A summary of some new reactions of Diazonium Chlorides

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A SUMMARY OF

SOME NEW REACTIONS OF DIAZONIUM CHLORIDES.

A THESIS

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FOR THE

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BY

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The thesis which consists of about 83 pages is divided into three parts.

Part I Is a historical survey of the earlier work carried out on the diazonium salts by such workers as Griess, Bamberger, and Hantzsch; followed by a discussion of the structural formulae proposed for the diazonium, normal diazo, and iso diazo salts, by these workers. The section is concluded by a summary of the decomposition reactions of diazonium salts in various aqueous solutions, e.g., in water alone, and in solutions of various salts..

Part II Consists of a survey of decomposition reactions carried out in non-ionic solvents. This work is of a more recent nature, and commences with the work of Pray in 1926, who showed that the mechanisms proposed by Hantzsch for such decompositions was no longer tenable. Examples from the work of Hey and Waters has led to an alternative mechanism being evolved - a free radical mechanism - this is discussed at length with illustrations and examples. A general survey is included of the preparation of organo metallic compounds via diazonium decompositions, and concluded with a summary of the various methods of preparation and properties of organic antimony compounds.

Part III Is a summary of the research work carried out by myself under the direction of Dr. Waters, and deals with the decomposition of the diazonium chlorides prepared from

p-chloraniline, p-bromoaniline, 4-chloro-o-toluidine, 5-chloro-o-toluidine, 4-chloro-o-anisidine, p-nitraniline, and ethyl anthanilinate, in acetone and ethyl acetate, in the presence of chalk alone, or together with mercury and antimony metal.

A summary of this work has already been communicated to the Chemical Society, and appeared in the Journal of this Society, June,1938, a copy of which is attached. A summary and conclusion terminates the thesis.

SOME NEW REACTIONS OF DIAZONIUM CHLORIDES.

Being

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by

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Acknowledgements.

I wish to express my gratitude to Dr. W.A. Waters for his constant interest and valuable criticism during the course of the investigation. Also for bringing to a successful conclusion the final elucidation of certain compounds, which time did not allow me to complete.

I am also indebted to the Principal of St. John's College, and the West Hartlepool Education Committee for their financial assistance which enabled me to undertake this work.

November,1938. F.B.M.

CONTENTS.

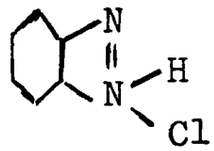
PART I.

(A). Historical Introduction.

With the possible exception of Wöhler's synthesis of urea from ammonium cyanate in 1828, no reaction is so emminent in the mind of the student of chemistry as the diazo reaction discovered by Peter Griess at Marburg in 1858, when he prepared the first diazonium salt from piramic acid[1]. During the eighty ensuing years these interesting compounds have been investigated far in excess of any others, both academically and industrially. The treatment of a primary aromatic amine with cold nitrous acid leads to the formation of a diazonium salt with such certainty and ease, that it has become the basis of a qualitative test for the former group; since the produced diazonium salt couples instantly with an alkaline solution of any phenol, precipitating an insoluble dye.

It was already known in 1858 that treatment of an aromatic amine with warm nitrous acid, led to the replacement of the amino group by a hydroxy group, i.e., the corresponding phenol could be obtained. It is reported that Kolbé suggested to Griess that treatment of piramic acid with nitrous acid would produce the corresponding hydroxy compound. Griess, in following up this suggestion, treated an alcoholic solution in the cold

with N_2O_3, and obtained a crystalline solid with none of the expected properties of hydroxy piramic acid. On extending this treatment to other primary aromatic amines, he came to the conclusion that he had discovered a reaction of general application. At first he imagined that the reaction could only be carried out in anhydrous solvents, and erroneously imagined that two hydrogen atoms of the aromatic nucleus had been replaced by nitrogen atoms as follows



and accordingly called them <u>diazo</u> compounds.

This structural hypothesis, and cumbersome method of diazotisation used by Griess were soon superseded by others of whom Hantzsch, Bamberger, Strecker, and Bloφmstrand were the most notable.

A summary of the general methods of diazotisation now available is given as follows

Table I

REACTION TECHNIQUE.	SPHERE OF EMPLOYMENT.
1. <u>Direct Method</u>:- <u>Martius 1866</u>. A solution of a metallic nitrite is added to a cold solution of the amine in Mineral acid $ArNH_2 + 2HX + NaNO_2 = ArN_2X + H_2O + NaX$ Quickest and cheapest method.	(a). Strongly basic amines whose salts are soluble in excess acid. (b). Sulphonated amines soluble in acids. (c). For the preparation of insoluble double salts.

Table I (Continued).

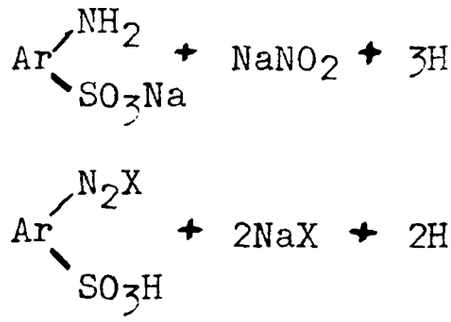
REACTION TECHNIQUE.	SPHERE OF EMPLOYMENT.
2. Inverted Method:- Schmitt 1859. Mixed alkaline solutions of a metallic nitrite and a salt of a sulphonated or carboxy amine are run into excess of cold mineral acid.  $Ar(NH_2)(SO_3Na) + NaNO_2 + 3HX =$ $Ar(N_2X)(SO_3H) + 2NaX + 2H_2O$	(a) Amino acids such as sulphanilic, naphthoic, amino benzoic, etc. (b) Some weakly basic amines, e.g., p-Nitraniline.
3. Claus' Method 1897:- Amine dissolved in concentrated acid (H_2SO_4, H_3PO_4, etc.) and diazotised with nitrosyl sulphuric acid. ($NaNO_2$ in conc. H_2SO_4). $ArNH_2 + NOHSO_4 \longrightarrow ArN_2HSO_4 + H_2O$.	For the most weakly basic amines easily nitrated or oxidised, e.g., ~~diphenylamine~~.
4. Witt's Method 1909:- Amine dissolved in nitric acid and meta-bisulphite added HNO_2 produced which diazotises the amine.	For weakly basic amines not easily nitrated or oxidised.
5. Griess Method 1858:- Amine suspended or dissolved in alcohol and N_2O_3 bubbled in	Can be used for most amines and gives the solid crystalline salt.
6. Knoevenagel's Method 1890:- The amine salt dissolved in inert solvent and diazotised by addition of alkyl nitrite.	Rapid method of obtaining the salt in crystalline state.

Table I (Continued)

REACTION TECHNIQUE.	SPHERE OF EMPLOYMENT.
7. Hantzsch and Jochem's Method: 1901:- Amine salt suspended in glacial acetic acid and alkyl nitrite stirred into mixture, precipitated with ether.	Rapid method of obtaining solid crystalline salt no advantage over Knoevenagel's method.

In general characteristics each of the above methods are similar, in that they ultimately treat the amine salt with cold nitrous acid, according to the equation

$$C_6H_5NH_2.HX + HNO_2 \longrightarrow C_6H_5N_2X + 2H_2O.$$

The object in dissolving the amine in an excess of acid being twofold; firstly, as a means of bringing the amine into solution and also liberating free nitrous acid, and secondly, to eliminate coupling reactions taking place between the diazonium salt and free amine, with the formation of insoluble diazo-amino compounds.

When diazo compounds are prepared as intermediaries for further reactions, such as the preparation of phenol from aniline, or the elimination of $-NH_2$ from an aromatic nucleus, it is not necessary to isolate the solid diazonium salts as crystalline solids; yet, in order to investigate the properties and decomposition mechanisms of these substances, they must be isolated in the solid state. The most useful method of obtaining solid diazonium salts is via the method of Knoevenagel[2], in which the amine salt is dissolved or

suspended in absolute alcohol, into which is blown a little dry HCl. By this means hydrolysis of the amyl nitrite which is allowed to drip slowly into the cold solution, rapidly takes place, nitrous acid being liberated and diazotisation ensuing without colouration of the product. The diazonium salt at this point is in solution in the alcohol. If dried ether is added to the alcoholic solution, cooled in ice and stirred, the solid diazonium salt rapidly crystallises out as a perfectly white, cubical crystalline solid, in most cases highly deliquescent and rapidly colouring in the air. The solid may then be filtered off and either washed with the solvent in which it is to be decomposed or alternatively, dried in a desiccator. This latter procedure has often proved dangerous, since diazonium salts are spontaneously explosive when perfectly dry, and several serious accidents have been attributed to this cause.

An alternative method of isolating solid diazonium salts in a stable condition, in which they can be handled with safety, is the precipitation of the zinc chloride double salt. Diazotisation is carried out as in the "direct method" above; to the cold solution is added the calculated quantity of zinc chloride in concentrated hydrochloric acid with stirring, almost immediately the double salt is precipitated as a white solid, which can be

filtered and dried for use. Various other double salts may be prepared (page 41).

(B). Structure and Theories of Reaction.

Theories of the structure of diazonium salts and the diazotates have been so voluminous and controversial that no attempt will be made to explore the labyrinths of all such theories, but only those of direct importance to decomposition reactions will be surveyed.

By altering the p_H of the solution of a diazonium salt, three broad zones can readily be distinguished, depending on their reactivity towards phenols. Hereafter they will be termed diazonium salts, normal diazotates, and iso-diazotates. A tabulated list of their properties and structures is given as follows[3]

Table II.

Zone.	Stability Range.	Nature of compound.	Reaction with Phenols.	Other major characteristics.	Formula.
Diazonium salts.	Up to pH 3.5	Strong salt-forming base unstable in solid state. Free hydroxide unisolatable.	Couples imperfectly.	Salts strongly ionised, readily forms double salts.	$\left(\text{Ph} - \underset{\text{III}}{\text{N}}\right)^{+}X'$ Blomstrand
Normal diazotates	pH 6.5–8.0	Very weak acid, salts unstable. Free hydroxide isolated, very unstable.	Couples readily.	Salts hydrolytically dissociated, weak oxidising agents, readily decompose liberating nitrogen.	$\text{Ph} - \underset{\text{HO}}{\overset{\text{II}}{\text{N}}}$ Hantzsch.
Iso-diazotates.	pH > 8.0	Weak acid, salts stable, isolation of free hydroxide doubtful.	Does not couple, or only slowly in cold aqueous solution.	Undergoes most reactions of normal diazotates though slower.	$\text{Ph} - \underset{\text{N} - \text{OH}}{\overset{\text{II}}{\text{N}}}$

The Diazonium Salts.

Griess originally gave the name diazo compounds to the substances he had isolated, on the erroneous assumption that two hydrogen atoms of the aromatic nucleus had been replaced by nitrogen atoms, and ascribed to them the formula given on page 2 . It was Kekulé in 1866 who first conceived the idea that they were probably related to the better known azo compounds, basing the single nitrogen attachment to the nucleus on the evidence that they usually gave rise to mono aryl derivatives, and accordingly wrote the formula $C_6H_5-N=N-X$. This was later substantiated by the diazotisation of penta-substituted aniline, by the usual methods. Blomstrand[4] and Strecker[5], independently put forward the proposition that one of the nitrogen atoms was pentavalent as in the ammonium salts, since the diazonium salts could hardly be classed with the stable, neutral azo compounds, and therefore proposed the formula $Ar - \underset{\underset{N}{\|}}{N} \rightarrow X$ for them.

Although today this is the recognised formula for the diazonium salts, it was not until 1890 that Blomstrand's work was recognised, since Emil Fischer who had determined the structure of phenyl hydrazine as $Ph - NH - NH_2$ whilst working on sugars, could not see how reduction of $Ph - \underset{\underset{N}{\|}}{N} - X$ could produce $Ph - NH - NH_2$.

The final recognition of Bloomstrand's formula in 1890 came from Bamberger and Hantzsch, the latter proposing the name diazonium salts from analogy with those of the ammonium radical, and suggesting that diazonium salts and diazotates were tautomeric. The only later modification to Bloomstrand's formula arose from the ionic theory which stipulated that the fifth nitrogen valency was ionic, and the true representation of the formula was $\left[Ar - \underset{\underset{N}{\|\|}}{N}\right]^{\blacklozenge} X'$

The Normal Diazotates.

Since despite numerous ingenious attempts by Hantzsch and his co-workers to isolate benzene diazonium hydroxide have failed[6], we can only presume that addition of alkali brings about rapid tautomeric change of the unstable diazonium hydroxide, to a more stable form - that of the normal diazotate. The equilibrium between these two forms does not appear clear cut, but is dependent on internal molecular conditions (i.e., substituents), as well as p_H and temperature. The following equilibria being effected

$$Ar - \underset{\underset{N}{\|\|}}{N^+} - X' \rightleftharpoons Ar - \underset{\underset{N}{\|\|}}{N^+} - OH' \rightleftharpoons Ar - N = NO'H^+ \rightleftharpoons$$

$$Ar - N = N - OH.$$

Hantzsch[7] suggested that with certain diazonium halides the following equilibrium may exist in the solid state

$$Ar - \underset{\underset{N}{\|}}{N^{+}} - Hal^{'} \rightleftharpoons Ar - N{=}N - Hal.$$

The Iso-diazotates.

Although the iso-diazotates are known to be more stable than the normal diazotates, the iso-hydroxide has never been isolated, although Hantzsch repeatedly made attempts to do so. It is now generally agreed that neither of the diazotates could have the nitrosamine formula $C_6H_5 - NH - N{=}O$ ascribed by **Pechmann**, since it represents a neutral molecule, incapable of salt formation, and the accepted formula is that of Hantzsch given in Table II.

Of the numerous and controversial theories which have been proposed for diazo compounds, only those having direct connection with the present-day theories will be mentioned.

The scientific investigation of the diazo compounds commenced with von Pechmann's discovery in 1892 that diazobenzene gave nitrosobenzanilide on **benzoylation**, and represented it as follows

$$Ar - \underset{\underset{M}{|}}{N} - N{=}O + Ar - COCl \longrightarrow Ar - \underset{\underset{\underset{Ar}{|}}{C_O}}{\overset{|}{N}} - N{=}O + HCl$$

In 1894 the iso-diazotates were independently discovered by Schraube and Schmidt, von Pechmann and Frobenius, and Bamberger, the nitrosamines being obtained from them by alkylation. The authors were all agreed in regarding the

iso-diazotates as nitrosamines Ar - NH - N=O, and the normal diazotates as true diazo compounds Ar - N = N - OH as assigned by Kekulé to them. In support of this theory Bamberger treated sodium iso-diazotate with methyl iodide, and obtained nitroso methyl aniline

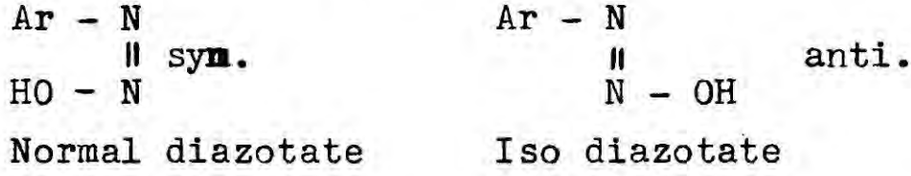
$$Ar - \underset{\underset{Na}{|}}{N} - N{=}O + CH_3I \longrightarrow Ar - \underset{\underset{CH_3}{|}}{N} - N{=}O + NaI$$

Pechmann, however, repeated using methyl iodide and silver iso-diazotate and obtained Ar - N = N - OMe, thus refuting Bamberger's nitrosamine formula, or at least, showed that the iso-diazotates were capable of yielding either -O or -N derivatives according to the method used. Hantzsch maintained that such results merely illustrated the tautomeric nature of the diazo compounds.

Hantzsch's first paper on the diazo compounds was published in 1894, in which he put forward his new theory in no uncertain terms, although it was based on very little experimental evidence, namely, that two forms of diazoamine-benzene and a second form of potassium diazo benzene sulphonate existed. Later, Bamberger showed that the former was actually a bis-diazoamino compound, whilst the analyses of the latter unstable compound were far from satisfactory. The main argument of Hantzsch's paper was to draw a comparison between the oximes and diazo compounds, and he presumed that an identical type of isomerism existed between the normal and iso-diazotates.

The contraversy which arose over this point between Hantzsch and Bamberger seems to have no parallel, and was probably due to the fact that whereas Bamberger studied these compounds on purely organic lines, Hantzsch approached it from a physico-chemical angle, of which Bamberger was very sceptical, but to which he was finally converted.

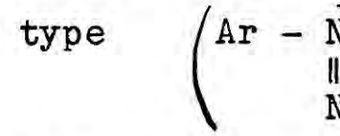
Hantzsch pointed out that it was most unlikely that the normal and iso-diazotates should be so different structurally, as their absorption spectra showed no such great differences, and accordingly he represented the diazo hydroxides as stereoisomers, viz:

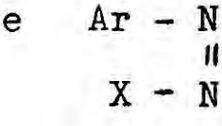


Normal diazotate Iso diazotate

Since the syn form may well be imagined to be subject to internal strain, it was considered to represent the active form - that of the normal diazotates. Hence he postulated that ALL decompositions took place via the intermediate formation of the syn diazo form, even the diazonium salts.

If Hantzsch's theory is correct then every diazo compound can exist in four modifications

(1) Diazonium of the type 

(2) N diazotate of the type 

(3) Iso diazotate of the type $Ar - \underset{\underset{N-X}{\|}}{N}$

and

(4) Nitrosamine of the type $Ar - \underset{\underset{N=O.}{|}}{NH}$

Although he was unable to obtain unequivocable evidence, he did isolate the three requisite diazo cyanides, together with the three members from diazo benzene /β-sulphonic acid. Whilst conductivity measurements of the salts of these latter have shown the normal salt to be a weaker acid than the iso, both having three ions, which strongly supports the stereo-chemical theory.

The nitrosamines were shown to be neutral substances containing no hydroxyl group, and can be produced by passing CO_2 into a solution of the sodium iso-diazotate. Bamberger maintained that by replacing the metallic atom in an iso-diazotate by hydrogen as above, a labile molecule results, which can be converted to the nitrosamine form

$$Ar - \underset{\underset{N-OH}{\|}}{N} \longrightarrow Ar - \underset{\underset{N=O.}{|}}{NH}$$

They are, therefore, pseudo acids, since treatment with alkali converts them to neutral salts - the iso-diazotates; whilst treatment with concentrated acid converts them slowly into diazonium salts.

By the action of N_2O_3 on acetanilide, nitroso acetanilide is produced which has been shown by Pechmann to be identical with iso-diazo benzene acetate (produced by acetylating Ar - N = N - OK), which illustrates the pseudo acidity of the nitrosamines $Ar - \underset{\underset{N = O}{|}}{N} - COCH_3 \rightleftharpoons Ar - \underset{\underset{N - OOCCH_3}{||}}{N}$.

Since Meisenheimer in 1921 showed that the oximes which originally had been termed cis were actually trans, and vice versa, considerable doubt was thrown on the syn and anti forms of the diazo compounds, as to which was the active tautomeric form in decomposition reactions. Le Fevre[8] has definitely established by determinations of dipole moments that the active form is the syn variety. He states that measurements of dipole moments of several pairs of isomeric diazo cyanides have provided definite evidence in support of Hantzsch's theory, viz, that the syn isomerides are the less stable, and are those primarily produced. The spontaneous isomerism which they undergo was followed by measurements of dielectric constant, and the anti isomerides are produced at rates obeying the unimolecular law.

The diazonium cyanides could not be isolated except as double salts with silver cyanide, as shown by Hantzsch[9], of the general formula, $RN_2Ag(CN)_2$. The labile normal cyanide always had the greater solubility and lower melting point, and coupled much the more readily in alcoholic solution with β-Naphthol.

A parallel has been found in azobenzene which exists in two isomeric forms, cis and trans. The transformation of cis into trans azobenzene has been shown by Hartley[10] to have a similar activation energy to the diazo cyanides, and it is therefore probable that the transformation mechanism is identical.

Le Fevre has also brought forward evidence that this isomerism in the diazo cyanides can take place in the solid state when exposed to ultra-violet light, thus upholding a further postulate made by Hantzsch[7].

(C) Decomposition Reactions in Aqueous Solution.

When aniline sulphate is diazotised at 0-5°C. by the addition of sodium nitrite, a solution of benzene diazonium sulphate is obtained whose properties are summarised as follows:-

Table III.

REACTANTS.	PRODUCTS OF REACTION.	REMARKS.
(a) Warming an aqueous solution.	Nitrogen is eliminated and a dark oil separates which can be shown to be phenol $Ar - N_2 - X + H_2O \rightarrow Ar - OH + N_2 +$ HX.	General property of all diazonium salts.
(b) Addition of bromine in KBr solution.	The perbromide is produced which collects as a black oil and solidifies. $Ar - N_2 - SO_4H + KBr + Br_2 =$ $ArNBrNBr_2 + KHSO_4$.	Treatment of this product with hot alcohol or inert solvent $N_2 + Br_2$ are eliminated $\rightarrow$ ArBr. $ArNBrNBr_2 \rightarrow$ $ArBr + N_2 + Br_2$.
(c) Addition of KI solution in the cold.	Nitrogen is evolved with the formation of iodobenzene. $ArN_2SO_4H + KI \rightarrow ArI + N_2 +$ $KHSO_4$.	This reaction with KI is unique, and is general with all diazonium salts.
(d) Alkaline $KMnO_4$	Yields nitrosobenzene and benzene diazoic acid $C_6H_5N = NOOH$.	Ref. 11 and 12.

TABLE III (Continued)

REACTANTS.	PRODUCTS OF REACTION.	REMARKS.
(e) Diazonium halide and Cu_2Cl_2 in HCl.	Vigorous evolution of N_2 in the cold with the formation of chlorobenzene.	Sandmeyer reaction. Cu_2Cl_2 in HCl → ArCl Cu_2Br_2 in HCl → ArBr KCN in $CuSO_4$ → ArCN
(f) Diazonium halide treated with copper powder.	Nitrogen vigorously evolved with formation of the aryl halide.	Gattermann reaction. Works with all diazonium halides in solution.
(g) Various double salts.		
(1) Cobalt thiocyanate.	The corresponding thiocyanate[13] is formed	None of these reactions require Copper powder or a copper salt.
(2) Double cyanide of Ni and K	Produces the corresponding nitrile.	
(3) Sodium sulphide or H_2S.	Can produce both diphenyl sulphide and diphenyl disulphide[14]	
(4) Diazonium fluoride and BF_3	The corresponding fluoro benzene is produced. $ArN_2F + BF_3 \rightarrow ArN_2BF_4 \rightarrow ArF + N_2 + BF_3$.	

(h) <u>Replacement of the diazo group in solution by radicals containing metals</u>.

The best known of these reactions is the Bart reaction, which consists of treating a diazonium salt in alkaline solution with sodium arsenite and thereby preparing phenyl arsenic acid, which crystallises in colourless prisms. Although no intermediate compound has been isolated in this reaction, Schmidt[15, 16] assumed that the arsenic acts in a pentavalent capacity as follows: $Ar - N_2 - Cl + Na_2HAsO_3 \longrightarrow$

$$\left[Ar - N = N - As(=O)(ONa)(OH)\right] \rightarrow Ar - As(=O)(OH)(ONa) + N_2.$$

The double salts of diazonium chlorides and $AsCl_3$, e.g., $ArN_2Cl.AsCl_3$, produce phenyl arsenic acids when treated with alkali. Similar treatment of the $SbCl_3$ double salts affords the corresponding aryl stibnic acids[17].

It is also reported by McClure and Lowy [18] that rapid stirring (2000 revs./min.) of mercury in a solution of benzene diazonium chloride leads to the formation of phenyl mercuric chloride.

When a solution of a diazonium chloride is treated with potassium xanthogenate a series of interesting compounds can be prepared, including thiophenols and thioethers.

$$Ar\text{-}N_2Cl + KS\text{-}C(=S)\text{-}OEt \rightarrow Ar\text{-}S\text{-}C(=S)\text{-}OEt + N_2 + KCl$$

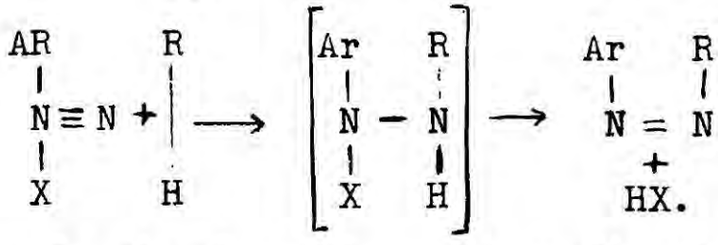
$$\xrightarrow{H_2O} ArSH + COS + EtOH. \qquad \xrightarrow{Heat} Ar\text{-}S\text{-}Et + COS.$$

(D) Mechanisms Suggested for the Decomposition Reactions.

(1) Hantzsch's cis diazo split.

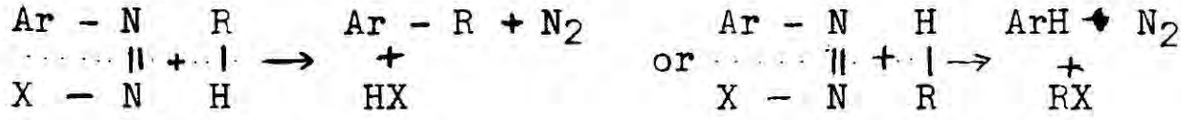
Hantzsch postulated in 1894 that the syn form of diazo salts was the more active and unstable, this has since been verified by Le Fèvre[8], and he maintained that ALL decompositions took place through this form. He argued from analogy with the isomerism of ethylenic compounds and considered his conclusions to be strongly supported by the fact that the labile cyanides decomposed readily in contact with copper powder, whereas the stable forms did not, assuming thereby that the elimination of nitrogen occurred more readily when the groups R & CN were closest together. Although this argument is fallacious as illustrated by the greater stability of the syn than the anti dichloroethylene, in view of Le Fèvre's recent work Hantzsch's original postulate regarding the diazo salts cannot be disputed as yet.

He formulated the following general scheme of reaction, which consists first of addition, and then scission, with liberation of nitrogen.



Similarly the formation of syn diazotates from KOH, diazosulphonates from K_2SO_3, and diazo cyanides from KCN, may be represented.

Decomposition of the normal diazo salts he represented as follows



(a) (b)

The reaction could take place as shown by (a) and/or (b), depending on both R.H and also the substituents in the aryl nucleus.

(2) <u>The Sandmeyer Reaction</u>.

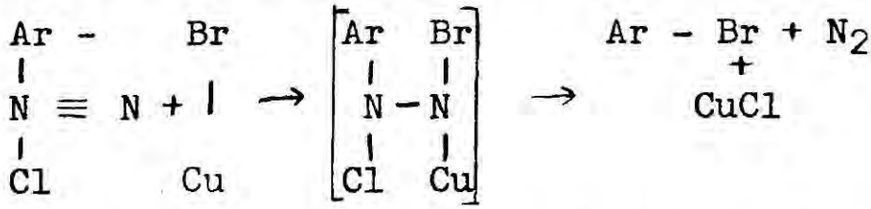
Because of its abnormality this reaction has aroused tremendous interest and research since its publication in 1884. Though various theories have been proposed from time to time, even today its mechanism is clouded in considerable doubt.

The reaction was discovered accidentally by Sandmeyer[19] in attempting to prepare phenyl acetylene by the action of copper acetylide on diazonium chloride, obtaining instead chlorobenzene in almost quantitative yield; whereas boiling a solution of a diazonium chloride saturated with HCl, leads to the formation of only a trace of chlorobenzene[20]. Further investigation revealed that the active agent in producing this unique decomposition was not copper acetylide, but cuprous chloride (Sandmeyer bubbled acetylene into a solution of diazo benzene chloride and cuprous chloride in HCl). Several other metallic chlorides have since been tried,

including $CuCl_2$, $FeCl_3$, $FeCl_2$, $AlCl_3$, etc., without anything like the success of Cu_2Cl_2, the former merely acting as accelerators for decomposition.

It has been suggested with some proof that an unstable intermediate complex is formed between the diazonium salt and the cuprous halide. Although Sandmeyer failed to isolate any such complex, Lillmann and Remey[21] isolated a red crystalline compound from β-diazo naphthalene bromide and Cu_2Br_2, whilst later Hantzsch[22] isolated the analogous benzene diazonium bromide/Cu_2Br_2 complex. It was found that these complexes readily broke down to give the aryl halide, nitrogen, and cuprous bromide in support of this theory. It is worthy of note that Griess[23, 24] obtained chlorobenzene from diazo benzene platinic chloride, diazo benzene auric chloride, and diazo benzene hexachloro stannate double salts. When it is remembered that diazonium chloride double salts are readily precipitated from aqueous solution by the addition of metallic chlorides in concentrated HCl, we notice that double salt formation by diazonium salts is a general characteristic, and it may be imagined that they could be graded in order of stability; the zinc chloride salts probably heading the list as the most stable, and decreasing in stability through the $SbCl_3$, $SnCl_4$ salts, etc., till finally the Cu_2Cl_2 double salts are reached which are so unstable that nitrogen splits out spontaneously, cuprous halide being regenerated and

the aryl halide formed. It cannot be dismissed, however, by assuming that a transient loose attachment of the cuprous halide takes place initially and is finally regenerated, for it has been definitely shown by Hantzsch and Blagden[25] that treatment of p-bromo diazonium bromide with Cu_2Cl_2 gave p-bromo chlorobenzene, and conversely, p-dibromo benzene was obtained from p-bromo diazonium chloride and Cu_2Br_2. Thus the halogen which finally replaces the -N=N-halide grouping is derived from the cuprous anion, and not from the diazonium anion. Some doubt is thrown upon the suggestion that the cuprous addition compound is similar to the normal double salts which are colourless, since they are not only highly coloured, but whereas decomposition of the cuprous compounds affords aryl halides, the normal metallic double salts yield phenol. Hantzsch maintained that the Sandmeyer reaction could be successfully explained by his usual method of decomposition, viz:-



and accordingly the compound in brackets would represent the unstable intermediate complex.

(3) <u>The Gattermann Reaction</u>.

Is probably even more mystifying than the Sandmeyer, since it consists of treating a diazonium halide in solution with copper powder, nitrogen being evolved, and the aryl

halide being obtained in almost quantitative yield. It is possible that the decomposition is not due solely to metallic copper, but to traces of cuprous halide formed by the interaction of the copper powder with the acid medium, in which it is carried out. In this connection it is interesting that Hantzsch and Vock[26] in attempting to prepare p-bromofluoro benzene by the action of copper powder on p-bromo benzene diazonium fluoride, obtained p-bromophenol, which may be expected, since according to Berzelius[27] cuprous fluoride is only stable in vacuo, being rapidly hydrolysed even in the ordinary atmosphere. If this suggestion is accepted as the true one, then the Gattermann and Sandmeyer reactions are fundamentally the same, but no present theory can explain how traces of diphenyl compounds are always isolatable from these reactions. An alternative mechanism will be discussed in the next section on free radical mechanisms.

(4) A Free Radical Mechanism.

In 1926 Pray[28] studied the rate of decomposition of benzene diazonium salts in water, and a series of aliphatic alcohols and acids. He found that for a series of aliphatic alcohols or acids, the observed reaction velocities, as measured by the rate of nitrogen evolution, were all of the same order, and in cases of the lower members of a series, were practically identical. As shown in 1(a) above, Hantzsch

(p.20)

represented decompositions to take place via the formation of an intermediate addition compound as illustrated below

(a) $Ar - N_2 - Cl + RH \longrightarrow Ar - N_2 - Cl.RH.$

(b) $Ar - N_2 - Cl.RH \longrightarrow Ar - N_2 - R + HCl$

(c) $ArN_2R \longrightarrow ArR + N_2$

(a) and (c) being regarded as rapid reactions.

According to Pray's results the rate of decomposition is independent of the nature of R, and he therefore claimed that Hantzsch's mechanism was no longer tenable, and that no known theory could explain these facts. Hey, in 1934, pointed out that a mechanism involving the formation of free radicals would satisfy all the requirements of both Pray and Hantzsch's work. The rate of nitrogen evolution being a measure of the rate of formation of free phenyl and atomic chlorine from PhN_2Cl, which would be truely unimolecular. This theory would also account for traces of polyphenyls formed during the Sandmeyer and Gattermann reactions. Further experimental evidence has been brought forward for this theory, from decompositions carried out in non-aqueous solvents, and will be submitted in Part II.

PART II.

Decomposition Reactions in Non-Aqueous Solvents.

Whereas decompositions carried out in aqueous acid solution usually take place via the diazonium salts, reactions carried out in non-aqueous solvents involve the diazo or covalent tautomers.

For this purpose the diazonium salts are first isolated in the solid state as very hygroscopic, white crystalline solids, which may be dried either in a vacuum desiccator as in the case of Hantzsch, or else washed with the solvent to be used, sucked as dry as possible on the filter, and rapidly transferred to the reaction vessel. With the exception of alcohols, diazonium salts are insoluble in all other organic solvents.

The first recorded decomposition reactions carried out in organic solvents were by Möhlau and Berger[29]; they decomposed benzene diazonium chloride in benzene, naphthalene and pyridine, and obtained diphenyl, phenyl naphthalene and α- and γ-Phenyl pyridines, respectively. The latter result is of great theoretical interest, in that no phenyl pyridinium chloride was detected, thus proving that attack of the nitrogen atom by phenyl kation and chloride anion did not take place, and is therefore evidence in support of a non-ionic decomposition mechanism.

Hantzsch[30] carried out a series of decompositions in glacial acetic acid, in different molecular concentrations.

Table IV.

Diazonium salt.	Sphere of Decomposition.	Reaction Products.
Benzene diazonium chloride.	1 mol of glacial acetic acid decomposition at 50°C.	57% phenyl acetate. 43% chloro benzene.
ψ-Cumene diazonium bromide.	2 mols of glacial acetic acid at 50°C.	47% cumyl acetate. 53% bromo-ψ-cumene.
ψ-Cumene diazonium bromide.	40 mols of glacial acetic acid at 50°C.	Only 28% of Bromo-ψ-cumene.

In 1901, Hantzsch and Jochem[31] decomposed various diazonium salts in methyl and ethyl alcohols, the results of their experiments showed that as the molecular weight of the alcohol increased, and as the number of negative substituents in the aromatic nucleus increased, the yield of aryl hydride increased and the aryl ether diminished.

Table V.

	Diazonium salt.	Sphere of Decomposition.	Reaction Products.
1.	Benzene diazonium chloride.	Decomposed in 10 times its weight of methyl alcohol at 50-55°C.	Nitrogen and formaldehyde evolved. Benzene and 71% Anisole produced.
2.	Benzene diazonium chloride.	Similarly decomposed in absolute ethyl alcohol.	Nitrogen and acetaldehyde evolved, a little benzene and 62% yield phenetole.
3.	Benzene diazonium sulphate.	Decomposed in absolute methyl alcohol.	Nitrogen and 69% anisole. No benzene or formaldehyde detected.
4.	Benzene diazonium sulphate.	Decomposed in absolute ethyl alcohol.	Nitrogen and 58% yield phenetole, a trace of benzene, but no acetaldehyde.
5.	p-Bromo benzene diazonium chloride.	Decomposed in absolute methyl alcohol.	Nitrogen and a mixture of bromobenzene and bromo-anisole obtained.
6.	p-Bromo benzene diazonium chloride.	Decomposed in absolute ethyl alcohol.	Nitrogen and acetaldehyde evolved 80% bromobenzene, no bromo-phenetole detected.

Table V (Continued).

	Diazonium salt.	Sphere of Decomposition.	Reaction Products.
7.	Tri-bromo benzene diazonium sulphate.	Decomposed in absolute methyl alcohol.	Nitrogen evolved, Tribromo benzene obtained in quantity, but no aldehyde or ether detected.
8.		Decomposed in absolute ethyl alcohol.	Identical result.

Hantzsch represented all these decompositions as taking place via the syn form of diazo structure as follows:

$$\begin{matrix} Ar - N & OEt \\ \| & | \\ Hal - N & H \end{matrix} \longrightarrow \begin{matrix} Ar - O - Et \\ + N_2 \\ + H.Hal \end{matrix}$$

(a)

or

$$\begin{matrix} Ar - N & H \\ \| & | \\ Hal - N & OEt \end{matrix} \longrightarrow \begin{matrix} Ar - H + N_2 + \\ EtO.Hal \\ \swarrow \\ CH_3CHO + H.Hal \end{matrix}$$

(b)

Thus he showed that (a) and (b) could take place with the formation of the aryl hydride and aryl ether, and that (b) predominated as the molecular weight etc. of the alcohol increased. If this is the course of the reaction, then whenever the hydrocarbon appears it must be accompanied by the aldehyde,

when a diazonium chloride is decomposed - reaction (b), yet Hantzsch and Jochem failed to detect any aldehyde in 5 above, though bromobenzene was produced.

As shown on page 24, Pray's results did not agree with this type of mechanism. A mechanism involving the formation of free radicals as proposed by Hey[33] and Waters[35], appears to satisfy the results of both workers, for the rate of nitrogen evolution being a measure of the rate of formation of free phenyl and atomic chlorine from $Ph.N_2Cl$, would be truly monomolecular; whilst the free phenyl radical would be capable of removing hydrogen from the solvent with the formation of benzene, or the chlorine atom of chlorinating the alcohol with the formation of an aldehyde as follows

$$C_2H_5OH + Ph^{\cdot} \longrightarrow C_6H_6 + C_2H_5O^{\cdot} \qquad (a)$$

$$C_2H_5OH + Cl^{\cdot} \longrightarrow C_2H_5OCl \longrightarrow CH_3CHO + HCl \qquad (b)$$

$$C_2H_5O^{\cdot} + Ph^{\cdot} \longrightarrow Ph - O - Et. \qquad (c)$$

Hantzsch[32] later extended decomposition in alcohols to the polyhydroxy and aromatic alcohols.

Table VI

Diazonium salt.	Sphere of Decomposition.	Reaction Products.
Benzene diazonium chloride.	n- or iso-propyl alcohol.	Phenyl propyl ethers, but no aldehyde.
	Amyl alcohol.	Phenyl amyl ether and valeraldehyde.
	Benzyl alcohol.	Benzaldehyde and phenyl benzyl ether.
	Glycerol.	Glyceryl phenyl ether.
	Mannitol.	Not attacked.
	Benzoin.	Not attacked.

During the last four years considerable experimental evidence has been brought forward for a free radical mechanism, in the decomposition of diazo benzene acetate, diazo benzene hydroxide, and benzene diazonium chlorides, the chief workers being Hey and Waters.

Benzene Diazo Acetate.

This compound has been shown to be isomeric with nitroso acetanilide, and was prepared by the action of N_2O_3 on acetanilide.

Grieve and Hey[33], in 1934, decomposed diazo benzene acetate at room temperature in various solvents and obtained the following results:-

(1) Benzene - Nitrogen evolved quantitatively - 80% yield of diphenyl obtained.

(2) Toluene - Nitrogen, acetaldehyde, acetic acid and methyl diphenyls.

(3) m-Xylene - Nitrogen, acetaldehyde, acetic acid and 2.4-dimethyl diphenyl.

(4) Ethyl benzoate - Ethyl diphenyl carboxylates were isolated.

(5) Benzaldehyde - Diphenyl-4-aldehyde was isolated.

These reactions of Grieve and Hey show that substitution always took place at the ortho and/or para position whatever the directive nature of the group in the aromatic solvent. Later, Grieve and Hey[34] studied the rate of decomposition of various p-substituted nitroso acetanilides in benzene, from which they came to the conclusion that although the diazonium salts can be graded in the following order of decreasing stability, p-OMe, p-Cl, p-Br, p-Me, H, m-Me, the following held for the nitroso acetanilides p-Cl, p-Br, H, p-Me. Equimolecular weights of the nitroso acetanilides were allowed to decompose at 20° in benzene previously saturated with nitrogen. The rate of decomposition being measured by the rate of evolution of nitrogen, and in each case good unimolecular velocity constants were obtained, all of which fell very close together, in marked contrast to the larger

differences observed with the diazonium salts.

Further decomposition reactions have been carried out by Waters[35] with diazo benzene acetate in aliphatic solvents, in each case a simple substituted aromatic compound was found amongst the decomposition product. Decompositions were carried out in hexane, cyclohexane, diethyl ether, dioxan, acetone, ethyl acetate, acetonitrile and acetic anhydride. The diazo compound was soluble and allowed to decompose at room temperature for several days, in each case benzene was readily isolated from the residue. From this evidence he concluded that the removal of hydrogen from the solvent by a free phenyl radical was a general characteristic.

Considerable evidence for such a free radical mechanism was the detection by Waters of carbon dioxide with the evolved nitrogen in ~~the latter solvent~~ CS_2 + CCl_4, which he attributed to the transient formation of the neutral acetate radical, since an acetate anion is incapable of splitting out CO_2.

Decompositions in methyl and ethyl iodides yielded iodobenzene.

Decompositions in ethyl bromide and bromoform produced bromobenzene.

Decompositions in chloroform and carbon tetrachloride produced chlorobenzene.

In carbon bisulphide decomposition led to the formation of diphenyl disulphide, whilst a solution of iodine in CS_2

yielded principally iodobenzene.

Waters also showed that in CS_2 and CCl_4 such metals as zinc, iron, copper, tin, lead, and antimony, were attacked yielding their acetates, even in the presence of an excess of chalk, thus eliminating attack by acetate ions.

In a recent publication, Butterworth and Hey[36] studied the effect of concentration and temperature on the rate of decomposition of nitroso acetanilide in benzene. Reactions were carried out with quantities of nitroso acetanilide varying from 2 to 20 grs. per 100 cc. of benzene at 20°C. Their tabulated results show that the maximum yield of diphenyl (80%) occurs at the lowest concentration and decreases to 46% with 20 grs. nitroso acetanilide, though the percentage of nitrogen evolved in each case was almost identical. The authors attribute the low yield of diphenyl in concentrated solution to the formation of ter and poly phenyls, which has been shown characteristic of these reactions. To test the effect of temperature, 2 gm. lots of the diazo acetate were decomposed in 100 cc. of benzene at 10°, 20°, 30° and 40°. The reaction velocity triples itself for each 10° rise, and the best yield of diphenyl was obtained at 20°C. Decompositions carried out in various solvents at 20°, showed the reaction velocity to be substantially constant, whatever the solvent.

Diazo Benzene Hydroxide.

Was decomposed in the following solvents by Grieve and Hey[33], finding only very slight differences between a solution kept neutral and a solution definitely alkaline.

(1) With benzene:- Benzene diazonium chloride solution prepared in the usual way and run into benzene and excess aqueous caustic soda, allowed to react at room temperature - yielded diphenyl.

(2) Toluene - similar procedure gave methyl diphenyls (o and p).

(3) m-Xylene - gave 2.4-dimethyl diphenyl.

(4) Chlorobenzene - chlorodiphenyls.

(5) Nitrobenzene - Nitro diphenyls.

(6) Ethyl benzoate - Ethyl diphenyl carboxylates.

(7) Mixture of toluene and nitrobenzene in equimolecular quantities.- Isomeric nitrodiphenyls, four times as great as yield of isomeric methyl diphenyls, showing that substitution took place in o and p positions much quicker with a m-directing group already present in the nucleus, than when an o and p directing group present.

Further reactions of diazo benzene hydroxide were carried out by Waters[37]. Benzene diazonium chloride being run into excess of caustic soda in (a) carbon bisulphide, (b) cyclohexane; decomposition was observed to take place only in the organic layer, diphenyl disulphide and benzene respectively being isolated from the decomposition products.

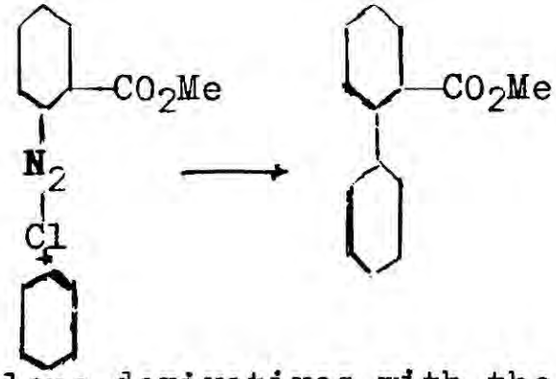
More recently Grieve and Hey[38] have carried out further experiments on the Gomberg reaction; a solution of benzene diazonium chloride being slowly added to benzene stirred with (a) an excess of caustic soda, (b) excess of calcium hydroxide, (c) excess of caustic soda, and an emulsifying agent, Linsapol A. The yield of diphenyl was principally the same in each case, and the authors showed conclusively that the reaction took place in the organic layer, which they assert supports the theory of a non-ionic mechanism. Reactions carried out between (a) diazotised aniline and aqueous sodium benzoate, (b) diazotised anthranilic acid and aqueous sodium benzoate, and (c) diazotised anthranilic acid and benzene in the presence of aqueous alkali, yielded no diphenyl carboxylates, though substitution of methyl anthranilate for anthranilic acid in the above does produce these compounds, showing that the essentials of this reaction is a two phase system, the success of which is dependent on the partition coefficient.

Aryl Diazonium Chlorides.

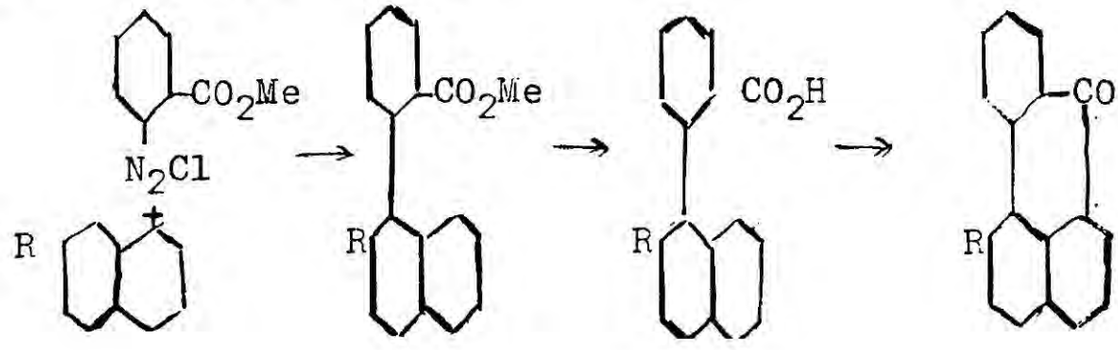
Solid benzene diazonium chloride prepared by the method of Hantzsch and Jochem (Table I) was decomposed under acetone, hexane, carbon tetrachloride, ethyl acetate and ethyl iodide, by Waters[39]. In all these reactions, HCl was evolved with the formation of chlorobenzene, with the exception of the latter solvent, which produced iodo benzene also. When

decomposition was carried out in acetone with excess of chalk present, benzene and chloro acetone were isolated, when mercury was present in the latter mixture, phenyl mercuric chloride could also be isolated. Since acetone is not attacked by chlorine ions, Waters postulated that the chloro acetone could only be produced by chlorination of the acetone, by atomic chlorine evolved during decomposition, the free phenyl simultaneously acquiring an atom of hydrogen from the acetone, with the formation of benzene.

Heilbron, Hey and Wilkinson[40] have decomposed diazotised methyl anthranilate in (a) aromatic solvents with the formation of diphenyl carboxylate esters as follows



(b) naphthalene derivatives with the formation of phenyl naphthalene derivatives as intermediaries in the formation of benzanthrone derivatives, viz:



More detailed decompositions of various aryl diazonium halides in acetone and ethyl acetate, with and without chalk, and in the presence of several metals, will be discussed in Part III, which is work carried out by myself.

Preparation of Organo metallic compounds from diazo salts.

1. Arsenic.

The isolation of phenyl arsenic acids via the Bart reaction[16] has already been mentioned, this reaction too was carried out in aqueous solution.

The formation of organic arsenicals can be prepared by the methods given below for antimony, the reactions being almost identical.

2. Mercury.

The aromatic mercury compounds have been prepared in numerous different ways. (a) action of aryl halides on sodium amalgam[41].

(b) aryl halides, $HgCl_2$ and sodium metal[42].

(c) Grignard reagents on mercury halides[43].

(d) direct mercuration[44].

(e) mercury salts, and aryl carboxylic acids[45].

(f) aryl sulphinic acids and mercuric chloride[46].

(g) aryl halides and mercuric acetate[47].

(h) Nesmejanov[48] prepared aromatic mercurials from mercury double salts of diazonium halides (for preparation see page 5).

Spontaneous decomposition of the double salt of benzene diazonium iodide and mercuric iodide produced iodo benzene, mercuric iodide, and a diphenyliodonium iodide. When the reaction was carried out in acetone or ethyl acetate in the presence of copper powder, the chief product isolated was phenyl mercuric iodide. Similarly, decomposition of benzene diazonium chloride mercuric chloride double salts, even naphthyl as well as subsfituted aryl diazonium chlorides, yields the corresponding phenyl, naphthyl, or substituted phenyl mercuric chlorides. A general conclusion Nesmejanov drew from his work, was that as the positive substituents in the aromatic nucleus increased, the yield of aryl mercuric halides increased likewise, and vice versa, e.g., o- and p-tolyl, o-anisyl, and p-phenetyl diazonium double salts gave the respective yields 66%, 66%, 72% and 77%, whilst with tribromo benzene diazonium chloride double salt no organic mercurial could be isolated.

$$Ar - N_2Cl + HgCl_2 + 2Cu = Ar - Hg - Cl + N_2 + 2CuCl$$

via this method he obtained p-chloro phenyl mercuric chloride - M.Pt. 240°C., and p-bromo phenyl mercuric chloride M.Pt. 249-5°C.

He showed also that by decomposing these double salts in the presence of a large excess of copper powder, mercury diaryls could be produced[48].

$$2ArN_2Cl.HgCl_2 + 6Cu = Ar_2Hg + 2N_2 + 3Cu_2Cl_2$$

Later, Nesmejanov[49] showed that liberation of mercury was not an intermediate phase in these reactions, since silver can be used to replace copper, which cannot displace mercury from solution. In addition the copper may be replaced by copper bronze, aluminium, iron, zinc, tin, or magnesium.

Decomposition of nitrosoacetanilide in CCl_4 in the presence of mercury metal yields besides mercurous and mercuric chlorides, phenyl mercuric chloride[50]. Whilst later Waters[39] showed that similarly when benzene diazonium chloride was decomposed in acetone in the presence of chalk and mercury, the same product could be isolated. This reaction has since been shown to be of general application by the preparation of p-chloro and p-bromo phenyl mercuric chlorides from the corresponding p-chloro and p-bromo diazonium chlorides, by Makin and Waters[51].

3. Tin.

Nesmejanov[52] extended his work to the preparation of aryl stannic chlorides, via the decomposition of salts of the general formula $\left[RN_2Cl\right]_2SnCl_4$. These were prepared in the usual manner by adding stannic chloride in concentrated

hydrochloric acid to a solution of the diazonium chloride when the double salt were precipitated as a white insoluble powder.

The tin double salt was added in small portions to boiling ethyl acetate containing a suspension of powdered tin; after the vigorous reaction had subsided the solvent was distilled away, and the residue extracted with petrol. They were generally low-melting, heavy crystalline solids of the general formula R_2SnCl_2, treatment of which with dilute ammonia gave the corresponding stannic oxide R_2SnO. These afforded the diaryl mercury compounds, by which they were identified by treatment with mercuric oxide. Nesmejanov maintained that compounds of the type $R_3Sn.OH$ or R_4Sn were not formed.

$$(ArN_2Cl)_2SnCl_4 + Sn \rightarrow Ar_2SnCl_2 + 2N_2 + SnCl_4$$

$$Ar_2SnCl_2 + 2NH_4OH \rightarrow Ar_2SnO + H_2O + 2NH_4Cl$$

$$Ar_2SnO + HgO \rightarrow Ar_2Hg + SnO_2$$

4. Lead.

Nesmejanov in the same communication described the formation of triaryl plumbic halides by the decomposition of the lead chloride double salts. Diaryl plumbic oxides were also obtained in very small yields.

He claims that the following general equation holds for the preparation of organo metallic compounds from diazonium double salt decompositions:

$$(RN_2Cl)_mXCl_n + 2m/p\ M^{(P)} = R_mX^{(n)}Cl_{n-m} + mN_2 + 2m/p\ M^{(p)}Cl_p,$$

where X = metallic atom of the double salt of valency n.

M = free metal of valency p.

m = number of mols of diazonium salt per mole of metallic chloride.

This equation can readily be followed in the preparation of Ar_2SnCl_2 above.

He has prepared the double salts of $ZnCl_2$, $CdCl_2$, $SnCl_4$, $PbCl_2$, $PtCl_4$, $TlCl_3$, $BiCl_3$, $FeCl_3$, $AuCl_3$ in HCl, from the following diazonium chlorides: phenyl, o-, m-, and p-Me, p-OH, p-OMe, o-, m-, p-Cl, p-Br, p-I, o-, m-, and p-NO_2, in about 5N HCl.

According to Nesmejanov's theory it is the metallic atom of the double salt which forms the organic compound, whereas Makin and Waters[51, 53] have conclusively shown that when the zinc chloride double salts are decomposed in the presence of Sb, Te, or Se powder in acetone or ethyl acetate, the corresponding organo metallic compounds are produced, but not that of zinc. It may be that initially the zinc aryl is formed, but decomposes in preference to the formation of the more stable Sb, Se, and Te compounds, or alternatively, if free aryl radicals and atomic chlorine are produced from the decomposing diazonium salt, these attack the more reactive metal. That this latter possibility is creditable is shown by the simultaneous

formation of Ar_3Sb, Ar_3SbCl_2 and Ar_2SbCl_2; as one would expect these radicals to combine independently wherever an uncompleted electronic shell was available.

5. Antimony.

Antimonials of the types Ar_3Sb, Ar_3SbCl_2, and Ar_2SbCl, may be produced as described above by decomposing the zinc chloride double salts in ethyl acetate or acetone in the presence of antimony powder and chalk.

An identical result is obtained by using the diazonium salt itself in place of the double salt[51]. The reaction proceeds in an identical manner, producing similar yields of the three antimonials.

6. Selenium and Tellurium.

Have been shown by Waters[53] to react in a similar manner with diazonium chlorides or their zinc chloride double salts in acetone and chalk, with the formation of diphenyl selenide and diphenyl tellurium dichloride, respectively.

The Preparation and Properties of Aryl Antimonials.

These compounds may conveniently be classified into two groups:

(A) Trivalent antimonials.

(B) Pentavalent antimonials.

Each of these groups are capable of further subdivision, but will be dealt with under these general headings.

A. 1. Tertiary Aryl Stibines. Ar_3Sb.

Four general methods of preparation are available:-

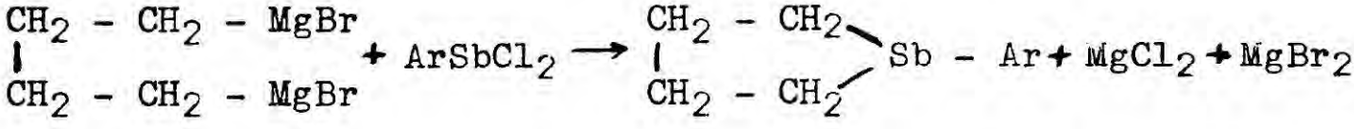
(a) Michaelis and Reese[54] showed that treatment of an aryl halide with $SbCl_3$ in the presence of sodium metal, in an inert solvent produced a preponderance of the tertiary aryl stibine, together with traces of the di and tri aryl stibnic halides Ar_2SbCl_3 and Ar_3SbCl_2, respectively.

$$3ArBr + SbCl_3 + 6Na \longrightarrow Ar_3Sb + 3NaCl + 3NaBr.$$

(b) The Grignard reagents too can be used for the preparation of these compounds, by decomposition in the presence of $SbCl_3$. Morgan and Micklethwait[55] claim to have obtained an almost quantitative yield of the tertiary stibines by this method.

$$3ArMgCl + SbCl_3 \longrightarrow Ar_3Sb + 3MgCl_2.$$

Via this method mixed stibines of the type ArR_2Sb and Ar_2RSb may be prepared, as well as heterocyclic antimony compounds, e.g.,



(c) Treatment of an organic halide with an alloy of antimony and sodium may be employed as follows[56]

$$3ArX + Na_3Sb \longrightarrow Ar_3Sb + 3NaX.$$

This is simply a variation of Michaelis and Reese's method.

(d) By treatment of mercury diaryls with $SbCl_3$, Michaelis and Reese[54] obtained aryl mercuric chlorides, but did not isolate any aryl stibine. Hasenbäumer[57], however, obtained the triaryl stibines by heating $SbCl_3$ and Ar_2Hg in a sealed tube with dry xylene to 130°C.

$$3Ar_2Hg + 2SbCl_3 \longrightarrow 2Ar_3Sb + 3HgCl_2$$

Properties of the Tertiary Stibines.

They are usually colourless crystalline solids of definite melting point, and which are quite stable in the air; they combine directly though not vigorously with free halogens to form the stibnic halides. However, with stibines containing bulky substituents attached in the ortho position in the aromatic nucleus, steric hindrance plays a definite part and the addition of halogens can only be achieved with difficulty. Consequently, whereas the simpler tertiary stibines show strong reducing properties converting cupric, ferric, and thallic chlorides to the corresponding -ous chlorides as follows: $Ar_3Sb + 2FeCl_3 \longrightarrow Ar_3SbCl_2 + 2FeCl_2$, the more complicated stibines must be refluxed with the halogen in chloroform or carbon tetrachloride.

Concentrated nitric or sulphuric acids convert these stibines into the corresponding stibinic nitrates or sulphates.

$$Ar_3Sb + 4HNO_3 \longrightarrow Ar_3Sb(NO_3)_2 + 2H_2O + 2NO_2$$

Oxidising agents convert them into the corresponding stibnic oxides ArSbO, or stibnic hydroxides $Ar_3Sb(OH)_2$, and whereas

cold dilute alkalis produce the hydroxides also, hot alkalis yield the sodium diphenyl stibnate $Ar_2Sb(=O)(ONa)$

Treatment of a stibine with $HgCl_2$ breaks the C - Sb linkage with the formation of Ar-Hg-Cl + $SbCl_3$ (Reverse of Hasenbaümer's reaction) and affords a method of elucidating the structure of the stibine.

2. Stibnous Halides. Ar_2SbCl and $ArSbCl_2$.

Preparation.

(a) Morgan and Micklethwait[55] found that treatment of a tertiary stibine with $SbCl_3$ involved two successive reactions:

$$2Ar_3Sb + SbCl_3 \longrightarrow 3Ar_2SbCl \qquad (a)$$

$$Ar_2SbCl + SbCl_3 \rightleftharpoons 2ArSbCl_2 \qquad (b)$$

and that the latter only, was reversible.

(b) In the presence of methyl alcoholic HCl the tertiary stibine can be dearylated with the formation of the diaryl stibnous chloride.

$$Ar_3Sb + HCl \xrightarrow{MeOH} Ar_2SbCl + ArH.$$

By successive treatment of the diaryl stibnous chloride with NaOH, HAC, and then HCl, the primary stibnous chloride can be obtained.

(i) $$2Ar_2SbCl + 2NaOH \longrightarrow (Ar_2Sb)_2O + 2NaCl + H_2O$$

(2) $(Ar_2Sb)_2O + 4Hac \longrightarrow 2Ar\text{-}Sb\begin{matrix}ac\\ac\end{matrix} + H_2O + 2ArH.$

(3) $Ar\text{-}Sb\begin{matrix}ac\\ac\end{matrix} + 2HCl \longrightarrow Ar\text{-}SbCl_2 + 2Hac.$

Properties of the Stibnous Halides.

The primary and secondary stibnous halides are white crystalline substances of definite melting point, readily precipitating silver halides when warmed with alcoholic silver nitrate. They are insoluble in water, but readily soluble in alcohol, ethyl acetate, acetone, and chloroform.

The stability of the secondary stibnous salts is greater than that of the primary, which, under certain conditions, are converted to the secondary or even tertiary compounds.

The primary halides react with NaOH, $H\overline{ac}$ and H_2S to form the corresponding oxides, diacetates and sulphides, respectively. Both add on halogens to form $ArSbCl_4$ and Ar_2SbCl_3 which upon hydrolysis afford primary and secondary stibnic acids, respectively.

B. 1. Aryl Stibonium salts of the type Ar_4SbCl do not exist in the aromatic series, as they do in the aliphatic, due no doubt to the influence of steric hindrance.

2. Triaryl Stibnic Halides. Ar_3SbCl_2.

Preparation.

(a) They are most readily prepared by direct halogenation of the tertiary stibines, which may be accomplished either

(1) By treatment with $CuCl_2$, as described by Loloff[58],

or (2) In more difficult case by refluxing with CCl_4 saturated with chlorine.

(b) They may be isolated from the by-products in the preparation of the tertiary stibines by Michaelis and Reese method (A.1.a).

Properties.

They are white needle-like crystalline solids, soluble in acetone, ethyl acetate, chloroform, benzene, and to a less extent 60-80° petrol, and readily precipitating AgCl quantitatively when refluxed with alcoholic silver nitrate or silver acetate in acetic acid. Treatment with alcoholic potash produces the triaryl stibinic oxide or hydroxide, which readily react with acids to form the dinitrates, sulphates, or even diacetates, which are prone to hydrolysis to the basic salt $Ar_3Sb\begin{matrix}X\\OH\end{matrix}$.

By treatment of the dichlorides with H_2S in alcoholic ammonia the sulphide may be obtained Ar_3SbS[59].

3. Diaryl Stibnic Halides Ar_2SbX_3.

Preparation.

(a) They may be obtained in the crystalline condition by cooling a solution of the diaryl stibnic acid in hot dilute halogen acid.

(b) By direct halogenation of the diaryl stibnous chloride and recrystallised from dilute HCl.

(c) They are obtained together with Ar_3SbCl_2 derivatives as by-products in the preparation of tertiary stibines (A.1. a) above.

(d) As a by-product in Hasenbaümer's method (A.1. d.) above for preparing tertiary stibines.

Properties.

They crystallise as long needles insoluble in water, but soluble in alcohol and dilute HCl. Treatment with alcoholic $AgNO_3$ produces the diaryl stibnic nitrate which rapidly hydrolyses to the basic nitrate.

4. Primary Stibnic Halides $ArSbCl_4$.

Preparation.

(a) By direct halogenation of primary stibnous halides dissolved in ether.

(b) Treatment of a primary stibnic acid with concentrated HCl and evaporation of the solution, yields an oil which solidifies and is $ArSbCl_4$.

Properties.

Very hygroscopic, low melting crystals, which are readily soluble in ether, hot chloroform, benzene, and HCl. Readily hydrolysed by water to the primary stibnic acid, and decompose on heating to give Ar_2SbCl_3 and $SbCl_3$.

5. Primary Stibnic Acids. $ArSbO_2.H_2O$

Preparation.

(a) To a diazotised solution of aniline, Sb_2O_3 in caustic soda is added, which produces phenyl stibnic acid (cf. Bart reaction). Treatment with HCl gives a solution of $ArSbCl_4$ which is precipitated as the $ArSbCl_4.NH_4Cl$ double salt by the addition of ammonium chloride. The precipitate is collected and hydrolysed with water to yield the primary stibnic acid Ar-Sb(=O)(OH)(OH) (60).

(b) The diazonium double salt $ArN_2Cl.SbCl_3$ is precipitated and decomposed in a 20% caustic soda solution, from which the stibnic acid is isolated by NH_4Cl treatment as in (a).

(c) By heating the tertiary stibine with $SbCl_3$ and thereby obtaining $ArSbCl_2$, which is chlorinated to $ArSbCl_4$, and hydrolysing with ammonia solution (a little diphenyl stibnic acid is precipitated) upon acidification of the filtrate with HCl the primary stibnic acid is precipitated.

$$ArSbCl_2 \xrightarrow{Cl_2} ArSbCl_4 \xrightarrow{H_2O} ArSbO_2.nH_2O.$$

Properties.

White infusible solids, insoluble in water or alcohol, slightly soluble in acetone, but soluble in glacial acetic acid, chloroform and amyl acetate. Treatment with conc. HCl converts them into the stibnic chloride, form salts with

alkalis, addition of H_2S to a solution of the acid in acetic acid precipitates the yellow aryl stibnic sulphide, whilst addition of $BaCl_2$ to an ammoniacal solution of the acid precipitates the barium salt.

6. Secondary Stibnic Acids. Ar_2SbO_2H.

Preparation.

(a) To a cold solution of diazotised aniline is added an aryl stibnous oxide (ArSbO) in glacial acetic acid; when made alkaline a vigorous reaction ensues and the filtrate on acidification precipitates the acid.

$$ArN_2Cl + ArSbO + 2KOH \longrightarrow Ar_2Sb(=O)(OH) + N_2 + KCl$$

(b) $$Ar_2SbCl \xrightarrow{Cl_2} Ar_2SbCl_3 \xrightarrow[\text{hydrolysis}]{\text{alkaline}} Ar_2Sb(=O)(OH)$$

(c) Oxidation of Ar_3Sb by hot alkaline hydrogen peroxide yields Ar_2SbO_2H also.

Properties.

They are usually slightly coloured powders of high melting point, insoluble in water or conc. HCl, but soluble in dilute HCl. Their solubility in alkalis depends upon their initial method of precipitation. The solution in hot dilute HCl is not precipitated with NH_4OH but is precipitated with pyridine hydrochloride. Treatment of an alcoholic HCl solution with mercuric chloride produces Ar-Hg-Cl and $SbCl_3$.

PART III.

Decomposition reactions were carried out in acetone and ethyl acetate with the diazonium chlorides from the following bases: p-chloraniline, p-bromoaniline, 4-chloro-o-toluidine, 5-chloro-o-toluidine, 4-chloro-o-anisidine, p-nitraniline and ethyl anthranilate.

p-Chloro benzene diazonium chloride.

Preparation.

Initially the diazonium salt was prepared by diazotising p-chloroaniline hydrochloride according to the method of Hantzsch and Jochem, the resulting solid was slightly coloured, and it was found advantageous to use a modified Knoevenagel method (see Table I).

21 grs. of p-chloraniline hydrochloride were dissolved with warming in 150 cc. of absolute alcohol, cooled to 10°C., a little HCl blown in and further cooled to 0° in a freezing mixture. Amyl nitrite (2½ cc.) were added drop by drop, the solution being slowly but efficiently stirred. After standing in ice for a further half hour, 200-250 cc. of sodium-dried ether were added, when the salt separated as an oil which later solidified. The diazonium salt was rapidly filtered off at the pump, and washed with the solvent to be used; the damp salt (35 grs.) was perfectly white and highly hygroscopic.

(1) Decomposition in acetone without chalk.

p-chloraniline hydrochloride (21 grs.) diazotised as above

was transferred whilst damp with acetone, to a flask containing 100 cc. of specially dried Analar acetone. A reflux condenser with calcium chloride guard tube was attached to the flask; on standing at room temperature the acetone became cherry pink, but no visible decomposition took place. The temperature of the acetone was slowly raised until a vigorous decomposition set in at 50°C, nitrogen was eliminated, and HCl detected at the top of the condenser by means of $AgNO_3$ solution, litmus paper, and ammonia. The mixture was finally refluxed for half hour to ensure complete decomposition of the diazonium salt. After removing the acetone by distillation up a long column, a dark residue remained which was transferred to a 25 cc. distilling flask provided with a short column. In this manner a fraction weighing 3 grs. was obtained boiling 118-120°, which was shown to be chloroacetone (pink colouration with NaOH, and the preparation of its semicarbazone M.Pt.147.5° alone or in admixture with an authentic specimen) and a fraction (1 g.) B.Pt. 131-133°which was shown to be chlorobenzene by nitration to 2.4-dinitro chlorobenzene B.Pt.51°C alone or in admixture with an authentic specimen.

(2) Decomposition in acetone in the presence of chalk.

The same quantities of the diazonium chloride and acetone were used together with 20 grs. of chalk. No reaction occurred in the cold, except that the colour of the acetone became pink, on raising the temperature to 50° decomposition set in, nitrogen alone being evolved.

After a final reflux on the water bath, the excess chalk was filtered off and the acetone distilled away leaving a residue, fractionation of which from a small flask yield

6 grs. of chloroacetone B.Pt.118-120° identified as in (1), and

1.5 grs. of chlorobenzene B.Pt.132-134° identified as in (1).

3 Decompositions in presence of lead, silver and bismuth.

Each experiment was carried out in 100 cc. of acetone with 6 grs. chalk present.

(a) 5 grs. of diazonium salt and 20 grs. lead filings.

(b) 5 grs. of diazonium salt and 5 grs. silver powder.

(c) 5 grs. of diazonium salt and 10 grs. precipitated bismuth.

In each case reaction set in in the cold (in contrast to 50° in acetone alone) and was completed by refluxing on the water bath. When cool, each solution was filtered, the residue and filtrate being separately investigated.

The residue from (a) was treated with boiling water, but no $PbCl_2$ could be extracted, treatment with warm dilute acetic acid, however, yielded a solution which precipitated PbS on passing H_2S, yellow $PbCrO_4$ on adding K_2CrO_4, and white $PbSO_4$ on adding H_2SO_4.

The residue from (b) was extracted with warm ammonia solution, the filtered extract gave 1.3 grs. of AgCl on acidification with nitric acid.

The residue from (c) was extracted with warm dilute HCl, but did not yield a solution containing bismuth ions.

The filtrates after removal of the acetone showed
(a) Contained some chlorobenzene as shown by the formation of its iodonium iodide (Masson's test).
(b) contained chlorobenzene detected by the above test, and also chloracetone shown by caustic soda colouration.
(c) extraction of the tarry residue with HCl gave a solution of $BiCl_3$, no chlorobenzene or chloracetone, however, could be detected.

4 Decomposition in the presence of Mercury.

Diazonium chloride (15 grs.) was placed in a flask containing 30 grs. of mercury, 20 grs. of chalk and 100 cc. of Analar acetone, a vigorous reaction set in at room temperature and the flask was vigorously shaken whilst standing in cold water, the reaction being completed by refluxing. When cool the excess chalk was filtered off and shown to contain both mercurous and mercuric ions. Acetone was distilled away from the filtrate leaving a semi-solid tarry residue which was extracted with hot alcohol. After repeated crystallisations and charcoalings, glistening silver plates of p-chloro phenyl mercuric chloride (1.5 g.) were obtained M.Pt.241°C.

(Found Hg 57.7%, total chlorine 20.4%. Calculated Hg 57.6%, chlorine 20.4%).

Hanke[61] gives M.Pt.225°, whilst Nesmejanov[48] gives M.Pt.240°. Treatment of a portion with fuming HNO_3 gave p-nitro chlorobenzene

M.Pt. 82°C. alone or mixed with authentic specimen.

5. Decomposition with Antimony Powder.

Diazonium chloride (20 grs.) were added to 20 grs. of chalk, 200 cc. of acetone and 30 grs. of antimony powder. A very vigorous reaction ensued whilst standing in cold water, the acetone actually refluxing. After the reaction had subsided the contents were refluxed for half hour, and the solid residue filtered off and extracted with boiling acetone. The acetone filtrates were collected and distilled leaving a brown semi-viscous residue which was repeatedly extracted with 60-80 petrol. Concentration and charcoaling of the petrol solution finally yielded a white crystalline product (1.4 grs.) which was shown to be tri(p-chlorophenyl) stibnic dichloride M.Pt.193°.

(Found Sb 23.0%, ionic chlorine 13.4%. $C_{18}H_{12}Cl_5Sb$ requires Sb 23.1%, ionic chlorine 13.4%).

A similar experiment without chalk present gave only .5 gr. of the above antimony compound.

6. Decomposition in Ethyl Acetate with Chalk.

20 grs. of the diazonium salt from p-chloraniline after washing with purified ethyl acetate were transferred to a flask containing ethyl acetate and 20 grs. of chalk. Although the solvent slowly developed a pink tint at room temperature, decomposition did not set in until warmed to 50-60°, the resulting mixture was refluxed to complete the

decomposition. After filtration the ethyl acetate was distilled away, the distillate giving positive tests for acetaldehyde (and in a later experiment was isolated by fractionation to give the 2,4-dinitro phenyl hydrazone M.Pt.162°), whilst the residue yielded a small quantity of a yellow oil boiling between 100-160° containing chlorine ions and having an acidic reaction. Vacuum distillation of the residue B.Pt. > 160°, yielded p-dichlorobenzene (0.4 g.) M.Pt.53.5° alone or in admixture with an authentic specimen prepared via the Gattermann reaction.

No chlorobenzene was detected in this reaction.

7 Decompositions with lead, silver and bismuth.

(a) 5 grs. of powdered lead, 7 grs. diazonium chloride, 100 cc. ethylacetate, 10 grs.chalk.

(b) 5 grs. powdered silver, 7 grs. diazonium chloride, 100 cc. ethyl acetate, 10 grs.chalk.

(c) 5 grs. precipitated bismuth, 7 grs. diazonium chloride, 100 cc. ethyl acetate, 10 grs.chalk.

The three flasks with contents stood at room temperature and were periodically shaken; decomposition ensued slowly and was completed by refluxing. The solid phase was separated and examined:-

(a) Solid residue extracted with hot water gave a solution of $PbCl_2$.

(b) Solid residue extracted with hot ammonia solution gave AgCl on acidification with nitric acid.

(c) Solid residue extracted with hot HCl showed no evidence of bismuth ions.

The filtrates:- In all cases acetaldehyde was detected during the removal of the ethyl acetate by distillation.

(a) Distillation of the residue gave fraction B.Pt.100-125° containing acetaldehyde, HCl, and acetic acid.

(b) Gave a fraction B.Pt.100-145° acid to litmus, containing acetic acid, HCl, and acetaldehyde.

(c) Residue deposited BiOCl on evaporation, soluble in HCl.

8 Decomposition in Ethyl Acetate with Mercury.

Diazonium salt (10 grs.) were covered with 100 cc. of ethyl acetate, 10 grs. of chalk and 20 grs. of mercury. No appreciable reaction took place until warmed to 50°. Acetaldehyde was readily detected at the top of the condenser by Schiff's reagent and ammoniacal silver nitrate. After filtration and removal of the ethyl acetate, no p-chloro phenyl mercuric chloride could be detected in the residue.

9 Decomposition in the presence of Antimony Powder.

10 grs. of the diazonium salt were added to 100 cc. of ethyl acetate, 10 grs. of chalk, and 20 grs. of powdered antimony. As soon as the mixture was shaken a brisk reaction ensued for almost an hour, acetaldehyde being continuously

evolved at the top of the condenser. After refluxing, the solid residue was filtered off and shown to contain $SbCl_3$; the filtrate was distilled to remove the ester, leaving a brown oily residue which crystallised on cooling in long needles. These were collected and recrystallised from ethyl acetate and petrol, from which long white needles separated having a M.Pt.192-3°. were shown to be tri(p-chlorophenyl) stibnic dichloride - yield .8 g.

p-Bromo benzene diazonium chloride.

Preparation.

p-bromaniline hydrochloride (26 grs.) was diazotised by the usual procedure at 10-15°C. in 200 cc. of absolute alcohol with 23 cc. amyl nitrite. The diazonium salt was obtained by an ether precipitation as perfectly white crystals which were highly hygroscopic.

1. Decomposition in Acetone with Chalk.

The diazonium salt (26 grs.) was placed in 200 cc. of Analar acetone with 20 grs. of precipitated chalk. On warming to 50-55°C. a vigorous decomposition set in with evolution of nitrogen. As soon as the reaction had abated the mixture was refluxed for 30 minutes and filtered hot. The acetone was distilled away up a long column, leaving a residue of 30 cc. which was transferred to a 50 cc. distilling flask and distilled from a sand bath. Three fractions were obtained:-

(1) B.Pt. 118-130° - 7.7 grs. gave tests for chloracetone.

(2) B.Pt. 130-155° - 6.4 grs. gave tests for chloracetone and a hydrocarbon.

(3) B.Pt. 155-170° - 4.3 grs. gave tests for a hydrocarbon only.

Redistillation of fraction (2) gave chloracetone 2.8 grs. and 3.6 grs. of a hydrocarbon. A semicarbazone from (1) melted at 148°C. (after recrystallisation from petrol) alone or in admixture with the authentic semicarbazone of chloracetone. Nitration of (2) and (3) yielded p-nitro bromobenzene M.Pt.126°C. alone or in admixture with an authentic specimen.

Thus actual yields were 10.5 grs. chloracetone.
7.9 grs. bromobenzene.

2. Decomposition with Mercury.

A similar weight of the diazonium salt was added to 200 cc. of acetone, 20 grs. of chalk and 30 grs. of mercury. A vigorous reaction ensued at room temperature on shaking, which was completed by a short reflux. After filtering, a trace of chloracetone was observed in the acetone distillate, and a dark semi-solid residue remained which on recrystallisation from alcohol yielded .8 g. of p-bromophenyl mercuric chloride M.Pt.248°C. Treatment of which with fuming nitric acid gave p-bromo nitrobenzene M.Pt.126° alone or in admixture with an authentic specimen.

3. Decomposition with Antimony Powder in Acetone.

26 grs. of p-bromo benzene diazonium chloride were placed in a 400 cc. flask with 30 grs. of powdered antimony, 20 grs. of chalk and 200 cc. of acetone. A very vigorous decomposition set in immediately, the acetone refluxing and nitrogen being evolved. After half hour's refluxing on the water bath, the solid phase was filtered off and extracted with hot acetone. Distillation of the combined acetone filtrates left a brown viscous residue which was extracted in a soxhlet with 60-80° petrol, from which was obtained long yellow needles, these were redissolved in petrol (in which they are only slightly soluble) and charcoaled, after several recrystallisations 3.0 grs. of tri-(bromo phenyl) stibine dichloride M.Pt.200°C. were obtained.

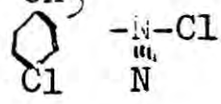
(Found Sb 18.5%, hydrolysable Cl 10.3%.

$C_{18}H_{12}Br_3Sb$ requires Sb 18.3%, hydrolysable Cl 10.7%)

4. Decomposition in Antimony Powder in Ethyl Acetate.

A similar weight of the diazonium chloride was covered with 200 cc. of ethyl acetate, 20 grs. of chalk, and 30 grs. of antimony powder. A slow reaction took place at room temperature which increased on warming and shaking. Acetaldehyde was detected at the top of the condenser, whilst after a short reflux and filtering off the solid phase, the solvent on distillation also contained acetaldehyde and HCl. Complete removal of the solvent left a brown viscous residue

which was poured into a basin to crystallise. The tarry crystals were extracted in a soxhlet with 500 cc. of 60-80 petrol for 3 hours, at the end of which time the thimble contained white needles which were recrystallised from a mixture of alcohol and ethyl acetate. These crystals were shown to be identical with those from the petrol extract, and melted at 200°C. - Yield 4.1 grs. tri(p-bromophenyl) stibine dichloride.

4-Chloro-o-tolyl diazonium chloride. 

Preparation.

20 grs. of 4-chloro-o-toluidine hydrochloride were diazotised by the usual procedure at 20°C. with 20 cc. of amyl nitrite. The resulting diazonium chloride was obtained as white cubical crystals only slightly hygroscopic.

1. Decomposition in Acetone with Antimony Powder.

20 grs. of the diazonium chloride were transferred to a flask containing 200 cc. of acetone, 20 grs. of chalk, and 30 grs. of antimony powder. A vigorous reaction set in in the cold, which shortly abated, the mixture was then refluxed for a few minutes before filtering away the solid phase and washing with acetone. Some of the antimony compound crystallised in the filter flask, the solution was therefore warmed to dissolve the crystals and set aside to slowly recrystallise. White needles M.Pt.224°C. were obtained (1.6 grs.).

Further concentration of the acetone solution yielded a further 4.6 grs. of the compound M.Pt.224°.

This substance gave qualitative tests for antimony, but contained no ionic chlorine. An antimony estimation gave Sb 22.36%, whereas the calculated Sb % for the stibine dichloride was 21.38% or 24.4% for the tertiary stibine. It was thought to be the stibine dihydroxide Sb % 22.87, since it reacted with thionyl chloride to give the dichloride M.Pt. 263°. Microscopic examination of the 224° compound showed it to be a heterogeneous mixture. Later recrystallisation from benzene by Waters gave a M.Pt. 226°C. and Sb = 24.4%, total chlorine 21.5%.

Calculated for tri(4-chloro-o-tolyl) stibine, Sb = 24.4%, chlorine 21.4%.

Thus this reaction yields the tertiary stibine which on treatment with chlorine in CCl_4 forms the stibine dichloride M.Pt.264°.

2. Decomposition with Antimony Powder in Ethyl Acetate.

A similar weight of the diazonium chloride was decomposed in 200 cc. of ethyl acetate in the presence of 20 grs. of chalk and 30 grs. of antimony powder. After completing the slow reaction by refluxing, and filtering away the residue, the ethyl acetate solution was distilled, acetaldehyde and HCl being detected in the distillate, a tarry

residue remained which was poured into a basin to crystallise. The crystals were filtered off, washed with dilute methyl alcohol to remove the tar; recrystallisation from ethyl acetate and alcohol gave crystals M.Pt.223-4°C. - yield 5.6 grs., a trace of a compound M.Pt.127° being obtained from the mother liquors.

As shown above the compound M.Pt.223-4° on recrystallisation, melted at 226°C. and was tri(4-chloro-o-tolyl) stibine.

Recrystallisation of the substance M.Pt.127° gave M.Pt.131° containing 29.0% Sb. Calculated for the stibnous chloride 29.8% Sb. Waters, from a larger specimen, obtained 29.8% Sb.

Hence, substance M.Pt.131° is di(4-chloro-o-tolyl) stibnous chloride.

Thus by decomposing 4-chloro-o-tolyl diazonium chloride in acetone were obtained

(a) tri(4-chloro-o-tolyl) stibine, M.Pt. 226° - 6.2 grs.

(b) tri(4-chloro-o-tolyl) stibine dichloride, M.Pt. 263° (later experiment).

In Ethyl Acetate

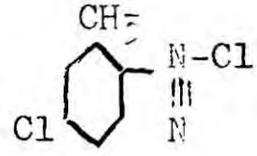
(a) tri(4-chloro-o-tolyl) stibine, M.Pt. 226° - 5.6 grs.

(b) di(4-chloro-o-tolyl) stibnous chloride, M.Pt. 131°.

Decomposition of 4-chloro-o-tolyl diazonium chloride, zinc chloride double salt in acetone in the presence of antimony and chalk.

20 grs. of 4-chloro-o-toluidine hydrochloride were dissolved in 40 cc. of 10N HCl and diazotised at 0° by the slow addition of 8.5 grs. of sodium nitrite in water. The resulting solution was filtered and added with stirring to 15.5 grs. of zinc chloride in concentrated HCl. The double salt was precipitated as a white powder which was filtered off, dried, and added to 200 cc. of acetone, 30 grs. of antimony powder and 20 grs. of chalk. A steady decomposition set in at room temperature which was completed by refluxing. The solid phase was separated and the acetone filtrate concentrated as usual. Crystals were obtained M.Pt.226° and shown to be tri(4-chloro-o-tolyl) stibine 1.4 grs.

From the mother liquors was obtained 1.6 grs. of crystals melting 131°C. shown to be di(4-chloro-o-tolyl) stibnous chloride.

5-Chloro-o-tolyl diazonium chloride 

Preparation.

The diazotisation is identical with that of 4-chloro-o-toluidine, the diazonium salt however, although white cubical crystals, was highly deliquescent.

1. Decomposition in Acetone with Antimony Powder.

20 grs. of the diazonium chloride were decomposed by the usual procedure in 200 cc. of acetone with 20 grs. of chalk and 30 grs. of antimony powder present. After completion of the decomposition by refluxing, the solid phase was filtered off whilst hot, and the acetone filtrate set aside to crystallise. The crystals obtained M.Pt.169°C. were recrystallised, together with those from the mother liquor; the resulting crystalline product melted sharply at 176°, further recrystallisation from petrol gave the same melting point. - Yield 3.2 grs.

Since the compound M.Pt.176° contained antimony, but no ionic chlorine, it was suspected of being the tertiary stibine. Duplicate analyses for antimony gave 24.55% and 24.54%. Calculated Sb for tri(5-chloro-o-tolyl) stibine 24.45%.

Later, Waters showed the total chlorine via a Carius estimation to be 21.5%; calculated for the stibine, total chlorine 21.4%.

Thus the decomposition in acetone has given 3.2 grs. of tri(5-chloro-o-tolyl) stibine M.Pt.176°.

2. Decomposition in Ethyl Acetate with Antimony Powder.

A similar weight of the diazonium salt was decomposed in 200 cc. of ethyl acetate, in the presence of 20 grs. of chalk and 30 grs. of antimony powder. Acetaldehyde was

detected at the top of the condenser during the decomposition. After filtering away the solid phase, and concentration of the ester filtrate, the solution was set aside to crystallise; 2.6 grs. of a crystalline derivative were obtained M.Pt.176° alone or in admixture with the above tertiary stibine. From the mother liquors a compound was obtained melting at 230°, this on recrystallisation from petrol had a M.Pt.238° and contained ionic chlorine. Sb analysis gave 21.5%. Sb calculated for tri(5-chloro-o-tolyl) stibine dichloride 21.4%.

Recrystallisation of the product obtained by treating the tertiary stibine M.Pt.176° with thionyl chloride yielded the dichloride M.Pt.238°.

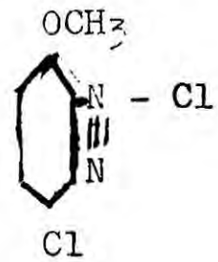
Thus the decomposition in ethyl acetate has yielded

(a) Tri(5-chloro-o-tolyl) stibine M.Pt.176°.

(b) Tri(5-chloro-o-tolyl) stibine dichloride M.Pt.238°.

Both the zinc chloride and antimony chloride double salts of this diazonium salt are soluble and could not be precipitated even with concentrated HCl present.

5-Chloro-2-Methoxy Benzene Diazonium chloride.



Preparation.

The diazotisation of 4-chloro-o-anisidine hydrochloride was carried out in the usual manner. The resulting diazonium

chloride was slightly yellow tinged and highly deliquescent.

(1) Decomposition with Antimony Powder in Acetone.

The diazonium salt (20 grs.) was decomposed in 200 cc. of acetone with 20 grs. of chalk and 30 grs. of antimomy powder. The solid phase was filtered off after refluxing, and the acetone filtrate concentrated by distillation. The crystals which separated were contaminated with tar, which was removed by a methyl alcohol wash. The resulting white crystals were recrystallised from petrol and melted at 146° - yield .6 grs. They contained ionic chlorine and an antimony analysis showed 26.46%.

Later recrystallisation from petrol by Waters gave M.Pt.144°. Sb 27.3%, ionic chlorine 8.1%.
Required for di(5-chloro-2-methoxy phenyl) stibnous chloride Sb 27.0%, ionic chlorine 8.05%.

Hence this reaction has yielded only .6 g. of di(5-chloro-2-methoxy phenyl) stibnous chloride M.Pt.144°C.

(2) Decomposition with Antimony Powder in Ethyl Acetate.

A similar weight of the diazonium salt was decomposed in 200 cc. of dry ethyl acetate in the presence of 30 grs. of antimony powder, and 20 grs. of chalk. After refluxing and filtering off the solid residue, the acetone filtrate was concentrated by distillation and allowed to crystallise. Tarry crystals were obtained which were filtered off and washed with dilute methyl alcohol. Recrystallisation from

petrol gave 1.8 grs. of a compound M.Pt.188°C. The mother liquors yielded .4 g. of a compound M.Pt.281° after charcoaling and recrystallisation from petrol.

Investigation of Compound M.Pt.281°C. was shown to contain ionic chlorine and to decompose on melting. An antimony estimation gave 20.04%. Calculated for tri(5-chloro-2-methoxy phenyl) stibine dichloride Sb 19.7%.

Later recrystallisation by Waters gave M.Pt.281° Sb = 19.7%.

Compound M.Pt.188°C. was shown to contain no ionic chlorine, and was suspected of being the tertiary stibine. An antimony analysis gave 22.1% Sb. Calculated for the tertiary stibine 22.2%.

Therefore the decomposition in ethyl acetate has afforded

(a) .4 g. of tri(5-chloro-2-methoxy phenyl) stibine dichloride M.Pt.281°C.

(b) 1.8 grs. of tri(5-chloro-2-methoxy phenyl) stibine M.Pt.188°C.

p-Nitrobenzene Diazonium chloride. $NO_2C_6H_4-N_2-Cl$

Preparation.

p-Nitroaniline was diazotised at 0°C. by the usual Knoevenagel method, giving a pale yellow diazonium salt, which was highly deliquescent.

1. Decomposition in Acetone with Antimony Powder.

The diazonium salt from 20 grs. of p-nitraniline was decomposed at room temperature in the presence of 200 cc. of acetone, 20 grs. of chalk and 30 grs. of antimony powder. The mixture was filtered after a short refluxing, and the acetone distilled away from the filtrate, leaving an oil smelling of nitrobenzene, which later solidified. This residue was taken up in light petrol and allowed to crystallise; the tarry crystals obtained were charcoaled and recrystallised from alcohol, giving 1 g. of a pale yellow substance M.Pt.225°C. containing 18.25% Sb. This compound contained ionisable chlorine as shown by an alcoholic solution of $AgNO_3$.

Time did not permit a thorough investigation of this compound, but it seems highly probable that it is the stibine dichloride in an impure state, i.e., tri(p-nitro phenyl) stibine dichloride.

2. Decomposition in Ethyl Acetate with Antimony Powder.

An identical amount of the diazonium chloride was decomposed in 200 cc. ethyl acetate, 30 grs. of antimony powder, and 20 grs. of chalk. The reaction was slow at room temperature, but increased on raising the temperature, acetaldehyde being evolved from the condenser. After refluxing and filtering hot, the ethyl acetate solution was distilled away from the filtrate, leaving a dark residue which was extracted with methyl alcohol. After charcoaling and

recrystallising .3 g. of the pale yellow compound M.Pt.225° was obtained, containing antimony and ionic chlorine.

(3) Decomposition of the $SbCl_3$ double salt.

Preparation.

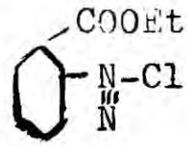
20 grs. of p-nitraniline were suspended in 300 cc. 7N HCl and diazotised at 5°C. by the addition of 14 grs. of $NaNO_2$. The resulting solution after filtering was added with stirring to 34 grs. of $SbCl_3$ in concentrated HCl. A copious white precipitate of $p\text{-}NO_2C_6H_4\text{-}N_2Cl.SbCl_3$ came down which was filtered off.

Decomposition in Acetone with Antimony Powder.

The above double salt was decomposed in 150 cc. of acetone with 25 grs. of antimony powder and 20 grs. of chalk. The decomposition, which was slow at room temperature, was increased by refluxing. The solid residue was filtered away, leaving a filtrate smelling strongly of nitrobenzene; after removal of the acetone on a water bath a dark oil was left, which distilled from a sand bath B.Pt.207-8° - yield 2 grs., and was shown to be nitrobenzene.

Hence this reaction afforded only nitrobenzene and no aromatic antimony compounds.

Ortho-Carbethoxy Benzene Diazonium chloride



Preparation.

20 grs. of ethyl anthanilate **hydrochloride** were

diazotised at 10°C. by 12 cc. of amyl nitrite, and the diazonium chloride isolated in the usual manner. The salt obtained was fleshy pink and hygroscopic.

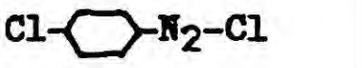
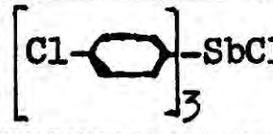
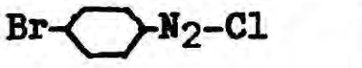
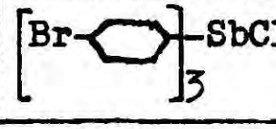
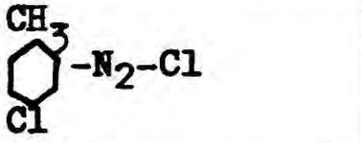
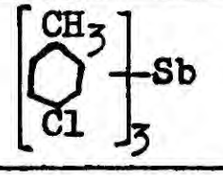
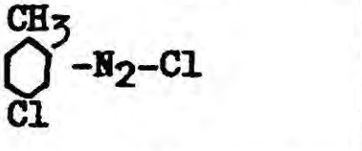
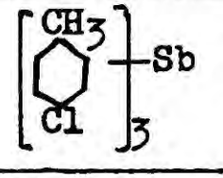
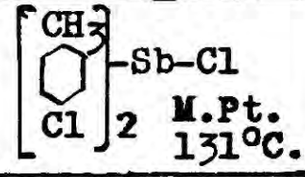
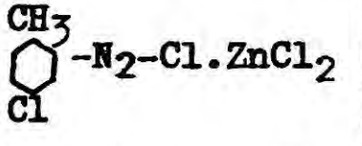
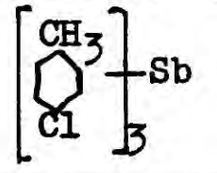
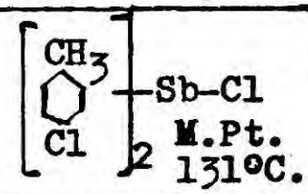
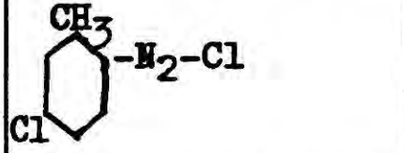
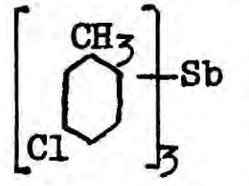
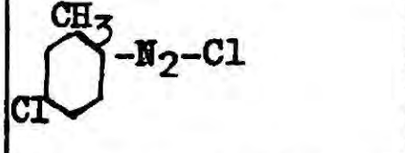
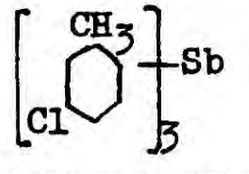
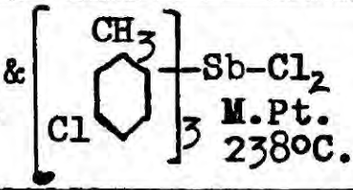
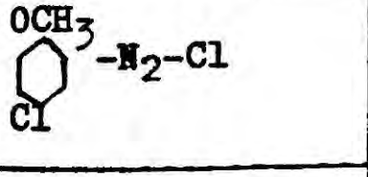
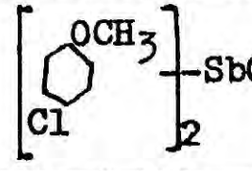
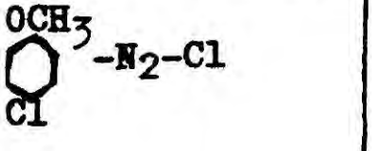
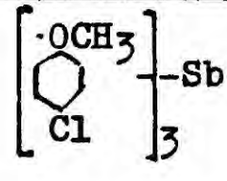
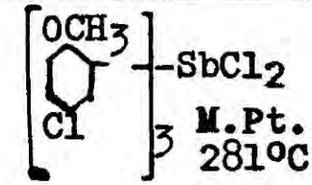
(1) Decomposition in Acetone with Antimony Metal.

20 grs. of the diazonium salt were taken with 200 cc. of acetone, 30 grs. of antimony and 20 grs. of chalk. Decomposition set in at room temperature and was completed by refluxing. Removal of the acetone after filtering left an oil smelling of ethyl benzoate. Vacuum distillation of the oil left a viscous residue, which gave tests for antimony. An alcohol extract of the residue did not recrystallise out, though when poured into water yielded a copious yellow precipitate which melted at 80° when dried. This substance seemed insoluble in all solvents except alcohol; it was therefore hydrolysed with alcoholic KOH, from which was obtained silky white needles containing antimony and burning with a sooty flame, though infusible. Thus it seems possible that the hydrolysis produced an aryl stibnic acid.

There was insufficient time for me to investigate this reaction fully.

SUMMARY OF THE DECOMPOSITIONS IN THE PRESENCE OF ANTIMONY POWDER AND CHALK.

Table VII.

Diazonium Salt.	Solvent.	Products of Reaction.
	Acetone or Ethyl acetate.	 M.Pt.193°C.
	Acetone or Ethyl acetate.	 M.Pt.200°C.
	Acetone.	 M.Pt.226°C.
	Ethyl acetate.	 M.Pt. & 226°C  M.Pt. 131°C.
	Acetone.	 M.Pt. & 226°C  M.Pt. 131°C.
	Acetone.	 M.Pt.176°C.
	Ethyl acetate.	 M.Pt. & 176°C.  M.Pt. 238°C.
	Acetone.	 M.Pt.144°C.
	Ethyl acetate.	 M.Pt. & 188°C.  M.Pt. 281°C.

Methods of Analysis:

Estimation of Mercury.

Approximately .2 g. of the aryl mercuric chloride was placed in a Carius tube with about 2 cc. of fuming nitric acid; the tube was sealed and the temperature raised during 6 hours to 300°C. in a Carius furnace. When cool the tube was cut open and the contents washed out into a 600 cc. beaker, caustic soda was added till alkaline, when HgO was precipitated, this was immediately redissolved in the minimum quantity of KCN. On passing H_2S, black HgS was precipitated, ammonium acetate was added, and the solution boiled till all ammonia had been expelled. The HgS was then filtered through a previously ignited and weighed Gooch crucible, washed with warm HCl and water and dried at 120°C.

Estimation of Antimony.

·1 to ·2 grs. of the antimony compound was weighed into an ignition tube and placed in a Kjeldahl flask with .2 g. of pure NaCl and 3 grs. of sodium bisulphate; 1.5 cc. of fuming nitric and 10 cc. of concentrated sulphuric acid were added, and the mixture was gently warmed for 20-30 minutes, during a second half hour stronger heating was applied to ensure complete rupture of the compound. When cool, 1 to 2 grs. of ammonium sulphate were added and the heating continued very strongly till no nitric acid remained. The mixture was cooled and washed into a beaker with 300 cc. of

water to which was added 1 g. of KBr, 10 cc. of concentrated HCl and an excess of SO_2 solution. After boiling to expel the excess SO_2, about 2 grs. of tartaric acid were added, and then made neutral by adding sodium bicarbonate. Titration of the solution with an N/40 solution of iodine gave an estimation of the antimony present as follows:

$$Sb_2O_3 + 2I_2 + 2H_2O \longrightarrow Sb_2O_5 + 4HI.$$

Estimation of total Chlorine.

This was carried out in the approved manner of a Carius estimation, the method proving to be more useful than those of Piria and Shiff, or Stepanow. The only modification necessary in this estimation was the addition of a little tartaric acid to prevent the precipitation of ~~silver tartrate~~. Sb_2O_3 etc.

Estimation of ionisable Chlorine.

Approximately .2 g. of the compound was refluxed with excess alcoholic caustic potash for 3 hours, water was added and the alcohol removed by distillation. The resulting alkaline solution was made acid by the addition of nitric acid and filtered, addition of silver nitrate to the filtrate gave a quantitative precipitate of silver chloride which was filtered through an ignited Gooch crucible, washed with nitric acid and water, and dried at 120°.

Conclusion and Summary:

In reading the papers of the '90s, one is struck by the broad generalisations drawn from a small range of experiments. In this respect Hantzsch was probably the most guilty; although several of his conclusions have since been verified by Le Fevre's work on dipole moments, and in academic quarters generally accepted and used as a vehicle to transmit ideas and express results, there are definite limits to its applicability and it should be regarded more as a method of convenience than as an exact hypothesis.

The recent work of Pray has shown that Hantzsch's cis diazo split, although capable of explaining the occurrence of his products of reaction, is quite untenable in view of the new evidence, and therefore that intermediate unstable addition compounds of the type proposed by Hantzsch do not exist. Hantzsch also postulated that it was possible in some cases for a diazonium salt to pass to the tautomeric diazo structure in the solid state, since on warming it coloured and on cooling in a freezing mixture reverted to its original white colour. This in itself is remarkable, since not only is it almost impossible to obtain diazonium salts completely dry without their exploding, but no other known substance isomerises in the solid state without a catalyst, which is frequently a solvent.

From work carried out by myself and others it appears that diazonium salts readily tautomerise to the diazo structure,

but only in the presence of a non-ionic solvent, although in which they may to all intents and purposes be insoluble. It seems impossible to explain the formation of aryl antimony compounds by Hantzsch's mechanism, since they cannot be prepared by the direct action of antimony on a hydrocarbon; further, it has been observed that whereas decomposition of a diazonium chloride does not take place until the temperature of the solvent has been raised to approximately 50°, a vigorous reaction ensues at 0°C. in the presence of metals.

This experimental evidence seems to indicate that even at 0° there is an equilibrium between the diazonium and diazo tautomers, and that whilst the n-diazo salts decompose extremely slowly at room temperature, but rapidly at 50° (probably the limit of stability), they are catalytically decomposed in the presence of metals. The extent of the tautomerism seems to be dependent upon the polar nature of the solvent, since although decomposition takes place at 0° when metals are present in the polar solvents, acetone and ethyl acetate, with non-polar solvents such as cyclohexane, benzene, CS_2, CCl_4, dioxan, and ethyl ether, no decomposition takes place until heated to 50° in the presence of the same metals.

Hantzsch declared that the Sandmeyer reaction could likewise be attributed to a cis diazo split following the intermediate formation of an unstable addition compound which

he succeeded in isolating.

It is rather hard to conceive of the tautomerism of a diazonium salt in a highly acid medium to the diazo salt, unless it takes place catalytically under the influence of cuprous chloride, or of copper powder in the Gattermann reaction; such a mechanism fails to afford any reason for the formation of di and poly phenyl derivatives which are found in traces in these reactions.

We may therefore say that Hantzsch's view that the normal and iso diazotates are stereoisomers containing trivalent nitrogen, and that the nitrosamines are pseudo acids with no free hydroxyl group, has not been superseded, and are the recognised formulae of today; but that his mechanism for decomposition reactions can no longer be considered tenable in the light of recent results. That such a position should arise may perhaps be explained by the fact that his structural hypothesis was contested at every point by the numerous workers in this field, such as Bloomstrand and Pechmann, whereas he was almost the sole worker engaged on decompositions in non-ionic solvents until recent years, and it was not until Pray in 1926 destroyed the addition mechanism that research on these lines became stimulated again.

During the last 10 years considerable work has been carried out by Hey and Waters and their co-workers on diazo acetates, diazo hydroxides, and diazonium chlorides, from which has been

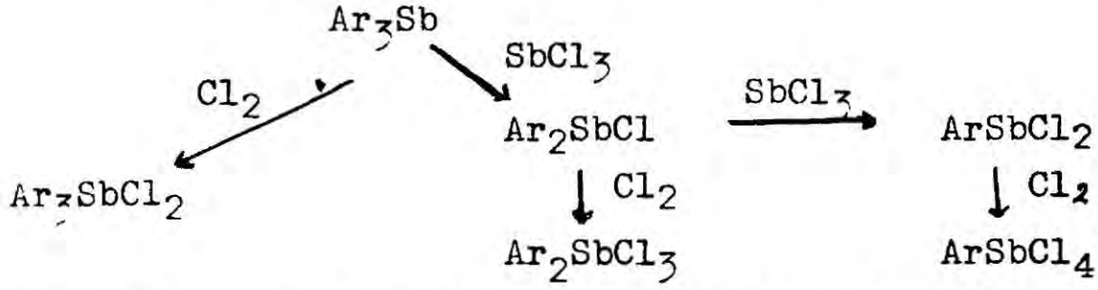
born a new theory, viz, the free radical mechanism, which has been able to interpret the results of Hantzsch and Pray satisfactorily, and also numerous reactions especially with metals inexplicable by Hantzsch's theory, though the Sandmeyer and Gattermann reactions still remain insoluble through lack of evidence.

According to the new theory, diazo compounds on decomposition in non-ionic solvents liberate a free aryl radical together with free acetate, hydroxide or atomic chlorine, respectively, with fission of nitrogen. Every reaction so far investigated has been capable of interpretation on this theory, though alternatives have been suggested by Professor Robinson of a less satisfactory nature. The experimen which have given impetus to this theory are the formation of di and poly phenyls when diazo acetates are decomposed in benzene, the liberation of carbon dioxide when decomposed in acetic anhydride, and the formation of aryl metallic compounds of Hg, Sb, Se and Te when diazonium chlorides are decomposed in acetone or ethyl acetate in the presence of these metals. All metals appear to be attacked under these conditions with the formation of their chlorides, and those forming organo-metallic compounds stable in boiling acetone or ethyl acetate appear to do so.

Nesmejanov by the decomposition of the double salts of diazonium chlorides and $SnCl_4$ and $PbCl_2$ has also obtained

Ar_2SnCl_2 and Ar_3SbCl compounds, but declared that it was always the metal contained in the double salt whose organic compound was formed; this has since been shown invalid, since the decomposition of double salts with zinc chloride in the presence of antimony metal, has afforded aryl antimony compounds from which it may be inferred that either preferential attack of the more reactive metal by the free radicals takes place, or that subsequent decomposition of the primary product may take place with the formation of the more stable aryl metallic compound.

From a study of the methods of preparation of aryl antimony compounds it will be noticed that the triaryl stibines form the gateway to all other derivatives as follows:-



Hence the preparation of any of these compounds depends primarily upon that of the corresponding tertiary stibine. For example by Michaelis and Reese method a chlorinated tertiary stibine cannot be prepared by taking a dihalogenated hydrocarbon, since both halogens will be attacked by the reagents employed, a similar drawback is experienced in the method of Morgan and Micklethwait which depends upon the preparation of the corresponding Grignard reagent. The only

method available is that of Hasenbäumer, which consists of heating the mercury diaryl with $SbCl_3$ in dry xylene under pressure. Apart from the inconvenience of such a method it is first necessary to prepare the mercury diaryl. By the method outlined in my experimental section it is possible to prepare substituted aryl antimonials from the corresponding amine hydrochlorides quite rapidly.

Steric hindrance appears to take a part in the preparation of these antimony compounds, since when a bulky substituent is present in the ortho position in the aromatic nucleus, the tertiary stibine is the usual product, instead of the stibine dichloride. This is upheld by the fact that whereas simple tertiary stibines show reducing properties, being able to convert cupric, thallic, and ferric chlorides to the corresponding -ous chlorides with the formation of the stibine dichloride, the ortho substituted stibines show no such properties and have to be refluxed with chlorine in CCl_4 to give stibine dichloride. The formation of aryl stibnous chlorides is almost certainly due to a secondary reaction between the tertiary stibine and $SbCl_3$ during the refluxing stage.

Every decomposition carried out in ethyl acetate and chalk was accompanied by the liberation of acetaldehyde from the top of the condenser. Moreover it was noticed that after separation of the chalk and removal of the ethyl acetate by

distillation, the ester distillate always contained both HCl and acetaldehyde. In several decompositions acetic acid was detected in the residue after complete removal of the ethyl acetate.

This cannot be due to hydrolysis of the ester by HCl, since an excess of chalk was always present. The simplest explanation is that tautomerism to the diazo chloride takes place in ethyl acetate, with decomposition at 500 into free phenyl and atomic chlorine, the latter chlorinating the ester to produce α-chloro ethyl acetate (cf. decomposition in acetone in presence of chalk), viz:-

$$Cl\cdot + C_2H_5OCOCH_3 \longrightarrow CH_3CHCl\text{-}OCOCH_3 + H\cdot$$

α-chloro ethyl acetate is known to be rapidly hydrolysed by moisture to acetaldehyde, acetic acid and HCl.

$$CH_3CHCl\text{-}OCOCH_3 + H_2O \longrightarrow CH_3CHO + HCl + CH_3COOH.$$

Further work is being carried out by Dr. Waters on these compounds; it is hoped that ultimately both the Sandmeyer and Gattermann reactions will yield the secret of their mechanisms and lower the veil which has so long enshrouded them in mystery.

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