Organic peroxide reactivity

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- ORGANIC PEROXIDE REACTIVITY -

The work described in this thesis was carried out both at King's College, Newcastle-on-Tyne, under the supervision of Professor G.R.Clemo, F.R.S., and at the laboratories of the British Rubber Producer's Research Association under the supervision of Dr.E.H.Farmer, F.R.S.
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INTRODUCTION.

The extreme importance of organic peroxides in many aspects of chemistry, biology and technology has, until recently, been but little recognised. During the past few years, however, research on and interest in the reactivities displayed by the various classes of organic peroxide has been greatly increased and it is now well recognised that this class of compounds is worthy of considerable study.

An organic peroxide may be defined as any compound containing an O-O bond linked directly at one or both ends to carbon atoms of organic groups. The various types of organic peroxide at present known are listed in Table (1).

From the standpoint of the present thesis the term "Organic Peroxide Reactivity" is intended to include the following aspects: (1) the preparation of organic peroxides, (2) the mode of thermal and photochemical decomposition of organic peroxides in the absence of solvents, and (3) the thermal and photochemical decomposition of organic peroxides (a) in the presence of olefins and olefinic compounds and (b) in the presence of non-olefinic organic solvents. Previous work on these various aspects has been reviewed up to April 1948 and the results summarised in this review show the complexity and diversity of the reactivities displayed by the various classes of peroxide and indicate the relevance of these reactions to many technologically important processes.

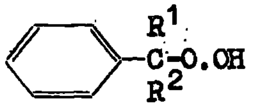
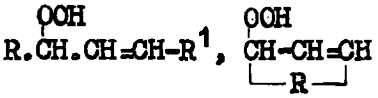
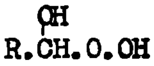
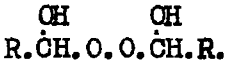
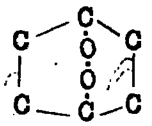
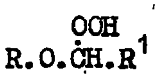
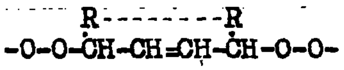
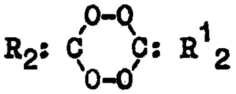
As will be described, olefins when photochemically or thermally reacted with molecular oxygen give, initially, unsaturated hydroperoxides which are highly reactive and which readily undergo secondary reactions resulting in their decay and a redistribution of the peroxidic oxygen. It is believed that these secondary reactions are responsible for the profound degradation which rubber suffers as the result of the incorporation of only a few units per cent of oxygen.

It is the primary aim of the present investigation to elucidate the nature of these secondary autoxidation processes, and to show to what extent they may be responsible for the oxidative degradation of rubber. To this end a study has been made of the thermal decomposition of three types of organic peroxide (a di-tert.-alkyl peroxide, a tert.-alkyl hydroperoxide and a saturated transannular peroxide) in the presence of low molecular weight cyclic and acyclic olefins.

Further, in order to compare the interaction of di-tert.-alkyl peroxides and non-olefinic compounds with that of these peroxides and olefins, a brief investigation has been made of the thermal decomposition of di-tert.-butyl peroxide in alkylbenzenes, cyclic and acyclic monoketones and cycloparaffins.

TABLE (1)

- CLASSIFICATION OF ORGANIC PEROXIDES.-

NAME	STRUCTURE
1. Alkyl peroxides	$R.O.OH$ ($R = CH_3, -CH(CH_3)_2, -C(CH_3)_3$ etc.)
2. Aralkyl hydroperoxides	 ($R^1 = R^2 =$ H or alkyl)
3. Alkenyl hydroperoxides	 $R.\overset{OOH}{C}H.CH{=}CH{-}R^1$, $\underbrace{\overset{OOH}{C}H{-}CH{=}CH}_{R}$
4. α-Hydroxy-alkyl hydroperoxides	 $R.\overset{OH}{C}H.O.OH$ (R = alkyl or *cyclo*alkyl)
5. Di-alkyl peroxides	$R.O.O.R^1$ (R = alkyl, R^1 = alkyl or *cyclo*alkyl.)
6. Alkyl-alkenyl peroxides	$R.O.O.R^1$ (R = alkyl, R^1 = *cyclo*alkenyl)
7. Di-α hydroxy-di-alkyl-peroxides	 $R.\overset{OH}{C}H.O.O.\overset{OH}{C}H.R.$ (R = alkyl)
8. Di-acyl- and di-aroyl peroxides	$R.CO.O.O.CO.R^1$ (R,R^1 = alkyl or aryl)
9. Transannular peroxides	
10. Ether hydroperoxides	 $R.O.\overset{OOH}{C}H.R^1$; (R,R^1 = alkyl)
11. Polymeric peroxides	 $-O-O-\overset{R}{C}H-CH{=}CH-\overset{R}{C}H-O-O-$
12. Ketone peroxides	

PART I

A REVIEW OF PREVIOUS WORK ON THE REACTIVITIES OF ORGANIC PEROXIDES.

SECTION (1)

- OLEFINIC REACTIVITY - THE AUTOXIDATION OF OLEFINS.-

The most important reactivity of olefinic systems has usually been regarded as residing in the double bond which can undergo additive reactions with many types of molecules (e.g. hydrogen, halogens, hydrogen halides, mercaptans, etc.). Recently, however, certain reagents have been shown to react substitutively with olefinic systems of the type $-CH_2-CH=CH-$, the point of attack being the α-methylene group (i.e. that adjacent to the double bond). This α-methylenic substitutive reactivity operates in the reactions of such reagents as N-bromo-succinimide (266), maleic anhydride (79), lead tetraacetate (58), selenium dioxide (112, 244), sulphur (24, 84) and oxygen (*vid.* below) with all olefins possessing the system $-CH_2-CH=CH-$. Certain of these reactions, e.g. substitutive attack by oxygen and sulphur, are now regarded as involving the formation of free radicals which result from the symmetrical (homolytic) breaking of covalent bonds (R.1) to give two groups X. and Y. each possessing an unshared electron. This type of bond fission is to be distinguished from the polar or heterolytic type (R.2.) in which the resulting groups X: and Y exist as charged ions.

$$X : Y \xrightarrow{\text{homolytic}} X. + Y. \qquad (R.1.)$$

$$X : Y \xrightarrow{\text{heterolytic}} \overset{-}{X:} + Y^+ \qquad (R.2.)$$

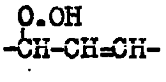
In this section are detailed the reactions of oxygen with unconjugated olefinic compounds possessing reactive α-methylene groups.

The results are of importance both from the standpoint of the reactivities displayed by various types of olefins and from that of the formation and reactivities of an important class of organic peroxides.

OLEFIN AUTOXIDATION.- In the thermally or photochemically promoted oxidation, at moderate temperatures (20°-40°), of mono-olefins containing the ethylenic system (I) the initial products are unsaturated hydroperoxides (II) in which the -OOH group is located at the α-methylenic carbon atom (59, 85, 128. 132, 231). Thus *cyclo*hexene (III) gives the hydroperoxide (IV) which retains the original unsaturation of the olefin and contains one -OH group (as -OOH). The constitution of the hydroperoxide as (IV) has been finally established by reduction to *cyclo*hexen-3-ol (V)

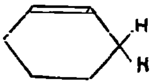
$-CH_2-CH=CH-$

(I)

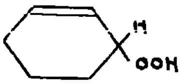


$\overset{O.OH}{-CH}-CH=CH-$

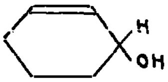
(II)



(III)



(IV)



(V)

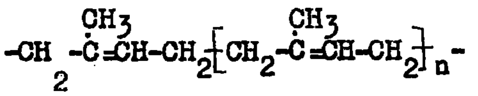
A similar course is pursued in the oxidation of low molecular weight polyisoprenes (e.g. dihydromyrcene (VI), dihydrofarnesene (VII), and squalene (VIII) containing the system $-CH_2-C(CH_3)=CH-CH_2$ (87), and by polyolefinic esters containing either a single double bond (methyl oleate) or the α-methylene interrupted polyolefinic systems (IX) and (X) as present in ethyl linoleate and ethyl linolenate respectively (6, 34, 88, 90, 114, 115).

(VI) $H.[CH_2.C(CH_3): CH.CH_2.]_2H$ (VII) $H.[CH_2.C(CH_3): CH.CH_2.]_3H$

$H.[CH_2.C(CH_3): CH.CH_2.]_3.[CH_2.CH: C(CH_3).CH_2.]_3H$
(VIII)

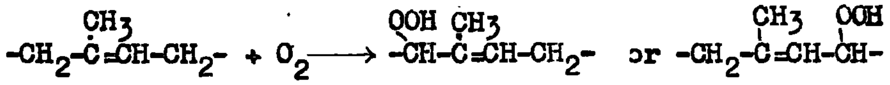
(IX) $-CH_2CH:CH.CH_2.CH:CH.CH_2-$ (X) $-CH:CH.CH_2.CH:CH:CH_2.CH:CH-$

Studies of the photochemical autoxidation of solutions of rubber (86) which contains the repeating isoprene system (XI) have shown that even in this complex molecule high yields of hydroperoxide are formed. Decay of the peroxide groups, however, occurs at an early stage of the oxidation, giving hydroxylated secondary products. Determinations of the unsaturation and active hydrogen values (32) of the peroxidised rubber give results which support the view that the initial peroxidation occurs at the α-methylene groups with the formation of hydroperoxides (R.3.) and preclude the possibility that oxygen adds at the double bonds of the rubber molecule (R.4.)

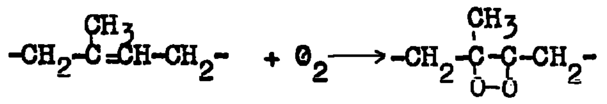


$$-CH_2-\overset{CH_3}{C}=CH-CH_2[CH_2-\overset{CH_3}{C}=CH-CH_2]_n- \qquad n = 4000-5000$$

(XI)



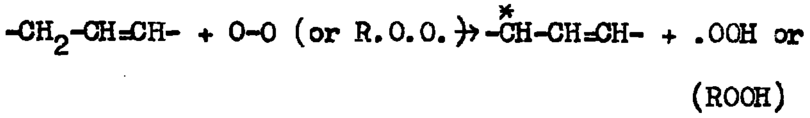
$$-CH_2-\overset{CH_3}{C}=CH-CH_2- + O_2 \longrightarrow -\overset{OOH}{CH}-\overset{CH_3}{C}=CH-CH_2- \text{ or } -CH_2-\overset{CH_3}{C}=CH-\overset{OOH}{CH}- \qquad (R.3.)$$



$$-CH_2-\overset{CH_3}{C}=CH-CH_2- + O_2 \longrightarrow -CH_2-\underset{O-}{\overset{CH_3}{C}}-\underset{O}{C}-CH_2- \qquad (R.4.)$$

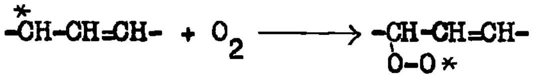
<u>Mechanism of Olefin Peroxidation.-</u> Farmer (82), proposed a radical chain mechanism for olefin peroxidation involving the following stages:-

(A) <u>Initiation.</u>

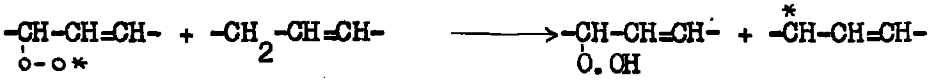


$-CH_2-CH{=}CH- + O{-}O \text{ (or } R.O.O.) \rightarrow -\overset{*}{C}H-CH{=}CH- + .OOH \text{ or } (ROOH)$ (R.5)

(B) <u>Propagation.</u>



$-\overset{*}{C}H-CH{=}CH- + O_2 \longrightarrow -\underset{O-O*}{CH}-CH{=}CH-$ (R.6)



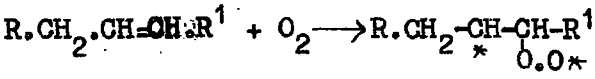
$-\underset{O-O*}{CH}-CH{=}CH- + -CH_2-CH{=}CH- \longrightarrow -\underset{O.OH}{CH}-CH{=}CH- + -\overset{*}{C}H-CH{=}CH-$ (R.7)

(C) <u>Termination.</u> of the reaction chains by combination of the radicals formed in (B).

The thermal decomposition of the initially formed hydroperoxide results in the production of new free radicals (e.g. R.O.O*, R.O*, HO*), which are capable of initiating new oxidation chains.

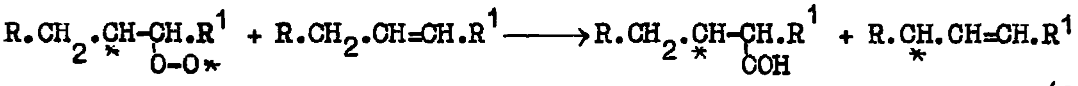
The possibility that chain initiation occurs by addition of oxygen at the double bonds has also been considered (33 (a)-(b), 78, 80, 115, 126).

Although Farmer's scheme (78), given below, involves <u>initiation</u> by addition of oxygen at one end of the ethylenic linkage, it does not result in saturation of the double bond but gives an olefinic hydroperoxide.



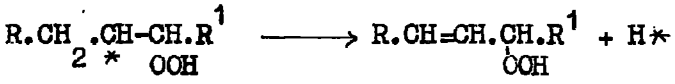
$R.CH_2.CH{=}CH.R^1 + O_2 \longrightarrow R.CH_2-\underset{*}{CH}-\underset{O.O*}{CH}-R^1$

(XII) (R.8)



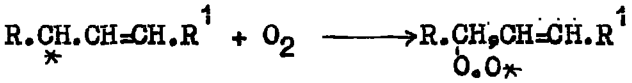
$R.CH_2.\underset{*}{CH}-\underset{O-O*}{CH}.R^1 + R.CH_2.CH{=}CH.R^1 \longrightarrow R.CH_2.\underset{*}{CH}-\underset{OOH}{CH}.R^1 + R.\underset{*}{CH}.CH{=}CH.R^1$

(R.9)

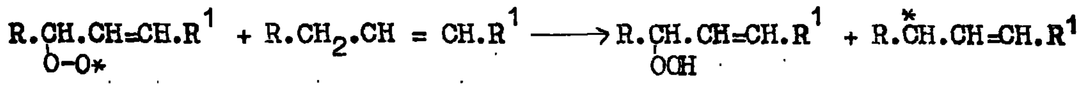


$R.CH_2.\underset{*}{CH}-\underset{OOH}{CH}.R^1 \longrightarrow R.CH{=}CH.\underset{OOH}{CH}.R^1 + H*$ (R.10)

(XIII)



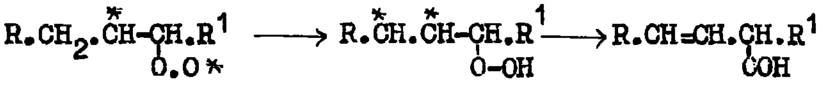
$R.\underset{*}{CH}.CH{=}CH.R^1 + O_2 \longrightarrow R.\underset{O.O*}{CH}.CH{=}CH.R^1$ (R.11)



$$\underset{\text{O-O*}}{\text{R.CH}}\text{.CH=CH.R}^1 + \text{R.CH}_2\text{.CH = CH.R}^1 \longrightarrow \underset{\text{OOH}}{\text{R.CH}}\text{.CH=CH.R}^1 + \text{R.}\overset{*}{\text{CH}}\text{.CH=CH.R}^1$$

(XIV) (R.12.)

The above intermolecular reactions resulting in stabilisation of the initially formed radical (XII) and the continuation of the peroxidation by radical chains (R.9 - R.12) was considered by Farmer as more likely than an intramolecular non-chain stabilisation reaction as represented by (R.13.).



$$\text{R.CH}_2\text{.}\overset{*}{\text{CH}}\text{-}\underset{\text{O.O*}}{\text{CH}}\text{.R}^1 \longrightarrow \text{R.}\overset{*}{\text{CH}}\text{.}\overset{*}{\text{CH}}\text{-}\underset{\text{O-OH}}{\text{CH}}\text{.R}^1 \longrightarrow \text{R.CH=CH.}\underset{\text{OOH}}{\text{CH}}\text{.R}^1$$

(R.13.)

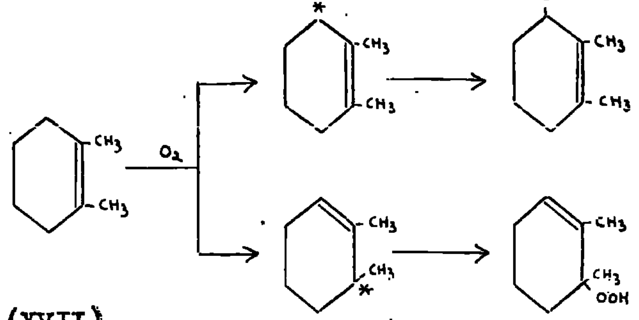
(XIII)

The reactions (R.8 - R.10) and reaction (R.13) are seen to result in a double bond shift in the original olefin. However, if the reaction proceeds by (R.8 - R.10) and the reaction chains are reasonably long, the number of hydroperoxide molecules possessing the redistributed double bond (XIII) will be of slight importance.

As the intramolecular mechanism would appear to give exclusively peroxides of the type (XIII) and the intermolecular mechanism predominantly those of type (XIV), it might be thought possible to distinguish between them, but this is not in fact feasible. An explanation of this is found in the fact that any alkenyl radical system $\text{R.}\overset{*}{\text{CH}}\text{.CH=CH.R}^1$, formed by the abstraction of hydrogen atoms from an α-CH_2 group, is potentially a resonating structure possessing the two canonical states (XV) and (XVI). Both (XV) and (XVI) can be stabilised(by -OOH) to give peroxides of type (XIV) and (XIII) respectively. The ability of any olefin to give both (XIII) and (XIV) as the result of resonance of the intermediate alkenyl radical would thus invalidate any quantitative estimates of the extent of double bond shift designed to discriminate between the <u>inter</u>- and <u>intra</u>- molecular mechanisms.

$$\underset{(XV)}{R.\overset{*}{C}H.CH{=}CH.R^1} \rightleftharpoons R.CH{\cdots}CH{\cdots}CH.R^1 \rightleftharpoons \underset{(XVI)}{R.CH{=}CH.\overset{*}{C}H.R^1}$$

<u>Verification of Double Bond Shift</u>.- That double bond shift does in fact occur in the autoxidation of olefins has been proved by both chemical and spectroscopic methods. Thus Farmer and Sutton (89) isolated and identified from the autoxidation of 1:2-dimethyl<u>cyclo</u>hexene (XVII) the two hydroperoxides (XVIII) and (XIX), the latter being formed by rearrangement of the original double bond.



(XVII) (XVIII) (XIX) (R.14.)

A number of workers have utilised U-V spectrographic analysis to detect double bond shift in the autoxidation of ethyl linoleate (XX) and ethyl linolenate. Thus Bolland and Koch (34), and Gunstone and Hilditch (114) demonstrated that the hydroperoxide resulting from the thermal oxidation of ethyl linoleate contained a high proportion of conjugated diene units. It was suggested that oxidative attack at the α-methylene group (a)* gave a free radical (XXI) composed of the three canonical structures

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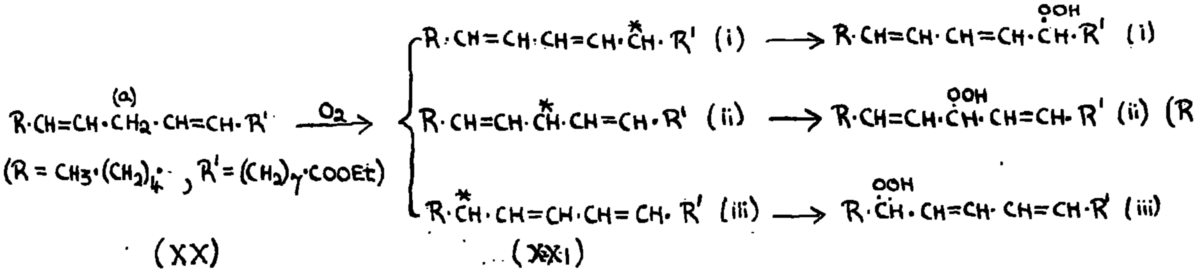
* This group being situated between two double bonds is more labile than either of the two terminal α-methylene groups.

(XXI (i) - XXI (iii)), two of which (XXI (i) and (iii)) would give conjugated diene hydroperoxides on stabilisation.



$$\underset{(XX)}{\overset{(R = CH_3\cdot(CH_2)_4\cdot\ ,\ R' = (CH_2)_7\cdot COOEt)}{R\cdot CH{=}CH\cdot \overset{(a)}{CH_2}\cdot CH{=}CH\cdot R'}} \xrightarrow{O_2} \underset{(XXI)}{\left\{\begin{array}{l} R\cdot CH{=}CH\cdot CH{=}CH\cdot \overset{*}{C}H\cdot R' \ (i) \longrightarrow R\cdot CH{=}CH\cdot CH{=}CH\cdot \overset{OOH}{C}H\cdot R' \ (i) \\ R\cdot CH{=}CH\cdot \overset{*}{C}H\cdot CH{=}CH\cdot R' \ (ii) \longrightarrow R\cdot CH{=}CH\cdot \overset{OOH}{C}H\cdot CH{=}CH\cdot R' \ (ii) \\ R\cdot \overset{*}{C}H\cdot CH{=}CH\cdot CH{=}CH\cdot R' \ (iii) \longrightarrow R\cdot \overset{OOH}{C}H\cdot CH{=}CH\cdot CH{=}CH\cdot R' \ (iii) \end{array}\right.}$$

(R.15)

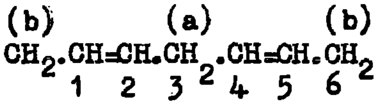
Similarly ethyl linolenate on oxidation gives hydroperoxides containing both diene and triene conjugation (90, 114).

Kinetics of Olefin Autoxidation.- Detailed kinetic studies by Bolland and Gee (31, 33(a)-(b)) of the initial stages of the thermal oxidation of ethyl linoleate and other non-conjugated olefinic esters and olefins have confirmed the radical-chain mechanism of Farmer. Under normal conditions of autoxidation, nearly all the chains are initiated by thermal decomposition of hydroperoxide (or added peroxide) and terminated by interaction of two peroxide free radicals to give stable end products.

Autoxidation at High Temperatures.- It is not certain that at higher temperatures (> 80°) oxygen attacks exclusively the α-methylene groups and in fact Hilditch et al. (6, 114), and Skellon (227) have recently presented evidence indicating that in the oxidation of methyl oleate at 120° considerable oxidative attack occurs at the double bond.

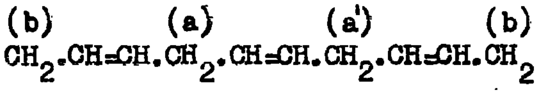
The Influence of Olefinic Structure on Rate and Nature of Autoxidation.-

(A) Rate of Autoxidation. The rate of autoxidation of any olefinic system will depend on the lability of its α-methylene hydrogen atoms, those systems possessing highly labile hydrogen atoms being the most rapidly oxidised. It is possible to classify unconjugated olefins into three main groups: (a) methylene interrupted 1:4- and 1:4:7- olefins (XXII (i) and (ii) respectively), (b) bi-spaced 1:5- and 1:5:9- olefins (XXIII), of which the polyisoprenes are important examples, and (c) mono-olefins (XXIV).



$$\overset{(b)}{CH_2}.\underset{1}{CH}{=}\underset{2}{CH}.\underset{3}{\overset{(a)}{CH_2}}.\underset{4}{CH}{=}\underset{5}{CH}.\underset{6}{\overset{(b)}{CH_2}}$$

(XXII (i))



$$\overset{(b)}{CH_2}.CH{=}CH.\overset{(a)}{CH_2}.CH{=}CH.\overset{(a')}{CH_2}.CH{=}CH.\overset{(b)}{CH_2}$$

(XXII(ii))

$CH_2.C(R){=}CH.CH_2.CH_2.C(R){=}CH{-}CH_2$

(XXIII)

$CH_2.CH{=}CH$

(XXIV)

It has been shown experimentally that the magnitude of the lability in these systems is in the order XXII (ii) > XXII (i) > XXIII > XXIV. Thus Gunstone and Hilditch (114) found that the rates of thermal oxidation at 20° of methyl linolenate (type XXII (ii)), methyl linoleate (type XXII (i)), and methyl oleate (type XXIV) were in the ratio of 25:12:1.

Alkyl substitution of the double bond also influences, presumably by its inductive effect, the lability of α-methylene hydrogen atoms. No detailed work has yet been published on the effect of this alkyl substitution on the rates of oxidation, but recently Bolland (private communication) has studied the relative oxidation rates of three series of olefins in which the members of each series differ in the extent of methyl substitution at the double bond. He found that the increasing degree of methyl substitution in the olefins (XV), (XVI), and (XVII) resulted in progressively increasing oxidation rates. When R = C_6H_5 the relative rates of the rate determining reaction (R.16) were in the order (XVII) > (XVI) > (XV) in the ratio of 16.5 : 4.9 : 1.

$R.CH_2.CH{=}CH_2$ (XV)

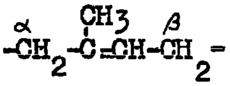
$R.CH_2.CH{=}CH.CH_3$ (XVI)

$R.CH_2.CH{=}C(CH_3)_2$ (XVII)

$$R.O_2^* + RH \longrightarrow R.O_2H + R \qquad (R.16)$$

(B) Position of Oxygen Attack.- The nature of the olefinic system not only controls the facility of oxidation but also determines the actual point of initial oxidative attack. In the systems (XXII (i)) and (XXII (ii)) the oxygen reacts almost exclusively at the methylene groups (a) and (a^1) situated midway between two double bonds (31, 33 (a)-(b), 90, 114).

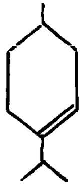
The introduction of alkyl substituents on the double bond is another factor determining the point of attack (as between C^{α} and C^{β}) in the system (XXVIII). Published work on this question is conflicting. Thus



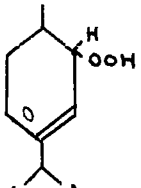
$$\overset{\alpha}{-CH_2}-\overset{CH_3}{C}{=}CH-\overset{\beta}{CH_2}=$$

(XXVIII)

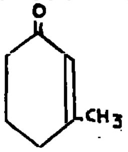
Hook and Lang (129) isolated the hydroperoxide (XXX) from the oxidation of p-menthene (XXIX), and Cook (53) obtained 3-methyl-Δ^2-cyclohexenone (XXXI) from the oxidation of 1-methylcyclohexene at 70° in the presence of ferrous phthalocyanine, both results indicating preferential attack at $-CH_2^{\beta}$.



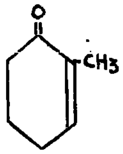
(XXIX)



(XXX)

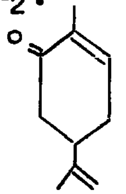


(XXXI)

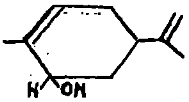


(XXXII)

(XXXIII)

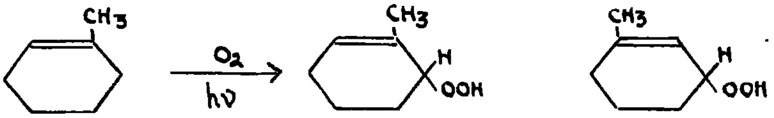


(XXXIV)



(XXXV)

Evidence for preferential attack at $-CH_2\alpha$ has been gained by Dupont (73) who found that oxidation of 1-methyl<u>cyclo</u>hexene at 95° gave 2-methyl-Δ^2-<u>cyclo</u>hexenone (XXXII), and by Blumann and Zeitschel (25) who showed that limonene (XXXIII) on oxidation gave carvone (XXXIV) and carveol (XXXV). More recently Farmer and Sundralingham (85) have adduced evidence for attack at both $-CH_2\alpha$ and $-CH_2\beta$ but they found that attack predominated at $-CH_2\alpha$. Their evidence was based on the isolation of both 1-methyl<u>cyclo</u>hexene-6- and -3-hydroperoxide ((XXXVI) and (XXXVII) respectively) from the photoxidation of 1-methyl<u>cyclo</u>hexene at 35°.



(XXXVI) (XXXVII) (R.17)

The problem is obviously one of considerable difficulty and awaits more detailed and accurate qualitative and kinetic investigations for its ultimate solution.

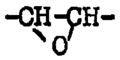
<u>SECONDARY AUTOXIDATION PROCESSES</u>.- The hydroperoxides initially formed in olefin autoxidation are extremely unstable and undergo extensive and complex rearrangement reactions involving the peroxide and unreacted olefin. The products resulting from this oxygen redistribution may then undergo further reactions with peroxide, olefin or other molecules. It is found that in any thermally or photochemically promoted autoxidation the products include, in addition to hydroperoxides, olefinic alcohols (XXXVIII), epoxides (XXXIX), and polymeric oxygenated compounds of uncertain composition, (85).

In the later stages of autoxidation of polyisoprenes (especially of rubber), ketones, aldehydes, carboxylic acids and esters become significant

(b) secondary products (86, 87).

$-CH{=}CH{-}CH(OH){-}$

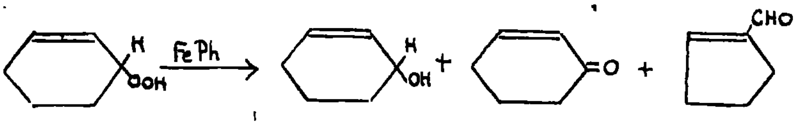
(XXXVIII)



$-CH{-}CH{-}$ (bridged by O)

(XXXIX)

If the autoxidation is carried out in the presence of metallic catalysts such as ferrous phthalocyanine or cabalt naphthenate the rate of oxidation is greatly increased and the secondary products become the major constituents (53, 191, 192, 219, 233). Farmer and Sundralingam (85) showed that pure olefin hydroperoxides were rapidly decomposed by traces of ferrous phthalocyanine giving complex mixtures of alcohols, aldehydes and ketones:

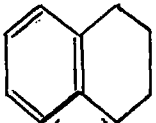


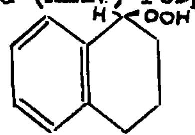
(R.18)

It is generally held that these secondary autoxidation processes are the causes of the oxidative breakdown of natural rubber, the production of rancidity and "off flavours" in oils and fats, and the hardening ("polymerisation") of paint and varnish films (237). A detailed discussion of the relevance of the course of autoxidation in these technically important processes is beyond the scope of this thesis. However, the relevance of the author's own findings on hydroperoxide/olefin reactions to the mechanism of oxidative scission and cross-linking of natural and synthetic rubbers, will be discussed in a later section (<u>vid</u>.p.100).

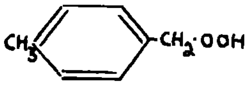
Little is known about the precise mechanisms involved in the decay of olefinic peroxides, mainly because of insufficient accurate qualitative and quantitative experiments. Many schemes have been proposed which explain, (plausibly or otherwise) the formation of the final products (36, 82), but until definite experimental proof of their correctness is obtained they must be regarded merely as tentative.

HYDROMATIC AND AROMATIC HYDROPEROXIDES.- Hydroaromatic hydrocarbons and alkyl benzenes containing labile C-H bonds vicinal to the aromatic nucleaus give, on thermal or photoxidation, hydroperoxides closely related to olefinic hydroperoxides. Tetralin (XL) was shown by Hartmann and Seiberth (120) and by Hock and Susemihl (133) to give on autoxidation the crystalline hydroperoxide (XLI). Similarly, *p*-xylene, ethyl benzene, and *iso*-propyl benzene form the hydroperoxides (XLII), (XLIII) and (XLIV) respectively (130, 131).

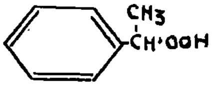

(XL)



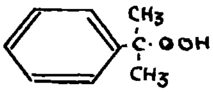
(XLI)



(XLII)



(XLIII)



(XLIV)

Detailed kinetic studies of tetralin autoxidation have shown that the process is analogous to that of aliphatic olefin autoxidation, involving free-radical chain reactions as in Farmer's proposed mechanism (109, 110, 135, 165, 169, 213). (*vid*.p. 6)

SECTION (2).

- PREPARATION OF ORGANIC PEROXIDES.-

1. ALKYL HYDROPEROXIDES and DI-ALKYL PEROXIDES.-

(A) PRIMARY ALKYL PEROXIDES.- Alkyl hydroperoxides (R.OOH) in which R. is a primary alkyl group are prepared by the half alkylation of hydrogen peroxide with the appropriate dialkyl sulphate in the presence of alkali (9, 116). Complete alkylation of hydrogen peroxide with two equivalents of dialkyl sulphate gives dialkyl peroxides R.O.O.R^1. (9), By this method the following peroxides have been prepared: dimethyl (210), methylethyl (8, 9, 234), diethyl and di-*n*-propyl (116, 258) peroxides.

(B) TERTIARY ALKYL PEROXIDES.- *tert*.-Butyl hydroperoxide, the first of this group to be prepared, was originally obtained by fractionation of an anhydrous solution of hydrogen peroxide in *tert*.-butanol in the presence of a dehydrating agent (173). Later, Milas and co-workers developed for preparation of *tert*.-alkyl hydroperoxides a general method involving reaction, in the cold, of *tert*.-alkyl hydrogen sulphates with 30% hydrogen peroxide (174-176). The alkyl hydrogen sulphate was prepared by reacting either a *tert*.-alcohol or an unsymmetrical dialkyl-ethylene with sulphuric acid:

$$R_2.C{=}CH_2 + H_2SO_4 \longrightarrow R_2.C(CH_3).O.SO_3H \qquad (R.19)$$

$$R.OH + H_2SO_4 \longrightarrow R.O.SO_3H + H_2O \qquad (R.20)$$

$$R.O.SO_3H + H_2O_2 \longrightarrow R.OOH + H_2SO_4 \qquad (R.21)$$

The reaction product always comprises a mixture of alkyl hydroperoxide and dialkyl peroxide, separation of which may be effected either by fractional distillation or by extraction of the hydroperoxide with alkali and regeneration with dilute mineral acid.

By adjustment of the concentration of sulphuric acid di-alkyl peroxides can be obtained as the major products. A better method of preparation of di-alkyl peroxides is by the reaction of the corresponding hydroperoxide with tert.-alkyl hydrogen sulphates (174-176).

$$(CH_3)_3C.O.OH + (CH_3)_3.C.HSO_4 \longrightarrow (CH_3)_3C.O.O.C(CH_3)_3 + H_2SO_4 \qquad (R.22)$$

Both di-tert.-alkyl peroxides and tert.-alkyl hydroperoxides have been prepared by Vaughan and Rust (241-243) by the controlled autoxidation at 150-250° of a trialkyl substituted methane R_3CH, hydrogen bromide being used as a catalyst (R.23).

$$R_3CH + O_2 \xrightarrow{HBr} R_3.C.OOH + R_3C.O.O.CR_3 \qquad (R.23)$$

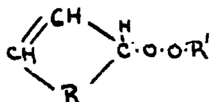
2. DI-ACYL AND DI-AROYL PEROXIDES.- Both diacyl and diaroyl peroxides, of which diacetyl peroxide and benzoyl peroxide may be taken as respective examples, are prepared by the action (below 0°) of the corresponding acid chloride, dissolved in a suitable solvent (e.g. ether or acetone) with either sodium peroxide or hydrogen peroxide and alkali (95, 184, 194, 239).

$$2R.CO.Cl + Na_2O_2 \longrightarrow R.CO.O.O.CO.R + 2NaCl \qquad (R.24)$$

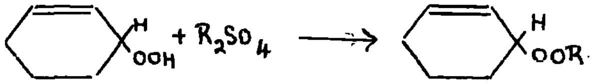
Diacetyl peroxide may also be prepared by reacting acetic anhydride in ether solution with sodium peroxide (96, 153). The peroxide is unstable and if required in the pure solid state must be kept at low temperatures (ca.-80°).

3. OLEFINIC HYDROPEROXIDES.- The preparation of olefinic and related hydroperoxides, such as tetralin hydroperoxide and alkyl-aryl hydroperoxides, have been described in the previous section.

4. cyclo-ALKENYL-ALKYL PEROXIDES.- These peroxides, having the general structure (XLV), have been prepared by Hook and Lang (129) by the alkylation, with di-alkyl sulphates in alkali, of cyclo-alkenyl hydroperoxides such as cyclo-hexene-3-hydroperoxide.



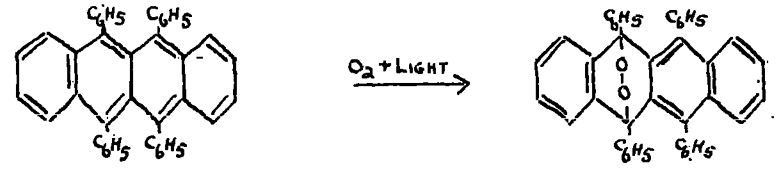
(XLV)



(R.25)

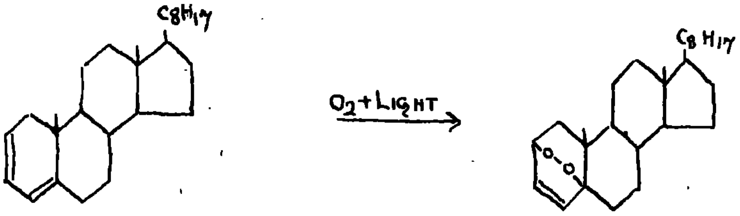
5. TRANSANNULAR and POLYMERIC PEROXIDES.- The transannular peroxides contain a 1:4- peroxide bridge across a six-membered carbon ring. They are generally derived from certain classes of polycyclic aromatic hydrocarbons (e.g. anthracene and naphthacene and their derivatives), but sterol-1:3-dienes also give well defined peroxides of this type (21). They are prepared by the photoxidation with molecular oxygen of conjugated dienes which undergo 1:4-addition. Thus rubrene (XLVI) gives rubrene peroxide (XLVII) (61, 179). As an example of a steroid peroxide may be cited 2:4-cholestadiene peroxide (XLIX) which is obtained when 2:4-cholestadiene (XLVIII) is irradiated, in the presence of oxygen, with a 200 watt Mazda bulb (225, 226).

(XLVI)



(XLVII) (R.26)

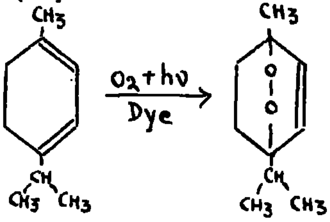
(XLVIII)



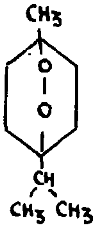
(XLIX) (R.27)

Monocyclic transannular peroxides are also known. The best known example is ascaridole (LI) which is unique in occurring naturally as the major anthelmintic constituent of chenopodium oil. Schenk and Ziegler (217) have recently synthesised ascaridole by the irradiation of dilute solutions of α-terpinene (L) with oxygen in the presence of a fluorescent dye such as chlorophyll. By the same method these workers obtained the two peroxides (LIII) and (LIV) from <u>cyclo</u>-hexa-1:3-diene and α-phellandrene respectively.

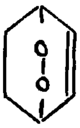
(L) (LI)



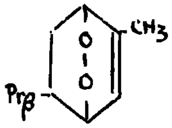
(LII)



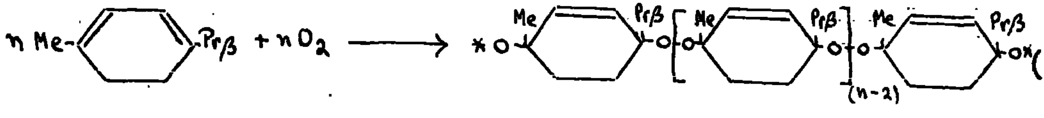
(LIII)



(LIV)



Previous attempts by Bodendorff (26) to prepare ascaridole from α-terpinene and oxygen gave polymeric peroxides (LV), in which the terminal peroxide radicals may be terminated by ring formation, disproportionation, or formation of hydroperoxide groups (80). The formation of polymeric peroxides such as (LV) appears to be a general reaction of all classes of non-aromatic cyclic and acyclic -1:3-dienes when the autoxidation is performed in high monomer concentration and in absence of photosensitisers (26, 80).



(R.28)

(LV)

These peroxides are notable for their great thermal stability and resistance to catalytic reduction, but the peroxide from butadiene is highly explosive (223).

Dihydroascaridole (LII) is of interest since it is the only known example of a completely saturated transannular peroxide. It is prepared by the reduction of the double bond in ascaridole using platinic oxide as catalyst (190).

SECTION (3).

THE THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF ORGANIC PEROXIDES.

In this section is given an account of the reactions involved in the thermal and photochemical decomposition of the major types of organic peroxide. The results have both advanced our understanding of the reactivities of free radicals and proved of value in studies of processes of technological importance, such as hydrocarbon fuel combustion and the deterioration of lubricating oils.

(1) PRIMARY ALKYL HYDROPEROXIDES.- Studies of the thermal decomposition of three primary alkyl hydroperoxides, CH_3OOH (168), $C_2H_5.OOH$ and $\underline{n}$-$C_3H_7.OOH$ (116, 118) have indicated that the reactions are complex, the products consisting mainly of aldehydes, alcohols and hydrocarbons but containing also significant amounts of carbon dioxide, carbon monoxide and oxygen.

Medvedev and Podjapolskaya (168) studied the decomposition of methyl hydroperoxide by the flow method and obtained results indicating a unimolecular decomposition into formaldehyde and water occurring alongside a bimolecular decomposition into methanol and oxygen.

Harris and Egerton (116, 118) showed that the main thermal decomposition reactions of ethyl- and n-propyl-hydroperoxide were heterogeneous dehydrations giving aldehydes and water:

$$CH_3CH_2OOH \longrightarrow CH_3.CHO + H_2O \qquad (R.29)$$

The existence of the corresponding alcohol (ethanol from $C_2H_5.OOH$ and n-propanol from n-Pr.OOH) and oxygen in the low temperature decompositions (170-200°) indicated that bimolecular reactions such as (R.30) also occurred.

$$2C_2H_5.OOH \longrightarrow 2C_2H_5.OH + O_2 \qquad (R.30)$$

A further reaction is a homogeneous, explosive, gas phase decomposition involving, in the first place, scission of the O-O- bond (R.31), the radical $CH_3CH_2.O*$ then decomposing to give formaldehyde (R.32)(238, 251).

$$CH_3.CH_2.O\text{-}OH \longrightarrow CH_3.CH_2.O* + \overset{*}{O}H \qquad (R.31)$$

$$CH_3.CH_2.O* \longrightarrow CH_3* + H.CHO \qquad (R.32)$$

Rice and Radowskas(209), studying the thermal decomposition of alkyl nitrites, have demonstrated by mirror experiments, that radicals of the type $R.CH_2.O*$ are unstable, readily undergoing scission into formaldehyde and an alkyl radical $R*$. The radical $R*$ can either by dimerisation give the hydrocarbon R_2, or by interaction with a molecule XH give RH.

(2) <u>DI-PRIMARY ALKYL PEROXIDES</u>.- Investigations of the thermal decomposition of di-ethyl peroxide(117, 119) and di-n-propyl peroxide(116) have indicated quite clearly that below a certain critical pressure the main mode of decomposition is a homogeneous, unimolecular reaction, but above this critical pressure explosive decomposition takes place and the nature of the products changes. This transition to an explosive mode of decomposition may be compared with a similar phenonemon in the decompositions of azomethane(4) and ethyl azide(42).

The products of the unimolecular decomposition of diethyl peroxide in the temperature range 130-190° are mainly acetaldehyde and ethanol (R.33).

$$C_2H_5.O.O.C_2H_5 \longrightarrow CH_3.CHO + C_2H_5.OH \qquad (R.33)$$

Above the critical pressure the peroxide decomposes to give mainly formaldehyde and ethane. The reaction most probably occurs according to the following scheme (R.34 - R.36) :

$$CH_3.CH_2.O.O.CH_2.CH_3 \longrightarrow 2\,CH_3.CH_2.O* \qquad (R.34)$$

$$CH_3.CH_2.O* \longrightarrow CH_3* + H.CHO \qquad (R.35)$$

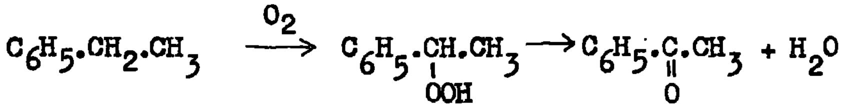
$$CH_3* + CH_3* \longrightarrow C_2H_6 \qquad (R.36)$$

Similarly the important products in the unimolecular decomposition of di-n-propyl peroxide at 180° are n-propanol and propionaldehyde (although significant amounts of formaldehyde and hydrocarbon indicate that the explosive mode of reaction also takes place to a small but constant extent). The explosive decomposition at 240° gives mainly formaldehyde and n-butane (R.37) :

$$CH_3.CH_2.CH_2.O.O.CH_2.CH_2.CH_3 \longrightarrow C_2H_5-C_2H_5 + 2H.CHO \qquad (R.37)$$

(3) SECONDARY ALKYL PEROXIDES.- Little work has been done on the decomposition of this type of peroxide. It may, however, be regarded as a general rule that they undergo, as the major reaction, dehydration to give a ketone, and by analogy with the reaction of primary hydroperoxides this is probably heterogeneous.

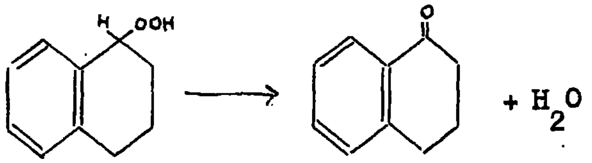
As examples: (I) Ethyl benzene on oxidation yields acetophenone the reaction occurring probably by the initial formation of the hydroperoxide (R.38)(230, 235, 267).



$$C_6H_5.CH_2.CH_3 \xrightarrow{O_2} C_6H_5.\underset{OOH}{CH}.CH_3 \rightarrow C_6H_5.\underset{\overset{\|}{O}}{C}.CH_3 + H_2O$$

(R.38)

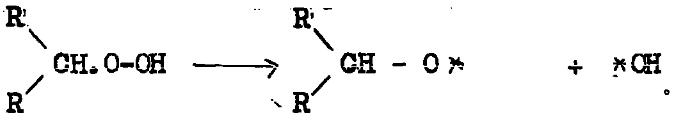
(II) Tetralin hydroperoxide (XLI) yields tetralone (LVI), the reaction being catalysed by such metallic salts as ferrous sulphate(120) and ferrous phthalocyanine(53):



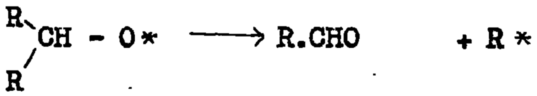
(XLI)   (LVI)   (R.39)

This peroxide may also undergo a radical decomposition reaction as evidenced by its ability to initiate the chain polymerisation of styrene, methyl methacrylate, vinyl cyanide(213) and 2-chlorobutadiene(116, 167) (vid.p. 46). This is further supported by the use of tetralin hydroperoxide as an initiator of tetralin autoxidation(213).

Walsh(251) believes that secondary alkyl hydroperoxides may also u undergo, at higher temperatures, a homogeneous explosive, gas phase decomposition similar to that occurring with primary and tertiary alkyl peroxides (vid.p. 20 and p. 24). The reaction involves the formation of RO* and *OH radicals by scission of the -O-O- bond, the RO* radical decomposing to give an aldehyde (R.40 and R.41).

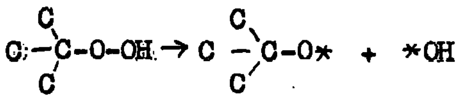


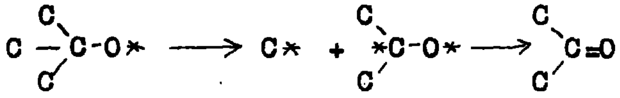
(R.40)



(R.41)

(4) <u>TERTIARY ALKYL HYDROPEROXIDES</u>.- Sufficient work has been recorded on the thermal decomposition of <u>tert</u>.-alkyl and -aryl hydroperoxides to lead George and Walsh (111) to make the following generalisation governing the mode of their decomposition: The reaction occurs in two stages: (i) scission of the -O-O bond to give an alkoxy radical R_3.C.O* and a hydroxyl radical *OH (R.42) ;
(ii) scission of a -C-C- bond adjacent to the -C-O- bond in the radical R_3.C.O* to yield a ketone (R.43)


(R.42)


(R.43)

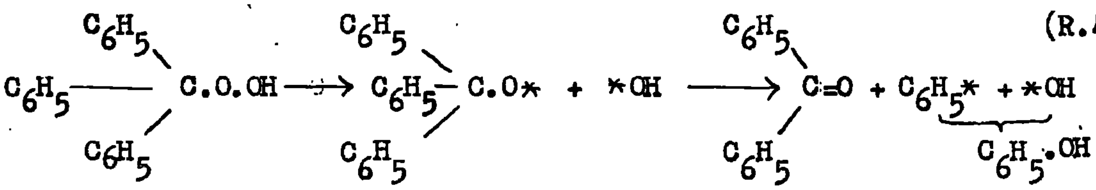
Energetically the second reaction (R.43) is favoured, being nearly thermoneutral since the energy required to break the -C-C- bond is counterbalanced by the energy released in forming the carbonyl group (111, 249). Raley, Rust and Vaughan (204) have calculated that in the case of di-<u>tert</u>.-butyl peroxide the step,

$$(CH_3)_3C.O* \longrightarrow (CH_3)_2C = O + CH_3 \qquad (R.44)$$

is <u>endothermic</u> to the extent of <u>ca</u>.5 k.cal.

The following examples may be cited in support of the above generalisation :

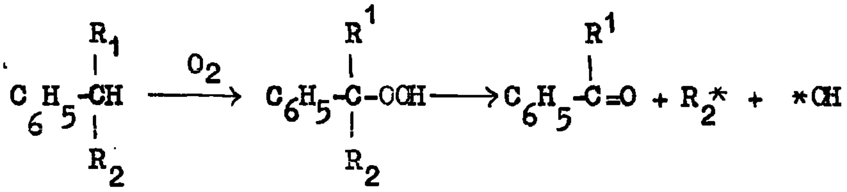
(i) Wieland and Maier (254) found that triphenylmethyl hydroperoxide decomposes to give benzophenone and phenol (R.45). This work has been confirmed by Stephens and Roduta (232) who obtained benzophenone and phenol as the only isolable products in the thermal oxidation of triphenylmethane at 119°.



$$(C_6H_5)_3C.O.OH \longrightarrow (C_6H_5)_3C.O* + *OH \longrightarrow (C_6H_5)_2C{=}O + \underbrace{C_6H_5* + *OH}_{C_6H_5.OH}$$

(R.45)

(ii) Stephens and Roduta (232) in a study of the oxidation at 119° of a series of secondary alkyl benzenes of the type $C_6H_5.CH(R_1R_2)$, (R_1=CH_3; R_2= C_2H_5, n-C_3H_7, n-C_4H_9) showed that in every case acetophenone was formed. Since hydroperoxides have been isolated as the initial products of alkyl benzene oxidations (130, 131) the oxidation probably occurs according to reaction (R.46).



$$C_6H_5\text{-}\underset{R_2}{\overset{R_1}{CH}} \xrightarrow{O_2} C_6H_5\text{-}\underset{R_2}{\overset{R^1}{C}}\text{-OOH} \longrightarrow C_6H_5\text{-}\overset{R^1}{C}{=}O + R_2* + *OH$$

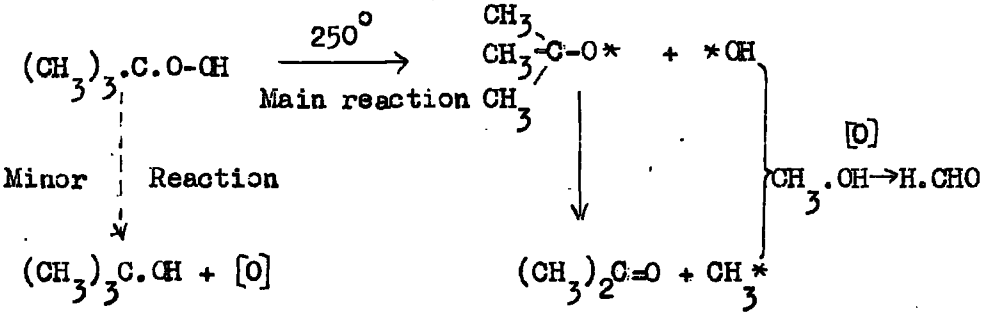
(R.46)

It should be noted that when the alkyl groups R_1 and R_2 attached to the -C-OOH group are dissimilar, it is the larger of these which is preferentially split off by scission of the C-C bond. Confirmation of this has been obtained in the thermal decomposition of di-tert.-alkyl peroxides (vid.p. 29). The greater strength of the C-C bond bearing the smaller of the alkyl groups is, as pointed out by George and Walsh (111), parallelled by the fact that the C-C dissociation energy in C_2H_5-C_2H_5 is less than that in C_2H_5-CH_3 (5).

(iii) The thermal decomposition of <u>tert</u>.-butyl hydroperoxide has been studied at various temperatures(175). Up to 75° no appreciable decomposition occurs. Between 95-100° regular decomposition takes place giving oxygen and <u>tert</u>.-butanol in almost quantitative yields (R.47).

$$(CH_3)_3.C.OOH \xrightarrow{95-100^{\circ}} (CH_3)_3.C.OH + [O] \qquad (R.47)$$

In the vapour phase decomposition at 250° the reaction follows, in the main, a different course. A gas, consisting largely of methane was obtained, and liquid products included acetone (38.7%), methanol (7%), <u>tert</u>.-butanol (11%), water (10%) and formaldehyde (not estimated). To account for these products Milas(175) proposed a free radical decomposition similar to that formulated by George and Walsh(111):



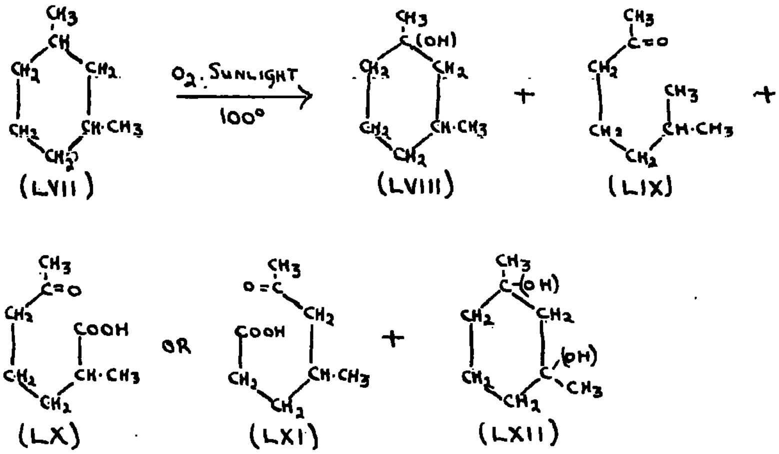
(R.48)

The formaldehyde resulted, according to Milas, from the reaction of methanol with an active oxidising group such as the HO* radical of the hydroperoxide. Experiments indicated that direct oxidation of methanol by molecular oxygen does not occur at 250° in the absence of a catalyst. The precise mechanism of methane formation was not included in the reaction scheme (vid. however, p. 50).

(iv) The work of Chavanne and co-workers has recently been shown by George and Walsh (111) to have considerable bearing on the problem of *tert*.-alkyl hydroperoxide decomposition.

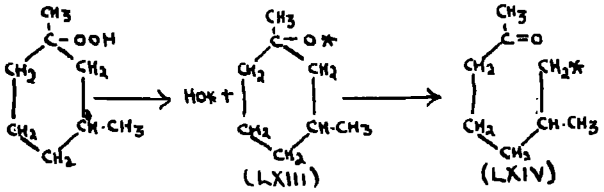
Chavanne has studied the uncatalysed thermal oxidation at 80-100° of a series of alkyl substituted *cyclo*pentanes and *cyclo*hexanes. The experiments included oxidation at 80° of 1:3-dimethyl-*cyclo*pentane (48), and at 100° of 1:2-dimethyl-*cyclo*hexane (47), 1:3-dimethyl-*cyclo*hexane (46) and 1:4-dimethyl-*cyclo*hexane (45). In all cases the oxidation products were complex, containing gaseous products (CO_2, CO, H_2, low molecular weight paraffins), water, acetic, formic and keto-acids, ketones, ketols, *tert*.-alcohols and diols.

One example will suffice. When 1:3-dimethyl-*cyclo*hexane (LVII) was oxidised in sunlight at 100° the products isolated included 1:3-dimethyl-*cyclo*-hexan-1-ol (LVIII) (the predominant oxidation product), 6-methyl-heptan-2-one (LIX), a keto-acid (either (LX) or (LXI)), 1:3-dimethyl-*cyclo*-hexan-1:3-diol (LXII), formic, acetic and two hexanoic acids (probably *iso*-butyl- and methyl propyl- acetic acids), together with carbon dioxide, carbon monoxide, hydrogen, methane and possibly propane. The predominant acidic products were the methyl acetyl valeric acid (LX) or (LXI), and acetic acid.



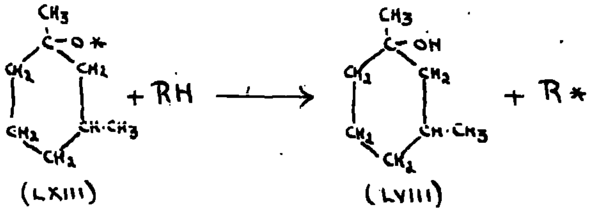
(R.49)

Although the existence of a tert.-alkyl hydroperoxide was not demonstrated by Chavanne, George and Walsh (111) have interpreted the reaction as the initial formation of a peroxide of this type by oxidation at a tert.-carbon atom, followed by its decomposition into free radicals which by further decomposition or reaction with other molecules give the observed products. The main reaction products are accounted for by the following reactions which are all energetically possible:



(R.50)

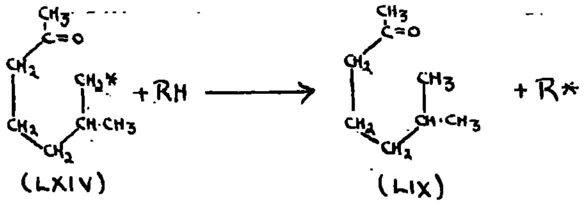
Reaction of the radical (LXIII) with a hydrocarbon RH (R.51) would give the cyclic tert.-alcohol (LVIII) :



(R.51)

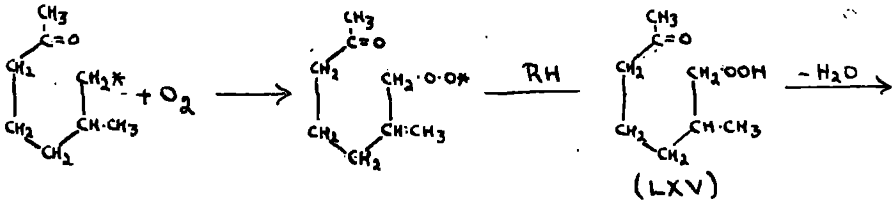
The keto alkyl radical (LXIV) may react in two ways: (a) to give the ketone (LIX) and a hydrocarbon radical R* which can continue the oxidation reaction and (b) by reaction with oxygen giving a keto peroxide (LXV) which by a unimolecular dehydration (cf.$C_2H_5.OOH$) would yield a keto-aldehyde (LXVI) and thence by further oxidation the keto acid (LXVII) :

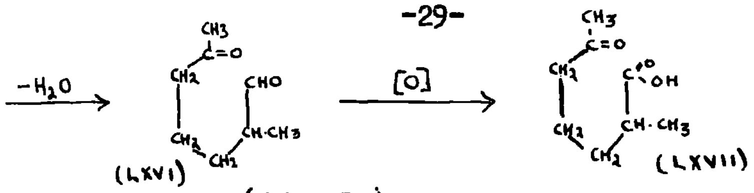
(a)



(R.52)

(b)





(R.53)

Walsh (251-253) has stressed the importance of these types of decompositions in an understanding of the processes involved in the oxidation of hydrocarbon fuels. A similar review of their relevance to the mechanism of the oxidation of lubricating oils has been given by Zuimeda (267).

(5) DI-*tert*.-ALKYL PEROXIDES.- These peroxides are remarkable for their great stability, being the most inert of all the di-alkyl peroxides known (di-*tert*.-butyl peroxide can be distilled at atmospheric pressure, b.p. 110°) without any appreciable decomposition). There appears to be a general gradation in the stability of the various classes of alkyl hydroperoxides and di-alkyl peroxides in the order: $R\text{-}O.O.R > R.O.O.H$, and $R_\gamma > R_\beta > R_\alpha$, where R = alkyl group. Walsh (249,250) has associated this increase in the -O-O- bond strength, in passing from primary to secondary to tertiary alkyl peroxides and di-alkyl peroxides, with the increased negative charge transference from the alkyl groups to the -O-O- bond.

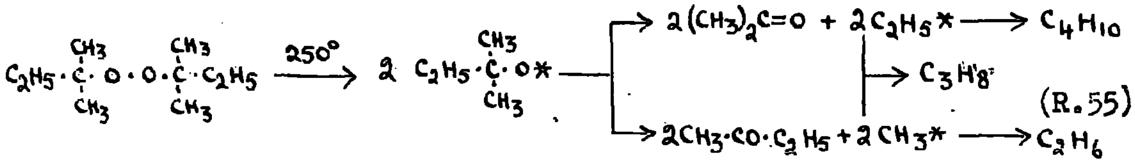
Since their first preparation in 1946 (*vid*.p. 15) much work has been done on the thermal decomposition of both symmetrical and asymmetrical di-alkyl peroxides. Of particular note is the pioneering work of Milas and his co-workers who studied di-*tert*.-butyl- (175), di-tert.-amyl- (176), di-trimethylethyl-, *tert*.-butyl-pentamethylethyl- and *tert*.-butyl-1-methyl-*cyclo*-hexyl-1 (174) peroxides.

In every case studied by Milas, vapour phase decomposition of the peroxides at ca. 250° yielded ketones and paraffins as the sole products. Di.-tert.-butyl peroxide gave acetone and ethane, a result which has been confirmed by George and Walsh (111). A free radical decomposition reaction was proposed, involving the initial formation of tert.-alkoxy radicals which degraded further by scission of a C-C bond adjacent to the C-O bond to give ketones and alkyl radicals, the latter dimerising to paraffin hydrocarbons:

$$(CH_3)_3.C.O.O.C(CH_3)_3 \xrightarrow{250^\circ} 2(CH_3)_3.C.O.* \longrightarrow 2(CH_3)_2C{=}O + 2CH_3* \longrightarrow C_2H_6$$

(R.54)

When the alkyl groups on the tertiary carbon atoms were dissimilar it was generally the larger of these that was preferentially eliminated. Thus di-tert.-amyl peroxide gave mainly acetone and n-butane with only minor amounts of methylethyl ketone, ethane and propane:



$$C_2H_5\cdot\overset{CH_3}{\underset{CH_3}{C}}\cdot O\cdot O\cdot\overset{CH_3}{\underset{CH_3}{C}}\cdot C_2H_5 \xrightarrow{250^\circ} 2\ C_2H_5\cdot\overset{CH_3}{\underset{CH_3}{C}}\cdot O* \longrightarrow \begin{cases} 2(CH_3)_2C{=}O + 2C_2H_5* \longrightarrow C_4H_{10} \\ \qquad\qquad\qquad\quad \longrightarrow C_3H_8 \\ 2CH_3\cdot CO\cdot C_2H_5 + 2CH_3* \longrightarrow C_2H_6 \end{cases}$$

(R.55)

More recently Raley, Rust and Vaughan (203) have stressed the importance of the reaction conditions in determining the nature of the pyrolysis products. In contrast to Milas, who used packed tubes, these workers have used large diameter, unpacked vessels and found that under these conditions interaction between alkyl radicals and ketone molecules became important. In the decomposition of di-tert.-butyl peroxide at 225°, besides acetone and ethane, significant amounts of methylethyl ketone and higher homologues and methane were isolated. The products were accounted for by initial substitutive attack of the methyl radical on the first formed ketone:

$$CH_3* + CH_3.CO.CH_3 \longrightarrow CH_4 + *CH_2.CO.CH_3 \qquad (R.56)$$

$$CH_3* + *CH_2.CO.CH_3 \longrightarrow CH_3.CH_2.CO.CH_3 \qquad (R.57)$$

In kinetic studies of the decomposition of this class of peroxide Raley, Rust and Vaughan (203) showed that the vapour phase decomposition of di-tert.-butyl peroxide at 140-160° was a homogeneous, first order, non-chain reaction, and that of di-tert.-amyl peroxide at 130-150° was homogeneous and approximately first order. It was further shown (204) that liquid phase decomposition of di-tert.-butyl peroxide in such solvents as iso-propyl benzene, tert.-butyl benzene and tri-n-butylamine was substantailly a first order reaction. The rate determining step was regarded as the unimolecular scission of the -0-0- peroxide bond:

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O.* \qquad (R.58)$$

The existence of tert.-alkoxy radicals was demonstrated by the formation of tert.-butanol when di-tert.-butyl peroxide decomposed in the above named solvents (203, 204) (R.59) (vid. the author's own work p. 110). The presence of alkyl radicals as intermediates was shown by the isolation, from the decomposition of the peroxide in the presence of nitric oxide, of formaldoxime, formed by interaction of methyl radicals and nitric oxide (R.60):

$$(CH_3)_3C.O.* + HR \longrightarrow (CH_3)_3C.OH + R* \qquad (R.59)$$

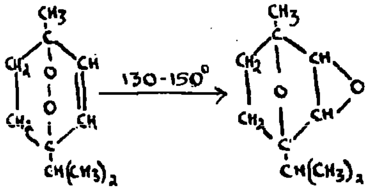
$$(CH_3* + NO \longrightarrow H_2C = NOH \qquad (R.60)$$

(6) TRANSANNULAR PEROXIDES.- The transannular peroxides

are best considered as a separate class since the reactivity encountered in their decomposition shows marked differences from that of the peroxides already considered, in which the intermediate formation of free radicals plays an important part. The characteristics of this group, together with the variations in reactivity within the group itself, are shown by the following account of the decomposition reactions of representative examples.

(1) Ascaridole (LI).-When heated alone to 130-150° ascaridole decomposes violently with a sudden rise in temperature to ca. 250° and the evolution of combustible gasses consisting chiefly of propane (218). A controlled decomposition has been effected by heating the peroxide at 130-150° in inert solvents such as cymene (182, 183) and xylene (121). The ascaridole isomerises into the dioxide (LXVIII), but the mechanism of this apparently simple reaction remains uncertain:

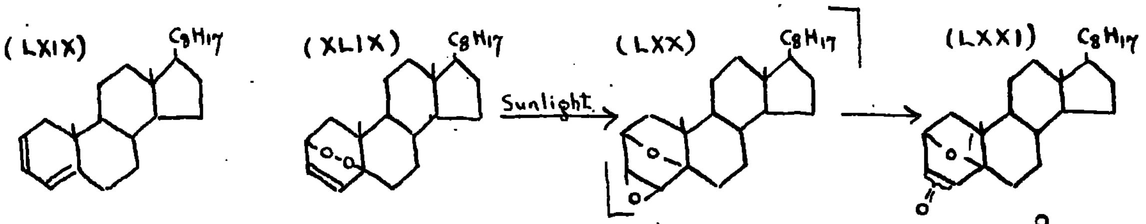
(LI)



(LXVIII) (R.61)

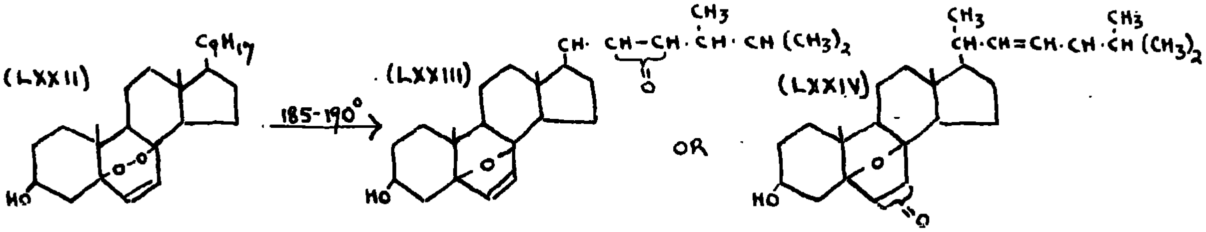
(2) Sterol Peroxides.- The peroxides, of which 2:4-cholestadiene peroxide (XLIX) and ergosterol peroxide (LXXII) are typical, undergo rearrangements into an oxido-ketone when heated or photochemically irradiated (21).

2:4-cholestadiene peroxide, on irradiation with sunlight, gives the oxido-ketone (LXXI) (20, 41). The same oxido-ketone is formed when 2:4-cholestadiene (LXIX) is oxidised with molecular oxygen in sunlight (225, 226). The dioxide (LXX) has been suggested as an intermediate in the isomerisation.



(R.62)

Ergosterol peroxide (LXXII) when heated at 185-190° isomerises into a hydroxy oxido-ketone (159, 263). Two possible structures (LXXIII) and(LXXIV) have been proposed for the isomer, (LXXIII) being preferred since the product failed to give 1:2-dimethyl-butryaldehyde on ozonolysis (113). This aldehyde would be an expected product of the ozonolysis of the double bond in the C_8 side chain in (LXXIV).



(3) Transannular peroxides of anthracene and naphthacene derivatives.-

A notable feature of these peroxides is the considerable variation in their ease and degree of dissociation into the parent hydrocarbon and oxygen. Quantitative studies of the extent of thermal dissociation on thermal treatment have been carried out, particularly by Moureu, Dufraisse and co-workers (21, 61). The results demonstrate that the dissociability of the peroxides is greatly influenced by the nature of the substituents in the meso positions of the anthracene and naphthacene nuclei. Findings with representative peroxides given in Tables (2) and (3) indicate that only in the cases of 9:10-diaryl-anthracene and 5:6:11:12-tetraarylnaphthacene peroxides does the dissociation approach 100%, as measured by the yields of oxygen liberated.

Of particular note is 1:4-dimethoxy-9:10-diphenyl-anthracene peroxide which undergoes quantitative dissociation in a few minutes at 80°(72). Replacement of one aryl group by an alkyl or hydrogen results in greatly reduced dissociability and replacement of two aryl groups gives non-dissociating peroxides.

Bergmann and McLean (21) believe that all the peroxides undergo thermal dissociation but that in the case of the peroxides with unsubstituted or alkyl substituted <u>meso</u> positions the liberated oxygen is used in further oxidation of the molecule; e.g. anthracene peroxide yields anthraquinone on heating.

TABLE (2)

Dissociation of 9:10-Transannular Peroxides of Anthracene Derivatives.

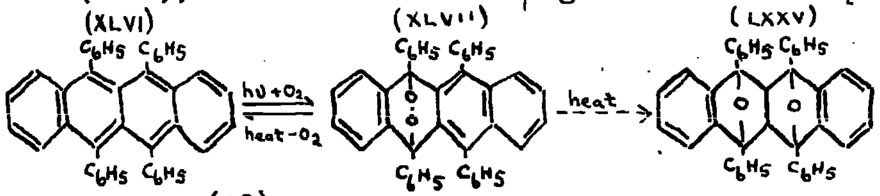
Peroxide of		% O_2 Liberated	Reference
	Anthracene	0	(65-67).
9:10-Dimethyl	"	0	(261, 262).
9-Phenyl	"	12	(70, 71).
9-Phenyl-10-methyl	"	20	(260).
9:10-Diphenyl	"	96	(63, 64).
1:4-Dimethoxy-9:10-Diphenyl	"	98	(72).

TABLE (3)

Dissociation of 6:11 Transannular Peroxides of Naphthacene Derivatives.

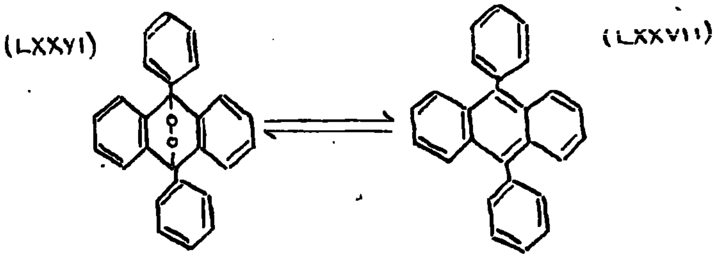
Peroxide of		% O_2 Liberated	Reference
	Naphthacene	0	(68).
6:11-Diphenyl	"	0	(69).
5:6:11-Triphenyl	"	15	(62).
5:6:11:12-Tetraphenyl (Rubrene)	"	80	(177,178).

The comparatively lower yield of oxygen obtained from the rubrene type of peroxide (Table (3)) has been attributed by Bergmann and McLean (21) to a partial isomerisation of the peroxide into a stable dioxide (LXXV), a reaction not occurring with anthracene peroxides:



(R.64)

Gee (98) asserts that the different stabilities of the various peroxides are dependent upon the magnitudes of the increased resonance energies of the hydrocarbons relative to those of the peroxides. In the case of 9:10-diphenylanthracene and its peroxide:



(R.65)

Gee has calculated that there is a gain in resonance energy of 43 k.cal.

in passing from the peroxide (LXXVI), with its four independently resonating systems, to the hydrocarbon (LXXVII) with its single resonating unit. Consequently the heat of dissociation of (R.65) has the very low value of 15 k.cal. That this mode of decomposition is the most facile is readily understandable on the basis of these figures. The difference in resonance energy between anthracene and its peroxide will be much lower due to the absence of aryl substituents in the meso positions and the consequent decrease in the number of resonating structures; the heat of dissociation into oxygen and hydrocarbon will thus have the much higher value of 31 k.cal. These considerations provide a theoretical basis for the observed fact that anthracene peroxide decomposes by an alternative course.

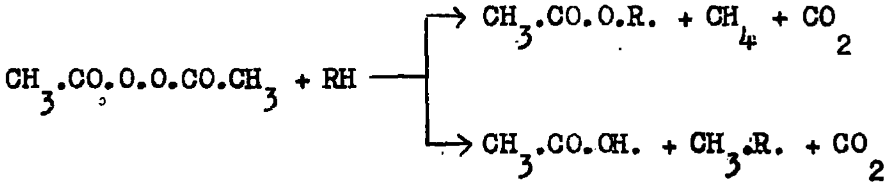
DI-ACYL PEROXIDES.- The best known and most frequently studied peroxide of this group is diacetyl peroxide. The researches of Walker and Wild on the thermal and photochemical decomposition of di-acetyl peroxide have shown that under favourable experimental conditions the reaction results in the formation of carbon dioxide and ethane according to (R.66):

$$\mathrm{CH_3.CO.O.O.CO.CH_3} \longrightarrow \mathrm{2CO_2 + C_2H_6} \qquad \text{(R.66)}$$

Reaction(R.66) is most nearly obeyed when the peroxide is decomposed, (a) by ultra-violet light irradiation of the solid at 16-18°(247) and (b) in the vapour phase at 100°(247). The reaction proceeds, probably, by initial formation of acetate radicals which decompose further into carbon dioxide and methyl radicals, the latter dimerising to ethane:

$$\mathrm{(CH_3).CO.O)_2} \longrightarrow \mathrm{2CH_3.CO.\overset{*}{O}} \longrightarrow \mathrm{2CO_2} + 2\overset{*}{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{C_2H_6} \qquad \text{(R.67)}$$

Under less favourable conditions, for example when the peroxide is heated in the liquid phase at 30-90°(245-246), the major products, apart from carbon dioxide, is methane, and only relatively small amounts of ethane arise. The formation of methane and the existence of large yields of gum-like material isolated under these conditions was attributed to reactions (R.68) and (R.69) involving the peroxide (or radicals derived from it) and certain of the decomposition products (RH):



$$CH_3.CO.O.O.CO.CH_3 + RH \longrightarrow CH_3.CO.O.R. + CH_4 + CO_2 \qquad (R.68)$$

$$CH_3.CO.O.O.CO.CH_3 + RH \longrightarrow CH_3.CO.OH. + CH_3.R. + CO_2 \qquad (R.69)$$

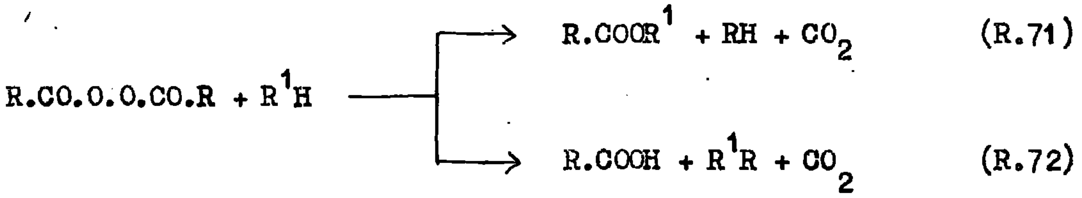
DI-AROYL PEROXIDES.- The considerable body of work that has been published on the thermal and photochemical decomposition of benzoyl peroxide, which is typical of this group, is both confusing and conflicting. An analogy with the decomposition of diacetyl peroxide is that of benzoyl peroxide to give under favourable conditions, carbon dioxide and diphenyl in yields approaching those required by reaction (R.70):

$$C_6H_5.CO.O.O.CO.C_6H_5 \longrightarrow C_6H_5.C_6H_5 + 2CO_2 \qquad (R.70)$$

Reaction conditions favouring this mode of decomposition include: (a) ultra-violet light irradiation (92), (b) pyrolysis alone (91, 207), or in the presence of certain catalysts (100).

That this is not the only reaction has been shown by many workers. Brodie (38, 39) found that the peroxide, when decomposed in sand at 85°, gave only one mol. of carbon dioxide per mol. of peroxide and not two as required by (R.70), a result that has been confirmed by

Gellissen and Hermans (100). Small amounts of benzene were formed, and benzoic acid was also a major product under certain conditions (74, 75). These results, taken in conjunction with the results of peroxide decomposition in solvents (<u>vid</u>.p. 52), suggest that reactions (R.71) and (R.72) may also be significant under certain conditions.



$$R.CO.O.O.CO.R + R^1H \longrightarrow R.COOR^1 + RH + CO_2 \qquad (R.71)$$

$$R.CO.O.O.CO.R + R^1H \longrightarrow R.COOH + R^1R + CO_2 \qquad (R.72)$$

SECTION (4).

THE REACTION OF ORGANIC PEROXIDES WITH OLEFINS AND OLEFINIC COMPOUNDS.

This section is the one most closely connected with the present author's contribution to organic peroxide reactivity. Little detailed work has been devoted to the reaction of organic peroxides with the various classes of conjugated and unconjugated olefins despite the extreme importance of these reactions. They must undoubtedly be involved in many processes of technological importance, for example the oxidative chain scission of natural and synthetic elastomers, peroxide vulcanisation of rubbers, the drying of paints, and the peroxide-catalysed polymerisation of vinylic olefins, which is the basis of the modern plastics and synthetic rubber industries. Only in the latter case has research been conducted on a scale appropriate to the importance of the subject.

The following is an account of the major contributions which have been made in this field.

Reaction of Benzoyl Peroxide with Olefins.- The ability of benzoyl peroxide to react with simple olefins was demonstrated by Lippmann in 1884 (107, 158) who reacted 2-pentene with the peroxide at 100°, obtaining definite reaction products, the correct identification of which is rendered doubtful by recent work.

(1) Cyclohexene.- Systematic investigations of benzoyl peroxide/olefin reactions are singularly lacking. The only reaction which has been studied in detail is that between benzoyl peroxide and cyclohexene

(83, 123).

Farmer and Michael (83) reacted the peroxide with a large excess of *cyclo*hexene at 140°. The products isolated and identified included carbon dioxide*, benzoic acid*, benzene, $\Delta^{2'}$-*cyclo*hexenyl benzoate* (LXXVIII), cyclohexyl benzoate* (LXXIX), $\Delta^{2'}$-*cyclo*hexenyl-Δ^{2}-*cyclo*hexene* (LXXX) and phenyl *cyclo*hexene (LXXXI). Higher boiling products present in small amounts included the benzoic esters of saturated and unsaturated C_{12} alcohols, and C_{18} hydrocarbons of uncertain composition. The major products are asterisked. Hermanns and van Eyk (123) conducting the reaction at 83°, obtained almost identical results. The latter investigators correlated the amount of peroxide decomposed with the yields of various products which together accounted for almost 100% of the peroxide. They found per mol. of peroxide: CO_2, 0.31 mols; $C_6H_5.COOH$, 0.31 mols.; $C_6H_5.COO-$ as esters, 1.35 equivalents (Total = 1.97 $C_6H_5.COO-$ groups).

Both groups of workers suggested the initial reaction to be the homolytic decomposition of the peroxide to give phenyl and benzoate radicals, a mechanism originally advanced by Hey and Waters (125):

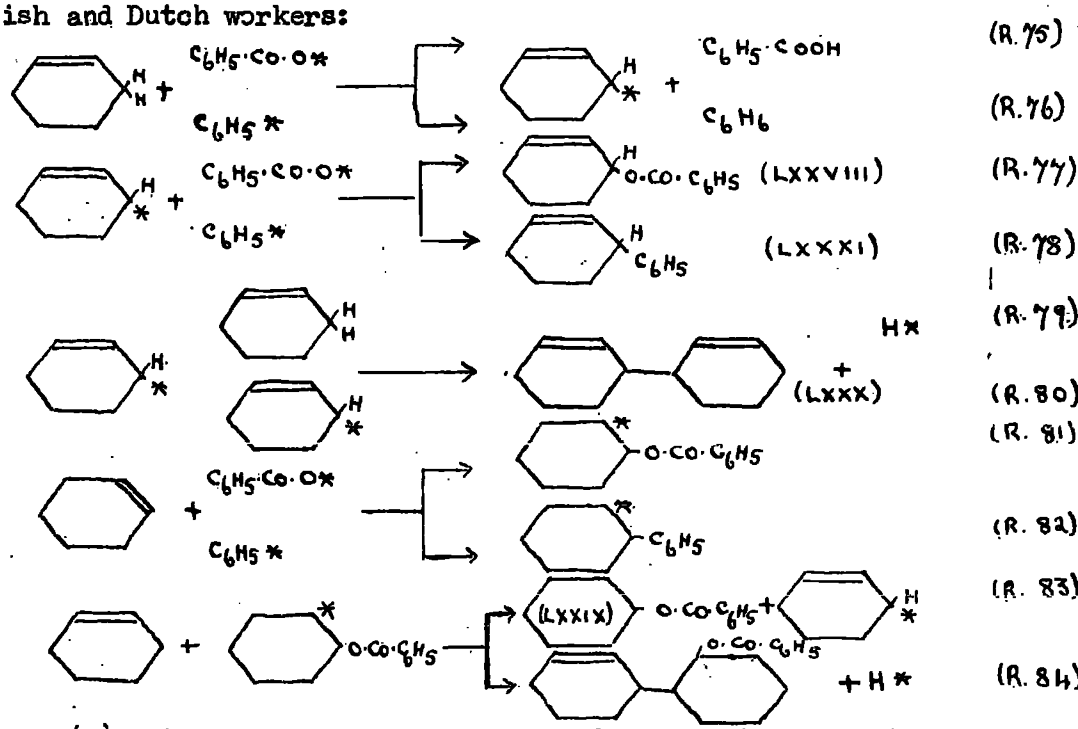
$$C_6H_5.CO.O.O.CO.C_6H_5 \longrightarrow 2C_6H_5.CO.O* \qquad (R.73)$$

$$C_6H_5.CO.O* \longrightarrow C_6H_5* + CO_2 \qquad (R.74)$$

The phenyl and benzoate radicals have two reactive centres to attack in the olefin molecule $R-CH_2-CH=CH-R^1$: (a) the α-CH_2 group, the lability of whose hydrogen atoms has been abundantly demonstrated (*vid*.p.5 *et seq*.), and (b) the double bond with its high additive reactivity.

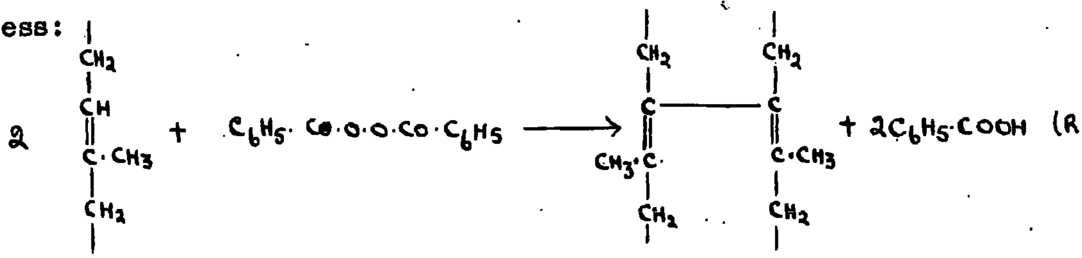
It was concluded from the character and quantitative proportions of the major products (a) that the peroxide decomposed to give mainly benzoate radicals (R.73) with only smaller amounts of phenyl radicals, (b) that these radicals reacted mainly with the double bond of the olefin, although considerable reaction also occurred at the α -CH_2 groups, (c) that the reaction resulted in a considerable degree of C-C linking of the olefin molecules at the α -CH_2 positions, as evidenced by the large yields of <u>cyclohexenyl-cyclohexene</u> (R.79-80).

The following free radical mechanism was advanced by both the English and Dutch workers:



(2) <u>Rubber Hydrocarbon</u>.- The above results are of value in interpreting the vulcanisation that occurs when rubber is heated with benzoyl peroxide. It is now well established (77, 97) that vulcanisation results from cross-linking of the isoprene $(-CH_2.\overset{CH_3}{C}{=}CH-CH_2-)$ units in the rubber molecules. With sulphur as vulcanising agent the cross-linkages consist probably of mono- and polysulphide groups, -C-S-C- and $>C-(S)_n-C-$ (24, 84, 180).

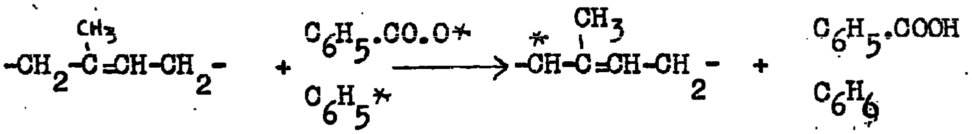
Ostromislenski (187, 188) was the first to discover that rubber was vulcanised when heated with benzoyl peroxide at 140°. Van Rossem and co-workers (214) showed that benzoic acid appeared during the reaction and found that some of the benzoate groups became united with the rubber. Van Rossem attributed the vulcanisation to dehydrogenation and -C-C- cross-linking of the rubber, benzoic acid being formed in the process:



(R.85)

(N.B., the abstracted hydrogen atoms were chosen arbitrarily)

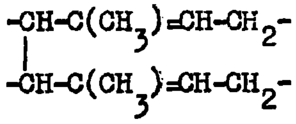
On the basis of the work with benzoyl peroxide and cyclohexene Farmer and Michael (83) advanced the view that peroxide vulcanisation of rubber was effected by attack of benzoate and phenyl radicals at the α-CH_2 groups of the isoprene units:



$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}- \;+\; \begin{matrix}\mathrm{C_6H_5.CO.O}^*\\ \mathrm{C_6H_5}^*\end{matrix} \longrightarrow \overset{*}{-\mathrm{CH}}-\overset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}- \;+\; \begin{matrix}\mathrm{C_6H_5.COOH}\\ \mathrm{C_6H_6}\end{matrix} \qquad (R.86)$$

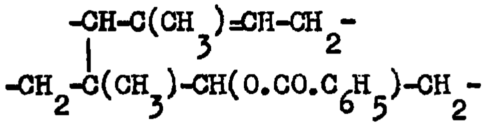
(LXXXII)

The radical (LXXXII) could by attack at the α-CH_2 of another isoprene unit give a cross-linked structure of the type (LXXXIII). Benzoate (and to a minor extent phenyl) radicals could also give cross-linked structures, e.g. (LXXXIV) by additive reactions analogous to (R.81 and R.82). Alternatively, structures such as (LXXXV) may result from substitutive attack of benzoate radicals at α-CH_2 groups (cf.R.77) but this, unlike (LXXXII) and (LXXXIII), will not contribute to cross-linking of the polyisoprene chains and therefore will not be significant in effecting vulcanisation.



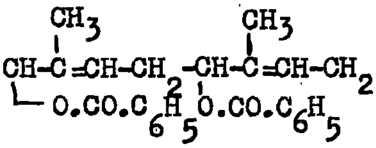
$$\begin{array}{l} -CH-C(CH_3)=CH-CH_2- \\ \;\;| \\ -CH-C(CH_3)=CH-CH_2- \end{array}$$

(LXXXIII)



$$\begin{array}{l} \qquad -CH-C(CH_3)=CH-CH_2- \\ \qquad\;\;| \\ -CH_2-C(CH_3)-CH(O.CO.C_6H_5)-CH_2- \end{array}$$

(LXXXIV)



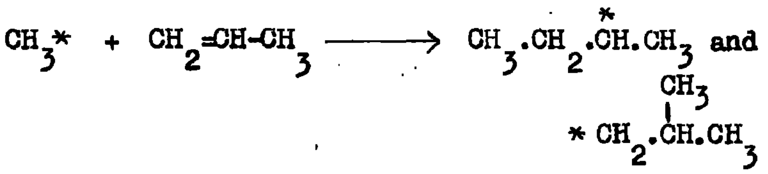
$$\begin{array}{l} \quad CH_3 \qquad\qquad\quad CH_3 \\ \quad\;| \qquad\qquad\qquad\;| \\ CH-C=CH-CH_2-CH-C=CH-CH_2 \\ \llcorner O.CO.C_6H_5\;\; O.CO.C_6H_5 \end{array}$$

(LXXXV)

The above hypothesis has recently been extended and the whole field of peroxide vulcanisation reviewed by Mark (et. al) (2, 3).

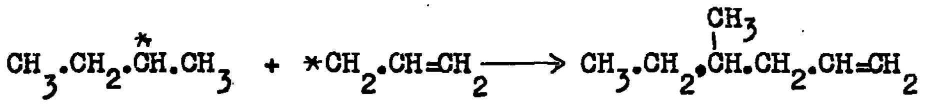
Reaction of Di-tert.-Butyl Peroxide with Olefins.- Rust, Seubold and Vaughan (215, 240) have recently studied the vapour phase reaction at 235° of di-tert.-butyl and di-tert.-amyl peroxides with the olefins, ethylene, propylene, 2-butene and iso-butylene. With propylene and di-tert.-butyl peroxide the products included, in addition to acetone, a mixture of paraffins and olefins varying from C_4 (butanes and butenes) to C_{10} (dimethyl-octanes). The products were accounted for by the initial reaction of methyl radicals, formed by decomposition of the peroxide, at either end of the double bond in the olefin. Representative reactions of this type are indicated below:

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2CH_3^{*} + 2(CH_3)_2C=O \quad (R.87)$$



$$CH_3^* + CH_2{=}CH{-}CH_3 \longrightarrow CH_3.CH_2.\overset{*}{C}H.CH_3 \text{ and } {}^*CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_3 \qquad (R.88)$$

$$CH_3.CH_2.\overset{*}{C}H.CH_3 + \begin{matrix} CH_3^* \\ CH_3.CH{=}CH_2 \end{matrix} \begin{matrix} \longrightarrow CH_3.CH_2.CH(CH_3)_2 & (R.89) \\ \longrightarrow CH_3.CH_2.CH_2.CH_3 + {}^*CH_2.CH{=}CH_2 & (R.90) \end{matrix}$$

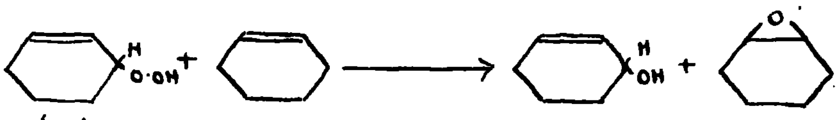


$$CH_3.CH_2.\overset{*}{C}H.CH_3 + {}^*CH_2.CH{=}CH_2 \longrightarrow CH_3.CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_2.CH{=}CH_2 \qquad (R.91)$$

<u>etc.</u>

As will be shown in the present author's contribution, this mode of reaction differs fundementally from that observed in the liquid-phase decomposition of di-alkyl-peroxides in olefins at the much lower temperature of 140°.

Reaction of Olefinic Hydroperoxides with Olefins.- Although, as stressed previously, the nature of olefin-hydroperoxide/olefin reactions is of importance in elucidating the reactions occurring in the later stages of olefin autoxidation, no detailed work has been reported on any such investigations. The only example given in the literature is that of Farmer and Sundralingam (85) who reacted *cyclo*hexenyl-3-hydroperoxide (IV) with *cyclo*hexene at 100° and obtained a small yield of *cyclo*hexen-3-ol and traces of epoxy*cyclo*hexane, together with high boiling oxygenated material. Insufficient work has been done to indicate any definite mechanism for the reaction, and (R.92) must be regarded as an over-simplification of the processes involved.



(IV)

(R.92)

THE PEROXIDE EFFECT.

In 1933 Kharasch and Mayo (146, 150, 151) found that in the presence of peroxides or oxygen, hydrogen bromide added to allyl bromide to give 1:3-dibromopropropane, contrary to the normal addition rule of Markownikow. Only when highly purified allylbromide was used in the absence of oxygen was the normal product, 1:2-dibromopropane, obtained. This reversal of normal addition has been termed the Peroxide Effect.

$$CH_2{=}CH.CH_2Br \;+\; HBr \xrightarrow{\text{Peroxides present.}} CH_2Br.CH_2.CH_2.Br \qquad (R.93)$$

$$CH_2{=}CH.CH_2Br \;+\; HBr \xrightarrow[\text{Peroxides absent.}]{} CH_3.CHBr.CH_2.Br \qquad (R.94)$$

Similar reversals of the direction of addition of olefins, in the presence of peroxides, have been reported to occur with mercaptans (136), thioacids (60), bisulphites (149) and halogenated hydrocarbons (147, 155). The peroxide effect does not apply to the additions of HF, HCl and HI to olefins.

Although the underlying principles are not fully understood it is believed that this effect is due to the ability of peroxide to initiate, by formation of bromine atoms (or RS*, R.CO.S* radicals etc.), a radical chain reaction as represented by (R.95 - R.97) (125, 142-144, 163). The radical $X{-}CH_2.\overset{R}{C}H{*}$ (X = Br*, RS* etc.) is believed to be more stable than $*CH_2.\overset{R}{C}H.X$ owing to the stabilising effect of the conjugated or hyperconjugated group R (162).

$$HBr \;+\; P{*} \longrightarrow HP \;+\; Br{*} \qquad (R.95)$$

$$Br{*} \;+\; CH_2 = CH.R \longrightarrow Br.CH_2 - \overset{*}{C}H.R \qquad (R.96)$$

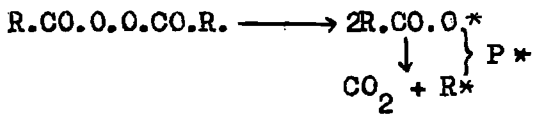
$$Br.CH_2.\overset{*}{C}H.R \ + \ HBr \longrightarrow Br.CH_2.CH_2.R \ + \ Br^{*} - \qquad (R.97)$$

(N.B. P* represents a peroxide radical or a radical formed by homolytic decomposition of a peroxide).

<u>Peroxide-initiated Vinyl Polymerisation</u>.- Vinyl olefins of the general structure $CH_2{=}\overset{R}{C}{-}X$ (R = H, CH_3; X = C_6H_5, $-O.CO.CH_3$, $-Cl$, $-CH_2.O.CO.CH_3$, CN and similar polar groups) may be polymerised by organic peroxides to give macromolecules of industrial importance. The organic peroxides commonly used are diaroyl- and diacyl peroxides (e.g. benzoyl peroxide), but recently dialkyl peroxides and alkyl hydroperoxides have been shown to be effective catalysts (195, 213). The polymerisation may be conducted in either a single or double phase system; the latter is termed <u>emulsion polymerisation</u>. The process may be either simple polymerisation involving a single monomer, or <u>co-polymerisation</u> involving two monomers, one of which may be a conjugated diene. The structural units in the vinyl polymers occur generally in a head to tail sequence, $-CH_2-\overset{X}{C}H-CH_2-\overset{X}{C}H-$, although in at least one instance, that of vinyl acetate polymerisation (94), a small percentage of head to head addition also takes place.

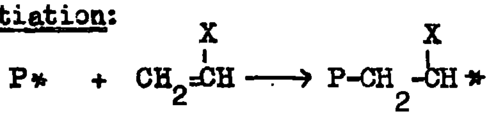
The concept, that addition polymerisations of this type proceed by a chain reaction involving successive additions of monomer units to an active free radical intermediates, is now widely accepted (93, 160, 170, 221, 229). The free radical chain reaction comprises the characteristic steps of activation, propagation, chain transfer, and termination (1, 197).

<u>Role of the Peroxide</u>.- Various investigators (137, 185,186) have proposed that organic peroxides initiate and catalyse vinyl polymerisation by their formation of active free radicals on thermal decomposition. The radical fragments P* (R.98 - R.99) adds to one end of the double bond of the vinyl monomer; it is generally assumed (94) that the radical $R.CH_2.\overset{X}{C}H*$ is more stable than $*CH_2.\overset{X}{C}H.P$ and consequently that attack by P* takes place at the <u>unsubstituted</u> carbon atom of the double bond (R.100) (cf. the "Peroxide Effect", p. 45)



$$R.CO.O.O.CO.R. \longrightarrow 2R.CO.O* \quad (R.98)$$
$$\downarrow \qquad \Big\} P*$$
$$CO_2 + R* \quad (R.99)$$

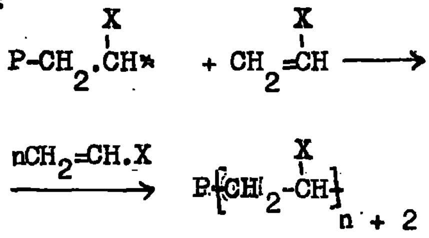
<u>Initiation:</u>



$$P* + CH_2{=}\overset{X}{C}H \longrightarrow P\text{-}CH_2\text{-}\overset{X}{C}H* \qquad (R.100)$$

The radical chains are <u>propagated</u> by the regular step-wise addition of monomer units to the growing polyvinyl radical in such a way that a new free radical is formed at each stage (R.101).

<u>Propagation:</u>



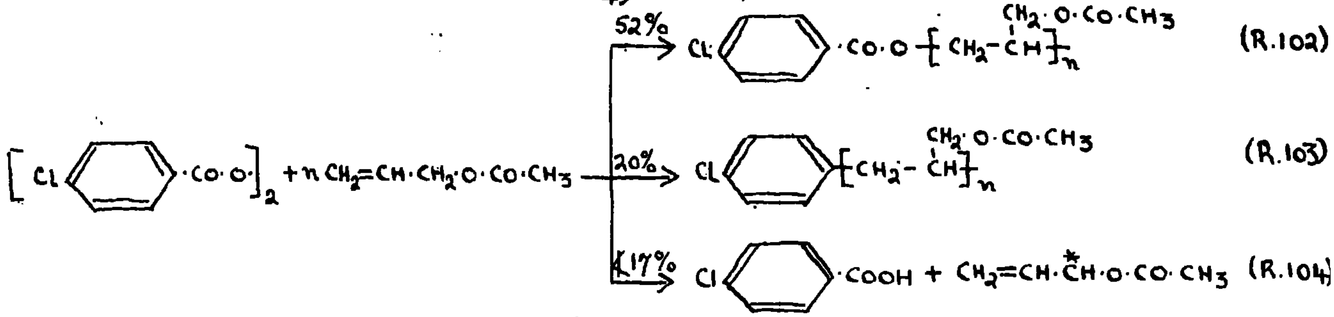
$$P\text{-}CH_2.\overset{X}{C}H* + CH_2{=}\overset{X}{C}H \longrightarrow P.CH_2.\overset{X}{C}H.CH_2.\overset{X}{C}H*$$
$$\xrightarrow{nCH_2=CH.X} P\{CH_2\text{-}\overset{X}{C}H\}_{n+2} \qquad (R.101)$$

The growing chains may be <u>terminated</u> in a number of ways the mechanisms of which are at present imperfectly understood. These may include: (i) chain transfer involving interaction between the polymer radicals and a monomer, solvent or previously formed polymer molecule, (ii) reaction of two polymer radicals with each other or of a polymer radical with a simple radical resulting either in radical linking, or in disproportionation to two stable molecules.

It is beyond the scope of the present thesis to give a more detailed discussion of the propagation and termination reactions and other important aspects such as the kinetics of polymerisation (1, 13, 200, 202) and co-polymerisation (171) and the mechanism of emulsion-polymerisation.

Fate of the Peroxide Fragments.- According to the proposed initiation reactions (R.98 - R.99) and (R.100) the peroxide radicals P* should become chemically united with the polymer. This has been established by a number of methods including chemical analysis (13, 14, 201, 202), radioactivity measurements (196), ultra-violet (138) and infra-red (197) analysis of the polymer.

In the chemical analysis method "marked" peroxides, usually halogenated benzoyl peroxides, are used to initiate the polymerisation, and the polymer is then analysed for halogen. For example, Bartlett and Altschul (13) polymerised allyl acetate with p-chloro-benzoyl peroxide and analysed the purified polymer for chlorine. Of the total halogen, 72.5% was bound to the polymer and of this ca.52% was present as p-chloro-benzoate groups and ca.20% as p-chloro-phenyl groups. These results provide further evidence that both aryloxy and aryl radicals act as polymerisation initiators. It is significant that not less than 17% of the decomposed peroxide was isolated as p-chlorobenzoic acid, a result that was attributed to the abstraction of hydrogen atoms from the α-CH_2 groups in the monomer by p-chloro-benzoate radicals (R.104):



Other classes of labile molecules which undergo homolytic decomposition have also been utilised as initiators, e.g. tetraphenylsuccinonitrile (222), phenylazotriphenylmethane (220) and p-bromobenzenediazohydroxide (199). Inorganic catalysts such as boron fluoride and stannic chloride can also initiate vinyl-polymerisation but these probably act by a polar mechanism (170).

Industrial Applications.- The modern plastics and synthetic rubber industries are both based on the polymerisation of vinyl monomers as described above.

Although polymers of a single vinyl monomer (e.g. vinyl chloride and methyl methacrylate) have found useful applications as plastics, the general industrial method is to co-polymerise two suitable monomers, one of which may be a conjugated dieme. The co-polymers of butadiene with styrene, acrylonitrile and isobutylene respectively are technically important as synthetic rubbers.

SECTION (5).

DECOMPOSITION OF PEROXIDES IN NON-OLEFINIC ORGANIC SOLVENTS.

1. DECOMPOSITION OF DI-ACYL PEROXIDES.- Kharasch and his collaborators have studied the thermal decomposition of diacetyl peroxide in a variety of solvents including ketones (152), alkyl benzenes (154), organic acids (141, 145) and their anhydrides (141), chlorides (148) and esters (148, 153). The peroxide decomposed to give methane and carbon dioxide with smaller amounts of methyl acetate. Ethane was formed in only a few solvents (e.g. methyl phenyl acetate) and then only in small amounts. Kharasch suggested that the methane resulted from the abstraction of hydrogen atoms from the solvent (R.106) by the highly reactive methyl radicals formed by the initial homolytic decomposition of the peroxide (R.105).

$$CH_3.CO.O.O.CO.CH_3 \longrightarrow CH_3* + CO_2 + CH_3.COO* \tag{R.105}$$

$$CH_3* + HR \longrightarrow CH_4 + R*, \tag{R.106}$$

The methyl acetate may have resulted in a number of ways as represented in (R.107 - R.109). In all cases the number of mols. of carbon dioxide formed was approximately equal to the sum of the number of mols. of methane and methyl acetate, in agreement with the postulated mechanism.

$$2CH_3.COO* \longrightarrow CH_3.CO.O.CH_3 + CO_2 \tag{R.107}$$

$$CH_3.COO* + (CH_3.COO)_2 \longrightarrow CH_3.COO.CH_3 + CO_2 + CH_3.COO* \tag{R.108}$$

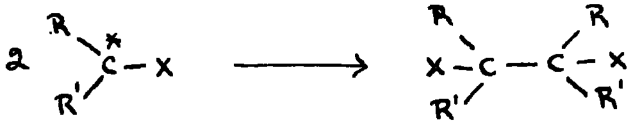
$$CH_3* + (CH_3.COO)_2 \longrightarrow CH_3.CO.O.CH_3 + CH_3.COO* \tag{R.109}$$

The methyl radical is highly selective in its action, attacking only the hydrogen atoms on the carbon atom alpha to the characteristic groupings ($X = COOH, COOR, >C = 0, C_6H_6$ etc.) of the solvents ($R,R^1 : CH\text{-}X$, for ketones, $X = >C = 0$, $R,R^1 : CH\text{-}X\text{-}CH: R,R^1$) as represented in (R.110):

(R.110)

(R,R^1 = H, Alkyl, Aryl, Chloralkyl etc.)

The solvent radical $R,R^1 : \overset{*}{C}\text{-}X$ is then stabilised by dimerisation (R.111). It was shown that in all decompositions "dimers"



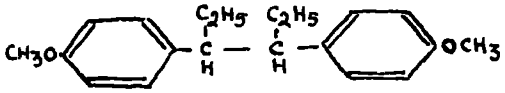
(R.111)

resulting from the solvent according to (R.111) were well represented, being the sole or major non-gaseous products. Thus, acetic acid gave succinic acid (R.112) and *iso*propyl benzene gave 2:3-dimethyl-2:3-diphenyl butane (R.113).

$$CH_3.COOH + CH_3^* \longrightarrow CH_4 + {}^*CH_2.COOH \xrightarrow{\text{dimerises}} [-CH_2.COOH]_2 \qquad (R.112)$$

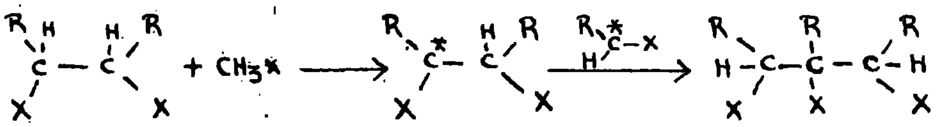
$$C_6H_5.CH(CH_3)_2 + CH_3^* \longrightarrow CH_4 + C_6H_5.\overset{*}{C}(CH_3)_2 \xrightarrow{\text{dimerises}} [C_6H_5.\overset{|}{C}(CH_3)_2]_2 \qquad (R.113)$$

The reactions are of great synthetic importance, being an easy route to succinic and alkyl-substituted succinic acids, 1:4-diketones and substituted dibenzyls. An important instance of the last example is the synthesis of the *meso* and *racemic* forms of hexoestrol dimethyl ether (LXXXVI) a source of the oestrogenic heoestrol - by decomposition of diacetyl peroxide in *p*-methoxy-*n*-propyl benzene.



(LXXXVI)

Those "dimers" possessing α-carbon hydrogen atoms are subject to further attack by CH_3* at the tertiary C-H groups to give "trimers" and higher polymers (R.114). Thus monochloromethyl acetate gives:



(R.114)

α:α¹-dichloro-succinic methyl ester and trichloro-tricarballylic methyl ester in the ratio of ca.2.3:1 based on monomer ester units. The yield of "trimer" is much greater than expected on a statistical basis and the results indicate that the relative concentrations of monomer and "dimer" molecules and radicals are not the major factors governing the final proportions of the various polymers. The determining factor appears to be the reaction of CH_3* with tertiary in preference to secondary C-H bonds, a suggestion in keeping with the weaker bond energy of C-Hγ than of C-Hβ (228).

2. THE DECOMPOSITION OF DIAROYL PEROXIDES.- The decompositions of diaroyl peroxides in the presence of non-olefinic organic solvents have received much attention in the past thirty years (27-30, 100-108, 123, 124, 206, 208, 255-257). As the results are too extensive to be discussed at length only the case of benzoyl peroxide will be considered here.

When high concentrations of benzoyl peroxide are decomposed thermally in benzene the major products are diphenyl, carbon dioxide and benzoic acid, with smaller amounts of phenyl benzoate, terphenyl and quarterphenyl (100). It was assumed that the solvent (R^1H) participates in the reaction and the reaction products were conveniently accounted for by the "R^1H" scheme of Gelissen and Hermans (100) which involved a main reaction (R.115) and a side reaction (R.116). The stoichiometry of the decomposition varies, however, from solvent to solvent. With benzene and other aromatic solvents (R.115) represents the main reaction (100, 101), but with isobutyl alcohol (R.116) becomes the principal course of action (104).

$$C_6H_5.CO.O.O.CO.C_6H_5 + R^1H \begin{cases} \xrightarrow{\text{Main}} C_6H_5.COOH + C_6H_5.R^1 + CO_2 & (R.115) \\ \xrightarrow{\text{Side}} C_6H_5.COO.R^1 + C_6H_6 + CO_2 & (R.116) \end{cases}$$

The participation of the solvent (R^1H) in the reaction has been proved by a number of workers (29, 100, 101, 124, 255, 257). Thus di-p-chlorobenzoyl peroxide in benzene gives 4-chlorodiphenyl and not $4{:}4^1$-dichlorodiphenyl, in agreement with (R.115) (100) and benzoyl peroxide decomposes in nitrobenzene gives 2- and 4-nitrophenyls but no diphenyl (124).

The R^1H scheme of Gelissen and Hermans as given above, although conveniently summarising the different end products possible in these decompositions, does not suggest the precise mechanism whereby these products are formed. A plausible mechanism was first proposed by Hey and Waters (125) and this is now widely accepted. According to these workers the initial reaction involves the homolysis of the peroxide R.CO.O.O.CO.R. to give two types of free radicals R* and R.CO.O* (R.117 - R.118) which by further interaction, either with themselves, with solvent molecules or with previously formed reaction products can give the hydrocarbons, acids and esters actually identified. The following scheme, in which R^1H is a solvent, summarises the initial and secondary reactions which explain the formation of the major reaction products:

$$
\begin{array}{lll}
R.CO.O.O.CO.R \longrightarrow R* + R.CO.O* + CO_2 & & (R.117) \\
R.CO.O* \longrightarrow R* + CO_2 & & (R.118) \\
R* + R^1H & \longrightarrow R.R^1 + H* & (R.119) \\
 & \longrightarrow RH + R^1* & (R.120) \\
R.CO.O* + R^1H & \longrightarrow R.COOH + R^1* & (R.121) \\
 & \longrightarrow R.COOR^1 + H* & (R.123) \\
R^1* + R.COO* \longrightarrow R.COOR^1 & & (R.124) \\
R* + R.R^1 & \longrightarrow R.R''.R^1 + H* & (R.125) \\
 & \longrightarrow RH + R^1R''* & (R.126)
\end{array}
$$

This scheme when applied to the reaction of benzoyl peroxide ($R = C_6H_5$) with benzene ($R^1 = C_6H_5$; $R'' = C_6H_4$) is seen to explain all the reaction products which have been isolated.

In recent years extensive investigations on diaroyl peroxide decomposition in many types of organic solvents have been made from the standpoint of the <u>reaction kinetics</u> rather than the isolation of end products.

It has been well established that both the <u>stoichiometry</u> and the <u>rate</u> of the peroxide decomposition varies widely from solvent to solvent (10, 11, 15, 16, 43). Also, in the same solvent the nature of the decomposition varies in relation to the initial peroxide decomposition (10, 11, 15, 16, 40, 43, 103).

Barnett and Vaughan (10), studying the kinetics of benzoyl peroxide decomposition in benzene at 80°, found that at infinite dilution the peroxide decomposes unimolecularly to give mainly diphenyl and carbon dioxide (R.128), the rate determining step being represented by (R.127). This reaction is comparable with that occurring when the pure peroxide is decomposed in the absence of solvents (<u>vid</u>. p. 37).

$$C_6H_5.CO.O.O.CO.C_6H_5 \longrightarrow 2C_6H_5.CO.O^* \qquad (R.127)$$

$$C_6H_5.CO.O.O.CO.C_6H_5 \longrightarrow C_6H_5.C_6H_5 + 2CO_2 \qquad (R.128)$$

At all finite concentrations (R.128) is accompanied by a bimolecular reaction, the latter predominating above a certain peroxide concentration. Initially the stoichiometry of this second order reaction is represented by (R.129) but this is gradually superceded with increasing peroxide concentration by a reaction represented by (R.130), which is the main reaction of the "R^1H^2" scheme of Gelissen and Hermans.

$$C_6H_5.CO.O.O.CO.C_6H_5 + C_6H_6 \longrightarrow C_6H_5.COOH + C_6H_5.CO.O.C_6H_5 \qquad (R.129)$$

$$C_6H_5.CO.O.O.CO.C_6H_5 + C_6H_6 \longrightarrow C_6H_5.COOH + CO_2 + C_6H_5.C_6H_5 \qquad (R.130)$$

Similar evidence for simultaneous first and second order decompositions of benzoyl peroxide in various solvents has been adduced by McClure <u>et</u> <u>al</u>.(103), Bartlett and Nozaki (15, 16), and Brown (40).

3. <u>DECOMPOSITION OF DI</u>-tert.-<u>ALKYL PEROXIDES</u>.- As previously stated (vid.p. 31) Raley, Rust, Seubold and Vaughan (203, 204, 215) have recently studied the decomposition of di-<u>tert</u>.-butyl peroxide in various organic solvents including alkyl benzenes, paraffins and tertiary amines. The peroxide decomposes to give large yields of <u>tert</u>.-butanol by abstraction of hydrogen from the solvent by the initially formed <u>tert</u>.-butoxy radical. The resulting solvent radicals are stabilised by dimerisation

For example, the peroxide when decomposed in iso-propyl benzene at 130° gives tert.-butanol and 2:3-dimethyl-2:3-diphenyl butane (LXXXVII). The reaction probably occurs according to (R.131 - R.132).

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \qquad (R,131)$$

$$(CH_3)_3C.O* + CH(CH_3)_2.C_6H_5 \longrightarrow (CH_3)_3.OH + \overset{*}{C}(CH_3)_2.C_6H_5 \xrightarrow{\text{dimerises}}$$

$$C_6H_5.C(CH_3)_2.C(CH_3)_2.C_6H_5 \qquad (R.132)$$

(LXXXVII)

Significant yields of acetone and methane in these decompositions (especially with tert.-butyl benzene as solvent) suggest that the peroxide may in part decompose according to (R.133) the CH_3* radicals then reacting as in (R.134) as proposed by Kharasch et al. (vid.p. 50)

$$(CH_3)_3C.O* \longrightarrow (CH_3)_2C = O + CH_3* \qquad (R.133)$$

$$CH_3* + RH \longrightarrow CH_4 + R* \qquad (R.134)$$

Certain of these results anticipate and confirm the findings of the present author (vid.p. 110).

PART (II).

NEW WORK ON THE REACTIVITIES OF ORGANIC PEROXIDES.

SECTION (I).

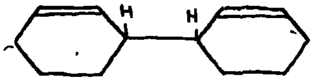
REACTION OF DI-*tert*.-ALKYL PEROXIDES WITH OLEFINS.

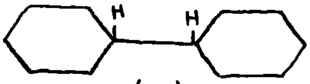
(A). REACTION OF DI-tert.-BUTYL PEROXIDE WITH cycloHEXENE.- The reaction of di-tert.-butyl peroxide with cyclohexene has been studied in detail and the nature and quantitative yields of the various reaction products have been carefully examined. The general experimental technique used in these and subsequent experiments was to react the peroxide and olefin (or other solvent reactant) in Carius tubes at 140° for times varying from 12-48 hours. The reactions were all conducted in the absence of oxygen. In the present instance both the relative proportions of peroxide to olefin and the reaction times were varied and the effects of these variations on the yield and nature of the reaction product determined.

Reaction of di-tert.-butyl peroxide and cyclohexene in the molar ratio of 1:6 for 24 or 48 hours at 140° resulted in complete decomposition of the peroxide, which was converted mainly into tert.-butanol and to a minor extent into acetone. In addition to recovered cyclohexene a mixture of cyclohexene "polymers" was obtained which contained no oxygenated constituents. By fractional distillation of the polymer mixture there were obtained three well defined polymer fractions: (i) a cyclohexene "dimer", $C_{12}H_{18}$; (2) a "trimer" $C_{18}H_{26}$; and (3) a "tetramer" $C_{24}H_{34}$ [4. The remainder of the polymer mixture was an undistillable residue consisting of cyclohexene "polymers" higher than "tetramer".

Detailed Examination of the Polymer Fractions.-

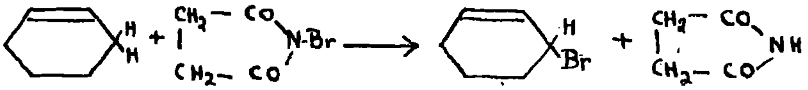
(I) The "Dimer" $C_{12}H_{18}$.- This consisted entirely of the dicyclic-$\Delta^{1:5}$-diolefin, $\Delta^{2'}$-cyclohexenyl-Δ^{2}-cyclohexene (I). The presence of two double bonds per C_{12} unit was confirmed both by iodine value determination (139, 140) and by catalytic micro-hydrogenation. Catalytic reduction of the olefin gave pure di*cyclo*hexyl (II).


(I)


(II)

Bromination of the olefin in chloroform gave almost quantitative yields of a mixture of two (presumably stereoisomeric) *cyclo*hexenyl-*cyclo*hexene tetrabromides, $C_{12}H_{18}Br_4$, which were separated by fractional crystallisation from chloroform into a major product, m.p. 159-160°, and a minor product, m.p. 188-190°. Both of these tetrabromides have been obtained by previous workers (22, 83) by brominating *cyclo*hexenyl-*cyclo*hexene.

Final confirmation of the structure of the "dimer" as (I) was obtained by its synthesis according to the following scheme:

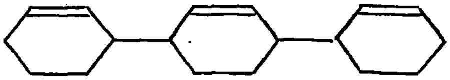

(R.1.)


(R.2.)

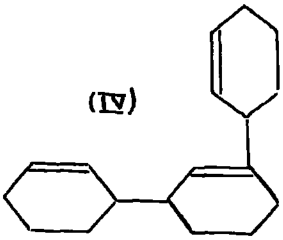
The physical constants of the *cyclo*hexenyl-*cyclo*hexene obtained by synthesis and by reaction of *cyclo*hexene with di-*tert*.-butyl peroxide were in good agreement, and the synthetic product gave the same two tetrabromides as were obtained from the *cyclo*hexene "dimer".

(2). The Trimer $C_{18}H_{26}$.- The "trimeric" fraction consisted of the two isomeric di*cyclo*hexenyl-*cyclo*hexenes (III) and (IV).

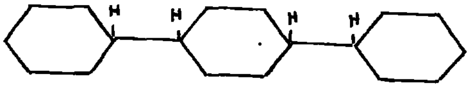
(III)



(IV)



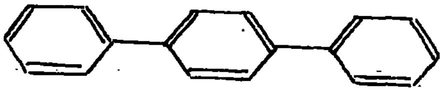
Evidence for the isomer (III) was obtained by catalytic reduction of the "trimer" which gave a reductant ($C_{18}H_{32}$) from which the high melting form of 1:4-di*cyclo*hexyl-*cyclo*hexane (m.p.162-163°) (V) was isolated. The substantial amounts of non-crystallisable di*cyclo*hexyl-*cyclo*hexanes in the reductant indicated the presence of other isomeric forms of the $C_{18}H_{26}$ "trimer".



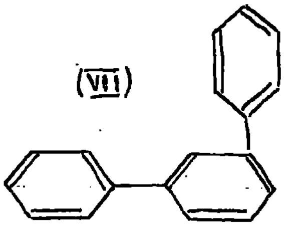
(V)

Selenium dehydrogenation of the "trimer" gave a mixture of 1:4- and 1:3-diphenylbenzenes (VI) and (VII) respectively, confirming the presence of the 1:4- linked *cyclo*hexene "trimer" (III) and establishing the presence of (IV) as one of the major "trimeric" constituents.* Although there was no evidence of any 1:2-diphenylbenzene in the dehydrogenated product, its complete absence was not definitely established.

(VI)



(VII)



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* Although, strictly speaking, the isolation of 1:3-diphenylbenzene establishes only the presence of a 1:3-di*cyclo*hexenyl substituted *cyclo*hexene in the "trimer" and does not indicate the actual positions of the olefinic unsaturation in this olefin, the reaction mechanism described later shows that (IV) is the most plausible structure.

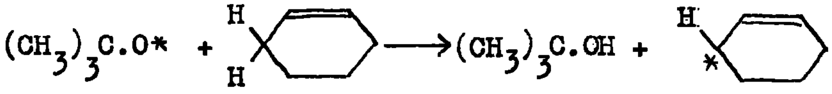
Bromination fo the "trimer" gave a complicated mixture of di*cyclo*hexenyl-*cyclo*hexene hexabromides which were difficult to separate. Three of these were isolated in substantailly pure form, but they were doubtless not the only hexabromides present, and their constitutions could not be established.

(3) *The"Tetramer" $C_{24}H_{34}$.-* The *cyclo*hexene "tetramer" fraction though molecularly homogeneous, consisted of many structural and stereoisomers. No detailed examination of the fraction was undertaken beyond establishing it as a tetracyclic olefin $C_{24}H_{34}$ containing four double bonds per molecule.

Mechanism of the Reaction.- From the experimental findings described above it is seen that di-*tert.*-butyl peroxide when decomposed in *cyclo*hexene is converted almost quantitatively into *tert.*-butanol, and the olefin is partially transformed into a mixture of *cyclo*hexene polymers which retain the original unsaturation of olefin and in which the *new C-C bonds are formed at the α-methylene positions.*

The mechanism advanced to explain these results involves the initial *homolytic* scission of thw O-O bond in the peroxide to give two *tert.*-butoxy radicals (R.3.). The latter are then stabilised by abstraction of labile α-methylene hydrogen atoms from *cyclo*hexene, yielding *tert.*-butanol and a *cyclo*hexenyl radical (R.4):

$$(CH_3)C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O^* \qquad (R.3)$$



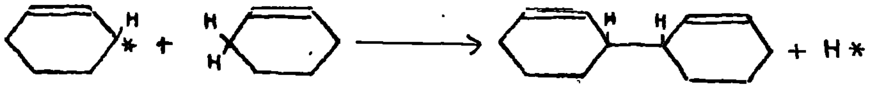
(R.4)

The existence of traces of acetone in these decompositions suggest that the peroxide undergoes, to a minor extent, unimolecular decomposition (R.5) in a manner analogous to the vapour phase pyrolysis of the peroxide in the absence of solvents (vid.p. 29):

$$(CH_3)_3C.O_2C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \longrightarrow 2(CH_3)_2C{=}O + 2CH_3* \qquad (R.5)$$

The cyclohexenyl radicals formed in (R.4) are stabilised either by radical-radical linking reactions (R.6) or by attacking a cyclohexene molecule (at the α-methylene group) by the replacement reaction (R.7), both processes leading to the formation of cyclohexenyl-cyclohexene.

(R.6.)



(R.7.)

$$(CH_3)_3C.O* \; + \; H* \longrightarrow (CH_3)_3C.OH \qquad (R.8)$$

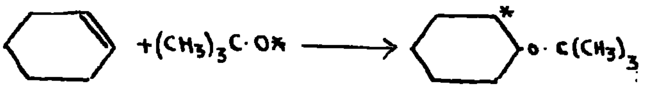
Chemically the two reactions (R.6) and (R.7) are indistinguishable and their relative importance can be estimated only by kinetic methods. The two major factors governing the relative rates (and thus the relative importance) of these two reactions will be the collision frequency factor, A, and theenergy of activation, E, as given in the Arrhenius equation (E.1) :

$$\text{Rate} = A\,e^{-E/RT} \qquad (E.1.)$$

On the one hand the collision frequency factor of (R.7) will be much greater than that of (R.6) because of the high concentration of *cyclo*hexene molecules compared with *cyclo*hexenyl radicals, and on this basis (R.7) will be the most favoured reaction. On the other hand the energy of activation of (R.6) is undoubtedly much lower than that of (R.7) and this factor would favour the radical-linking process.

Thermochemically the reaction sequences involved in the above mechanism are all energetically possible.. Using the latest bond energies reported in the literature* the two alternatives processes (R.3)→(R.4)→(R.6) and (R.3)⟶(R.4)⟶(R.7)⟶ (R.8) leading to the formation of *tert.*-butanol and *cyclo*hexenyl-*cyclo*hexene are found to be exothermic to the extent of *ca.*54 k.cal.

The absence of any oxygenated constituents in the *cyclo*hexene polymers demonstrates the highly specific reactivity of *tert.*-butoxy radicals, which are obviously limited in their reactions to hydrogen abstraction from the olefinic α-methylene groups and which show *no additive* reactivity towards the double bonds (R.9) or *substitutive* reactivity at the α-methylene groups (R.10) :



(R.9)

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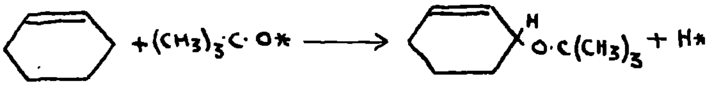
* The following are the bond energies used in the above calculations:

D_{O-O} (for $(CH_3)_3C.O.O.C(CH_3)_3$ = 39 k.cal. (203)

D_{C-H} (for α-CH_2 group in *cyclo*hexene) = 80 k.cal. This is computed from D_{C-H} = 99 for a paraffin hydrocarbon (18) and the resonance energy (ca.19 k.cal.) calculated to be gained in the mesomeric system $-\overset{*}{C}H.CH{=}CH- \rightleftharpoons CH{=}CH.\underset{*}{C}H$ (33(6)).

D_{C-C} (for α-CH_2 groups in *cyclo*hexenyl-*cyclo*hexene) = 81-2x19 = 43 k.cal. (33(6), 193).

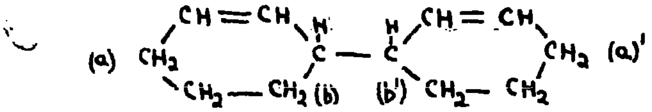
D_{O-H} (for $(CH_3)_3C.OH$) = 105 k.cal. (203)


(R.10)

This lack of additive and substitutive reactivity of tert.-butoxy radicals is in contrast with that of phenyl and benzoate radicals (from decomposing benzoyl peroxide) which were shown by Farmer (83) and Hermans (123) to undergo all the three types of reactions analogous to (R.4), (R.9) and (R.10) (vid.p. 37).

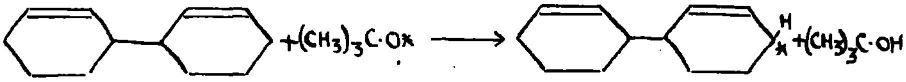
Mechanism of the formation of the higher cyclohexene"polymers".- The same basic reactions advanced to explain the formation of cyclohexenyl-cyclohexene may also be used to account for that of the cyclohexene "trimer" isomers and the higher boiling "polymers". The initially formed cyclohexenyl-cyclohexene will compete with the monomer olefin for reaction with tert.-butoxy radicals to give tert.-butanol and cyclohexenyl-cyclohexenyl radicals, and the latter will then, by radical-radical linking or by radical-molecule reactions, form higher molecular weight "polymers".

The cyclohexenyl-cyclohexene molecule contains (as shown in (VIII) four reactive α -methylene groups, (a), (a^1), (b) and (b^1):

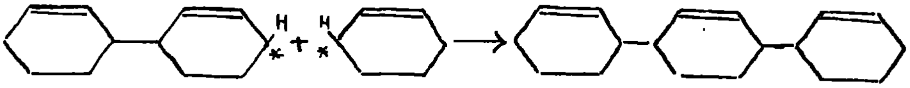


(VIII)

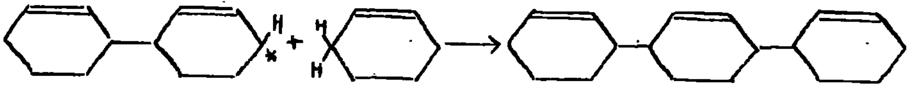
Attack at the α -methylene positions (a) and (a^1) in (VIII) by tert.-butoxy radicals may explain the formation of 1:4-dicyclohexenyl-cyclohexene. The following scheme gives the possible reactions leading to the formation of this isomer:



(R.11)

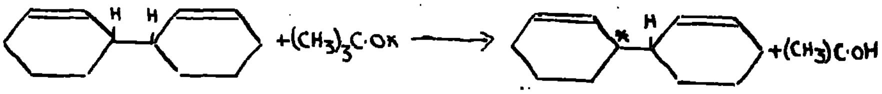


(R.12)



+ H* (R.13)

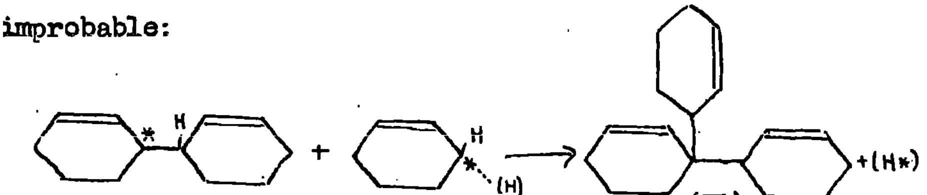
Reaction of *tert.*-butoxy radicals at the α-methylene groups (b) and (b^1) will give the *cyclo*hexenyl-*cyclo*hexenyl radical (IX):



(R.14)

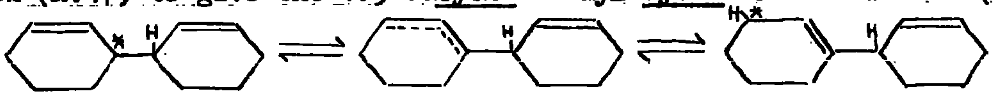
(IX)

The stabilisation of this radical by a *cyclo*hexene molecule or *cyclo*hexenyl radical to give the "trimer" (X), (R.15) would be sterically improbable:

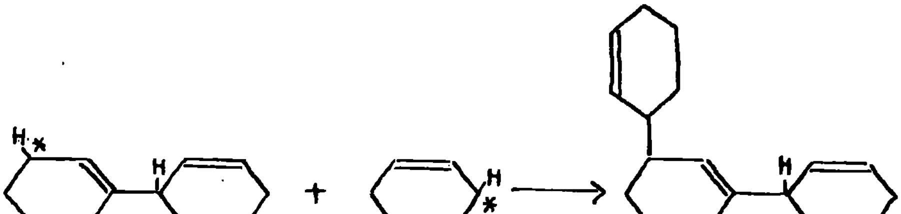


(X)
(R.15)

Alternatively the radical (IX) can mesomerise to its other canonical structure (XI) in which steric factors preventing radical linking will not be operative. The radical (XI) may then be stabilised as in (R.17) to give the 1:3-di*cyclo*hexenyl-*cyclo*hexene "trimer" (IV)



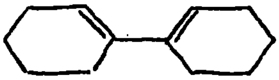
(IX) (XI)
(R.16)



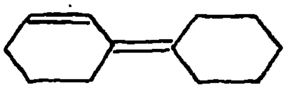
(XII) (IV)
(R.17)

Similar processes as described above may be envisaged to explain the formation of the cyclohexene "tetramer" and higher polymer fractions. It is to be expected that these higher polymer will contain increasingly greater numbers of structural isomers as their molecular weights rise, owing to the many differently situated α-methylene groups in the molecules and the possibility of extensive double bond rearrangements as in (R.16 - R.17).

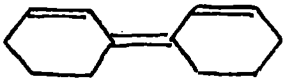
The Significance of Conjugation in the High "Polymers".- The cyclohexene recovered from the reaction product and representative samples of the various "polymer" fractions were analysed for conjugation by ultra-violet spectrography. The recovered cyclohexene, the "dimer" and the "trimer" contained no conjugated groups. A sample of "tetramer" (A, Table 5), and two samples of "polymeric" residues (B and C, Table 5) all gave absorption maxima near 2423°A and at 2860°A. The following conclusions were made from the positions of maximum absorption and the magnitude of the extinction coefficients: (i) The spectra preclude the possibility of two conjugated double bonds in one ring, as in cyclohexadiene-1:3, which would give a maximum at ca. 2550°A (35, 265). (ii) The absorption at $\lambda_{max} = 2430$°A may be due to either of the two conjugated diene systems (XII) and (XIII) (35, 265). This conjugation is of the order of $<5\%$ in the "tetramer" A, and is between 10-20% in the polymer residues B and C. (iii) The unresolved bond at $\lambda_{max} = 2860$°A may be due to relatively small amounts of conjugated trienes such as (XIV) and (XV) which give selective absorption at $\lambda_{max} \sim 2800$°A (157). However, since conjugated diene ketones also absorb at λ_{max} 2690-3170°A the precise value being dependant upon the degree of alkyl substitution at the double bonds (76), the spectrographic data do not alone preclude the possibility of this type of triene conjugation in the polymers.



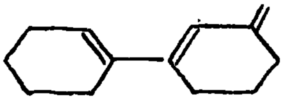
(XII)



(XIII)



(XIV)



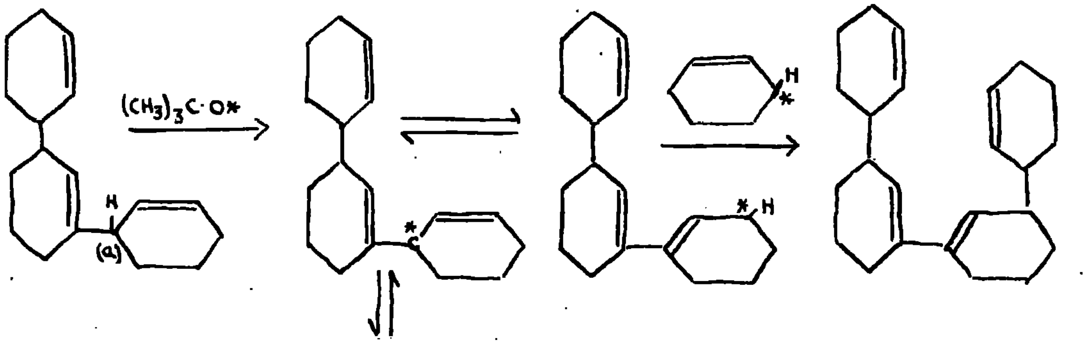
(XV)

It is suggested that the formation of diene conjugation in the "tetramer" and higher polymers is due to double bond shift resulting from mesomerism of an alkenyl radical system (R.19) which is initially formed as in (R.18) :

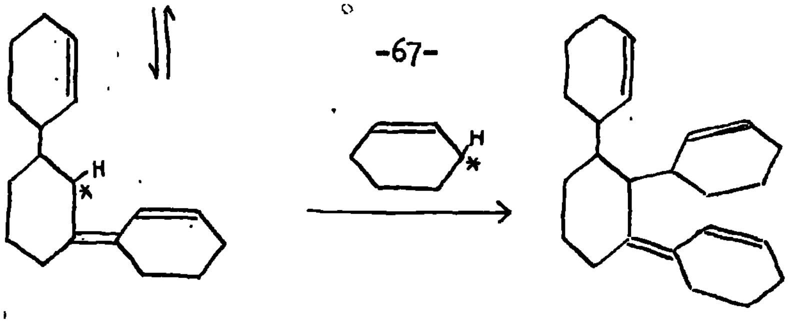
$$R.CH_2.CH{=}CH.R1 + (CH_3)_3C.O^* \longrightarrow R.\overset{*}{C}H.CH{=}CH.R^1 + (CH_3)_3C.OH \qquad (R.18)$$

$$R.\overset{*}{C}H.CH{=}CH.R^1 \longrightarrow R.CH{=}CH.\overset{*}{C}H.R^1 \qquad (R.19)$$

Thus the following scheme shows how diene conjugation (both of types (XII) and (XIII)) may be formed from 1:3-di*cyclo*hexenyl-*cyclo*hexene (IV) by reaction of *tert*.-butoxy radicals at the α-CH group (a) Attack at this point rather than at any other of the five α-methylene positions in (IV) will be preferred since C-H$_a$ is present in a 1:4-diene system $CH{:}CH.\overset{\overset{R}{|}}{C}H.CH{:}CH$, and such α-methylene groups are known to be more labile than those present in the mono-olefin systems $-CH_2-CH{=}CH-$ and $-\overset{\overset{R}{|}}{C}H.CH{=}CH-$ (vid.p. 11)



(R.20)
(i)



(R.20)
(ii)

Processes similar to those described above will account for conjugated dienes in the higher "polymers". It is significant that the above mechanism of double bond shift through mesomeric effects will not result in conjugation in the cyclohexene polymers of a lower order than "tetramer" which is in agreement with the observed facts.

Correlation of the Yields.- The stoichiometries of the reactions leading to the observed products are represented by the following equations:

$$2C_6H_{10} + (CH_3)_3C.O.O.C(CH_3)_3 = C_{12}H_{18} + 2(CH_3)_3C.OH \qquad (E.2)$$

$$3C_6H_{10} + 2(CH_3)_3C.O.O.C(CH_3)_3 = C_{18}H_{26} + 4(CH_3)_3C.OH \qquad (E.3)$$

$$4C_6H_{10} + 3(CH_3)_3C.O.O.C(CH_3)_3 = C_{24}H_{34} + 6(CH_3)_3C.OH \qquad (E.4)$$

etc.

Using these equations, the yields of tert.-butanol and the cyclohexene "polymers" have been correlated with the amount of peroxide decomposed. These data, which are given in Tables (4-5), are in very good agreement and support the postulated reaction mechanism.

From Table (4) it is seen that all the peroxide had reacted in the 6:1 run after reaction times of 24 and 48 hours, but that 12 hours heating resulted in incomplete decomposition of the peroxide. The relative proportions of the "polymer" fractions remained constant in experiments conducted with a constant ratio of olefin to peroxide for different reaction times. Comparison of Tables(4-5) shows that variation of the ratio of peroxide to olefin causes great differences in the ratios of the "polymers". Thus in the 6:1 run the order of polymer abundance is "dimer"8 : "trimer 2.7: "tetramer" 1, whereas in the 2:1 run this order has changed to "dimer" 1.75 : "trimer" 1.1 : "tetramer" 1.

The high yields of "trimer" and higher "polymers" would not be expectedon a statistical basis since when the peroxide is decomposed in a large excess of olefin the monomer olefin molecules would always be more abundant than the dimer molecules and would therefore be expected to react preferentially with the peroxide. This should result in large amounts of "dimer" with only minor amounts of higher "polymers". The lack of statistical balance in these reactions evidently results from the increasing reactivity of the α-methylene C-H bonds in the olefins as the latter increase in molecular complexity. Thus in passing from cyclohexene to the "dimer" and to the two "trimers" (III) and (IV) it is seen that, although the number of α-methylene groups per C_6 unit remains constant, the nature of these groups alters enormously. In the monomer there are two α-CH_2 groups, in the "dimer" two α-CH_2 and two α-CHR groups and in "trimer" (IV) three α-CH_2 and three α-CHR groups. One of the latter will be highly reactive since it is present in the 1:4-diene system $\text{-CH:CH.}\overset{R}{\text{C}}\text{H.CH:CH,}$ ~~CH~~- (vid.p.11). It is now well established that the lability of C-H bonds is in the order $C\text{-}H_\gamma > C\text{-}H_\beta > C\text{-}H_\alpha$, and on this basis the relative reactivities of the olefins in this reaction will be in the order "trimer" > "dimer" > "monomer". This reactivity factor will act in opposition to, and may well counterbalance, the collision frequency factor and thus result in larger proportions of the higher "polymers" than expected. statistically.

These findings are comparable with those obtained by

Kharasch *et al.* (vid.p. 52) in a study of the reaction of monochloromethyl acetate with methyl radicals. In this work the authors explained the lack of statistical balance between "dimer" and "trimer" by reactivity factors similar to those outlined above.

(B). REACTION OF DI.*tert.*-BUTYL PEROXIDE WITH 1-METHYL*cyclo*HEXENE AND *cyclo*HEXENYL-*cyclo*HEXENE.- The reactions of di-*tert.*-butyl peroxide with 1-methyl*cyclo*hexene and with *cyclo*hexenyl-*cyclo*hexene at 140° were analogous to the reaction just described. The results, which provide useful confirmatory evidence of the nature of peroxide/*cyclo*olefin reactions, will not be detailed in full here, but two specific points will be made.

(I). The "dimer" $C_{14}H_{22}\Gamma 2$ resulting from methyl*cyclo*hexene, although molecularly homogeneous, appeared to consist of a mixture of structural isomers. Owing to methyl substitution at one of the ethylenic carbon atoms, the abstraction of hydrogen atoms from the two dissimilar α-methylene groups in the olefin by *tert.*-butoxy radicals would result in two different methyl-*cyclo*hexenyl radicals (R^1) and (R^2). The latter would further give by mesomerism a third radical (R^3). Dimerisation of these radicals would thus result in the formation of a maximum of six dimethyl*cyclo*hexenyl-*cyclo*hexenes and the presence of all or some of these is to be expected and, indeed, is suggested by the wide boiling point range of the "dimer".

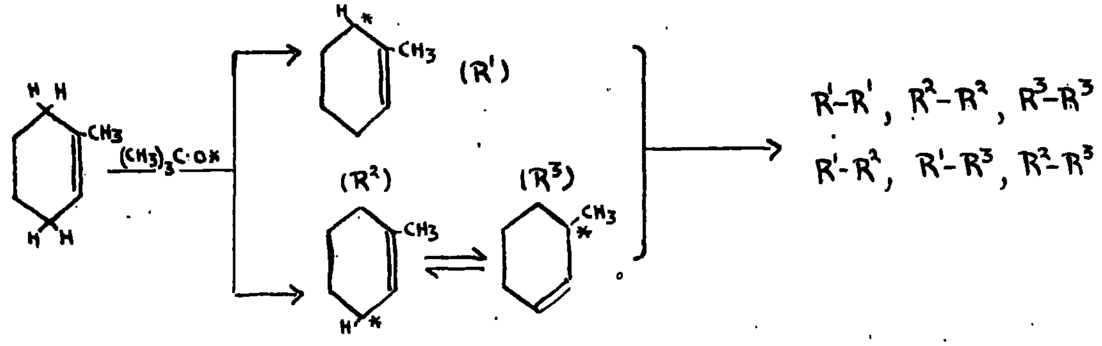


TABLE (4).

REACTION OF DI-tert.-BUTYL PEROXIDE (48.7g.) WITH cycloHEXENE (164.0g.)

(Temp. 140°, Molar Ratio 1:6)

TIME	12 HOURS			24 HOURS			48 HOURS		
PRODUCTS.	WT.(G.)	%Total Polymer.	%Peroxide Accntd. for.	WT.(G.)	%Total Polymer.	%Peroxide Accntd. for.	WT.(G.)	%Total Polymer.	%Peroxide Accntd. for.
tert.-BUTANOL	43.0	-	87.25	47.4	-	96.2	46.0	-	93.3
POLYMER MIXTURE	42.0	(25.6% cycloHexene)		45.5	(27.75% cycloHexene)		45.0	(27.45% cycloHexene)	
"DIMER" $C_{12}H_{18}$	25.8	61.44	47.75	28.15	61.85	52.1	27.2	60.45	50.35
"TRIMER" $C_{18}H_{26}$	8.8	20.95	21.8	9.5	20.9	23.55	9.75	21.75	24.2
"TETRAMER" $C_{24}H_{34}$.	3.3	7.86	9.2	3.55	7.8	9.9	3.5	7.8	9.8
HIGHER "POLYMER" (Assumed "HEXAMER")	3.8	9.06	11.8	3.85	8.45	11.95	4.2	9.3	13.05
	(TOTAL)	99.3	90.55	(TOTAL)	99.0	97.5	(TOTAL)	99.3	97.4

TABLE (5).

REACTION OF DI-tert.-BUTYL PEROXIDE WITH cycloHEXENE (140°; 24 HOURS).

REACTANTS	WT½(G.)	Molar Ratio	WT.(G.)	Molar Ratio
cycloHEXENE	109.3	4:1	54.65	2:1
DI-tert.-BUTYL PEROXIDE.	48.7		48.7	

PRODUCTS.	WT.(G)	%Total Polymer.	% Peroxide Accntd.for.	WT.(G.)	%Total Polymer.	%Peroxide Accntd.for.
tert.-BUTANOL	46.3	-	93.9	46.0	-	93.3
POLYMER MIXYURE.	44.4	(40.6% cycloHEXENE)		35.8	(65.5% cycloHEXENE)	
"DIMER" $C_{12}H_{18}$	20.4	45.95	37.75	7.14	19.95	13.2
"TRIMER" $C_{18}H_{26}$	9.5	21.4	23.55	4.56	12.75	11.3
"TETRAMER" $C_{24}H_{34}$	4.6[(a)]	10.35	12.85	4.1	11.45	11.45
HIGHER "POLYMER"	8.0[(b)]	18.0	24.9	18.7[(c)]	52.25	59.85 - 61.1
-	-	(TOTAL)	99.05	-	(TOTAL)	95.8 - 97.05.

(a) "Tetramer" Sample (A).

(b) "Polymer" Sample (B). Average "Hexameric" composition (Found M (benzene) 470. Calc. for $C_{36}H_{50}$: M, 482.

X (c) "Polymer" Sample (C). Average composition between "Septamer" and "Octamer" (Found: C, 89.55; H, 10.25; M (benzene), 605, 615. $C_{42}H_{58}$ requires C, 896; H, 10.4; M, 562; $C_{48}H_{66}$ requires C, 89.65; H, 10.35%; M, 642.)

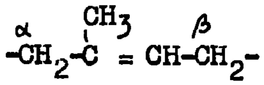
(2). When *cyclo*hexenyl-*cyclo*hexene and di-*tert*.-butyl peroxide were reacted together *in the molar ratio of 2:1* for 48 hours at 140° all the peroxide decomposed yielding *tert*.-butanol (≡ 92% of the peroxide). Of particular significance were the facts: (i) that 35.8% of the olefin was recovered unchanged, (ii) that 18.5% was converted to *bis*-*cyclo*hexenyl *cyclo*hexene ($C_{24}H_{34}$ F4), and (iii) that 40.75% was converted into a mixture of undistillable *cyclo*hexene "polymers" having an average composition of an "octamer" ($C_{48}H_{66}$ F8). These results confirm the earlier findings that the radical linking polymerisation of the olefin is *not* limited to the "dimeric" stage as represented by (R.21 - R.22). Had such a simple mechanism been operative in this instance no *cyclo*hexenyl-*cyclo*hexene would have remained and the olefin product would have consisted *entirely* of *bis*-*cyclo*hexenyl-*cyclo*hexene. On the contrary the "dimer" olefin when formed competes successfully with the monomer for reaction with *tert*.-butoxy radicals and thus builds up successive radical linking reactions a mixture of higher olefin "polymers".

$$X\text{-}H + (CH_3)_3C.O{*} \longrightarrow X{*} + (CH_3)_3C.OH \qquad (R.21)$$

$$X{*} + X{*} \longrightarrow X\text{-}X \qquad (R.22)$$

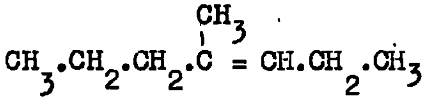
[X = *cyclo*hexenyl-*cyclo*hexenyl]

(6) REACTION OF DI-tert.-BUTYL PEROXIDE WITH 4-METHYLHEPTENE-3.- This investigation was undertaken to determine the relative reactivities of the two methylene groups $-CH_2^{\alpha}$ and $-CH_2^{\beta}$ bordering an unsymmetrical double bond:



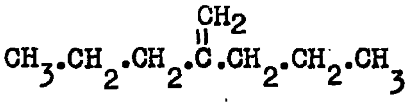
$$\overset{\alpha}{-CH_2}-\overset{CH_3}{\overset{|}{C}} = CH-\overset{\beta}{CH_2}-$$

4-methylheptene-3 (XVI) was chosen because of the unambiguity of its preparation by the dehydration of 4-methylheptan-4-ol, the only possible isomer being 4-methyl$^{\text{ene}}$heptane (XVII) :



$CH_3.CH_2.CH_2.\overset{CH_3}{C} = CH.CH_2.CH_3$

(XVI)



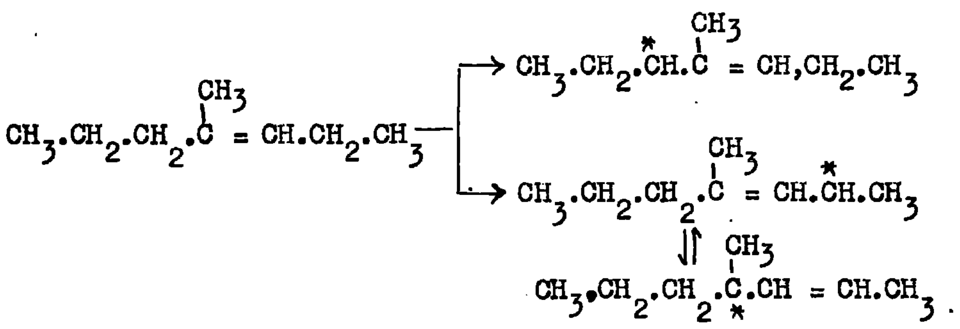
$CH_3.CH_2.CH_2.\overset{CH_2}{\overset{\|}{C}}.CH_2.CH_2.CH_3$

(XVII)

Infra-red analysis of the carefully fractionated olefin (spectrum 3) showed a large preponderance of (XVI) with only a small amount (≯ 10%) of (XVII).

Heating the olefin and di-tert.-butyl peroxide in a molar ratio of 4:1 at 140° gave a reaction product containing unchanged olefin, tert.-butanol (97.3% of peroxide), traces of acetone, and a polymeric olefin mixture which was shown by analysis to consist entirely of hydrocarbon constituents. The latter observation confirms the previous finding that tert.-butoxy groups do not combine with the olefin molecule. Distillation of the polymer mixture led to the separation of a methylheptene "dimer" $C_{16}H_{30}$ F2, which on catalytic reduction gave a hexadecane $C_{16}H_{34}$.

The "dimer" is probably formed by a mechanism allied to that outlined for the formation of cyclohexenyl-cyclohexene from cyclohexene and di-tert.-butyl peroxide. Consideration of the possible points of attack, by tert.-butoxy radicals, in 4-methylheptene-3 show that three possible alkenyl radicals (XVIII), (XIX) and (XX) can result from the abstraction of α-methylene hydrogen atoms from the olefin, the radical (XX) being a mesomeric form of (XIX):



$$CH_3.CH_2.CH_2.\overset{\displaystyle CH_3}{\overset{|}{C}} = CH.CH_2.CH_3 \rightarrow CH_3.CH_2.\overset{*}{C}H.\overset{\displaystyle CH_3}{\overset{|}{C}} = CH,CH_2.CH_3 \quad (XVIII)$$

$$CH_3.CH_2.CH_2.\overset{\displaystyle CH_3}{\overset{|}{C}} = CH.CH_2.CH_3 \rightarrow CH_3.CH_2.CH_2.\overset{\displaystyle CH_3}{\overset{|}{C}} = CH.\overset{*}{C}H.CH_3 \quad (XIX)$$

$$\rightleftharpoons CH_3.CH_2.CH_2.\underset{*}{\overset{\displaystyle CH_3}{\overset{|}{C}}}.CH = CH.CH_3. \quad (XX)$$

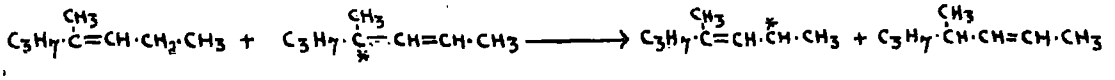
The nature of the "dimer" will depend on the relative labilities of the α-methylene groups $-CH_2^{\alpha}$ and $-CH_2^{\beta}$ and thus upon the relative preponderance of the radical forms (XVIII), (XIX) and (XX). Any estimate of the relative amounts of these radicals in the "dimer" will therefore indicate the relative activities of the two α-methylene groups.

Infra-red analysis of the "dimer" (Spectrum 4) showed the presence of a new type of unsaturation (band at 975 cm^{-1}) attributed to $R.CH{=}CH.R^1$, in addition to the olefinic types $R_2.C{=}CH_2$ and $R_2.C{=}CH.R^1$, and the presence of this new unsaturation is taken as evidence for the presence of the radical form (XX) in the "dimer". As olefins of the type $R.CH{=}CH.R^1$ usually give a characteristic band at 965 cm^{-1} the attributing of the 975 cm^{-1} band to this grouping naturally requires justification. This is found in the facts that 4-octene absorbs at 973 cm^{-1} (205) and the observation by Koch (private communication) of similar exalted wave numbers in other olefinic systems containing, indisputably, $R.CH{=}CH.R^1$ groups. Finally, strong experimental proof of the correct assignment of the 975 cm^{-1} band was found in the fact that this band completely disappeared when the "dimer" was reduced. This exaltation fo the wave number is provisionally attributed to the tertiary grouping adjacent to the double bond in the "dimer" resulting from (XX). On the basis of the measured extinction coefficient of the 965 cm^{-1} absorption of the CH=CH. grouping in a related olefin (Koch, private communication) it is estimated that the "dimer" contains about 15% of $R_3C.CH{=}CH{-}R^1$.

These results indicate that a considerable degree of attack (by <u>tert</u>.-butoxy radicals) occurs at $-CH_2^{\beta}$ and that the resulting radical (XIX) mesomerises to give (XX) resulting in a partial double bond shift of the original unsaturation. No evidence has been adduced of attack at $-CH_2^{\alpha}$.

Attempts to determine the nature and proportions of the olefinic groupings in the "dimer" by ozonolysis were unsuccessful. From many ozonolyses there resulted mixtures of aldehydes and ketones which defied attempts at their separation and characterisation. Repeated fractional crystallisation of the aldehyde dimedones gave no pure derivatives and chromatographic analysis of the mixed aldehyde and ketone dinitrophenylhydrazones resulted in only partial separation of the constituents and indicated only that the number of aldehydes and ketones was great.

It is significant that the recovered methylheptene had physical properties slightly at variance with those of the original olefin and contained, as shown by infra-red analysis, <u>traces</u> of $-CH{=}CH-$ unsaturation. This double bond shift is attributed to hydrogen transfer reactions between methylheptene molecules and the methylheptenyl radicals (XX):



$$C_3H_7{\cdot}\overset{CH_3}{C}{=}CH{\cdot}CH_2{\cdot}CH_3 + C_3H_7{\cdot}\underset{*}{\overset{CH_3}{C}}{=}CH{=}CH{\cdot}CH_3 \longrightarrow C_3H_7{\cdot}\overset{CH_3}{C}{=}CH{\cdot}\overset{*}{C}H{\cdot}CH_3 + C_3H_7{\cdot}\overset{CH_3}{C}H{\cdot}CH{=}CH{\cdot}CH_3 \quad (R.23)$$

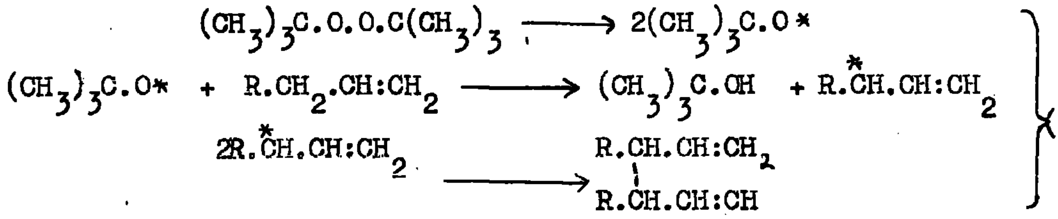
(D). <u>REACTION OF DI-tert.-BUTYL PEROXIDE WITH 1-HEPTENE</u>.- So far the reactions of di-<u>tert</u>.-butyl peroxide have been conducted with olefinic systmes of the types $R.CH_2.CH{:}CH.CH_2.R^1$ and $R.CH_2.C(CH_3){:}\ CH.R^1$. It was considered pertinent to investigate the reactivity of tert.-butoxy radicals with a vinylic olefin CH_2:CH.CH_2.R to determine the effect of olefinic structure on the nature of the reaction. To this end di-tert.-butyl peroxide was reacted with 1-heptene at 140°, in the molar ratio of 1:4. tert.-Butanol (≡ 85.5% of the peroxide) was isolated from the reaction product, and only a small amount (6.35%) of heptene was recovered. Fractionation of the higher boiling product gave three heptene "dimers" (ii) A, B and C containing traces of oxygenated constituents, and a large amount (ca.76% of the olefin) of an undistillable polymer having an average composition of a "hexamer". The three "dimer" fractions and the polymer residue had considerably lower unsaturation values than the original olefin as shown by quantitative hydrogenation, C/H ratios, and infra-red analysis.

Infra-red spectrographic analysis of the original and recovered heptene, and the three "dimer" fractions (ii) A, (ii) B (spectrum 2), and (ii) C provided valuable information concerning the mechanism of the reaction. Thus, the occurrence of double bond shift was indicated by the presence of traces of R.CH:CH.R unsaturation in the recovered heptene, and of a considerable proportion of this type of unsaturation, in addition to the original CH_2:CH.R, in the "dimers" and the higher polymer. Bands consistent with the presence of small amounts of ether groups and possibly traces of carbonyl groups were also found in the "dimers".

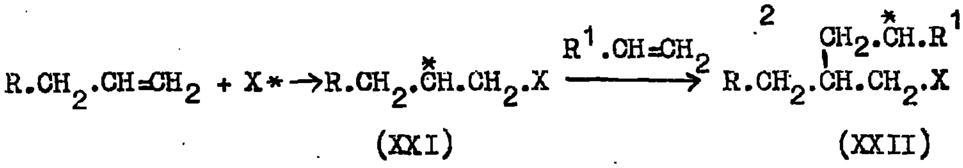
The main conclusions reached from this investigation are:
(I) A large amount of the peroxide decomposes to give tert.-butanol.
(2) Extensive polymerisation of the olefin results, and this lack of balance between the relative proportions of recovered heptene, "dimer"

and polymer is completely at variance with the proportions of these products obtained when olefins of the type $R.CH_2.CH{:}CH.R^1$ are reacted with the peroxide under comparable conditions. (3) The polymers show a significant decrease in the unsaturation. (4) Extensive rearrangement of the olefinic unsaturation occurs.

It is inferred from these results that two different types of polymerisation are being effected by means of *tert*.-butoxy radicals, these being (i) a radical linking reaction (R.24) at α -methylene groups, typical of *cyclo*alkene/peroxide reactions and (ii) vinyl addition polymerisation (R.25) initiated either by *tert*.-butoxy or alkenyl radicals as formed in (R.24) (*vid.*p.47):



$$\left.\begin{array}{l} (CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O^* \\ (CH_3)_3C.O^* + R.CH_2.CH{:}CH_2 \longrightarrow (CH_3)_3C.OH + R.\overset{*}{C}H.CH{:}CH_2 \\ 2R.\overset{*}{C}H.CH{:}CH_2 \longrightarrow \begin{array}{l} R.CH.CH{:}CH_2 \\ \quad | \\ R.CH.CH{:}CH_2 \end{array} \end{array}\right\} \quad (R.24)$$



$$\underset{}{R.CH_2.CH{=}CH_2} + X^* \rightarrow \underset{(XXI)}{R.CH_2.\overset{*}{C}H.CH_2.X} \xrightarrow{R^1.CH{=}CH_2} \underset{(XXII)}{R.CH_2.\overset{\overset{CH_2.\overset{*}{C}H.R^1}{|}}{C}H.CH_2.X} \quad (R.25)$$

[X* = an alkenyl or alkoxy radical.]

The radicals (XXI) and (XXII) may be stabilised by dismutation (R.26), by radical linking either with themselves (R.27) or with alkenyl or alkoxy radicals (R.28), or by capturing a hydrogen atom from another olefin molecule (R.29) :

$$R.CH_2.\overset{*}{C}H.CH_2.X \longrightarrow R.CH{=}CH.CH_2.X + H^* \quad (R.26)$$

$$R.CH_2.\overset{*}{C}H.CH_2.X + R.CH_2.\overset{*}{C}H.CH_2.X \longrightarrow [R.CH_2.\overset{|}{C}H.CH_2.X]_2 \quad (R.27)$$

$$R.CH_2.\overset{*}{C}H.CH_2.X + X* \longrightarrow R.CH_2.CH(X).CH_2.X \qquad (R.28)$$

$$R.CH_2.\overset{*}{C}H.CH_2.X + R^1H \longrightarrow R.CH_2.CH_2.CH_2.X + R* \qquad (R.29)$$

etc.

Reactions (R.27 - R.29) all result in polymer formation with decrease in the unsaturation, and the fact that the major product is a high polymer indicates that these reactions compete favourably with (R.24) and that their chain lengths must be reasonably long.

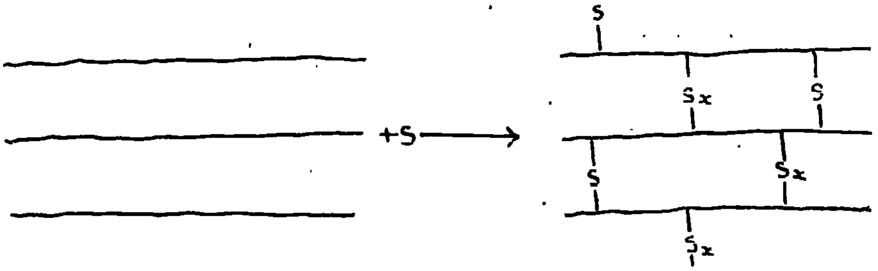
The presence of $R.CH{=}CH.R^1$ unsaturation is explicable by the dimutation reaction (R.26) and by mesomerism of the radical $R.\overset{*}{C}H.CH{:}CH_2$ to its alternative canonical state $R.CH{:}CH.CH_2*$ (R.30). The presence of the latter type of unsaturation in the recovered heptene further indicates that transfer reactions between heptene molecules and $R.CH{:}CH.CH_2*$ radicals (R.31) must occur to some extent:

$$R.\overset{*}{C}H.CH{=}CH_2 \rightleftharpoons R.CH{=}CH.CH_2* \qquad (R.30)$$

$$R.CH_2.CH{=}CH_2 + R.CH{=}CH.CH_2* \longrightarrow R.\overset{*}{C}H.CH{=}CH_2 + R.CH{=}CH.CH_3 \qquad (R.31)$$

The mechanism postulated above explains in a reasonable way the observed experimental facts and demonstrates the profound effect of the nature of an olefinic system on the course of peroxide/olefin reactions.

(E). REACTION OF DI-tert.-BUTYL PEROXIDE WITH RUBBER HYDROCARBON.- The results of the model experiments involving the reaction of di-tert.-butyl peroxide with simple cyclic and acyclic olefins were sufficiently encouraging to suggest a study of the reaction of rubber with this peroxide. Should the reactions occurring with the simple olefins also apply to rubber this would mean that di-tert.-alkyl peroxides could be used as efficient reagents for cross-linking the polyisoprene chains in rubber, which process is known to be one of the major factors in the phenomenon of vulcanisation. Rubber is usually vulcanised by heating it with sulphur at ca. 140° in the presence of other compounding ingredients including accelerators, oxygen inhibitors and strengtheners, whicheach play a specific role in modifying the physical and chemical properties of the vulcanisate. It is now established that the rubber is vulcanised by forming mono- and polysulphide cross-links between different rubber molecules (R.32), resulting in a nett increase in the average molecular weight of the rubber chains. Within certain limits the increased cross-linking reduces the solubility of rubber in solvents and increases such physical properties as tensile strength, elasticity and modulus.



(R.32)

Rubber Molecules. Vulcanised Rubber

In the present investigation two series of experiments were conducted in which (a) raw "smooth smoked sheet" rubber and (b) acetone-extracted smoked sheet were reacted (140° for 6 hours) with varying amounts of di-tert.-butyl peroxide in the complete absence of oxygen. Vulcanisation of the rubber samples had obviously been effected; they became completely insoluble in benzene and other solvents. The mechanical properties and the equilibrium swelling constant in benzene (Qm)* of all the samples were measured immediately after reaction.

The data are given in Tables (6) and (7). The measurement of Qm permits an estimate of the average molecular weight between junction points (Mc) in the cross-linked rubber molecules, and the value is proportional to the number of new cross-links formed. The evaluation of Mc from Qm is based on equation (E.5) derived by Gee (97, 99):

$$\ln\left[1+\frac{1}{Q_m}\right] - \left[Q_m+1\right]^{-1} = \mu\left[Q_m+1\right]^{-2} + \frac{\rho_r V_o}{M_c}\left[Q_m+1\right]^{-1/3} \quad (E.5)$$

(ρ_r = Density of Rubber; Vo = Molar volume of swelling liquid.;
μ = Constant (0.395 for benzene)).

Gee established that the values of $10^4/Mc$ obtained from (E.5) for a series of sulphur vulcanisates were in good agreement with values determined for similar samples by an independant method (99). The use of (E.5) can therefore be regarded as a reliable method of tracing the changes in the degree of cross-linking produced by different peroxide concentrations.

<u>Significance of the Physical Measurements</u>.- The results given in Tables (6) and (7) demonstrate that di-<u>tert</u>.-butyl peroxide is highly effective in producing good rubber vulcanisates and the nature of the samples indicates that uniform vulcanisation has been effected. The values of Qm and Mc steadily decrease with the increasing peroxide concentration indicating a progressive increase in the degree

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* Qm is defined as the volume of solvent (benzene) imbibed at equilbrium swelling by unit volume of rubber.

of cross-linking.

Fig.5 shows the effect of peroxide concentration on the tensilestrengths of the samples. The two curves show the characteristic feature of well defined maxima, the tensile strengths increasing with increasingamounts of peroxide to a certain critical peroxide concentration beyond which they fall very sharply.[*] The effect of acetone-extraction of the rubber before reaction is to increase the maximum attainable tensile strength and also to reduce the peroxide concentration required to produce this maximum figure. Thus "raw smoked sheet" requires ca.2.9% of peroxide to give a maximum tensile strength of 178 kg.cm.$^{-2}$, whereas acetone extracted "smoked sheet" gives a vulcanisate with a maximum tensile strength of 206 kg.cm.$^{-2}$ with only 1.45% of peroxide. Acetone extraction of the rubber removes non-rubber constituents (natural antioxidants, resin acids, etc.) which presumably compete with the polyisoprene units for reaction with the peroxide and thus reduce the utility of the peroxide as a cross-linking agent.

As the peroxide concentration increases beyond a certain optimum value the desirable properties of the vulcanisates (good tensile strength and elasticity) deteriorate, and with peroxide concentrations of ca.5-16% (for series (a) rubbers) the samples show no rubber-like properties, being brittle, having low tensiles and possessing negligible elastic properties. The results demonstrate that cross-linking of rubber chains must be restricted within very critical limits to give useful products.

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[*] The same phenomenon is observed in rubber-sulphur vulcanisates (97).

TABLE (6).

REACTION OF RAW RUBBER/DI-tert.-BUTYL PEROXIDE. 6 HOURS AT 140°.

% Peroxide. (W/W)	Qm.	10^4/Mc.	Mc.	T.S. (Kg.cm^{-2})	% Elongation at break.	Modulus (Kg.cm^{-2}) 100 %	300%	500%	700%
0	-	-	-	54	925	3.1	3.6	4.85	18.0
1.45	4.42	1.33	7500	141	645	5.4	12.6	28.8	-
2.1	3.92	1.63	6150	145	580	7.4	18.0	60.0	-
2.5	3.72	1.77	5660	162	570	6.2	19.5	82.0	-
2.9	3.44	2.12	4720	178	555	11.0	22.0	93.0	-
3.4	2.63	3.18	3150	123	470	8.2	24.6	-	-
5.4	2.22	4.34	2300	29.5	250	13.0	-	-	-
7.65	2.12	4.61	2170	16.0	85	-	-	-	-
10.1	1.29	9.91	1010	12.3	40	-	-	-	-
15.7	1.01	11.85	840	12.0	20	-	-	-	-

TABLE (7).

REACTION OF ACETONE-EXTRACTED RUBBER/DI-tert.-BUTYL PEROXIDE

6 HOURS AT 140°.

% Peroxide (W/W)	Qm.	10^4/Mc.	Mc.	T.S. (Kg.cm^{-2})	% Elongation. at break.	Modulus (Kg.Cm^{-2}) 100%	300%	500%	700%
0	-	-	-	80.3	900	3.3	5.7	10.6	34.4
1.0	4.31	1.35	7380	155	705	7.25	13.7	32.3	154
1.45	4.13	1.45	6840	206	660	6.54	15.6	55.5	-
1.7	4.08	1.51	6610	190	625	6.55	17.2	63.5	-
3.1	2.56	3.32	3010	22.1	210	11.8	-	-	-
3.95	2.11	4.55	2200	16.1	100	16.1	--	-	-
51.5	0.73$_5$	22.7	440	-	-	-	-	-	-

Chemistry of the Reaction.- Two experiments were conducted using large percentages of di-*tert*.-butyl peroxide in order to determine the chemical nature of the reaction:

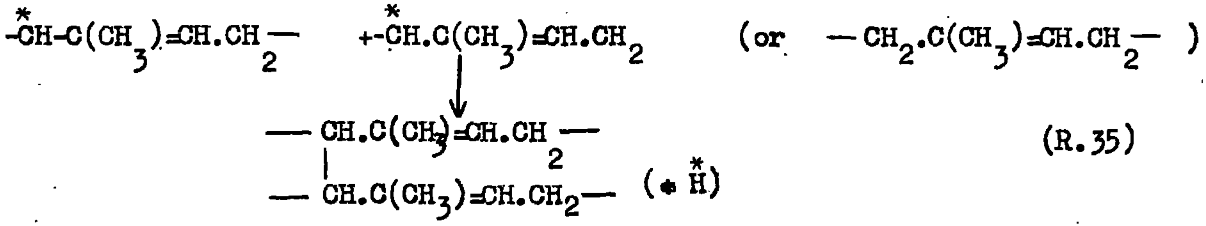
1) A sample of acetone-extracted "smoked sheet" was reacted with 51.5% of its weight of peroxide for 6 hours at 140°. The increase in oxygen content of the vulcanised product was found to be only 0.34 - 0.355% based on direct oxygen determination(44).

2) Reaction of a rubber sample similar to that used in 1), with 48.2% w.w. of peroxide for 6 hours at 140° gave a liquid product consisting entirely of a mixture of *tert*.-butanol (41.1% of the peroxide) and acetone (36.6% of the peroxide).

It is seen that little oxygenation of the rubber has occurred and that the peroxide decomposes to give mainly *tert*.-butanol and acetone. On the basis of these results it is suggested that the major, if not sole, reaction involved in peroxide-vulcanisation of rubber is the dehydrogenation of the isoprenic α-methylene groups by *tert*.- butoxy radicals, the resulting alkenyl radicals being stabilised to give a three dimensional cross-linked structure in which *the cross links are entirely formed of C-C bonds*.

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \qquad (R.33)$$

$$(CH_3)_3C.O* + \quad -CH_2.C(CH_3) = CH.CH_2- \longrightarrow (CH_3)_3C.OH + -\overset{*}{C}H.C(CH_3) = CH.CH_2 \qquad (R.34)$$



$$\begin{array}{l} -\overset{*}{C}H-C(CH_3)=CH.CH_2- \quad + -\overset{*}{C}H.C(CH_3)=CH.CH_2 \quad (\text{or } -CH_2.C(CH_3)=CH.CH_2-) \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad -CH.C(CH_3)=CH.CH_2- \\ \qquad\qquad -CH.C(CH_3)=CH.CH_2- \quad (+\overset{*}{H}) \end{array} \qquad (R.35)$$

(The α-CH_2's attacked are abbitrarily chosen in this scheme).

The existance of acetone in the reaction product when high concentrations of peroxide are used indicates that the tert.-butoxy radicals can, inpart, decompose according to (R.36):

$$(CH_3)_3C.O* \longrightarrow (CH_3)_2C=O + CH_3* \qquad (R.36)$$

The resulting methyl radicals may then dimerise to give ethane or they may play an effective part in cross-linking the polyisoprene units as they do with organic solvent molecules (vid.p.51):

$$RH + CH_3* \longrightarrow R* + CH_4 \qquad (R.37)$$

$$R* + R* \longrightarrow R\text{-}R \qquad (R.38)$$

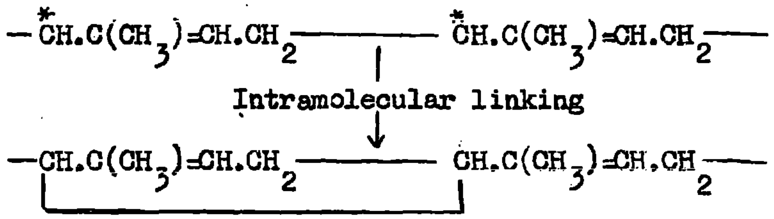
$$R* + RH \longrightarrow R\text{-}R + H* \qquad (R.39)$$

$$(R = -\overset{*}{C}H.C(CH_3)=CH.CH_2-)$$

The possibility of (R.36) and the succeeding reactions (R.37 - R.39) occurring will become less as the peroxide concentration decreases, and the above reactions are probably insignificant when only 1-3% of the peroxide is used.

The fact that negligible oxygenation of the rubber occurs (even when large amounts of peroxide are used) shows that substitution of such groups as tert.-butoxy in the isoprene units plays no important role in the overall reaction. This is incontrast with the findings of van Rossem *et.al.*(214) who showed that in the vulcanisation of rubber with benzoyl peroxide a considerable degree of benzoyloxylation of the rubber occurred (*vid*.p. 42). Analogous differences between the reactivities of *tert*.-butoxy and benzoate radicals have proved to exist in the reactions of these radicals with *cyclo*hexene (*vid*.p. 62 and p. 39).

The utility of *tert*.-butoxy radicals in forming, in the main, C-C bonds and not being wastefully employed in producing ethers (which process in no way aids vulcanisation) is naturally advantageous. A second possible wasteful process is the intramolecular linking of alkenyl radicals, produced within the same rubber chain, to give a cyclic rubber (R.40). However the fact that as little as 1-2%



$$-\overset{*}{C}H.C(CH_3){=}CH.CH_2 - \overset{*}{C}H.C(CH_3){=}CH.CH_2 -$$

$$\downarrow \text{Intramolecular linking}$$

$$-CH.C(CH_3){=}CH.CH_2 - CH.C(CH_3){=}CH.CH_2 -$$

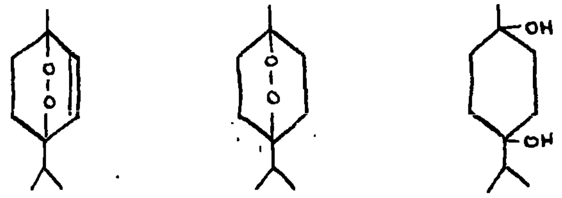
(R.40)

of di-*tert*.-butyl peroxide is effective in producing highly cross-linked products would indicate that this is not a serious competetive raction.

Technical Applications.- The production of a vulcanised rubber consisting entirely of hydrocarbon constituents is obviously of importance in the rubber industry, since sulphurated vulcanisates often have serious disadvantages. Thus peroxide vulcanisates may be used as gaskets for pressure hydrogenation, in place of sulphur vulcanisates which often poison the hydrogenation catalyst. Recently, Bellamy and Watt (19) have found that rubber tubing which has been vulcanised with sulphur or sulphur compounds strongly deactivates penicillin solution. This deactivation has been traced to the presence of certain sulphurated compounds in the tubing; and it is significant that synthetic polyvinyl chloride and polyethylene tubing are completely inactive towards penicillin solutions. A pure hydrocarbon rubber produced by peroxide-vulcanisation would also be expected to be inactive.

(F). THE THERMAL DECOMPOSITION OF DIHYDROASCARIDOLE AND ITS REACTION WITH cycloHEXENE.-

Preparation of Dihydroascaridole.- The observation of Paget (190) that ascaridole (XXIII) may be reduced to dihydroascaridole (XXIV) by using platinic acid as catalyst has now been confirmed by quantitative micro-hydrogenation of the pure peroxide.

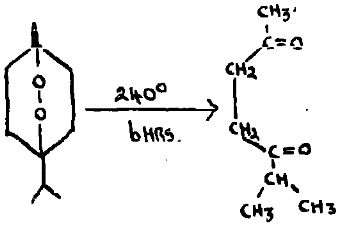


(XXIII) (XXIV) (XXV) (R.41)

The rate of hydrogenation (Fig.4) indicates that one mol. of hydrogen per mol. of ascaridole was rapidly absorbed and a second mol. of hydrogen was slowly absorbed over a much longer period, resulting in complete reduction of the peroxide to cis-1:4-terpin (XXV). In Fig.4. the curve OA corresponds to the reduction of the ethylenic link and the curve AB to the reduction of the O-O bond.

In macro-hydrogenations it was found that, if reduction was stopped when one mol. of hydrogen per mol. of ascaridole had been taken up, dihydroascaridole was the major product although some ascaridole had escaped reaction and some dihydroascaridole had been further reduced to <u>cis</u>-1:4-terpin.

<u>Thermal Decomposition of Dihydroascaridole</u>.- Dihydroascaridole, unlike ascaridole and other transannular peroxides, is remarkable for its thermal stability. It has been found that it can be heated in bulk to temperatures approaching 250° without occurrence of explosive decomposition. When heated at 240° for several hours the peroxide undergoes a regular non-explosive decomposition with evolution of gaseous products and the formation of a 1:4 diketone, 2-methylheptandione-3:6 (XXVI) which is obtained in a yield of 43.8% based on the peroxide decomposed. There also results a large amount of polymeric material the constituents of which were not identifiable.



(XXVI) (R.42)

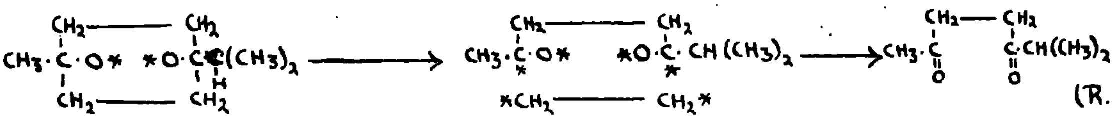
<u>Mechanism of the Reaction</u>.- Since the O-O bond in dihydroascaridole is linked at tertiary carbon atoms the peroxide can be regarded as a di-<u>tert</u>.-alkyl peroxide and should resemble di-<u>tert</u>.-butyl peroxide in its mode of thermal decomposition and general chemical reactivity[1]. This resemblance in the thermal decompositions of the two peroxides is apparent since they both result in the formation of ketones with evolution of gaseous products. By analogy with the mechanism formulated by George and Walsh and by Milas (<u>vid</u>.p. 29) to explain the formation of acetone and ethane from di-<u>tert</u>.-butyl peroxide it is

proposed that dihydroascaridole decomposes thermally by the initial scission of the peroxide bond to give the di-alkoxy di-radical (XXVII) (R.43):

(XXVII)

(R.43)

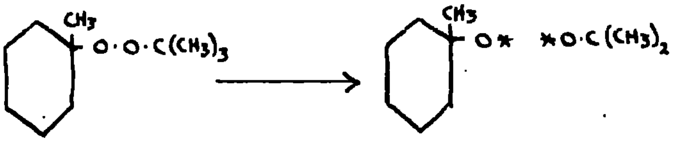
The consecutive or simultaneous breaking of two C-C bonds in the C_6 ring of the di-radical (XXVII) then gives 2-methyl heptandione-3:6 and a hydrocarbon di-radical $*CH_2-CH_2*$ (R.44).



(R.44)

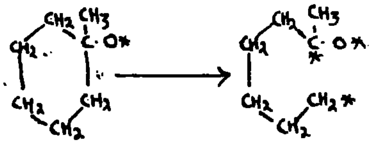
The radical $*CH_2-CH_2*$ may be stabilised to give ethylene or undergo a number of other stabilising reactions by interaction with other radical species or hydrogen containing molecules, but, since no detailed examination of the gaseous products was made, further speculation on the subsequent reactions of this radical is fruitless.

The above scheme necessitates the scission of C-C bonds in the ring adjacent to the C-O bonds and would require these bonds to be weaker than the CH_3-C and $(CH_3)_2$CH-C bonds in dihydroascaridole. Confirmation of this, as shown by Milas and Perry (174), is found in the fact that the peroxide (XXVIII) on thermal decomposition yields the radical (XXIX) which then decomposes further by scission of a ring C-C bond in preference to the C-CH_3 bond.



(XXVIII) (XXIX)

(R.45)



(XXIX)

(R.46)

Reaction of Dihydroascaridole.with *cyclo*Hexene.- When dihydroascaridole was heated with a large excess of *cyclo*hexene at 140° for 18 hours it was found that the peroxide and olefin were recovered completely unchanged. The result is suprising and in marked contrast with the reaction of di-*tert*.-butyl peroxide with *cyclo*hexene and other olefins. This difference may be explained by the great stability of dihydroascaridole even at temperatures as high as 140° and it may well be that insufficient energy is supplied at this temperature to cause tha initial scission of the O-O bond which, on the basis of the work with di-*tert*.-butyl peroxide, is a necessary preliminary to further interaction of the resulting alkoxy radicals with the olefin. Alternatively the unreactivity may be attributable to steric factors. If the initial scission of the O-O bond is assumed to occur the resulting alkoxy radicals will remain rigidly held in close proximity to one another by the cyclic C_6 structure, and recombination reactions to give the peroxide may be preferred to interaction with olefin molecules which may be prevented sterically from undergoing the collissions with the R-C.O* radicals necessary for reaction.

SECTION (2).

REACTION OF tert.-ALKYL HYDROPEROXIDES WITH OLEFINS.

(1). REACTION OF tert.-BUTYL HYDROPEROXIDE WITH cycloHEXENE.-

The present study of the thermal decomposition of tert.-butyl hydroperoxide in cyclohexene at 140° is the only detailed examination which has been reported of the reactivities of organic hydroperoxides with olefins. As will be described later, the results obtained in this investigation are of importance in elucidating the complex secondary changes occurring in olefin autoxidation, and the particular relevance of the nature of these reactions to the oxidative chain scission of rubber will also be considered.

Reaction of tert.-butyl hydroperoxide with cyclohexene in a molar ratio of 1:6 for 24 hours at 140° resulted in the complete decomposition of the hydroperoxide and formation of a complex mixture of products including water, tert.-butanol, acetone, olefinic alcohols and ketones, and cyclic polyolefins. The products which have been isolated and characterised are given in (Table 8).

Nature of the Reaction Products.- Examination of Table (8) shows that tert.-butyl hydroperoxide is converted mainly into tert.-butanol but small amounts of acetone are also formed. The hydroperoxide is seen to display four important reactivities towards the olefinic systems $-CH_2-CH=CH-$, (i) hydroxylation of the α-methylene groups to give an olefinic alcohol, (ii) oxidation of the olefinic alcohol to give an α-β-unsaturated ketone, (iii) cross-linking of olefin molecules at the α-methylene position to give olefinic "polymers", and (iv) saturation of the olefinic double bond by hydroxyl groups to give 1:2 diols.

TABLE (8)

REACTION OF tert.-BUTYL HYDROPEROXIDE WITH *cyclo*HEXENE.

(140°, 24 hours)

Reactants.	Wt.(g.)	Mols.
*cyclo*Hexene	328	4.0
$(CH_3)_3.C.OOH$	60	0.67

Products.

$(CH_3)_3.C.OH$	46.7 (94.8% C_4H_9OOH)	0.62	≡ 0.62 C_4H_9OOH
Water	3.4	0.19	≡ 0.19 "
Acetone	0.05	0.00086	≡ 0.0_386 "
*cyclo*Hexen-3-ol	*ca.* 17.4	0.178	≡ 0.178 "
*cyclo*Hexen-3-one	*ca.* 3.1	0.323	≡ ≯ 0.097 "
*cyclo*Hexenyl-*cyclo*hexene	> 28.25	> 0.174	≡ 0.35 C_6H_{10}
trans.-*cyclo*Hexan-1:2-diol	1.25	0.011	≡ 0.022 C_4H_9COH
*cyclo*Hexenyl-*cyclo*hexenol, $C_{12}H_{18}O$.	≯ 5.2	≯ 0.029	≡ ≯ 0.029 "
*cyclo*Hexenyl-*cyclo*hexenone, $C_{12}H_{16}O$.	≯ 0.92	≯ 0.0052	≡ ≯ 0.016 "
Di*cyclo*hexenyl-*cyclo*hexene $C_{18}H_{26}$	*ca.* 2.7	0.011	≡ ≯ 0.033 C_6H_{10}
Residue	5.1	-	-

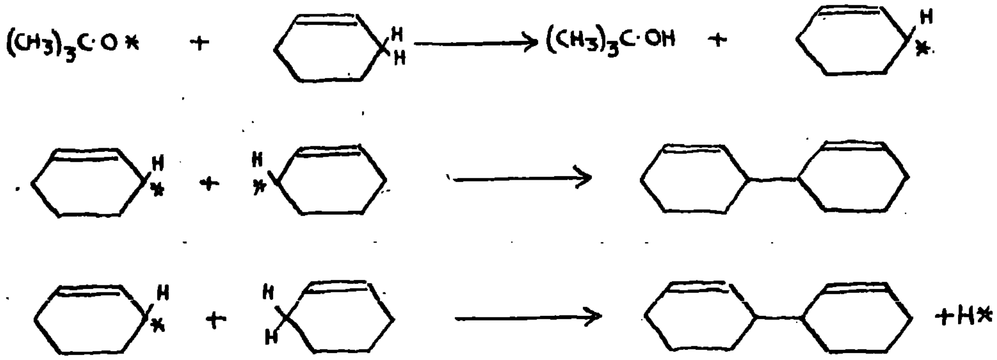
Oxygenated ≡ *ca.* 0.53 .OH groups.
Product.

Proposed Mechanism of the Reaction.- The nature of the reaction products disclosed above suggests that the initial reaction involved in the decomposition of tert.-butyl hydroperoxide with an olefin is the homolytic scission of the O-O peroxide bond to give tert.-butoxy and hydroxyl radicals (R.47):

$$(CH_3)_3C.O\text{-}CH \longrightarrow (CH_3)_3C.O* + HO* \qquad (R.47)$$

The resultant radicals then display their own unique reactivities with reactive centres in the olefin system $-CH_2-CH{=}CH-$ and thus achieve stabilisation. The types of reactions occurring with $(CH_3)_3C.O*$ and $HO*$ will be considered in turn.

(1) The tert.-butoxy radical.- As was shown in the reaction of di-tert.-butyl peroxide with cyclohexene, the tert.-butoxy radical reacts specifically by abstracting hydrogen atoms from the olefinic α-methylene groups to yield tert.-butanol and an olefinic radical (R.48)[1]. The latter radical then dimerises or reacts with an olefin molecule giving a stable olefin dimer (R.49 - R.50):



(R.48)

(R.49)

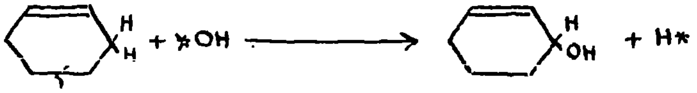
(R.50)

The presence of almost quantitative yields of tert.-butanol (based on the reaction $(CH_3)_3C.OOH \longrightarrow (CH_3)_{\cancel{3}}C.OH$) strongly supports (R.48) as the major reaction pursued by tert.-butoxy radicals. The minute amounts of acetone formed in the reaction indicate that (R.51) occurs to an insignificant extent.

$$(CH_3)_3C.O* \longrightarrow (CH_3)_2C{=}O + CH_3* \qquad (R.51)$$

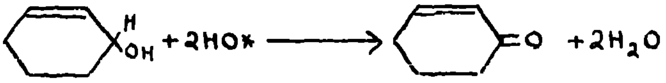
(2) The hydroxyl radical.- The many types of oxygenated products isolated in this reaction indicate that the role of the hydroxyl radical is manifold. The predominance of cyclohexen-3-ol suggests that the major reaction of the hydroxyl radical involves either its linking with a cyclohexenyl radical,(produced according to R.48) or a displacement reaction at the α-methylene group of the olefin (R.52 and R.53 respectively).

(R.52)



(R.53)

The cyclohexen-3-one is obviously formed by further-oxidation of the cyclohexenol by an oxidising agent which may be the hydroperoxide itself or more likely the hydroxyl or tert.-butoxy radicals.* The presence of water in the reaction product strongly supports the view that the active oxidising agent is the hydroxyl radical (R.54):



(R.54)

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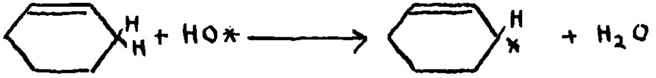
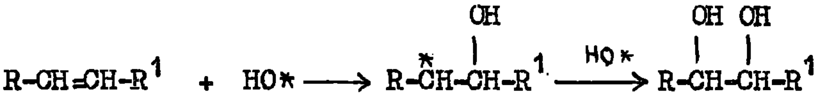
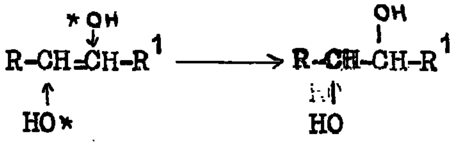
* That ketones do result from therreaction of alcohols with tert.-butyl hydroperoxide was proved experimentally by heating the latter both with cyclohexen-3-ol and cyclohexanol at 130°for 24 hours, when the corresponding

However, the yield of water is much greater than would be expected on the basis of (R.54) and the amount of ketones present, suggesting that the hydroxyl radical may also be capable of reacting analogously to the tert.-butoxy radical to give an olefin radical and water according to (R.55).


(R.55)

The presence of small amounts of trans.-cyclohexandiol indicates that the hydroxyl radicals possess, to a minor extent, an additive reactivity with olefinic double bonds. It is not possible to decide whether the diol results by successive or simultaneous additions of HO* to the double bond. The two possible reactions are :

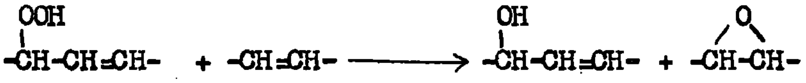

$$R-CH=CH-R^1 + HO\ast \longrightarrow R-\overset{\ast}{C}H-\overset{OH}{C}H-R^1 \xrightarrow{HO\ast} R-\overset{OH}{C}H-\overset{OH}{C}H-R^1 \quad (R.56)$$


$$R-\underset{\overset{\uparrow}{HO\ast}}{C}H=\overset{\ast OH \downarrow}{C}H-R^1 \longrightarrow R-\underset{HO}{C}H-\overset{OH}{C}H-R^1 \quad (R.57)$$

Since it has been found that in the secondary reactions of

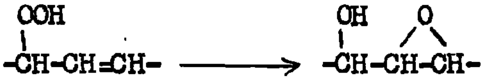
CONT, from Page 94. ketones were obtained in substantial yields.

olefin autoxidation (*vid*.p. 13) significant quantities of epoxides result, a careful search was made for *cyclo*hexanepoxide in the reaction product. No evidence could be found for its presence and careful analysis of the distribution of oxygen (between -OH and -C=O) in the major oxygenated product proved that the epoxide, if present at all, must be formed in undetectable quantities. On the basis of these results there is no experimental foundation for such reactions as (R.58 - R.59) which have been suggested (81) as possible routes to the formation of epoxides by secondary decomposition reactions of olefinic peroxides.



$$-\overset{\text{OOH}}{\text{CH}}-\text{CH}=\text{CH}- + -\text{CH}=\text{CH}- \longrightarrow -\overset{\text{OH}}{\text{CH}}-\text{CH}=\text{CH}- + -\overset{\text{O}}{\overbrace{\text{CH}-\text{CH}}}-$$

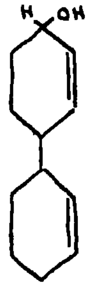
(R.58)



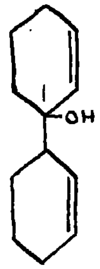
$$-\overset{\text{OOH}}{\text{CH}}-\text{CH}=\text{CH}- \longrightarrow -\overset{\text{OH}}{\text{CH}}-\overset{\text{O}}{\overbrace{\text{CH}-\text{CH}}}-$$

(R.59)

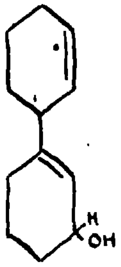
Formation of Higher Boiling Products.- It is to be expected that, since it is formed as one of the major initial reaction products, *cyclo*hexenyl-*cyclo*hexene will compete with *cyclo*hexene for reaction with *tert*.-butoxy and hydroxyl radicals and thus act as the progenator of higher molecular weight products. From the complicated mixture of the higher boiling product a fraction was isolated consisting predominantly of *cyclo*hexenyl-*cyclo*hexenol with some α-β- unsaturated *cyclo*hexenyl-*cyclo*hexenone. These products were obtained in too small amounts to permit rigid experimental determination of their constitutions, but, applying the previous considerations of the nature of hydroxyl radical attack on an olefin and the resonance possibilities of a *cyclo*alkenyl radical, it is suggested that the alcohol would be a mixture of the three isomers (XXX), (XXXI) and (XXXII), and the ketone a mixture of the two isomers (XXXIII) and (XXXIV). The mechanism of formation of these products will be similar to that applicable to their lower analogues cyclohexen-3-ol and cyclohexen-3-one (R.52 - R.54).



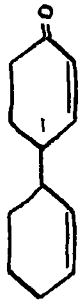
(XXX)



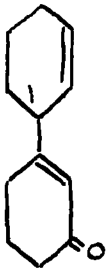
(XXXI)



(XXXII)



(XXXIII)



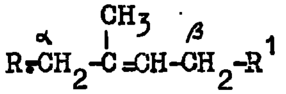
(XXXIV)

The formation of dicyclohexenyl-cyclohexene indicates that cyclohexenyl-cyclohexene is also attacked by tert.-butoxy radicals (according to R.48 - R.50) giving cyclohexenyl-cyclohexenyl radicals, which by stabilisation with cyclohexene radicals or molecules form the "trimer".

The presence of a substantial yield of undistillable material indicates that the reactions outlined above can operate with the higher molecular weight products to give polymers consisting of olefins, olefinic alcohols and ketones, and diols.

Summary fo the Reaction.- The following conclusions may be drawn from the character and quantitative proportions of the chief reaction products: (1) The free radicals $(CH_3)_3C.O^*$ and HO^* formed by decomposition of tert.-butyl hydroperoxide react mainly within the α-methylene groups of the olefin, resulting in the conversion of the hydroperoxide to tert.-butanol. (2) Additive attack at the double bond by tert.-butoxy radicals is non-existent and by hydroxyl radicals is insignificant. (3) Reaction of tert.-butyl hydroperoxide with an olefin does not yield an epoxide. (4) Hydroperoxide/olefin reactions do not lead to degradation of the olefin molecule, but lead partly to its "polymerisation" and partly to its transformation into olefinic alcohols and ketones. (5) The majority of thenew bonds, whether C-C, C-OH or C=O, are formed at the α-methylenic carbon atoms of the olefin.

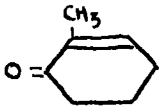
(2) <u>REACTION OF</u> tert.-<u>BUTYL HYDROPEROXIDE WITH 1-METHYL</u> cyclo<u>HEXENE</u>.- A brief examination of this reaction was undertaken with the specific aim of establishing the effect of alkyl substitution at the double bond on the relative reactivities of the two α-methylene groups in the system (XXXV) (cf. pp.12, 72).



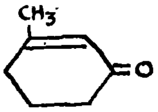
$$R-\overset{\alpha}{CH_2}-\overset{CH_3}{\overset{|}{C}}=CH-\overset{\beta}{CH_2}-R^1$$

(XXXV)

The course of the reaction was in general similar to that of the reaction just described, the hydroperoxide being converted almost quantitatively into <u>tert</u>.-butanol. From the reaction product there was isolated a major oxygenated fraction containing both methyl<u>cyclo</u>hexenols and α-β-unsaturated methyl<u>cyclo</u>hexenones. Ultra-violet spectrographic analysis indicated 12% of unsaturated ketones in the fraction. On treatment with 2:4-dinitrophenylhydrazine the fraction gave a mixture of two products which were separated by chromatographic analysis (alumina) into the 2:4-dinitrophenylhydrazones of 2-methyl Δ^2-<u>cyclo</u>hexenone (XXXVI) and 3-methyl-Δ^2-<u>cyclo</u>hexenone (XXXVII). The relative yields of the hydrazones



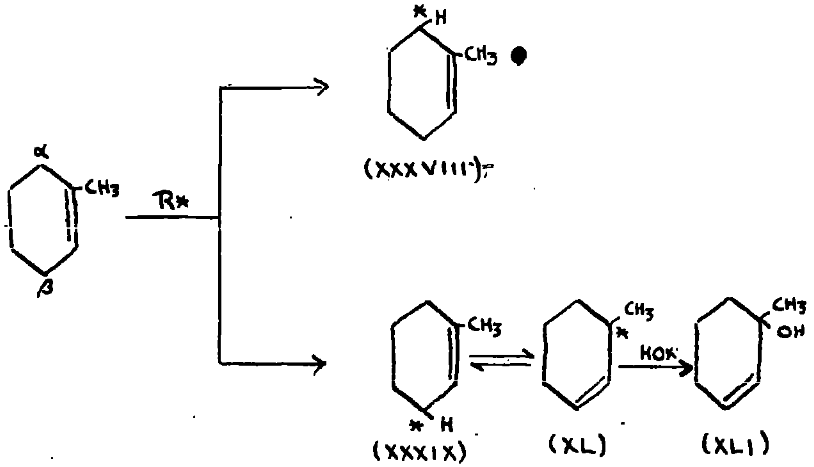
(XXXVI)



(XXXVII)

indicated that the ketones (XXXVI) and (XXXVII) were present in the ratio of *ca.* 2.2:1. The alcohol portion evidently consisted of a mixture of isomeric methyl*cyclo*hexenols since it was impossible to prepare derivatives (α -naphthyl urethanes) of constant or sharp melting point. Oxidation of the alcohol-ketone mixture with chromic acid in acetic acid yielded a ketone fraction which gave the dinitrophenylhydrazones of (XXXVI) and (XXXVII) in the proportions of 2.4:1.

These results clearly indicate that active radicals (in this case hydroxyl radicals) can attack both $-CH_2^{\alpha}$ and $-CH_2^{\beta}$ in (XXXV) and they suggest that the two radical species (XXXVIII) and (XXXIX) are present in *stabilised form*, in the proportions of about 2.2-2.4:1.



It must be stressed that the present results should not be interpreted as indicating that $-CH_2^{\alpha}$ is the most reactive methylene group, i.e. that (XXXVIII) and (XXXIX) are *formed* in the ratio of 2.2-2.4:1. Mesomerism of the radical (XXIX) to (XL) is always possible and stabilisation of the latter by *OH to give 1-methyl-Δ^2-*cyclo*hexen-1-ol (XLI) would invalidate any estimate of the relative reactivities of $-CH_2^{\alpha}$ and $-CH_2^{\beta}$ based on the proportions of products resulting from the two initially formed radicals (XXXVIII) and (XXIX).

The present investigation, although not wholly successful, provides additional evidence that the difference in the reactivities of $-CH_2^{\alpha}$ and $-CH_2^{\beta}$ is small, and suggests that earlier work (*vid*.p. 12) indicating complete reaction at either $-CH_2^{\alpha}$ or $-CH_2^{\beta}$ to the exclusion of the other should be accepted only with the greatest caution.

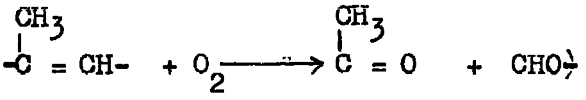
RELEVANCE OF THE PRESENT WORK TO THE OXIDATIVE BREAKDOWN OF RUBBER.

A brief review of the data previously obtained in connection with the oxidative breakdown of rubber is considered relevant to a fuller understanding of the problem and to the hypothesis which is now advanced to explain the processes involved in the secondary reactions of peroxidised rubber.

The results of oxidative attack on the rubber molecule are of immense technologocal importance in the aging by thermal oxidation of unvulcanised and vulcanised rubbers. For industrial utility rubber must possess good aging qualities, i.e. must be little effected by such factors as heat, light, oxygen and ozone. Two opposite [illegible] effects may ensue as the result of thermal oxidation of rubber, these being *chain-scission* and *cross-linking* of the rubber molecules. Tobolsky and co-workers (172, 236), from studies carried out mainly on synthetic rubbers, have shown that chain-scission and cross-linking reactions occur simultaneously so that the relative rates of these competing reactions are the controlling factors governing the physical properties of the oxidised products.

Although thermal oxidation of *natural rubber* usually results in an overall chain-scission effect, with polybutadiene and polybutadiene-styrene rubbers the reverse takes place, the oxidised products showing an increased degree of cross-linking (51, 172). This difference has been attributed to differences between the chemical reactivities of the polyisoprene and polybutadiene systems, $-CH_2.C(CH_3)=CH.CH_2-$ and $-CH_2-CH=CH.CH_2-$ and to variations in polymer structure such as cis-trans. isomerism, relative amounts of 1:2 and 1:4- polymerisation and the degree of branching in the polymer chains.

Farmer and Sundralingam (86) have demonstrated that oxygen is relatively uneconomical in causing chain-scission, when natural rubber solutions are photo-oxidised. For example, they found that although 2.9% of oxygen was sufficient to reduce the molecular weight of rubber from 324,000 to 55,000, 120 atoms of oxygen were absorbed for each double bond broken. The results at once show that no simple scheme for the utilisation of oxygen in scission reactions, such as (R.60) proposed by Staudinger, is permissible.



$$-\overset{CH_3}{\overset{|}{C}}=CH- \; + \; O_2 \longrightarrow \overset{CH_3}{\overset{|}{C}}=O \; + \; CHO- \qquad (R.60)$$

A further point of importance in connection with this problem is the nature of the distribution of oxygen in oxidised rubbers between various types of groupings such as -OH, C=O, -COOH, -COOR, $-\overset{O}{\widehat{C-C}}-$ -C.O.C- etc. Hilton (127) and Naylor (181) have estimated this distribution of oxygen in highly oxidised rubbers (Rubbones B and C; 11 and 13.3% oxygen respectively). Their results are given in Table (9). It is seen that 50-60% of the total oxygen is accounted for in these analyses and the residual 40-50% was presumed to be present largely as ether groups, although

TABLE (9).

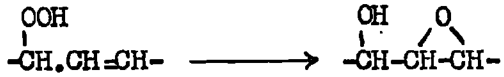
DISTRIBUTION OF OXYGEN IN RUBBERS.

O as % of total oxygen.

Oxygen Functional Group.	Rubbone B.	Rubbone C.
Peroxide -OOH	<1	<1
Hydroxyl -OH	31	30
Carboxyl -COOH	4	2
Ester -COOR	18	5
Carbonyl -C=O	4	7
Epoxide  $\overset{O}{C-C}$ plus carbonyl	4	-

recently it has been suggested (81) that stable peroxide groups (C-O-O-C) may also be present.

The precise mechanism of the degradative and aggregative processes in the oxidation of rubber still remains obscure. Farmer (80,81) believes that both chain-scission and cross-linking occur by various secondary reactions of the initially formed unsaturated hydroperoxide (vid.p. 13). According to Farmer, interaction of the peroxide with the double bond yields epoxides and alcohols (R.61 - R.62), the epoxides being the precursors of chain-scission reactions leading to ketones and aldehydes and, in later stages of oxidation, carboxylic acids and esters. Cross-linking reactions were attributed to the formation of stable peroxides ($R.O.O.R^1$) and ethers ($R.O.R^1$) (R.63 - R.64).



$$-\overset{OOH}{CH}.CH{=}CH- \longrightarrow -\overset{OH}{CH}-\overset{\;\;O}{\widehat{CH-CH}}- \qquad (R.61)$$

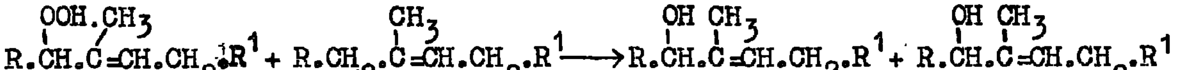
$$-\overset{OOH}{CH}.CH{=}CH- \;+\; -CH{=}CH- \longrightarrow -\overset{OH}{CH}-CH{=}CH- \;+\; -\overset{O}{\widehat{CH-CH}}- \qquad (R.62)$$

$$R.OOH + R^1.COH \longrightarrow R.O.R^1 + R.O.O.R^1 \qquad (R.63)$$

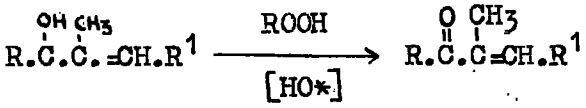
$$R.O.O.* + -CH{=}CH- \longrightarrow R.O.O.CH-\overset{*}{CH}- \xrightarrow{H*} R.O.O.CH-CH_2- \qquad (R.64)$$

New Conception of Polyisoprene Hydroperoxide Decomposition, Leading to Oxidative Degradation of Rubber.- The present author's work on the reaction of *tert.*-butyl hydroperoxide with *cyclohexene* would appear relevant to the elucidation of the processes occurring in rubber oxidation.

The general nature of the reaction of *tert.*-butyl hydroperoxide with *cyclohexene* would lead to the expectation that *inter*- or *intra*-molecular reactions of polyisoprene hydroperoxides with other isoprene units would occur to give olefinic secondary alcohol (R.65). The latter might then be oxidised further by radicals (e.g. HO*) from the decomposing peroxide to give α-β-unsaturated ketones (R.66)



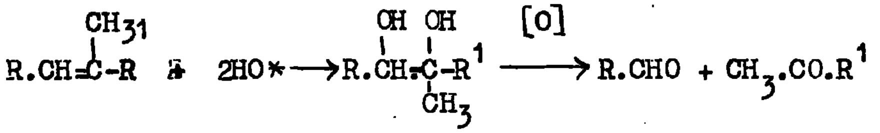
$$R.\overset{OOH}{CH}.\overset{CH_3}{C}{=}CH.CH_2.R^1 + R.CH_2.\overset{CH_3}{C}{=}CH.CH_2.R^1 \longrightarrow R.\overset{OH}{CH}.\overset{CH_3}{C}{=}CH.CH_2.R^1 + R.\overset{OH}{CH}.\overset{CH_3}{C}{=}CH.CH_2.R^1 \qquad (R.65)$$



$$R.\overset{OH}{C}.\overset{CH_3}{C}.{=}CH.R^1 \xrightarrow[{[HO*]}]{ROOH} R.\overset{O}{\overset{\|}{C}}.\overset{CH_3}{C}{=}CH.R^1 \qquad (R.66)$$

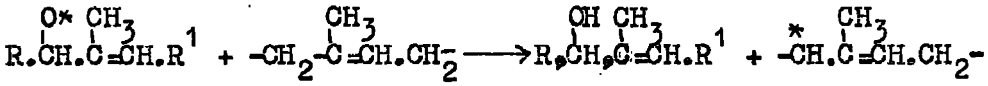
These reactions entail redistribution of hydroperoxide groups *without chain-scission of the rubber molecule* and on the basis of the "model" experiments appear to be the predominant modes of decomposition of the peroxide. The predominant occurrence of such reactions would confirm the observed presence of large proportions of hydroxyl groups and the inefficacy of oxygen in causing chain-scission.

A small proportion of the hydroxyl radicals from the decomposing peroxide may be successful in hydroxylating the double bonds to give glycols (R.69), which are probably precursors of aldehydic and ketonic chain-scission products.

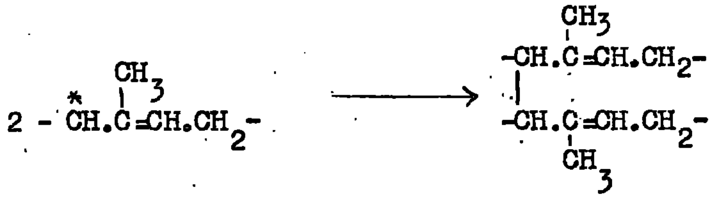


$$R.CH{=}\overset{CH_3}{C}{-}R^1 + 2HO* \longrightarrow R.\overset{OH}{C}H{-}\underset{CH_3}{\overset{OH}{C}}{-}R^1 \xrightarrow{[O]} R.CHO + CH_3.CO.R^1 \qquad (R.69)$$

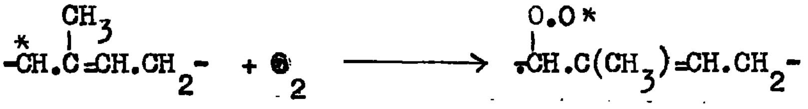
Cross-linking reactions may result from the action of the alkenyloxy radicals (from the decomposing peroxide) at the α-methylene groups in other isoprene units according to (R.70 - R.71). The oxidation of the isoprene radical (XLII) to give new peroxide radicals (R.72) will compete with the cross-linking reaction (R.71) and the relative efficacy of these two reactions will depend on the reaction conditions.



$$R.\overset{O*}{C}H.\overset{CH_3}{C}{=}CH.R^1 + {-}CH_2{-}\overset{CH_3}{C}{=}CH.CH_2{-} \longrightarrow R.\overset{OH}{C}H.\overset{CH_3}{C}{=}CH.R^1 + {-}\overset{*}{C}H.\overset{CH_3}{C}{=}CH.CH_2{-} \qquad (R.70)$$

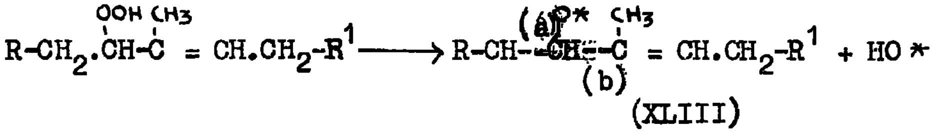


$$2\ {-}\overset{*}{C}H.\overset{CH_3}{C}{=}CH.CH_2{-} \longrightarrow \begin{array}{l} {-}CH.\overset{CH_3}{C}{=}CH.CH_2{-} \\ \quad | \\ {-}CH.\underset{CH_3}{C}{=}CH.CH_2{-} \end{array} \qquad (R.71)$$



$${-}\overset{*}{C}H.\overset{CH_3}{C}{=}CH.CH_2{-} + O_2 \longrightarrow {-}\overset{O.O*}{C}H.C(CH_3){=}CH.CH_2{-} \qquad (R.72)$$

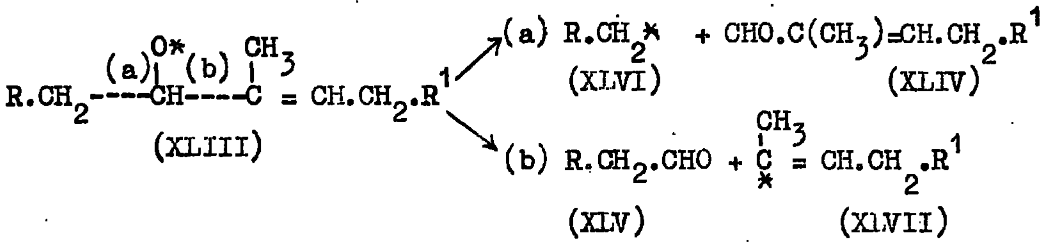
The above reactions involve the interaction of hydroperoxides with other isoprene units. An alternative mode of chain-scission involves the thermal unimolecular decomposition of the peroxide to give an alkenyloxy and a hydroxyl radical (cf. the decomposition of tert.-butyl hydroperoxide, p. 26):



$$R{-}CH_2.\overset{OOH}{CH}{-}\overset{CH_3}{C} = CH.CH_2{-}R^1 \longrightarrow R{-}CH{\overset{(a)}{-}}\overset{O*}{CH}\underset{(b)}{-}\overset{CH_3}{C} = CH.CH_2{-}R^1 + HO* \qquad (R.73)$$

(XLIII)

The radical (XLIII) may decompose by scission of the C-C bonds (a) and (b) adjacent to the C-O bond, to give the aldehydes (XLIV) and (XLV):

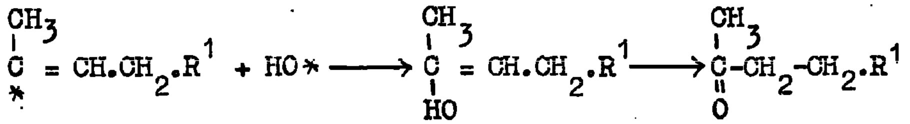


$$R.CH_2\overset{(a)}{----}\overset{O*}{CH}\overset{(b)}{----}\overset{CH_3}{C} = CH.CH_2.R^1 \begin{cases} \nearrow (a)\ R.CH_2* + CHO.C(CH_3){=}CH.CH_2.R^1 & (R.74) \\ \searrow (b)\ R.CH_2.CHO + \underset{*}{\overset{CH_3}{C}} = CH.CH_2.R^1 & (R.75) \end{cases}$$

(XLIII) (XLVI) (XLIV) (XLV) (XLVII)

The radicals (XLVI) and (XLVII) could then initiate new oxidation chains or react with nearby hydroxyl radicals to give alcohols (R.76) or ketones (R.77)

$$R.CH_2* + HO* \longrightarrow R.CH_2.OH \qquad (R.76)$$



$$\underset{*}{\overset{CH_3}{C}} = CH.CH_2.R^1 + HO* \longrightarrow \underset{HO}{\overset{CH_3}{C}} = CH.CH_2.R^1 \longrightarrow \underset{O}{\overset{CH_3}{C}}{-}CH_2{-}CH_2.R^1 \qquad (R.77)$$

The above schemes, although mainly speculative, are all based on established reactions occurring with related but simpler molecules, and afford a reasonable explanation of many of the phenomena observed in the attack of rubber by oxygen. Further elucidation of the mechanism of the oxidative breakdown of rubber could be obtained only by studies of the decomposition of olefinic hydroperoxides alone and in the presence of isoprenic olefins[1].

SECTION (3).

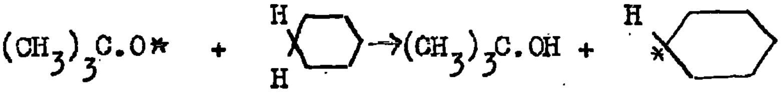
DECOMPOSITION OF DI-tert.-ALKYL PEROXIDES IN NON-OLEFINIC SOLVENTS.

A series of investigations has been made of the liquid phase decomposition of di-*tert.*-butyl peroxide at 140° in various classes of organic solvents, including saturated cyclic hydrocarbons, alkyl benzenes and cyclic and acyclic ketones, to determine whether the reactions involved paralleled those associated with peroxide decomposition in olefinic media. This analogy was, in fact, found.

(1) *Saturated Hydrocarbons*.- Di-*tert.*-butyl peroxide was reacted with a large excess of *cyclo*hexane for 24 hours at 140°. Complete decomposition of the peroxide occurred, giving *tert.*-butanol as the major product (*ca.*92.5%) with only traces of acetone. In addition to unchanged *cyclo*hexane there was found a mixture of hydrocarbon polymers from which pure di*cyclo*hexyl (22.6% of polymer) and a low yield of di*cyclo*hexyl-*cyclo*hexane ($C_{18}H_{32}$) were isolated. The latter hydrocarbon contained traces of oxygenated impurities; owing to the chemical inertness of the *cyclo*hexane structure it was not possible to obtain evidence of its structural composition. The major portion (*ca.*52%) of the reaction product was an orange polymeric residue which was largely hydrocarbon. It had a mean molecular weight of 630 indicating an average of between seven and eight *cyclo*hexane units per mol. Ultra-violet spectrographic analysis of the polymer showed the presence of *unsaturation* including *conjugated* cyclo*hexadiene* groupings. The insolubility of the polymer in the usual hydrogenating solvents prevented a quantitative determination of the unsaturation and made it impossible to establish whether the unsaturation was *entirely* or only *partially* present in conjugated diene groups.

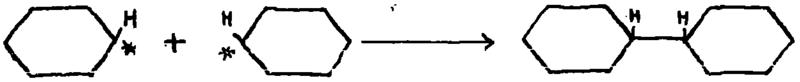
The results clearly indicate that di-*tert.*-butyl peroxide is an effective agent for the polymerisation of saturated hydrocarbons by the introduction of C-C cross-links. The large yields of *tert.*-butanol and significant amounts of di*cyclo*hexyl suggest that the initial reactions involved are as given in the scheme below:

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \qquad (R.78)$$

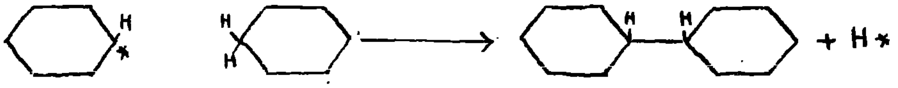


(R.79)

The *cyclo*hexyl radicals may then achieve stabilisation to give di*cyclo*hexyl by reactions (R.80 - R.81). These two possible reactions are chemically indistinguishable although kinetically (R.80) may be preferred since it doubtless has the lower activation energy (cf.p. 61).



(R.80)



(R.81)

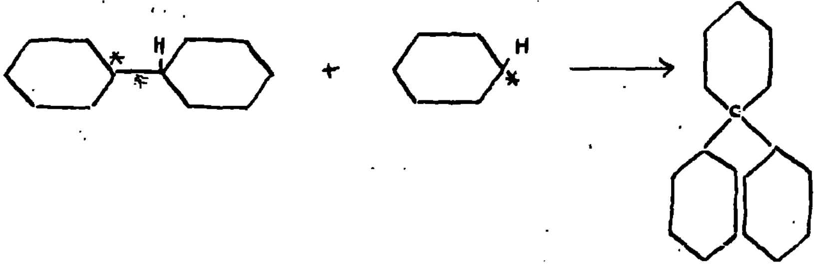
To this point the reaction of di-*tert.*-butyl peroxide with saturated hydrocarbons closely parallels its reaction with olefins. Some explanation, however, is necessary for the suprisingly large proportion of polymeric material formed in spite of the low peroxide concentration, and for the presence of *diene conjugation* in this polymer. This lack of statistical balance in the proportions of the various polymers is attributed to the greater lability of the two $C\text{-}H\gamma$ bonds in di*cyclo*hexyl than the $C\text{-}H\beta$ bonds in *cyclo*hexane, a fact which conforms with the estimate by Smith and Taylor[228] of the weaker bond energy of a $C\text{-}H\gamma$ bond as compared with that of a C-Hβ bond.

On this basis tert.-butoxy radicals react, preferentially, according to (R.82) to give dicyclohexyl radicals (XLVIII) and tert.-butanol:

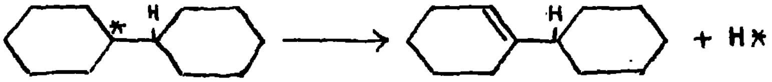
(XLVIII)

(R.82)

Stabilisation of the radical (XLVIII) may proceed by either or both of two possible reactions: (i) linking with a cyclohexyl radical to give 1:1-dicyclohexyl-cyclohexane (R.83); (ii) dismutation to give 1-cyclohexyl-cyclohexene (R.84).

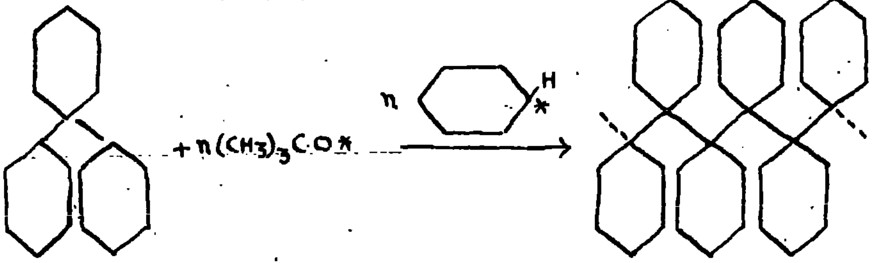


(R.83)



(R.84)

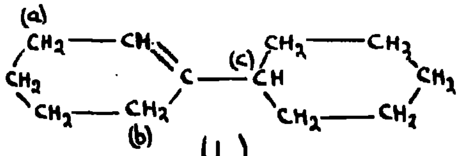
Sterically (R.83) would not appear to be favoured and repetitions of this reaction to build up a high polymer such as (XLIX) are regarded as highly probable.



(XLIX)

(R.85)

On the other hand (R.84) is not only a feasible reaction but also provides a very plausible explanation of the formation of large amounts of high polymers and of the introduction of ethylenic bonds into these polymers. Of the three molecules, cyclohexane, dicyclohexyl and cyclohexyl-cyclohexene, the latter will certainly possess the most labile C-H bonds, since it contains three active methylene groups ((a), (b) and (c) (L)) adjacent to the double bond. These methylene groups will be further activated by the cycloalkyl substitution at the double bond (cf. p. 11) and (c) will possess a highly labile C-H bond since it is tertiary.

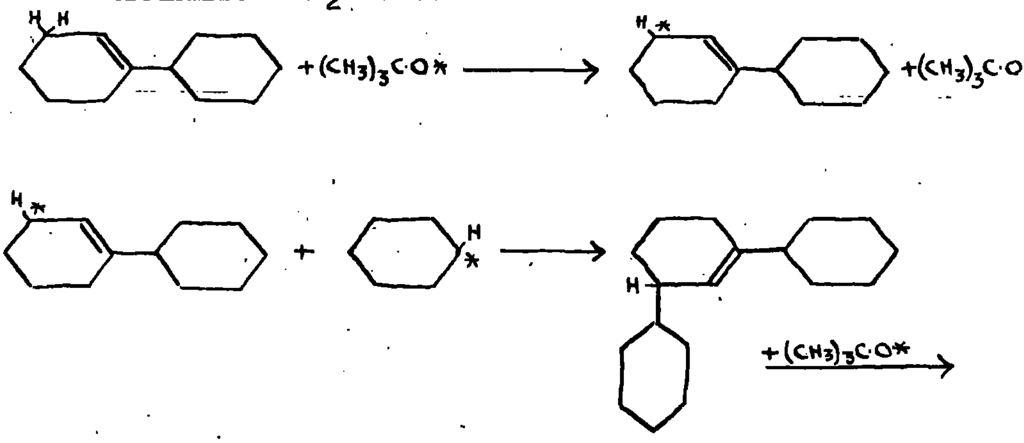


(L)

(L)

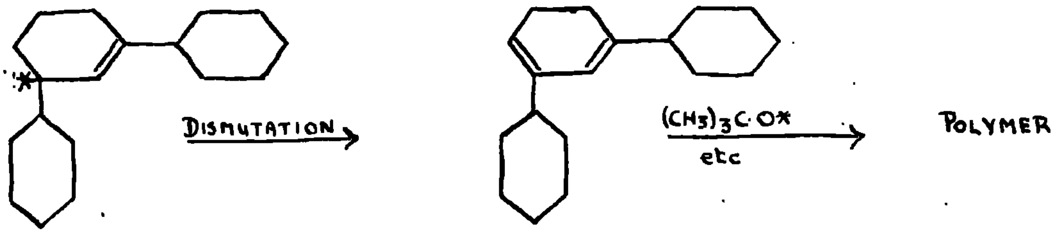
Any one, or all, of the α-methylene groups (a), (b), and (c) can be the site of attack by tert.-butoxy radicals according to (R.79). There are many possible subsequent reactions, but the following scheme indicates how attack at two of the reactive points (a) and (c) in (L) may result in conjugated diene formation. Repetition of these reactions, which will be more favoured owing to the greater reactivity of the C-H bonds adjacent to the double bonds in the newly formed molecules than of the C-H bonds in cyclohexane and dicyclohexyl, will thus build up a high polymer possessing unsaturated groupings which are wholly or partly conjugated.

(i) Attack at $-CH_2$ (a).-



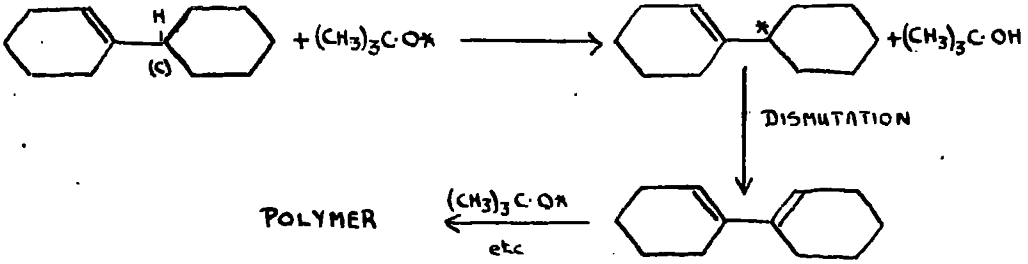
(R.86)

(R.87)



(R.89)

(ii) *Attack at -CH (c)*.-

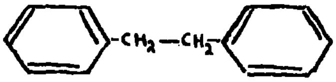


(R.90)

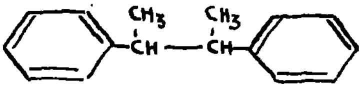
Obviously the whole reaction mechanism is not as simple as that outlined above, but the important points have been established, (i) that C-H bonds in *cyclo*paraffins can be broken by *tert.*-butoxy radicals and (ii) that di*cyclo*hexyl radicals can dismutate by hydrogen removal to give cyclic olefins which then become the most reactive species. The resulting reactions are complex, involving reactions of alkoxy radicals with *cyclo*paraffins, *cyclo*olefins and cyclic-1:3-diens to give hydrocarbon radicals which are stabilised by various means. The necessity for further detailed investigations of this type of reaction is evident and such studies will doubtless prove of value in interpreting both peroxide and hydrocarbon reactivities.

(2) *Alkyl Benzenes*.- The dehydrogenating activity of *tert.*-butoxy radicals applies not only to olefins and saturated hydrocarbons but also to the three alkyl benzenes, toluene, ethylbenzene and *iso*propylbenzene. Decomposition of di-*tert.*-butyl peroxide in all three solvents

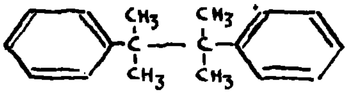
at 140° results in the formation of dibenzyl or substituted dibenzyls and tert.-butanol. The initial reaction closely parallels that of the peroxide with olefins and that of diacetyl peroxide with organic molecules (vid. work of Kharasch et.al.p. 50). The hydrogen atoms vicinal to the aromatic nucleus are the most labile and it is these which are abstracted by tert.-butoxy radicals. Thus, toluene gives dibenzyl (LI), ethylbenzene gives a mixture of meso-and racemic-2:3-diphenylbutanes (LII), and isopropylbenzene gives 2:3-diphenyl-2:3-dimethylbutane (LIII).



(LI)



(LII)



(LIII)

The mechanism of the reaction is similar to that proposed for the peroxide/olefin reactions. By way of example, the following scheme shows how (LIII) results from the reaction of di-tert.-butyl peroxide and isopropylbenzene:

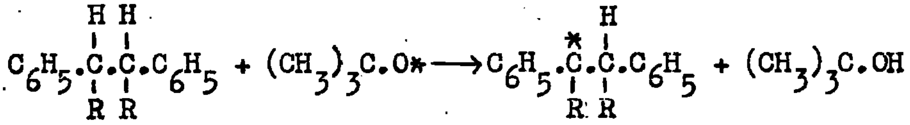
$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \qquad (R.92)$$

(R.93)

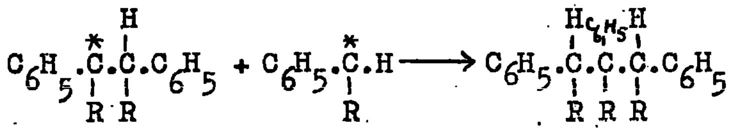
(R.94)

The existence of dimethyl-diphenylbutane as the sole aromatic product from the isopropylbenzene/peroxide reaction is proof of the greater lability of the $C-H_\gamma$ bond than of the $C-H_\alpha$ bonds of the methyl groups in the isopropyl group, a result in accord both with the work of Kharasch et al.(vid.p.51) who demonstrated the preferential attack at the C-Hγ bond in isopropylbenzene by CH_3* radicals (from decomposing di-acetyl peroxide), and the estimate by Smith and Taylor (228) that the strengths of C-H bonds are in the order $C\text{-}H_\alpha > C\text{-}H_\beta > C\text{-}H_\gamma$.

The "dimers" (LI) ans (LII) from toluene and ethylbenzene respectively retain C-H bonds vicinal to the phenyl groups and may, therefore, react further with tert.-butoxy radicals according to (R.95 - R.96) to yield "trimers" and higher "polymers". Higher polymers were, indeed, found with these two hydrocarbons and in the case of toluene a fraction was isolated which approximated in composition to the "trimer" 1:2:3-triphenylpropane (LIV).

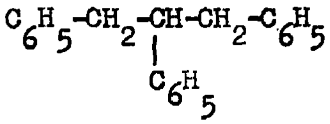


$$C_6H_5.\overset{H}{\underset{R}{C}}.\overset{H}{\underset{R}{C}}.C_6H_5 + (CH_3)_3C.O* \longrightarrow C_6H_5.\overset{*}{\underset{R}{C}}.\overset{H}{\underset{R}{C}}.C_6H_5 + (CH_3)_3C.OH$$ (R.95)



$$C_6H_5.\overset{*}{\underset{R}{C}}.\overset{H}{\underset{R}{C}}.C_6H_5 + C_6H_5.\overset{*}{\underset{R}{C}}.H \longrightarrow C_6H_5.\overset{H}{\underset{R}{C}}.\overset{C_6H_5}{\underset{R}{C}}.\overset{H}{\underset{R}{C}}.C_6H_5$$ (R.96)

etc.



$$C_6H_5-CH_2-\underset{C_6H_5}{CH}-CH_2-C_6H_5$$ (LIV)

The major aromatic product (49.5% of total polymer) from the toluene/peroxide reaction was an undistillable polymer which although containing traces of oxygenated material was mainly hydrocarbon. This high yield of polymer, although unexpected on statistical grounds since the peroxide was decomposed in a three mol. excess of toluene, may be explained by the preferential attack of *tert.*-butoxy radicals at the $C-H_\gamma$ bond in (LIV) rather than at the $C-H_\alpha$ or $C-H_\beta$ bonds in toluene and dibenzyl respectively. Continuation of (R.95 - R.96) on this basis would lead to a high molecular weight polymer.

The fact that significant yields of acetone were formed in these decompositions indicates that *tert.*-butoxy radicals are not stablised entirely as *tert.*-butanol but they do in part decompose according to(R.97).* The methyl radicals may then compete with *tert.*-butoxy radicals as hydrogen abstractors (R.98) or may dimerise to give ethane.

$$(CH_3)_3C.O* \longrightarrow (CH_3)_2C{=}O + CH_3* \qquad (R.97)$$

$$CH_3* + RH \longrightarrow CH_4 + R* \qquad (R.98)$$

As will be shown later *tert.*-butoxy radicals react with ketones according to (R.99) to give ketonyl radicals which are then stabilised by radical linking reactions. The formation of acetonyl radicals by this means from the pre-formed acetone and the linking of these with alkyl benzene radicals (R.100, where R = alkyl benzene radical) would effectively explain the traces of oxygenated material in the toluene polymers.

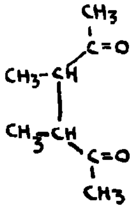
$$CH_3.CO.CH_3 + (CH_3)_3C.O* \longrightarrow *CH_2.CO.CH_3 + (CH_3)_3C.OH \qquad (R.99)$$

$$R* + *CH_2.CO.CH_3 \longrightarrow R.CH_2.CO.CH_3 \qquad (R.100)$$

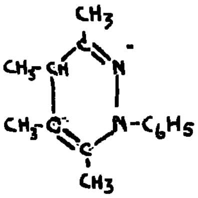
---

* In the decomposition of di-*tert.*-butyl peroxide in toluene the molar yields of *tert.*-butanol and acetone were in the ratio of *ca.*9.25:1, indicating that (R.93) rather than (R.97) is the preferred mode of decomposition.

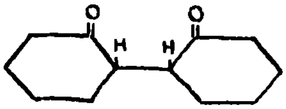
(3) *Cyclic and Acyclic Mono-ketones*.- Di-*tert*.-butyl peroxide has been found to be a highly effective reagent for synthesising 1:4-diketones from cyclic and acyclic monoketones containing α-methylene groups. Thus the peroxide on heating with a large excess of methyl ethyl ketone at 140° gave a mixture of ketone polymers from which 3:4-dimethyl hexandione-2:5 (LV) was isolated in pure form. The constitution of (LV) as a *1:4-diketone* was proved by the formation of the pyridazine derivative (LVI) on reaction with phenylhydrazine.



(LV)



(LVI)

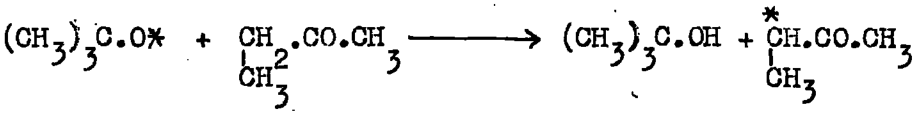


(LVIII)

Similarly, *cyclo*hexanone when heated with di-*tert*.-butyl peroxide at 140° gave, inaddition to a large amount of higher ketone-polymer, a mixture of stereoisomeric 2:2^1-diketodi*cyclo*hexyls (LVIII) from which the high melting form (m.p. 73-74°) was separated. This same ketone has been synthesised by unambiguous means by Plant (198), and recently has been obtained by Kharasch *et al*. (152) by the decomposition of diacetyl peroxide in *cyclo*hexanone (vid.p. 51).

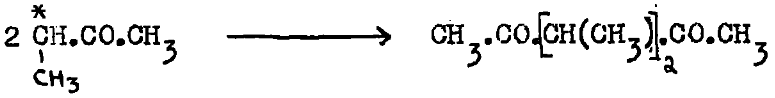
The formation of 1:4-diketones by direct linking of α-methylene carbon atoms demonstrates the analogy of the reaction of di-*tert*.-butyl peroxide with mono-ketones, and its reaction with olefins, *cyclo*-paraffins and alkyl benzenes. A similar reaction mechanism is probably operative:

$$(CH_3)_3C.O.O.C(CH_3)_3 \longrightarrow 2(CH_3)_3C.O* \qquad (R.101)$$



$$(CH_3)_3C.O^* + \underset{CH_3}{\underset{|}{CH_2}}.CO.CH_3 \longrightarrow (CH_3)_3C.OH + \underset{CH_3}{\underset{|}{\overset{*}{CH}}}.CO.CH_3$$

(R.102)

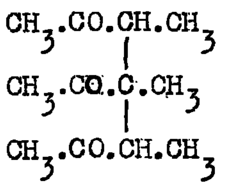


$$2\ \underset{CH_3}{\underset{|}{\overset{*}{CH}}}.CO.CH_3 \longrightarrow CH_3.CO[CH(CH_3)]_2.CO.CH_3$$

(R.103)

The presence of 3:4-dimethylhexandione-2:5 as the only diketone indicates the greater lability of the α-CH_2 group than either the α-CH_3 or β-CH_3 groups in methyl ethyl ketone.

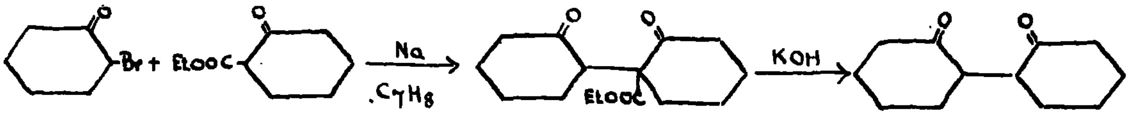
Further reaction of the initially formed diketone with tert.-butoxy radicals accoding to (R.102- R.103) gave a slightly impure triketone (LIX) together with a large amount of higher ketone polymers.



$$\begin{array}{c} CH_3.CO.CH.CH_3 \\ | \\ CH_3.CO.C.CH_3 \\ | \\ CH_3.CO.CH.CH_3 \end{array}$$

(LIX)

The reaction of the di-tert.-butyl peroxide with alkyl benzenes and monoketones is seen to provide new and readily accessible synthetic routes to the preparation of substituted dibenzyls and 1:4-diketones respectively. The latter reaction is of especial value since 1:4-diketones act as intermediates in the synthesis of many heterocyclic systems. The greater accessibility of 1:4-diketones by this method than by other existing methods is well demonstrated when the route used by Plant (198) to prepare $2:2^1$-diketodicyclohexyl is considered :



The ease of preparation in pure form and the relative freedom from hazard in reaction of the di-tert.-alkyl peroxides further suggest that these peroxides will be of greater synthetic value than the di-acetyl peroxide used by Kharasch (vid.p. 50)

CONCLUSIONS.

CONCLUSIONS.

The foregoing investigations have shown that the nature of the thermally promoted reaction of di-tert.-butyl peroxide with cyclic and acyclic olefins depends upon the structural pattern of the olefin. With those olefins containing the systems $-CH_2-CH{=}CH-$ and $-CH_2-C(CH_3){=}CH-$ the major reactivity of the peroxide involves the direct linking of the olefinic α-methylene carbon atoms to form "dimers" and higher "polymers" in which the original unsaturation of the olefin is retained. The peroxide is, in all cases, converted almost quantitatively into tert.-butanol, decomposition to acetone and methyl radicals occurring to an insignificant degree. This process, when applied to rubber hydrocarbon, results in its vulcanisation, the vulcanisate containing almost entirely hydrocarbon constituents and possessing properties similar to those found for rubber/sulphur vulcanisates.

The observed results have all been explained by a free-radical mechanism involving the initial scission of the O-O bond of the peroxide to give tert.-butoxy radicals. The latter are highly specific in their reactivity, abstracting labile (α -methylene) hydrogen atoms from the olefin and thus aquiring stabilisation as tert.-butanol.

Reaction of di-tert.-butyl peroxide with a vinylic olefin $CH_2{=}CH.CH_2-R$ involves two competitive reactions, (1) radical-linking processes typical of the olefins considered above, and (2) radical addition polymerisation typical of the reactions involved in the formation of synthetic rubbers, and plastics. The combined effect of these two processes results in a higher degree of polymerisation than that observed in the reactions with non-vinylic olefins and the resulting polymers possess considerably reduced unsaturation.

The complexity of reaction products resulting from the thermal decomposition of tert.-butyl hydroperoxide in cyclohexene demonstrates the diverse reactivities displayed by organic hydroperoxides when reacted with olefins. The peroxide is converted into the corresponding alcohol and the olefin is converted into a mixture of hydrocarbon and oxygenated products, the formation of which is explained by the initial decomposition of the hydroperoxide to give tert.-butoxy and hydroxyl radicals. The tert.-butoxy radicals give rise to olefin polymers described above and the hydroxyl radicals react mainly at the α-methylene positions of the olefin to give olefinic alcohols and ketones. Only a minor amount of attack by hydroxyl radicals at the double bonds is observed.

The relevance of these reactions to the processes involved in the oxidative degradation of rubber has been considered and a possible reaction scheme has been detailed to account for the redistribution of the oxygen of the initially formed polyisoprene hydroperoxide.

The thermal decomposition of dihydroascaridole, which can be considered as a cyclic di-tert.-alkyl peroxide, has been shown to follow a course identical with that for acyclic di-tert.-alkyl peroxides. Dihydroascaridole is remarkably stable and does not react with cyclohexene at 140°.

Investigations have been made of the thermal decomposition of di-tert.-butyl peroxide in non-olefinic compounds, including cycloparaffins alkyl benzenes, and cyclic and acyclic monoketones. The reactions involved closely parallel those observed with the peroxide and olefins and the results are in accord with a free radical mechanism involving the formation of new C-C bonds between the solvent molecules. The reactions are very similar to those of diacetyl peroxide with organic solvents studied by

Kharasch *et al.*

The results of the present investigation have advanced our knowledge of free-radical reactivities, especially those displayed by organic peroxides and various types of olefinic and related systems. All the many reactions encountered can be consistently explained by mechanisms involving the formation and subsequent stabilisation of free-radicals. The α-methylenic reactivity displayed by the olefinic systems $-CH_2.CH{=}CH-$ and $-CH_2-C(R){=}CH-$ towards alkoxy and hydroxyl radicals have been shown to be similar to that exhibited towards oxygen and sulphur.

PART (3).

EXPERIMENTAL.

ACKNOWEDGEMENT.

I wish to thank Dr.W.T.Chambers, Miss H.Rhodes and Miss E.Farquhar for the analytical data, Dr.H.P.Koch for the Spectrographic data and their interpretation , and Mr. T.A.Sharpley for the mechanical testing of the rubber samples.

In addition I express my appreciation to Dr.R.F.Naylor and Dr.J.L.Bolland for valuable discussions at various stages of the work.

EXPERIMENTAL.

(All melting points are uncorrected)

Di-tert.-butyl peroxide. This peroxide was prepared by both methods given by Milas and Surgenor (175).

(a) Di-tert.-butyl peroxide from tert.-butyl hydroperoxide and tert.-butyl hydrogen sulphate had b.p. 109.0-110/761.5 mm., n_D^{16} 1.3905. Yield 73%. (Found: C,65.45; H,12.65. Calc. for $C_8H_{18}O_2$: C,65.7; H,12.4%.)

(b) Di-tert.-butyl peroxide from tert.-butanol and hydrogen peroxide. When performed on a three mol. scale (based on tert.-butanol) using a reaction time of 4 hours and temperature of 0 to -5° the yield of crude product was 125g., n_D^{20} 1.3961. Fractionation of this gave the pure peroxide b.p. 109.0-110.0/760 mm., n_D^{20} 1.3882 (Found: C,65.7; H,12.3%), together with 16.5g. of higher boiling material which contained tri-isobutylenes, b.p. 177-186°/765mm., n_D^{20} 1.4320, and a small amount of higher polyisobutylenes.

(Milas and Surgenor (175) give for the peroxide, b.p. 109.0-109.2°/760mm., n_D^{20} 1.3872. Milas and Perry (175) give b.p. 12-13°/20mm., n_D^{25} 1.3838. Vaughan and Rust (241) give b.p. 108-110°, n_D^{20} 1.3893.).

The percentage of peroxidic oxygen in the peroxide was determined by the following method. About 0.1g. was heated with freshly distilled hydriodic acid (3.0c.c.) in sealed tubes at 80-90° for 3 hours. The liberated iodine was estimated by titration with standard sodium thiosulphate solution. A suitable correction for the hydriodic acid decomposed by oxygen in the tubes was made by heating 3.0c.c. of the acid under comparable conditions.(Found: P.O.C.,21.7, 21.95.Calc. for $C_8H_{18}O_2$: P.O.C.,21.9%).

REACTION of DI-tert.-BUTYL PEROXIDE with OLEFINS.

(A) REACTION with CYCLIC OLEFINES.

(1) cycloHEXENE.- The olefin was purified by repeated washing with sodium hydrosulphite solution, then water. It was dried for 24 hours over calcium chloride, then over sodium wire and finally was distilled over sodium wire in an atmosphere of purified nitrogen using a 14in. Fenske column, packed with glass helices, with a reflux head. The fraction b.p.82.50°/744.5mm.,n_D^{20}1.4463 was used.

The reaction was conducted under various conditions of molar ratio of olefin to peroxide and reaction time; the following being a representative example.

cycloHexene (164g., 2.0 mols.) with di-tert-butyl peroxide (48.7g., 0.33 mols.) was heated for 48 hours at 140° in Carius tubes sealed in an atmosphere of pure nitrogen. The product (212.0g.) was a colourless mobile liquid which on fractionation through a 10in. Vigreux column under nitrogen gave a forerun b.p.74-83°/764mm. (160.5g.). After removal of the last traces of volatile material by warming the residue at 50° for a short while on the water pump there remained a colourless oily product (45.0g.). The latter was distilled at oil pump pressure giving the fractions, (i) b.p.68-71°/1mm. (27.2g.), n_D^{20}1.5095, (ii) b.p.130-140°/1mm. (9.75g.), (iii) b.p.180-192°/1mm. (3.5g.) and an undistillable residue (*ca.* 4.2g.), which set to a glass on cooling.

Examination of the fractions.- The *forerun* consisted of a mixture of *tert.*-butanol, unchanged *cyclo*hexene and a trace of acetone. By aqueous extraction with 6 x 50g. of water 46.0g. of aqueous soluble material was obtained. This was found to be almost entirely *tert.*-butanol. In one experiment the aqueous extract was distilled giving an azeotrope of *tert.*-butanol/water, b.p.80°/763mm. This was dried over potassium hydroxide, the organic layer separated and distilled over sodium giving *tert.*-butanol, b.p.80-82°/765mm., identified as its phenyl urethane derivative m.p. and mixed m.p. with an authentic sample 135-136°. (Found: C,68.5; H,8.3; N 7.0. Calc. for $C_{11}H_{15}O_2N$: C,68.4; H,7.83; N,7.25%).

In a further experiment the aqueous extract was treated with an excess of saturated 2:4-dinitrophenylhydrazine solution (in 2N HCl). Acetone 2:4-dinitrophenylhydrazone was obtained, (0.24g. acetone), which on crystallisation from light petroleum, (b.p.100-120°), had m.p. 122-123° and mixed m.p. with an authentic sample 123-124°. (Found: C,45.7; H, 4.55. Calc. for $C_9H_{10}O_4N_4$: C,45.4; H,4.2%).

The yield of *tert.*-butanol represents 93.3% of the peroxide, the yield of acetone being insignificant, ($\ngtr$ 0.1% of peroxide).

The recovered *cyclo*hexene (114.5g.) was dried over calcium chloride and distilled over sodium in nitrogen, b.p., 83.0°/763m.m. A sample of the olefin on ultra-violet spectrographic analysis showed the almost complete absence of conjugated diene (Found 0.05-0.1% of 1:3 *cyclo*hexadiene), and the complete absence of benzene.

The *fraction (i)*, a colourless oily liquid, consisted mainly of the dimeric olefin $\Delta^{2'}$-*cyclo*hexenyl-Δ^{2}-*cyclo*hexene .

(Found: C;88.0; H,11.2). On careful fractionation (6in. Vigreux) over sodium in nitrogen, the pure hydrocarbon was obtained, b.p.62-63°/0.5mm., b.p.68-69°/1.0mm., $\underline{n}_D^{18}$1.5092. (Found: C,88.65; H,11.23; Iodine Value, 302.5,302.2; M(micro-Rast), 167.5. Calc. for $C_{12}H_{18}$: C,88.8; H,11.2%; Iodine Value, 313.6; M,162).

Quantitative catalytic hydrogenation of the $C_{12}H_{18}$ olefin.- A value of 1.97 double bonds per molecule was obtained. (Calc. for $C_{12}H_{18}$: $\vert^{=}2$). The olefin (31.46 mg.) in absolute ethanol (5.0c.c.) over Adams catalyst (10mg.) absorbed 9.06c.c. of hydrogen at 15° and 758mm. ≡ 8.57c.c. at N.T.P. (Calc.for $C_{12}H_{18}$,$\vert^{=}2$: 8.70c.c. at N.T.P.). The rate of hydrogenation is given in Fig. (1).

Hydrogenation of the $C_{12}H_{18}$ olefin.- The olefin (1.5g.) dissolved in absolute ethanol (20c.c.) was hydrogenated over previously reduced platinic oxide (75mg.), at room temperature and pressure. The hydrogen uptake on completion (ca. 6 hours) was 425c.c. at 16° and 753mm. ≡ 398c.c. at N.T.P. (Calc. for $\vert^{=}2$: 415c.c. at N.T.P.). After the removal of catalyst and solvent, distillation of the product over sodium yielded pure dicyclohexyl, b.p.72-73°/ca.1mm., $\underline{n}_D^{20}$1.4803, (1.3g.,86.7%). (Found: C,86.65; H,13.4, Calc. for $C_{12}H_{22}$: C,86.65; H,13.35%).

Bromination of the $C_{12}H_{18}$ olefin.- The olefin (2.0g.) dissolved in chloroform (20c.c.) was cooled in an ice/salt bath. To this was added , with stirring during one hour, a solution of bromine (3.75g.) in chloroform (20c.c.) until there remained a slight permanent excess of bromine. On removal of the solvent and excess bromine the bromide was obtained as a colourless crystalline solid, (5.75g., 96.6%). It was found to consist of a mixture of two, presumably stereoisomeric, cyclohexenyl-cyclohexene tetrabromides, which were separated by repeated fractional crystallisation from chloroform: (A), the more soluble form, predominated and separated in colourless prismatic plates m.p.159-162°, (Found: C, 29.9; H, 3.8; Br, 66.65. Calc. for $C_{12}H_{18}Br_4$: C, 29.9; H, 3.76; Br, 66.35%); (B), the less soluble form, was obtained in small amount. It crystallised in large colourless rectangular prisms m.p.188-190°, (Found: C, 29.85; H, 3.75; Br, 66.75%).

Both tetrabromides have been reported separately in the literature. (Farmer and Michael (83) give for (A) m.p.159°. Berlande (22), gives for (B) m.p.189-190°).

Nitric acid oxidation of the $C_{12}H_{18}$ olefin.- (cf. Berlande (22).). When the olefin (1.0g.) was oxidised with nitric acid (6c.c., d.1.42) at 100° the only product isolated was oxalic acid dihydrate (0.32g.). It crystallised from benzene/acetone in colourless prismatic needles m.p. 100-101.5°, m.p. (anhydrous acid) 187-188°, undepressed in mixed m.p. with authentic sample, (Found: E.W.63.0. Calc. for $C_2H_2O_4.2H_2O$: E.W.63.0).

Synthesis of $\Delta^{2'}$-cyclohexenyl-Δ^{2}-cyclohexene.-

(1). Preparation of 3-bromo-cyclohexene-1.- (cf. Ziegler et al. (266). N-bromosuccinimide (36.6g.) and cyclohexene (103c.c.) were gently refluxed for 30 minutes in pure dry carbon tetrachloride (150c.c.) in the presence of a little benzoyl peroxide as catalyst. The succinimide which separated out from the cold reaction mixture was filtered off (20.2g., Calc. 20.35g.). After removal of the solvent through a column, bromocyclohexene distilled over at b.p.58-60°/12mm., $n_D^{18.5}$ 1.5309, (25.0g., 75.5%). (Found: C, 44.75; H, 5.6. Calc. for C_6H_9Br: C, 44.75; H, 5.65%).

(2). Reaction of 3-bromo-cyclohexene-1 with magnesium.- The brome-cyclohexene (20.0g.) dissolved in ether (75c.c.) was added during 40 minutes to magnesium (2.0g.) just covered with ether. The reaction began on gentle heating. After completion the product was stirred for a further hour, decomposed with ice-cold ammonium chloride solution, the ether layer separated and dried over calcium chloride. The ether was removed on the water bath and the product distilled over sodium in nitrogen giving cyclohexenyl-cyclohexene, b.p. 62-63°/0.5 mm., n_D^{19} 1.5093, (9.4g., 94%). (Found: C,88.5; H,11.35. Calc. for $C_{12}H_{18}$: C,88.8; H, 11.2%.)

Bromination of the synthetic $C_{12}H_{18}$ olefin.- Adopting the method previously described (p.123) 2.0g. of the olefin gave 5.95g. (100%) of the tetrabromide mixture which on fractional crystallisation from chloroform gave the two cyclohexenyl-cyclohexene tetrabromides: (A) m.p. 160°. (Found: C,29.85; H,3.85; Br,66.3%), and (B) m.p. 189-190°. (Found: C,29.9; H,3.8; Br,66.4. Calc. for $C_{12}H_{18}Br_4$: C,29.9; H,3.75; Br,66.35%). The lower melting form (A) was as before, the major product.

The fraction (ii) was a colourless viscous liquid which on refractionation over sodium in nitrogen distilled mainly at b.p.133-134°/ 1 mm., n_D^{20} 1.5330. It analysed to the olefinic hydrocarbon di-cyclohexenyl cyclohexene, $C_{18}H_{26}$, F3. (Found: C,88.9; H,10.85; Iodine value, 282, 284, 287; M (micro-Rast)239. $C_{18}H_{26}$ requires C,89.2; H,10.8%; Iodine Value, 315; M,242.

Quantitative catalytic hydrogenation of the $C_{18}H_{26}$ olefin. - A value of 2.94 double bonds per molecule was obtained. (Calc. for $C_{18}H_{26}$: F3). The olefin (28.94m.g.), distilled immediately prior to hydrogenation (b.p.128-130°/1 mm.), dissolved in glacial acetic acid (5.0c.c.) was reduced over Adam's catalyst (10 mg.). 8.38 c.c.of hydrogen were absorbed at 15° and 754mm. ≡ 7.88c.c. at N.T.P. (calc. for $C_{18}H_{26}$ Γ3: 8.04c.c. at N.T.P.). The rate of hydrogenation is given in Fig(2).

Hydrogenation of the $C_{18}H_{26}$ olefin.- A solution of the olefin (5.0g.) in a mixture of glacial acetic acid and ethyl acetate (15c.c.) was hydrogenated over previously reduced Adam's catalyst (0.15g.) at room temperature and pressure. The hydrogen uptake was 1435c.c. at N.T.P. (Calc.: 1390c.c. at N.T.P.). During the reduction a colourless crystalline solid separated out. The solution was warmed to dissolve the solid, the catalyst removed and the solvent distilled off under reduced pressure, leaving the saturated hydrocarbon (4.95g.). Distillation of this gave a fraction (i) b.p.147-150°/2 mm., (3.5g.) which partially crystallised on cooling, and (ii) a colourless crystalline residue (1.45g.). The latter, when combined with the solid in fraction (i) (0.2g.), gave the high melting form of 1:4-di<u>cyclo</u>hexyl-<u>cyclo</u>hexane obtained as colourless feathery plates from ethyl acetate, m.p. 162-163°. (Found: C,86.9; H,13.0; Calc. for $C_{18}H_{32}$: C,87.0; H,13.0%). (Von Braun, Irmisch and Nelles (37) give m.p.162°; Corsen and Ipatieff (55) give m.p.159.5-161°).

The colourless liquid in fraction (i) had b.p.122-128°/1 mm., n_D^{18} 1.5072. It could not be induced to crystallise and consisted, presumably of a mixture of 1:4- and 1:3-di<u>cyclo</u>hexyl-<u>cyclo</u>hexane stereoisomers. (Found: C,87.05; H,12.60%). (Corson and Ipatieff (55) report for the low melting 1:4-isomer, m.p.54-56° and later (56) for the two 1:3 isomers, m.p.62.5-63.5° and mp.57-59°).

Selenium dehydrogenation of the $C_{18}H_{26}$ olefin.- The olefin (2.0g.) and powdered selenium (6.0g.) were heated in an atmosphere of nitrogen for 40 hours at a metal bath temperature of 320°. Hydrogen selenide was evolved almost immediately. The product, which solidified on cooling, was extracted with boiling benzene and on removal of the solvent gave a solid (1.8g.). Sublimation of this over molten sodium at 0.05 mm. (bath temperature, 200-250°) gave a colourless crystalline solid (1.53g.) melting over a considerable range <u>ca</u>.50° - <u>ca</u>.175°. Crystallisation from benzene gave 1:4-diphenylbenzene (0.4g.) as lustrous plates m.p.211-212° (literature records m.p.213°). (Found: C,93.35; H,6.15. Calc. for $C_{18}H_{14}$: C,93.9; H,6.1%) The benzene mother liquor on evaporation to dryness gave a solid (0.99g.) which on repeated fractional crystallisation from absolute methanol gave the following fractions: (i) a mixture of 1:4- and 1:3-diphenylbenzene (0.6g.); (ii) 1:3-diphenylbenzene as colourless needles m.p.82°(softening) -84°, (0.15g.). (Found: C,94.0; H,6.1. Calc. for $C_{18}H_{14}$: C,93.9; H,6.1%) and (iii) a less pure 1:3-diphenylbenzene m.p.82-83°, (0.13g.). (The highest recorded m.p. for 1:3-diphenylbenzene is 87°).

<u>Bromination of the $C_{18}H_{26}$ olefin</u>.- A solution of the olefin (2.0g.) in chloroform (20c.c.) was cooled to 0°. To this was added, during 1 hour with constant stirring, a solution of bromine (1.5c.c.) in chloroform (20c.c.) until a permanent excess of bromine was present. Removal of the solvent under reduced pressure gave a colourless solid bromination product (5.4g.) This proved to be a mixture of difficulty seperable isomeric <u>hexabromides</u> of di-<u>cyclo</u>hexenyl-<u>cyclo</u>hexene. Crystallisation from chloroform gave the following, (A) a very insoluble colourless crystalline powder (0.1g.), m.p.285-287° (sublimation). (Found: C,29.95; H,3.7; Br, 66.55. $C_{18}H_{26}Br_6$ requires C,29.94; H,3.65%; Br,66.45%); (B) a micro-crystalline powder, m.p.249-250° (<u>ca</u>.50mg.); (C) the major product, micro-crystals, m.p.217-219°) (Found: C,29.95; H,3.7; Br,67.0.). Other isomers though probably present, were not isolated.

The fraction (iii) was a colourless extremely viscous liquid which on refractionation over sodium in nitrogen had b.p.180-193°/1 mm., n_D^{20} 1.5478. It analysed to a cyclohexene "tetramer", bis-cyclohexenylcyclohexene. (Found: C,89.05; H,10.7; Iodine Value, 282, 284; M (micro-Rast),313. $C_{24}H_{34}$ requires C,89.35; H,10.65%; Iodine Value, 315.5; M,322.). Though molecularly homogeneous it doubtless contained many structural isomers.

Quantitative catalytic hydrogenation of the $C_{24}H_{34}$ olefin.- A value of 3.98 double bonds per molecule was obtained. (Calc.for $C_{24}H_{34}$ F4). The olefin (29.62mg.), distilled immediately prior to hydrogenation, in glacial acetic acid (5.0c.c.) over Adam's catalyst (10mg.), absorbed 8.66c.c. of hydrogen at 13° and 753mm. $\equiv$ 8.20c.c. at N.T.P. (Calc. for $C_{24}H_{34}$ F4: 8.24(5)c.c. at N.T.P.). The rate of hydrogenation is given in Fig.(3).

Ultra-violet spectrographic analysis of the cyclohexene polymer products.- Representative samples of the various polymer fractions were submitted to ultra-violet spectrographic analysis.

(1). Cyclohexenylcyclohexene and dicyclohexenyl-cyclohexene.- showed no selective absorption consistent with the presence of conjugated diene units.

(2). Bis-cyclohexenyl cyclohexene from the 6:1 run (Table 4), in cyclohexane/10% ethanol as solvent, showed selective absorption near λ max2450A, $E^{1\%}_{1cm.} \sim 45$ and also at ~ λ_{max}2830A, $E^{1\%}_{1cm.} \sim 50$.

(3) Bis-cyclohexenylcyclohexene from the 4:1 run (Table 5), in 1:1 cyclohexane/ethanol as solvent, showed selective absorption at λ_{max}2430A, $E^{1\%}_{1cm.}$ 50 and at λ max2860A, $E^{1\%}_{1cm} \doteqdot 65$.

(4) The polymeric mixture obtained as the undistillable residue from the 4:1 run, ((A), Table (5), in 1:1 *cyclo*hexane/ethanol as solvent, showed selective absorption at λ_{max}2430A, $E^{1\%}_{1cm.}$ 140 and at λ_{max}2860A, $E^{1\%}_{1cm.}$45. The polymeric mixture in the 2:1 run, ((B), Table (5) gave similar bands at λ_{max}2430A, $E^{1\%}_{1cm.}$180 and at λ_{max}2860A, $E^{1\%}_{1cm}$ 90.

(2) Δ^1METHYL-*cyclo*HEXENE.-

Preparation of the olefin.- 1-Methyl-*cyclo*hexanol-1 was prepared by the Grignard reaction of *cyclo*hexanone (b.p.56-56.5°/20 mm., n_D^{21}1.4508) with methyl magnesium iodide. (Yield: 72.4%; b.p.62.5-64°/16 mm., n_D^{17}1.4618). Dehydration of the alcohol with 1% of iodine, at 140°, gave methyl*cyclo*hexene b.p.109.0-110.0°/760 mm., $n_D^{19.5}$1.4503.

Reaction with Di-tert.-Butyl Peroxide.- The olefin (50g., approximately 0.5 mol.) amd di-*tert*.-butyl peroxide (18.25g., 0.125 mol.) were heated in a Carius tube sealed under nitrogen, at 140° for 24 hours. The product (66.0g.) was a colourless mobile liquid which on fractionation gave the fractions, (i) b.p.82-110° (44.2g.); (ii) b.p. < 86°/1 mm., (0.35g.); (iii) b.p. 86-94°/ 1mm., (10.15g.); (iv) b.p.94-146°/1 mm., (0.45g.); (v) b.p. 146-149°/1 mm., (3.85g.); (vi) b.p.203-204.5°/1 mm., (2.4g.); (vii) a residue in the still (a polymeric colourless glass not further investigated) *ca*.4.0g.

Examination of the fractions.- **Fraction (i)** was shown, on aqueous extraction, to contain 18.0g. of water soluble compounds being mainly *tert*.-butanol, isolated as previously described, b.p. 82-82.5°/760 mm. Only traces of acetone were present, being identified and estimated as its 2:4-dinitrophenylhydrazone, m.p.124-125° (yield 0.11g.

≡0.027g. acetone). The non-aqueous layer was unchanged methyl*cyclo*hexene which after drying (calcium chloride) and distilling over sodium amounted to 25.0g. and had b.p.109-110°/760mm., $n_D^{17.5}$ 1.4510.

Fraction (iii), a colourless oily liquid, was identified as *dimethyl*-cyclo*hexenyl*-cyclo*hexene*. It was molecularly homogeneous but probably consisted of a mixture of structural isomers. Redistillation over sodium in nitrogen gave a main fraction b.p.74-78°/0.5mm., n_D^{20}1.5116. (Found two different samples): C,88.35; 88.55; H, 11.80; 11.65; M(micro-Rast),214; M(benzene),233; Unsaturation value (by catalytic hydrogenation) F2.00. $C_{14}H_{22}$ requires C,88.35; H,11.65; M,190; F2.).

Hydrogenation of the $C_{14}H_{22}$ olefin.- The olefin (1.37g.) in absolute alcohol (150c.c.) was hydrogenated over palladium-charcoal (200 mg.). The hydrogen uptake was 305.0c.c (N.T.P.); Calc; 322.9c.c. (N.T.P.) After removal of the catalyst and solvent the reductant, dimethyl*cycl*ohexyl-*cyclo*hexane, was distilled over sodium giving two fractions: (i) b.p.64-68.0°/0.5mm., n_D^{20} 1.4827, (0.56g.) (Found: C, 86.7; H, 13.45.); and (ii) b.p. 68.0°/0.5mm., n_D^{20} 1.4831, (0.47g.) (Found: C, 86.6; H, 13.5. Calc. for $C_{14}H_{26}$: C, 86.5; H, 13.5%). Both products (i) and (ii) were colourless mobile liquids stable towards potassium permanganate solution and bromine.

Bromination of the $C_{14}H_{22}$ olefin.- Bromination of the olefin at 0° in chloroform showed that the theoretical amount of bromine for addition to two double bonds was consumed. The product, however, on removal of the solvent rapidly lost hydrogen bromide and darkened. No solid tetrabromides could be isolated.

Fraction (v) was a viscous colourless liquid. On redistillation (4" Vigreux column) over sodium in nitrogen it had b.p. 144-148°/1mm., n_D^{20} 1.5339. Elementary analysis, molecular weight and unsaturation determinations showed it to be a *trimethyl-di-cyclohexenyl-cyclohexene*, (probably a mixture of structural isomers) (Found: C, 88.75, 88.8; H, 11.25; 11.35; M(benzene) 268, 280, 300; Unsaturation value (catalytic hydrogenation: Γ2.87. $C_{21}H_{32}$requires C, 88.65; H, 11.35; M, 284; Γ3.).

Fraction (vi) was an extremely viscous colourless "semi-glass". Distillation through a 4 inch Vigreux column over sodium gave a small forerun b.p. $<$ 186°/0.1mm. and a main fraction b.p. 186-192°/0.1mm. The latter fraction analysed to a *methylcyclohexene* "*tetramer*". (Found: C, 89.0; H, 11.35. $C_{28}H_{42}$ requires C, 88.8; H, 11.2%).

(3) $\Delta^{2'}$-cyclo*HEXENYL*-Δ^{2} -cyclo*HEXENE*.-

The olefin (b.p.68-70°/1mm., 16.2g.) and di-*tert*.-butyl peroxide (7.3) were heated at 140° for 48 hours in an evacuated sealed tube. The product (23.0g.) on fractionation gave the following fractions: (i) *tert*.-butanol, b.p. 80-82.5°/751mm., (6.8g., 92% of the peroxide); (ii) unchanged olefin, b.p. 64-67°/ca.1mm., n_D^{20}1.5090, (5.8g., 35.8% of the original olefin). Found: C, 88.45; H, 11.4. Calc. for $C_{12}H_{18}$: C, 88.8; H, 11.2%); (iii) b.p. 180-190°/1mm., n_D^{20}1.5468, (3.0g.); (iv) residue in the still (6.6g.) which set on cooling to a bright orange resin.

Fraction (iii) was identified as a cyclohexene "tetramer", bis,-cyclohexenylcyclohexene. (Found: C, 89.35; H, 10.8; Iodine Value, 289, 292; Unsaturation value (catalytic hydrogention) Γ3.84. $C_{24}H_{34}$ requires C, 89.36; H, 10.64%; Iodine Value, 315.5; Γ4).

The residue, fraction (v), consisted mainly of a cyclohexene polymer mixture, of an average "octameric" complexity. (Found: Iodine value, 307.3; 307.5; M(micro-Rast), 666. $C_{48}H_{66}$ Γ8 requires Iodine value, 316, M, 643).

(B) REACTION with ACYLIC OLEFINS.

(1) 1-HEPTENE.- The olefin was prepared by the reaction of allyl bromide with n-butyl magnesium bromide, (cf. Wilkinson (259)). The crude olefin had b.p. 90-95°/743mm. It was carefully refractionated over sodium wire in an atmosphere of purified nitrogen through a three foot Widmer column, a middle fraction b.p. 92.0-93.2°/746mm., n_D^{20} 1.3999, being collected (Found: C, 85.6; H, 14.8. Calc. for C_7H_{14}: C, 85.6; H, 14.4%).

A mixture of the olefin (85.0g.) and di-tert.butyl peroxide (31.7g.) was heated at 140° for 24 hours in nitrogen-filled Carius tubes. The product (116.0g.), a light yellow oil, on fractionation gave; (i) b.p. 75-86°(32.5g.); (ii) b.p.84-100°/1mm., n_D^{20} 1.4410, (9.1g.)(Found: C, 84.6; H, 14.35%; (iii) residue (64.5g.)

Examination of the fractions.- Aqueous extraction of the forerun (i) gave tert.-butanol (27.1g., 85.5% of the peroxide) and recovered olefin (5.4g.) which, after drying over calcium chloride and distilling over sodium, had b.p. 94.0-96.5°/766mm., $\underline{n}_D^{20}$ 1.4000.

A portion of the <u>fraction (ii)</u> (5.0g.) was carefully refractionated over sodium through a 6 in. Vigreux column. It gave the fractions, (ii) (A), b.p. 58-70°/0.1mm., $\underline{n}_D^{24}$ 1.4420 (1.1g.) (Found: C, 85.2; H, 14.35; M(benzene), 196. Calc. for $C_{14}H_{28}$: C, 85.6; H, 14.35%; M, 196. Calc. for $C_{14}H_{26}$: C, 86.5; H, 13.5%; M, 194.); (ii) (B) b.p. 70-76°/0.1mm., $\underline{n}_D^{24}$ 1.4440, (1.85g.) (Found: C, 85.8; H, 14.45; M(benzene), 207,208,209); (ii)(C), b.p. 76-78°/0.1mm., $\underline{n}_D^{24}$ 1.4430, (1.65g.) (Found: C, 85.1; H, 14.6; M(benzene), 211). Quantitative catalytic hydrogenations of (ii)A-(ii)(C) in glacial acetic acid over Adam's catalyst gave the following unsaturation values: (ii)(A), 98.6c.c.H_2/g 97.85 c.c. H_2/g. (N.T.P.); (ii)(B), 83.8c.c./g.; (ii)(C) 93.7c.c./g. (Calc. for $C_{14}H_{28}$, Γ1 : 114.3 c.c./g.; Calc. for $C_{14}H_{26}$, Γ2: 231.0c.c./g.

The residue (iii) was a mixture of polymeric hydrocarbons of unsaturation value considerably lower than in the parent olefin. No attempt was made at any separation or further investigation of the components. (Found: C, 85.7; H, 14.0; n_D^{20} 1.4737; M(benzene) 590. Calc. for $C_{42}H_{84}$, Γ1: C, 85.6; H, 14.4%; M, 588. Catalytic hydrogenation gave a hydrogen uptake of 34.7c.c./g.(N.T.P.) Calc. for $C_{42}H_{84}$, Γ1: 38.1c.c./g., compare heptene, 228.4c.c./g.).

Infra-red spectrographic analysis of 1-heptene and 1-heptene products.

The various samples were examined as the pure liquids in rock salts absorption cells of path length 0.1mm. on a Hilger double - beam research instrument run on single-beam photographic recording.

The Synthetic 1-heptene had very strong bands at 909 and 990cm^{-1}. Selective absorption of other characteristic frequencies was absent. (Spectrum I).

The recovered 1-heptene contained, in addition to the 909 and 990cm^{-1} bands, an extremely weak band at 965cm^{-1}.

The dimer fractions (ii) (A), (B), (C) had spectra very similar to one another. In addition to strong absorption at 910 and 990cm^{-1} they displayed a strong band at 965cm^{-1} and other bands at 1082 and 1198cm^{-1}. There was also a weak band at 887cm^{-1}. (Spectrum 2, Fraction (ii)(B).

The polymer mixture.- In this case by far the strongest absorption occurred at 965cm^{-1}.

(2) 4-METHYL-Δ^3-HEPTENE.-

Preparation of the olefin.- 4-Methylheptan-4-ol was prepared by the Grignard reaction of methyl-n-propylketone with n-propyl magnesium bromide. The carbinol was obtained as a colourless oily liquid, b.p. 70-78°/20-23mm., n_D^{20} 1.4258. Yield: 66.3%.

Dehydration of the carbinol was effected by refluxing it with ca. 0.5% of iodine at 140-150° for 3.5 hours in a slow stream of nitrogen. The azeotrope, b.p.88-120° of olefin and water was distilled off through a short column, the olefin separated and dried over calcium chloride. It was carefully fractionated, over sodium in a nitrogen atmosphere, through a 14 inch glass helices packed Fenske column using a reflux head and reflux ratio of 5:1. A main fraction, b.p. 116.0-117.0°/738mm., n_D^{20} 1.4175 (50% yield) was collected and used. An infra-red spectrographic analysis of the olefin (Spectrum 3) indicated that the main type of unsaturation was trialkyl ($R'CH{=}C\langle^{R^2}_{R^3}$), but there was also a small amount of as.-dialkyl ($R_2C{=}CH_2$) present, indicative of the 4-methyleneheptane isomer. Other types of unsaturation were definitely absent.

Reaction with di-tert.-butyl peroxide.- A mixture of the olefin (112g., ∝ 4 mols.) and the peroxide (36.5g., ∝ 1 mol.) was heated at 140° for 24 hours in Carius tubes sealed in an atmosphere of nitrogen. The colourless liquid product (148.0g.) on fractionation gave a forerun (i) b.p.80-120°/742mm., (89.3g.). The remaining product (57.0g.) when heated on a water bath to 95°/21mm., gave a fraction (ii) b.p. $<28°$/21mm., n_D^{20} 1.4187, (8.9g.) and a residual liquid (iii) n_D^{20} 1.4641, (47.9g., 42.7% of olefin), which contained entirely olefinic hydrocarbon constituents (Found: C, 86.35, 86.1; H, 13.65, 13.65). A portion (46.8g.) of (iii) on fractionation under nitrogen gave the following fractions: (iv) b.p. $<71°$/0.05mm., n_D^{20} 1.4510 (2.0g.); (v) b.p.67°/0.01mm.-72°/0.05mm., n_D^{20} 1.4586 (25.3g.) and a residue (vi) n_D^{20} 1.4775 (19.0g.) which was not further investigated (Found: C, 86.15; H, 13.4%)

Examination of the fractions.- The forerun (i) was extracted with water (300g., then 200g.) and gave water soluble constituents (36.0g.). Treatment of the aqueous extract with aqueous 2:4-dinitrophenylhydrazine

(2N,HCl) gave acetone-2:4-dinitrophenylhydrazone (0.32g. ≡ 0.08g. acetone). The only other water soluble material was *tert.*-butanol (ca. 36.0g., corresponding to 97.3% of the peroxide).

The olefin present in fractions (i) and (ii) was combined and on distillation over sodium under nitrogen gave a fraction, b.p. 117.0-120.0°/755mm., n_D^{20} 1.4184, (cf. constants for original olefin).

The fraction (v), a colourless oily liquid, analysed to the methylheptene "dimer", *hexadecadiene* (Found: C, 86.1; H, 13.6, M(benzene) 246. $C_{16}H_{30}$ requires C, 86.4; H, 13.6%; M, 222).

Reduction of the $C_{16}H_{30}$ olefin.- The redistilled olefin (3.1g.) was dissolved in absolute ethanol (50cc.) was hydrogenated over palladium/charcoal catalyst (1.0g.) at room temperature and pressure. The hydrogen uptake (535cc. at N.T.P.) corresponded to 85.6% of theoretical for $C_{16}H_{30}$ $\ulcorner$ 2. After removal of the catalyst and solvent and distillation of the reductant, hexadecane was obtained as a colourless liquid, b.p. 64-67°/0.1mm., n_D^{20} 1.4439 (2.3g.) Found: C, 84.9; H, 14.95. Calc. for $C_{16}H_{34}$: C, 84.85; H, 15.15%). The product was stable towards aqueous potassium permanganate over a long period.

Infra-red spectrographic analysis of 4-methyl-3-heptene products.

The samples were examined as the pure liquids in rock salt absorption cells of path length 0.1mm. on a Hilger double-beam research instrument run on single-beam photographic recording.

(1) *The recovered 4-methyl-3-heptene* had a higher ratio of $CH_2 = C-R_2$ to $R-CH = C.R_2$ than in the original olefin, and

also gave a band at 963cm^{-1} consistent with a trace of $R.\ CH = CH - R$ which was absent in the original hydrocarbon.

(2) The methylheptene "dimer" (Spectrum 4). In the dimer the ratio of $CH_2 = C - R_2$ to $R.\ CH = C.R_2$ was about the same as in the original olefin. A strong new band appeared at 975 cm.$^{-1}$ and there was broadening of the 1640 cm.$^{-1}$ double-bond absorption band. This has been attributed to the presence of a new form of unsaturation, $R_3.\ C.\ CH = CH - R$ not present in the original olefin.

(3) Hexadecane; methyl heptene dimer reductant. The unsaturation absorption in the 1650 cm.$^{-1}$ region and the strong bands at 847 cm.$^{-1}$ and 975 cm.$^{-1}$, assigned to $R_2.\ C = CH - R$ and $R.\ CH = CH - R$ respectively, were all absent.

(3) RUBBER HYDROCARBON.- Two series of experiments were made in which (a) raw "smooth smoked sheet" rubber and (b) acetone-extracted smoked sheet were reacted with varying amounts of peroxide in the absence of oxygen for 6 hours at 140°. The general experimental technique was as follows: Strips of the rubber (ca. 4 x 0.5 x 0.1 inches) of known weight were left in contact with the appropriate amounts of peroxide in tubes sealed in an atmosphere of purified nitrogen. After 24-48 hours contact it was assumed that even distribution of the peroxide in the rubber had been attained. The samples were quickly weighed and, while cooled in liquid air to prevent loss of peroxide, were sealed in Carius tubes in a nitrogen atmosphere of ca. 0.05 mm. and heated at 140° for 6 hours. In the case of the acetone-extracted samples the rubber was extracted for 24 hours in a nitrogen atmosphere, both

before and after reaction, and were then dried for 3-5 days at 10^{-5}mm.

Mechanical properties and the equilibrium swelling constant (Qm) in benzene of all the samples were measured immediately after reaction. The latter measurement enabled an estimate of the average molecular weight between junction points (Mc) in the cross-linked rubber molecules to be made (vid. p. 80).

Determination of Qm. Pieces (ca. 0.5-1.0 g.) of the various rubbers, of known density, were left in contact with an excess of benzene in a thermostat at 25.0°. After 5-7 days, equilibrium swelling had been attained. The samples were quickly surface dried and weighed. The weight and thus the volume of benzene imbibed by unit volume of rubber (Qm) was readily calculated. All the above data are given in Tables (6) and (7)[1].

Chemistry of the reaction:

Experiment (1).- A sample of acetone-extracted "smooth smoked sheet" rubber was dried for 4 days at 10^{-5} mm. and then immediately analysed (Found: C, 86.3; H, 11.45; C/H, 7.54:1; O, 0.98, 0.965; ash, 0.25%). This sample was reacted with 51.5% of di-*tert*.-butyl peroxide for 6 hours at 140°. A liquid which separated from the product after reaction was shown to be mainly *tert*.-butanol, together with some acetone but no peroxide. The rubber product (a hard brittle solid having no rubber-like properties), was acetone-extracted and dried for 7-9 days at 10^{-5}mm. (Found: C, 87.3, 86.6; H, 11.3, 11.55; C/H, 7.725-7.50:1; O, 1.32, 1.32; ash, 0.95%).

Experiment (2).- A sample of rubber (17.0 g.) as in experiment (1) was allowed to imbibe di-tert.-butyl peroxide (8.2 g., 48.2% w.w. of rubber) in an atmosphere of purified nitrogen over a period of two weeks. The rubber/peroxide mixture was then heated in the absence of oxygen at 140° for 6 hours. The liquid product (5.8 g.) which separated out after reaction was pumped off at 1 mm. pressure and collected in a liquid air trap. It was a colourless liquid boiling entirely over the range 56-80° and was shown to consist of a mixture of acetone and tert.-butanol. The acetone (36.6% of original peroxide) was estimated and identified as its 2:4-dinitrophenylhydrazone, m.p. 124-125°, mixed m.p. 125°. the Tert.-butanol (41.1% of original peroxide) was identifed as its phenyl urethane, m.p. and mixed m.p. 136°. No unchanged peroxide was found.

REACTION OF DIHYDROASCARIDOLE WITH OLEFINS.

Ascaridole was freshly distilled before use, the fraction b.p. 66-67°/1mm., n_D^{15} 1.4752, being used. (Found: C, 71.7; H, 9.6. Calc. for $C_{10}H_{16}O_2$: C, 71.41; H, 9.6%).

Quantitative hydrogenation of Ascaridole.- The peroxide (30.38 mg.) was hydrogenated in absolute ethanol (10.0 c.c.) over platinic oxide catalyst (10 mg.) A total of 8.01 c.c. (N.T.P.), of hydrogen was absorbed representing 98.8% of the theoretical of complete reduction to cis-1:4-terpin. The rate of hydrogenation (Fig. 4) shows that 1 molecule of hydrogen per molecule of peroxide is absorbed rapidly (ca. 5 minutes) and a second molecule is absorbed more slowly taking a total of 18 hours for complete reduction.

Preparation of Dihydroascaridole.- (cf. Paget(190)).

Ascaridole (60g.) in absolute alcohol (100c.c.) was reduced over platinic oxide catalyst (0.5 g.) at room temperature and pressure. Hydrogenation was stopped when approximately 1 molecule of hydrogen per molecule of peroxide had been absorbed. Found: 8.7ℓ. at 18° and 752 mm. Calc. for 1 mol. H_2:8.62ℓ. The catalyst and solvent were removed and on distillation of the product (58.0 g.), dihydroascaridole was obtained as a light green oily liquid, b.p. 58-60°/1mm. (41.2g.). It was purified by crystallisation from an equal volume of light petroleum (b.p.40-60°) cooled in an ice-salt mixture; the process was extremely wasteful owing to the ready solubility of the peroxide in the solvent and its low melting point. Dihydroascaridole separated in large colourless prisms, m.p.19-20°, n_D^{15} 1.4690, (17.0g.) (Paget,(190) gives m.p. 19.5°) (Found: C, 70.3; H, 10.65; Iodine Value, O. Calc. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.70; Iodine Value, O.).

The residue in the still (17.8g.) was a brown viscous gum consisting of unchanged ascaridole and cis-1:4-terpin. On trituration with a little benzene and crystallisation from the same solvent, cis-1:4-terpin was obtained in colourless plates, m.p. 117°.

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(A). cycloHEXENE.-

A mixture of dihydroascaridole (8.2g.) and cyclohexene (45.0g.) was heated in a nitrogen filled sealed tube at 140° for 18 hours. There was no pressure increase on opening the tube.

The product (53.2g.) on fractionation gave *cyclo*hexene, b.p. 83-84°, and on removal of the last traces of olefin on the water pump, dihydroascaridole (8.2g., 100%) was recovered completely unchanged. All physical constants were in agreement with those of the original peroxide. B.p. 58-60°/1mm., $\underline{n}_D^{15}$ 1.4690, m.p.18-19° (Found: C, 70.85; H, 10.6. Calc. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.70).

Catalytic hydrogentation of the product in ethanol and over palladium-charcoal gave *cis*-1:4-terpin in 96% yield. Colourless plates from benzene, m.p. 117°, (literature gives m.p.117°). (Found: C, 70.2; H, 11.9. Calc. for $C_{10}H_{20}O_2$:C, 69.7; H, 11.7%).

PYROLYTIC DECOMPOSITION OF DIHYDROASCARIDOLE.

Dihydroascaridole (10.0g.) was heated under an *efficient* reflux at an oil bath temperature of 240° for 6 hours. The liquid refluxed gently and no explosive decomposition occurred. The product weighed 8.50g., showing a loss in weight (presumably by gaseous evolution) of 1.50g. On fractional distillation it gave the fractions; (i) b.p. 79-82°/9mm., (3.1g.); (ii) unchanged peroxide, b.p. 104-106°/10mm., (1.4g.); (iii) a dark brown viscous polymeric residue (*ca.* 4.0g.) which was not further investigated.

Fraction (i) was identified as the 1:4-diketone, 2-methylheptandione-3:6. (Found: C, 67.7; H, 9.85; $\underline{n}_D^{20}$ 1.4322. Calc. for $C_8H_{14}O_2$:C, 67.55; H, 9.9%). (Semmler(224) gives b.p.82-86°/10m m.,

n_D 1.433. Von Auwers and Hinterseber(7) give b.p. 90-91°/16 mm., n_D^{20}1.4330.

Refluxing the ketone with hydroxylamine hydrochloride and sodium acetate in aqueous ethanol for 5 hours, gave the dioxime which separated from acetone in colourless rectangular prisms, m.p. 137° (Wallach and Meister(248); Ciamician and Silber(50) both record m.p. 137°). (Found: C, 55.95; H, 9.5; N, 16.25. Calc. for $C_8H_{16}O_2N_2$: C, 55.8; H, 9.35; N, 16.3%). The semicarbazide derivative (1-ureido-2-methyl-5-*iso*-propyl pyrole) separated from absolute ethanol (in which it was difficultly soluble) in colourless micro-crystals, m.p.199-200°. (Henry and Paget(122) and Ciamician and Silber(50) record m.p.201°).

REACTION of tert.-BUTYL HYDROPEROXIDE with OLEFINS.

tert.-Butyl hydroperoxide was prepared according to the method of Milas and Surgenor(175). The final product, after drying over magnesium perchlorate, had b.p. 37.5-38.0°/20mm., n_D^{20} 1.4004, n_D^{25}1.3980. (Milas and Surgenor(175) give n_D^{20}1.4013, Milas and Perry(175) give b.p. 33-34°/17mm., n_D^{25}1.3983).

(1) REACTION with cycloHEXENE.- A mixture of cyclohexene (328g., 4 mol.) and *tert.*-butyl hydroperoxide (60g., 0.66 mol.) was heated at 140° (± 1°) for 24 hours in nitrogen-filled Carius tubes. The product (386.2g.) separated into two layers, the upper layer which predominated being light yellow in colour, and the lower layer being colourless and consisting mainly of water.

Fractionation of the product in nitrogen gave a *forerun* (i) b.p. 66.0 - 82.5°/750mm., (257.2g.). The residue (126.4g.) on evacuation on the water pump at room temperature gave *cyclo*hexene (ii) n^{20}_{D} 1.4460, (47.0g.) which was collected in a liquid air trap. The residue (iii) was a light yellow oxygenated material amounting to 78.4g. (Found: C, 81.25; H, 11.05; O(by difference), 7.7; OH, 6.75, 6.85, 6.95; O(as OH) 6.35-6.54%). A portion (74.6g.) of (iii) on fractionation in nitrogen through a 7" Vigreux column gave the following main fractions:(iv) b.p. (small amount) 53°- (mainly) 62.0 - 62.5°/10mm., n^{20}_{D} 1.4740, (22.1g., *23.2g.*); (v) b.p.62.5°/10mm.-63°/0.6mm., n^{20}_{D} 1.4798, (4.8g., *5.05g.*); (vi) b.p. 63-68°/0.6-0.7mm., n^{20}_{D} 1.5000, (28.1g., *29.5g.*) (vii) a residual viscous yellow liquid, (15.9., *16.7g.*).(The weights underlined correspond to 78.4g. of (iii)) A portion of fraction (vii) (14.8g.) was transferred to a smaller still and on distillation gave: (viii) b.p. 72-106°/1mm., n^{20}_{D} 1.5080, (0.6g., *0.68g.*); (ix) b.p. 106-132°/1mm., n^{20}_{D} 1.5210, (5.8g., *6.55g.*); (x) b.p. 132-142°/1mm., n^{20}_{D} 1.5319, (2.4g., *2.7g.*); (xi) a residual viscous orange liquid, undistillable at a bath temperature of 200°/1mm., n^{20}_{D} 1.5455, (4.5g., *5.1g.*). (The weights underlined correspond to 16.7g. of (vii).

Examination of the fractions.- The fraction (i) consisted of a mixture of *cyclo*hexene, *tert.*-butanol, water and a trace of acetone. In one experiment the total water soluble material was estimated by extraction with water (3 x 400g.) yielding water soluble compounds (50.1g.) In a second experiment an approximate estimation of the water present was made by shaking the bulk fraction with anhydrous potassium carbonate (30.0g.) The latter when separated increased in weight to 33.4g. indicating the presence of 3.4g. of water. In a third experiment the total aqueous extract was treated with excess dinitrophenylhydrazine solution giving acetone-2:4-dinitrophenylhydrazone, (0.21g. ≡ 0.05g. acetone). In a fourth experiment the total aqueous extract was distilled giving a tert.- butanol/water azeotrope, b.p. 79-81°/748mm. which after drying (potassium hydroxide) and distillation over sodium gave tert.-butanol, b.p. 80-82.5°, (Found: C, 64.6; H, 13.75. Calc. for $C_4H_{10}O$: C, 64.80; H, 13.60%). It was further identified by its phenyl urethane, m.p. and mixed m.p. with an authentic specimen 136° (Found: C, 68.6; H, 8.1; N, 7.4. Calc. for $C_{11}H_{15}O_2N$: C, 68.4; H, 7.8; N, 7.25%).

The above results indicate the presence of tert.-butanol (ca. 46.7g. ≡ 94.8% of the hydroperoxide), water (3.4g.) and acetone (0.05g.).

The cyclohexene present in fractions (i) and (ii) was combined, and after drying (calcium chloride) and distillation over sodium in nitrogen had b.p. 82.5°/750mm., n_D^{20} 1.4461. (cf. constants for original olefin).

The fraction (iv) was a colourless oily liquid, having a penetrating smell. It was shown to consist of cyclohexen-3-ol, with a smaller amount of the corresponding ketone, cyclohexen-3-one. There was also present a little olefinic material (probably cyclohexenyl-cyclohexene), which repeated refractionation could not remove. (Found: C, 74.6; H, 10.65; OH, 13.0. Calc. for $C_6H_{10}O$:C, 73.4;

H, 10.3; OH 17.35%. Calc. for C_6H_8O:C, 75.0; H, 8.40%).

The *cyclo*-hexen-3-ol- was characterised by its α-naphthyl urethane derivative which crystallised from absolute ethanol in long colourless needles, m.p. and mixed m.p. 156° (literature gives 156°) (Found: C, 76.05; H, 6.35; N, 5.15, 5.20. Calc. for $C_{17}H_{17}O_2N$: C, 76.40; H, 6.4; N, 5.25%). Treatment of a little of the fraction with 3:5-dinitrobenzoyl-chloride in benzene gave cyclo*hexen-3-ol-3:5-dinitrobenzoate*, which crystallised as colourless needles from light petroleum (b.p. 60-80°) m.p. 113-114° (Found: C, 53.0; H, 3.95; N, 9.6, 9.9. $C_{13}H_{12}O_6N_2$ requires C, 53.5; H, 4.1; N, 9.6%).

The *cyclo*hexen-3-one was characterised by its 2:4-dinitrophenylhydrazone, obtained as deep red-orange needles from light petroleum (b.p. 100-120°) m.p. 162-3°(Found: C, 52.2; H, 4.45; N, 20.5. Calc. for $C_{12}H_{12}O_4N_4$: C, 52.2; H, 4.4; N, 20.3%). For purposes of comparison *cyclo*hexen-3-one was prepared by the oxidative hydrolysis of 3-bromo-*cyclo*hexene (*vid*. Courtot and Pierron(57)). It was obtained as a colourless liquid b.p. 53.5 - 54.5°/10mm., n_D^{19} 1.4890, containing a small amount of brominated material as impurity (Found: C, 74.2; H, 8.45. Calc. for C_6H_8O : C, 75.0; H, 8.4%). It gave a 2:4-dinitrophenylhydrazone, which crystallised from alcohol as deep red-orange needles, m.p. 163° and mixed m.p. with specimen above 162-163° (Found: C, 52.0; H, 4.25; N, 20.3%). Bartlett and Woods(17) give m.p. 163°; Marvel and Walton(161) give m.p. 165-166°(from ethanol), m.p. 167.5 - 168° (from ethyl acetate).

A quantitative estimation by the method of Iddles, Low, Rosen and Hart(134) of the ketonic content of fraction (iv) indicated the presence of 13.35% of *cyclo*hexen-3-one.

An ultra-violet spectrographic analysis of fraction (iv) showed an absorption maximum at 2250Å, compatible with the presence of an α-β-unsaturated ketone (as in *cyclo*hexen-3-one). Found: $\epsilon_{2250} = 1350$; assuming $\epsilon = 10{,}000$ for pure *cyclo*hexen-3-one (cf. Cooke and Woodward(264); Birch(23), this would indicate *ca.* 10-13% of this ketone.

Catalytic reduction of a portion of (iv) with palladium/charcoal in absolute ethanol gave a reductant which on treatment with 2:4-dinitrophenylhydrazine gave *cyclo*hexanone-2:4-dinitrophenylhydrazone, as orange-yellow plates from ethanol, m.p. and mixed m.p. 156-158° (Found: C, 52.15; H, 5.2. Calc. for $C_{12}H_{14}O_4N_4$: C, 51.8; H, 5.05%).

The above analyses indicate that in fraction (iv) the percentage of oxygen as -OH = 12.23 and as $>C = O$ = 2.23 giving a total oxygen content (as -OH + C = O) = 14.46%. This compares well with the oxygen content of 14.75% obtained (by difference) by elementary analysis and indicates that other types of oxygenated groups must be absent.

The *fraction (vi)* was a colourless oily liquid which on cooling deposited a colourless crystalline solid; in some cases solid crystallised out during the later stages of distillation of the fraction. The latter (1.25g.) was filtered off and washed with a little light petroleum (b.p. 40-60°) in which it was completely insoluble. On crystallisation from ether, *trans*-*cyclo*hexan-1:2

diol was obtained in colourless plates, m.p. 102-104° (literature records m.p. 104°) Found: C, 62.25; H, 10.4. Calc. for $C_6H_{12}O_2$: C, 62.05; H, 10.4%).

The liquid product consisted of *cyclo*hexenyl-*cyclo*hexene, contaminated with a little oxygenated material (Found: C, 87.85; H, 11.3%). Various methods were attempted to remove the latter including the following:

(a) Repeated distillation of the olefin over sodium did not prove effective.

(b) The olefin, dissolved in light petroleum (b.p. 60-80°), was passed through a column of activated alumina. The solution which passed through was freed from solvent; distillation of the residue over sodium gave the almost pure olefin, b.p. 69-71°/1mm., n_D^{16} 1.5099 (Found C, 88.65, 88.25; H, 11.6, 11.3; M (micro-Rast) 159, 160. Calc. for $C_{12}H_{18}$: C, 88.8; H, 11.2%; M, 162). The light buff band adsorbed on the column was eluted with absolute ethanol. Removal of the solvent and crystallisation of the product from ether gave *trans*-*cyclo*hexan-1:2~~:2~~-diol, m.p. 104° (Found: C, 62.4; H, 10.15; Calc. for $C_6H_{12}O_2$: C, 62.05; M, 10.4%).

(c) The olefin was shaken repeatedly with small quantities of water. The organic layer was taken up in a little ether, dried over calcium chloride and the ether removed. The residue on distillation over sodium in an atmosphere of nitrogen had b.p. 61-62°/ 0.5 mm., n_D^{20} 1.5082 (Found: C, 88.3; H, 11.3%).

Quantitative catalytic hydrogenation of the olefin gave a value of 1.92 double bonds per molecule (Calc. for $C_{12}H_{18}$: Γ2).

Bromination of the olefin.- A solution of the olefin (1.0g.) in chloroform (25 c.c.) was brominated at 0° with bromine (2.0g.) in chloroform (20 c,c,). After completion, the solvent and slight excess of bromine were removed, leaving a colourless crystalline solid (2.85 g.) Fractional crystallisation of this from chloroform gave two stereoisomeric tetrabromides, (a) the major portion, colourless prismatic plates m.p. 159-160° (Found: C, 30.15; H, 3.75. Calc. for $C_{12}H_{18}Br_4$: C, 29.9; H, 3.75%), and (b) in small amount, large colourless prisms, m.p. 189-191° (Found: C, 29.6; H, 3,85%). These two tetrabromides were identical with those obtained from synthetic $\Delta^{2'}$-*cyclo*hexenyl-Δ^{2}-*cyclo*hexene (*vid.* p. 125).

The fraction (ix), a colourless viscous liquid, was highly oxygenated (Found: C, 81.6; H, 10.3%). A portion (2.7g.) on refractionation through a 4 inch Vigreux column gave the following fractions: (a) b.p. <87.5°/0.05mm., n_D^{20} 1.5110, (0.4g.); (b) b.p. 87.5 - 90°0/0.04 mm., n_D^{20} 1.5160, (1.0g.); (c) b.p. 90.0 - 105°/0.04 mm., n_D^{20} 1.5253, (1.0g.) The fraction (b) contained, on the basis of analytical data, *ca.* 81% of cyclo*hexenyl*-cyclo*hexenol* $C_{12}H_{18}O$ and *ca.* 14% of cyclo*hexenyl*-cyclo*hexenone* (Found: C, 79.9; H, 10.25; OH, 7.6; λ_{max} 226, ϵ_{max} = 1400. $C_{12}H_{18}O$ requires C, 80.85; H, 10.2; OH, 9.55%). A similar sample, b.p. 110-126°/1mm., n_D^{17} 1.5160 gave C, 80.75; H, 10.05; Γ1.7. Fraction (c) was a mixture of the alcohol and ketone with a little higher boiling olefin

(Found: C, 81.6; H, 10.35%). Owing to the small amounts of the alcohol/ketone mixture isolated no structural investigation was possible.

The fraction (x), a colourless oily liquid, was shown to be mainly dicyclohexenyl-cyclohexene with a little oxygenated material as impurity. On redistillation over sodium a main fraction was obtained, b.p. 108-110°/0.5mm., n_D^{20} 1.5328 (Found: C, 88.0; H, 10.85. Calc. for $C_{18}H_{26}$:C, 89.2; H, 10.8%).

The residue (xi) consisted of a mixture of high boiling alcohols and olefins (Found: C, 85.1; H, 10.5). No attempt was made to separate the constituents of this mixture.

Reaction of tert.-Butyl Hydroperoxide with cycloHexanol

cycloHexanol (b.p. 64°/17 mm., 10g.∝1 mol.) and tert.-butyl hydroperoxide (9.0g.∝ 1 mol.) were heated under reflux at 130° for 24 hours. The product on fractionation gave (i) tert.-butanol, b.p. 80-83°/747 mm., (5.5g., 74.3% of peroxide), (ii) a fraction b.p. 140-156°/747 mm. (9.8 g.) and (iii) a residue (2.0 g.), containing a small amount of adipic acid which after crystallisation from ether had m.p. 147-148.5 (literature give m.p. 151°). Fraction (ii) contained 19% of cyclohexanone which was estimated and identified as its 2:4-dinitrophenylhydrazone, m.p. 157-158°, mixed m.p. with authentic specimen 157-158° (Found: C, 52.0; H, 5.35. Calc. for $C_{12}H_{14}O_4N_4$: C, 51.8; H, 5.05%).

Reaction of tert.-Butyl Hydroperoxide with cycloHexen-3-ol.-

The cyclohexenol was treated with saturated sodium bisulphite solution to remove any ketonic material. It had b.p. 162-165°/752 mm., α-naphthyl urethane m.p. 156°(Found: C, 76.4; H, 6.7; N, 5.3. Calc. for $C_{17}O_{17}O_2N$: C, 76.4; H, 6.4; N, 5.25%).

The alcohol (4.0g.) and hydroperoxide (9.0g.) were heated under reflux at 130° for 24 hours. The product on fractionation gave (i) *tert.*- butanol (3.3g., 44.6% peroxide), (ii) unchanged peroxide (3.6g.), (iii) a fraction b.p. 150-163°(3.55g.) and (iv) a dark brown oily residue which contained unidentified acidic material. Fraction (iii) contained *ca.*18.2% of *cyclo*hexen-3-one estimated and identified as its 2:4-dinitrophenylhydrazone, m.p. and mixed m.p. 158-160° (Found: C, 52.3; H, 4.5. Calc. for $C_{12}H_{12}O_4N_4$: C, 52.2; H, 4.4%).

(2) REACTION WITH 1-METHYL*cyclo*HEXENE.- A mixture of 1-methyl*cyclo*hexene (144g., 1.5 mol.) and *tert.*-butyl hydroperoxide (45g., 0.5 mol) was reacted at 140° for 24 hours in nitrogen-filled Carius tubes. The product (187.2g.), a light yellow liquid, gave on fractionation the following fractions: (i) b.p. 78-112°/735mm., (104.7g.) containing a small aqueous layer; (ii) a fraction collected in a liquid air trap at 13 mm., (7.0g.); (iii) b.p.<53°/13mm., n_D^{20}1.4520, (20.5g.), (iv) b.p. 53-77° (mainly 67-77°)/13mm.,(14.2g.); (v) a yellow viscous residue which was not investigated further.

Extraction of fraction (i) with water (250g.+100g.) gave an aqueous extract (37.1g.) consisting *mainly* of *tert.*-butanol together with smaller amounts of water and *traces* of acetone. The non-aqueous portion of fraction (i) and fractions (ii) and (iii) consisted of unchanged olefin. They were combined, dried ($CaCl_2$)

and on distillation over sodium under nitrogen gave a main fraction b.p. 107-108°, $\underline{n}_D^{20}$ 1.4501, (73.6g.)

Fraction (iv).- This was a colourless oily liquid containing a mixture of methyl*cyclo*hexenols and methyl*cyclo*hexenones (Found: C, 76.1; H, 10.55. Calc. for $C_7H_{12}O$: C, 74.95; H, 10.7%). Ultra-violet spectrographic analysis gave a selective absorption band at 2310Å., ϵ_{max} = 1200, consistent with the presence of ~12% of conjugated methyl*cyclo*hexenones.

Treatment of a portion (0.5g.) of this fraction with 2:4-dinitrophenylhydrazine in absolute ethanol gave a mixture of deep red dinitrophenylhydrazones (0.25g.). The latter (0.025g.) dissolved in light petroleum (b.p. 40-60°) (150c.c.) was chromatographed on a column of alumina (30g., 600 x 9 mm.) and the chromatogram was developed with the same solvent (350 c.c.). Two distinct bands were formed, the upper band (35 mm.) consisted of 3-methyl-Δ^2-cyclohexenone dinitrophenylhydrazone, m.p. 168-170° (4.4 mg.) and the lower band (55mm.) contained 2-methyl-Δ^2-cyclohexenone dinitrophenylhydrazone, m.p. 198-200°, mixed m.p. 199-201° (9.7mg.).

Oxidation of Fraction (iv).- To a portion (6.0g.) of (iv) in glacial acetic acid (10 c.c.) there was added with cooling a solution of chromic acid (CrO_3, 4.0g.) in 75% aqueous acetic acid (10c.c.). The oxidation was completed by warming the mixture on the water bath for half an hour. The ketone portion was extracted with ether (200 c.c.) and the etherial layer neutralised (sat. Na_2CO_3 aq.) and then dried ($CaCl_2$). After removal of the solvent the product was distilled giving a fraction (i) b.p. 62-70°/13 mm., $\underline{n}_D^{20}$ 1.4672, (2.2g.)

and a higher boiling residue (ii) (1.2g.).

The ketone content of fraction (i) was estimated by precipitation of its dinitrophenylhydrazone as ca. 64%. Chromatagraphic separation of the mixed dinitrophenylhydrazone (30mg.) as described above gave the dinitrophenylhydrazones of 2-methyl-Δ^2-cyclohexenone (12.1 mg.) and 3-methyl-Δ^2-cyclohexenone (5.0mg.).

REACTION of DI-tert.-BUTYL PEROXIDE with SATURATED HYDROCARBONS.

(I) cycloHEXANE.- The peroxide (24.3g., $\propto$ 1 mol.) and spectroscopically pure cyclohexane (84g., $\propto$ 6 mols. n^{20}_{D} 1.4262) were heated together in Carius tubes at 140° for 24 hours. The reaction product (107.9g.), a light yellow liquid, on distillation gave a forerun, b.p. 70-91°/766mm., (92.5g.) shown by aqueous extraction and treatment of the aqueous extract with 2:4-dinitrophenylhydrazine soln (2N.HCl) to contain tert.- butanol (22.8g., 92.45% of peroxide), acetone (0.085 g.), and unchanged cyclohexane, which after drying (calcium chloride) was recovered virtually unchanged (ca. 69g., n^{20}_{D} 1.4261).

The residual product (13.6g., 16.2% of hydrocarbon), a viscous yellow liquid, on fractionation through a 6 in. Vigreux column under reduced pressure gave, (i) b.p. $<$100°/11mm., n^{20}_{D} 1.4711, (0.34g.); (ii) b.p. 100.0 - 102.3°/11mm., n^{20}_{D} 1.4784, (3.08g.);

(iii) b.p. $<$124°/0.1mm., n_D^{20} 1.4825, (0.57g.); (iv) b.p. 124 - 134°/0.1mm., n_D^{20}1.5035, (0.57g.); (v) an orange polymeric residue (7.1g.), which on cooling set to a brittle solid glass.

The fraction (ii) consisted mainly of di*cyclo*hexyl. On refractionation over sodium it gave a small forerun, b.p. $<$ 99.5°/10mm., n_D^{20} 1.4792, and a main fraction, b.p. 99.5 - 100.0°/10mm., n_D^{20} 1.4801 (Found: C, 86.8; H, 13.4. Calc. for $C_{12}H_{22}$: C, 86.65; H, 13.35%). *The fraction (iv)* was mainly di*cyclo*hexyl-*cyclo*hexane $C_{18}H_{32}$, containing a small amount of oxygenated material (Found: C, 86.3; H, 12.6; M(benzene), 242. Calc. for $C_{18}H_{32}$: C, 87.0; H, 13.0%; M, 248). *Fraction (v)* was mainly a mixture of polymeric hydrocarbons but also contained a small amount of oxygenated material (Found:C, 87.0; H, 11.5%; M(benzene), 630). An ultra-violet spectrographic examination of this polymer indicated the definite presence of unsaturation and in particular, showed the presence of selective absorption near 2550Å, which may be due to not more than 5% of conjugated cyclohexadiene groupings. It was not possible to determine the extent of unsaturation or to establish whether the unsaturation was entirely or only partially present in conjugated diene groups.

REACTION OF DI-tert.-BUTYL PEROXIDE with ALKYL BENZENES

(I) TOLUENE.- A mixture of the peroxide (18.25g., α1 mol.) and toluene (46.0g., α4 mols., b.p. 100.0 - 100.2°/761mm., $n_D^{18.2}$ 1.4974 was heated at 140° for 24 hours in a Carius tube sealed in an atmosphere of nitrogen. On opening the tube a considerable amount of gas was evolved. The liquid product, a light yellow liquid, amounted to almost 64g. Distillation of this gave the following fractions, (i) b.p. 79 - 110°, (31.5g.); (ii) b.p. 110°, (1515g.), n_D^{20} 1.4927, being mainly recovered toluene; (iii) b.p. 84 - 85°/0.1mm., (0.4g.); (iv) b.p. 85 - 86°/0.1mm., (4.2g.) which solidified to a mass of colourless crystals; (v) b.p. 86 - 138°/0.1mm., (0.4g.); (vi) b.p. 138 - 144°/0.1mm., $n_D^{19.2}$ 1.5872, (2.3 g.); (vii) an undistillable residue, (7.15g.), which set to a clear light yellow glass.

Examination of the fractions.- The fraction (i). Heating a small portion of this fraction with phenyl-isocyanate for 1 hour gave tert.-butanol phenylurethane, colourless needles from petroleum ether (b.p. 100 - 120°), m.p. 135.5 - 136° (Found: C, 68.3; H, 7.65; N, 7.4. Calc. for $C_{11}H_{15}O_2N$: C, 68.4; H, 7.8; N, 7.25%). Aqueous extraction of a portion (29.4g.) of the fraction gave water soluble constituents (13.4g.) consisting of tert.-butanol (92.2%) and acetone (7.8%), estimated and identified as its 2:4-dinitrophenylhydrazone, orange plates from absolute ethanol, m.p. 124 - 125° (Found: C, 45.45; H, 4.35. Calc. for $C_9H_{10}O_4N_4$:

C, 45.4; H, 4.25%). The water-insoluble material was a mixture of toluene and unreacted peroxide.

The fraction (iv) was pure dibenzyl. On crystallisation from absolute ethanol it formed prismatic plates, m.p. 51.0 - 51.5° (Found: C, 92.25; H, 7.75. Calc. for $C_{14}H_{14}$: C, 92.25; H, 7.75%).

The *fraction (vi)* probably consisted mainly of a slightly impure *1:2:3-triphenylpropane* (Found: C, 92.05; H, 7.6. $C_{21}H_{20}$ requires C, 92.6; H, 7.4%).

The *residue (vii)* was mainly hydrocarbon, but contained a little oxygenated material (Found: C, 90.75; H, 7.65%).

(2) *ETHYL BENZENE*.- The peroxide (36.5g.$\propto$1 mol.) and ethylbenzene (106g.$\propto$ 4 mols. b.p. 135°/755mm., n^{20}_{D}1.4959) were heated on an oil bath under an efficient reflux at 140° for 24 hours, a slow stream of purified nitrogen being passed through the apparatus. The product, a colourless liquid (142.0g.) on fractionation gave a forerun b.p. 83-136°/760mm. (125.0g.) which was shown by aqueous extraction to contain *tert*.- butanol (*ca*. 12.7g.). Removal of the last traces of ethylbenzene by heating on the water bath under slight vacuum left a higher boiling residue (16.3g.) which on standing partially crystallised out. The solid (7.5g.) was separated, washed with a little methanol and identified as *meso*-2:3-diphenylbutane, colourless gleaming crystals from absolute ethanol, m.p. 125 - 126°(Found: C, 91.5; H, 8.75. Calc. for $C_{16}H_{18}$: C, 91.35; H, 8.65%). Conant and Blatt(52) give m.p.

124 - 125°; Ott(189) gives m.p. 126 - 127°.

The oily liquid (8.8g.), after removal of the methanol, gave on distillation a fraction, b.p. 85 - 86°/1mm.(6.3g.), from which more solid (0.9g), m.p. 126°, separated. The resulting colourless oily liquid (5.4g.) was racemic-2:3-diphenylbutane. On redistillation over sodium it had b.p. 136°/9mm., $\underline{n}_{D}^{20}$ 1.5537 (Found: C, 91.25; H, 8.8. Calc. for $C_{16}H_{18}$: C, 91.35; H, 8.65%). Kharasch et.al.(154) give b.p. 106°/2mm., $\underline{n}_{D}^{20}$ 1.5517.

Isomerisation of the racemic to the meso -diphenylbutane was effected by heating the former in an evacuated sealed tube at 250° for 17 hours in the presence of a catalytic quantity of iodine ($<$ 1mg. per g. of liquid). Yield, 42%, m.p.126°.

The residue in the still (2.5g.), a colourless viscous liquid, consisted of higher polymeric hydrocarbons which were not further investigated.

(3) iso-PROPYLBENZENE.- Experiment (A): A mixture of the peroxide (12.2g. $\propto$ 1 mol.) and iso-propylbenzene (20.0g. $\propto$ 2 mols.; b.p. 148.0 - 148.5°/725mm $\underline{n}_{D}^{20}$ 1.4910) was heated under an efficient reflux on an oil bath held at 140° for 46 hours, a slow stream of purified nitrogen being passed through the apparatus. The product on fractionation gave (i) mainly tert.-butanol (5.1g.) identified by its b.p., 82 - 83°, its complete water solubility and its phenyl urethane derivative, m.p. 136°, (ii) unchanged peroxide (6.2g.), b.p.110 - 114°; (iii) unchanged iso-propylbenzene (11.25g.), b.p.

150 - 152°. On removal of the last traces of hydrocarbon by warming under water pump vacuum there remained a colourless crystalline solid (8.45g.), identified as 2:3-dimethyl-2:3-diphenylbutane. It crystallised from absolute ethanol in long colourless needles, m.p. 118 - 119°(Found: C, 90.6; H, 9.4. Calc. for $C_{18}H_{22}$: C, 90.7; H, 9.3%). Klages(156) gives m.p. 119 - 120°; Kharasch et al(154) give m.p. 115°.

Experiment (B): A mixture of the peroxide (12.2 g. ∝ 1 mol.) and iso-propylbenzene (40.0g. ∝ 4 mols.) was heated in nitrogen-filled Carius tubes at 140° for 24 hours. The product (51.5g.) on distillation gave a fraction b.p. 82 - 150°(33.6g.) shown by aqueous extraction to consist of water soluble constituents (10.3g.) and water insoluble compounds (23.3g., mixture of unchanged peroxide and hydrocarbon). The water extract consisted of acetone, (0.52g.) estimated and identified as its 2:4-dinitrophenylhydrazone (2.15g.), and tert.-butanol (9.78g., 79.5% of peroxide). After the removal of the last traces of volatile products by heating to 50° at 12 mm., there remained in the still, dimethyldiphenylbutane (17.1g.)(85.5% yield based on peroxide), m.p. 118-119.5°.

REACTION OF DI-tert. BUTYL PEROXIDE WITH KETONES.

(1). METHYL ETHYL KETONE.- A mixture of methyl ethyl ketone (b.p. 79 - 80°/760mm., 72g.) and di-tert.-butyl peroxide (36.5g.) was heated in sealed tubes at 140° for 24 hours. The product, an orange liquid, on distillation gave the fractions;

(i) b.p. $73-80^{\circ}/760$ mm., (78.65g.), being a mixture of *tert*.-butanol and unreacted ketone; (ii) small intermediate fraction b.p. $<74^{\circ}/8$ mm., (0.94 g.); (iii) b.p. $74-76^{\circ}/8$ mm., n_D^{20} 1.4342, (11.55 g.); (iv) viscous orange liquid, b.p. $76-84^{\circ}/1$mm., n_D^{20} 1.4651, (2.45 g.) and (v) a dark orange polymeric residue (8.8g.) which set to a glass on cooling. The latter was not further investigated.

The fraction (iii) was a sweet smelling colourless liquid identified as 3:4-dimethylhexandione-2:5 (Found: C, 67.6; H, 9.9; M (acetone), 138 ± 12. Calc. for $C_8H_{14}O_2$: C, 67.6; H, 9.9%; M, 142). Heating the diketone (0.5g.) with hydroxylamine hydrochloride (0.75 g.) and anhydrous sodium acetate (1.0g.) in aqueous alcohol on the water bath for 3 hours gave the dioxime (0.2g.), which crystallised as its monohydrate from aqueous ethanol (charcoal) in colourless needles, m.p. 200-201° (Found: C, 50.7; H, 9.7; N, 14.5. Calc. for $C_8H_{16}O_2N_2.H_2O$: C, 50.5; H, 9.55; N, 14.75%. Found: (sample heated at 100-120° under high vacuum) C, 55.95; H, 9.45; 16.1. Calc. for $C_8H_{16}O_2N_2$: C, 55.8; H, 9.3; N, 16.3%). Ciamician and Silber(49) give m.p. 202°. Treatment of the diketone with phenylhydrazine in aqueous acetic acid gave the pyridazine derivative (LVI), which crystallised from aqueous ethanol in colourless needles, m.p. 126 - 127° (Found: C, 78.5; H, 8.5; N, 12.9. Calc. for $C_{14}H_{18}N_2$: C, 78.5; H, 8.4; N, 13.1%). Ciamician and Silber(49) give m.p. 130°; Kharasch, McBay and Urry(152) give m.p. 127-128°.

The fraction (iv) was shown by analysis and molecular weight determination to be a "trimeric" ketone, presumably (LIX), (Found: C, 68.6; H, 9.5; M(acetone), 215 ± 24. $C_{12}H_{20}O_3$ requires C, 67.95; H, 9.45%; M, 212. Although the liquid gave a positive reaction to aqueous 2:4-dinitrophenylhydrazine sulphate no pure derivative could be obtained, nor could a pure oxime be prepared under the usual conditions.

(2) CYCLO*HEXANONE*.- The ketone (98 g., b.p. 56-56.5°/20mm., $\underline{n}_D^{20}$ 1.4508) and di-*tert*.-butyl peroxide (24.4g.) were heated under reflux at 140-150° for 48 hours. On distillation, the product, a bright red liquid, gave (i) *tert*.-butanol, b.p. 80-83°/763 mm., (17.6g.); unreacted peroxide, b.p. 110°/763 mm., (2.5g.); (iii) unchanged *cyclo*hexanone, b.p. 48-50°/13mm., (82.4g.) and a higher boiling material (13.1g.). The latter on fractionation at 1 mm. pressure gave a fraction (iv) b.p. 117 -120°/ca. 1mm., (5.0g.) and an undistillable residue (*ca*.8.0g.) which, on cooling, set to a brittle resin.

The *fraction (iv)* on refractionation gave a mixture of stereoisomeric 2:2'-diketodi*cyclo*hexyls as a colourless oil, b.p. 110 - 117°/1mm. (mainly 116 - 117°/1mm.) $\underline{n}_D^{20}$ 1.4999. (Found: C, 74.2; H, 9.4. Calc. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.35%). On cooling in solid carbon dioxide and continued scratching the oil partially crystallised. The solid, when separated and crystallised from light petroleum (b.p. 40 - 60°), gave the higher melting form of 2:2'-diketodicyclohexyl as long colourless prismatic needles, m.p. 73-74° (Found: C, 74.2; H, 9.35%). Plant(198) and Kharasch et al.(152) give m.p. 70 - 71°.

The resin obtained as a residue in the reaction was readily soluble in acetone, benzene and chloroform, moderately soluble in alcohol and insoluble in petrols. Its analysis and molecular weight indicated it to have, approximately, the average composition of a cyclohexanone "tetramer" (Found: C, 76.7, 76.1; H, 8.9, 8.65; M(benzene), 360, 370. $C_{24}H_{34}O_4$ requires C, 74.6; H, 8.9%; M, 386).

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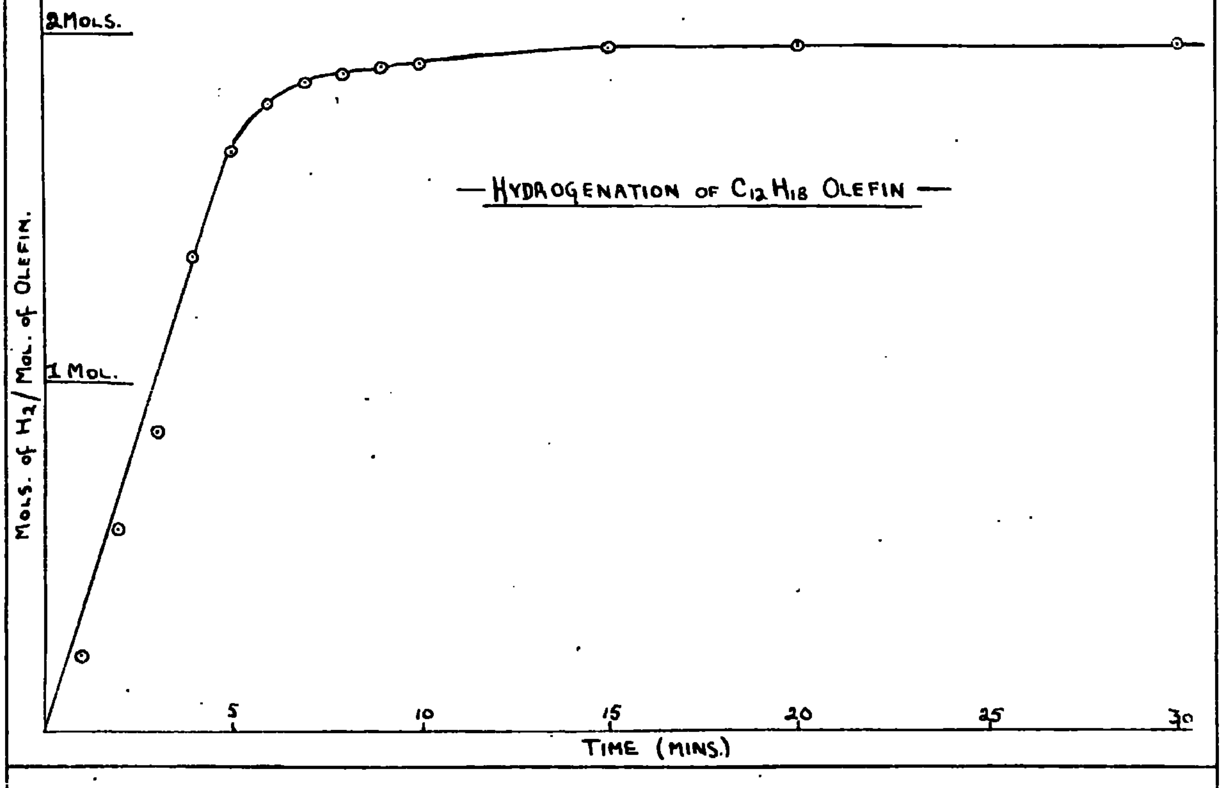
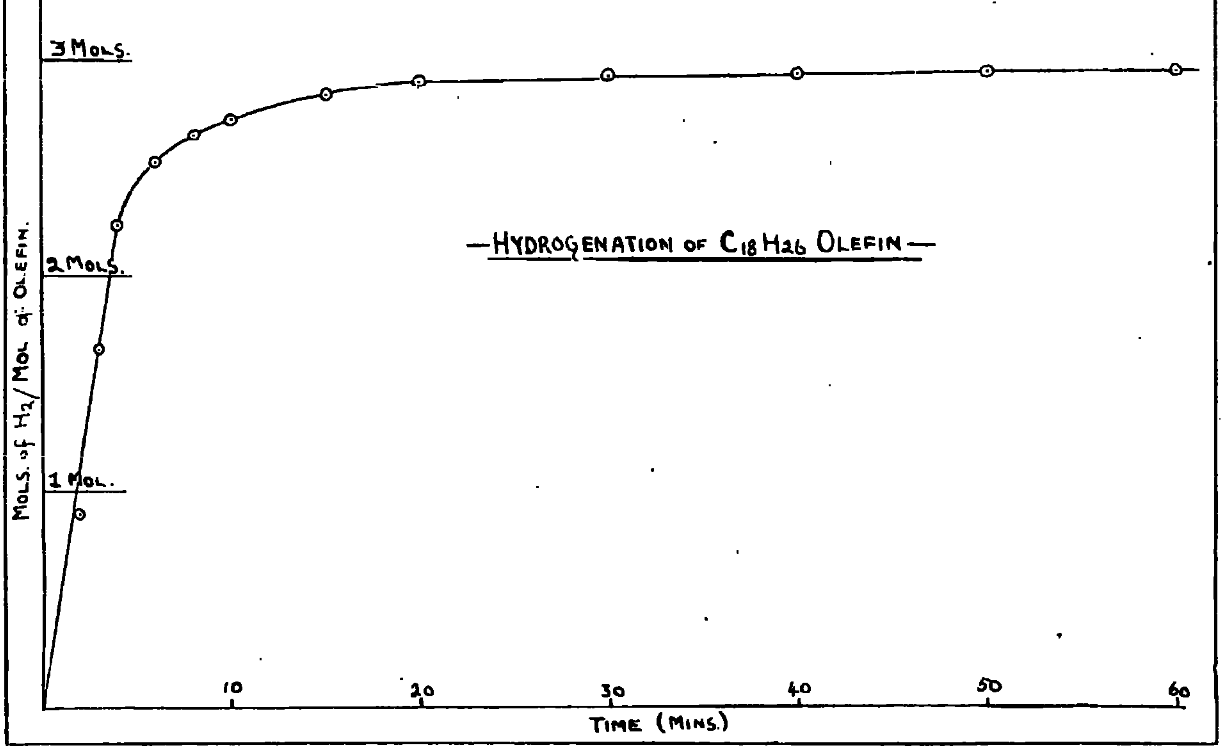
Fig 1



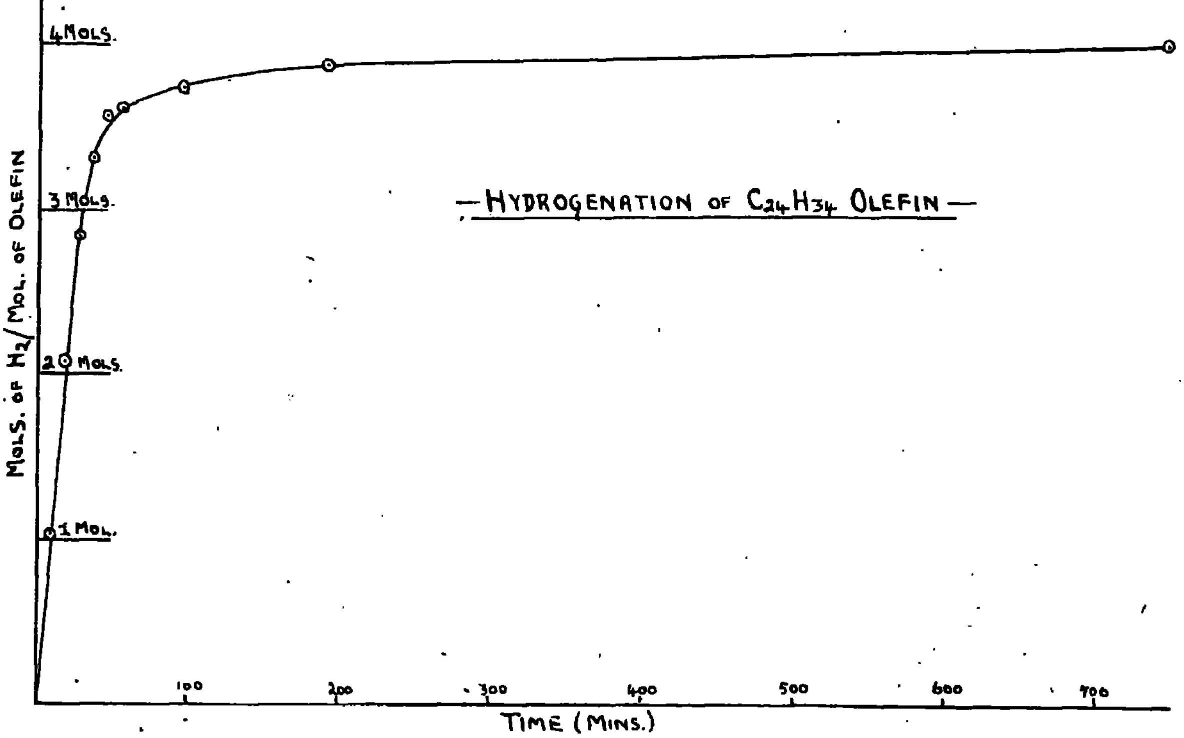
—Hydrogenation of $C_{12}H_{18}$ Olefin—

Fig 2



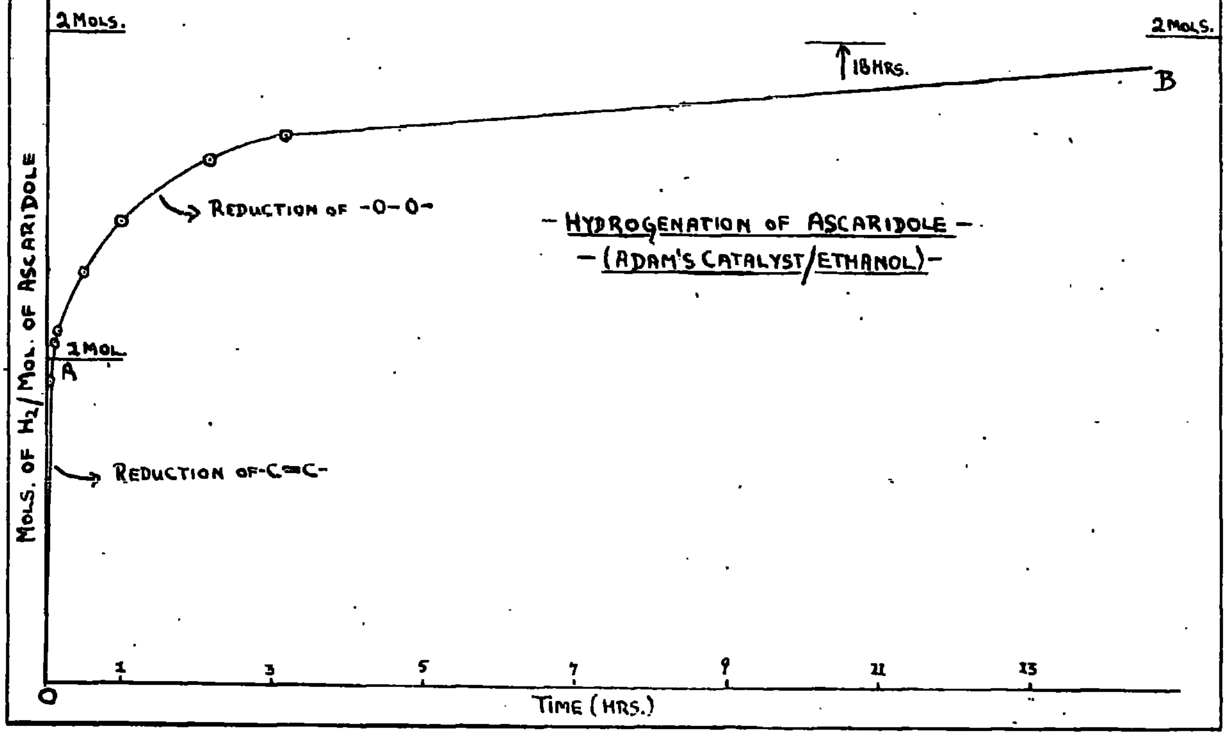
—Hydrogenation of $C_{18}H_{26}$ Olefin—

-Fig 3-



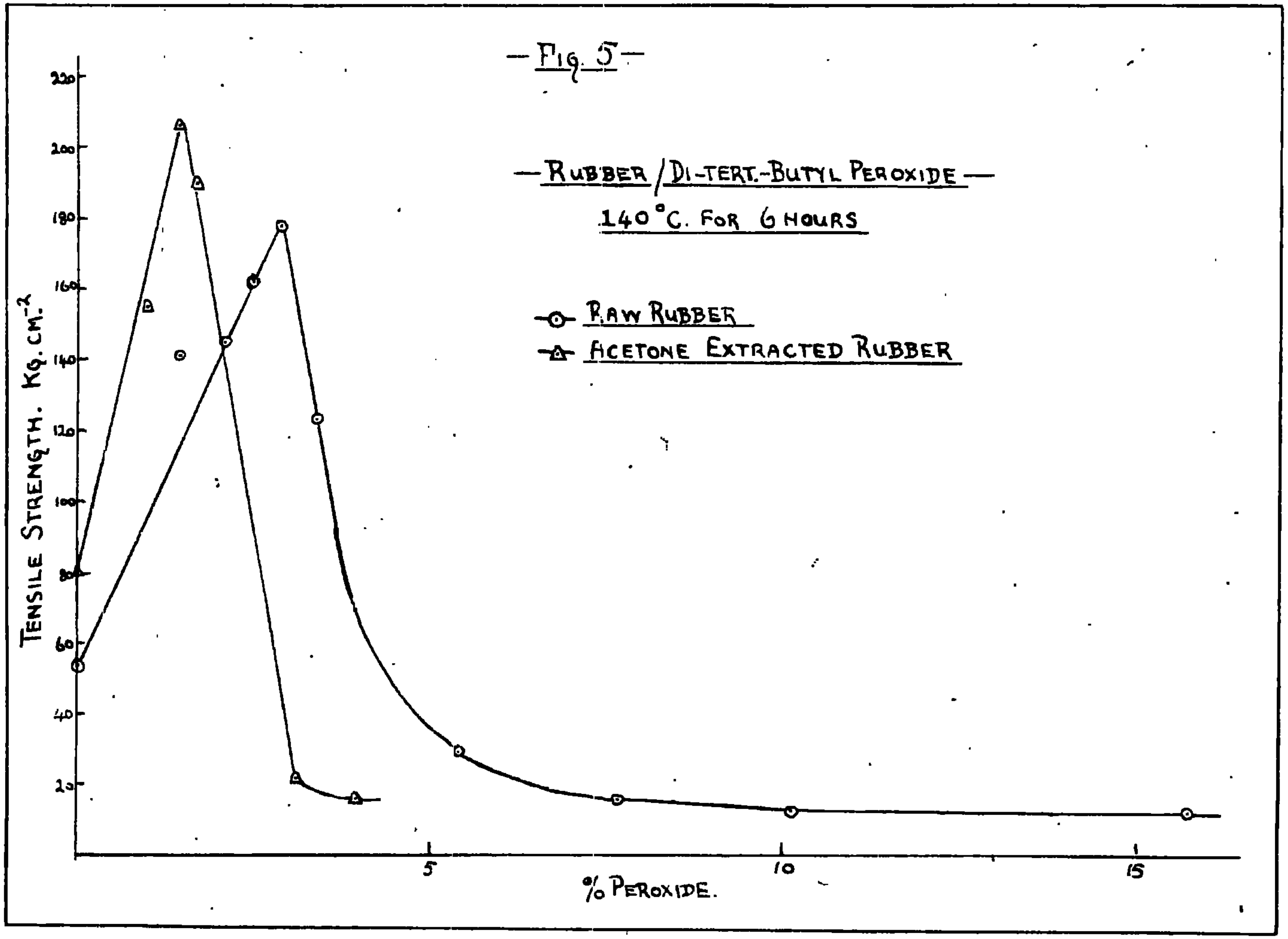
—Hydrogenation of $C_{24}H_{34}$ Olefin—

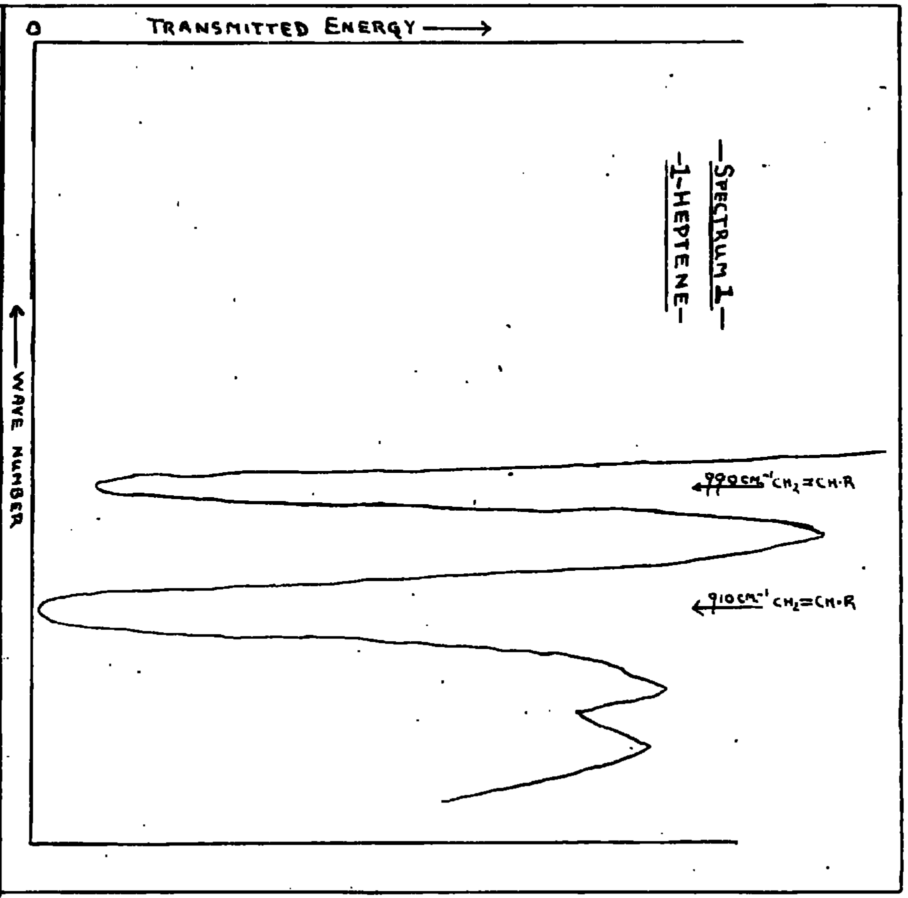
-Fig 4-



—Hydrogenation of Ascaridole—
—(Adam's Catalyst/Ethanol)—

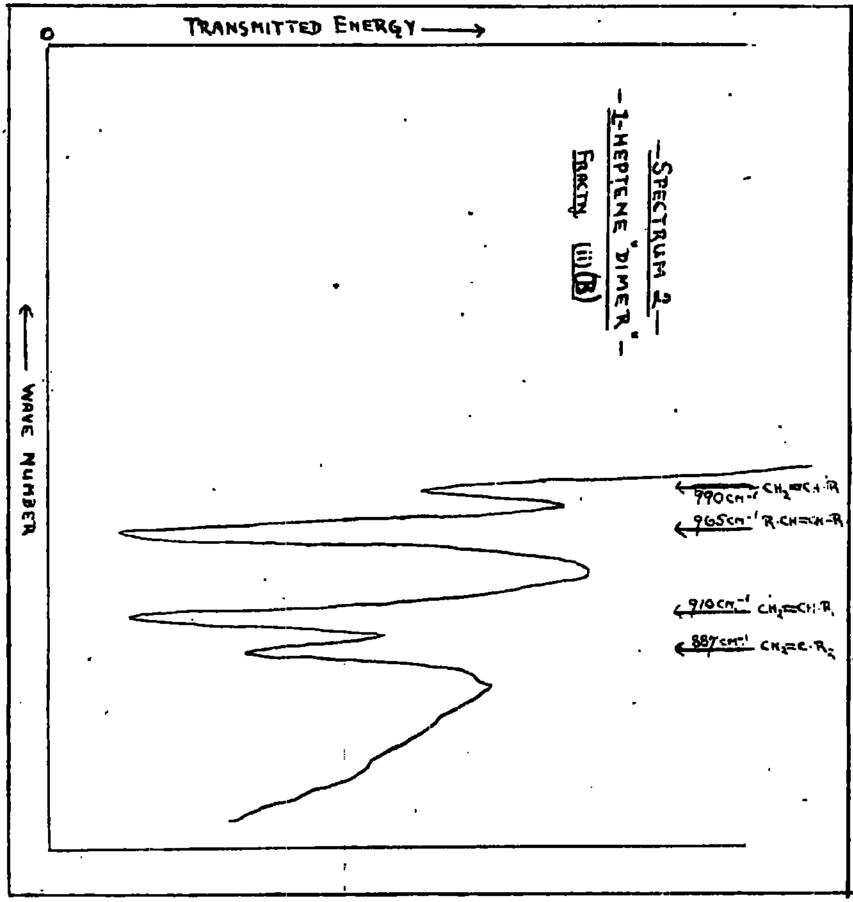
— Fig. 5 —


— Rubber / Di-tert.-Butyl Peroxide —
140 °C. For 6 hours
Raw Rubber
Acetone Extracted Rubber
Tensile Strength. Kg. cm.$^{-2}$
220
200
180
160
140
120
100
80
60
40
20
5
10
15
% Peroxide.



-SPECTRUM 1-

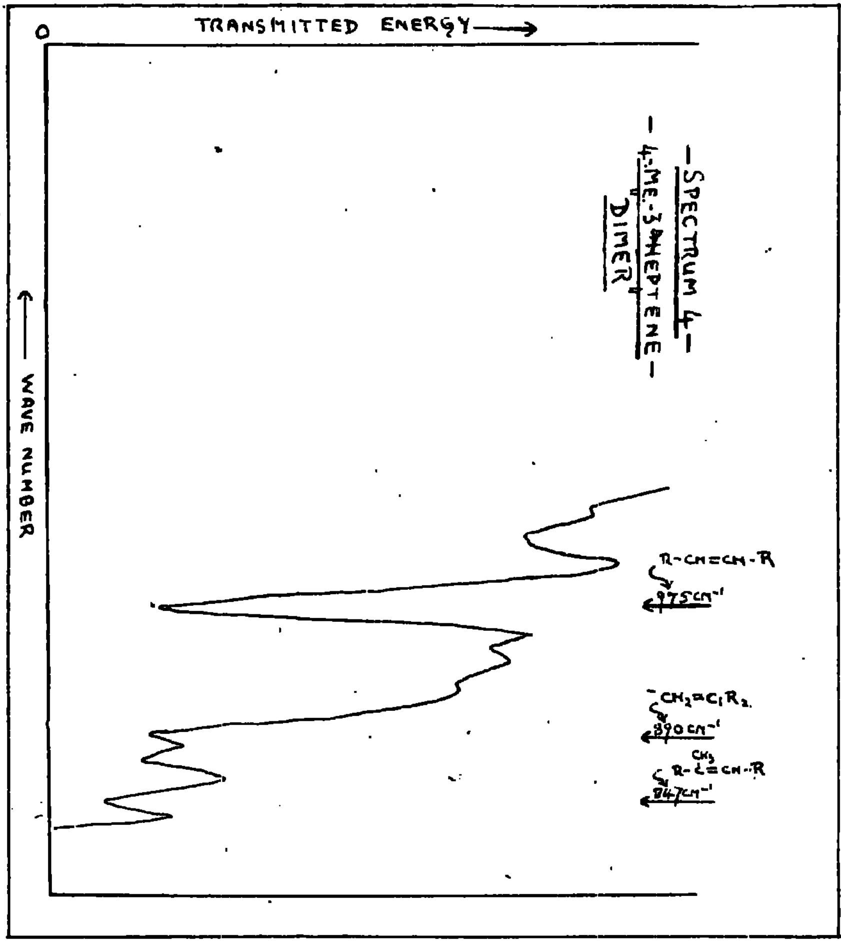
-1-HEPTENE-



-SPECTRUM 2-

-1-HEPTENE "DIMER"-

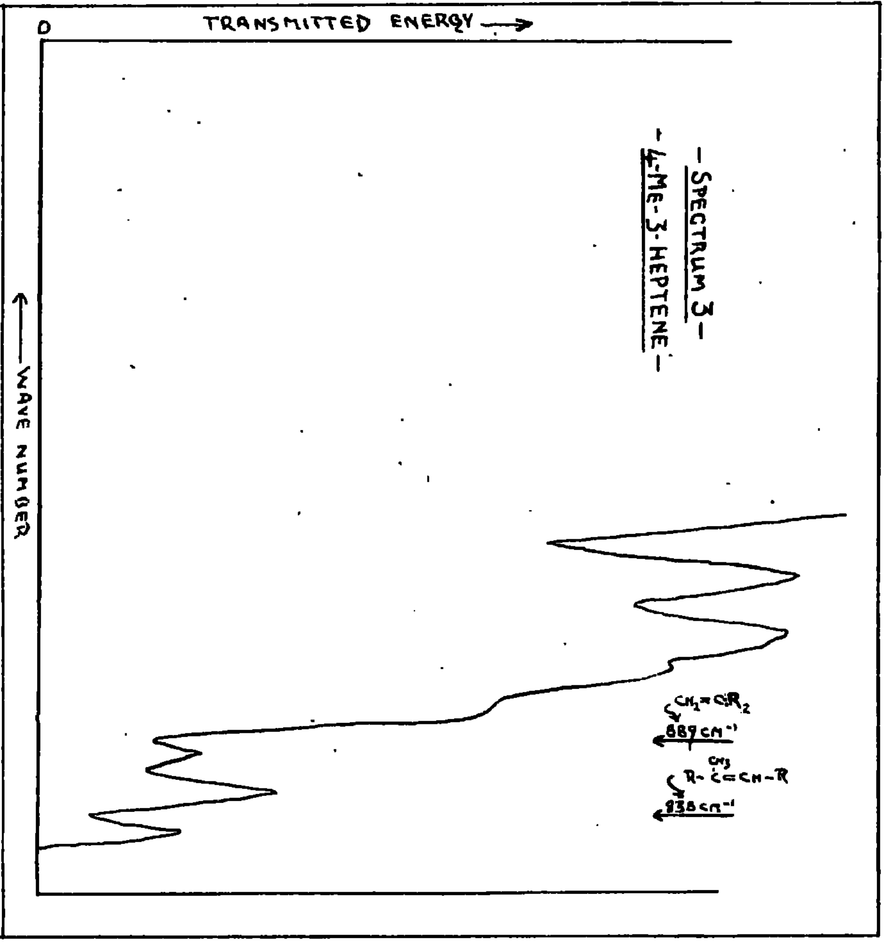
FRACTN (iii)(B)



-SPECTRUM 4-

-4-ME-3-HEPTENE-

DIMER



-SPECTRUM 3-

-4-ME-3-HEPTENE-