Halogen and interhalogen adducts of substituted amido-ions

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HALOGEN AND INTERHALOGEN ADDUCTS OF SUBSTITUTED AMIDO-IONS

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A B S T R A C T

The reaction between N-dimethylchloramine and iodomethane - which yields the species $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ - has been investigated with a view to elucidating possible mechanisms, and a number of analagous and related compounds have been prepared.

Variation of initial molar ratios gives rise to different products and ratios of products. A large excess of N-dimethylchloramine yields a mixture of $(CH_3)_3N.ICl$ and $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ (1:1.55) whereas a one hundredfold excess of iodomethane yields iodine only. With nearly equal ratios of starting materials, $(CH_3)_4N^+I^-$ is formed. These results suggest a number of competing reactions which became more or less favourable depending on initial reactant concentrations.

A proposed mechanism for the reaction leading to the formation of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ has been suggested:

(i) $(CH_3)_2NCl + CH_3I \longrightarrow (CH_3)_3NClI$

(ii) $(CH_3)_3NClI \longrightarrow (CH_3)_3N + ICl$

(iii) $(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4N^+ I^-$

(iv) $(CH_3)_2NCl + ICl \longrightarrow (CH_3)_2N(Cl)(ICl)$

(v) $(CH_3)_2N(Cl)(ICl) + (CH_3)_4N^+I^- \longrightarrow (CH_3)_4N^+ (CH_3)_2N(ICl)_2^-$

The adduct $(CH_3)_2NCl.ICl$ is a proposed intermediate, and this substance has been prepared, together with two other previously unknown related compounds $(CH_3)_2NCl.IBr$ and $(CH_3)_2NCl.Br_2$. The analagous N-dibenzylchloramine compound $(C_6H_5CH_2)_2NCl.ICl$ has also been prepared.

Various adducts of N-halamines have been reacted with large cation halides. The reaction between $(CH_3)_2NCl.ICl$ and $(CH_3)_4N^+I^-$ yields $(CH_3)_4N^+ (CH_3)_2N (ICl)_2^-$, and analagous reactions have produced the new compounds $Cs^+(CH_3)_2N(ICl)_2^-$, $(C_6H_5)_2I^+(CH_3)_2N(ICl)_2^-$ and $(CH_3)_4N^+(CH_3)_2NI_4^-$. Attempts to synthesise these and related compounds from N-halamine adducts and large cation tri-iodides have yielded the novel $Tl^+ (CH_3)_2N(ICl)_2^-$ besides providing a faster route to $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ and $(CH_3)_4N^+(CH_3)_2NI_4^-$

A number of halide insertion reactions have been tried and have been shown to produce simple polyhalides or polyhalide mixtures in the majority of cases. Reaction of $(CH_3)_2NCl.I_2$ with $(CH_3)_4N^+Br^-$ yielded the new substance $(CH_3)_4N^+(CH_3)_2NIBrCl_2^-$, while with $(CH_3)_4N^+I^-$, the similarly novel $(CH_3)_4N^+(CH_3)_2NI_3Cl^-$ is formed.

Reaction of N-dimethyliodamine with iodomethane gives excellent yields of $(CH_3)_4N^+(CH_3)_2NI_4^-$, but various attempts to alkylate N-halamines with allyl iodide failed. Benzyl iodide, on the other hand, produced complex mixtures or simple polyhalides, one such being $(CH_6H_5CH_2)_2 (CH_3)_2N^+I_3^-$ which does not appear to have been previously reported.

TO MY MOTHER.

A C K N O W L E D G E M E N T S

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INTRODUCTION

INTRODUCTION

N-halamines were discovered by Wurtz during his wider work on aminoalkanes (1). He found that addition of halogens to chilled solutions of free amines produced a variety of derivatives which in general possessed sharp odours and exhibited considerable reactivity; he suggested that these new substances were effectively amines with their original hydrogen atoms replaced by halogens, e.g.

$$3CH_3NH_2 + 2Cl_2 \longrightarrow CH_3NCl_2 + 2CH_3NH_2.HCl$$

Tscherniak disovered another route to these compounds which employed the reaction between alkylammonium chlorides and chlorates(I)

e.g. $$(C_2H_5)_2NH_2Cl + NaClO \longrightarrow (C_2H_5)_2NCl + H_2O + NaCl$$

and this method of preparation (2) is still widely used. It was modified and greatly extended in 1894 by Berg (3) who described the preparation and properties of nineteen N-halamines in sufficient detail for the results to be reproduceable, and his methods have become more or less standard since.

N-halamines are in general highly reactive substances. They possess two active centres - a nitrogen atom and a halogen atom which together provide the basis of an extensive and diverse chemistry. The nitrogen atom plays a dominant role in various bicyclic re-arrangements and hydrazine formation and acts as a base (in nucleophilic substitution), a radical cation (in the Hoffman-Loffler reaction) and a radical (in a number of addition and photolytic reactions).

The halogen can act as a cation in halogenation reactions and as an anion in Grignard reactions. Reaction of N-halamines with Grignard reagents was extensively investigated by Coleman (4) who showed the former's valuable potential as synthetic reagents, a potential which has been well exploited since (5). There is as yet no complete review of the chemistry of N-halamines, but an important step towards this has been undertaken by Kovacic et al (6).

N-halamine chemistry covers such a wide field that it would clearly be neither possible or desirable to cover it - even superficially - here. In any case, much of it although extremely interesting is not strictly relevant to the brief provided by the title, so it is perhaps more appropriate to concentrate on an aspect which has a more direct bearing on the subject matter of the thesis - the reaction of N-halamines with haloalkanes, which can produce a variety of unusual and unexpected substances.

1. The formation of trialkylhalammonium cations.

For many years studies of both amine-halogen addition compounds and the reaction between tri-alkylamines and chlorates (I) have suggested the existence of tri-alkylhalammonium ions. For example, Hantzch (7) reacted aqueous trimethylamine with chloric (I) acid and obtained N-dimethylchloramine and methanol as products. He proposed that an intermediate species was formed, which in modern terms would be

$$(CH_3)_3N + HOCl \longrightarrow (CH_3)_3NClOH \longrightarrow (CH_3)_2NCl + CH_3OH$$

formulated $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{OH}$. Ellis (8) adduced kinetic, spectroscopic and colligative evidence for this or similar species but no solid products were obtained until Cowan (9) isolated salts by precipitating the trialkylhalammonium ions with large, stabilising anions such as $\overset{-}{BF_4}$ or $\overset{-}{ClO_4}$. These salts were prepared via three routes:

(i) by reaction of aqueous trimethylammonium-chlorine complex with sodium tetrafluoborate (III) or chlorate (VII)

$$(CH_3)_3NCl_2\ (aq) \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \overset{-}{Cl}\ (aq) \xrightarrow{\overset{-}{BF_4}} (CH_3)_3\overset{+}{N}Cl\ \overset{-}{BF_4}(c)$$

(ii) by reaction of trimethylamine-chlorine complex with Lewis acids in a sealed tube, e.g:

$$(CH_3)_3NCl_2 + BCl_3 \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \ \overset{-}{BCl_4}$$

(iii) by reaction of dimethylhalamines with alkylating agents, e.g.

$$(CH_3)_2NCl + CH_3O\ ClO_3 \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \overset{-}{ClO_4}$$

This last method was extensively investigated and the following results were obtained:

(a) N-Dimethylchloramine reacts with dimethyl sulphate, methyl fluosulphonate and methyl perchlorate producing, respectively,

$(CH_3)_3\overset{+}{N}Cl\ \overset{-}{O_3SOCH_3}$, $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{SO_3F}$, $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{ClO_4}$

The reactions were performed simply by condensing an appropriate amount of N-dimethylchloramine on to a solution of the alkylating agent in diethyl ether or carbon tetrachloride on the vacuum line at liquid nitrogen temperature ($-196^{\circ}C$). The mixture was allowed to warm up in a refrigerator to $-5^{\circ}C$ and the solid salt isolated either by filtration in a glove box or by pumping away all volatile material.

Methyl nitrate did not react, but iodomethane gave an unexpected and most interesting product which is discussed below.

(b) N-dimethylbromamine reacts with methyl fluosulphonate to give highly water soluble $(CH_3)_3\overset{+}{N}Br\ \overset{-}{SO_3F}$ which can be precipitated by aqueous sodium chlorate (VII) as $(CH_3)_3\overset{+}{N}Br\ \overset{-}{ClO_4}$. The bromo-compounds are much less stable than their chloro-equivalents, samples changing rapidly from white to red at room temperature.

2. Reaction of N-halamines with alkylhalides.

Reaction of aminoalkanes with haloalkanes produces successively dialkyl and trialkylamines and finally quaternary ammonium salts thus:

$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI \longrightarrow (CH_3)_2\overset{+}{N}H_2\ \overset{-}{I}$$

$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI \longrightarrow (CH_3)_3\overset{+}{N}H\ \overset{-}{I}$$

$$(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4\overset{+}{N}\ \overset{-}{I}$$

The reactions proceed via nucleophilic attack of the haloalkane by the basic amine:

$$(CH_3)_3N: \rightarrow CH_3{-}I \longrightarrow (CH_3)_4\overset{+-}{N}I$$

which is exactly parallelled by the reaction of N-dimethylchloramine with methyl perchlorate mentioned previously

$$(CH_3)_2ClN: \rightarrow CH_3{-}O{-}ClO_3 \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \overset{-}{ClO_4}$$

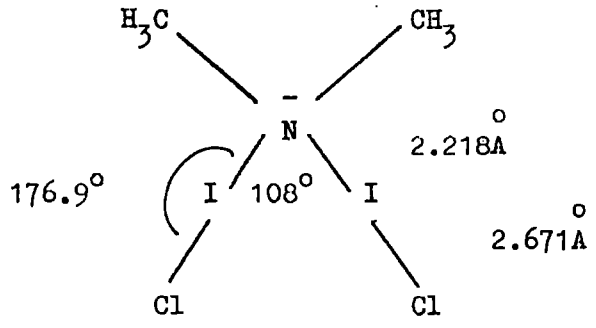
It might well be assumed that N-dimethylchloramine would react with iodomethane in an entirely analagous manner yielding trimethyl-chloroammonium iodide:

$$(CH_3)_2ClN: \rightarrow CH_3{-}I \longrightarrow (CH_3)_3\overset{+}{N}Cl\ \overset{-}{I}$$

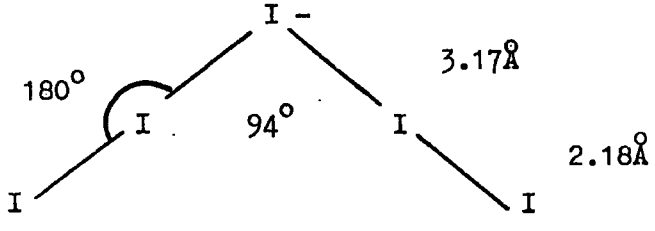
but it has been found (10) that in fact when N-dimethylchloramine is mixed with excess iodomethane a yellow solid soon deposits which, although having the empirical formula C_3H_9NICl is neither the iodine (I) chloride adduct of trimethylamine $(CH_3)_3N$. ICl or trimethylchlorammonium iodide but an entirely novel substance, formulated as

$$(CH_3)_4\overset{+}{N}\ \ (CH_3)_2N(ICl)_2^{-}$$

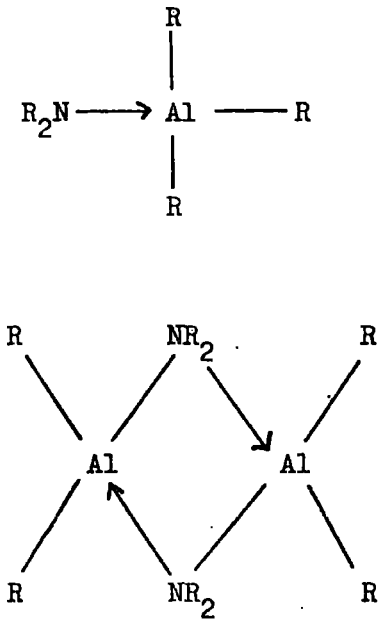
i.e. tetramethylammonium dimethylamido <u>bis</u> iodine (I) chloride. The structure of the $(CH_3)_2N(ICl)_2^-$ anion has been determined by low temperature X ray analysis (11) to be



and appears to be a pseudo-polyhalide showing analogies to the structure of the I_5^- ion:



The dimethylamido group ——$N(CH_3)_2$ can be considered as a new pseudohalide and has been shown to exist in compounds derived from aluminium alkyls e.g:



(53)

In a similar way, N-dimethybromamine reacts with excess iodomethane giving tetramethylammonium dimethylamido bis iodine (I) bromide

$$(CH_3)_4\overset{+}{N} \quad (CH_3)_2N\,(IBr)_2^-$$

but reaction of N-dimethylchloramine with bromomethane produces the bromine (I) chloride addition product of trimethylamine $(CH_3)_3N.BrCl$ while chloromethane does not appear to react at all.

In this work, the reaction between N-dimethylchloramine and iodomethane will be investigated with a view to throwing some light on the mechanism and generally opening up the chemistry of the ion $Me_2N(ICl)_2^-$. The preparation of intermediates and analogues will also be described together with their characterisation and it is hoped that the associated discussion will relate this new field to our existing knowledge of nitrogen-halogen chemistry.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

1. Preparation of reagents.

(a) Dimethylchloramine.

This substance has been prepared in the past by a variety of methods. Hoffman (12) and Tcherniak prepared it by reacting dimethylammonium chloride with sodium chlorate (I).

$$(CH_3)_2NH_2^+ + Cl\bar{O} \longrightarrow (CH_3)_2NCl + H_2O$$

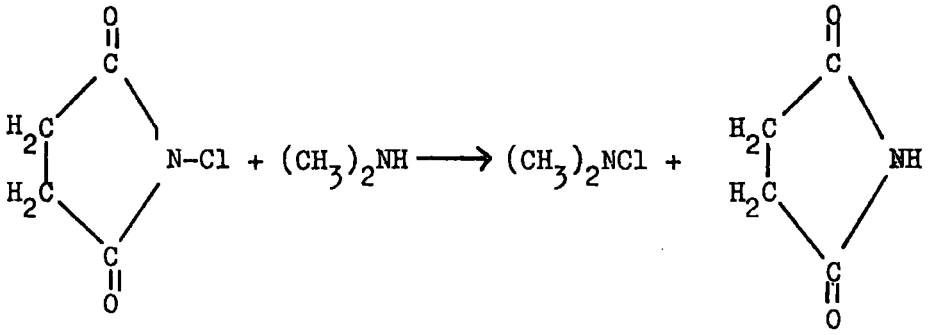
and the method was described carefully by Berg (3). Coleman (4) used the same method but simultaneously extracted the product with organic solvents. Meisenheimer (13) cleared tertiary amines with chloric (I) acid.

$$Me_3N + HOCl \longrightarrow Me_2NCl + MeOH$$

a reaction now known to take place via formation of $(CH_3)_3\overset{+}{N}Cl\ \overset{-}{O}H$; Ellis (8) found methanal CH_2O as a product:

$$(CH_3)_3N + 2HOCl \longrightarrow (CH_3)_2NCl + HCHO + HCl + H_2O$$

Schönberg reacted N-dimethylamine with N-chlorosuccinimide, a useful method where small quantities of very pure product are required:(14):



and Seppelt (15) prepared trichloromethane solutions of N-dimethylchloramine by reacting bis (dimethylamido) dimethylsilane with chlorine:

$$(CH_3)_2N\diagdown\!\!\diagup Si(CH_3)_2 + Cl_2 \longrightarrow 2(CH_3)_2NCl + (CH_3)_2SiCl_2$$
$$(CH_3)_2N\diagup\!\!\diagdown$$

The method suffers from the rather obvious drawback of a difficult starting material.

Jackson et al (16) prepared a number of alkyldichloramines such as $CH_3CH_2CH_2NCl_2$ by passing chlorine into aqueous solutions of the corresponding amines containing sodium hydrogen carbonate to remove acid; a modification of the method could presumably be used for the dialkylchloramines.

The method employed here uses the reaction between dimethylammonium chloride and sodium chlorate (I) as described by Berg (3). Some initial difficulty was found in the preparation of the chlorate (I)

solution but this was overcome by employing the method of Sterling (17).

Sodium chlorate (I) solution.

109g (ca.2.7 moles) of sodium hydroxide was dissolved in $150cm^3$ of water in a wide necked, $2dm^3$ conical flask. After cooling to room temperature, 625g of ice was added and chlorine passed in rapidly from a cylinder, with shaking until all but a little of the ice remained unmelted by the heat of the reaction. Using this method, no continuous weighing is necessary to monitor chlorine up-take and the final temperature of the reaction mixture is 0^oC.

$$Cl_2 + 2\bar{O}H \longrightarrow \bar{C}l + O\bar{C}l + H_2O$$

N-Dimethylchloramine.

To the solution of sodium chlorate (I) prepared above was added 82g (1 mole) of dimethylammonium chloride in small portions, the flask being well cooled externally in ice and shaken frequently. N-dimethylchloramine appeared as a pale yellow upper layer which was quickly separated and kept in a small stoppered flask over anhydrous calcium chloride at -30^oC (freezer).

This preparation is not without its dangers: on more than one occasion there was a sharp rise in temperature, evolution of chlorine and the appearance of a dense yellow oil. This unwelcome substance is probably methyl N-dichloramine CH_3NCl_2 - known to have an explosive rating comparable to that of nitroglycerine (18) - but the chlorination could quite possibly proceed further and produce the notoriously dangerous nitrogen (III) chloride NCl_3 which has

caused serious injury in the past, Dulong, for instance, having lost an eye and three fingers (19) in an explosion.

The crude N-dimethylchloramine was fractionated <u>in vacuo</u> in $10cm^3$ portions which were first cooled to $-196^{\circ}C$ in liquid nitrogen and allowed to warm spontaneously, thus removing dissolved, non-condensable gases. The following cooling baths were used around the traps on the vacuum line:

Trap A - liquid nitrogen/carbon tetrachloride slush - $23^{\circ}C$

Trap B, Trap C - acetone/dry ice slush - $78^{\circ}C$

Trap D - liquid nitrogen $-196^{\circ}C$

N-dimethylchloramine distilled largely into traps B and C, each batch taking about 30 minutes; a little condensate appeared in trap D and was retained for analysis which showed it to be dimethylamine $(CH_3)_2NH$. The pure N-dimethylchloramine was distilled into an ampoule fitted with a Rotaflow stopper and stored at $-30^{\circ}C$ to prevent decomposition. Yields are variable, but in an average preparation, $25cm^3$ of pure product was typical, which is poor, based on dimethylammonium chloride.

<u>Properties of N-dimethylchloramine</u>.

Pale yellow, almost colourless liquid.

Density = $0.9555g/cm^3$ @ $20^{\circ}C$.

B.p. = $43.0^{\circ}C$ @ 756 Torr (with decomposition).

n_D = 1.4021 (20)

$$N{-}Cl = 1.77 \pm 0.02A$$

$$CNCl = 107^{\circ} \pm 2^{\circ} \qquad (21)$$

The liquid is unstable at room temperature but the decomposition products are so far unknown except that one of these is dimethylammonium chloride, which deposits as small crystals on standing.

(b) N-dibenzylchloramine.

$$(C_6H_5CH_2)_2NH + HCl \longrightarrow (C_6H_5CH_2)_2NH_2^+Cl^-$$

$$(C_6H_5CH_2)_2\overset{+}{N}H_2\overset{-}{Cl} + OCl^- \longrightarrow (C_6H_5CH_2)_2NCl + H_2O$$

$96cm^3$ (0.5 mole) of dibenzylamine (BDH) was poured slowly into $120cm^3$ of 50% hydrochloric acid with stirring. More water ($300cm^3$) was added when the slurry of dibenzylammonium chloride became too thick. The dibenzylammonium chloride - which formed glittering plates - was filtered at the pump, washed with copious quantities (ca.$2dm^3$) of cold water and then added (without drying) to an ice-cold sodium chlorate (I) solution prepared as before from 54g sodium hydroxide, $75cm^3$ water, and 312g ice. The addition was performed slowly and carefully with external cooling in ice/water, since some benzylchloramines, notably $C_2H_5CH_2NCl_2$ are spontaneously inflammable and their formation via accidental over-heating of the mixture has to be avoided.

After standing for 15 minutes, the product was extracted with 2 x $100cm^3$ portions of diethyl ether, the ethereal solutions subsequently being separated, dried over anhydrous sodium sulphate and allowed to evaporate spontaneously in the fume cupboard. Quite

magnificent colourless crystals - up to 1cm long - were formed, which, as Berg reported (22) possess "un odeur assez agreable d'essence de noyau". They were dried over silica gel in the freezer and used without further purification; the yield was 40g (57%)

N-dibenzylchloramine has a remarkable solubility in ethanol:

$$3.20g/100cm^3 \text{ @ } 16^oC \text{ , } 493.60g/100cm^3 \text{ (!) @ } 53^oC$$

(c) Halogens and interhalogens.

Bromine and iodine were ANALAR grade and were used without further purification.

Iodine (I) chloride was obtained as a commercial sample (BDH) and purified by melting (m.p.27.2°C) and cooling slowly until ca.80% had solidified. The supernatant liquor was decanted, and the procedure was repeated twice on the solid which was finally ampouled (23)

Iodine (I) bromide was prepared in solution as needed. Typically, 2.54g iodine and 1.6g bromine - equivalent to 4.14g (0.02 mole) of iodine (I) bromide - were dissolved in carbon tetrachloride:

$$I_2 + Br_2 \longrightarrow 2IBr \qquad (24)$$

A commercial sample (Hopkin & Williams) was also used on occasion with no significantly different results.

(d) Halides.

Iodomethane was obtained as pure grade; it was stored over phosphorus (V) oxide in the dark to prevent photolytic decomposition.

Allyl iodide was obtained as a commercial sample (BDH) and was purified by distillation over silver powder in the absence of light. It was stored in a stoppered flask wrapped in foil to prevent photolytic decomposition. (25)

Benzyl iodide ($C_6H_5CH_2I$ was prepared as follows:

$$NaI + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2I + NaCl$$

100g sodium iodide (0.66 mole) and 63g benzylchloride (0.5 mole) were added to 500cm^3 acetone and the mixture was refluxed for 1 hour, after which it was poured into 1500cm^3 water. The liquid benzyl iodide was separated and chilled in ice/salt until it solidified and was then recrystallised from ethanol. (26)

The substance melts at 25°C and is an extremely powerful lachymator. Residues cling persistently to glassware (even hot, aqueous sodium hydroxide has little effect) but can be removed by an overnight soak in saturated, aqueous potassium permanganate.

Benzyl iodide was stored in a dark, stoppered bottle at -30°C.

(c) Pseudo-halides

Cyanogen iodide was prepared as follows:

$$NaCN + I_2 \longrightarrow CNI + NaI$$

9g (0.18 mole) of sodium cyanide was dissolved in $30cm^3$ water in a $250cm^3$ three necked flask and the solution cooled to 0^oC. 43g (0.17 mole) of iodine was added in ca.2g portions over 40 minutes, with careful stirring. $40cm^3$ of peroxide-free diethyl ether was added and after a little further stirring the resulting ethereal solution of iodine was separated. The aqueous layer was extracted again successively with 30 and $25cm^3$ portions of diethyl ether and the combined extracts evaporated to dryness at room temperature in vacuo. $40cm^3$ water was added to the residue and the solution heated at 50^oC for 15 minutes under filter-pump vacuum (this removes NaI and so prevents formation of NaI_2CN)). On cooling to 0^oC, cyanogen iodide precipitated and was filtered, air-dried and re-crystallised from trichloromethane. (27) The product (19g) had a m.p. of 147^oC and was stored in a dark, stoppered bottle.

Iodine azide was prepared in solution by the method of Hantzsch (28) by reaction of freshly precipitated silver (I) azide and ice-cold ethereal iodine solution

$$AgN_3(c) + I_2(s) \longrightarrow AgI(c) + IN_3(s)$$

but the method is dangerous in that not only is the product liable to explode when dry, but silver (I) azide is a notorious explosive as well. After an initial trial on a 0.1g scale, there was an explosion and a more reliable method was sought and found:

$$NaN_3(c) + ICl)s) \longrightarrow IN_3(s) + NaCl(c)$$

6.5g (.1 mole) of sodium azide was slurried with $25cm^3$ acetonitrile and the suspension cooled in ice/salt. A solution of $5.1cm^3$ (0.1 mole) iodine (I) chloride in $25cm^3$ acetonitrile was added dropwise over 30 minutes, the temperature being kept below 0^oC at all times. The deep orange solution of iodine azide was filtered through a pre-cooled frit and used at once, although it can be stored safely at -30^oC. (29)

(f) Polyhalides.

Rubidium tri-iodide was prepared by adding 2.1g (o.01 mole) rubidium iodide to 3.0g (excess) powdered iodine in $30cm^3$ warm water. After cooling in the refigerator (a modern alternative to the "low winter temperature" recommended by the reference authors!) the deep red-brown crystals were filtered and air dried. (30)

Caesium tri-iodide was similarly prepared using 2.6g (0.01 mole) caesium iodide (31). Both products appeared to be completely stable at room temperature.

Thallium (I) tri-iodide was prepared by dissolving 8g (0.03 mole) of iodine in the minimum of constant boiling hydriodic acid and adding to this 6g (0.02 mole) thallium (I) iodide. The mixture was taken to dryness in vacuo over silica gel (32). On another occasion, the substance was prepared by refluxing thallium (I) iodide with excess methanolic iodine for several hours; filtration yielded glittering, black crystals of the polyiodide. (33)

Tetramethylammonium tri-iodide was made by two methods:

(i) 2.0g (0.01 mole) tetramethylammonium iodide was mixed with $30cm^3$ methanol and 3.3g (0.013 mole) iodine was added. After shaking to dissolve the reactants, the mixture was allowed to stand overnight; the deposited purple-brown needles were then filtered and air-dried. (34)

(ii) 3.1g (0.015 mole) of tetramethylammonium iodide was mixed with $80cm^3$ methanol and 4g (excess) iodine was added. The mixture was warmed to 45^oC very gently and shaken until a red solution resulted. (A slight residue was removed by filtration). The solution was left overnight and the deposited needles were filtered and air-dried. This method - essentially that of Chattaway and Hoyle (35) - is the better of the two, but care was needed since the desired compound tends to disproportionate on warming:

$$2(CH_3)_4\overset{+}{N}\overset{-}{I_3} \longrightarrow (CH_3)_4\overset{+-}{N}I \quad + \quad (CH_3)_4\overset{+}{N}\overset{-}{I_5}$$

Tetra n-butylammonium tri-iodide was made by dissolving 3.7g (0.01 mole) of tetra n-butylammonium iodide and 2.54 (0.01 mole) iodine in $25cm^3$ of hot methonal. An oily layer formed which solidified on cooling. The substance was recrystallised from 95% ethanol and the short, purple needles which formed were air-dried. (36)

(g) Solvents.

Solvents were of ANALAR grade and were stored over molecular sieves.

(h) Other substances.

Tetramethylammonium azide was prepared by reacting barium azide and tetramethylammonium sulphate solutions metathetically. This method was devised in order to avoid the potentially hazardous literature procedure based on the reaction

$$AgN_3(aq) + (CH_3)_4\overset{+-}{N}I(aq) \longrightarrow AgI(c) + (CH_3)_4\overset{+-}{N}N_3(aq)$$

which involves shaking silver (I) azide (!) in a flask (37). Barium azide was prepared by reacting potassium azide and barium perchlorate solutions and removing precipitated potassium perchlorate while tetramethylammonium sulphate was prepared by reacting thallium(I) sulphate and tetramethylammonium bromide solutions:

$$KN_3(aq) + Ba(ClO_4)_2(aq) \longrightarrow 2KClO_4(c) + Ba(N_3)_2(aq)$$

$$2(CH_3)_4NBr(aq) + Tl_2SO_4(aq) \longrightarrow ((CH_3)_4N)_2SO_4(aq) + 2TlBr(c)$$

$$Ba(N_3)_2(aq) + ((CH_3)_4N)_2SO_4(aq) \longrightarrow 2(CH_3)_4NN_3(aq) + BaSO_4(c)$$

16.2g (0.2 mole) of potassium azide - prepared by reacting I-nitrobutane with hydrazine hydrate and ethandic potassium hydroxide (38) - was dissolved in $75cm^3$ and the solution poured into one of 33.6g (0.1 mole) of barium perchlorate in $75cm^3$ water. The mixture was cooled to $-5^{\circ}C$ and the precipitated potassium perchlorate filtered. The solution of barium azide thus formed was kept in a refigerator.

50.48g (0.1 mole) of thallium (I) sulphate was dissolved in $500cm^3$ of hot water and a solution of .31g (0.2 mole) tetramethylammonium bromide in $150cm^3$ hot water was added. The mixture was cooled and the dense, white precipitate of thallium (I) bromide removed by filtration. The filtrate (which was tested for absence of Tl^+ by means of aqueous potassium iodide) was added to the solution of barium azide prepared as above and the precipitated barium sulphate flocculated by heating over steam for half an hour. Filtration through Hi-flo gave a colourless solution of tetramethylammonium azide which was taken to dryness over steam. The product was dried *in vacuo* over silica gel, giving 11g (95% yield) of colourless, tetragonal crystals.

Analysis:	(%)	Found:	C 41.05	H 10.83	N 47.91
		Calcd:	C 51.36	H.10.41	N 48.23

2. Methods.

In the great majority of cases, methods of investigation were confined to simple mixing of reagents in $100cm^3$ stoppered, conical flasks which were subsequently kept at room temperature, 5^oC or -30^oC as dictated by the individual reaction in question. Precipitates were filtered through sintered glass, washed with pure reaction solvent and dried *in vacuo*. Those products which were unstable at room temperature were kept in a small evacuated desiccator in the freezer.

Safety.

Great care was taken to avoid any exposure to organic

solvents, particularly halo-alkanes. Similarly, amines and halamines were treated with considerable respect, since quite apart from their unpleasant odours they are known to be toxic and commercial samples are thought to contain nitrosamines - known carcinogens - as impurities.

Particular care was taken with cyano compounds and the insidiously toxic thallium (I) salts; at no time were these handled outside a fume hood or vacuum line and all residues were very carefully disposed of in the recommended manner.

Azides were prepared in small quantities and, with the exception of tetramethylammonium azide which is known to be very stable, were used at once. No reaction involving more than 50mg of material was performed, and even these quantities were handled at arms length with clamps and tongs.

C H A P T E R T H R E E

ALKYLATION OF N-DIMETHYLCHLORAMINE

ALKYLATION OF N-DIMETHYLCHLORAMINE

Reaction of N-dimethylchloramine with excess iodomethane has been shown to yield a novel tetramethylammonium pseudo-polyhalide which has the formula $(CH_3)_4\overset{+}{N}\ \ (CH_3)_2N(\overset{-}{ICl})_2$ showing some analogies with $(CH_3)_4\overset{+}{N}\ \overset{-}{I_5}$. (11) A mechanism has been suggested (39) for this reaction:

(i) $(CH_3)_2NCl + CH_3I \longrightarrow (CH_3)_3NClI$

(ii) $(CH_3)_3NClI \longrightarrow (CH_3)_3N + ICl$

(iii) $(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4\overset{+}{N}\ \overset{-}{I}$

(iv) $(CH_3)_2NCl + ICl \longrightarrow (CH_3)_2N\begin{matrix}Cl\\ \diagdown\\ \diagup\\ ICl\end{matrix}$

(v) $(CH_3)_2N\begin{matrix}Cl\\ \diagdown\\ \diagup\\ ICl\end{matrix} + (CH_3)_4\overset{+}{N}\ \overset{-}{I} \longrightarrow (CH_3)_4\overset{+}{N}\ \ (CH_3)_2N(\overset{-}{ICl})_2$

and this section will describe various experiments designed to test its validity. There are broadly two aspects to this work, i.e.

(a) investigation of the role of initial reactant ratios on the product(s) of reaction

(b) attempts to synthesize intermediates such as the iodine (I) chloride adduct in (iv) and use them in reactions such as (v).

1. Variation of initial reactant ratios.

The reactions were performed in stoppered test tubes at refrigerator temperature (ca.5°C). The reactants were measured by volume using 1 cm^3 and 10 cm^3 graduated pipettes and carbon tetrachloride added as appropriate to maintain constant volume. After leaving overnight, any precipitate was filtered through sintered glass and dried *in vacuo*, while filtrates were evaporated to dryness on the vacuum line and any solid products kept. Infra-red spectra were obtained for all products.

The results are summarised overleaf, and it can be seen that initial molar ratios are important in determining the products of the reaction. Determination of the approximate ratios of products in mixtures was undertaken by examination of IR spectra. The transmittances were corrected by an empirical formula (40)

$$T = \frac{100\,(t - 2.5)}{t_o} + 2.5$$

where T = true % transmittance, t = observed % transmittance and t_o = background % transmittance. The corrected transmittances were converted to absorbances using the relationship

$$\text{Absorbance} = \log \frac{100}{\text{true \% transmittance}}$$

and the following results were obtained: (Table 3,02)

TABLE 3,01

VARIATION OF INITIAL MOLAR RATIOS

OF $(CH_3)_2NCl$ AND CH_3I - RESULTS

Me_2NCl cm^3	CH_3I cm^3	Molar ratio	Yield of solid	ANALYSIS
8.3	0.61	10.1	0.835	Mixture of $Me_4\overset{+}{N}$ $Me_2N(ICl)_2^-$ and $Me_3N.ICl$
4.15	0.61	5 : 1	0.194	"
2.07	0.61	2.5 : 1	0.019	$(CH_3)_4\overset{+}{N}$ $\overset{-}{I}$
0.83	0.61	1 : 1	0.003	"
0.83	6.1	1 : 10	1.960	Mixture of $Me_4\overset{+}{N}$ $Me_2N(ICl)_2^-$
0.83	3.05	1 : 5	0.382	"
0.83	1.5	1 : 2.5	0.030	"
0.83	61.0	1 : 100	4.73	Iodine only

TABLE 3,02

RATIO OF $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$

$(CH_3)_3N.ICl$ IN REACTION MIXTURES

SAMPLE	MOLAR RATIO $(CH_3)_2NCl$: CH_3I	RATIO OF PRODUCTS
1A	10 : 1	1 : 1.55
1B	5 : 1	1 : 1
2A	1 : 10	1 : 2
2B	1 : 5	1 : 0.84
2C	1 : 2.5	3 : 1

None of the reaction mixtures produced a pure product, and since this is at variance with the results reported by Cowan *et al* (10), a further experiment was performed, this time at room temperature:

2. Preparation of tetramethylammonium dimethylamido bis iodine (I) chloride

1.66 cm^3 (0.02 moles) of pure N-dimethylchloramine was added to 3.0 cm^3 (ca. 0.05 moles) of pure iodomethane in a stoppered test tube and the mixture left at room temperature with occasional shaking for half an hour. The resulting yellow solid was filtered, washed with a little iodomethane and dried *in vacuo* over soda-lime. The mass of the product, 3.84g, showed that the reaction

$$(CH_3)_2NCl + CH_3I \longrightarrow C_3H_9NClI$$

had gone nearly to completion, and IR examination showed that $(CH_3)_4^+N\ \ (CH_3)_2N\ (ICl)_2^-$ was the only substance present. These results confirm previous investigations. Optimum conditions for the production of the novel polyhalide thus appear to be a moderate excess of iodomethane and a temperature of ca. 20-25°C. It is, however, difficult to rationalise observations on the reactions at 5°C in terms of the mechanism proposed above. Those reactions which involve ratios of $(CH_3)_2NCl$: CH_3I at 1:1 and 2.5:1 produce simply tetramethylammonium iodide; this could be explained simply by there not being enough chloramine for the reaction scheme to go to completion:

(i) $(CH_3)_2NCl + CH_3I \longrightarrow (CH_3)_3NClI$

(ii) $(CH_3)_3NClI \longrightarrow (CH_3)_3N + ICl$

(iii) $(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4\overset{+}{N}\overset{-}{I}$

The iodine (I) chloride on this basis presumably stays in solution and is prevented from forming the adduct $(CH_3)_3N.ICl$ by rapid methylation. No precipitate of any adduct was found and there was no evidence of the formation of tetramethylammonium dichloro-iodate (I) $(CH_3)_4\overset{+}{N}\ \overset{-}{ICl_2}$ which would have probably revealed itself as a bright yellow crystalline precipitate giving bands in the very low infra-red region. These arguments are, nevertheless, extremely tentative.

On the other hand, the small amount of product obtained is puzzling, since ionic tetramethylammonium salts would be completely insoluble in the covalent solvent and the equations show that not all the chloramine is accounted for. Another problem is the dilution factor - by altering the initial concentrations (as opposed to simple volumes) it is entirely possible that alternative reactions become kinetically more favourable. A further difficulty is the proposed decomposition of the unstable substance $(CH_3)_3N.ClI$ in (2) which presumably must be concerted, i.e.iodine (I) chloride splits off as the further methylation in (iii) occurs, otherwise there is little to prevent the formation of $(CH_3)_3N.ICl$, a known stable compound.

3. Attempted methylation of trimethylamine-iodine (I) chloride adduct

Since direct experiment on $(CH_3)_3NClI$ is not likely to be possible, it was thought that it might prove instructive to attempt a methylation of its isomer $(CH_3)_3N.ICl$

2.21g (0.01 mole) of trimethylamine-iodine (I) chloride adduct was dissolved in 6.1cm^3 (0.1 mole) of iodomethane. The solution was left at 5°C overnight and the resulting deep, purple-brown solid was filtered, washed with a little cold iodomethane and dried *in vacuo*.

Yield: 3g.

Analysis:	Calcd:	C 10.56	H 2.65	N 3.20	I 83.50
	Found:	C 10.30	H 2.71	N 2.98	I 83.55

The infra-red spectrum was that of a simple polyhalide, and the analysis is consistent with tetramethylammonium tri-iodide $(CH_3)_4\overset{+}{N}\,\overset{-}{I_3}$, presumably formed by the following reactions:

(a) $$(CH_3)_3N.ICl + CH_3I \longrightarrow (CH_3)_4\overset{+}{N}\,\overset{-}{I} + ICl$$

(b) $$ICl + CH_3I \longrightarrow CH_3Cl + I_2$$

(c) $$(CH_3)_4\overset{+}{N}\,\overset{-}{I} + I_2 \longrightarrow (CH_3)_4\overset{+}{N}\,\overset{-}{I_3}$$

This reaction shows the possibility of methylating trimethylamine adducts as proposed in reaction (a) of the above mechanism. Infra-red evidence of CH_3Cl was at best unconvincing however.

4. Attempted synthesis of N-dimethylchloramine adducts

The proposed mechanism for the reaction of N-dimethylchloramine with iodomethane involves an intermediate adduct $(CH_3)_2NCl.ICl$, and since the literature does not appear to mention previous syntheses of this and similar compounds it was thought appropriate to attempt their preparation:

$$(CH_3)_2NCl + ICl \longrightarrow (CH_3)_2NCl.ICl$$

1.66cm^3 (0.02 mole) of pure N-dimethylchloramine was mixed with 20cm^3 of carbon tetrachloride and the resulting solution was added to one of 1.0cm^3 (0.02 mole) of iodine (I) chloride in 20cm^3 carbon tetrachloride. There was an immediate reaction, the dark red colour of the iodine (I) chloride being discharged, and a bright yellow precipitate formed. After cooling in a freezer (ca. -30°C) for half an hour, the product was filtered, washed with carbon tetrachloride and dried in vacuo at -30°C.

Yield: 2.30g (43,98% calcd. as adduct)

Analysis:					
	Calcd.	C 9.92	H 2.48	N 5.79	Halogen 81.78
	Found.	C 9.66	H 2.37	N 5.56	Halogen 82.05

The adduct is a bright yellow, crystalline solid which is unstable at room temperature, slowly evolving N-dimethylchloramine. It is, however, stable at -30°C but reacts with water. The infra-red spectrum is consistent with its formulation as $(CH_3)_2NCl.ICl$ (See Chapter 6. p.64).

The iodine (I) bromide adduct is formed in a similar way using either a mixture of 2.54g of iodine and 1.6g bromine - equivalent

to 4.14g (0.02 mole) of iodine (I) bromide - or simply 4.14g iodine (I) bromide in place of the iodine (I) chloride. The adduct is a deep golden yellow crystalline solid with similar properties to the iodine (I) chloride adduct, but more stable at room temperature.

Yield: 1.43g (50% calcd. as adduct)

Analysis:	Calcd.	C 8.39	H 2.11	N 4.89	Halogen 84.61
	Found	C 8.13	H 2.10	N 4.91	Halogen 84.89

The iodine adduct is formed in an identical way substituting a solution of 2.54g (0.02 mole) iodine in $50cm^3$ of carbon tetrachloride for that of the iodine(I) chloride. The adduct is an orange microcrystalline substance which appears to be more stable than the iodine (I) chloride and iodine (I) bromide analogues, which it otherwise resembles.

Yield: 2.52g (75.68% calcd. as adduct)

Analysis:	Calcd.	C 7.20	H 4.20	N 1.80	Halogen 86.78
	Found	C 7.16	H 4.20	N 1.87	Halogen 87.24

The same substance was made by Cowan (41) who obtained an identical infra-red spectrum but reported the colour of the substance as yellow, a difference probably due to a finer state of division.

The bromine adduct was (presumably) prepared in analogous fashion substituting a solution of $0.57cm^3$ (0.02 mole) of bromine in $20cm^3$

of carbon tetrachloride for that of the iodine(I) chloride. After several hours at -30°C, a bright yellow crystalline solid deposited which was subsequently filtered, washed with carbon tetrachloride and dried rapidly in vacuo.

Yield: 1.03g (30.7% calcd. as adduct)

The product was too unstable to be analysed but there was nothing to suggest that it was other than $(CH_3)_2NCl.Br_2$

An attempt was made to prepare the iodine (I) cyanide adduct by mixing a solution of 1.53g (0.01 mole) of iodine (I) cyanide in $10cm^3$ of dichloromethane with $0.83cm^3$ (0.01 mole) of N-dimethy-chloramine in $10cm^3$ dichloromethane. A slight yellow colour was produced, but all attempts to isolate a solid failed.

The comparable electron affinities of ICN (0.9e) and I_2 (1.7e) suggest that iodine (I) cyanide is a considerably weaker acceptor than iodine; the iodine molecule is more polarisable and hence forms adducts more readily (42). Further, Hageman points out (43) that bromine (I) cyanide cleaves tertiary amines:

$$R_3N + CNBr \longrightarrow R.Br + R_2N.CN$$

so it is possible that iodine cyanide gives some equivalent reaction.

The iodine azide adduct was probably prepared, however, by mixing $5cm^3$ of the iodine azide solution prepared as described on p. 16

to one of 1.66cm^3 (0.02 mole) of N-dimethlychloramine; the resulting solution on evaporation <u>in vacuo</u> (using a water pump rather than the vacuum line, for safety reasons) produced a yellow solid. This exploded violently, shattering the containing flask, and the investigation was discontinued.

5. <u>Attempted syntheses of N-dibenzylchloramine adducts</u>.

An interesting extension of the work described in Chapter 2, Part 4, is the attempted preparation of adducts of an aryl chloramine.

$$(C_6H_5CH_2)_2NCl + ICl \longrightarrow (C_6H_5CH_2)_2NCl.ICl$$

1.41g N-dibenzylchloramine (0.01 mole) was dissolved in 10cm^3 of dichloromethane and to this was added a solution of 0.51cm^3 of iodine (I) chloride in 10cm^3 of the same solvent. After cooling to -30°C for some hours, the bright yellow, crystalline product was filtered, washed with a little cold dichloromethane and dried <u>in vacuo</u>.

<u>Yield</u>: 1.81g (58.4% calcd.as adduct)

<u>Analysis:</u>	Calcd:	C 42.67	H 3.58	N 3.55	Halogen 50.11
	Found:	C 41.94	H 4.63	N 3.75	Halogen 51.83

Attempts to make other adducts failed, those tried being the iodine (I) bromide, iodine (I) cyanide, iodine (I) azide, iodine,

bromine and chlorine adducts, all of which resembled each other by producing complex mixtures of what appeared to be free halogens and halogen substituted benzyl derivatives.

These reactions show that the formation of intermediates of the type $R_2NCl.XX$[1] from N-halamines and alkyl halides is certainly possible. This does not mean, however, that the presence of such intermediates has been shown to play a role in the alkylation of N-halamines, merely that step (iv) in the proposed mechanism, i.e.

$$(CH_3)_2NCl + ICl \longrightarrow (CH_3)_2N\begin{matrix}\diagup Cl \\ \diagdown ICl\end{matrix}$$

could well be a correct postulate. The possible role of such an adduct in the overall reaction will be discussed in Chapter Four.

CHAPTER FOUR

REACTIONS OF N-DIMETHYLCHLORAMINE ADDUCTS WITH LARGE CATION HALIDES

REACTIONS OF N-DIMETHYLCHLORAMINE ADDUCTS WITH LARGE CATION HALIDES

In the mechanism proposed for the reaction of N-dimethylchloramine with iodomethane, it is suggested that the final stage involves reaction of an iodine (I) chloride adduct of N-dimethylchloramine with tetramethylammonium iodide generated *in situ*:

$$(CH_3)_2N\begin{matrix}Cl\\ \diagdown\\ \diagup\\ ICl\end{matrix} + (CH_3)_4\overset{+}{N}I^{-} \longrightarrow (CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^{-}$$

In order to test the feasability of such a reaction, adducts of N-dimethylchloramine - prepared as in the previous chapter - were mixed in a 1.1 molar ratio with a variety of halides containing large cations, initially iodides such as caesium or tetramethylammonium iodide. Generally the method consisted of the addition of finely powdered halide to a solution of the adduct in dichloromethane the mixture then being allowed to stand at room temperature until there was no apparent sign of any further reaction. The products were filtered, washed with cold dichloromethane and dried *in vacuo*. It will be noted that these reactions, if any, are solid phase, since the ionic halides are largely insoluble in dichloromethane, and this meant, of course, that reactions took place slowly, sometimes over many hours.

1. Attempted synthesis of $(CH_3)_4\overset{+}{N}\ (CH_3)_2N(ICl)_2^{-}$

1.05g (0.005 mole) of tetramethylammonium iodide and 1.21g (0.005 mole) of N-dimethylchloramine-iodine (I) chloride adduct were

reacted as described above in $10cm^3$ dichloromethane. An initial brown colouration (iodine?) soon gave way to an orange and finally orange-yellow solid.

Yield: 2.06g (91.15% calcd. as desired product)

Analysis: calcd. for $(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^-$

	C 16.26	H 4.07	N 6.32	Cl 16.03	I 57.32
found:	C 16.32	H 4.25	N 6.02	Cl 16.21	I 56.01

The infra-red spectrum of the substance was consistent with that of $(CH_3)_4N^+ (CH_3)_2N(ICl)_2^-$, so the reaction

$$(CH_3)_2N\begin{matrix}Cl\\ \diagdown\\ \diagup\\ ICl\end{matrix} + (CH_3)_4\overset{+-}{N}I \longrightarrow (CH_3)_4N^+ (CH_3)_2N(ICl)_2^-$$

appears to take place under the conditions described, suggesting that this particular stage in the overall mechanism is possible. It would be unwise, however, to conclude that because it is possible then it does in fact take place - much more evidence would be needed.

2. Attempted synthesis of $Cs^+ (CH_3)_2N(ICl)_2^-$

1.30g (0.0005 mole) of caesium iodide was finely ground and reacted with 1.21g (0.0005 mole) of N-dimethylchloramine-iodide (I) chloride adduct in $10cm^3$ dichloromethane. The reaction was performed at 5^oC, as it took several days and there was a danger of side/decomposition reactions. More than one product was apparent at the end of three days; the light yellow crystalline material which

was thought to be the desired product was readily decanted from one or two dark coloured aggregates, which turned out to be caesium tri-iodide.

Yield: 1.0g

Analysis:	Calcd: for $Cs^+ (CH_3)_2((ICl)_2^-$					
	C 4.79	H 1.21	N 2.79	Cl 14.13	I 50-59	Cs 26.49
Found:	C 4.52	H 0.91	N 2.49	Cl 13.90	I 50.14	Cs 23.51

The product is stable at -30°C and appears to be soluble in water and most organic solvents; its infra-red spectrum was consistent with its formulation as $Cs^+ (CH_3)_2N(ICl)_2^-$

3. Attempted synthesis of $(C_6H_5)_2I^+ (CH_3)_2N(ICl)_2^-$

1.03g (0.005 mole) of diphenyliodonium iodide, prepared by the method quoted by Vogel (44), was reacted with 1.21g N-dimethyl-chloramine iodine (I) chloride adduct in $10cm^3$ dichloromethane. The resulting red-brown solid was found to be stable at room temperature for some hours and does not appear to react with water.

Yield: 1.16g

Analysis:	Calcd: for $(C_6H_5)_2I^+ (CH_3)_2N(ICl)_2^-$				
	C 25.87	H 2.48	N 2.15	I 58.58	Cl 10.91
Found:	C 25.43	H 2.90	N 2.16	I 57 92	Cl 10.88

The infra-red spectrum was consistent with the formulation of the substance as $(C_6H_5)_2I^+ (CH_3)_2N(ICl)_2^-$

Attempts to prepare other analogues were unsuccessful. Thallium (I), pyridinium and rubidium iodides failed to react at all, while larger cation quaternary ammonium halides such as tetra n-butylammonium iodide gave deep reddish solutions which either deposited iodine or quaternary ammonium tri-iodides. This is probably because of the different ionic radii.

One problem associated with these reactions is the fact that one reactant is solid and hence the reaction is very slow, thus opening up the possibility of side-reations. It was then thought that if the lattice energy of the reacting halides was lowered by converting them to the tri-iodides, the latter might be sufficiently soluble to react in one phase. The method was identical with that described for the simple iodides, i.e. 0.005 mole of the tri-iodide was reacted with 0.005 mole of the N-dimethylchloramine adduct in $10cm^3$ dichloromethane. When no further reaction was apparent, the solid product was filtered, washed with dichloromethane and dried *in vacuo*.

The following tri-iodides were used: rubidium, caesium, thallium (I) tetramethylammonium and tetra n-butylammonium, and of these only the thallium (I) and tetramethylammonium compounds produced solids.

(i) Thallium (I) compound.

Yield: 1.05g

The product is bright yellow and micro-crystalline. It is decomposed by water with the liberation of iodine, but appears to be soluble in acetone.

Analysis: Calcd: for $Tl^+ (CH_3)_2N(ICl)_2^-$.

C 4.19	H 1.06	N 2.44	Cl 12.37	I 44.28	Tl 35.66
Found: C 3.97	H 1.20	N 2.41	Cl 12.00	I 44.05	Tl 33.09

(ii) Tetramethylammonium compound

Yield: 1.80g

Analysis: Calcd: for $(CH_3)_4N^+ (CH_3)_2N(ICl)_2^-$

C 16.3	H 4.1	N 6.3	I 57.3	Cl 16.0
Found: C 16.2	H 4.1	N 5.9	I 56.2	Cl 16.5

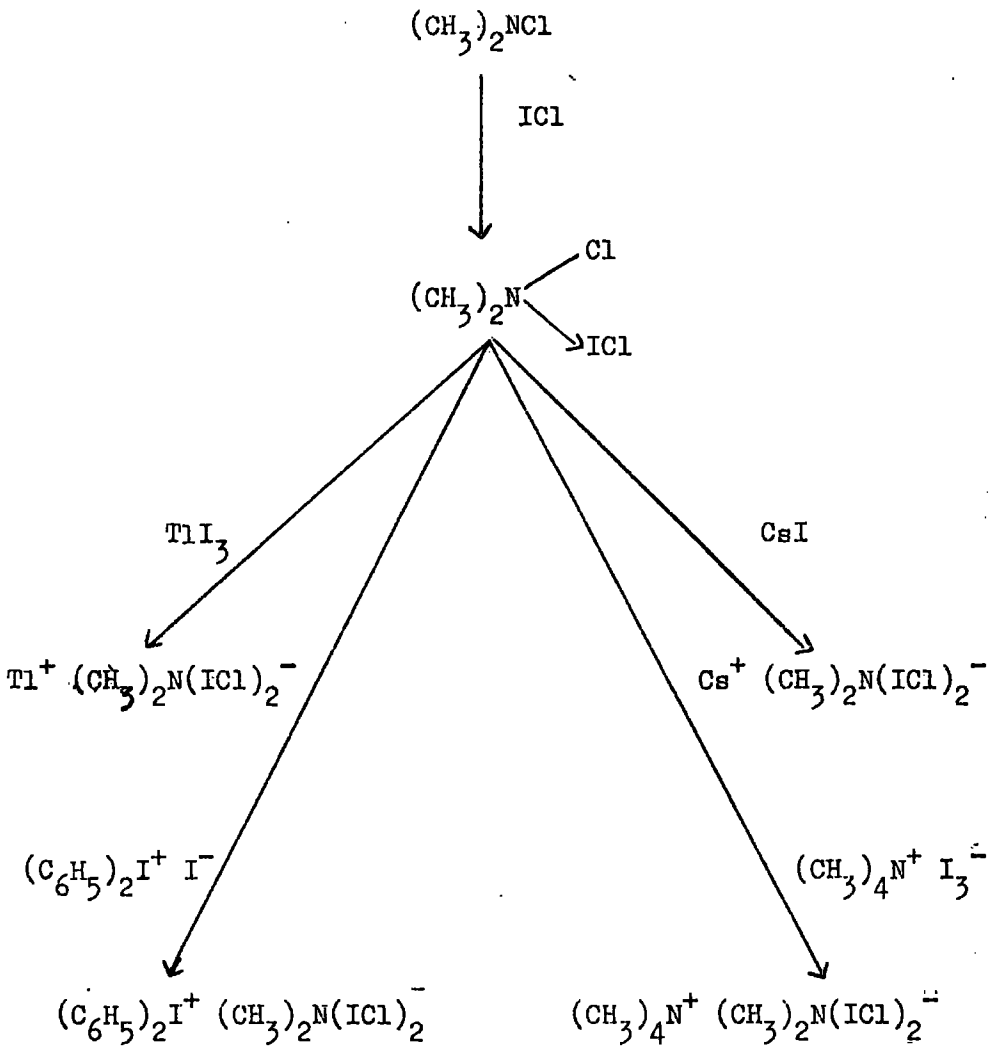
The infra-red spectra of both these compounds showed them to contain the ion $(CH_3)_2N(ICl)_2^-$, and the tetramethylammonium salt (i.e. the original compound) had thus been prepared by a different route:

$$(CH_3)_2NH \xrightarrow{HCl} (CH_3)_2NH^+2\ Cl^- \xrightarrow{OCl} (CH_3)_2NCl \xrightarrow{ICl} (CH_3)_2NCl.ICl \xrightarrow{(CH_3)_4N^+I_3^-} (CH_3)_4N^+(CH_3)_2N(ICl)_2^-$$

Presumably the reaction between N-dimethylchloramine-iodine (I) chloride adduct and tetramethylammonium iodide can be formulated as

$$(CH_3)_2NCl.ICl + (CH_3)_4\overset{+}{N}\overset{-}{I_3} \longrightarrow (CH_3)_4\overset{+}{N}\ \overset{-}{(CH_3)_2N(ICl)_2} + I_2$$

The filtrate from the reaction was in fact found to contain iodine. A surprising result was the failure of caesium tri-iodide to react - particularly odd in view of the reaction of the simple caesium iodide reported previously. The reactions described above can be summarised as follows:



Infra-red spectra are recorded in Chapter Eight.

C H A P T E R F I V E

FURTHER REACTIONS OF N-HALAMINES

FURTHER REACTIONS OF N-HALAMINES

A rather obvious extension of the work already described is to use other N-halamines and other alkylating agents, and some experimental investigations are described in this chapter pertaining to this rather wider field. The choice of N-halamines was governed as much by their availability and ease of handling as well as their suitability in a strictly chemical sense; thus, for example, N-benzylchloramine $C_6H_5CH_2NClH$ was considered too dangerous to handle - it decomposes violently at room temperature (48) - and N-dimethylbromamine was also thought inappropriate because of the very lengthy work involved in its preparation (49).

Clearly, it would have been possible to try an ascending series of N-chloramines $(CH_3CH_2)_2NCl$.....$(CH_3CH_2CH_2CH_2)_2NCl$ but it was decided that a more interesting line of attack would perhaps be to investigate the reactions of an N-dialkyliodamine and an N-diarylchloramine, the first because of the attractively small amount of reliable information on this class of compound - and the latter because of the possibility of extending the chosen type of reaction into the aryl field. The compounds selected were in fact N-dimethyliodamine $(CH_3)_2NI$ and N-dibenzylchloramine $(C_6H_5CH_2)_2NCl$. N-dimethyliodamine, $(CH_3)_2NI$, is, as already noted, a comparatively rare substance inasmuch as it has only recently been prepared in a reproduceable manner (50) despite many previous claims, including that of Berg (51) who thought

that he had obtained the substance by the reaction

$$(CH_3)_2NCl + KI \longrightarrow (CH_3)_2NI + KCl$$

(he probably only produced a mixture of N-iodamine decomposition products, KI_3 and such like).

Its pale yellow appearance provides evidence for its simple monomeric nature (cf. $NI_3.NH_3$ - "nitrogen tri-iodide" - which is black and polymeric, consisting of NI_4 tetrahedra (52)) so that in the reactions studied here polymeric starting materials would not prove an added complication.

The reaction studied was that between N-dimethyliodamine and iodomethane, a reaction which appears to proceed in an entirely analagous fashion to that between N-dimethylchloramine and iodomethane, thus:

$$(CH_3)_2NI + CH_3I \longrightarrow C_3H_9NI_2$$

The product is an orange microcrystalline solid whose infra-red spectrum is consistent with its formulation as $(CH_3)_4N^+ (CH_3)_2NI_4^-$ and is the iodine equivalent of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$. It is stable at room temperature if kept over soda-lime and has not been shown to exhibit any marked photosensitivity. A reaction mechanism analagous to that of the N-dimethylchloramine reaction would be:

(1) $(CH_3)_2NI + CH_3I \longrightarrow (CH_3)_3NI_2$

(2) $(CH_3)_3NI_2 \longrightarrow (CH_3)_3N + I_2$

(3) $(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4N^+I^-$

(4) $(CH_3)_2NI + I_2 \longrightarrow (CH_3)_2N\begin{matrix}I\\ \searrow I_2\end{matrix}$

(5) $(CH_3)_2N\begin{matrix}I\\ \searrow I_2\end{matrix} + (CH_3)_4N^+I^- \longrightarrow (CH_3)_4N^+(CH_3)_2NI_4^-$

(Reactions 2 and 3 would probably be concerted) and the evidence in favour of this is:

(a) The iodine adduct of trimethylamine is known and is a stable substance. It was in fact prepared by reacting iodine with trimethylamine:

$$(CH_3)_3N + I_2 \longrightarrow (CH_3)_3N.I_2$$

and its infra red spectrum was examined in comparison with those of N-dimethyliodamine - iodine adduct and $(CH_3)_4N^+(CH_3)_2NI_4^-$

(b) Reaction of trimethylamine and iodomethane does give tetramethylammonium iodide; this is a long established method, in fact, of preparing the latter substance.

(c) The iodine adduct of N-dimethyliodamine is also known, having been prepared by Jander (47)

(d) Reaction between the iodine adduct of N-dimethyliodamine and tetramethylammonium iodide has been found to yield $(CH_3)_4N^+(CH_3)_2NI_4^-$ and in addition, tetramethylammonium tri-iodide has also been shown to react similarly. These reactions are very similar to those previously described for the corresponding chloro-compounds (p.33 - 38).

It must, of course, be emphasized that this evidence does not prove that the purported mechanism is correct: it merely makes it more likely in that proposed intermediates and some reactions are possible. Reactions involving N-dibenzylchloramine proved rather less successful in that the products were either mixtures (including, regrettably, iodine) or simple polyhalides; so far it has not proved possible to prepare an aryl analogue. Reaction with excess iodomethane produced an orange coloured solution which subsequently deposited white crystals shown by analysis to be dimethyldibenzylammonium iodide, the reaction possibly being

$$(C_6H_5CH_2)_2NCl + 2CH_3I \longrightarrow (C_6H_5CH_2)_2(CH_3)_2N^+I^- + ICl$$

and the orange colour of the solution being due to the iodine (I) chloride simultaneously formed. The trouble with this proposed reaction is that iodine (I) chloride would normally be expected to react with a quaternary ammonium iodide and produce a polyhalide, i.e.

$$(C_6H_5CH_2)_2(CH_3)_2N^+I^- + ICl \longrightarrow (C_6H_5CH_2)_2(CH_3)_2N^+I_2Cl^-$$

The orange colour could perhaps be due to a new pseudopolyhalide anion, but this would be even more difficult to describe by balanced equations.

On the other hand, reaction of N-dibenzylchloramine with excess benzyl iodide simply produced a black iodine containing "mess" which proved almost impossible to analyse fully in the time available; a guess at the products would include tetrabenzylammonium tri-iodide. Reaction of N-dibenzylchloramine-iodine (I) chloride adduct with tetramethylammonium iodide produced, surprisingly, tetramethylammonium dichloro-iodate (I) $(CH_3)_4NICl_2$ and a possible reaction is

$$(C_6H_5CH_2)_2NCl.ICl + (CH_3)_4N^+I^- \longrightarrow (CH_3)_4N^+ICl^-_2 + (C_6H_5CH_2)_2NI$$

Any N-dibenzyliodamine would presumably remain in solution, but as neither this compound or its decomposition products have been reported in the literature, this must remain very tentative.

As far as different alkylating agents are concerned, the choice is restricted to those which are known to react reasonably easily, so that CH_3CN, for example, is not suitable for the type of reaction described here since it is a less effective alkylating agent. Two compounds were briefly investigated and these are benzyl iodide $C_6H_5CH_2I$ and allyl iodide $CH_3CH{=}CH_2I$; both of which proved singularly unsuccessful! Reaction of N-dimethylchloramine with a five-fold excess of benzyl iodide at ca.5°C gave a yellowish suspension which darkened rapidly and deposited a mass of glittering black crystals. These proved to be dimethyldibenzylammonium tri-iodide $(CH_3)_2(C_6H_5CH_2)_2N^+I^-_3$ and possible reactions are:

(1) $2C_6H_5CH_2I + 2(CH_3)_2NCl \longrightarrow 2C_6H_5CH_2Cl + (CH_3)_2N{-}{-}N(CH_3)_2 + I_2$

(2) $(CH_3)_2NCl + 2C_6H_5CH_2I \longrightarrow (CH_3)_2(C_6H_5CH_2)_2N^+I^{-\ +} + ICl$

(3) $(CH_3)_2(C_6H_5CH_2)_2N^+I^- + I_2 \longrightarrow (CH_3)_2(C_6H_5CH_2)_2N^+I^-_3$

Reaction (1) is particularly hypothetical since it is not known whether tetramethyl hydrazine is derivable from N-dimethyl-chloramine. A further difficulty is that one might legitimately expect the reaction:

$$2I^- + 2ICl \longrightarrow I_3^- + ICl_2^-$$

to take place. The analysis of the solid product showed only one substance present, however.

Reaction of allyl iodide with N-dimethylchloramine simply produced a dark brown solution containing some free iodine; no solid materials were isolated despite attempts at evaporation and it would thus seem that the reaction:

$$2CH_3CH{=}CH_2I + (CH_3)_2NCl \longrightarrow 2CH_3CH{=}CH_2Cl + I_2 + (CH_3)_2N{-}{-}N(CH_3)_2$$

had occurred, with complicating further halogenation of the products and reactant. No further investigation was undertaken.

E X P E R I M E N T A L

1. Reaction of N-dimethyliodamine with iodomethane.

1.69g (0.01 mole) of N-dimethyliodamine (47) was dissolved in $15cm^3$ (ca.0.25 mole) of iodomethane and the solution left with occasional shaking for ten minutes at ca.5°C (refrigerator). The initially clear, light orange solution rapidly became cloudy and a dull orange microcrystalline solid was deposited which was subsequently filtered, washed with a little ice-cold iodomethane and dried in vacuo.

Yield: 2.89g (92.9%)

Analysis: Calcd. for $(CH_3)_4N^+(CH_3)_2NI_4^-$

C 9.93 H 2.49 N 3.86 I 83.71

Found: C 10.12 H 2.84 N 3.82 I 84.05

Infra-red examination confirmed the presence of the ion $(CH_3)_2NI_4^-$

2. Reaction of N-dimethyliodamine-iodine adduct with tetramethylammonium tri-iodide.

2.13g (0.005 mole) of N-dimethyliodamine-iodine adduct was dissolved in $15cm^3$ dichloromethane and 2.08g (0.005 mole) of finely powdered tetramethylammonium tri-iodide was added. After leaving at refrigerator temperature (ca.5°C) overnight, the orange solid was filtered, washed with a little dichloromethane and dried in vacuo.

Yield: 1.85g (48.6%)

Analysis: The identical appearance and infra-red spectrum to those of the previous compound confirmed that the substance was $(CH_3)_4N^+(CH_3)_2NI_4^-$

3. Reaction of N-dibenzylchloramine with iodomethane.

1.41g (0.01 mole) N-dibenzylchloramine was dissolved in $15cm^3$ (ca.0.25 mole) iodomethane. The solution, kept at ca.5°C (refrigerator) turned orange and a white, crystalline solid floated to the surface; after 24 hours this solid was filtered off, washed with iodomethane and air dried as it appeared quite stable.

Yield: 1.0g

Analysis: Calcd. for $(C_6H_5CH_2)_2(CH_3)_2^+ I^-$

C 54.40 H 5.71 N 3.97 I 35.93

Found: C 53.85 H 4.80 N 3.88 I 36.42

4. Reaction of N-dibenzylchloramine with benzyl iodide.

1.41g (0.01 mole) N-dibenzylchloramine was added to a solution of 10.90g (0.01 mole) benzyl iodide in $20cm^3$ dichloromethane, care being taken to avoid eye exposure since benzyl iodide is a dangerous lachrymator. After a period of 24 hours at ca.5°C, a black "mess" had resulted which could not be analysed; some free iodine seemed to be present. No further investigation of the reaction was undertaken.

5. Reaction ofN-dibenzylchloramine iodine (I) chloride adduct with tetramethylammonium iodide.

3.03g (0.01 mole) N-dibenzylchloramine iodine (I) chloride adduct was dissolved in $20cm^3$ dichloromethane and 2.01g (0.01 mole) tetramethylammonium iodide was added. The mixture slowly yielded a bright yellow crystalline solid.

Yield: 2.1g

Analysis: Calcd. for $(CH_3)_4N^+ICl_2^-$

C 17.67 H 4.45 N 5.15 Cl 26.07 I 46.67

Found: C 17.55 H 5.32 N 5.09 Cl 25.24 I 47.44

The substance is tetramethylammonium dichloro-iodate (I)

6. Reaction of N-dimethylchloramine with benzyl iodide.

0.83cm^3 (0.01 mole) of N-dimethylchloramine was added to a solution of 10.90g (0.05 mole) benzyl iodide in 20cm^3 carbon tetrachloride and the mixture was kept at ca.5°C (refrigerator) overnight. A yellowish opalescence initially produced soon gave way to a deposit of glittering black crystals which were filtered, washed with carbon tetrachloride and dried in vacuo.

Yield: 6g

Analysis: Calcd. for $(C_6H_5CH_2)_2(CH_3)_2N^+I_3^-$

C 31.75 H 3.32 N 2.31 I 62.71

Found: C 29.05 H 3.15 N 2.42 I 63.06

The substance is thus dibenzyldimethylammonium tri-iodide $(C_6H_5CH_2)_2(CH_3)_2N^+I_3^-$

7. Reaction of N-dimethylchloramine with allyl iodide.

0.83cm^3 (0.01 mole) N-dimethylchloramine was dissolved in 10cm^3 (ca.0.15 mole) allyl iodide. A dark solution resulted which did not change during a 24 hour stand at ca.5°C, and a repeat experiment using a solution of 8.45g (0.05 moles) of tri-iodide in 20cm^3 carbon tetrachloride gave the same result, so the reaction was not further investigated.

CHAPTER SIX

HALIDE INSERTION REACTIONS

HALIDE INSERTION REACTIONS

A previous chapter described experiments whose aims were (a) to establish the feasability of preparing tetramethylammonium dimethyl amido bis (iodine (I) chloride) from the iodine (I) chloride adduct of N-dimethylchloramine and tetramethylammonium iodide, and (b) to replace the tetramethylammonium cation by other large cations. It is obviously possible to try a whole series of permutations and combinations based on (a) since the basic reaction involves an adduct of N-dimethylchloramine and a tetramethylammonium halide; the reaction has three potentially variable halogen groups, i.e. the halamine itself, the halogen Lewis acid and the tetralkylammonium halide. However, because time did not permit a full investigation, a selection of reactions was examined and these produced interesting results.

The four adducts of N-dimethylchloramine already described in Chapter Three were reacted with a variety of quaternary ammonium salts, and in addition the iodine adduct of N-dimethyl iodamine was reacted with tetramethylammonium iodide. Three of these reactions produced new compounds containing anions of the type $(CH_3)_2NX_4^-$, and the results are summarised in Table 5,01. The preparation of tetramethylammonium dimethylamido tetra iodide $(CH_3)_4N^+(CH_3)_2NI^-_4$ was particularly interesting as it has been found possible to prepare it in an analagous manner to the bis (iodide chloride) compound, i.e. from the halamine and excess iodomethane, showing that these reactions are to some extent general.

TABLE 5,01

REACTIONS OF HALAMINE ADDUCTS

WITH QUATERNARY AMMONIUM COMPOUNDS

	QUATERNARY AMMONIUM HALIDE				
ADDUCT	$Me_4N^+F^-$	$Me_4N^+Br^-$	$Me_4N^+I^-$	$Me_4N^+N_3^-$	Bu_4NBr
$Me_2NCl.ICl$	$Me_4N^+ICl_2^-$	Polyhalide mixture	Me_4N^+ $Me_2N(ICl)_2^-$	No reaction	Bu_4N^+ $IBrCl^-$
$Me_2NCl.IBr$	-	$Me_4N^+IBrCl^-$	-	-	-
$Me_2NCl.I_2$	-	Me_4N^+ Me_2N $IBrCl_2^-$	Me_4N^+ Me_2N I_3Cl^-	-	-
$Me_2NCl.Br_2$	-	No reaction	-	-	-
$Me_2NI.I_2$	-	-	Me_4N^+ Me_2N I_4^-	-	-

— indicates not tried.

It is also of interest that the high iodine - containing adducts - $(CH_3)_2NCl.I_2$ and $(CH_3)_2NI.I_2$ - were the only substances to produce the desired compounds and indeed, the chemistry of this type of compound appears to be dominated by iodine and methyl groups, which is probably a function of size, rate of reaction and the high polarisability of iodine more than anything else. Other reactions produced polyhalides, the simplest and most stable of these being tetramethylammonium dichloro-iodate (I) $Me_4N^+ICl_2^-$, a bright yellow crystalline solid which has been known for many years (45), and in some cases, mixtures appeared to have been produced, indicative of a highly complex set of reactions. Further attempts to react chloramine adducts with other quaternary ammonium halides such as tetraethyl and tetra n-propylammonium iodides gave deep reddish solutions from which it did not prove possible to isolate solids, again confirming the dominance of methyl derivatives.

EXPERIMENTAL

1. Reaction of $(CH_3)_2NCl.ICl$ with tetramethylammonium fluoride.

1.21g (0.005 mole) of N-dimethylchloramine iodine (I) chloride adduct was dissolved in $10cm^3$ dichloromethane and 0.46g (0.005 mole) of tetramethylammonium fluoride (46). There was an immediate reaction with some fuming and, on leaving, a bright yellow solid deposited which was subsequently filtered, washed with dichloromethane and dried *in vacuo*.

Yield: 0.90g (66.2%)

Analysis: Calcd. for $(CH_3)_4N^+ICl_2^-$

C 17.67 H 4.45 N 5.15 Cl 26.07 I 46.47

Found: C 17.37 H 4.47 N 4.77 Cl 26.15 I 44.38

The I.R. spectrum was consistent with that of a simple polyhalide.

2. Reaction of $(CH_3)_2NCl.ICl$ with tetramethylammonium bromide.

The procedure described in (1) above was repeated except that 0.77g (0.005 mole) of tetramethylammonium bromide was used in place of the fluoride. A mixture of bright yellow and orange crystals were deposited, and since a repeat gave a similar product with different analysis for carbon, hydrogen and nitrogen, this was assumed to be a mixture of simple polyhalides.

Possible reactions here are:

(i) $(CH_3)_2NCl.ICl + (CH_3)_4N^+Br^- \longrightarrow (CH_3)_4N^+IBrCl^- + (CH_3)_2NCl$

(ii) $(CH_3)_2NCl.ICl + (CH_3)_4N^+Br^- \longrightarrow (CH_3)_4N^+ICl_2^- + (CH_3)_2NBr$

(iii) $(CH_3)_2NCl.ICl + (CH_3)_4N^+Br^- \longrightarrow (CH_3)_4N^+BrCl_2^- + (CH_3)_2NI$

The N-halamines would presumably then decompose.

3. Reaction of $(CH_3)_2NCl.ICl$ with tetramethylammonium azide.

The procedure described in (1) above was repeated except that 0.58g (0.005 mole) of tetramethylammonium azide was substituted for the fluoride. There was no reaction even when the mixture was left at ca.5°C for some weeks, and the azide was recovered unchanged.

4. Reaction of $(CH_3)_2NCl.ICl$ with tetra n-butylammonium bromide

The procedure described in (1) above was repeated except that 1.61g (0.005 mole) of tetra n-butylammonium bromide was subsituted for the fluoride. A deep reddish solution resulted which on careful evaporation yielded a mass of golden yellow crystals.

Yield: 2.0g (82.6%)

Analysis:	Calcd. for: $(C_4H_9)_4N^+ClBrI^-$					
	C 39.64	H 7.47	N 2.58	Cl 7.31	Br 16.48	I 26.18
Found:	C 40.33	H 9.00	N 3.14	Cl 9.54	Br 13.30	I 19.75 (low)

These figures and the simple I.R. spectrum of the compound suggest - despite low halogens - that the substance is tetra n-butylammonium chloride bromide iodide $(C_4H_9)_4N^+ClBrI$

A possible reaction here is:

$$(CH_3)_2NCl.ICl + (C_4H_9)_4N^+Br^- \longrightarrow (C_4H_9)_4N^+ClBrI^- + (CH_3)_2NCl$$

The solution did smell very strongly of N-dimethylchloramine.

5. Reaction of $(CH_3)_2NCl.IBr$ with tetramethylammonium bromide.

1.43g (0.005 mole) of dimethylchloramine iodine (I) bromide adduct was dissolved in $10cm^3$ of methylene chloride and 0.77g (0.005 mole) of tetramethylammonium bromide was added. A yellow colour soon gave way to a deposit of bright orange crystals which were filtered, washed with a little methylene chloride and dried in vacuo.

Yield: 1.22 (85.6%)

Analysis: Calcd. for $(CH_3)_4N^+ClBrI^-$

	C 16.77	H 4.22	N 4.89	Cl 12.38	Br 27.89	I 44.31
Found:	C 16.54	H 5.61	N 4.82	Cl 14.52	Br 27.64	I 42.16

These figures and the simple I.R. spectrum suggest that the compound is tetramethylammonium chloride bromide iodide $(CH_3)_4N^+ClBrI^-$

A possible reaction here is:

$$(CH_3)_2NCl.IBr + (CH_3)_4N^+Br^- \longrightarrow (CH_3)_4N^+ClBr^- + (CH_3)_2NBr$$

6. Reaction of $(CH_3)_2NCl.I_2$ with tetramethylammonium bromide

1.67g (0.005 mole) of N-dimethylchloramine-iodine adduct was dissolved in $10cm^3$ of dichloromethane and 0.77g (0.005 mole) of tetramethylammonium bromide was added. After leaving overnight at 5°C, the yellow, microcrystalline deposit was filtered, washed with dichloromethane and dried in vacuo.

Yield: 1.95g (98.5%)

Analysis: Calcd. for $(CH_3)_4N^+ (CH_3)_2NIBrCl_2^-$

	C 18.20	H 4.58	N 7.08	Cl 17.91	Br 20.19	I 32.05
Found:	C 17.35	H 5.48	N 5.98	Cl 14.85	Br 20.94	I 32.05

The I. R. spectrum confirmed that the substance is $(CH_3)_4N^+(CH_3)_2NIBrCl_2^-$

7. Reaction of $(CH_3)_2NCl.I_2$ with tetramethylammonium iodide

The procedure described in (6) above was repeated, using 1.01g (0.005 mole) tetramethylammonium iodide in place of the bromide. There was an immediate reaction and on standing, an orange solid was deposited.

Yield: 2.21g (87.7%)

Analysis: Calcd. for $(CH_3)_4N^+(CH_3)_2NI_3Cl^-$

C 13.20 H 3.39 N 5.24 Cl 6.66 I 71.51

Found: C 13.89 H 3.79 N 5.39 Cl 6.43 I 72.20

These figures and the supporting I. R. spectrum show the compound to be $(CH_3)_4N^+ (CH_3)_2N^-I_3Cl$

8. Reaction of $(CH_3)_2NCl.Br_2$ with tetramethylammonium bromide

The bromine adduct of N-dimethylchloramine was prepared as described previously (page 28) and 1.19g (0.005 mole) was rapidly added to 0.77g (0.005 mole) of tetramethylammonium bromide in $10cm^3$ of dichloromethane. After some days at ca 5°C the white solid was filtered, washed with dichloromethane and dried. The melting point of 228°C (cf 230°d) confirmed this as unreacted tetramethylammonium bromide.

9. Reaction of $(CH_3)_2NI.I_2$ with tetramethylammonium iodide

The iodine adduct of N-dimethyliodamine was prepared by the method of Jander (47) as follows:

3g (0.0175 mole) of N-dimethyliodamine was added to $50cm^3$ of a saturated solution of iodine in ethoxyethane at -30°C and was left for two days with gentle stirring, the temperature being kept below -25°C (the freezer was used overnight). The resulting brownish adduct was filtered, washed rapidly with ethoxyethane then pentane and was dried at -30°C in vacuo.

Yield: 4.05g

$$(CH_3)_2NI + I_2 \longrightarrow (CH_3)_2NI.I_2$$

2.13g (0.005 mole) of the adduct was dissolved in 15cm^3 of dichloromethane and 1.01g (0.0005 mole) of tetramethylammonium iodide was added. After an overnight stand at ca.5°C, the deep orange solid was filtered, washed with dichloromethane and dried in vacuo.

Yield: 2.81g (89.8%)

Analysis: Calcd. for $(CH_3)_4N^+(CH_3)_2NI_4^-$

C 9.93 H 2.49 N 3.86 I 83.71

Found: C 10.01 H 3.53 N 3.92 I 81.12

The I. R. spectrum confirmed the compound as $(CH_3)_4N^+(CH_3)_2N^-I_4$

CHAPTER SEVEN

REACTION OF N-DIMETHYLCHLORAMINE WITH TETRAMETHYLAMMONIUM IODIDE

REACTION OF N-DIMETHYLCHLORAMINE WITH TETRAMETHYLAMMONIUM IODIDE

A possible synthetic route to polyhalides containing the bis (dimethylamido) group is presented by the direct reaction of N-halamines with quaternary ammonium halides. Unfortunately, time did not permit much investigation along these lines, such work as was done being restricted to one reaction only, i.e. that between N-dimethylchloramine and tetramethylammonium iodide.

When these substances are reacted together on a 1:1 molar basis in carbon tetrachloride, a yellow colour is soon apparent. After a few hours at room temperature, a bright yellow solid precipitates out, which on filtering in air slowly turns red. Simple investigation has shown that the colour change is due to reaction with atmospheric moisture rather than with oxygen and the red substance is probably thus a hydrolysis product of some presumed polyhalide.

Properties of the reaction product.

The apparently new substance is deep brick-red, crystalline and stable at room temperature. It resists the action of cold water for many hours but eventually, or rapidly on warming, a brown solution of iodine and white crystals of tetramethylammonium iodide (identified by melting point 198°d cf 209 result. If heated dry, darkening occurs, a white sublimate forms (which appears to be a mixture of amine halides), and free amine (s) are liberated as detected by their odour. No iodine vapour is produced. The infra-red spectrum indicates the presence of $(CH_3)_4N^+$

There was, regrettably, no further time to investigate this material and reaction more fully.

EXPERIMENTAL

A solution of 0.83 cm^3 (0.01 mole) of N-dimethylchloramine in 20 cm^3 of carbon tetrachloride was mixed with a suspension of 2.02g (0.01 mole) of tetramethylammonium iodide in 10 cm^3 of the same solvent. After standing overnight at room temperature the yellow solid which formed was filtered, washed with a few cm^3 of carbon tetrachloride and air was drawn through the filter until no further colour change was apparent. The red solid produced was dried in vacuo.

Yield: 2.0g

Analysis: the compound gave the following figures:

C 23.40 H 5.80 N 7.03 Cl 12.75 I 51.94

These correspond fairly well to those calculated for $(CH_3)_4N^+(CH_3)_2N^-ICl$

C 25.68 H 6.47 N 9.98 Cl 12.64 I 45.23

C H A P T E R E I G H T

INFRA RED SPECTROSCOPY

INFRA RED SPECTROSCOPY

Infra red spectroscopy provides information about molecular modes of vibration and hence structure. It is a particularly valuable technique when dealing with a series of very similar compounds such as those described in this work, and has been used here almost exclusively as an analytical tool, i.e. as a means of identifying substances.

The spectra of ten new nitrogen-halogen compounds have been recorded as well as those of a variety of known substances for reference purposes, using a Perkin-Elmer 457 grating spectrometer in the range 4000 - 250 cm^{-1}. The region 400 - 40 cm^{-1} was explored using a Beckman R11C FS 720 interferometer.

For examination in the 400 - 250 cm^{-1} region, specimens were carefully dried either <u>in vacuo</u> or over silica-gel, ground quickly in a dry agate mortar and made into a mull with either Nujol or hexachlorobutadiene. The plates used were sodium chloride, potassium bromide or (more usually) caesium iodide; the two last were protected from oxidation by thin polythene film. Samples for examination on the interferometer were simply mulled with Nujol as before and supported on black polythene.

The purpose of this chapter is to bring together all the infra red evidence which has been used to support claims previously described in this work with appropriate comments, and it is perhaps best to begin by examination of the spectrum of the first compound of the series $M^{+}R_2NX_4^{-}$ to be discovered, i.e. $(CH_3)_4N^{+}(CH_3)_2N(ICl)_2^{-}$. This substance was first prepared by

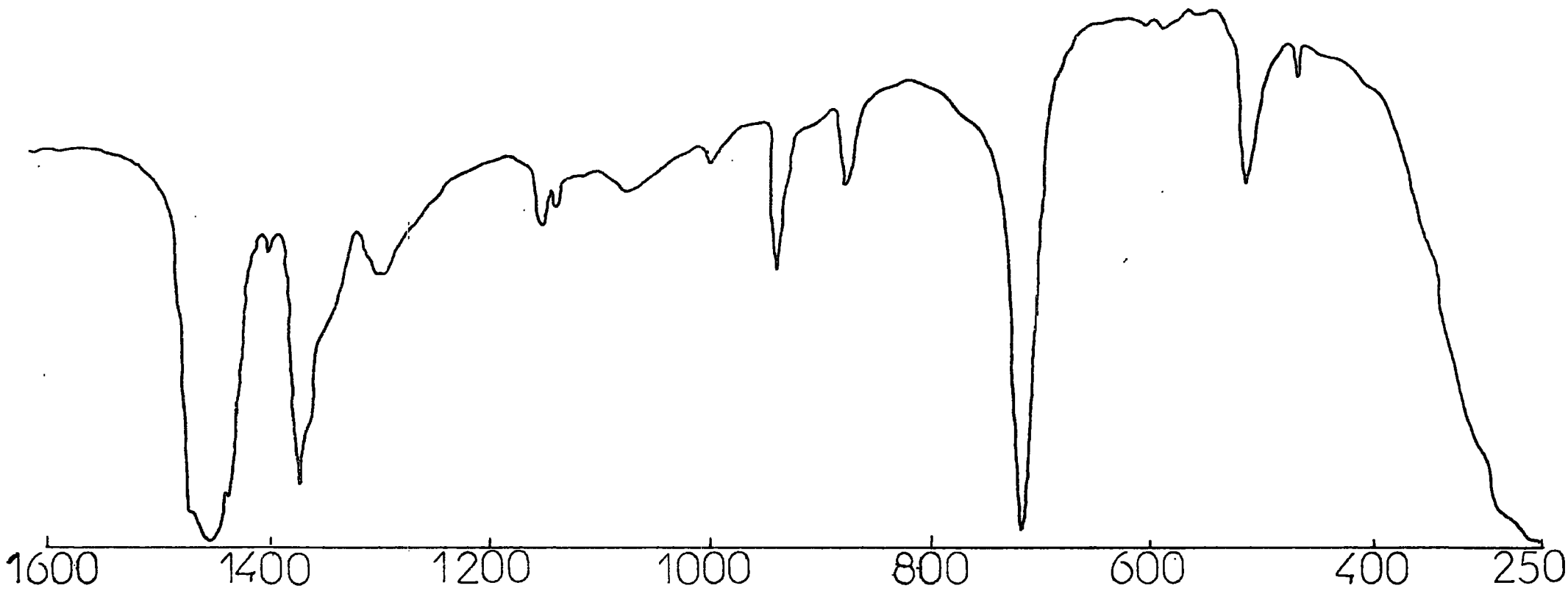
reaction of N-dimethylchloramine with excess iodomethane (10) and in an investigation of the connection between initial molar ratios of reactants and resulting products (page 23) no single reaction gave a pure product, so a deliberate synthesis was undertaken (page 24). This gave an almost quantitative yield of yellow solid whose spectrum was as follows:

TABLE 8,01

COMPARISON OF THE I.R. SPECTRA OF TWO SPECIMENS OF $(CH_3)_4N^+CH_3)_2N(ICl)_2^-$

Synthesised compound	Reported compound (41)
cm^{-1}	cm^{-1}
3025	3025
2965	2965
2905	2910
2855	2856
1494	1494
1480	1483
1460	1461
1438	1437
1400	1402
1159	1159
1145	1145
1010	1010
945	945
880	880
516	520
473	475

These values are consistent, confirming the identity of the product as pure $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ as compared with those obtained by Cowan. (41)



INFRA RED SPECTRUM OF $(CH_3)_4^+N\ (CH_3)_2N\ (ICl)_2^-$

FIG 8,01

One of the intermediates proposed in the reaction mechanism is the substance $(CH_3)_3NClI$ and since this has never been reported, an attempt was made to methylate its isomer $(CH_3)_3NICl$ using a 10:1 molar excess of iodomethane (page 26). A deep purple-brown solid resulted which gave the following infra red spectrum:

TABLE 8,02

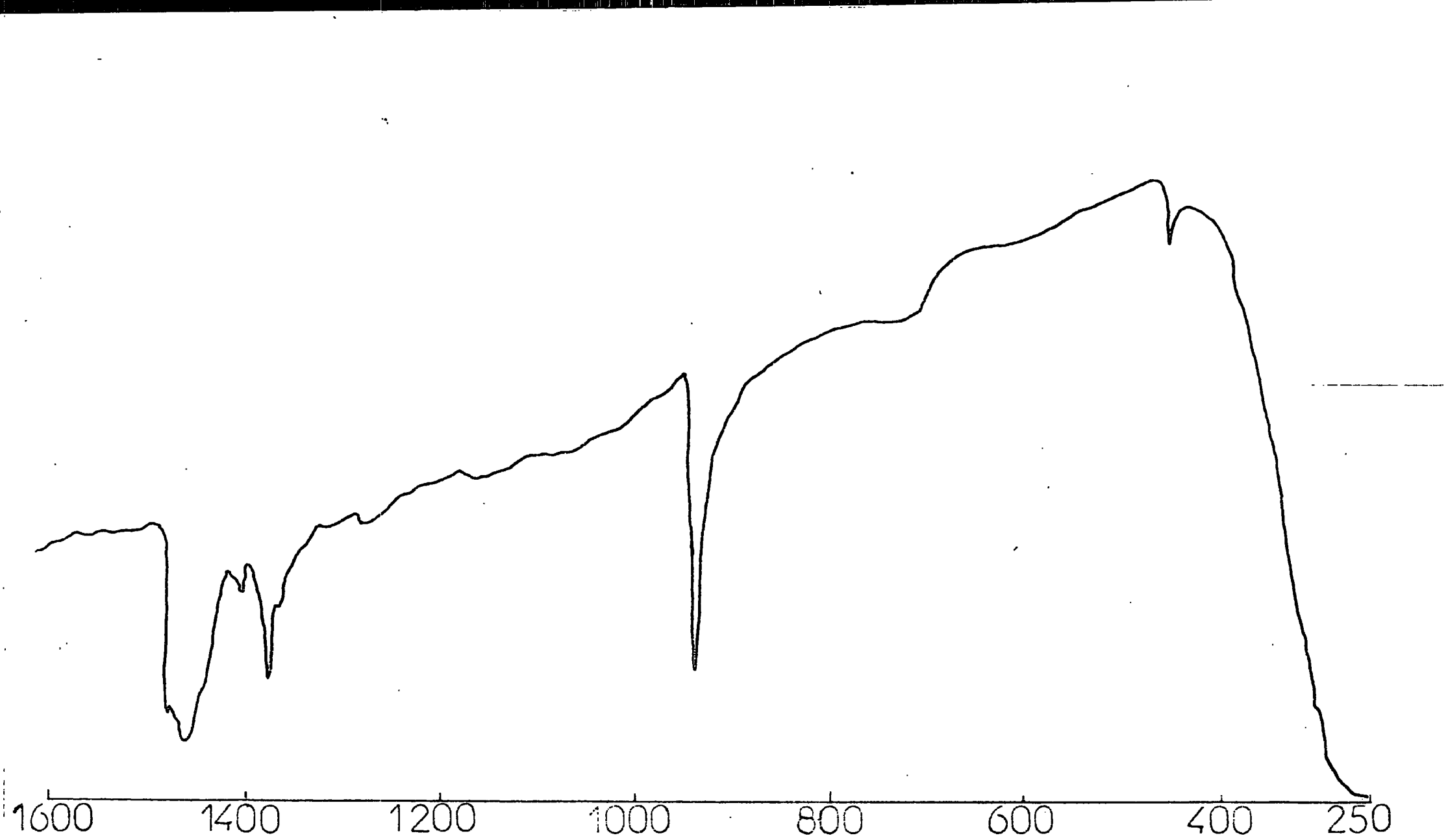
INFRA RED SPECTRUM OF $(CH_3)_3NICl$ / CH_3I REACTION PRODUCT

Reaction product	$(CH_3)_4N^+I_3^-$
cm^{-1}	cm^{-1}
3020	3018
1478	1478
1415	1417
1405	1409
945	945
455	456

The substance is thus tetramethylammonium tri-iodide.

The synthesis of N-dimethylchloramine adducts with various halogens or interhalogens was achieved by mixing of the reagents in an appropriate solvent followed by chilling (page 27 et seq). The iodine (I) chloride and iodine (I) bromide adducts were stable enough to be examined spectroscopically and gave the following results:

See Table 8,03 (Overleaf)



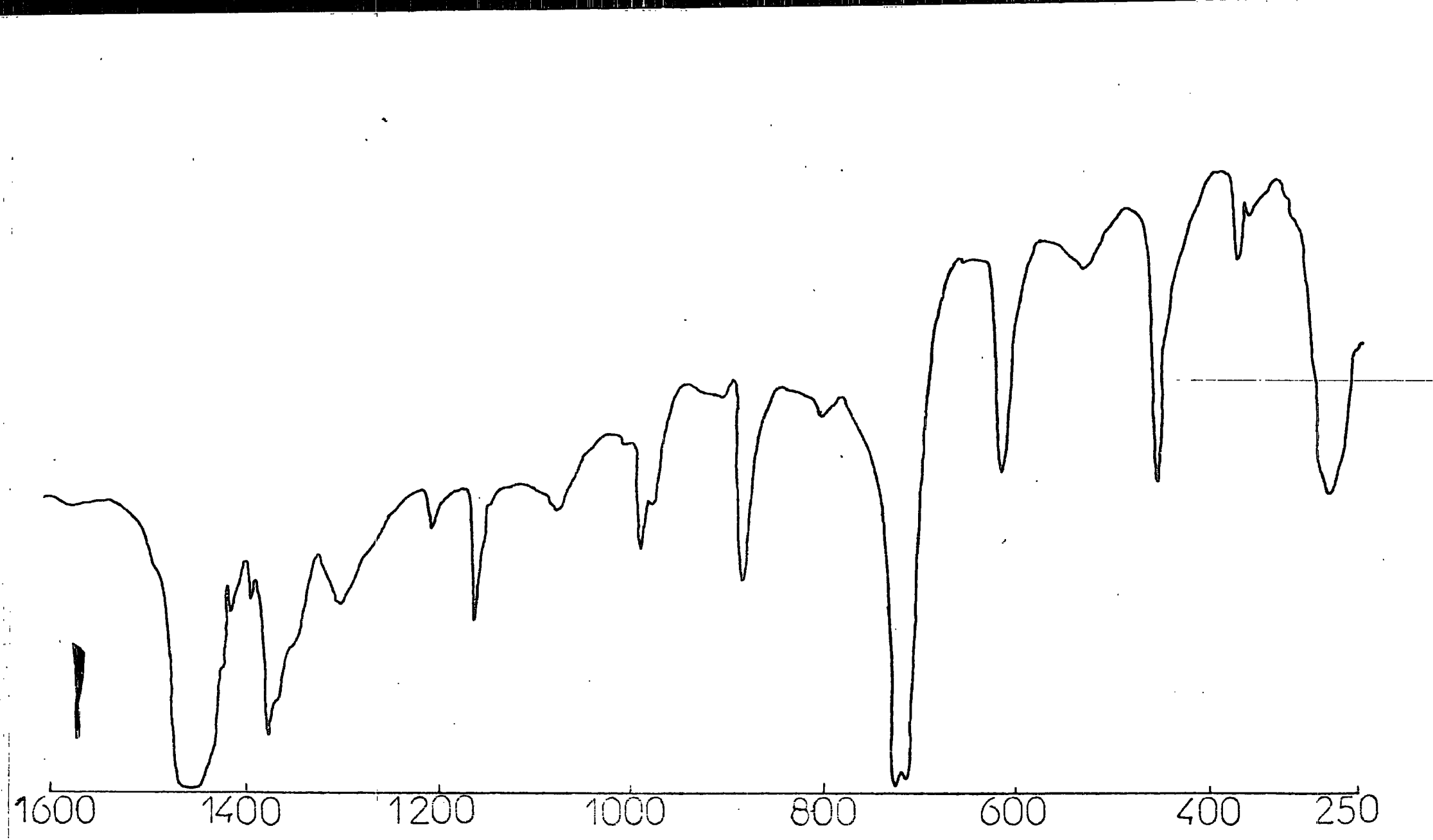
INFRA RED SPECTRUM OF $(CH_3)_4N^+ I_3^-$

FIG 8.02

TABLE 8,03

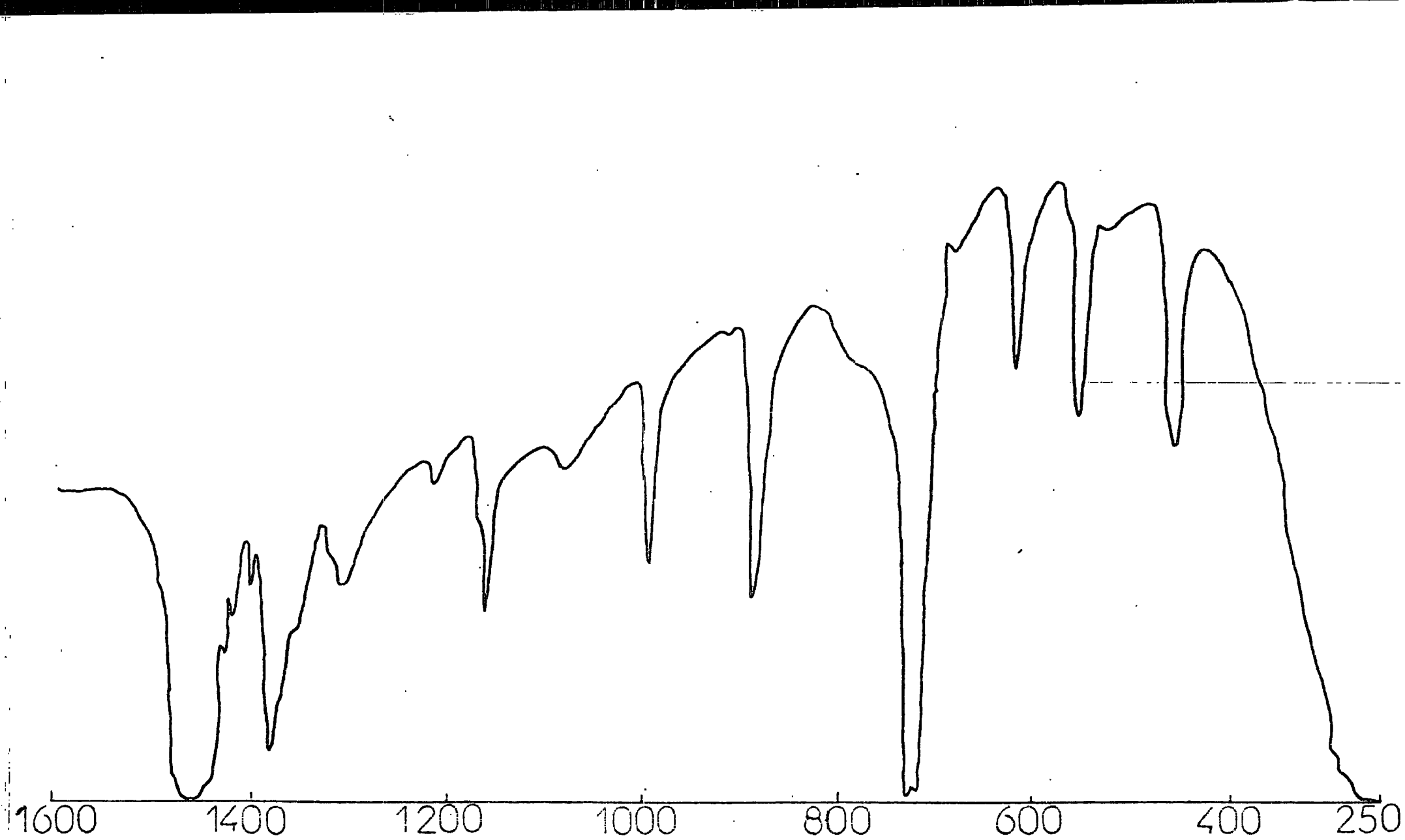
INFRA RED SPECTRUM OF ICl AND IBr ADDUCTS OF $(CH_3)_2NCl$

$(CH_3)_2NCl.ICl$	$(CH_3)_2NCl.IBr$
cm^{-1}	cm^{-1}
3599 (w)	3600 (vvw)
3330 (w)	
2020 (w)	2020 (vw)
1445 (w)	1415 (w)
1395 (vw)	1395 (w)
1210 (w)	1210 (w)
1165 (s)	1155 (s)
1150 (vvw)	
1080 (w)	1080 (vw)
990 (s)	990 (s)
980 (m)	
890 (vs)	890 (vs)
623 (vs)	620 (s)
535 (w)	555 (s)
460 (vs)	460 (s)
380 (m)	
280 (s)	



INFRA RED SPECTRUM OF $(CH_3)_2NCl \cdot ICl$

FIG 8.03



INFRA RED SPECTRUM OF $(CH_3)_2NCl \cdot IBr$

FIG 8.04

The corresponding iodine compound $(CH_3)_2NCl.I_2$ was also prepared and although its colour (orange) was different from the yellow specimen reported by Cowan (41) the following comparable infra red spectrum was obtained:

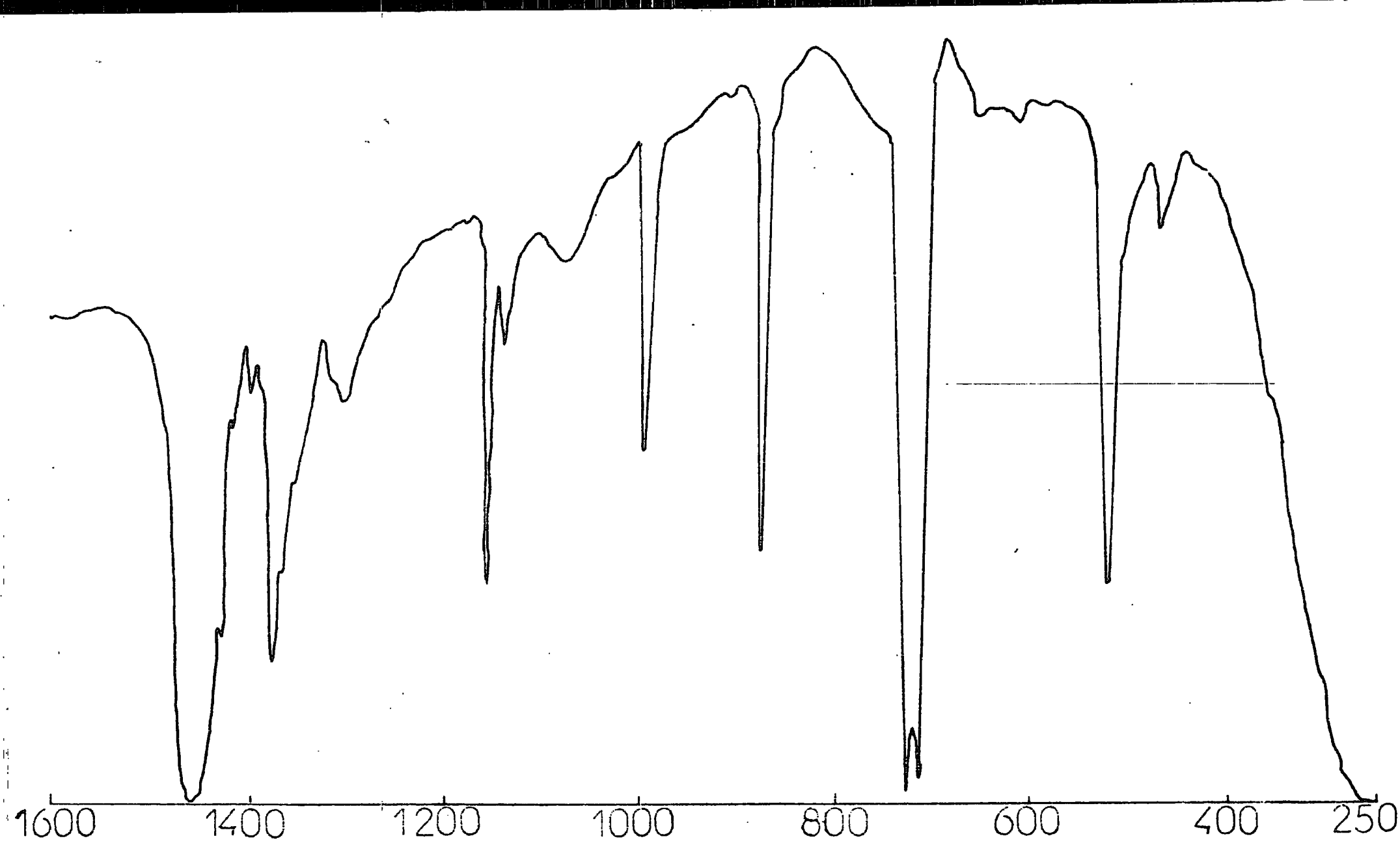
TABLE 8,04

INFRA RED SPECTRA OF TWO SAMPLES OF $(CH_3)_2NCl.I_2$

New specimen	Reported specimen (41)
cm^{-1}	cm^{-1}
1430	1435
1415	1415
1399	1400
1154	1155
1145	1145
1000	1010
880	880
525	505
470	455

In these adducts it seems probable that bands at 1150, 1145 880 and 520 cm^{-1} are due to skeletal modes of vibration of the $(CH_3)_2N$--group, the 1150/1145 cm^{-1} split band being caused by C-N stretching, while bands in the region 550-450 cm^{-1} may well be due to twisting or rocking of the $(CH_3)_2N$ moiety. Cowan suggests that the strong absorption at 880 cm^{-1} may be due to a CNC deformation mode, while the band at 280 cm^{-1} in $(CH_3)_2NCl.ICl$ could be due to an I-Cl stretch, previously reported at 249 cm^{-1} in $(CH_3)_4N^+ICl_2^-$ (54).

Reaction of these adducts with large cation halides has in some cases produced compounds containing $Me_2NX_4^-$-type ions, whose



INFRA RED SPECTRUM OF $(CH_3)_2NCl \cdot I_2$

FIG 8.05

identity was checked by comparison of their infra red spectra with those of known compounds. The first successful synthesis of this type resulted in the preparation of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ from the iodine (I) chloride adduct of N-dimethylchloramine and tetramethylammonium iodide, and this was followed by a very similar synthesis using tetramethylammonium tri-iodide in place of the simple iodide.

$$(CH_3)_2NCl.\ ICl + (CH_3)_4N^+I^- \longrightarrow (CH_3)_4N^+(CH_3)_2N(ICl)_2^-$$

$$(CH_3)_2NCl.\ ICl + (CH_3)_4N^+I_3^- \longrightarrow (CH_3)_4N^+(CH_3)_2N(ICl)_2^- + I_2$$

The products gave the following infra red spectra:

TABLE 8.05

INFRA RED SPECTRA OF $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$

PREPARED VIA INTERMEDIATES

Product ex $(CH_3)_4NI$	Product ex $(CH_3)_4NI_3$	Reported (41)
cm^{-1}	cm^{-1}	cm^{-1}
1437	1437	1437
1405	1405	1402
1155	1155	1159
1145	1145	1145
1000	1005	1010
943	945	945
880	880	880
520	520	520
465	460	475

These results are close enough to confirm the analytical data which check for $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$

In a similar way, the iodine (I) chloride adduct of N-dimethylchloramine reacted slowly with a suspension of caesium iodide in dichloromethane to form the corresponding caesium compound, and analagous results were obtained with diphenyl-iodonium iodide and thallium tri-iodide (but not TlI). The identity of the products was confirmed by their infra red spectra which were compared with that reported for $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$; results are shown in Table 8,06.

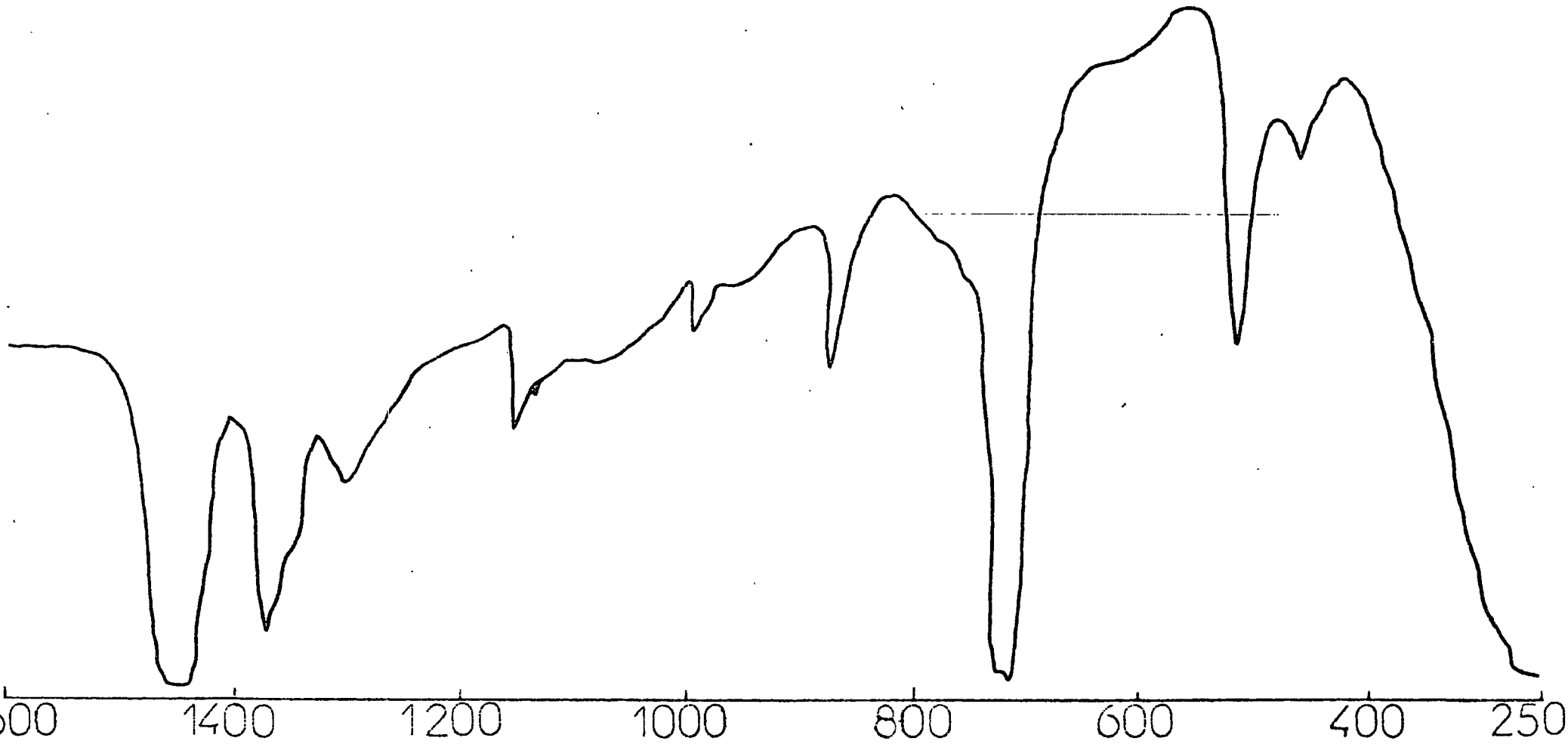
The non-appearance of the bands at 1437, 1402 and 945 cm^{-1} in the new compounds are due to the absence of $(CH_3)_4N^+$ while the relevant bands at 1150-1140 and 880-520 cm^{-1} are due to skeletal $(CH_3)_2N$ vibrations - good evidence for its preservation as a discreet entity.

The reaction of N-dimethyliodamine with excess iodomethane proceeds rapidly at room temperature and produces an orange solid whose analysis corresponds to $(C_3H_9NI_2)_x$. This could be the iodine adduct of trimethyliodamine $(CH_3)_3N.I_2$ or alternatively $(CH_3)_4N^+(CH_3)_2NI_4^-$ and the infra red spectrum confirms the latter. It is interesting to compare the spectrum of this new compound with those of $(CH_3)_3N.I_2$, $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ and the iodine adduct of dimethyliodamine $(CH_3)_2NI.I_2$, and the results are shown in Table 8,07. It is clear that the new substance more closely resembles the known $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ than it does the most likely alternative, i.e. $(CH_3)_2NI.I_2$. In particular, the 1150/1140 cm^{-1} splitting due to C-N bond stretching is present - a characteristic absorbance of ions of the type $(CH_3)_2NX_4^-$ - and so is the very strong and typical band at 945 cm^{-1}, due to an

TABLE 8,06

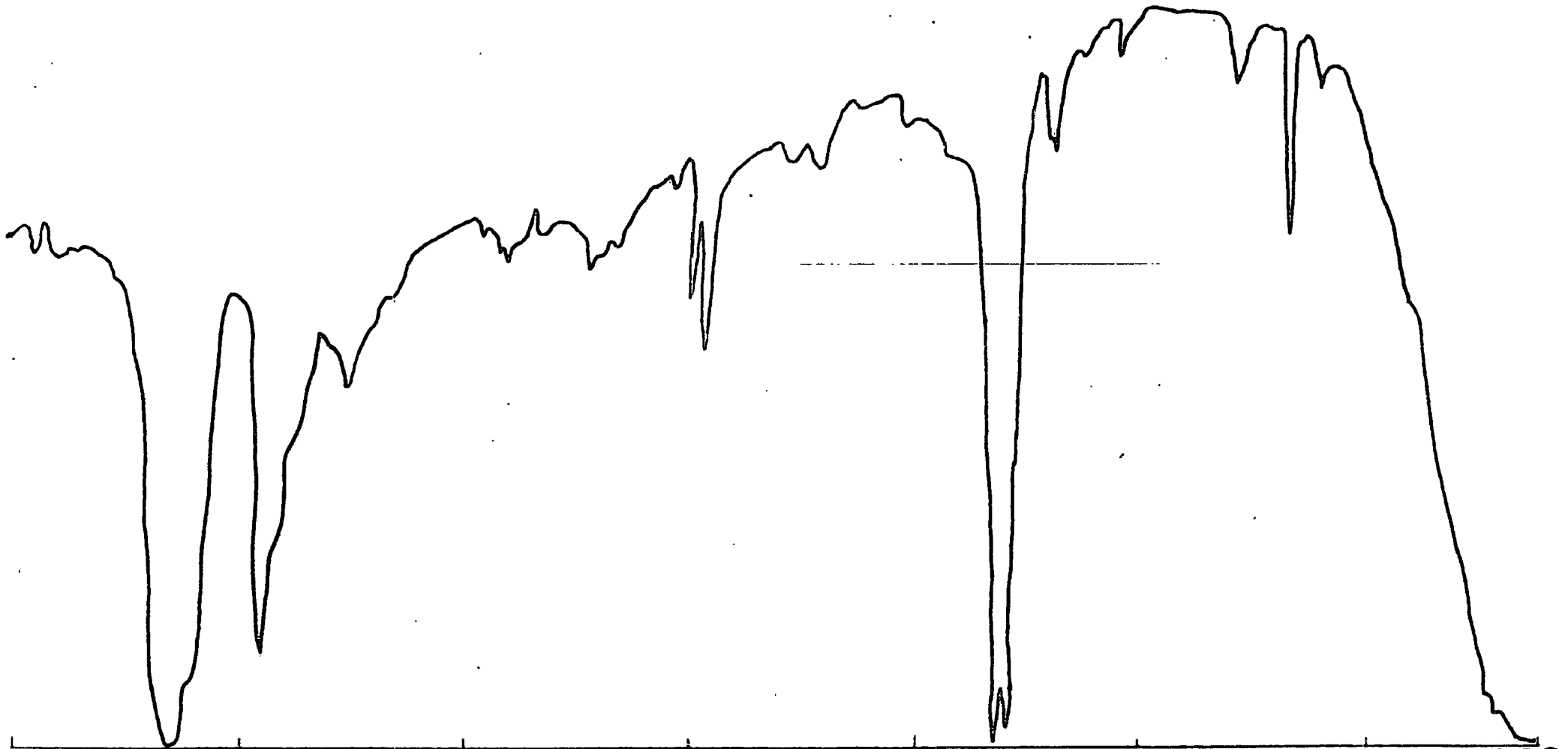
INFRA RED SPECTRA OF $M^{+}(CH_3)_2N(ICl)_2^{-}$ 1600 - 250 cm^{-1}

M=Cs	M= $(C_6H_5)_2I$	M= Tl	M=$(CH_3)_4N$
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
	3590 (w)		3025
			2965
			2910
			2856
			2330
			1494
			1483
			1461
			1437
			1402
1155 (m)	1155 (m)	1155 (m)	1149
1145 (w)		1145 (w)	1145
998 (w)	998 (s)	998 (s)	1010
	998 (s)		945
878 (s)	882 (w)	880 (s)	880
	682 (m)		
	615 (w)		
520 (vs)	517 (w)	520 (s)	520
475 (m)	468 (m)	475 (s)	475



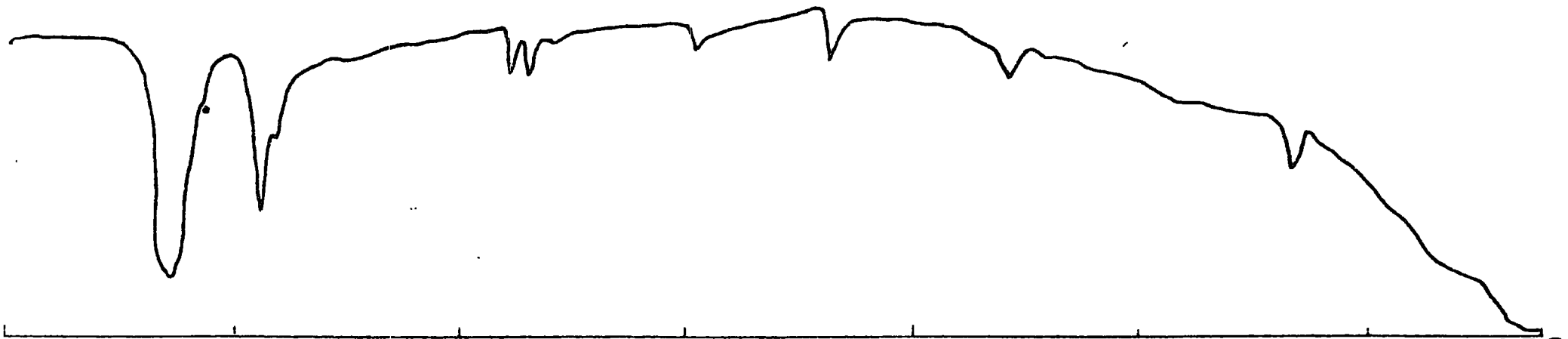
INFRA RED SPECTRUM OF $Cs^{+}(CH_3)_2N(ICl)_2^{-}$

FIG 8.06



INFRA RED SPECTRUM OF $(C_6H_5)_2I^+ (CH_3)_2N (ICl)_2$

FIG 8.07



INFRA RED SPECTRUM OF $Tl^{+}(CH_3)_2N(ICl)_2^{-}$ FIG 8,08

TABLE 8.07

INFRA RED SPECTRUM OF $(CH_3)_4N^+(CH_3)_2NI_4^-$ AND RELATED COMPOUNDS

$(CH_3)_4N^+(CH_3)_2NI_4^-$	$(CH_3)_2NI.I_2$	$(CH_3)_3N.I_2$	1600 - 100 cm^{-1} $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
1445 (m)		1440 (vw)	1437
1402 (m)		1400 (w)	1402
	1300 (m)	1255 (m)	
1150 (s)	1150 (s)	1205 (vw)	1159
1140 (s)		1100 (m)	1145
1010 (w)	1015 (w)	1000 (s)	1010
945 (vs)			945
	895 (m)		
875 (s)	885 (m)	805 (vs)	880
			520
475 (vs)	492 (s)	470 (vs)	474
430 (w)			
246 (m)			
208 (m)			
190 (m)			
142 (m)			
108 (m)			

overall deformation of $(CH_3)_4N^+$, both providing good evidence for the new substance being $(CH_3)_4N^+(CH_3)_2NI_4^-$.

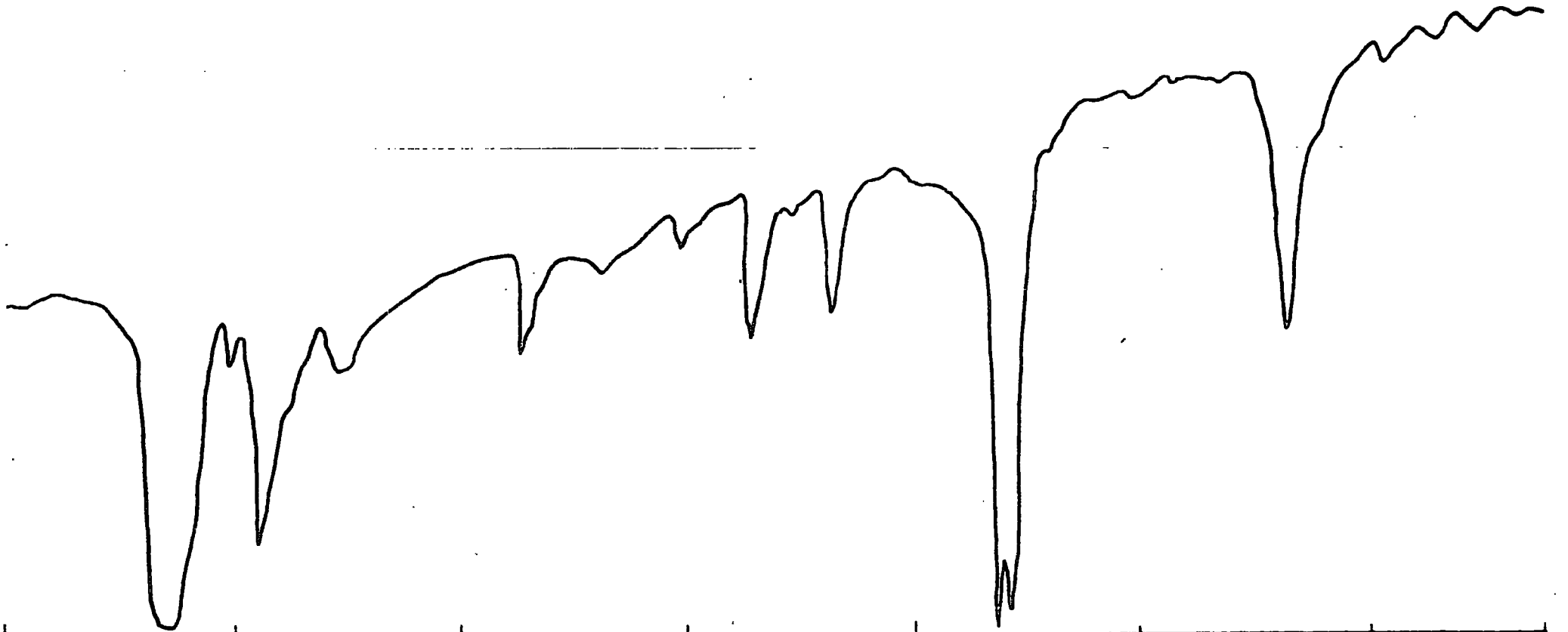
The low bands in the far infra red region at 142 and 108 cm^{-1} are probably associated with the I — I function. N — I vibrations are reported at 196 cm^{-1} in $(CH_3)_3N.ICl$ and 172 cm^{-1} in $(CH_3)_3N.IBr$ (54). If the N — I band was shorter because of adjacent groups it would be expected that the absorption frequency would rise so the bands at 190 and 208 cm^{-1} could be due to N — I stretching.

The new compound $(CH_3)_4N^+(CH_3)_2NI_4^-$ was also prepared by two other methods, i.e. by reacting the iodine adduct of N-dimethyl-iodamine with either tetramethylammonium iodide or the tri-iodide:

$$(CH_3)_2NI.I_2 + (CH_3)_4N^+I^- \qquad (CH_3)_4N^+(CH_3)_2NI_4^-$$

$$(CH_3)_2NI.I_2 + (CH_3)_4N^+I_3^- \qquad (CH_3)_4N^+(CH_3)_2NI_4^- + I_2$$

and the identity of the analytically satisfactory products was checked by infra red examination, results being shown in Table 8,08, overleaf.



INFRA RED SPECTRUM OF $(CH_3)_4N^+ (CH_3)_2NI_4^-$

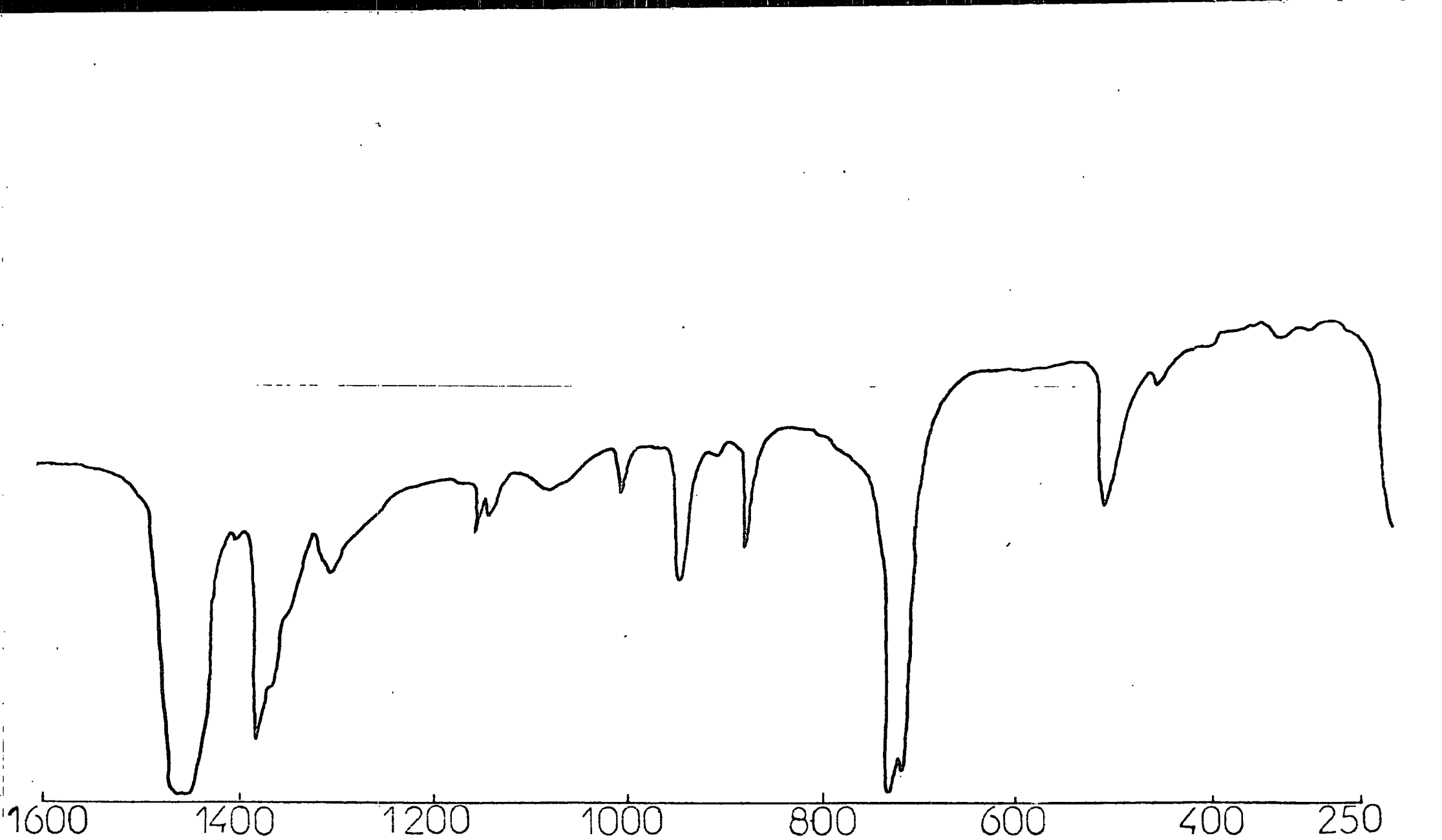
FIG 8.09

TABLE 8,08

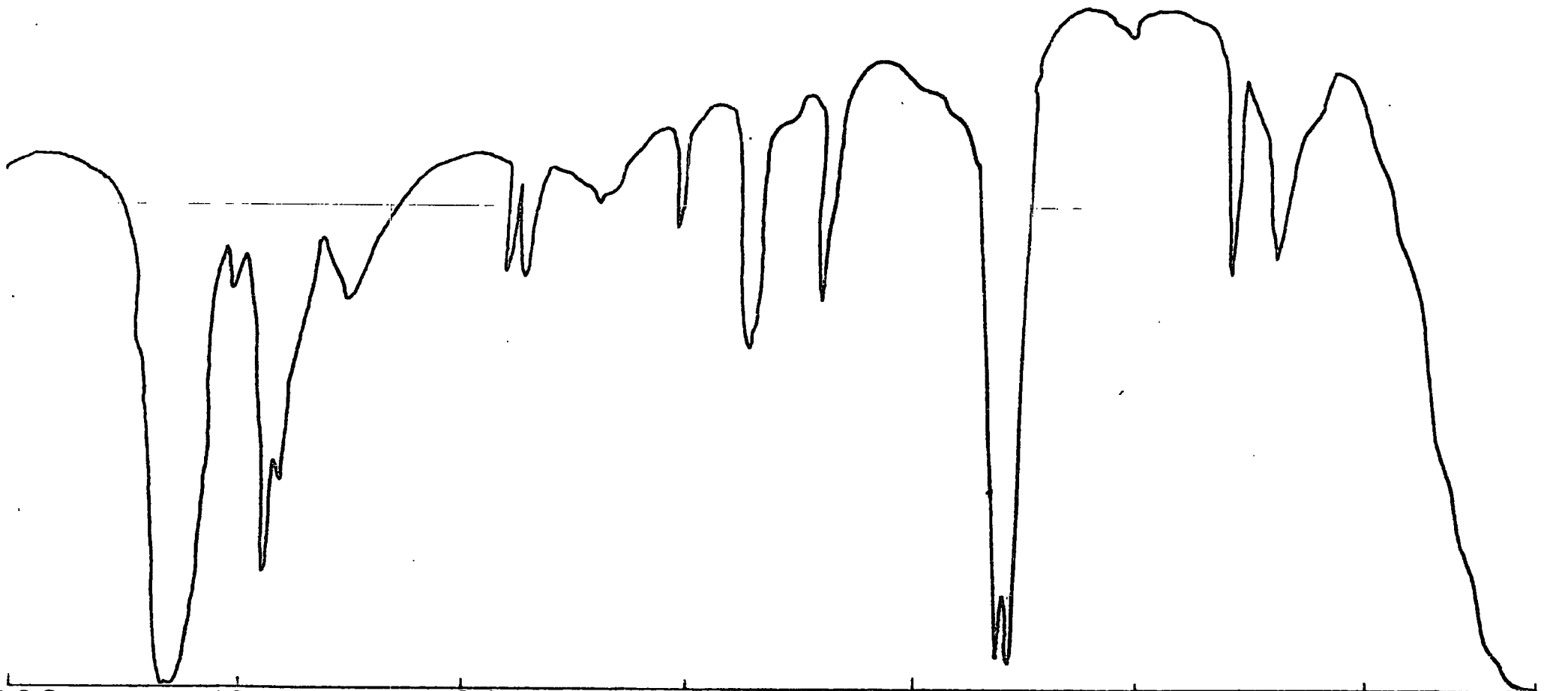
INFRA RED SPECTRA OF $(CH_3)_4N^+(CH_3)_2NI_4^-$ SPECIMENS

Original	Prepared via $(CH_3)_4N^+I^-$	Prepared via $(CH_3)_4N^+I_3^-$
cm^{-1}	cm^{-1}	cm^{-1}
1445	1445	1440
1402	1405	1402
1150	1150	1155
1140	1145	1145
1010	1010	1010
945	945	945
875	875	875
475	480	480

Halide insertion reactions to date have provided two new species containing ions of the type $(CH_3)_2NX_4^-$. The first of these, prepared by reaction of tetramethylammonium bromide with the iodine adduct of dimethylchloramine analysed at $(C_6H_{18}N_2Cl_2BrI)_x$ but its infra red spectrum confirmed the presence of the anion $(CH_3)_2NIBrCl_2^-$. Similarly, reaction of the same adduct with tetramethylammonium iodid gave $(CH_3)_4N^+(CH_3)_2NI_3Cl^-$. The infra red spectra of these compounds is shown in Table 8, 09 overleaf.

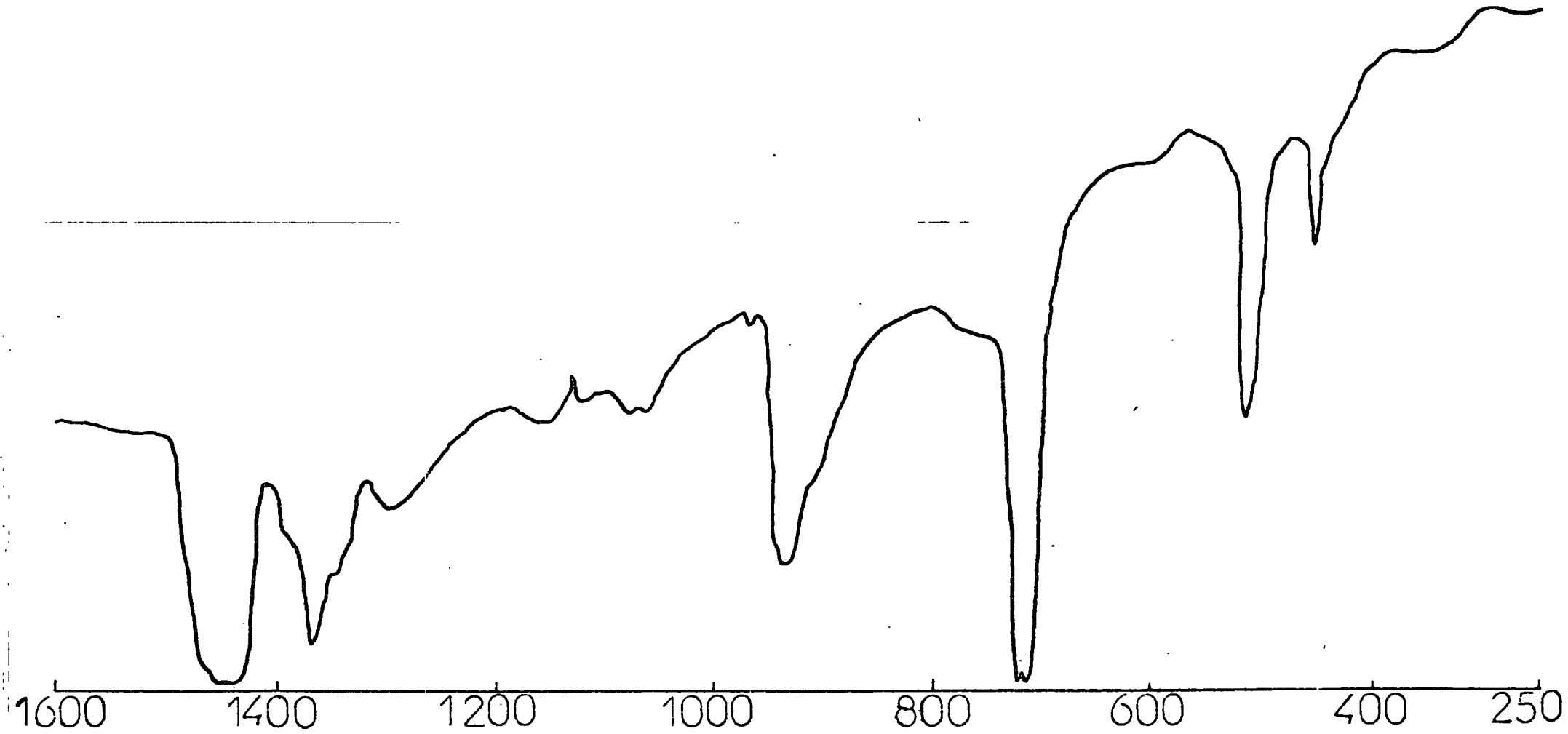


INFRA RED SPECTRUM OF $(CH_3)_4N^+ IBrCl_2^-$ FIG 8.10



INFRA RED SPECTRUM OF $(CH_3)_4N^+ I_3Cl^-$

FIG 8.11



INFRA RED SPECTRUM OF INITIAL REACTION PRODUCT OF $(CH_3)_2NCl$ & $(CH_3)_4NI$

FIG 8,12

TABLE 8,09

INFRA RED SPECTRA OF THREE COMPOUNDS CONTAINING Me_2NX_4 TYPE IONS

$(CH_3)_4N^+(CH_3)_2NIBrCl_2^-$	$(CH_3)_4N^+(CH_3)_2NI_3Cl^-$	$(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$
cm^{-1}	cm^{-1}	cm^{-1}
1405 (w)	1405 (w)	1402
1155 (w)	1155 (m)	1159
1143 (w)	1145 (m)	1145
1010 (m)	1010 (m)	1010
945 (s)	945 (s)	945
880 (s)	880 (s)	880
510 (vs)	520 (vs)	520
460 (w)	480 (s)	475
197 (w)		
175 (w)		
141 (m)		
102 (w)		

These results show typical bands at 1405, 945 and 460 cm^{-1} for $(CH_3)_4N^+$ and bands at 1150/1140, 880, 520 and 475 cm^{-1} associated with $(CH_3)_2N$. The four bands in the far infra red probably represent N — I stretching (197, 175 cm^{-1}) and halogen-halogen stretching (141, 102 cm^{-1}). The compound containing the ion $(CH_3)_2NI_3Cl^-$ apparently decomposed during examination.

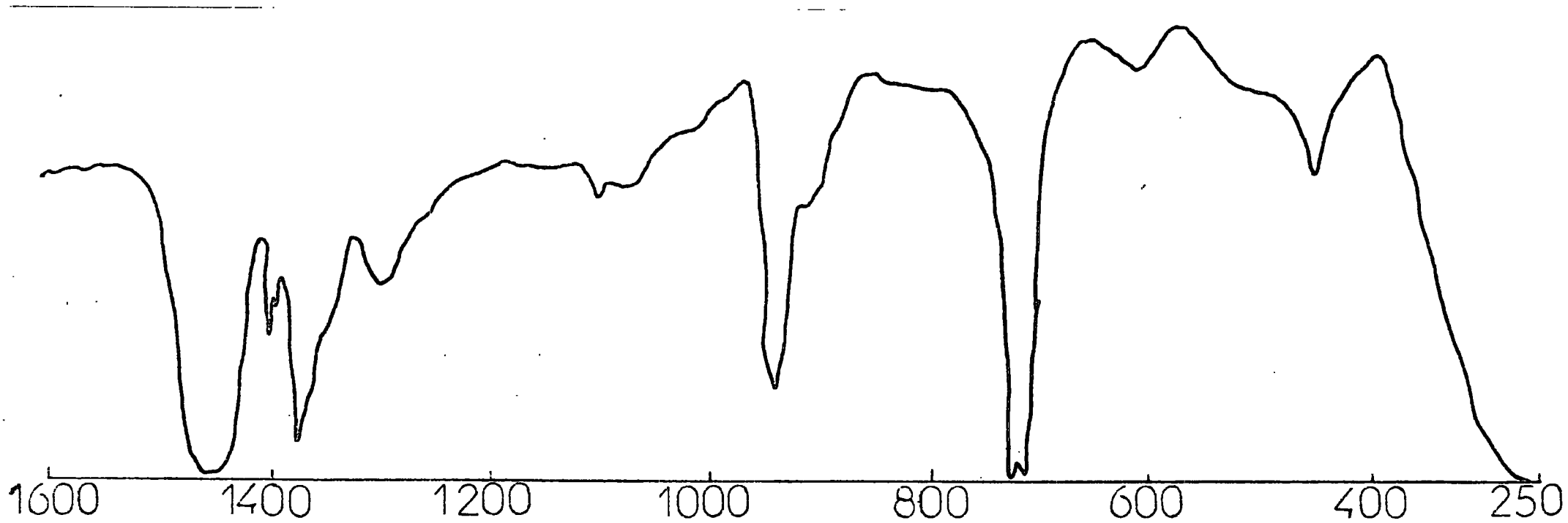
The reaction of N-dimethylchloramine with tetramethylammonium iodide gives a yellow solid which turns red on the addition of water or if left in ordinary (damp) air. Lack of time prevented a full examination of these substances, but their infra red spectra are as follows overleaf..

TABLE 8,10

INFRA RED SPECTRA OF $(CH_3)_2NCl/(CH_3)_4N^+I^-$ REACTION PRODUCTS

Yellow Solid	Red Solid
cm^{-1}	cm^{-1}
2015 (w)	2010 (w)
1400 (w)	1400 (m)
1150)	1390 (w)
1140) w ?	1110 (w)
1070 (m)	
940 (vs)	945 (vs)
518 (vs)	620 (w) (broad)
455 (s)	460 (s)

These rather odd looking spectra both show the presence of $(CH_3)_4N^+$ - bands at 1400, 945 and 460 cm^{-1} but very little else of interest. This suggests that they are simple polyhalides, but an attempt to look for halogen-halogen vibrations in the far infra red region resulted in decomposition in each case.



INFRA RED SPECTRUM OF REACTION PRODUCT OF $(CH_3)_2NCl$ & $(CH_3)_4NI$ FIG8,13

DISCUSSION AND CONCLUSIONS

DISCUSSION AND CONCLUSIONS

The two principal objectives at the outset of this work were:

(i) To obtain evidence for a reaction mechanism proposed to explain the synthesis of $(CH_3)_4N^+(CH_3)_2(ICl)_2^-$ from N-dimethylchloramine and iodomethane.

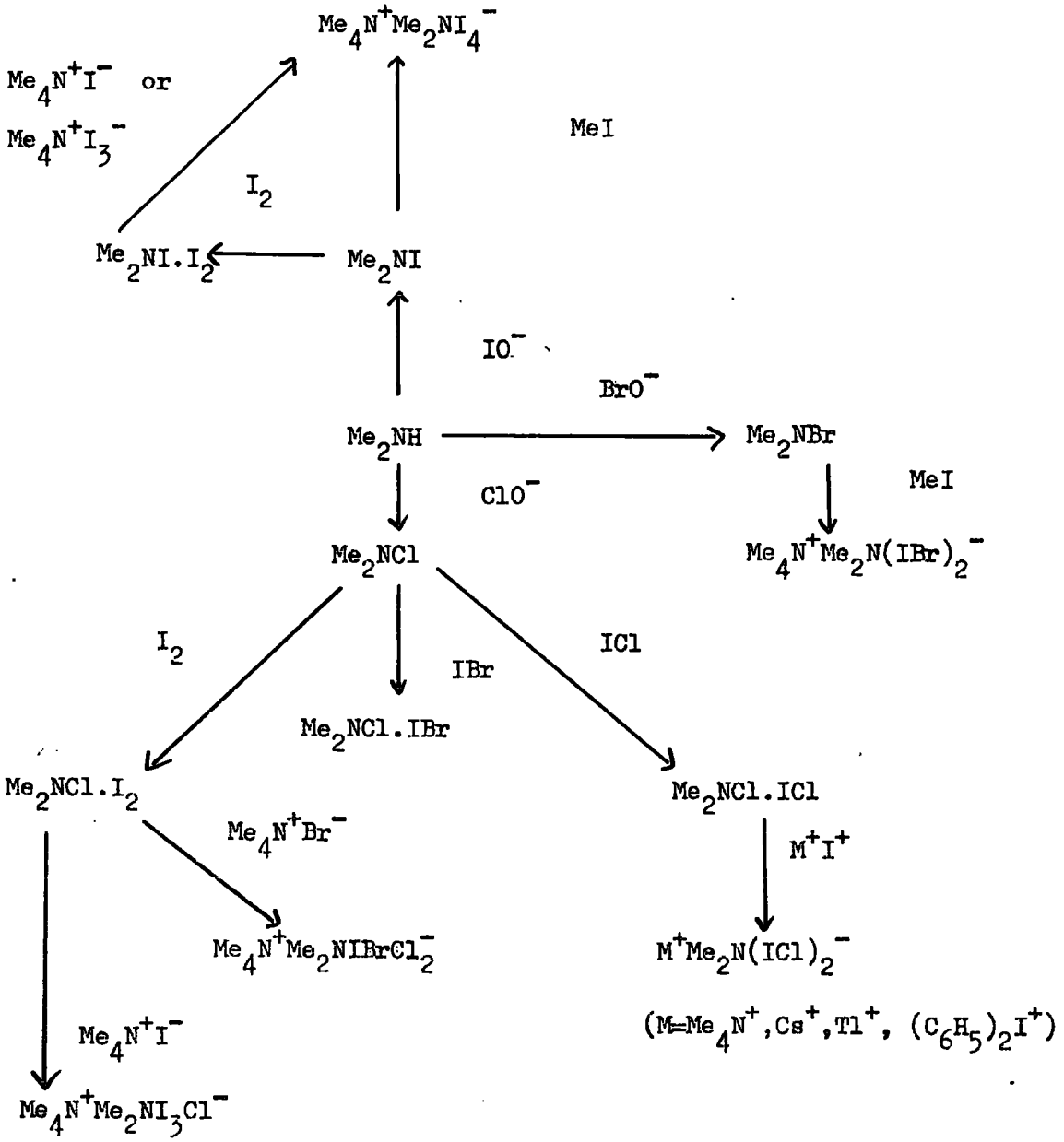
(ii) To prepare analagous and other compounds related to $(CH_3)_4\overset{+}{N}(CH_3)_2N(ICl)_2^-$ within the overall aim of generally "opening up" this small area of nitrogen-halogen chemistry. It is now appropriate to evaluate what has been achieved.

The relevant reactions of N-halamines and their related compounds are shown schematically overleaf, and it can be seem that there are certain general conclusions to be drawn. N-halamines of the methyl series react readily with iodomethane to produce pseudo-polyhalides of the type $M^+ R_2NX_4^-$ where M^+ is a large cation and X is a halogen or combination of different halogens. Compounds containing three new anions have been prepared, i.e. $(CH_3)_2NI_4^-$, $(CH_3)_2N\ IBrCl_2^-$ and $(CH_3)_2NI_3Cl^-$ which makes the total numberknown to date five.

It does not appear very likely that analagous compounds containing larger alkyl or aryl groups can be prepared by the methods described in previous chapters, this probably being due to more favourable reaction rates with $-CH_3$ containing materials, but at least it is now clear that the novel pseudo-polyhalide ion $(CH_3)_2N(ICl)_2^-$ is not unique, being in fact a member of a small group of like ions. Furthermore, the cation associated with

DISCUSSION AND CONCLUSIONS

TABLE 1



anions of this type can be changed, at least as far as $(CH_3)_2N(ICl)_2^-$ is concerned (and there does not appear to be any reason other than perhaps finding optimum conditions for reaction why this should not also be true for other anions as well) so extending the total range of compounds. None of these, however, has proved suitable for nuclear quadruple resonance spectroscopy, although all have possible potential as synthetic intermediates - potential which remains to be exploited.

One of the first priorities in the work described here was to find some evidence for this reaction mechanism

(i) $(CH_3)_2NCl + CH_3I \longrightarrow (CH_3)_3NClI$

(ii) $(CH_3)_3NClI \longrightarrow (CH_3)_3N + ICl$

(iii) $(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4N^+I^-$

(iv) $(CH_3)_2NCl + ICl \longrightarrow (CH_3)_2N(Cl)(ICl)$

(v) $(CH_3)_2N(Cl)(ICl) + (CH_3)_4N^+I^- \longrightarrow (CH_3)_4N^+(CH_3)_2N(ICl)_2^-$

and while such experiments as have been undertaken in this area do not in themselves establish the accuracy of such a mechanism, they have at least showed nothing that would contradict it. In particular, two discoveries can be regarded as providing evidence as to the <u>possibility</u> , at least, that such a mechanism is responsible for the synthesis of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$, i.e.

the formation of N-halamine adducts with Lewis acids:

$$\text{e.g. } (CH_3)_2NCl + ICl \longrightarrow (CH_3)_2N\begin{matrix}\diagup Cl \\ \diagdown ICl\end{matrix}$$

and, more interestingly, the reaction of such adducts with large cation halides:

$$\text{e.g. } (CH_3)_2NCl.ICl + (CH_3)_4\overset{+-}{N}I \longrightarrow (CH_3)_4N^+(CH_3)_2N(ICl)_2^-$$

An improvement can be made on this reaction by employing a large cation polyiodide, e.g. $(CH_3)_4N^+I_3^-$; the reaction time is then very much reduced, presumably because of the polyiodide's lower lattice energy and thus enhanced solubility in the solvent. The method appears to be of fairly general application since $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$, $(CH_3)_4N^+(CH_3)_2NI_4^-$ and $Tl^+ (CH_3)_2N(ICl)_2^-$ have all been prepared in this way.

Variation of initial molar ratios of reactants gives rise to different products and ratios of products and this suggests that there are competing reactions which become more or less favourable depending on conditions. There is some difference in behaviour between N-dimethylchloramine and N-dimethyliodamine in their reactions with iodomethane in that the iodamine reacts rapidly and quantitatively even with vast excesses of iodomethane whereas the chloramine simply produces iodine. A full kinetic investigation would be needed to resolve this puzzle.

Halide insertion reactions, while not yet fully explored, have also been shown to provide a route to anions of the type $R_2NX_4^-$.

Many permutations and combinations of N-halamine - halogen/interhalogen adduct and large cation halides are possible; of those tried, only two gave rise to desired compounds and these provided the new substances $(CH_3)_4N^+IBrCl_2^-$ and $(CH_3)_4N^+I_3Cl^-$. The others gave simple polyhalides or mixtures of polyhalides, again possibly a function of kinetic factors.

Attempts to prepare aryl analogues have proved singularly unsuccessful to date despite several methods of attack. The synthesis of aryl N-halamines is surprisingly easy (22) but adducts with appropriate Lewis acids are much more difficult. Reaction of N-dibenzylchloramine with iodine (I) chloride did, however, give a fairly stable bright yellow crystalline solid whose analysis corresponded to $(C_6H_5CH_2)_2NCl.ICl$, although the reaction was very slow. Unfortunately, its reaction with tetramethylammonium iodide produced, of all things, tetramethylammonium dichloro-iodate (I) $(CH_3)_4N^+ICl_2^-$ instead of the expected substance $(CH_3)_4N^+ (C_6H_5CH_2)_2N (ICl)_2^-$, a reaction whose attempted explanation appears on page 44. Similarly, reactions of N-dibenzylchloramine with excess benzyl iodide or iodomethane also failed to produce the desired type of compound, although in the latter instance an apparently new polyhalide $(C_6H_5CH_2)_2(CH_3)_2N^+I_3^-$ resulted.

The main problem with the work described here was the lack of time to follow up all the various possibilities which continually presented themselves as matters progressed, and this has meant, of course, that the chosen field of N-halamine chemistry has not yet been even nearly fully explored. A particular

disappointment was the failure of new substances to respond to N.Q.R. investigation, so there is as yet no information on N-halogen bond type.

Nevertheless, it is hoped that sufficient has been achieved to show the extent of this field of enquiry, together with its associated investigative problems, besides raising questions whose solution should prove very interesting indeed.

SUGGESTIONS FOR FURTHER WORK

The work described in this thesis has, hopefully, opened up a little more of the chemistry of nitrogen-halogen compounds, but has simultaneously shown that a very great deal more research is needed before an overall picture will be possible. It is perhaps appropriate now to consider the lines along which work might profitably proceed.

1. N-halamine variation.

Most of the work to date has involved reactions of N-dimethylchloramine and N-dibenzylchloramine, and this could readily be extended by exploiting all the possible variations of both halogen and alkyl/aryl groups. In particular it would be interesting to attempt syntheses involving N-iodamines, since these are not only little known but are likely to give rapid reactions leading to products of the desired type $R_4N^+ R_2N^-X_4$ if the example described on page 46 is at all typical.

Similar changes in the reaction of N-halamine adducts with large cation halides would fairly certainly yield some new analogues of $(CH_3)_4N^+ (CH_3)_2N(ICl)_2^-$ and even those combinations of reactants which failed in this respect would probably prove interesting from a mechanistic point of view or because of production of new polyhalides. A very obvious possibility here is for adducts of N-dimethylbromamine - which do not appear to be known - to be prepared and reacted with a variety of tetramethylammonium salts. The reaction between $(CH_3)_2NBr.IBr$

and tetramethylammonium bromide should yield $(CH_3)_4N^+(CH_3)_2NIBr_3^-$ while that between $(CH_3)_2NBr.ICl$ - if stable - and tetramethylammonium chloride might give $(CH_3)_4N^+(CH_3)_2N^-IBrCl_2$ a compound already prepared by a different combination of adduct and halide (page 54). Similarly, heterocyclic base adducts, e.g. piperidine - ICl might give some interesting products, and other large cation halides such as trimethylsulphonium iodide $(CH_3)_3S^+I^-$ could also be tried.

A more extensive investigation of the N-dibenzylhalamine series could well produce the first aryl analogue of the bis (dimethylamido) - halogen-containing anion, and this might well be soluble in, say, heptane, which would facilitate kinetic studies via ultra-violet/visible spectroscopy.

2. Reactions with polyhalides.

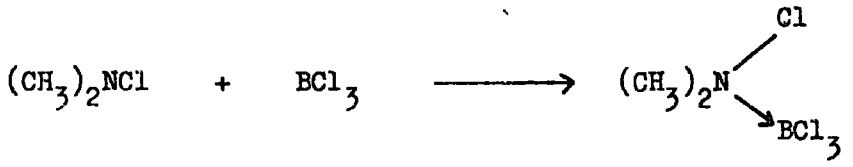
It should prove interesting to react N-halamines and their adducts with a number of polyhalides. The reaction described on page 36 et seq between $(CH_3)_4N^+I^-_3$ and the iodine (I) chloride adduct of N-dimethylchloramine produces a good yield of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$ so it is likely that variation here might produce other known compounds or new ones. An example would be the reaction between $(CH_3)_2NCl.IBr$ and $(CH_3)_4N^+I_2Cl^-$ which could yield $(CH_3)_4N^+$ $(CH_3)_2N^-I_3Cl$ - a known compound - or $(CH_3)_4N^+$ $(CH_3)_2N^-I_2BrCl$ - not known - or mixtures.

3. Other N-halamine adducts.

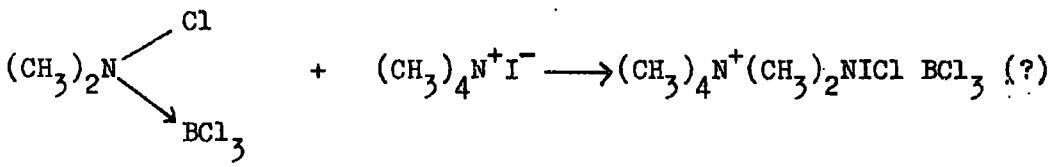
Reactions via intermediate N-halamine adducts described in Chapter Four have been limited to very few actual adducts. The

pseudo-halogens iodine (I) cyanate and thiocyanate might well yield suitable adducts with some N-halamines, and since their preparations (50,51) are relatively easy - with none of the potential hazards of iodine (I) azide - this line of enquiry would be worth pursuing.

More interestingly the reaction of Lewis acids like the boron (III) halides with N-halamines is known to yield adducts, e.g.



and it should prove very profitable to react these (colourless) substances with large cation halides. There was, unfortunately, insufficient time to pursue this, but sufficient preliminary work was done to show that such reactions - performed under strictly anhydrous conditions - yield chocolate-coloured precipitates which <u>might</u> be due to reactions like



and since the number of convenient Lewis acids is enormous, this area of investigation is potentially very rich in new nitrogen-halogen compounds.

4. <u>Physical measurements</u>.

One of the reasons for wishing to have more compounds of the type described in previous chapters is that one or more might

prove suitable for physical measurements. Two particular areas of interest are:

(i) Measurement of the nuclear quadrupole resonance spectrum (NQR) of one of the new nitrogen-halogen compounds, which would give some indication of the distribution of charge across the N-halogen bond. Compounds examined to date have so far failed to give satisfactory signals.

(ii) Investigation of the kinetics of various reactions leading to synthesis of $(CH_3)_4N^+(CH_3)_2N(ICl)_2^-$, probably using ultra-violet/visible spectroscopy. If a satisfactory compound can be made, this would probably give decisive information on the actual reaction mechanism of formation.

One thing certain is that the solution of the problem mentioned in previous pages will provide much interest - and not a few surprises, perhaps.

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