Studies on the co-ordination chemistry of Amides, Imides and related compounds

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STUDIES ON THE CO-ORDINATION CHEMISTRY OF AMIDES, IMIDES AND RELATED COMPOUNDS

THESIS

presented in candidature for the
degree of

MASTER OF SCIENCE

of the

UNIVERSITY OF DURHAM

by

P. K. UMMAT, B.Sc., (LONDON).

October, 1966.

For my parents

The work described in this thesis was performed in the chemistry laboratories of the Sunderland Technical College, during the period from October 1964 to August 1966, under the supervision of Dr. K. Wade, Lecturer in Inorganic Chemistry, University of Durham, and Dr. D. Hall, Senior Lecturer in Inorganic Chemistry, Sunderland Technical College. This thesis contains the results of some original research by the author, and no part of the material has previously been submitted by the candidate for a degree in this or any other University. Where use has been made of the results and conclusions of other authors in relevant studies care has been taken to ensure that the source of information is always clearly indicated, unless it is of such general nature that indication is impracticable.

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Summary

The reactions of the imidchlorides PhCCl:NR (where R=Ph, Et or Me) with boron trichloride have been shown to give 1:1 adducts which, on the basis of their infrared spectra, are assigned ionic structures PhCNR^{+} , $\mathrm{BCl_4}^{-}$. When heated these nitrilium tetrachloroborates decompose irreversibly into benzonitrile - boron trichloride, PhCN, $\mathrm{BCl_3}$, and aryl or alkyl chloride RCl. Hydrolysis affords the amide PhCONHR, boric acid and hydrochloric acid. Features of the infrared spectra of the nitrilium salts are discussed and compared with the spectra of related compounds.

The imidchloride PhCCl:NCOPh also reacts with boron trichloride to give a 1:1 adduct, for which spectroscopic evidence of a covalent structure is presented.

Adducts of certain acid amides RCONHR and imides RCONHCOR with the Lewis acids $\mathrm{BCl_3}$, $\mathrm{BF_3}$ and $\mathrm{SnCl_4}$ have also been studied. In all cases where adducts were obtained, their infrared spectra were consistent with structures involving co-ordination through oxygen.

Attempts to prepare tetrachloroborates RCO^{+} , $\mathrm{BCl_4}^{-}$ from boron trichloride and certain acid chlorides RCOCl were unsuccessful.

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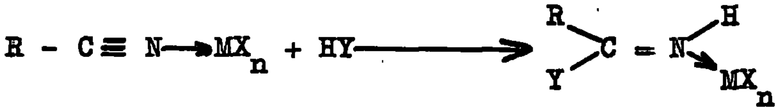
PART I

INTRODUCTION

Introduction

A general investigation of the addition reactions of nitrile adducts with Lewis Acids is being undertaken in these laboratories. Nitrile adducts RCN, MX_n (where MX_n is a Lewis Acid, normally a metal halide) appear to be capable of undergoing two distinct types of addition reactions (1-5):-

(a)



$$R-C\equiv N\rightarrow MX_n + HY \longrightarrow \begin{matrix}R\\Y\end{matrix}\!>\!C=N\begin{matrix}H\\ \searrow MX_n\end{matrix}$$

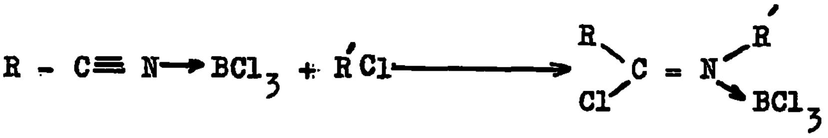
(b) $R-C\equiv N\rightarrow MX_n + R'Y \longrightarrow [R-C\equiv N-R']^+\ [MX_nY]^-$

where R = an organic group (alkyl or aryl) or hydrogen, and

Y = an electronegative group such as $-NR_2$, -OR or halogen.

When Y = $-NR_2$ or -OR, the reaction generally follows equation (a); when Y = halogen the general reaction is represented by equation (b); examples of types (a) and (b) are known (4,5).

This thesis is concerned with those systems having Y = halogen, particularly chlorine, and for which the Lewis Acid is BCl_3, i.e. a study of the possible reaction.



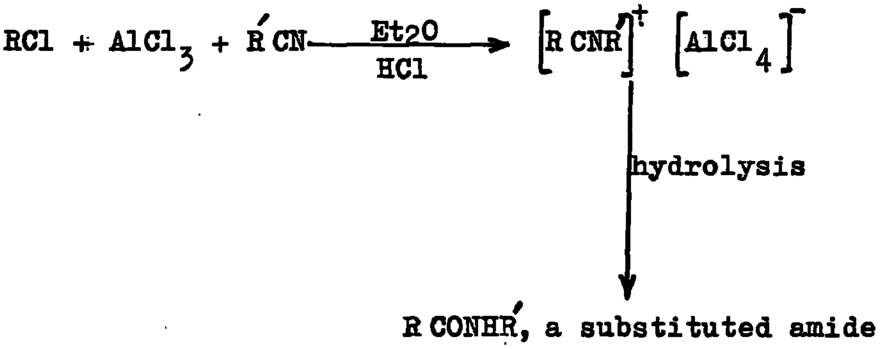
$$R-C\equiv N\rightarrow BCl_3 + R'Cl \longrightarrow \begin{matrix}R\\Cl\end{matrix}\!>\!C=N\begin{matrix}R'\\ \searrow BCl_3\end{matrix}$$

or

$$[R-C\equiv N-R']^+\ [BCl_4]^-$$

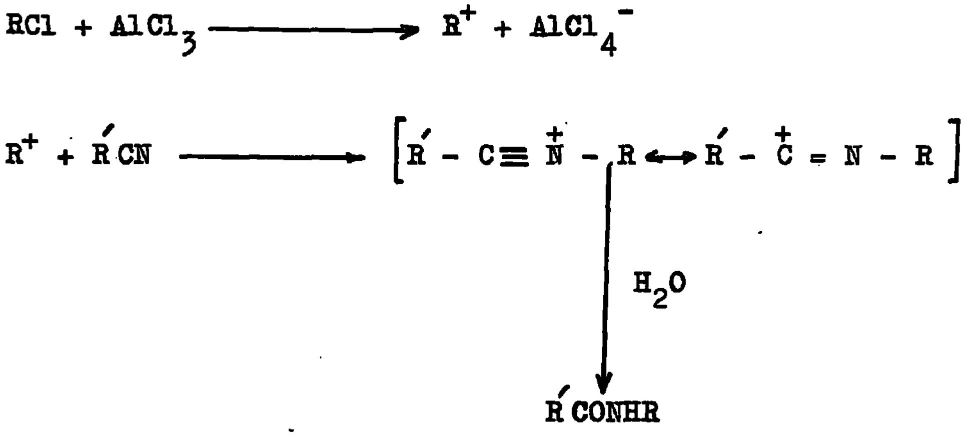
(A) Nitrilium Salts $RCNR^{+}\ MX_{n+1}^{-}$

Canon and Co-workers (1) first reported the N- alkylation of nitriles in the presence of aluminium trichloride.



$$RCl + AlCl_3 + R'CN \xrightarrow[HCl]{Et_2O} [RCNR']^{+}\,[AlCl_4]^{-} \xrightarrow{\text{hydrolysis}} RCONHR'\text{, a substituted amide}$$

where R = *n*-Cyclopentyl or *n*-Cyclohexyl groups and R' = aryl group. They proposed a simple carbonium ion type mechanism

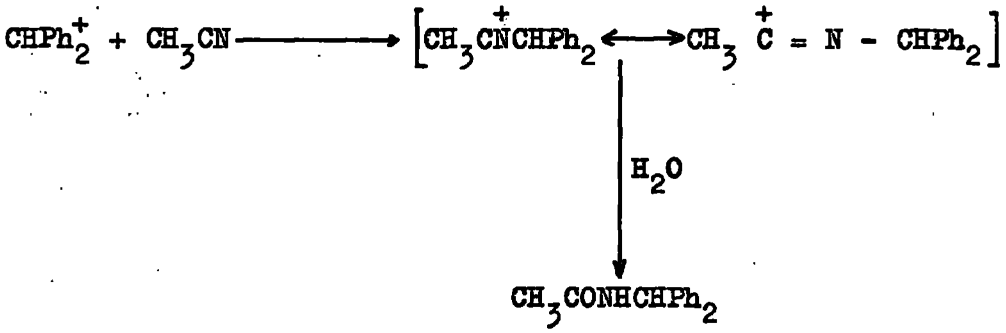


$$RCl + AlCl_3 \longrightarrow R^{+} + AlCl_4^{-}$$

$$R^{+} + R'CN \longrightarrow \left[R' - C \equiv \overset{+}{N} - R \longleftrightarrow R' - \overset{+}{C} = N - R\right] \xrightarrow{H_2O} R'CONHR$$

In the same year Cast and Stevens (2) reported a similar type of N-alkylation of nitriles with diphenylmethylbromide, but in the presence of silver sulphate instead of aluminium trichloride

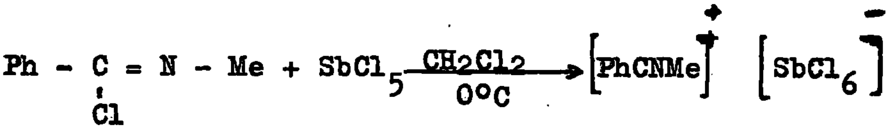
$$CH\ Ph_2Br + Ag^{+} \longrightarrow CHPh_2^{+} + AgBr$$



$$\mathrm{CHPh_2^+ + CH_3CN \longrightarrow \left[CH_3C\overset{+}{N}CHPh_2 \longleftrightarrow CH_3\,\overset{+}{C} = N - CHPh_2\right]}$$
$$\Big\downarrow \mathrm{H_2O}$$
$$\mathrm{CH_3CONHCHPh_2}$$

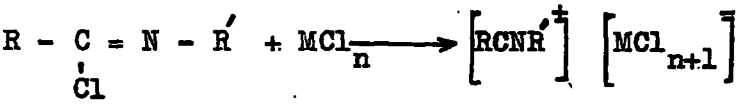
The reaction intermediate, N-diphenylmethyl acetonitrilium salt was not isolated but its presence was inferred from the nature of the hydrolysis product, N-diphenylmethylacetamide. A similar conclusion was reached by Davies and Co-workers in experiments using propionitrile (3).

Following these results attempts were made to isolate the proposed reaction intermediate and this was first successfully performed by Klages and Grill (4) using the reaction represented by the equation:-



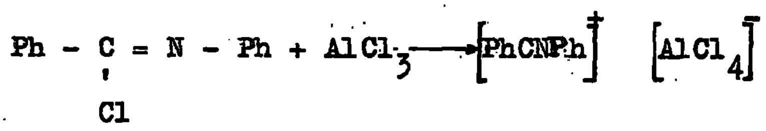
$$\mathrm{Ph - \underset{Cl}{C} = N - Me + SbCl_5 \xrightarrow[0^{o}C]{CH_2Cl_2} \left[PhCNMe\right]^{+} \left[SbCl_6\right]^{-}}$$

Since then similar and alternative routes for the formation of N-alkylnitrilium salts have been reported by Meerwein, Laasch, Mersch and Nentwing (5)



$$\mathrm{R - \underset{Cl}{C} = N - R' + MCl_n \longrightarrow \left[RCNR'\right]^{+} \left[MCl_{n+1}\right]^{-}}$$

e.g.



$$Ph-\underset{Cl}{C}=N-Ph + AlCl_3 \longrightarrow [PhCNPh]^{+}\ [AlCl_4]^{-}$$

$$Ph-C\equiv N\rightarrow SbCl_5 + C_2H_5Cl \longrightarrow [PhCNC_2H_5]^{+}\ [SbCl_6]^{-}$$

Direct N-alkylation of the nitrile with trialkyloxonium salts or with aryldiazonium salts are among the other various possible routes for the formation of nitrilium salts e.g.:-

$$[(C_2H_5)_3O]^{+}\ [AlCl_4]^{-} + PhCN \longrightarrow [PhCNC_2H_5]^{+}\ [AlCl_4]^{-} + (C_2H_5)_2O$$

$$[Ar.N{=}N]^{+}\ [BF_4]^{-} + RCN \longrightarrow [RCNAr]^{+}\ [BF_4]^{-} + N_2\uparrow$$

The possibility of preparing nitrilium salts containing an -NH group was demonstrated by Klages, Ruhnan and Hauser (6) in 1959.

$$(PhCN)_2,\ SnCl_4 \xrightarrow[\text{room temp.}]{\text{HCl (1 mole)}} (PhCNH)^{+}_2\ SnCl_6^{2-}$$

The salt structure of this latter compound being confirmed by conductivity measurements in liquid sulphur dioxide. However, when the same reaction was performed at 50°C, 2 moles of HCl were consumed per mole of nitrile with the formation of the benzimide hexachlorostannate.

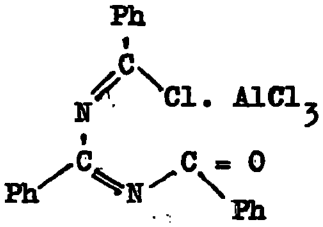
$$(PhCN)_2\ SnCl_4 \xrightarrow[50^{\circ}C]{HCl} (PhCCl{:}NH_2)^{+}_2\ SnCl_6^{2-}$$

In contrast to the direct N-alkylation of the nitriles, N-acylation has been found to yield only one stable nitrilium salt.

The only reported example is the isolation of N-benzoylbenzimide trichlorozincate, $\overset{+}{\text{PhCNCOPh}}$ $\overset{-}{\text{ZnCl}_3}$ from the reaction of the benzonitrile complex of zinc chloride and benzoyl chloride as reported Meerwein et al (5):-

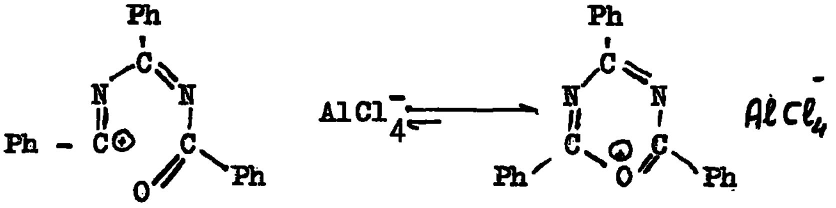
$$\text{PhCN} \rightarrow \text{ZnCl}_2 + \text{PhCOCl} \xrightarrow[5\ \text{min}]{150^{\circ}\text{C}} [\text{PhCNCOPh}]^{+} \quad [\text{ZnCl}_3]^{-}$$

P. Eitner and F. Kraft (7) in 1892 first investigated the reaction between benzonitrile, benzoyl chloride and aluminium trichloride, and showed that 2 moles of benzonitrile reacted with 1 mole of benzoyl chloride and 1 mole of aluminium trichloride. The structure (I)



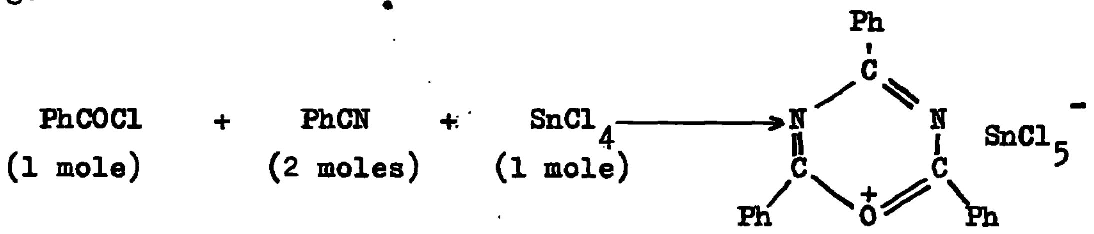
(I)

was assigned to the product. The modern interpretation of this reaction product favours the formation of a heterocyclic structure i.e.:-

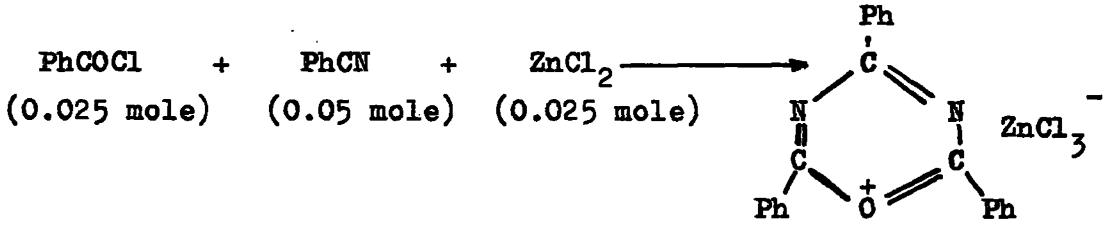


2, 4, 6-triphenyl - 3,5 diazapyrylium tetrachloroaluminate.

This has been shown to be generally true for other Lewis Acids in similar reactions in the recently reported work of Schmidt (8), e.g.:-

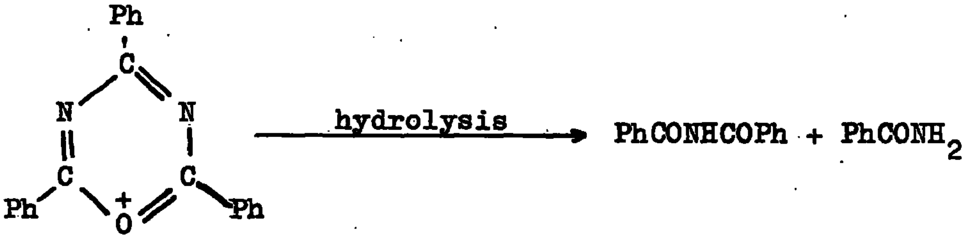


and



The nitrilium trichlorozincate A , and the pyrylium trichlorozincate B are crystalline products, the melting point of A is reported (5) to be 196-199°C while the latter melts at 184-188°C. These two types of product may easily be distinguished by examining the hydrolysis product in each case. The nitrilium salt would be expected to yield dibenzamide (m.pt. 148°C) quantitatively while the pyrylium salt would give two components, dibenzamide and benzamide.

$$\underset{\textstyle A}{PhCNCOPh^+,\ ZnCl_3^-} \xrightarrow{\text{hydrolysis}} PhCONHCOPh$$



B

The main requirements for the formation of these nitrilium salts appear to be that the Lewis Acid is strong and capable of forming a stable complex anion, MX_n^-.

Among the many reported examples of anions of nitrilium salts no mention is made of the tetrachloroborates. It was proposed therefore to investigate the possibility of preparing nitrilium salts of tetrachloroborate ion, $RCNR^+$, BCl_4^- or $RCNCOR^+$, BCl_4^-.

The problem can be approached in two ways:-

(a) Possible addition of HCl, $R'Cl$ or $R'COCl$ to RCN, BCl_3 adduct.
i.e.

$$RC\equiv N, BCl_3 + HCl \longrightarrow R-\underset{Cl}{\underset{|}{C}}=NH, BCl_3 \text{ or } RCNH^+, BCl_4^-$$

$$RC\equiv N, BCl_3 + R'Cl \longrightarrow R-\underset{Cl}{\underset{|}{C}}=NR', BCl_3 \text{ or } RCNR'^+, BCl_4^-$$

$$RC\equiv N, BCl_3 + R''Cl \longrightarrow R-\underset{Cl}{\underset{|}{C}}=NR'', BCl_3 \text{ or } RCNR''^+, BCl_4^-$$

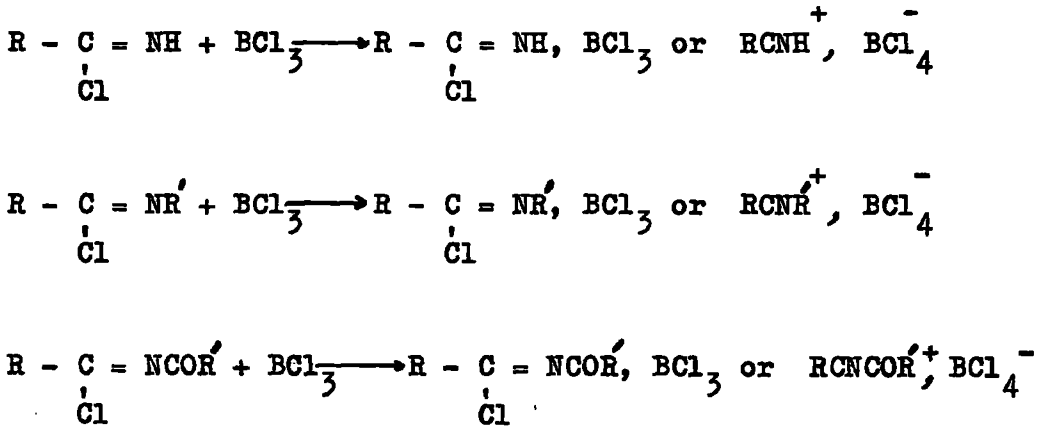
where R = alkyl or aryl

R' = aryl

and R'' = benzoyl or acyl group.

(b) An alternative route to the same products as above might possibly be the addition of boron trichloride to various N-substituted imidechlorides.

i.e.



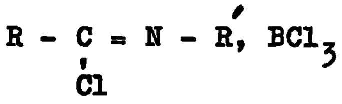
$$R-\underset{Cl}{C}=NH + BCl_3 \longrightarrow R-\underset{Cl}{C}=NH, BCl_3 \text{ or } RCNH^+, BCl_4^-$$

$$R-\underset{Cl}{C}=NR' + BCl_3 \longrightarrow R-\underset{Cl}{C}=NR', BCl_3 \text{ or } RCNR'^+, BCl_4^-$$

$$R-\underset{Cl}{C}=NCOR' + BCl_3 \longrightarrow R-\underset{Cl}{C}=NCOR', BCl_3 \text{ or } RCNCOR'^+, BCl_4^-$$

If a tetrachloroborate is not formed in these reactions, there is still the possibility that a covalent adduct might be formed, e.g.:-

Covalent adduct



$$R-\underset{Cl}{C}=N-R', BCl_3$$

or

Ionic adduct $\left[R-\overset{+}{C}=NR' \longleftrightarrow R-C\equiv\overset{+}{N}R'\right]\left[BCl_4\right]^-$

Infrared spectroscopy would be the most useful tool in distinguishing between these two possible structures. Vibrational bands due to the tetrachloroborate anion, BCl_4^-, have been recently well characterised as also the stretching frequency of $-C\equiv\overset{+}{N}-$ group (9, 10). In the case of a covalent adduct the only expected spectroscopic feature would be the lowering of the $-C = N-$ stretching frequency, while in the case of an ionic complex, in addition to a characteristic tetrachloroborate region, a new peak due to $-\overset{+}{C}\equiv N-$ should be observed.

(B) Tetrachloroborates, M^+, BCl_4^-

During the past few years there has been considerable interest in compounds containing the tetrachloroborate anion (12-20). Some of these are listed in tables I, II and III. Although the tetrafluoroborates are well established, relatively stable compounds, the other tetrahalogenoborate ions have been characterised only recently, and show decreasing stability in the order $BF_4^- > BCl_4^-$ $BBr_4 > BI_4^-$ (41).

The tetrachloroborate ion was first postulated in certain adducts of borontrichloride with halogen compounds (21-29). For example Wiberg (23) has reported a 1:1 complex of borontrichloride and triphenylmethyl chloride (correct analysis but no m.pt. below 200°C). Though not so identified this was the first ionic chloroborate having the structure $(Ph)_3C^+$, BCl_4^- (47).

TABLE I

Cations of Tetrachloroborate ion, BCl_4^-

No.	Cation R^+	Preparation a) Solvent b) Temperature c) Pressure	M.Pt. x°C (decomp.)	Characteristic Absorption Frequencies.	Ref.
1	NO	a) CF_2Cl_2 b) $-50^{\circ}C$ c) Normal	24-25	630-750 cm^{-1} (Vs, br.)	44,19
2	C_5H_5NH	a) CH_2Cl_2 b) $23^{\circ}C.$ c) Normal	118-121	630-750 cm^{-1} (Vs, br.)	28,45
3* (i) (ii) (iii)	K Rb Cs	a) - b) $400-500^{\circ}C$ c) 1 atm.	-	630-750 cm^{-1} (Vs, br.)	18,11

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*Heats of dissociation in the range 8-15 KCal as compared to 27-29 KCal for the corresponding tetrafluoroborates (46).

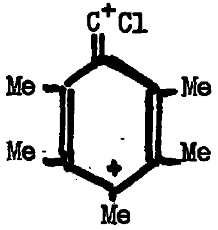
TABLE I

(continued.)

No.	Cation R^+	Preparation a) Solvent b) Temperature c) Pressure	M.Pt. x^oC (decomp.)	Characteristic Absorption Frequencies.	Ref.
4	NH_4	a) Chloroform b) r.t. c) -	166-170	649 (S), 665 (S), 694 (S), 722 (S).	17,31
5 (i)	Me_4N	Same as for 4.	264	665 (S), 695 (S), 723 (S), 667 (S), 693 (S), 718 (S).	
(ii)	Et_4N		222-224		
6 (i)	RNH_3 R = benzoyl	a) CH_2Cl_2 b) -80^oC c) -	-	630-750 (Vs, br.)	32
(ii)	R = cyclohexyl	Same as 6 (i)	142-143	630-750 (Vs, br.)	
7	C_7H_7	a) CH_2Cl_2 b) r.t. for 24 hrs. c) -	119-120	-	29

TABLE I

(continued.)

No.	Cation R^+	Preparation a) Solvent b) Temperature c) Pressure	M.Pt. x^oC (decomp.)	Characteristic Absorption Frequencies.	Ref.
	Ar_2N	a) -			
8	(Aryldiazonium)	b) -15°C	84-85	-	19
		c) Normal			
		a) Benzene		630-750 cm^{-1}	
9	$(Ph)_3C$	b) -15°C	200	(with maxima at	23,47
		c) Normal		667 & 695 cm^{-1})	
		a) Liquid SO_2			
*10		b) -	152-153	737-763 cm^{-1}	48
		c) -		(Vs, br.)	

* Trichloromethyl pentamethyl benzene.

TABLE II

Cations of Tetrabromoborate ion, BBr_4^-

No.	Cation R^+	Preparation a) Solvent b) Temperature c) Pressure	M.Pt. x°C (decomp.)	Characteristic Absorption Frequencies.	Ref.
1	C_5H_5NH	a) CH_2Cl_2 b) r.t.	140-142	590 cm^{-1}	28
2	NH_4	a) Chloroform b) 70°C	-	586, 607 cm^{-1} (S, br.)	17
3	$(Ph)_3C$	a) CH_2Cl_2 b) r.t.	150	590 cm^{-1}	49
4	C_7H_7	a) CH_2Cl_2 b) 0°C.	171-173	590 cm^{-1}	49
5	Ar_2N	a) Chloroform	82	-	19

TABLE III

Cations of Tetraiodoborate, BI_4^-

No.	Cation R^+	Preparation a) Solvent b) Temperature c) Pressure.	M.Pt. x°C (decomp.)	Characteristic Absorption Frequencies.	Ref.
1	C_7H_7	a) CH_2Cl_2 b) 20°C.	223	517 cm^{-1}	50,41
2*	$(Ph)_3C$	a) CH_2Cl_2 b) 20°C	-	-	50
3	C_5H_5NH	a) liquid anhydrous hydrogen iodide			
4	Me_4N		-	517 cm^{-1}	41,40
5	Et_4N				

* $(Ph)_3C^+,BI_4^-$ - viciously hygroscopic and is light sensitive. Satisfactory analysis could not be obtained.

Routes to simple chloroborate salts have generally involved high temperature and pressure (11), long milling of solids (17), or liquid hydrogen chloride (15, 16) solvent; and the products often gave unsatisfactory analysis. Exceptions include the synthesis of pyridinium chloroborate, $C_5H_5NH^+$, BCl_4^- from pyridinium chloride, $C_5H_5NH^+Cl^-$ and boron trichloride in methylene chloride (28) and of tropenium haloborate from cycloheptatriene and boron halide in methylene chloride (29, 30).

The preparation of K, Rb and Cs tetrachloroborates (11) have required high temperature and pressure and even under these conditions attempts to prepare lithium and sodium tetrachloroborates have been unsuccessful. Ammonium tetrachloroborates (31) were first prepared by the action of boron trichloride with alkylammonium chloride in boiling chloroform, the method was later improved by milling the chlorides at room temperature with glass beads in chloroform. Tetrachloroborates have also been obtained by a disproportionation following the reactions of certain primary and secondary amines with boron trichloride (32, 33).

Waddington and Klanberg first reported the conductivities of halides of groups III - V elements in anhydrous liquid hydrogen chloride (16, 17) in 1959. Some of the solutions thus obtained have such a high conductance that they closely resemble aqueous solutions of electrolytes. To account for the self-conductance of liquid hydrogen chloride, self ionisation is assumed,

$$HCl \rightleftharpoons H^+ + Cl^-$$

or allowing for solvation effects the equilibrium is perhaps better represented by:-

$$3HCl \rightleftharpoons H_2Cl^+ \ (37, 38) + HCl_2^- \ (34, 35, 36)$$

Tetramethylammonium chloride with hydrogen chloride gives the corresponding hydrogen dichloride,

$$Me_4NCl + HCl \longrightarrow Me_4N^+ + HCl_2^-$$

The high conductance of the solution indicates that Me_4NCl is a good chloride donor.

A graph illustrating the conductometric titration of Me_4NCl with boron trichloride is shown in FIG. I. The conductance of Me_4NCl varied uniformly with the molar ratio until a ratio of 1:1 was reached. The resulting tetramethylammonium tetrachloroborate, Me_4N^+, BCl_4^- was soluble in liquid hydrogen chloride but could be isolated upon evaporation of the solvent. The use of the ionising solvent was later extended to liquid hydrogen bromide (39, 40) and hydrogen iodide (40, 41) to aid the preparation of tetrabromo and tetraiodoborates, BBr_4^- and BI_4^- respectively.

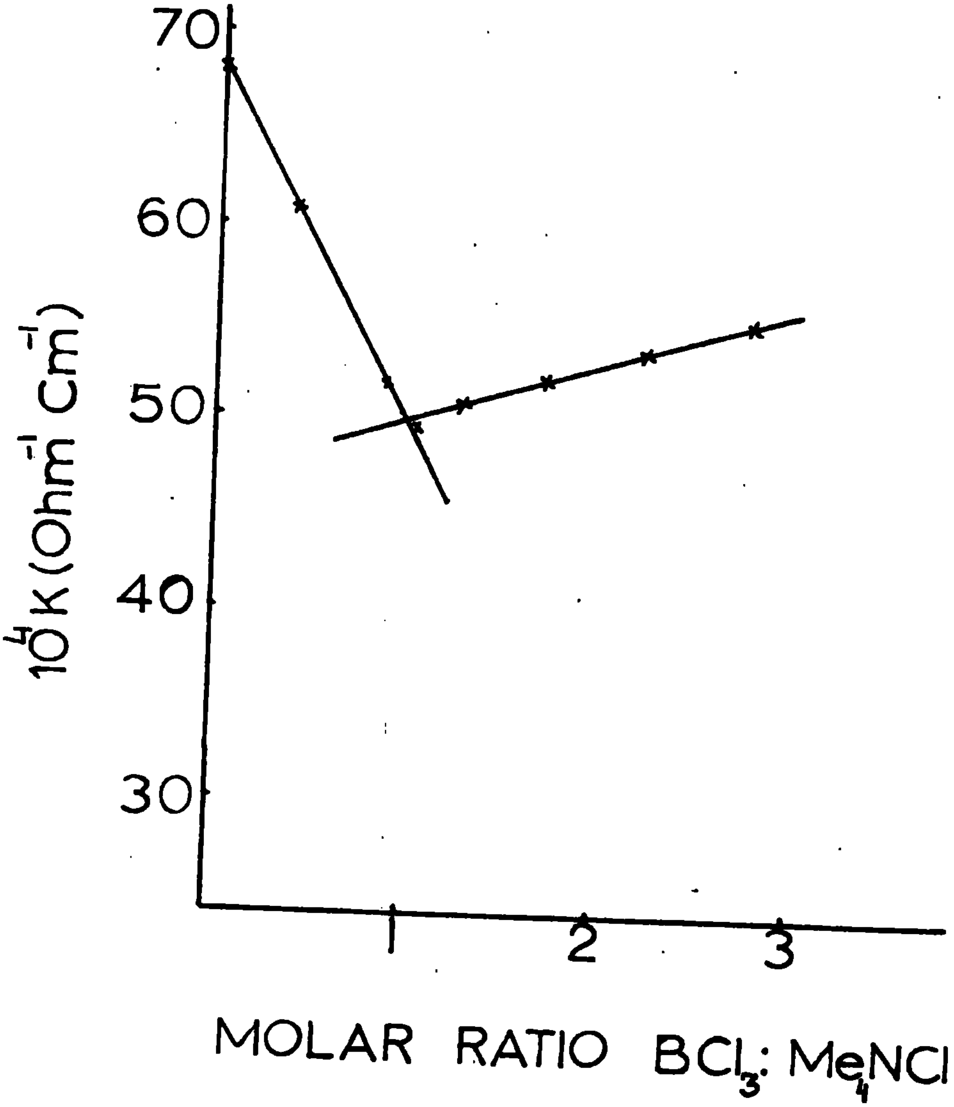
For a given cation Waddington observed the order of stability to be

$$BCl_4^- > BBr_4^- > BI_4^-$$

Tetraiodoborates tended to be light sensitive becoming purple on exposure to sunlight due to the release of iodine (41).

FIG. 1

CONDUCTOMETRIC TITRATION PLOT : ·32M-Me_4NCl + BCl_3.



The use of the Infrared spectroscopic data has aided in assigning characteristic frequencies to the tetrahalogenoborates. The infrared spectra of the tetrachloroborates of the following cations, Me_4N^+, Et_4N^+, $C_5H_5NH^+$, PH_4^+ and PCl_4^+ were recorded and the contribution of the BCl_4^- ion was identified by comparison with the infrared spectra of other salts with the same cations. The spectra showed a very broad strong band in the 630-750 cm^{-1} region, ($\Delta\nu_{\frac{1}{2}} \sim 120$ cm^{-1}) with the maxima at 699 and 664 cm^{-1} and three bands of medium intensity at 1449, 1382 and 1265 cm^{-1}. The last three bands fall in the region where CH deformation and CH_3 and NH_3 vibration occurs and are not easily recognised in ammonium salts. The frequencies and force constants are similar to those of the isoelectronic carbon tetrachloride.

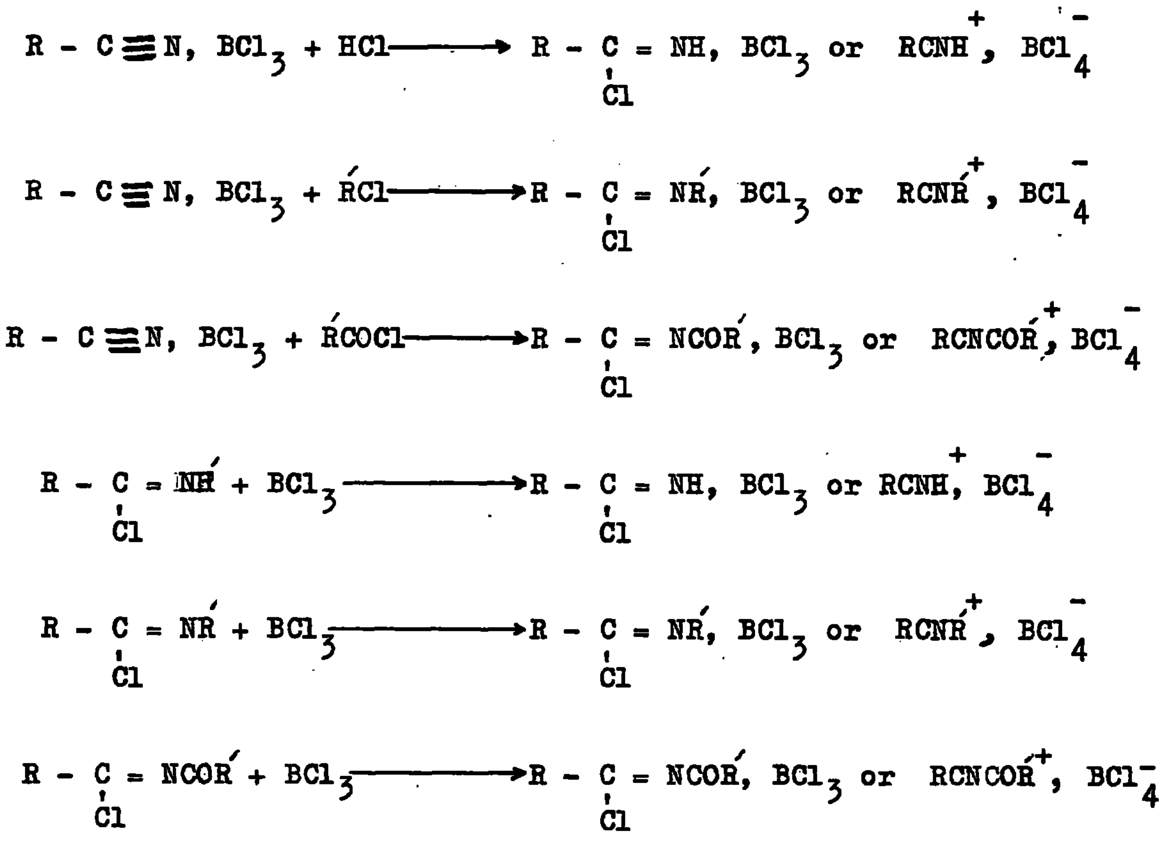
The tetrabromoborate ion, BBr_4^- has a strong and characteristic absorption at 593 cm^{-1} (39), this is very probably ν_3, the asymmetric stretching vibration. Similarly the characteristic absorption due to tetraiodoborate ion, BI_4^- is at 517 cm^{-1} (41). It is much less intense than the corresponding absorption in the tetrachloroborate and tetrabromoborate ions.

Some recent studies of vibration spectra of the ions BCl_4^- and BBr_4^- have been reported by Wynne and George (42) and Grieghton (43). All the fundamental vibration frequency of tetrachloro-and tetrabromoborates have now been obtained from Raman and Infrared measurements on solutions. The tetrachloroborate ion was studied in sulphur dioxide solution, while tetrabromoborate ion was examined in solution in methylene chloride as its ethyldi -

isopropylammonium salt, Et $\mathrm{Pr^i_2NH^+}$, since tetrabromoborate reacts rapidly with sulphur dioxide to form thionyl bromide and boric oxide. The values of υ_3, the boron-halogen stretching frequency, agree well with the published infrared spectral data (17).

(C) Object of Research

Investigation of the following and related types of reaction with the view to preparing nitrilium salts of the tetrachloroborate ion.



$$\mathrm{R-C\equiv N,\ BCl_3 + HCl \longrightarrow R-\underset{Cl}{C}=NH,\ BCl_3\ \ or\ \ \overset{+}{RCNH},\ \overset{-}{BCl_4}}$$

$$\mathrm{R-C\equiv N,\ BCl_3 + R'Cl \longrightarrow R-\underset{Cl}{C}=NR',\ BCl_3\ \ or\ \ \overset{+}{RCNR'},\ \overset{-}{BCl_4}}$$

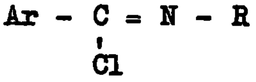
$$\mathrm{R-C\equiv N,\ BCl_3 + R'COCl \longrightarrow R-\underset{Cl}{C}=NCOR',\ BCl_3\ \ or\ \ \overset{+}{RCNCOR'},\ \overset{-}{BCl_4}}$$

$$\mathrm{R-\underset{Cl}{C}=NH' + BCl_3 \longrightarrow R-\underset{Cl}{C}=NH,\ BCl_3\ \ or\ \ \overset{+}{RCNH},\ \overset{-}{BCl_4}}$$

$$\mathrm{R-\underset{Cl}{C}=NR' + BCl_3 \longrightarrow R-\underset{Cl}{C}=NR',\ BCl_3\ \ or\ \ \overset{+}{RCNR'},\ \overset{-}{BCl_4}}$$

$$\mathrm{R-\underset{Cl}{C}=NCOR' + BCl_3 \longrightarrow R-\underset{Cl}{C}=NCOR',\ BCl_3\ \ or\ \ \overset{+}{RCNCOR'},\ BCl_4^-}$$

The obvious starting compounds would include PhCN, BCl_3, PhCCl:N Ph, and PhCCl:N CO Ph. Adducts of the related amides PhCONHPh and Ph CO NH CO Ph could also be prepared for comparison. These too would be new compounds. Further variations include the study of MeCN, BCl_3, MeCONHCOMe, Phthalimide and chloroderivatives of these.

In concluding the introduction it may be added that a reliable knowledge of the structure and chemistry of the stable N- alkyl or aryl nitrilium salt may be expected to improve our understanding of reactions which may involve nitrilium cations as reaction intermediate e.g.:- (the Beckmann rearrangement of oximes and derivatives, various alkylations of nitriles and reactions of the imidechlorides,  $Ar - \underset{Cl}{\overset{|}{C}} = N - R$ and sulphonate esters,

$$Ar - C(OSO_2R) = NR \quad).$$

References

Part I

1. Cannon, Grebber and Y.-K. HSU, J.Org.Chem. 1953, 18, 516
2. Cast and Stevens, J.Chem. Soc. 1953, 4180
3. Davies, Ramsay, and Stone, J.Chem.Soc. 1949, 2633.
4. Klages and Grill, Annalen 1955, 594, 21-32
5. Meerwein and Co-workers, Ber. 1956, 89, 209, 204.
6. Klages, Ruhnau and Hauser, Annalen 1959, 626, 60
7. P. Eitner and F. Krafft, Ber.dtsch,Chem.Ges. 1892, 25, 2267
8. R. R. Schmidt, Chem.Ber. 1965, 98, 334.
9. J. E. Gordon and G.C. Furrell, J.Org.Chem. 1959, 24, 269.
10. G. C. Turrell and J. E. Gorden, J.Chem.Phys. 1959, 30, 895.
11. E. L. Muetterties, J.Amer.Chem.Soc. 1957, 79, 6563.
12. A. B. Burge and E. R. Birnbaum, J.Inorg,Nucl.Chemistry 1958, 7, 146.
13. D. E. Burge, H. Freund and T. H. Norris, J.Phys.Chem, 1959, 63, 1969.
14. T. C. Waddington and F. Klanberg, Naturwiss 1959, 20, 578.
15. T. C. Waddington and F. Klanberg, J.Chem.Soc. 1960, 2329.
16. T. C. Waddington and F. Klanberg, J.Chem.Soc. 1960, 2332.
17. W. Kynastron, B. E. Larcombe and H.S. Turner, J.Chem.Soc, 1960, 1772.
18. E. L. Muetterties, J.Inorg.Nucl.Chem, 1960, 12, 355.

19. G. A. Olah and W. S. Tolgyesi, J.Org.Chem, 1961, 26, 2319.

20. Geuther, J.Prakt.Chem, 1874, 8, 354.

21. Meerwein and Maier-Hüser, J.Prakt.Chem, 1932, 134, 51.

22. N. N. Greenwood and K. Wade, J.Chem.Soc. 1956, 1527.

23. Wiberg and Heubaum, Z.Anorg.Chem, 1935, 222, 98.

24. Martin, J.Phys.Chem, 1947, 51, 1400.

25. Groeuerdeld, Rec.Trav.Chim, 1952, 71, 1152.

26. Lappert M.F, J.Chem.Soc, 1953, 2784.

27. Hewitt and Holiday, J.Chem.Soc, 1953, 530.

28. Lappert, Proc.Chem.Soc, 1957, 21.

29. K. M. Harmon, A.B. Harmon & F. E. Cummings, J.Chem.Soc, 1961, 83, 3912.

30. K. M. Harmon, A. B. Harmon, & F. E. Cummings, J.Chem.Soc, 1964, 86, 5511.

31. Kynastron and Turner, Proc.Chem.Soc, 1958, 304.

32. Gerrard and Mooney, Chem.Ind., 1958, 1259.

33. Gerrard and Mooney, Chem.Ind., 1959, 432.

34. Herbrandson, Dickenson and Weinstein, J.Am.Chem.Soc., 1954, 76, 4046.

35. West, J.Am.Chem.Soc., 1957, 79, 4568.

36. Sharp, J.Am.Chem.Soc., 1958, 2558.

37. Schisler and Stevenson, J.Chem.Phys, 1956, 24, 926.

38. Field and Lampe, J.Am.Chem.Soc, 1958, 80, 5583.

39. Waddington and White, Proc.Chem.Soc, 1960, 85.

40. Waddington and White, J.Chem.Soc, 1963, 2701-7.

41. Waddington and White, Proc.Chem.Soc, 1960, 315.

42. K. J. Wynne & J. W. George, J.Am.Chem.Soc, 1965, 87, 4750.

43. J. A. Greighton, J.Chem.Soc., 1965, 6589.

44. Partington and Whyne, J.Chem.Soc, 1949, 3135.

45. Gerrard and Lappert, Chem.Rev.1958, 58, 1081.

46. J. H. de Boer and J. A. M. Van Liempt, Rect.trav.chim, 1927, 46, 124.

47. Kemmitt, Milner and Sharp, J.Chem.Soc., 1963, 111.

48. Tetrahedron Letters 1962,983-6.

49. K. Harmon and A. Harmon., J.Amer.Chem.Soc, 1961, 865.

50. K. Harmon and Cummings, J.Am.Chem.Soc, 1962, 84, 1751.

PART II

EXPERIMENTAL METHODS.

(A) Materials and Manipulative techniuqes

Two methods have been used for the preparation of the boron halide co-ordination complexes discussed in this thesis. The first of these involved the direct addition of boron halide to the ligand in absence of solvent, and the second method used a solvent medium.

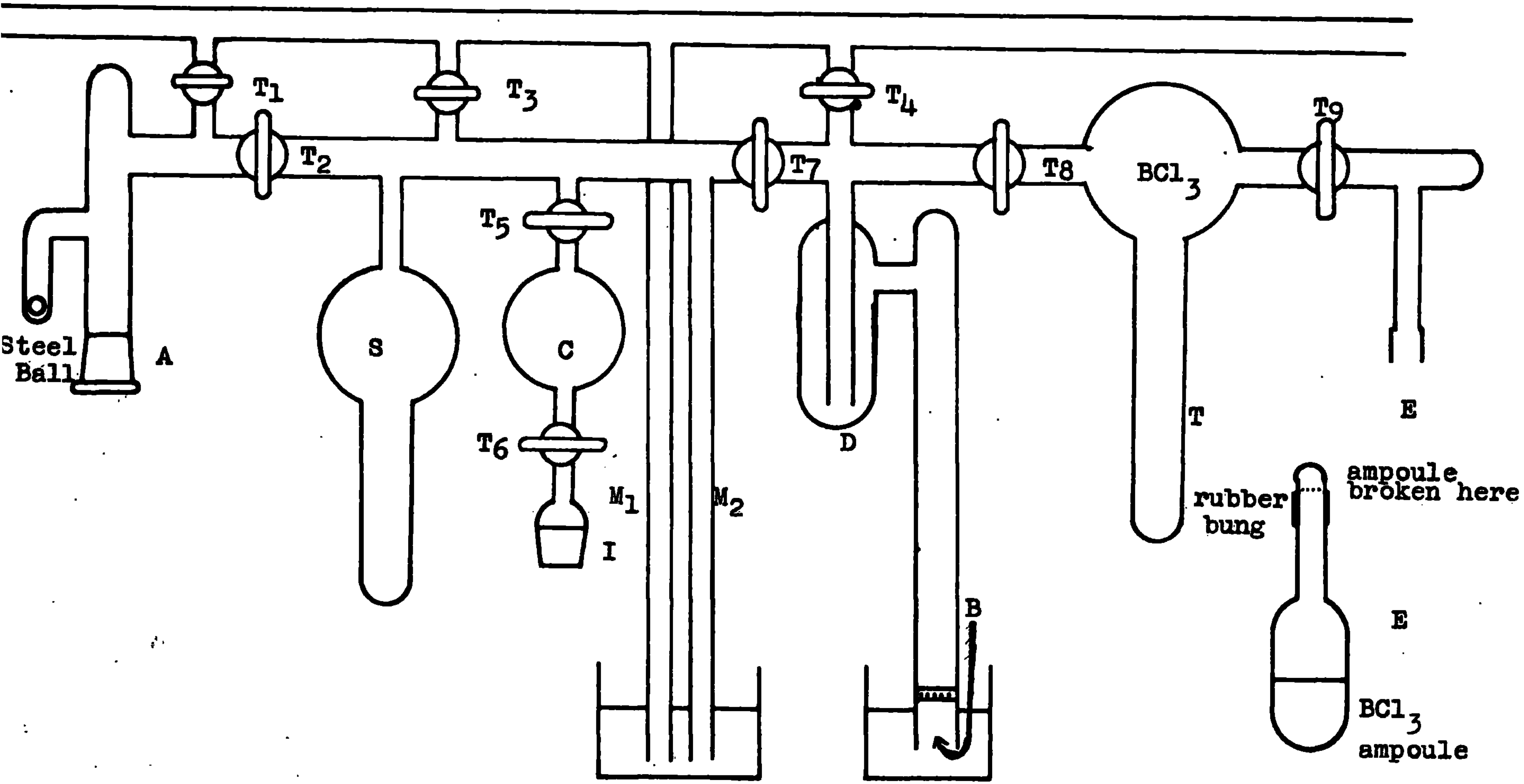
Method I - No Solvent

The apparatus used is illustrated in Fig. 2 and Fig. 3. Fig. 2 shows the detail of the reaction vessel. The ligand material is introduced through the side tube X which is then sealed. Attachment to the vacuum system is made at A (Fig. 3) through the ground glass joint B_{19}. After evacuation the vessel is filled with a measured quantity of boron halide and the vessel sealed at the point V. When the reaction is complete the vessel can be attached again to the vacuum system through the ground joint Z, and opened to the system by breaking the seal Y. A sintered glass disc is included at W in order to prevent loss of solid material from the reaction vessel by mechanical carry-over during the vacuum operations.

The main vacuum system (Fig. 3) included facilities for the introduction, storage and purification of reagent materials as well as a system for the accurate measurement of the quantity of reagent added to and removed from the reaction vessel.

FIG. 3

VACUUM LINE



The materials used were 50 gm. ampoules of BCl_3 (B.D.H. reagent quality) and BF_3 stored in a metal cylinder (Imperial Smelting Corporation). The BCl_3 was introduced into the system in the following way:-

A rubber bung was fitted closely to the neck of the ampoule (see inset Fig. 3), the content of which was then frozen solid. The top of the ampoule was cracked off and the bung immediately fitted into the ground joint E. After removal of air from the intervening tubing the BCl_3 was distilled from the ampoule by cooling the tube T in liquid air. The tap T_9 was closed and the vessel exhausted of residual air. The BCl_3 was allowed to volatise into the storage bulb and then frozen again and the air exhaustion repeated. This operation was repeated several times to ensure removal of all air from the system. The BCl_3 was then stored in the storage bulb, a capacity of 10 litres being available.

BF_3 was not stored in the system but was introduced in the following way as required:-

The BF_3 gas from the cylinder was bubbled through mercury at B, the vacuum system being closed at this point by a sintered glass disc impermeable to mercury but allowing free passage of the gas. The BF_3 was thus passed to the trap D, cooled in liquid air, which condensed out the BF_3, the trap being kept open to the pumps to remove entrained air. The BF_3 was further treated by trap to trap distillation; the sequence of traps used for this is not shown in the diagram.

Boron trifluoride was used direct from the cylinder without any further purification. The complexes analysed satisfactorily, therefore further purification of BF_3 through formation and subsequent decomposition of the benzonitrile-boron trifluoride adduct (vapour pressure at $-111.6^{\circ}C$, 301 mm), (1), was considered to be unnecessary.

The storage system was isolated from the measurement system through the tap T_7.

Measurement of the quantity of gaseous reagents used were made by P,V,T measurements in that part of the apparatus enclosed by taps T_2, T_3, T_6 and T_7. Pressure of gas in the system was measured by the manometers M_1 and M_2. The manometer M_1 was connected directly to the main vacuum line, and M_2 to the measurement volume, the difference in level between the mercury columns giving the pressure of gas enclosed. No meniscus corrections were applied as these were not considered necessary. The volume of the measurement system was calibrated using the gas pipette C, the volume of which was previously measured by determination of the weight of water which could be contained between taps T_5 and T_6. For calibration the tap T_6 was opened to dry air admitted through a $CaCl_2$ tube and the atmospheric pressure measured on a laboratory barometer. Tap T_6 was then closed and T_5 opened to admit the measured sample into the measurement volume. The final pressure being observed on the manometers

M_1 and M_2. The volume of the measurement system was then calculated.

Boron halide gas could then be introduced into the measurement volume and P,V,T measurements completed.

The reaction vessel attached at A was exhaused through tap T_1 which was then closed. Tap T_2 was opened and the reaction vessel cooled in liquid air to condense the boron halide into the vessel which was then sealed. After completion of the reaction the vessel was again attached at A, the seal broken by the steel ball and the excess of boron halide condensed into the measured volume by cooling the tube S. T_2 was then closed and after allowing the boron halide to volatalise into the measurement volume, pressure and temperature measurements were again taken. The measurements allowed one to calculate the amount of boron halide taken up by the ligand. Confirmation of this was obtained by also observing the gain in weight of the ligand.

Advantages of Solid-Gas reactions:-

(1) Analysis simple and direct.

(2) Manipulation in vacuum.

Disadvantages of Solid-Gas reactions:-

(1) Reaction is heterogenous and hence uncertain that reaction is complete.

(2) The product is generally non-crystalline.

These disadvantages suggested that homogenous reaction be tried - maintaining manipulation in isolation.

Advantages of reactions in a solvent medium:-

(1) The reaction is homogenous and therefore more likely to go to completion.

(2) The product is crystalline and therefore better characterised.

Disadvantages of reactions in a solvent medium:-

(1) The complete elemental analysis is required.

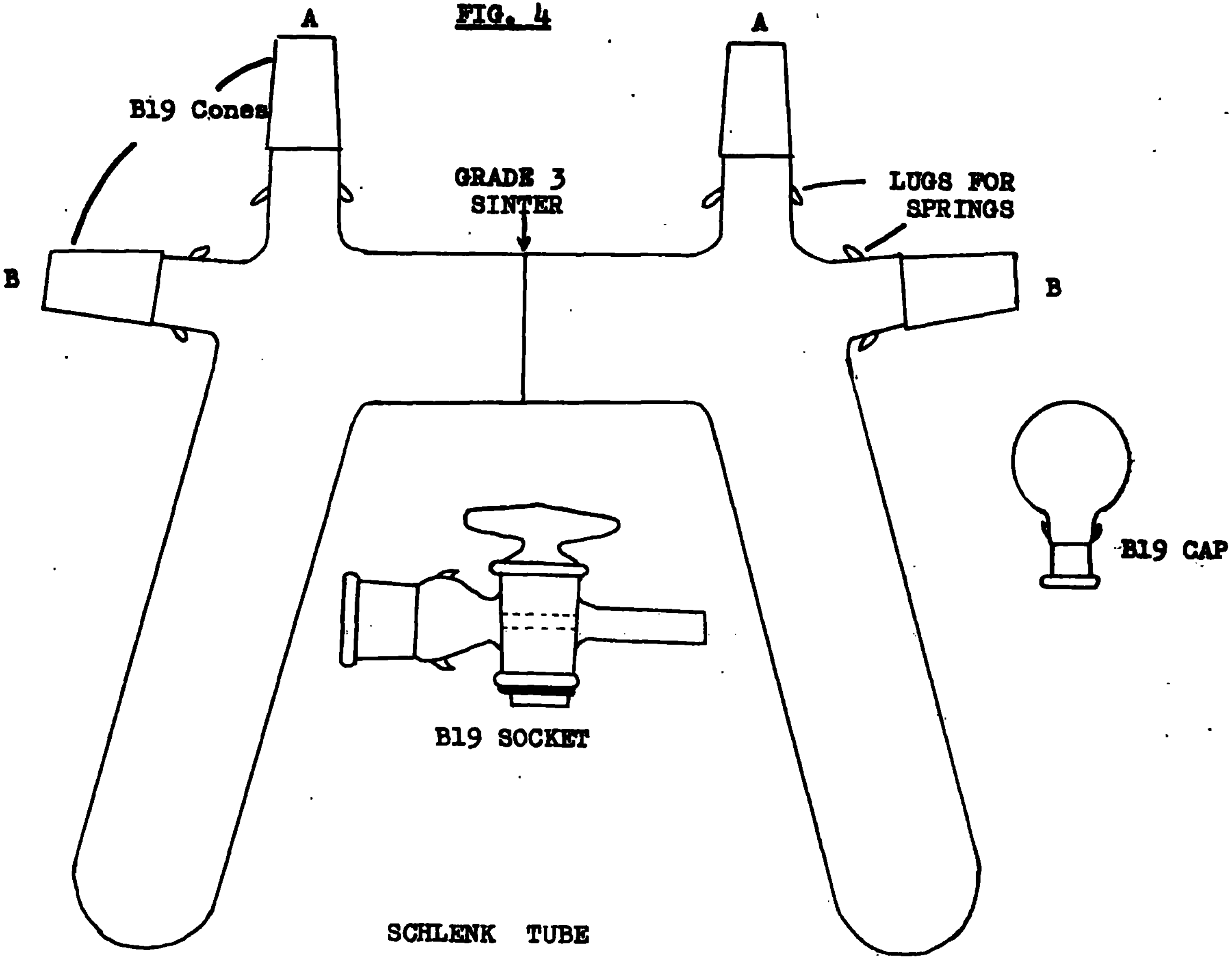
(2) It is more difficult to exclude water.

Method 2 - Solvent medium

The solution of the ligand material was introduced in one limb of a double Schlenk tube (31). The apparatus is illustrated in Fig. 4. Two B_{19} sockets with taps were fitted at B and two B_{19} caps at A (see insets Fig. 4). The Schlenk tube was continuously flushed with dry nitrogen. An excess boron halide was bubbled through the solution and after the reaction was complete the crystals of pure compound were collected, by filtration, on the glass sinter and dried in vacuo. Finally, although necks A are not co-axial with the limbs, solid can be readily removed from the bottom of these with a bent spatula. Compounds which were sensitive to the moist air were generally purified by recrystalliaation in a Schlenk tube of this type.

Manipulation of the complexes was generally performed in a dry box. The dry box was maintained with P_2O_5.

FIG. 4



SCHLENK TUBE

(B) Analysis:- Carbon and hydrogen were determined by using the Baird and Tatlock micro-combustion unit; whenever necessary, hygroscopic compounds were weighed into a boat in a dry box. For comparison purposes some carbon and hydrogen analyses were carried out by the microanalytical section of the chemistry department, Durham University, under the direction of Mr. T. Holmes.

Chlorine was determined gravimetrically as silver chloride. Since the complexes were generally very hygroscopic, these were hydrolysed in a closed vessel followed by the addition of silver nitrate solution.

Boron (2, 3) was determined in a sample of hydrolysate by preliminary neutralisation of any hydrochloric acid (using methyl-red), addition of excess mannitol, and titration to phenolphthalein end-point. The method was checked with a known mixture of pure boric and hydrochloric acid. Satisfactory results were obtained.

In a typical experiment, a small amount of solid was weighed accurately and dissolved in 20 mls of water. The liquid was diluted with 30 mls and gently warmed to eliminate any dissolved carbon dioxide. To keep the volume 30-35 ml, the hydro chloric acid was almost neutralised with N- NaOH to the first appearance of a yellow colour. 6 gms of mannitol were dissolved (the red colour of the indicator returning), and two drops of phenolphthalein added. The volume of N/10 NaOH necessary to produce distinct pink colour was noted and this corresponded to the boric acid present.

Aluminium (4) was determined gravimetrically by 8- Hydroxy Quinoline (oxine) method.

Nitrogen was determined by semimicro Kjeldahl method.

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(C) SPECTRA:- Infrared spectra in the range 650-4000 cm^{-1} were obtained from mulls of the various complexes in nujol using a unicam SP 100 mark 2 and SP 200 spectrophotometer. Wave length calibration was performed using a polystyrene film.

Abbreviations used for Infrared absorption frequencies:-

S - strong, VS - very strong, M - medium, W - weak,

VW - very weak, br. - broad, Sh - shoulder.

Due to moisture sensitivity of the complexes, a thick opaque mull of the complex was prepared in a dry box using a minimum amount of nujol and was sandwiched between sodium chloride windows. Sometimes the sample in the form of potassium bromide disc has also been used for less hygroscopic products. The SP 200 spectrophotometer was used only for qualitative work.

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(D.) Preparation of Potential Ligands

The commercially available amides, imides and anhydrides were purified by recrystallisation. The purity of the samples was checked by their melting point.

N- substituted benzamides, PhCONHR where R = CH_3, C_2H_5 and t.butyl $C(CH_3)_3$, were prepared by the Schotten-Baumann reaction (5).

$$PhCOCl + RNH_2 \text{ (aq. soln)} \longrightarrow PhCONHR + NaCl + H_2O$$

These were all further purified by recrystallisation from aq/alcoholic solution.

(a) Diacetamide, $(CH_3CO)_2NH$ (6)

A mixture of acetamide (50 gms.), freshly distilled acetic anhydride (102 gms.), and acetyl chloride (5 gms.) was refluxed for 45 minutes. Fractions of boiling point up to 125°C were removed by distillation at atmospheric pressure and the residue was distilled in vacuum. The fraction of boiling point 105°C/7 mm was collected and the crude diacetamide was purified by recrystallisation from dry ether. M.pt. was found to be 77-78°C (quoted 76-77°C) (7).

Analysis:- Found: C, 46.6; H, 6.80%

Calc. for $C_4H_7NO_2$: C, 47.6; H, 6.98%

I.R. Spectrum (7) - KBr disc

535 (M), 618 (M), 668 (VW), 746-769 (M. br.), 1022 (M), 1238 (VS), 1374 (S), 1422 (M), 1515 (VS), 1695 (M), 1745 (VS), 1854 (VW), 2717 (VW), 2959 (S), 3145 (S), 3215 (S), 3419 (M.br) cm^{-1}

(b) Dibenzamide, $(PhCO)_2NH$ (8)

Pure benzamide (30 g) was dissolved in 5 times its weight of freshly distilled pyridine. Purified benzoyl chloride (29 mls) was added gradually to this solution and the mixture was kept cool during addition. The deep red solution gradually deposited pyridine hydrochloride during a few hours. The mixture was then treated with water to remove most of the pyridine. An oil separated which was extracted with ether and this etheral solution was washed with dilute sulphuric acid to remove the remaining pyridine. White needles of dibenzamide immediately separated. The aq. solution obtained by shaking the original product with water slowly deposited long needles of dibenzamide. The crude product was recrystallised from pet. ether (b.pt. 100-120°C). The m.pt. was found to be 148°C (quoted 144° and 148-149°) (9). Recrystallisation from pet. ether gave very poor yields of dibenzamide. Toluene was found to be much more effective in that the yield and purity of the product was considerably improved.

Analysis:- Found: C, 74.20; H, 4.93 %

Calcd. for $C_{14}H_{11}NO_2$: C, 74.17; H, 4.90 %

I.R. Spectrum - KBr disc

609 (VS), 694, 689 (W. doublet), 709 (VS), 718 (VS), 779 (M), 789 (M), 806 (M), 960 (M), 977 (W), 1002 (M), 1028 (S), 1073 (S), 1128, 1118 (S. doublet), 1160 (W), 1181 (M), 1231 (VS), 1305 (W), 1448 (VW), 1475 (S. br.) 1500 (S), 1584 (W), 1602 (M), 1685 (VW), 1704 (VS), 3065 (W), 3125 (VW), 3240 (S).

(c) Benzanilide - imidchloride, PhCCl:NPh

This was prepared by the method described by Braun (10), using thionyl chloride as the chlorinating agent. Details are as follows:-

Purified benzanilide (1 mol.) and redistilled thionyl chloride (rather more than 1 mol.) was refluxed for an hour on the water bath. After one hour the dark yellow oil was distilled under vacuum. The fraction boiling point 158°C/5 mm was collected. The compound could not be recrystallised. The m.pt. was found to be 41-42°C (quoted 40°C and 40.5-42°C) (11). Since benzanilide-imidchloride is moisture sensitive, its reaction was carried out under dry nitrogen.

Analysis:- Found: Cl, 16.20 %

Calcd. for $C_{13}H_{10}NCl$: Cl, 16.47 %

Phosgene (12) and Phosphorous pentachloride (11) can also be used in the preparation of the above mentioned compound. Since the benzanilide imidchloride prepared by thionyl chloride analysed satisfactorily and the m.pt. agreed well with the literature value, the other two preparations were not attempted.

<u>I.R. Spectrum</u> - Nujol Mull

524 (W. br.), 553 (W), 603 (VS), 612 (VS), 641 (S), 659 (VS), 687 (VS), 761 (VS), 827 (S), 855 (VS), 921 (VS), 929 (S), 1000 (M), 1026 (S), 1075 (S), 1105 (VW), 1169 (VS), 1252 (S), 1316 (M), 1380 (VS), 1450 (VS), 1490 (S), 1532 (VW), 1593 (S), 1661 (VS), 2850 (M), 2920 (S), 3080 (M).

(d) N- methylbenzimidchloride and N- ethylbenzimidchloride
PhCCl:NR (R = Me or Et).

Two methods of chlorinating the respective N- substituted amides have been attempted:-

(a) Thionyl chloride Method (10)

N- alkylbenzamide PhCONHR (where R = CH_3 or C_2H_5) and rather more than 1 mole of thionyl chloride was heated on water bath. HCl and SO_2 gases evolved and after an hour the yellow oil was distilled under reduced pressure; fractions boiling 116°C/25 mm (when R = C_2H_5) and 70°C/3 mm (when R = CH_3) were collected.

(b) Phosphorous pentachloride Method (13)

Finely powdered PCl_5 and ethylbenzamide were mixed in molecular proportion. Gentle warming gave a greenish/yellow clear liquid. $POCl_3$ was then distilled off under reduced pressure and the imidchloride collected at 110-111°C/14 mm.

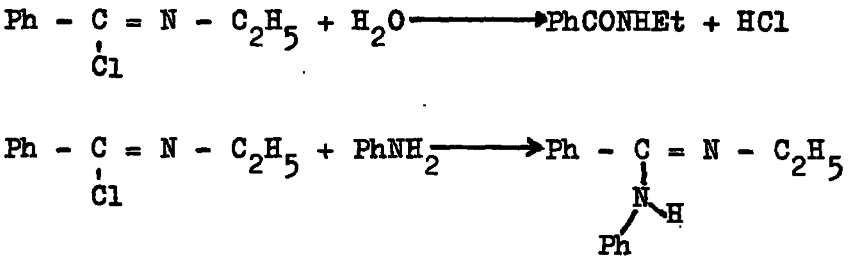
Analysis:- Found:- Cl, 22.90

Calcd. for C_8H_8NCl:- Cl, 23.10

Found:- C, 64.50; H, 6.37

Calcd. for C_9H_9NCl:- C, 64.46; H, 6.01

These imidchlorides are colourless, extremely hygroscopic liquids. Both reacted with cold water to give the respective N- substituted amides. Another way the identity of N- ethyl benzimidchloride was established was its reaction with aniline to give N- ethyl, N′ phenylbenzamidine, m.pt. 77-78°C (quoted 74-76°C).



$$Ph - \underset{Cl}{C} = N - C_2H_5 + H_2O \longrightarrow PhCONHEt + HCl$$

$$Ph - \underset{Cl}{C} = N - C_2H_5 + PhNH_2 \longrightarrow Ph - \underset{\underset{Ph}{N}\text{-}H}{C} = N - C_2H_5$$

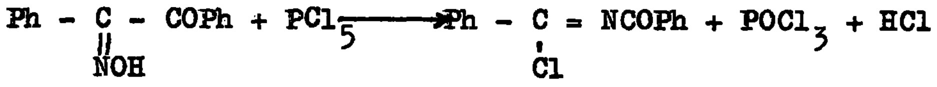
I.R. Spectrum of PhCCl: NCH_3 – Neat

673 (M), 690 (VS), 767.5 (VS), 810 (W), 880 (VS), 928 (M), 998 (VS), 1035 (S), 1083 (M), 1185 (S), 1210 (M), 1237 (VS), 1317 (M), 1340 (M), 1405 (S), 1453 (VS), 1492.5 (S), 1586 (M), 1600 (m), 1678 (VS), 1740 (M), 1780 (S), 2975 (S br.) 3072 (S).

(e) α-Chloro-N-Benzoylbenzimide, $Ph - \underset{Cl}{C} = NCOPh$ (14)

5 gms finely powdered dibenzamide and 7 gms of phosphorous pentachloride were treated with 40 mls dried chloroform and occasionally shaken. HCl gas was evolved and after an hour or so the reaction was complete. The resulting chloroform solution was diluted with 50 mls ether and shaken with iced water to remove any phosphoryl chloride. The solution was dried with magnesium sulphate and allowed to evaporate. Colourless needles separated. The crude product was recrystallised from light petroleum (b.pt. 60-80°C). The m.pt. was found to be 86°C (quoted 87°). (14) The yield was about 80%.

This compound was also prepared according to the method of Beckmann and Sandel (15). Rearrangement of benzilmonoxime was effected in presence of phosphorus pentachloride.



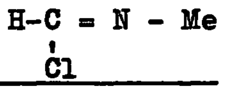
$$Ph - \underset{NOH}{\overset{}{C}} - COPh + PCl_5 \longrightarrow Ph - \underset{Cl}{C} = NCOPh + POCl_3 + HCl$$

The m.pt. was found to be 84°C (quoted 84°C) (15), however the yield was only 20%.

<u>I.R. Spectrum</u> - Nujol Mull.

650 (M), 678 (M), 685 (M), 720 (VS), 770 (S), 795 (S), 910 (VS), 1000(M), 1020 (S), 1045 (S), 1080 (W), 1100 (VW), 1175 (S), 1210 (VS) 1260(S), 1320 (S), 1380 (S), 1580 (W), 1600 (M), 1648 (VS), 1680 (W).

(f) N- Methylformimidchloride, $\mathrm{H{-}\underset{Cl}{C}{=}N{-}Me}$ (12)



4 mls of N- Methylformamide was added dropwise to a phosgene solution in benzene at ice temperature. A vigorous reaction takes place with the evolution of carbon dioxide. During one hour a white ppt. deposited which was filtered, washed twice with hexane and dried under vacuum. It is a hygroscopic solid, m.pt. 75-80°C.

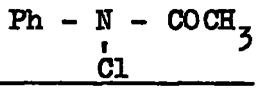
<u>Analysis</u>:-

Found:	Cl, 45.2 %
Calcd. for C_2H_4NCl:	Cl, 45.7 %

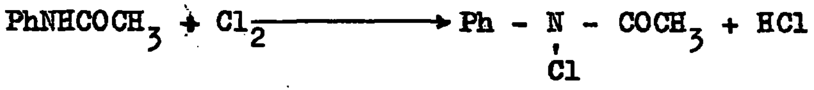
<u>I.R. Spectrum (SP 200)</u> - Nujol Mull

725 (S br. W Sh. around 760 cm^{-1}), 830 (M), 880 (S), 1020 (M), 1083 (S), 1140 (M), 1268 (S), 1500 (W), 1690 (VS).

(g) N- Chloroacetanilide (16), $\mathrm{Ph{-}\underset{Cl}{N}{-}COCH_3}$



Acetanilide was suspended in an excess of a solution of potassium bicarbonate. Domestos solution (17%) was added to the above suspension. A heavy ppt. deposited immediately, which was filtered and dried under vacuum. It was further purified by recrystallisation from a mixture of chloroform and ligroin. M.pt. 91°C.



$$\mathrm{PhNHCOCH_3 + Cl_2 \longrightarrow Ph{-}\underset{Cl}{N}{-}COCH_3 + HCl}$$

I.R. Spectrum - KBr disc

682 (M), 708 (VS), 776 (VS), 1045 (M br.), 1243 (S), 1330 (VS), 1370-1460 (br. maxima at 1400), 1500 (VS), 1560 (W), 1603 (S), 1700 (VS), 2148 (M), 2160 (S), 3055 (M), 3330-3550 (S br.)

(h) p-chloroacetanilide, $pClC_6H_4NHCOCH_3$

This compound was prepared simply by heating the N-chloroacetanilide with dilute acetic acid. On cooling long needles of p chloroacetanilide separated m.pt. 179-180°C.

I.R. Spectrum - KBr disc.

720 (M), 765 (M), 858 (S), 980 (W), 1030 (M), 1100 (M), 1190 (W), 1274 (M), 1330 (VS), 1415 (M br.), 1557 (VS), 1620 (VS), 1685 (VS), 2348 (S), 2365 (VS), 2930 (W br.), 3130 (M), 3193 (M), 3264 (M), 3300 (VS).

(i) Benzonitrile - boron trichloride Complex, PhCN, BCl_3

This adduct was prepared by the method of Gerrard, Lappert and Wallis (17). An excess of boron trichloride gas was bubbled through the benzonitrile solution in dry benzene at 0°C. The reaction was carried out under dry nitrogen in a Schlenk tube. White solid separated, which was filtered, washed with the solvent several times and finally dried at 20°C/1 mm. The adduct was further purified by recrystallisation from anhydrous toluene.

I.R. Spectrum - Nujol Mull

510 (VS), 557 (VS), 625 (W), 670 (S), 690-762 (S br. maxima at 706), 888 (M br.), 937 (M), 975 (M), 1000 (M), 1010 (W), 1026 (S), 1064 (M), 1096 (M), 1171-1174 (S doublet), 1300 (M), 1342 (W), 1377 (S), 1590 (S), 2317 (S), 2348 (W), 2423 (W).

(E) Attempted preparation of potential ligands:-

(a) N-Methylacetimidchloride, Me CCl: NMe (12)

(i) Phosgene route:-

10 gms of N- methylacetamide (B.D.H reagent) was dissolved in 100 ml carbon tetrachloride. This solution was kept at ice temperature while phosgene was bubbled through it. (Phosgene was available as a solution in toluene or benzene, 12.5% w/w, B.D.H. reagent in 100 ml ampoules. The gas was obtained by gently warming the ampoule). A white solid separated which was filtered and dried under vacuum. It is a hygroscopic solid, M.pt. 87-92°C (under sealed capillary tube).

Analysis:-		
	Found:	Cl; 19.20 %
	Calcd. for C_3H_6NCl:	Cl; 38.85 %

I.R. Spectrum (SP 200) - Nujol Mull

725 (S), 820 (S), 870 (S), 1015 (M), 1043 (S), 1150 (S br.) 1330 (W), 1540-1710 (S br. with maxima at 1640).

(ii) Thionyl chloride route:-

6.5 gms of N-Methylacetamide was dissolved in 100 ml. dry ether. 6ml of re-distilled thionyl chloride was added to this solution at ice temperature. A homogenous solution was obtained but immediately white crystalline solid separated. The solid was filtered, washed twice with pet. ether and finally dried under vacuum. It is slightly moisture sensitive, m.pt. 89-92°C.

Analysis:-

Found:	Cl, 19.40 %
Calcd. for C_3H_6NCl :	Cl, 38.85 %

Its infrared spectrum was identical with the product from reaction (i).

(b) N-Methylacetamid hydrochloride, $(CH_3CONHCH_3)_2.HCl$ (18, 19).

Hydrochloric acid gas was bubbled through a solution of N-methylacetamide in dry ether at ice temperature. A white solid separated, which was filtered, washed twice with ether and finally allowed to dry under vacuum. It is a hygroscopic solid, m.pt. 89-92°C (quoted 87-89°C).

Analysis:-

Found:	Cl, 19.40 %
Calcd. for $C_6H_{15}ClNO$:	Cl, 19.43 %

Infrared spectrum was identical to the reaction products of (i) and (ii).

The reaction product from above was shown to be a hydrochloride of the dimer, $(CH_3CONHCH_3)_2.HCl$ by treating it with water, followed by the addition of potassium bicarbonate. A vigorous reaction ensued with the evolution of carbon dioxide -

a typical reaction of a hydrochloride. After the reaction had subsided the liquid was treated with ether and the etheral layer was evaporated to dryness. Large crystals deposited, which were identified as N-Methylacetamide by their infrared spectrum.

In a similar experiment, except alcohol was used instead of water, the final product was found to be the same as above.

$$2(CH_3CONHCH_3)_2.HCl + K_2CO_3 \text{ (aq. or alc.)}$$
$$\xrightarrow{\qquad\qquad} 4CH_3CONHCH_3 + KCl + H_2O + CO_2$$

(c) N-t.Butylbenzimidchloride, $PhCCl{:}NBu^t$

In a similar manner to the preparation of the other N-substituted benzimidchlorides (10) an attempt was made to prepare the t- butyl benzimidchloride as follows:-

7 gms of t. butylbenzamide, $PhCONHBu^t$ and rather more than 1 mole of re-distilled thionyl chloride were refluxed on the water bath for an hour. After the evolution of HCl and SO_2 gases had stopped the solution was distilled under vacuum. The liquid was collected at   /mm. The yield was quantitative. The spectrum of the colourless liquid was recorded and was found to be identical to the spectrum benzonitrile.

$$PhCONHC(CH_3)_3 + SOCl_2 \xrightarrow{\qquad\qquad} PhCN + SO_2 + HCl$$
$$+ (CH_3)_3CCl.$$

(d)N-Phenylacetimidchlor~~die~~ide:- via Phosgene method (12)

Phosgene gas was obtained as described on page and was used without any further purification. This gas was then bubbled through a solution of acetanilide in dry chloroform at 0°C. A white precipitate separated which was washed a few times with the solvent. The product was filtered and dried under vacuum. It is a slightly hygroscopic, white solid, m.pt. 124-126°C.

Analysis:- Found:- C, 61.8; H, 5.87;
Cl, 13.2%
Calcd. for C_8H_8NCl:- C, 62.5; H, 5.24;
Cl, 23.1 %

I.R. Spectrum - Nujol Mull

695 (S), 725 (M), 745 (S), 770 (S), 798 (S), 830 (W), 850 (W), 865 (W), 877 (W), 928 (S), 990 (VS with steps at 1050 (M), 1080 (M)), 1165 (M), 1238 (M), 1282 (M), 1293 (W Sh), 1315 (M), 1352 (M), 1493 (M), 1537 (S), 1575 (W), 1600 (S), 1663 (S), 2300 (S), 220 (W. Sh).

Since other imidchlorides (10) are easily prepared by the thionyl chloride route, an attempt was made to prepare the N-phenylacetimidchloride via this route.

5 gms of acetanilide were dissolved in 100 ml dry chloroform. 2.7 mls of thionyl chloride were gradually added to this solution at 0°C. There was an immediate reaction resulting

the separation of a white product. This was collected on a filter, washed twice with ether and dried under vacuum. It is slightly hygroscopic, m.pt. 121.5-123.5°C. Lassaignes test showed the presence of nitrogen and chlorine, but sulphur was absent.

Analysis:- Found:- C, 62.0; H, 5.93;
Cl, 13.32 %
Calcd. for C_8H_8NCl:- C, 62.5; H, 5.24;
Cl, 23.1 %

Infrared spectrum was found to be identical to the product obtained via phosgene route.

PART III

EXPERIMENTAL RESULTS

1. Addition reactions of chlorides with nitrile adducts

(A) Benzonitrile-boron trichloride complex and HCl Gas.

HCl gas was produced by dropwise addition of concentrated H_2SO_4 to concentrated HCl and dried by passing it through concentrated sulphuric acid. The gas was then bubbled through a solution of PhCN, BCl_3 in toluene for 2 hours under dry nitrogen atmosphere. A solid separated, which after washing several times with hexane was filtered and dried under vacuum at 24°/1 mm. The spectrum of the solid was identical to that of PhCN,BCl_3 complex.

(B) PhCN,BCl_3 complex and acetyl chloride.

This reaction was carried out on the vacuum line. To 1.1991 gms (5.45 millimole) of PhCN,BCl_3 in a break seal tube were 0.461 gms (5.86 millimole) of acetyl chloride. The reaction vessel was left for 12 hours at room temperature. The white PhCN,BCl_3 complex had dissolved in acetyl chloride giving a yellow solution. When excess acetyl chloride was recovered under vacuum the complex changed to reddish brown colouration. All the acetyl chloride was recoverable. Infrared spectrum of the product was similar to that of the PhCN,BCl_3 complex.

(C) PhCN,BCl_3 complex and benzoyl chloride

A molar quantity of benzoyl chloride was added to a solution of the complex in toluene. A solid separated, which was filtered and dried under vacuum. The infrared spectrum was identical to $PhCN,BCl_3$ adduct.

(D) Reaction of p chlorobenzoylchloride, $pClC_6H_4COCl$ benzonitrile and boron trichloride

2.93 gms (0.025 mol.) boron trichloride gas was condensed on to a mixture of 5.15 gms (0.05 mol.) benzonitrile and 4.5 gms (0.025 mol.) of p chlorobenzoylchloride in a reaction vessel. The reaction vessel was sealed off. A solid separated from a yellow liquid. The solid and the liquid were separated in the Schlenk tube under dry nitrogen atmosphere. The solid was filtered and dried under vacuum at 23°C/1 mm. The infrared spectrum of the solid was found to be identical to that of the $PhCN,BCl_3$ complex. The spectrum of the liquid indicated the presence of p chlorobenzoylchloride and benzonitrile.

$$\text{p Cl } C_6H_5COCl + C_6H_5CN + BCl_3 + C_6H_5CN$$

$$\longrightarrow \text{p Cl } C_6H_5COCl \ \& \ C_6H_5CN \text{ mixture} + C_6H_5CN,BCl_3$$

(E) Reaction of chlorobenzene, benzonitrile and aluminium trichloride

2.245 gms (0.02 moles) of chlorobenzene and 2.06 gms (0.02 moles) of benzonitrile were mixed together with 20 mls of O dichlorobenzene in a Schlenk tube. 2.67 gms (0.02 moles) of anhydrous aluminium trichloride were added to this solution and the solution was heated gently until all the aluminium trichloride dissolved. The solution was then cooled in an ice-bath for a few minutes. The addition of the pet. ether to this solution deposited a yellow solid. This was further washed six times with pet. ether, filtered and dried under vacuum. It is a light yellow solid which can be recrystallised from anhydrous toluene. It is an extremely hygroscopic product, does not melt but starts decomposing at 90°C.

<u>Analysis</u>:- Found: Cl, 30.80 %

Calcd. for $C_{14}H_{10}N_2AlCl_3$: Cl, 31.30 %
(20,21,22).

<u>I.R. Spectrum</u> - Nujol Mull recorded on SP200

680 (S), 760 (VS), 800 (W), 825 (M), 920 (M), 1005 (W), 1027 (S), 1040 (S), 1128 (S), 1155 (W), 1180 (S), 1205 (M), 1300 (S), 1603 (VS)), 1625 (S), 2310 (VS), 2410 (M).

The complex reacted vigorously with water giving off HCl gas. The resulting solution which had two layers, was shaken with dry ether and the etheral layer was dried with $MgSO_4$ and finally allowed to evaporate under vacuum. The residue was a clear liquid which was identified as benzonitrile by its infrared spectrum.

$$(Ph\ CN)_2,\ AlCl_3 + \text{excess } H_2O \longrightarrow 2PhCN + Al(OH)_3 + HCl$$

2. Reactions of the following ligands with boron trichloride:-

(A) p chlorobenzoylchloride, p Cl C_6H_4COCl

5.36 gms (45.8 millimoles) of boron trichloride gas was condensed on 6.3007 gms (36 millimoles) of p chlorobenzoylchloride in a reaction vessel. The reaction vessel was left at room temperature for three days, during which time a homogenous solution was obtained. All the boron trichloride was found to be recoverable. Hence it appears that under these conditions there is no reaction.

(B) 3:5 dinitrobenzoyl chloride, 3,5 $(NO_2)_2C_6H_3COCl$

3.55 gms (30.3 millimole) of boron trichloride was condensed on to 2.2700 gms (9.85 millimole) of 3:5 dinitrobenzoyl chloride in a reaction vessel. The reaction vessel was gradually allowed to warm to room temperature. The texture of the light yellow 3,5 dinitrobenzoyl chloride remained unchanged and after two weeks time the excess boron trichloride was removed under vacuum. All BCl_3 was found to be recoverable, the gas spectrum indicated no other component except pure boron trichloride.

After the failure of this solid-gas reaction, a solution reaction (chloroform as solvent) was attempted in a Schlenk tube. Excess BCl_3 was bubbled through the solution of 3,5 dinitrobenzoyl chloride. No solid product deposited and after removal of the solvent under vacuum the parent compound was obtained.

(C) (a) Triphenylmethylchloride, $(Ph)_3CCl$

Triphenylmethylchloride(23)(B.D.H. reagent) was further purified by recrystallisation (24) from dry benzene. An excess of boron trichloride gas was bubbled through a solution of triphenylmethyl chloride (m.pt. 110-112°C Lit.^{25}value 109-111°C) in petroleum ether (80-100°C range) at ice temperature in a Schlenk tube under dry nitrogen. A deep yellow ppt. deposited which was further washed four times with pet. ether to give a brilliant bright yellow product. The product was finally filtered and dried under vacuum for a few hours. It is an extremely hygroscopic solid, m.pt. $>$ 200°C.

Analysis:-			
	Found:-	B, 2.50;	Cl, 35.40%
	Calcd. for $C_{19}H_{15}BCl_4$:-	B, 2.73;	Cl, 35.85%

I.R. Spectrum - Nujol Mull

621 (S), 662, 700 (S br.), 726 (W), 767 (S), 804 (S), 838 (S), 916 (M), 949 (M), 978 (S), 998 (S), 1012 (M), 1041 (W), 1063 (S), 1095 (S), 1102 (S), 117 (S), 1180 (M), 1297 (S), 1359 (S), 1451 (S), 1480 (S), 1580 (S), 2950 (W).

The complex reacted vigorously even with cold water to yield triphenyl carbional, $(Ph)_3OH$, identified by m.pt. (165°C) and infrared spectrum.

$$(Ph)_3\overset{+}{C}\ ,\ \ \overset{-}{BCl_4}\ + 4H_2O\ \ (\text{excess})$$

$$\xrightarrow{\qquad\qquad} (Ph)_3OH + B\,(OH)_3\ + 4HCl$$

(c) (b). Triphenylmethyl chloride, $(Ph)_3CCl$ - no solvent.

2.445 gms (20.90 millimoles) of boron trichloride was allowed to come in contact with 3.05 gms (10.93 millimoles) of finely powdered triphenylmethyl chloride in a reaction vessel on the high vacuum line. The white triphenylmethyl chloride immediately changed to a uniform brilliant bright yellow colouration. All the boron trichloride was then condensed on it by liquid air and finally the reaction vessel was sealed off and left at room temperature. After a period of two days, excess boron trichloride was removed on the vacuum line, leaving the yellow product. The amount of boron trichloride which reacted with triphenylmethyl chloride was found to be 0.613 gms (5.23 millimoles) i.e. only 5.23 millimoles of BCl_3 reacted with 10.93 millimoles of $(Ph)_3CCl$

(D) N- chloroacetanilide, MeCON(Cl)Ph

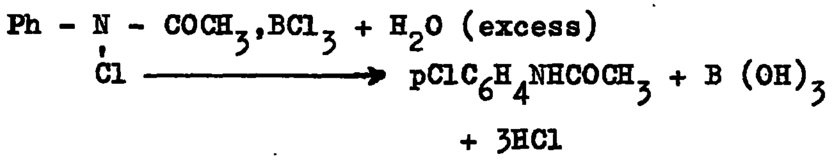
An excess of boron trichloride was bubbled through a solution of N-chloroacetanilide in chloroform at 0°C. An oily layer formed which on shaking vigorously for a few minutes resulted in a heavy precipitate. The product was dried under vacuum. It is a white hygroscopic solid, M.Pt. 136°C (at 140°C it started swelling in a sealed tube).

Analysis:-	Found:- ionisable Cl, 36.71; B, 3.62%
$C_8H_8NCl_4OB$ requires:-	ionisable Cl, 37.15; B, 3.76%

<u>I.R. Spectrum</u> - KBr disc

737 (S), 785 (M), 845 (S), 1025 (W Sh.), 1053 (VS), 1100 (S), 1210 (M), 1260 (M), 1308 (M), 1340 (VW), 1362 (M), 1417 (S), 1455 (S), 1502 (VS), 1550 (S), 1590 (S), 1630 (VS), 1650,1655 (w steps), 3190 - 3370 ($\nu_{1/2} \sim 180$) [S br. with maxima at 3270 cm^{-1}].

On treatment with water, N chloroacetanilide boron trichloride adduct gave needle shaped crystals which were identified as p chloroacetanilide, m.pt. 179-180°C.



$$\mathrm{Ph - \underset{Cl}{N} - COCH_3{,}BCl_3 + H_2O\ (excess) \longrightarrow pClC_6H_4NHCOCH_3 + B(OH)_3 + 3HCl}$$

(E) <u>p chloroacetanilide, $pClC_6H_4CONHCH_3$</u>

An excess of boron trichloride gas was bubbled through a suspension of p-chloroacetanilide in methylene chloride. A white crystalline product separated which was filtered and dried under vacuum. The product melts at 156-158°C with decomposition.

<u>Analysis</u>:- Found:- ionisable Cl, 36.75;
B , 3.78%

$C_8H_8NCl_4OB$ requires:- ionisable Cl, 37.15;
B , 3.76%

I.R. Spectrum - KBr disc

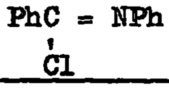
737 (S), 785 (M), 845 (S), 1025 (W Sh.), 1053 (VS), 1100 (S), 1210 (M), 1260 (M), 1308 (M), 1340 (VW), 1362 (M), 1417 (S), 1455 (S), 1498 (S), 1548 (S), 1585 (S), 1630 (VS), 1650, 1668 (W steps), 2350 (W), 2365 (M), 3160-3297 (S br. with maxima at 3225), 3280 (VW) cm^{-1}.

The complex reacted vigorously with water and the solid product was identified as p-chloroacetanilide, m.pt. 179-180°C.

$$\mathrm{p\ ClC_6H_4NHCOCH_4,BCl_3 + H_2O}\quad \text{(excess)}$$

$$\xrightarrow{\qquad\qquad} \mathrm{pClC_6H_4NHCOCH_3 + B(OH)_3 + 3HCl}$$

(3) Addition reaction of Imidchlorides



(A) Benzanilide-imidchloride, $\underset{\mathrm{Cl}}{\mathrm{PhC}} = \mathrm{NPh}$ and BCl_3

An excess boron trichloride gas was bubbled through a solution of benzanilide-imidchloride in o-dichlorobenzene in a Schlenk tube under dry nitrogen atmosphere at 0°C. A heavy ppt. immediately separated. The complex filtered, washed twice with carbon tetrachloride and was dried under vacuum at 20°C/1 mm. It is a very light pinkish hygroscopic solid, m.pt. 154° (decomp.).

Analysis:- Found: C, 45.7; H, 3.14; B, 3.20, 3.23
Cl, 42.5%

$C_{13}H_{10}NCl_4B$ requires: C, 46.8; H, 3.04; B, 3.26; Cl, 42.7%

I.R. Spectrum - Nujol Mull

492 (M br.), 531 (S), 550 (M br.), 602 (M), 616 (M), 719, 694 676 (VS br.), 763 (VS), 800 (M), 835 (VW), 883.5 (M), 943, 926 and 917 (M br.), 971 (M), 1000 (M), 1026 (M), 1094 (VW), 1124 (W), 1166 (M), 1176 (M), 1190 (W), 1261 (S), 1294 (W), 1572,(1592 (M br), 1613 (M), 1667 (M), 2318 (S), 2353 (W), 2855 (S).

Reaction with Water:-

The complex reacted vigorously even with cold water. Hydrochloric acid gas evolved and the residue was identified as benzanilide by its m.pt. (163°C) and infrared spectrum.

$$\left[\mathrm{Ph} - \mathrm{C} \equiv \overset{+}{\mathrm{N}} - \mathrm{Ph} \longleftrightarrow \mathrm{Ph} - \overset{+}{\mathrm{C}} = \mathrm{N} - \mathrm{Ph}\right] + \mathrm{BCl}_4^- \xrightarrow{\mathrm{H_2O\ (excess)}} \mathrm{PhCONHPh} + \mathrm{B(OH)_3} + 4\mathrm{HCl}\uparrow$$

Solubility:-

The complex was found to be insoluble in methylene chloride, acetonitrile, benzonitrile and nitrobenzene.

(B) Benzanilide-imidchloride, PhCCl:NPh and BF_3

Boron trifluoride gas was allowed to bubble through a solution of benzanilide-imidchloride in o dichlorobenzene, until the solution was saturated with it. The reaction which was carried out at room temperature did not yield any solid complex.

(C) Benzanilide imidchloride, PhCCl:NPh and anhydrous $AlCl_3$

To a solution of benzanilide-imidchloride in nitrobenzene was added a molar quantity of freshly sublimed aluminium trichloride in the same solvent. A deep red colour was observed when excess of aluminium trichloride was used. The reaction was carried out at ice temperature. The complex was filtered and washed a few times with carbon tetrachloride. It is a hygroscopic, light yellow crystalline solid and melts with decomposition at 175-179°C (quoted 215°C).26. However, when commercially available anhydrous Aluminium trichloride was used the melting point was found to be 145°C (decomp.) H. H. Bosshard and HCh. Zollinger (27) have prepared the complex using methylene chloride as the solvent. They report the m.pt. to be 142-145°C. The melting point appears to depend on the quality of aluminium trichloride, but since our complex analysed quite satisfactory, no further investigation was attempted.

Analysis:- Found: Cl, 39.84; Al, 7.58 %

Calcd. for $C_{13}H_{10}NCl_4Al$: Cl, 40.64; Al, 7.73%

I.R. Spectrum:- The spectrum was recorded on SP200 and the only significant feature was a strong peak at 2312 cm^{-1}. Bosshard and Zollinger (27) have reported that Infrared spectrum of their complex showed a strong band at 2309 cm^{-1}.

Reaction with Water:-

The complex does not react as vigorously as its analogue, $PhCNPh,BCl_4$. The hydrolysis product was the same as for 3 (I), namely benzanilide (m.pt 163°C).

(IV) N-ethylbenzimidchloride, PhCCl: NEt and BCl_3

Two experiments have been carried out, one on the high vacuum line using a reaction vessel and the other as a solution reaction using chloroform as a solvent.

(i) Vacuum line experiment:-

3.07 gms (26.2 millimoles) of boron trichloride were condensed on 3.3575 gms (20.0 millimole) of N-ethylbenzimidchloride in a reaction vessel. The reaction vessel was allowed to stand in ice water for a few hours and then left for 12 hours at room temperature. A bright yellow solid was obtained. Excess BCl_3 was taken off under vacuum. Stoichiometry was as follows (Ration $BCl_3/_{PhCCl:NEt}$):-

By P, V, T measurement	By gain in weight
0.98	0.96

(ii) Solution reaction

The solution reaction was performed in the usual manner in chloroform. This time a very light yellow amorphous solid was obtained. It is a hygroscopic solid m.pt. 110°-115°C.

Analysis:-			
	Found:	Cl, 48.87;	B, 3.76 %
	$C_9H_{10}NCl_4B$ requires:	Cl, 49.83;	B, 3.82 %

I.R. Spectrum - Neat

542 (S), 630-750 (VS br. with maxima at 660, 675 and 737), 775 (S), 807 (S), 885 (M), 912 (M), 925 (M), 946 (S), 970 (S), 1005 (S), 1034 (S), 1050 (S), 1070 (S), 1088 (M), 1097 (W), 110 (S), 1176 (M), 1187 (S), 1262 (S), 1305 (S), 1345 (S), 1526 (S), 1600 (S), 1635 (S), 1785 (M), 1917 (M), cm^{-1}.

Hydrolysis:-

The complex reacted vigorously even with cold water. After hydrolysis with aq/NaOH, the product was identified as Nethylbenzamide by its m.pt. (68°C) and infrared spectrum

$$Ph-\underset{Cl}{C}=N-C_2H_5,BCl_3 + 4H_2O \longrightarrow PhCONHC_2H_5 + HCl + H_3BO_3$$

Decomposition of $PhCNEt^{+}$ BCl_4^{-} under vacuum at 150°C

The complex was gradually heated to 150°C. The gaseous s spectrum indicated the presence of two components. EtCl and BCl_3. A white crystalline product sublimed on to the cooler part of the tube. This was shown to be benzonitrile-boron trichloride complex by Infrared spectrum.

(E) N-Methylbenzimidchloride, PhCCl:NMe and boron trichloride

4.79 gms (40.8 millimoles of boron trichloride was condensed on 4.685 gms (30.55 millimoles) of N- methylbenzimidchloride in a reaction vessel. The reaction vessel was left in ice water for a few hours and then left at room temperature for 12 hours.

A yellow amorphous powder was obtained. It is a hygroscopic solid, m.pt. 140° (decomp.). However the solid started softening at 120°C. By P, V, T measurements, the stoichometry (moles PhCCl:NMe per mole BCl_3) was found to be 1:0.95.

The solution reaction afforded a yellow product with needle shaped crystals.

Analysis:- Found:- Cl, 51.60 %

$C_8H_8NCl_4B$ requires:- Cl, 52.30 %

I.R. Spectrum:- Nujol Mull

543 (M), 630-750 (VS br.), 762 (VS), 880 (M), 956 (S), 1032 (S), 1237 (S), 1275 (M), 1305 (M), 1600 (S), 1645 (S), 1790 (M), 2380 (VS), 2475 (M).

Hydrolysis:-

The complex reacted vigorously even with cold water. The hydrolysis product was identified as N-methylbenzamide by its m.pt. (80°C) and Infrared spectrum.

Decomposition of $[PhCNMe]^{+}$ $[BCl_4]^{-}$ under vacuum at 150°C

The gaseous spectrum indicated the presence of two components, MeCl and BCl_3. A white crystalline product which sublimed on the cooler part of the tube gave a similar spectrum to PhCN, BCl_3 complex.

$$\overset{+}{PhCNCH_3}, \overset{-}{BCl_4} \xrightarrow{heat} PhCN, BCl_3 + CH_3Cl$$

$$+ \text{ some free } BCl_3.$$

(F)I. N-methylformimidchloride, HCCl:NMe and boron trichloride in chloroform

An excess of boron trichloride gas was allowed to bubble through a suspension of N-methylformimidchloride in dry chloroform at 0°C. Boron trichloride reacted immediately with the formation of an oil. After shaking the Schlenk tube for 10 minutes the oil solidified to a white crystalline mass. The solution was filtered and the crystals were dried under vacuum. While drying, the white solid gradually changed to uniform brown colouration.

The product is extremely hygroscopic, m.pt. 50-55°C.

Analysis:- Found: Cl, 60.50; B, 5.65, 5.69%

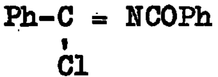
$C_2H_4NBCl_4$ requires: Cl, 72.93; B, 5.58%

$C_2H_3NBCl_3$ requires: Cl, 66.83; B, 6.83%

Decomposition under vacuum

The brown product was gently heated to approx. 80°C on a water bath for half an hour. The gaseous product was condensed with liquid air and a representative sample was introduced in a gas cell for the infrared spectrum. The spectrum showed the presence of a single component, methyl chloride. The residue was a black crystalline material which was not analysed.

(G). α-chloro-N-benzoylbenzimide, $\underset{\text{Cl}}{\text{Ph-C}} = \text{NCOPh}$ and BCl_3



Boron trichloride gas was bubbled through a chloroform solution of α-chloro-N-Benzoylbenzimide. The reaction was carried out at 0°C using a Schlenk tube under dry nitrogen atmosphere. A heavy white ppt. separated after an excess of BCl_3 was used. The excess BCl_3 was removed by using a slow stream of dry nitrogen. The solution was filtered and dried at 24°C/1 mm. It is an off-white hygroscopic solid, melting point 122°C.

The reaction was also carried out on the vacuum line. 12.48 gms (106.4 mm) of BCl_3 gas was condensed on 2.0865 gms (85.7 millimoles) of α-chloro-N benzoylbenzimide in a reaction vessel. The reaction vessel was left at room temperature for 2 days. Only 0.248 gms (21.1 millimoles) of BCl_3 reacted with α-chloro-N benzoylbenzimide. The non-stoichiometric ratio in which boron trichloride reacts with the parent compound is believed to be due to incomplete reaction in the solid-gas phase.

Analysis:- Found: C, 47.70; H, 2.75;

B, 3.02, 3.05 %

C H NOCl B requires: C, 46.50; H, 2.77;

B, 3.01 %

I.R. Spectrum:- Nujol Mull

504 (S br.), 550 (S br.), 615 (S), 672 (VS), 685 (W), 708 (M), 704-775 (VS br), 796 (S), 840 (S), 917 (S), 1000 (S), 1023 (S), 1040 (S), 1117 (S), 1177 (S), 1220 (S), 1240 (S), 1262 (W), 1316 (W), 1370 (VS), 1450 (VS), 1586 (S), 1653 (Sh.), 1704 (VS), 1830 (W).

4. Addition reactions of acid amides and imides.

(A) Phthalimide and boron trichloride

0.955 gms (8.15 millimoles) of boron trichloride was condensed on 0.5915 gms (4.02 millimoles) of Phthalimide in a reaction vessel. The reaction vessel was left at room temp. for 2 days. A yellow colouration of the white Phthalimide was observed in the reaction vessel, when BCl_3 was condensed on Phthalimide at liquid air temperature. The yellow colour only appears while reaction vessel is at low temperature, it gradually disappears when reaction vessel is allowed to warm up to room temperature. After 2 days the excess BCl_3 was pumped off, leaving a white amorphous solid. The gas spectrum was identical to boron trichloride. No impurities were detected in infrared spectrum of the gas.

Three experiments were carried out on the high vacuum line:-

1. Phthalimide + 1 mole of BCl_3
2. Phthalimide + 2 moles of BCl_3

3. Phthalimide + 3 moles of BCl_3.

In each of these three cases only 1:1 adduct was formed. Stoichiometric ratio of Phthalimide/BCl_3 was found to be 1:0.98 by P,V,T measurements and 1:0.99 by gain in weight.

<u>Analysis</u>:-			
	Found:	Cl, 39.80;	B, 4.00 %
	$C_8H_5NOBCl_3$ requires:	Cl, 40.30;	B, 4.09 %

The complex reacted vigorously with water and the hydrolysis product was identified as phthalimide by its m.pt. (237°C) and infrared spectrum.

<u>Melting point of complex; Phthalimide, BCl_3</u>

The adduct does not melt but chars. Charring starts at 195°C, the product gradually darkens.

<u>I.R. Spectrum</u> - KBr disc

725 (VS), 755 (M), 800 (M), 830 (M), 893 (M), 1068 (VS), 1085 (M), 1100 (S), 1157 (M), 1208 (S), 1320 (VS), 1360-1510 (S br. with maxima at 1400 and 1480), 1617 (S), 1760 (VS), 1785 (S), 3140-3310 (VS br. with maxima at 3230) cm^{-1}.

(Bi) <u>Phthalimide and boron trifluoride at room temperature.</u>

Solid-gas reaction between phthalimide and boron trifluoride did not yield any complex.

(C). Phthalimide and boron trifluoride at -80°C

0.992 gms (14.63 millimoles) of boron trifluoride were condensed on 0.7903 gms (5.85 millimoles) of Phthalimide in a reaction vessel. The reaction vessel was then placed in a cold bath at -80°C and left at this temperature for four hours. After this period, the reaction vessel was opened to the vacuum line for a few hours and 0.588 gms (8.67 millimoles) of boron trifluoride gas was recovered. Therefore only 0.404 gms (5.95 millimoles) of BF_3 reacted with phthalimide at -80°C. This amount of BF_3 absorbed corresponded to a 1:1 adduct with Phthalimide. The latter changed its colour from white to light green colouration.

(D.) Diacetimide, $(CH_3CO)_2NH$ and boron trifluoride

At room temperature, diacetimide did not react with boron trifluoride, however at -80°C diacetimide absorbed 2 moles of BF_3. Details are given as follows:-

3.025 gms (20.5 millimoles) of BF_3 gas was condensed on 0.7809 gms (7.73 millimoles) of diacetimide in a reaction vessel. The reaction vessel was then left at -80°C for 6 hours. During this time 0.738 gms (5.0 millimoles) of BF_3 was recovered. Therefore 2.287 gms (15.5 millimoles) of BF_3 reacted with phthalimide at -80°C. This corresponded to 2 moles absorption of boron trifluoride.

(E). Diacetimide,$(CH_3CO)_2NH$ and Stannic (IV) Chloride in 1,2 Dichloroethane

Stannic chloride (B.D.H. reagent grade) was further purified by keeping it over mercury and then redistilling under dry nitrogen. Stannic chloride was added in molar proportion to a solution of diacetimide in 1,2 dichloroethane at room temperature. A white precipitate separated, which was washed several times with chloroform and finally with ether. The product was dried under vacuum. It is a hygroscopic, white, solid and melts with decomposition at 210°C.

Analysis:- Found:- Sn, 31.9; Cl, 46.67%

$C_8H_{14}O_4SnCl_4$ requires:-Sn, 25.7; Cl, 30.70%

I.R. Spectrum - Nujol Mull (recorded on SP.200)

695 (VW), 730 (W br.), 780 (S), 935 (S), 1030 (S), 1045 (Sh.), 1250 (VS), 1380 (VS), 1405 (VW), 1460 (VS), 1685 (VS), 3150 (M).

INDICATOR TITRATION OF STANNIC CHLORIDE

The indicator titration of stannic chloride was carried out as described by Luder and Co-workers (28) in 1,2 dichloroethane using crystal violet as indicator. Standard solution of $SnCl_4$ was made in a dry box. The acidic solution of known molarity was placed in a burette with $CaCl_2$ guard tubes. Many runs were made in order to determine the end point (yellow). The results represented below are typical of those obtained after preliminary difficulties were overcome.

System:- Stannic (IV) chloride and diacetimide.

c.c. $SnCl_4$ (A)	c.c. Diacetimide (B)	Moles $^B/_A$
0.0435 M	0.0294 M	
3.50	10	1.935
3.50	10	1.935
3.43	10	1.970

The molar ratio in which diacetimide reacts with stannic chloride is found to be approximately 2.0 viz. $SnCl_4\ 2(CH_3CO)_2NH$.

(F) Benzanilide, PhCONHPh and boron trifluoride

0.300 gms (4.42 millimoles) of boron trifluoride gas was condensed on to 0.8382 gms (4.25 millimoles) of pure benzanilide in a reaction vessel. The reaction vessel was left for 2 days at room temperature. During this time the texture of white crystalline benzanilide had changed to off-white uniform powder. The stoichiometric ratio of benzanilide/boron trifluoride was found to be 1:0.95 by P,V,T measurements and 1:0.96 by gain in weight. The product melted in the range of 50-55°C.

Analysis:- Found:- C, 58.7; H, 4.85 %

$C_{13}H_{11}NOBF_3$ requires:-C, 58.9; H, 4.20 %

I.R. Spectrum - Nujol Mull

507 (M), 520 (M), 532 (M), 582 (M), 619 (Q), 645 (S br.), 690 (S), 716 (S), 749 (VS), 770 (Sh.), 790 (M), 882 (M), 909 (M), 925 (M), 1000 (VW), 1036,(1122 (S br.), 1083 (S), 1169 (W), 1190 (W), 1262 (S), 1299 (Sh.), 1322 (S), 1439 (S), 1495 (Sh.), 1528 (S), 1575 (W), 1595 (S), 1660 (VS), 3030 (Sh.), 3340 (W br.), cm^{-1}.

(G). Benzanilide, PhCONHPh and boron trichloride.

1.682 gms (14.46 millimoles) of boron trichloride gas was condensed on 2.0386 gms (10.30 millimoles) of benzanilide in a reaction vessel. The reaction vessel was left for 12 hours at room temperature. The excess boron trichloride was then removed under vacuum. After half an hour of pumping, it was found that an exact 1:1 complex had formed. The reaction vessel was left pumping for a further period of 2 hours. During this period only a further 0.298 moles of boron trichloride were removed. The product was then transferred to a two neck flask under dry nitrogen. The complex decomposes very slowly at room temperature evolving boron trichloride. The chemical analysis and infrared study under these conditions were unsatisfactory and therefore not even attempted.

(H)I. N-Ethylbenzamide, PhCONHEt and boron trifluoride in Methylene Chloride.

An excess of boron trifluoride gas was bubbled through a methylene chloride solution of N-ethylbenzamide at 0°C in a Schlenk tube under dry nitrogen atmosphere. A yellow oily product separated and the solvent was removed under vacuum. The residue was an off-white solid, m.pt. 95°C (although it started softening at about 87°C). It is slightly sensitive to moisture.

Analysis:- Found: C, 49.20; H, 5.20 %
$C_9H_{11}ONBF_3$ requires: C, 49.70: H, 5.06 %

I.R. Spectrum - Nujol Mull.
657 (M), 700 (W), 730 (S), 800 (M), 870 (S br.), 900 (M), 920-1000 (S br.), 1040 (W), 1060-1200 (br.), 1300 (M), 1340 (M), 1380 (VS), 1460 (VS), 1500 (W), 1540, 1555 (S doublet), 1587 (M), 1610 (M), 1820 (M), 3335 (S br.).

The complex reacted very slowly with water, but on warming it dissolved and on addition of N-NaOH, the clear solution deposited white crystalline solid which was identified as N-ethylbenzamide, m.pt. 68°C.

5. Purification of Solvents (29):-

Pyridine ("Analar". B.D.H. grade, b.pt. 115.3°C) was dried, by refluxing for some hours over potassium hydroxide pellets, before being distilled.

Chloroform (30) ("Analar". B.D.H. grade, b.pt. 61.2°C) was washed several times with concentrated sulphuric acid, then with dilute sodium hydroxide and finally with ice water. It was dried over potassium carbonate and distilled shortly before use.

Benzene (b.pt. 80.1°C) was dried by refluxing with phosphorous pentaoxide and distilled.

Toluene ("Analar". B.D.H. grade, b.pt. 110.6°C) was dried by refluxing over phosphorous pentaoxide before being distilled.

Thionyl chloride (b.pt. 78.8°C) was purified by redistilling the commercial product at low pressures under dry nitrogen atmosphere.

Carbon tetrachloride (b.pt. 76.8°C) was dried similarly to toluene.

Ether was dried by sodium and distilled.

References - Pt. II & III

1. H. C. Brown and R. B. Johannsen
   J. Amer. Chem. Soc. 1950, 72, 2937
2. W. W. Scott
   Standard Methods of Chemical Analysis 1950 p.170.
3. J. R. Partington and A. L. Whynes
   J. Chem. Soc. 1949, 3135.
4. W. W. Scott
   Standard Methods of Chemical Analysis 195 p.12.
5. A. I. Vogel
   "Practical Organic Chemistry" 1954, p.559.
6. J. B. Polya and Tardrew
   J. Chem. Soc. 1948, 1081.
7. J. Uno and K. Machida
   Bull. Chem. Soc. Japan 1961, 34, 545
8. A. W. Titherley
   J. Chem. Soc. 1904, 85, 1684
9. O. E. Thompson
   J. Amer. Chem. Soc. 1951, 73, 5841.
10. J. V. Braun and W. Pinkenell
    Ber, 1934, 67, 1219
11. O. Wallach and M. Hoffmann
    Ann. 1877, 184, 79.
12. H. H. Bosshard and Hch. Zollinger
    Helv. Chim. Acta, 1959, 42, 1659.

13. G. D. Lander

J. Chem. Soc. 1903, 83, 320.

14. A. W. Titherley and Elizabeth Worrall

J. Chem. Soc. 1910, 97, 839.

15. E. Beckmann and K. Sandel

Annalen 1897, 296, 279.

16. F. D. Chattaway and K. J. P. Orton,

J. Chem. Soc., 1899, 75, 1050.

17. Gerrard, Lappert and Wallis

J. Chem. Soc., 1960, 2178.

18. C. Naegeli, Lydia Gruntuch and P. Lendoff.

Helv. Chim. Acta 1929, 12, 255.

19. Hofmann, Ber. 1881, 14, 2729,

20. Meerwein, H, E. Batlenberg, H. Cooled, E. Pteil and G. Willfang.

J. Prakt. Chem. 1939, 154, 83.

21. Perrier, G.

Comp t. rend, 1895, 120, 1424

22. Perrier, G.

Bull. Soc. Chim. France, 1895, 13, 1031

Ref. 20, 21, 22 through G. A. Olah.

Friedel-Crafts and related reactions 1963, p. 571.

23. W. E. Backmann, "Organic Synthesis", Coll. Vol. III, E. C. Horning, Ed, John Wiley & Sons, inc. New York, N.Y. 1955, p.841.

24. Kemmitt, Milner and Sharp
J. Chem. Soc. 1963, 111.

25. K. M. Harmon, A. B. Harmon, and F. E. Cummings,
J. Amer. Chem. Soc. 1964, 86, 5511.

26. Meerwein et al Ber. 1956, p. 125.

27. see reference 12.

28. E. B. Garber, L.E.D. Pease and W. F. Luder
Analytic. Chem. 1953, 25, 581.

29. Technique of Organic Chemistry Vol. VII Organic Solvents.
A. Weissberger and E. S. Proskauer. Interscience publishers,
Inc., New York 1955.

30. Morgan, S. O and H. H. Lowery
J. Phy. Chem. 1930, 34, 2385.

31. E. O. Fischer, W. Hafner, and H. O. Stahl
Z. Anorg. Chem., 1955, 282, 47.

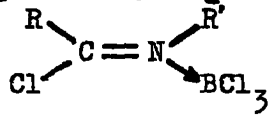
PART IV

DISCUSSION.

(A.) Reactions between imidchloride and boron trichloride

Imidchlorides are formulated, RCCl:NR' where R and R' are organic radicals. As outlined in Part I, we considered that an imidchloride might interact with boron trichloride according to one of the following reaction paths:-

either $RCCl{:}NR' + BCl_3 \longrightarrow [RC\equiv NR']^{+} [BCl_4]^{-}$

or $RCCl{:}NR' + BCl_3 \longrightarrow$ 

The nature of the product can be determined by examination of its infrared spectrum. A characteristic band in the spectra of nitrilium salts is $\nu\, C\equiv N$ in the region 2300-2400 cm^{-1}, whereas a co-ordinated azomethine group such as would occur in a covalent adduct would give rise to a band near 1600 cm^{-1} i.e. at slightly lower frequency than the band assigned $\nu\, C=N$ in the parent imidchloride. Also, the spectra of tetrachloroborates have a characteristic broad absorption in the region 600-750 cm^{-1}.

1:1 adducts of boron trichloride with the imidchlorides listed in Table IV were prepared, and their infrared spectra compared with those of two reference compounds, the nitrilium tetrachloroaluminate $PhCNPh^{+}\ AlCl_4^{-}$, for which the ionic structure had already been established (1) and the tetrachloroborate $Ph_3\overset{+}{C}, \overset{-}{BCl_4}$ (2). The relevant frequencies are listed in Table IV, and the spectra themselves are illustrated in Figures 5, 6, 7 and 8. It is clear that the imidchloride-boron trichloride adducts are nitrilium tetrachloroborates $PhCN\overset{+}{R}$, BCl_4^- ($R = Me$, Et or Ph).

TABLE IV

Ligand	Preparation Conditions Solvent	Temperature.	M.Pt. x °C(dec)	BCl_4^- region cm^{-1}	$-C\equiv\overset{+}{N}-$ cm^{-1}
PhCCl:NPh	$OCl_2C_6H_4$	0°C	154	616-719 (br)	2318 (s)
PhCCl:NEt	$CHCl_3$	0°C	110-115	630-750 (br)	2365(s)
PhCCl:NMe	$CHCl_3$	0°C	120	630-750 (br)	2380 (s)

Fig. 5 illustrates the infrared spectrum of N-methylbenzonitrile tetrachloroborate, $\left[Ph-C\equiv NMe\right]^{+}$ $\left[BCl_4\right]^{-}$, and that of triphenyl-methyl tetrachloroborate is shown in Figure 6. The BCl_4^- region in both of these Figures shows a broad absopption around 630-750 cm^{-1} with maxima at 669 cm^{-1} and 676 cm^{-1}. In addition the spectrum of N-methyl benzonitrilium compound (Fig.5) shows a new infrared absorption band at 2380 cm^{-1} which is absent from the spectrum of the parent imidchloride. An example of an imidchloride spectrum, that of N- ethylbenzimidchloride, is shown in Figure 7. In Figure 8 the BCl_4^- and $-C\equiv\overset{+}{N}-$ absorption bands of N- phenylbenzonitrilium tetrachloroborate are illustrated in detail.

Further characterisation of the compounds was made by examination of their hydrolysis products. In all cases the tetrachloroborates of the nitrilium salts gave their respective N- substituted amides on treatment with dilute alkali.

FIG. 5

INFRARED SPECTRUM OF $(PhCNMe)^{+},(BCl_4)^{-}$

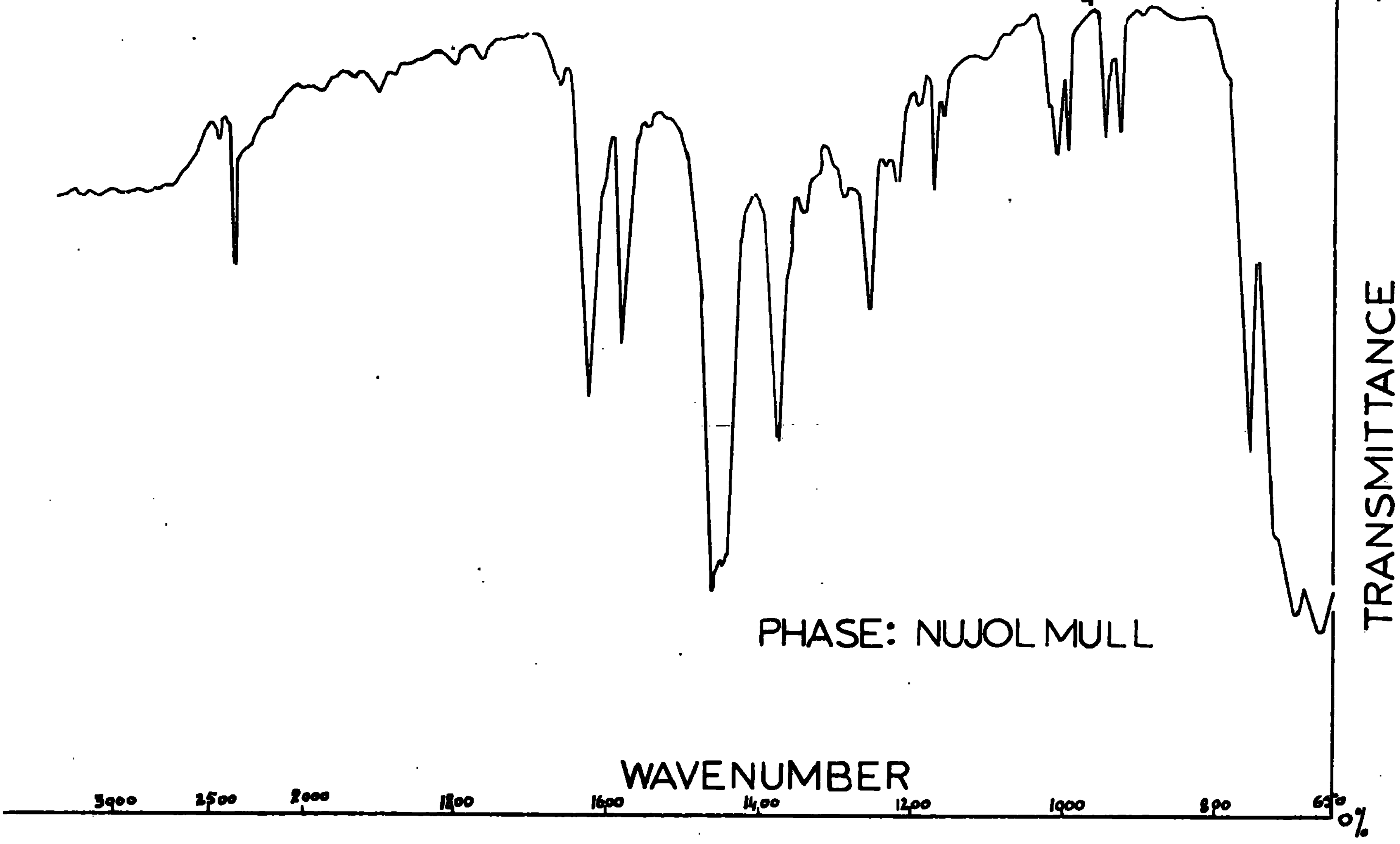
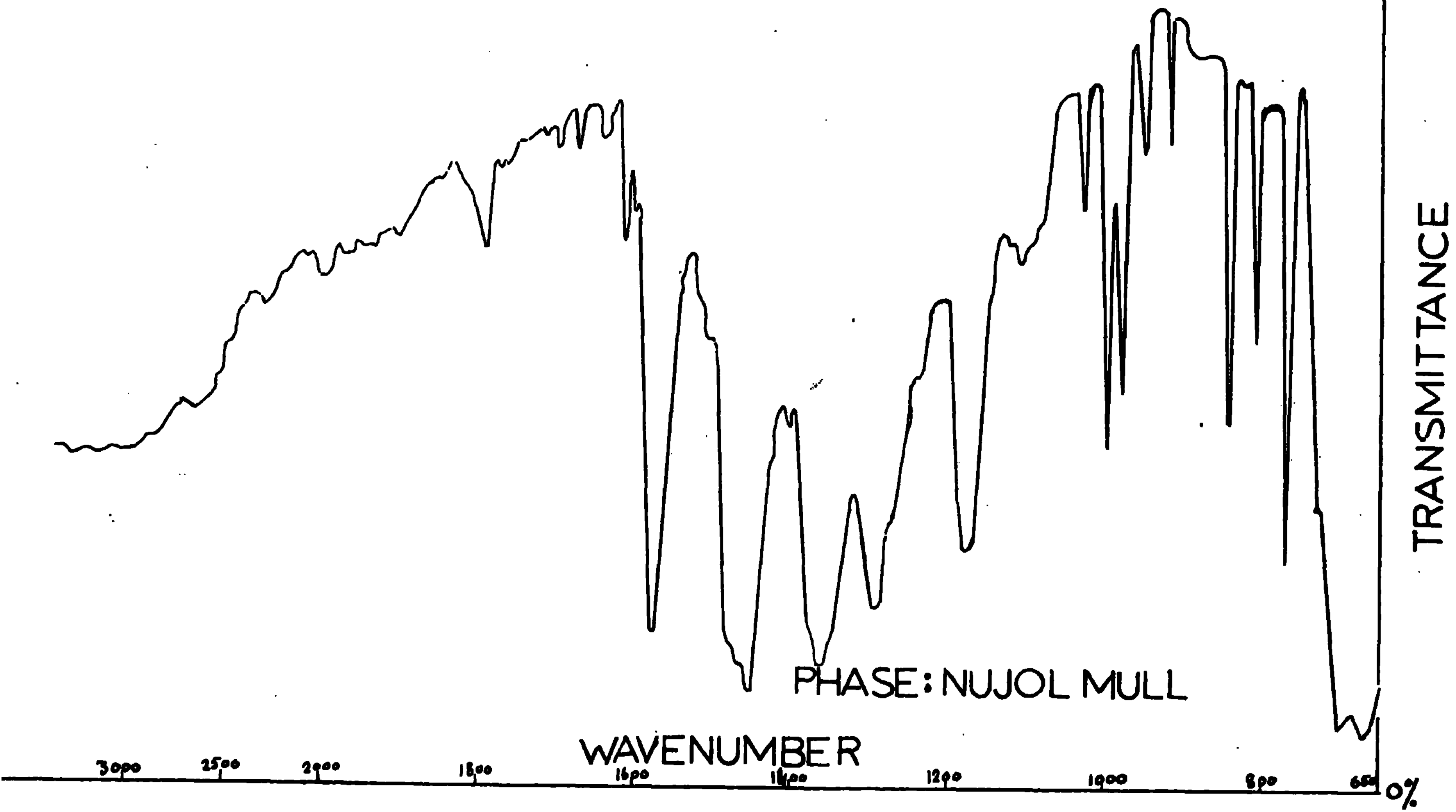


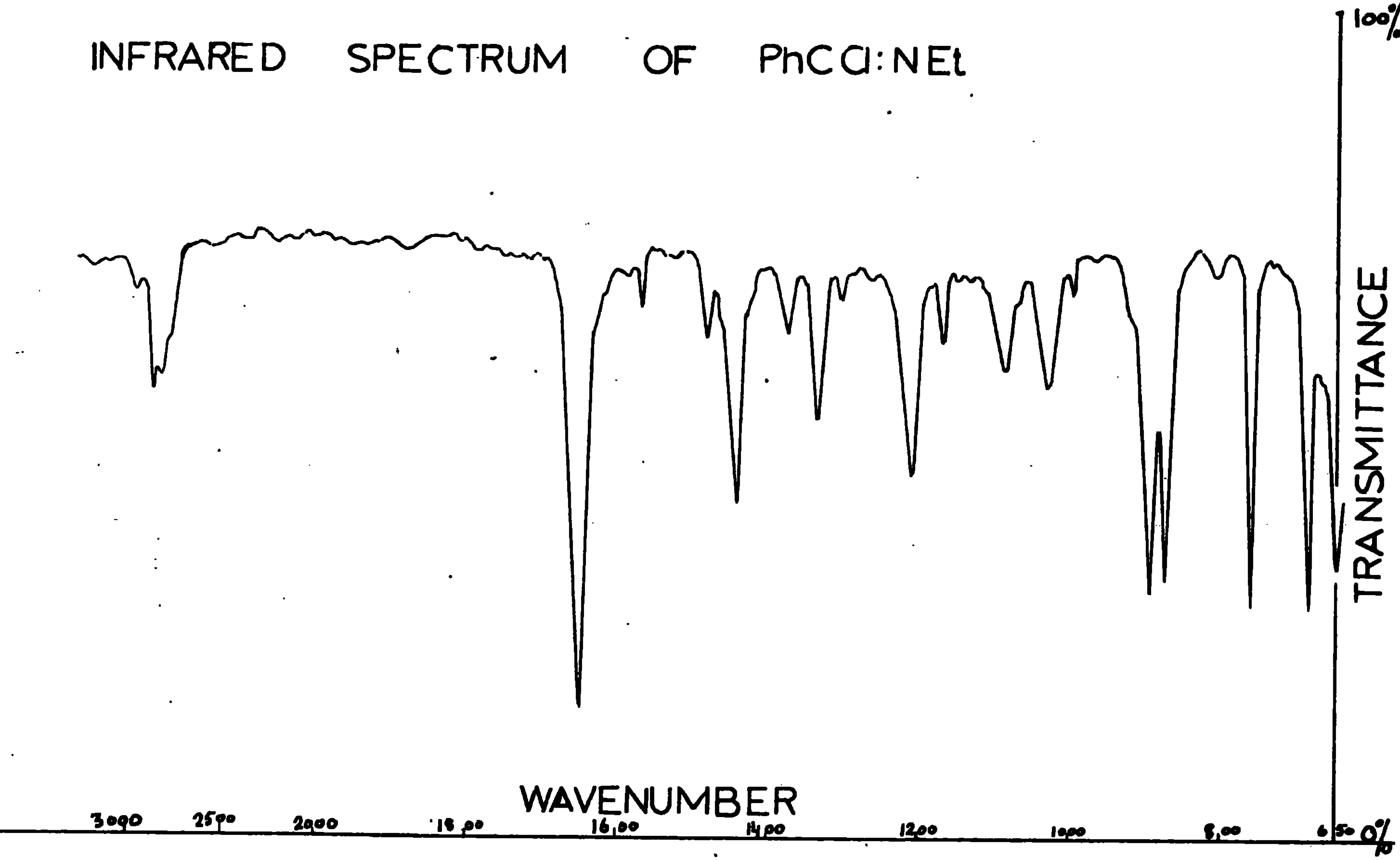
FIG. 6

INFRARED SPECTRUM OF $(Ph)_3C^+, BCl_4^-$



PHASE: NUJOL MULL

FIG. 7

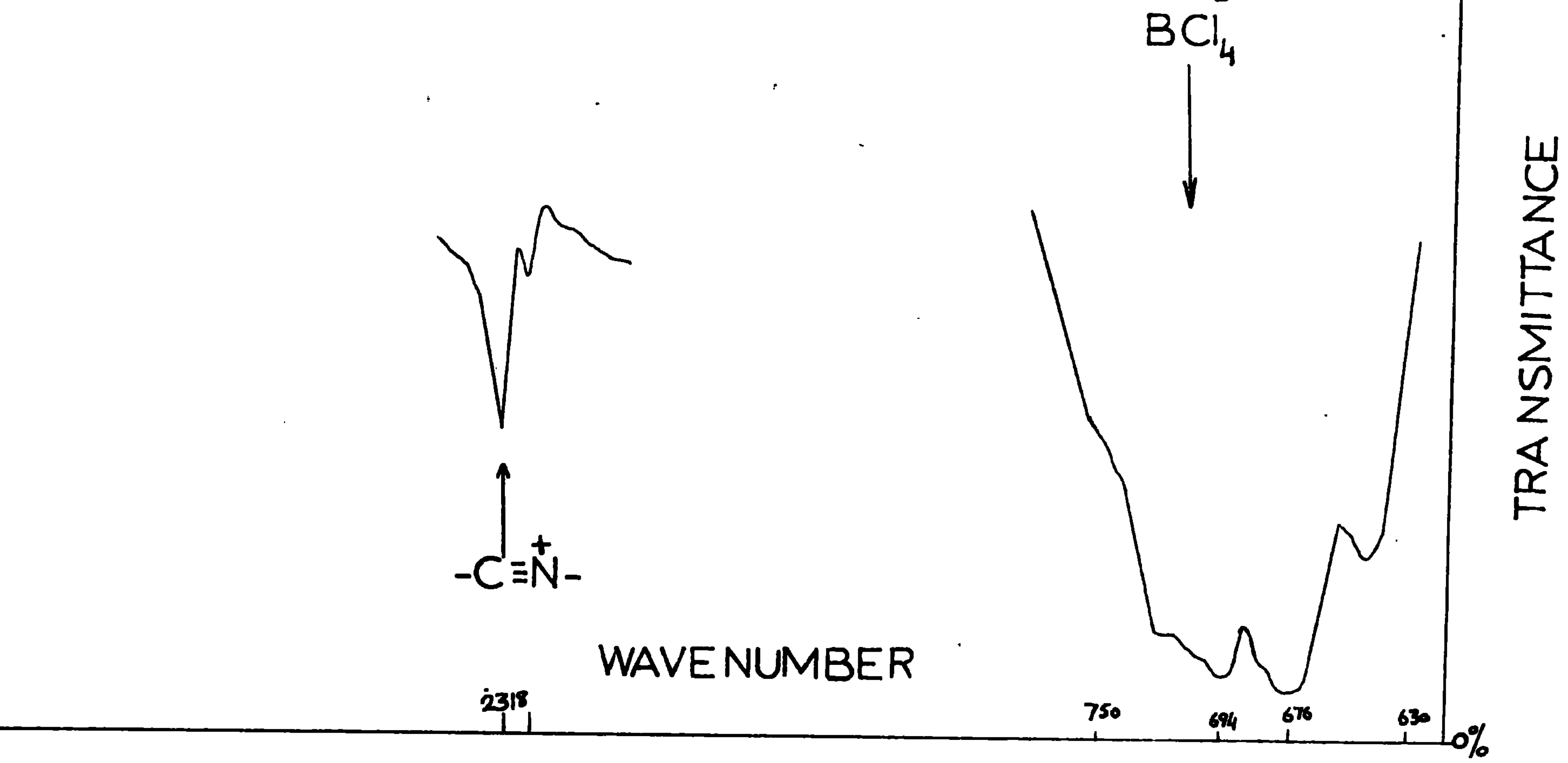


INFRARED SPECTRUM OF PhCCl:NEt

FIG. 8

INFRARED SPECTRUM OF $\mathrm{PhC\overset{+}{N}Ph}, \mathrm{BCl_4^-}$

$\mathrm{BCl_4^-}$ & $-\mathrm{C{\equiv}\overset{+}{N}}-$ ABSORPTION REGIONS



$$[\mathrm{PhCNR'}]^{+}\,[\mathrm{BCl_4}]^{-} \longrightarrow \mathrm{PhCONHR'}$$

The products of the thermal decomposition of the N-methyl and N- ethyl benzonitrilium salts were the appropriate alkyl chloride together with the solid BCl_3 adduct of benzonitrile, i.e. PhCN, BCl_3. The gaseous infrared spectrum of the products also showed the presence of some unco-ordinated BCl_3. (PhCN, BCl_3 itself dissociates slightly at room temperature).

$$[\mathrm{PhCNR}]^{+}\,[\mathrm{BCl_4}]^{-} \longrightarrow \mathrm{PhCN,\ BCl_3 + RCl.}$$

It is worth noting that the products of the hydrolysis and pyrolysis experiments can be explained in terms of either the ionic or covalent structure for the adducts.

Conductivity measurements on the nitrilium salts were not made because of their limited solubility in suitable solvents. However, it may yet be possible to make measurements on the N-methylbenzonitrilium tetrachloroborate, as this shows some solubility in methylene chloride. It is possible that confirmation of the ionic nature of the salts might also be obtained by ^{11}B N.M.R. measurements. The chemical shift for BCl_3 adducts is reported as S = -9 to -10 P.P.M. relative to $BF_3.Et_2O$ as standard, whereas that for BCl_4^- is S = -11 to -12 (3). However, the chemical shift differences might prove too small to allow unambiguous interpretation. The chemical shift difference for the comparable bromides show a much larger effect, the BBr_3 adduct shift being S = +6 to +10 P.P.M. compared to

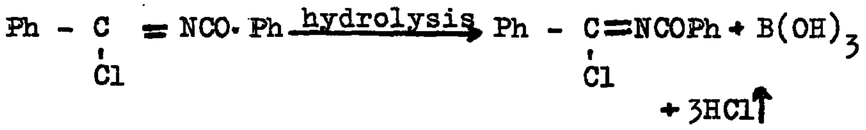
BBr_4^- having S = + 26 P.P.M. (3).

BF_3 addition to the imidchlorides was expected to yield one of the two possibilities

(a) a covalent adduct

(b) a mixed tetrahalogenoborate i.e. BF_3Cl^- such as that observed by Sharp (1) on treatment of triphenylmethyl chloride with boron trifluoride. No reaction however occurred.

In the reaction of boron trichloride with N- benzoylbenzimidchloride, PhCCl:NCOPh and with N- methylformimidchloride, HCCl:NMe adduct formation occured but no evidence for the formation of a tetrachloroborate was found. The nature of the former adduct was shown by examining the infrared spectrum and hydrolysis products. The hydrolysis product was identified as N-benzoylbenzimidchloride (p.   ) i.e.



$$\mathrm{Ph-\underset{Cl}{C}=NCO\cdot Ph \xrightarrow{hydrolysis} Ph-\underset{Cl}{C}=NCOPh + B(OH)_3 + 3HCl\uparrow}$$

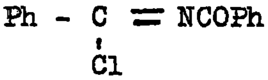
This is consistent with the covalent structure for the adduct; the boron trichloride molecular structure remains intact and the hydrolysis products are those expected from boron trichloride itself. In the case of an ionic structure, $\mathrm{Ph-C\equiv NCOPh^+}$ BCl_4^- , one would have expected dibenzamide (M.Pt. 148°C) as one of the hydrolysis products.

$$\mathrm{\left[PhC\equiv NCOPh\right]^+ \left[BCl_4\right]^- \xrightarrow{hydrolysis} PhCONHCOPh + B(OH)_3 + 4HCl}$$

The hydrolysis of N- benzoylbenzonitrilium trichlorozincate, $Ph\overset{+}{C}NCOPh$, $Zn\overset{-}{Cl}_3$, was reported by Meerwein et al to give dibenzamide in quantitative yield (4).

$$\left[PhC\equiv NCOPh\right]^{+}\left[ZNCl_3\right]^{-}\xrightarrow{\text{hydrolysis}} PhCONHCOPh$$

Furthermore, the infrared spectrum of PhCCl:NCOPh, BCl_3 (Fig.9) showed no characteristic absorption frequencies due to BCl_4^- anion or $-C\equiv\overset{+}{N}-$. An ionic structure, $Ph\overset{+}{C}NCOPh$ $\overset{-}{BCl_4}$ for this compound can therefore be ruled out. It is not possible, however, to decide on the position of attachment of the BCl_3 unit to

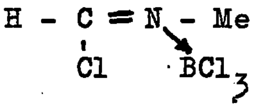


$Ph-\underset{Cl}{\underset{|}{C}}=NCOPh$

on the basis of the infrared spectrum alone. The bands at 1600 cm^{-1} and 1648 cm^{-1} in the parent imidchloride are replaced by bands at 1586 cm^{-1} and 1704 cm^{-1} in the adduct.

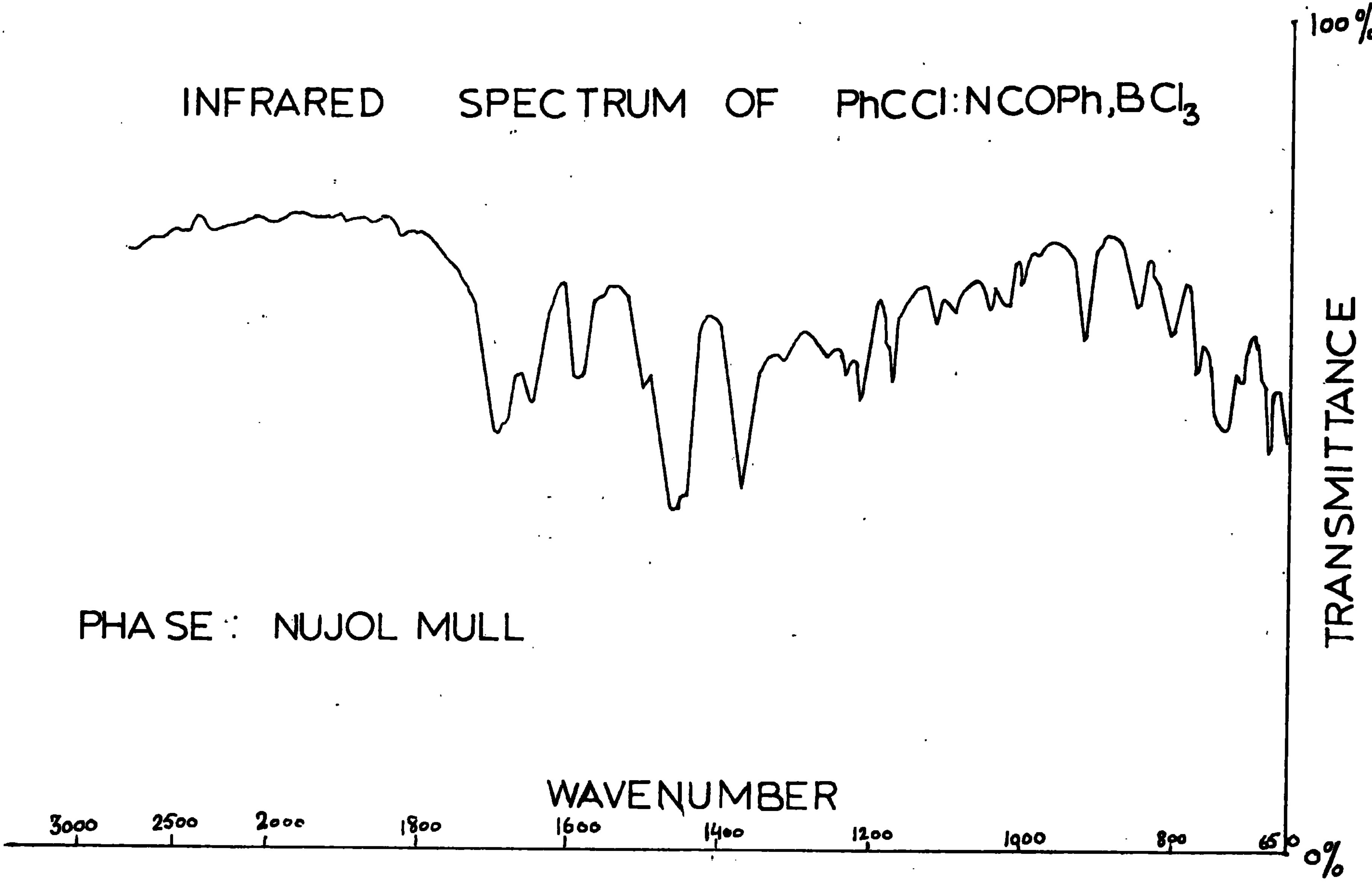
It would be of interest to attempt the preparation of N- benzoylbenzonitrilium tetrachlorozincate by interaction of N- benzoylbenzimidchloride and $ZnCl_2$.

Whilst the nature of the adduct formed by N- methylformimidchloride, HCCl:NMe is obscure, the evidence for the non-formation of a tetrachloroborate is conclusive. The analytical, spectroscopic and thermal decomposition data suggests that the product is a mixture. Simple adduct formation would give



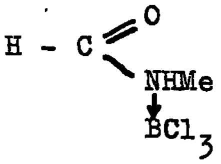
$H-\underset{Cl}{\underset{|}{C}}=\underset{BCl_3}{\underset{\searrow}{N}}-Me$

FIG·9



INFRARED SPECTRUM OF PhCCl:NCOPh,BCl_3

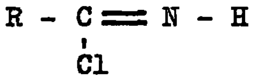
indicating a Cl:B ratio of 4:1 in conflict with the observed value of3·3:1. The appearance in the infrared spectrum of an N-H stretching frequency around 3300 cm^{-1} would not be expected on this formulation. The preparation conditions were exactly the same as in the previous experiments, there being no doubt about the purity of the starting materials. It is considered that 1:1 adduct formation occurs but the extremely hygroscopic nature of the product leads to partial hydrolysis with the formation of some N- methylformamide boron trichloride adduct i.e.



The pure amide adduct HCONHMe, BCl_3 (5) is a viscous liquid which when heated at 110°C for 17 hours under vacuum gives only HCl gas.

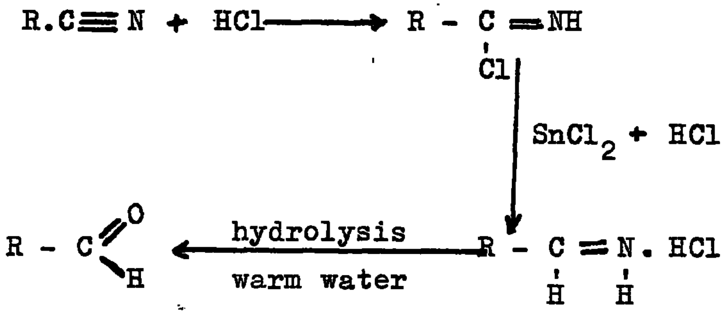
Attempts were made to prepare a wider range of imidchlorides than those so far presented. A wider range of organic groupings attached to the central imidchloride group would have made intercomparison of observed properties easier. However, of the range of imidchlorides explored in the time available, only those already mentioned were prepared in sufficient quantity and purity for adduct formation.

The simplest imidchlorides would be the family represented by the formula



$$R - \underset{\displaystyle Cl}{C} = N - H$$

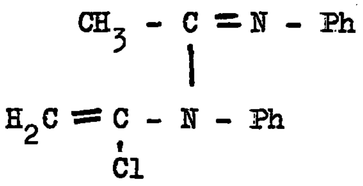
where R is an alkyl or aryl group. It seems doubtful whether these compounds can be isolated in a pure condition, although their formation when an ethereal solution of a nitrile is saturated with gaseous HCl has been claimed by a number of workers (6, 7, 8). For example Stephen (7) postulates the formation of R - CClN-H as an intermediate in the conversion of a nitrile into an aldehyde containing the same number of carbon atoms e.g.



The intermediate has not been isolated. The compound $C_2H_5 - \underset{\displaystyle Cl}{C} = N - H$ was reported (9) as resulting from the saturation of propionitrile with HCl gas, and allowing the solution to stand for a period of two months. However, the fact that the author reports purification by recrystallisation from hot <u>water</u> casts doubt on the preparation. The imidchlorides successfully prepared during this work are all extremely sensitive to the presence of moisture, being hydrolysed to the corresponding amide. Attempts were made to prepare imidchlorides of this kind by the action of hydrogen chloride on nitriles but without success.

The N- substituted acetimidchlorides $CH_3 - \underset{Cl}{C} = N - R$ were next considered. N- phenylacetimidchloride is reported (2) as the product of reaction between phosgene and acetanilide, being a white solid whose analysis corresponded to the formation of $CH_3 - \underset{Cl}{C} = N - Ph$ and having a melting point of 118-120°C. Repetition of this reaction in the present work resulted in a white solid (M.Pt. 123°C) but the analysis of this product gave a significantly low value for chlorine. Thionyl chloride and acetanilide gave an identical product. The identity of the product is not yet established.

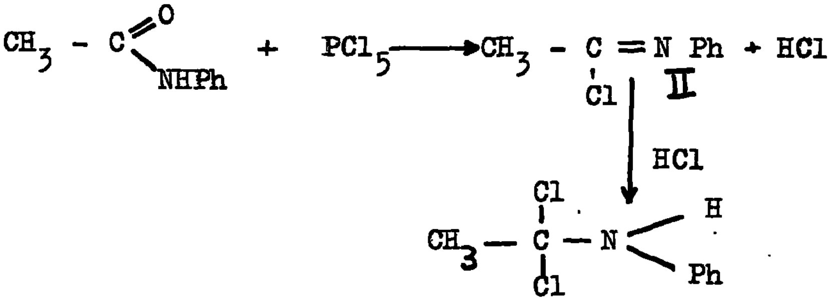
Wallach (10) has reported that PCl_5 forms with acetanilide the product



$$\begin{array}{l} \quad\; CH_3 - C = N - Ph \\ \qquad\qquad\;\; | \\ H_2C = \underset{Cl}{C} - N - Ph \end{array}$$

I.

and a mechanism for this preparation is given by von Braun and Josted (11) i.e.



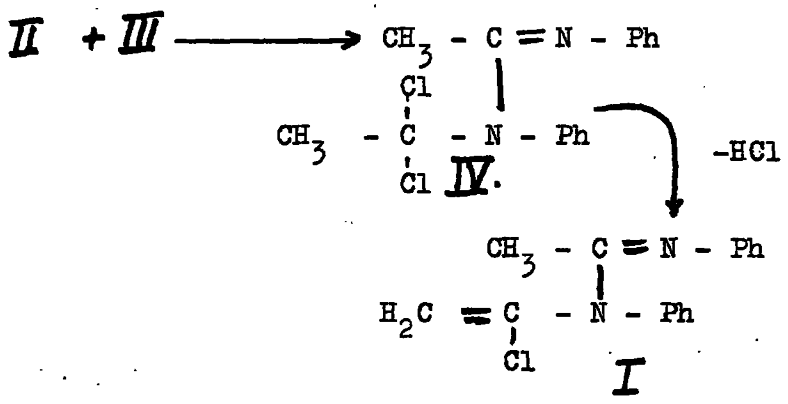
$$CH_3 - C\begin{smallmatrix} \nearrow O \\ \searrow NHPh \end{smallmatrix} + PCl_5 \longrightarrow \underset{\text{II}}{CH_3 - \underset{Cl}{C} = N\,Ph} + HCl$$

$$\Big\downarrow HCl$$

$$CH_3 - \underset{Cl}{\overset{Cl}{C}} - N \begin{smallmatrix} H \\ Ph \end{smallmatrix}$$

III

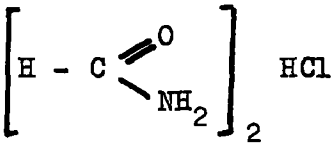
further



The formation of I by loss of HCl from the intermediate condensation product, IV, giving the ethylidene structure in a basic molecule, may be compared with the formation of vinyl chloride from ethylidene dichloride.

Since the reaction of both thionyl chloride and phosgene would be expected to produce the imidchloride II in the presence of HCl the possibility of the formation of I cannot be ignored. The analysis of the product does not correspond to I but from the nature of the reaction the formation of a mixture of I and II would seem possible.

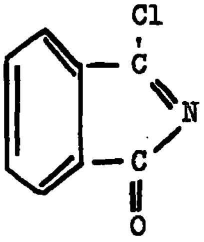
N- methylacetimidchloride is reported (2) to be formed in the reaction between phosgene and methylacetamide, as a white solid (M.Pt. 45-65°C). The reported analysis was concerned only with the percentage of Cl, and this corresponded to a 51% yield of the imidchloride. No mention was made of the nature of the remaining 49%. In the present work this preparation was attempted using both thionyl chloride and phosgene, the product being identical in each case. The analytical results and melting point (89-92°C) show this to be the hydrochloride of the methylacetamide dimer $(CH_3CONHMe)_2.HCl$. The formation of a similar dimer is reported (11) for the reaction between formamide and phosgene, i.e.:-



$$\left[H-C{\overset{O}{\diagup\!\!\!\!/}}\!\!\!\!\diagdown_{NH_2}\right]_2 HCl$$

It will be noted in Table IV that successful preparation of imidchlorides and their subsequent conversion into tetrachloroborates by the action of boron trichloride has been achieved only for those imidchlorides in which a phenyl group is attached to the carbon atom of the imidchloride grouping.

In addition preparation of a cyclic imidchloride, 1 chloro, 3 oxoisoindolemine was attempted, i.e:-



This compound has been previously reported (12), but the yields in this work were too low for study of adduct formation.

B. The Infrared Spectra of Nitrilium Salts.

It has already been noted that the presence of a band in the region 2300-2400 cm^{-1} in the infrared spectra of the boron trichloride adducts was used as evidence for their formulation as nitrilium salts. It is worth stressing that these bands occur always at a higher frequency than the analogous band in the spectrum of the parent nitrile. Some observed values are listed below in Table V:-

Table V

Nitrilium Salt	ν - $C\equiv\overset{+}{N}$ - (cm^{-1})	Ref.
$PhC\equiv\overset{+}{N}Me$, BCl_4^-	2380	this work
$PhC\equiv\overset{+}{N}Et$, BCl_4^-	2365	this work
$PhC\equiv\overset{+}{N}Ph$, BCl_4^-	2318	this work
$PhC\equiv\overset{+}{N}Ph$, $SbCl_6^-$	2300 (approx)	(13)
$MeC\equiv\overset{+}{N}\text{-}Me$, $SbCl_6^-$	2416	(14)

$\nu C\equiv N$ PhCN = 2229 cm^{-1}

$\nu C\equiv N$ EtCN = 2247 cm^{-1}

$\nu C\equiv N$ MeCN = 2253 cm^{-1}

The increase is similar to that observed when a nitrile adduct is formed e.g.

νCN for $PhC\equiv N$ = 2229 cm^{-1}

νCN for $PhC\equiv N\rightarrow BCl_3$ = 2314 cm^{-1}

Frequency shift $\Delta\nu = \nu$CN (adduct) - νCN (free nitrile) = 85 cm^{-1}.

An explanation of the observed stretching frequency of nitrilium cations might be made in the following way:- the nitrilium cation may be regarded as formed from a nitrile by donation of the nitrogen lone pair to a carbonium ion e.g.

$$PhC\equiv N + \overset{+}{R} \longrightarrow PhC\equiv N\rightarrow\overset{+}{R}$$

A list of frequency shifts $\Delta\nu$ for a number of nitrile adducts is given in Table VI.

Table VI

Adduct	$\Delta\nu$ for adducts of:- PhCN	EtCN	MeCN
RCN, BF_3	107	90	106
RCN, BCl_3	85	81	72
$(RCN)_2$, $TiCl_4$	41	38	51
RCN, Me_3Al	43	47	43
RCN, Me^+	151	-	153
RCN, Et^+	136	-	-
RCN, Ph^+	89	-	-

A number of suggestions have been advanced to account for the increase $\Delta\nu$ of the $-C\equiv N-$ stretching frequency on adduct formation by nitriles e.g.

a) Kinematic coupling of the $C\equiv N$ and M-N stretching vibrations (15).

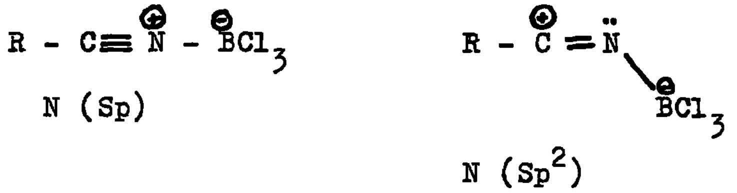
b) Mass effect of the Lewis acid (15).

c) Increase in the $-C\equiv N-$ force constant upon co-ordination.

Gerrard and Lappert (15) considered that $-C\equiv N-$, B-N kinematic coupling was unlikely because of the wide frequency separation of these modes, and further showed that the mass effect to be expected for the Lewis acids was too small to account for the observed variation. These authors based their arguments for the observed increase on a change in bond order of the -C$\equiv$N- link on co-ordination. Thus in the free nitrile the bonding was considered to arise from mesomerism between the structures

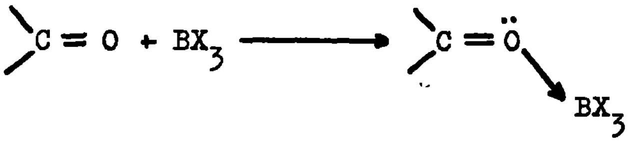
$$R - C\equiv\ddot{N} \longleftrightarrow R - \overset{\oplus}{C}=\overset{\ominus}{\ddot{N}}$$

In the co-ordinated nitrile such mesomerism should not be possible since different geometrical structures would be involved, i.e.



on this basis the adduct would have the higher bond order and correspondingly higher force constant.

In contrast to the increase in -C$\equiv$N- stretching frequency on co-ordination the carbonyl frequency is decreased for systems in which the Carbonyl group is the donor. Beattie and Gilson (16) suggest that this arises from the different geometries of the two types of complex. Thus in the BX_3 complexes of C O the resulting group is non linear.



whereas in nitrile complexes the group is linear.

$$-C \equiv N + BX_3 \longrightarrow -C \equiv N \rightarrow BX_3$$

The unsymmetrical disposition of the X atom relative to the $C = O$ bond in the carbonyl complexes will be such as to repel electrons out of the $C = O$ link, whereas the disposition of the X atoms is symmetrical for the $-C \equiv N$ system and such repulsion will occur along the bond direction.

Purcell and Drago (17) have more recently presented molecular orbital calculations for 1:1 adducts of acetonitrile with a number of Lewis acids, and have calculated the force constants for $C \equiv N$ in these adducts (Table VIII).

Table VIII

Vibrational frequencies and force constants for 1:1 acetonitrile adducts.

$CH_3CN \rightarrow L$ where L Lewis Acid		ν_{CN} cm^{-1}	F_{CN} (mdynes/°A)
CH_3CN		2266	
CH_3CN	ICl	2278	17.896
CH_3CN	$SnCl_4$	2302	18.225
CH_3CN	$AlCl_3$	2330	18.611
CH_3CN	BF_3	2355	19.022

F_{CN} force constant in mdynes/°A

ν_{CN} vibration frequency of $-C \equiv N-$

The mass effect of the adduct on the $-C \equiv N-$ stretching frequency is shown to be only of significance for adducts of mass less than 10. By far the greatest effect is that due to increase in the $-C \equiv N-$ force constant on adduct formation. A minor contribution arises from the $-C \equiv N$, $B - N$ kinematic coupling.

It would also appear to be worthwhile making a comparison of $\nu\, C \equiv N$ for the nitrilium salts with $\nu\, C \equiv C$ for the homologous di-substituted acetylenes the two systems being isoelectronic. Such a comparison has been made for the dimethylacetylene and the N- methylacetonitrilium ion (14). The comparison of $\nu\, C \equiv \overset{+}{N}$ and $\nu\, C \equiv C$ is made difficult for two reasons.

1. Data are available in the literature only for dimethylacetylene and phenylmethyl acetylene. A complete comparison would require values of $\nu\, C \equiv C$ for phenyl ethylacetylene and diphenylacetylene.

2. The assignment of $\nu\, C \equiv C$ for the available acetylenes is made difficult by the existence of a very strong doublet in the $C \equiv C$ stretching region. The peaks of the doublet are quoted as being of equal intensity (18). Herzberg (19) assigns the higher frequency band of the doublet as being due to the $C \equiv C$ stretching vibration for the molecule dimethylacetylene, and the lower frequency member of the doublet as due to a combination band. However the possibility of Fermi resonance between these two bands makes the actual assignment of the $\nu\, C \equiv C$ fundamental

uncertain for if this occurs the peak positions will be displaced from their true values.

In presenting the frequencies for comparison the practice of Herzberg has been followed and the $C \equiv C$ stretching frequency quoted is that of the higher frequency component of the doublet. Although a doublet also appears for the nitrilium ions the intensities are not equal. The value quoted is for the lower frequency component of the doublet which has in this case the greater intensity. This assignment is similar to that adopted by Turrell and Gordon (13).

	$\nu\ C \equiv \overset{+}{N}$		$\nu\ C \equiv C$ cm^{-1}
Ph CN $\overset{+}{\text{Me}}$	2380 cm^{-1}	Ph $C \equiv C$ Me	2253 (20)
Ph CN $\overset{+}{\text{Et}}$	2365	Ph $C \equiv C$ Et	
Ph CN $\overset{+}{\text{Ph}}$	2318	Ph $C \equiv C$ Ph	
Me CN $\overset{+}{\text{Me}}$ (14)	2416	Me $C \equiv C$ Me	2313 (21)

It will be observed that $\nu C \equiv \overset{+}{N}$ is higher than $\nu\ C \equiv C$ for the corresponding acetylene. The absence of data on PhCCEt and PhCCPh does not permit comment on the trend noted for the comparable nitrilium cation where the frequency for PhCNR increases in the sequence

$$R = Me > Et > Ph$$

The increase in value of the $-C \equiv \overset{+}{N}$ as against $C \equiv C$ suggests on increase in the triple band stretching force constant on replacing $\equiv C-$ by $\equiv \overset{\oplus}{N}-$.

(C). Reaction of Chlorides with Nitrile Adducts

The possibility of carrying out the following reaction

$$RCN,BCl_3 + R'Cl \longrightarrow [RCNR']^{+} [BCl_4]^{-}$$

was investigated using the chlorides HCl, MeCOCl, $pClC_6H_4COCl$ and chlorobenzene. The results are discussed below.

(a) The System $PhCN/BCl_3/HCl$

The reaction of HCl gas with benzonitrile-stannic chloride adduct, $(PhCN)_2SnCl_4$ has been reported (23) to yield benzonitrilium hexchlorostannate (IV).

$$Ph(CN)_2.SnCl_4 \xrightarrow[\text{room temp.}]{2HCl\ (g)} [PhCNH]^{+}_2 [SnCl_6]^{--}$$

This, the only reaction of the kind so far reported, suggested that a similar type of reaction with the adducts of boron trichloride would be an alternative to that using imidchlorides for the synthesis of nitrilium salts e.g.

$$RCN,BCl_3 + HCl \longrightarrow [RCNH]^{+} [BCl_4]^{-}$$

However, hydrogen chloride had no effect on $PhCN,BCl_3$.

(b) The System $PhCN/BCl_3/PhCOCl$

The zinc chloride adduct of benzonitrile on treatment with benzoyl chloride has been shown to yield benzoyl benzonitrilium trichlorozincate (4) i.e.

$$PhCN,ZnCl_2 + PhCOCl \longrightarrow [PhCNCOPh]^{+} [ZnCl_3]^{-}$$

This suggests that formation of a tetrachloroborate might follow the interaction of the benzonitrile-boron trichloride adduct with benzoyl chloride i.e.

$$\mathrm{PhCN,BCl_3 + PhCOCl \longrightarrow \overset{+}{[PhCNCOPh]}\ \overset{-}{[BCl_4]}}$$

However no interaction was found to occur in this investigation. The benzoyl chloride and nitrile adduct could be recovered unchanged.

(c) The System PhCN/BCl_3/CH_3COCl

When benzonitrile-boron trichloride adduct was treated with acetyl chloride in toluene at room temperature, no reaction was observed. The reactants were recovered unchanged.

It seems probable that the lack of success in systems (a), (b), and (c) is due to the fact that the route is thermodynamically unfavourable. Thermal decomposition of the nitrilium salts of benzonitrile, prepared from the imidchloride, occurs readily yielding alkyl halide and benzonitrile-boron trichloride adduct.

$$\mathrm{\overset{+}{[RCNR']}\ \overset{-}{[BCl_4]} \xrightarrow{heat} R'Cl + RCN,BCl_3}$$

where R = Ph

R′ = Ph,Et or Me.

A similar observation has been made by Lappert (24) in the case of pyridinium tetrachloroborate, C_5H_5NH,BCl_4. HCl was lost on heating to give the pyridine - boron trichloride adduct.

$$\mathrm{\overset{+}{[C_5H_5NH]}\ \overset{-}{[BCl_4]} \xrightarrow{heat} C_5H_5N,BCl_3 + HCl}$$

Lappert also showed that the reverse reaction was not possible.

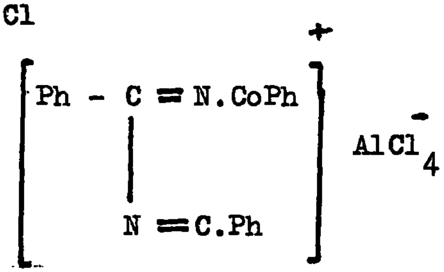
(d) The System $PhCN/BCl_3/p\text{-}ClC_6H_4COCl$

When boron trichloride was added to a mixture of pchlorobenzoyl chloride and benzonitrile, the solid separating from the system was identified as benzonitrile - boron trichloride adduct.

$$PhCN + pCl\ C_6H_4COCl + BCl_3 \longrightarrow PhCN,BCl_3 + pCl\ C_6H_4COCl$$

In contrast to this, aluminium trichloride forms the tetrachloroaluminate of the N, acyl-acyl nitrilium salt (4).

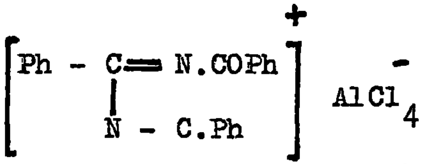
$$2\ PhCN + AlCl_3 + pCl\ C_6H_4COCl$$



$$\left[\begin{array}{l}\mathrm{Ph - C = N.CoPh}\\ \qquad\;\; | \\ \qquad\;\; \mathrm{N = C.Ph}\end{array}\right]^{+} AlCl_4^{-}$$

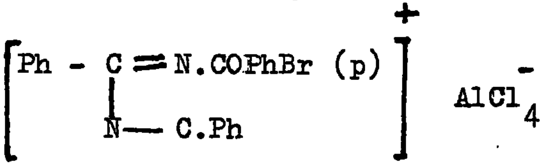
It is significant, however, that two nitrile molecules are involved here. Related salts which have been described include the following:-

1.



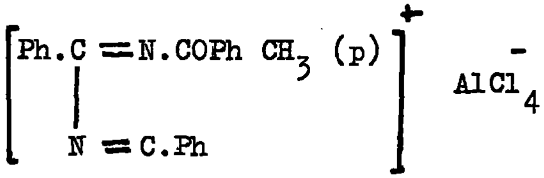
$$\left[\begin{array}{l}\mathrm{Ph - C = N.COPh}\\ \qquad\;\; | \\ \qquad\;\; \mathrm{N - C.Ph}\end{array}\right]^{+} AlCl_4^{-}$$

2.



$$\left[\begin{array}{l}\mathrm{Ph - C = N.COPhBr\ (p)}\\ \qquad\;\; | \\ \qquad\;\; \mathrm{N - C.Ph}\end{array}\right]^{+} AlCl_4^{-}$$

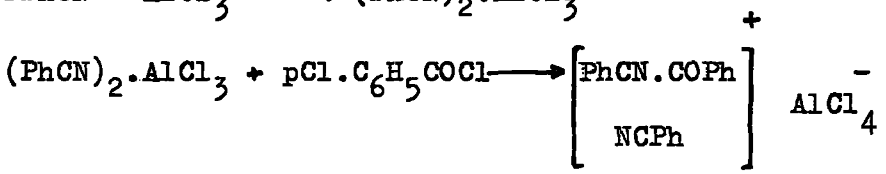
3.



$$\left[\begin{array}{l}\mathrm{Ph.C = N.COPh\ CH_3\ (p)}\\ \qquad | \\ \qquad \mathrm{N = C.Ph}\end{array}\right]^{+} AlCl_4^{-}$$

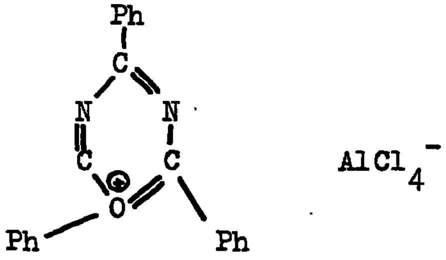
Nitrilium salts of chlorostannate and chloroantimonate anions have also been prepared. During an investigation of the reaction between benzonitrile, chlorobenzene and aluminium trichloride in which 1:1:1 molar ratios of the reactants were used, the product obtained was $(PhCN)_2.AlCl_3$, despite the fact that a 1:1 adduct $PhCN,AlCl_3$ is known. It is suggested that $(PhCN)_2,AlCl_3$ is an intermediate in the formation of compounds 1, 2 and 3 and that this product subsequently undergoes reaction with p-chlorobenzoyl chloride to give the N, acyl-acyl nitrilium salt; e.g.

$$2PhCN + AlCl_3 \longrightarrow (PhCN)_2.AlCl_3$$



$$(PhCN)_2.AlCl_3 + pCl.C_6H_5COCl \longrightarrow \begin{bmatrix} PhCN.COPh \\ NCPh \end{bmatrix}^{+} AlCl_4^{-}$$

The weight of the evidence as described in Part I suggests that the cation in such compounds has the heterocyclic structure:-



(e) The System $PhCN/BCl_3/PhCl$.

The reaction of chlorobenzene with benzonitrile and boron trichloride gave the benzonitrile - boron trichloride adduct, $PhCN,BCl_3$. When boron trichloride was replaced by aluminium trichloride a similar reaction took place which resulted in the formation of benzonitrile - aluminium trichloride adduct, $(PhCN)_2.AlCl_3$.

In contrast alkyl halides have been reported to react with some nitrile adducts to form ionic complexes. For example acetonitrile - antimony pentachloride adduct when treated with an excess of methyl chloride gives the nitrilium hexachloroantimonate (14):-

$$CH_3CN,SbCl_5 + CH_3Cl \longrightarrow \left[CH_3CNCH_3\right]^+ \left[SbCl_6\right]^-$$

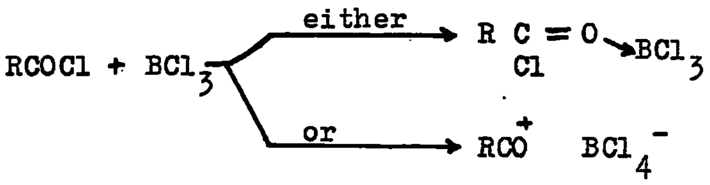
This difference between reactions of alkyl halides and aryl halides may be attributed to the well known higher reactivity of alkyl halides as compared to aryl halide.

(D) Reactions of Chlorides with Boron trichloride

(a) The Systems $pClC_6H_4COCl/BCl_3$

Benzoyl chloride forms addition compounds with a range of Lewis acids but no adduct is reported with boron trichloride (24,25,26,27,28). The aluminium (24,29) and gallium (30) trichlorides however do form adducts with benzoyl chloride.

Acid chlorides might in theory give either covalent adducts by co-ordination through the carbonyl oxygen or ionic acylium adducts by cleavage of Cl^-:-



$$RCOCl + BCl_3 \begin{cases} \xrightarrow{\text{either}} R\underset{Cl}{C}=O \rightarrow BCl_3 \\ \xrightarrow{\text{or}} RCO^+ \quad BCl_4^- \end{cases}$$

Formation of the ionic type of adduct would be most likely in cases where the nature of R favours cleavage of Cl^- and therefore formation of the acylium ion. The behaviour towards BCl_3 of the acid chlorides $p\text{-}ClC_6H_4COCl$ and $3,5(NO_2)_2C_6H_3COCl$

was therefore investigated, but no evidence of complex formation was obtained.

(b) The System Ph_3CCl/BCl_3

The triphenyl methyl cation, Ph_3C , is one of the most stable hydrocarbon cations, the chloride behaving as an ionic compound forming a 1:1 adduct with BCl_3, the adduct having the tetrachloroborate structure, Ph_3C^{+} , BCl_4^{-} (1). The adduct was prepared in this instance to provide the characteristic I.R. frequencies of the tetrachloroborate anion for comparison with the tetrachloroborates prepared in this work (see p.).

As described earlier the compound Ph_3C , BCl_4 was precipitated from a benzene solution of Ph_3C Cl , by addition of BCl_3, as a deep yellow solid. The deep yellow colour is also obtained on contact of the solid Ph_3C Cl with gaseous BCl_3 giving the appearance of complete reaction in this system. However this solid-gas reaction is incomplete, the conversion to Ph_3C , BCl_4 being only of the order of 1% even after contact of the reactants for a period of 3 days.

The intense colour of these adducts appears to be characteristic of salts of triphenyl methyl cation with large anions and it is possible that the colour arises from an electron transfer process i.e.

$$Ph_4C^{+}\ ,\ BCl_4^{-} \longrightarrow Ph_3C.BCl_4$$

Such a transfer of charge could be regarded as reforming the Ph_3C free radical, which itself has an intense yellow colour. The tetrachloroborate compound was examined in an E.S.R. spectrometer and showed a paramagnetic resonance signal at about the free electron region. Whilst this is not regarded as conclusive it would seem that further work on this point might yield useful results, but further discussion of this point will not be made here.

(C) The Systems MeCON (Cl) Ph/BCl_3 and $MeCONHC_6H_4Cl/BCl_3$

The compound MeCON(Cl)Ph was prepared in order that its reaction with boron trichloride could be studied and compared with the behaviour of acid amides RCONHR towards BCl_3. There appeared to be 3 possible donor sites in the N-chloro amide, viz. the carbonyl oxygen, the nitrogen and the chlorine atom.

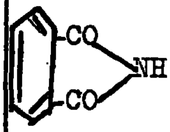
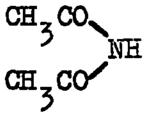
When treated with boron trichloride, N-chloroacetanilide gave a 1:1 adduct, the infrared spectrum of which did not show the bands characteristic of the tetrachloroborate anion, but did however contain a band at 3270 cm^{-1} in the region expected for an N-H stretching vibration. A possible explanation was that the N-chloroacetanilide had rearranged on contact with BCl_3 to p-chloroacetanilide. The boron trichloride adduct of p-chloroacetanilide was therefore prepared and the comparison showed it to be one and the same compound.

(E) Reactions of amides and Imides with BCl_3 and BF_3

Some amides RCONH and imides $(RCO)_2NH$ were used in the preparation of imidchlorides discussed in Section A. The adducts of these amides and imides were also prepared during this investigation mainly for the purpose of comparison with the products of adduct formation on the corresponding imidchloride. The adducts have not previously been reported and their composition is recorded in Table IX. The column headed "Ratio" gives the number of moles of ligand per mole of the Lewis acid.

Table IX

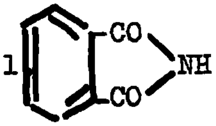
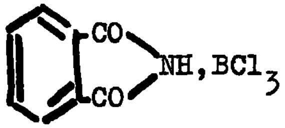
Complexes of some Lewis Acids with amides and imides.

Ligand	Lewis Acid	Ratio	M.Pt°C.
	BF_3		
	BF_3	1	
	BCl_3	1	195 (dec.)
 $(CH_3CO)_2NH$	BF_3		
	BF_3	½	
PhCONHPh	$SnCl_4$	2	210 (dec.)
	BF_3	1	50-55
	BCl_3	1*	
PhCONHEt	BF_3	1	95

*The benzanilide - boron trichloride adduct dissociates into its components at room temperature.

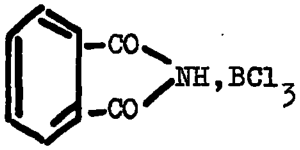
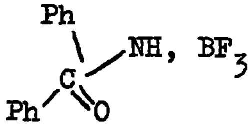
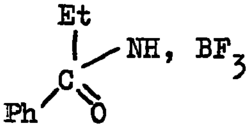
The frequencies of the absorption bands in the infra-red spectra of these adducts are listed in Pt III (pp.   ), and the values for a number of selected bands are shown in Table X. The amide I band arises almost exclusively (> 80%) from the carbonyl stretching mode (6).

Table X

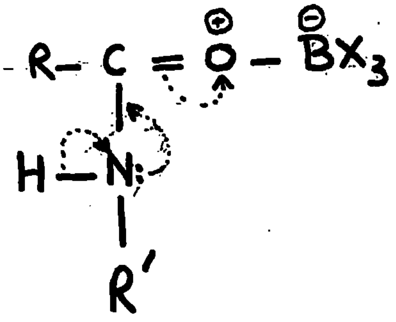
Compound	Phase	N-H St. cm^{-1}	Amide I	C-N St. cm^{-1}
1 	KBr disc	3200	1784	1063
2 	Nujol	3230	1760	1068
1. $(CH_3CO)_2NH$	KBr	3145	1745	1022
2. $SnCl_4.2(CH_3CO)_2NH$	Nujol	3200	1690	1026
1. PhCONHPh	Nujol	3334	1661	1002
2. BF_3.PhCONHPh	Nujol	3340	1660	1036
1. PhCONHEt	Nujol	3335	1640	1005
2. BF_3.PhCONHEt	Nujol	3345	1610	1020

Adduct formation leads to frequency shifts of the infra-red absorption bands, and the shifts for the compounds examined in the present work are shown in Table XI.

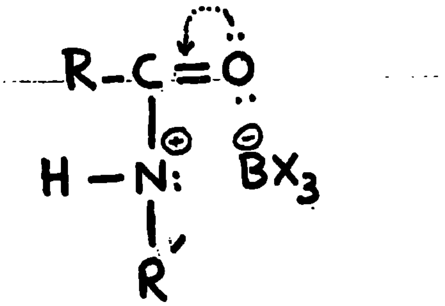
Table XI

Complex	$\Delta\nu$ N-H cm^{-1}	$\Delta\nu$ (Amide I) cm^{-1}	$\Delta\nu$ C-N cm^{-1}
	+30	-24	+5
$(CH_3CO)_2NH.\ SnCl_4$	+55	-55	+4
	+6	-1	+34
	+10	-30	+15

A number of authors (5, 31, 32) have used such frequency shifts to decide the question of the co-ordination site in related compounds, the problem being whether co-ordination occurs through the O or N atom. Gerrard and co-workers (5) discuss their results in terms of the structures I and II, and predict the indicated frequency shifts $\Delta\nu$.



I



II

$\Delta\nu$ C = O	-ive	$\Delta\nu$ C = O	+ive
$\Delta\nu$ C - N	+ive	$\Delta\nu$ C - N	-ive
$\Delta\nu$ N - H	+ive	$\Delta\nu$ N - H	+ive
I		II	

The frequency shifts observed by these authors are consistent with structure I, i.e. co-ordination through the O atom. The range of published values (5, 31, 32) for frequency shifts in related compounds are:-

$\Delta\nu$ C = O	-ive	0 → 38 cm^{-1}
$\Delta\nu$ C - N	+ive	7 → 30 cm^{-1}
$\Delta\nu$ N - H	+ive	25 → 75 cm^{-1}

The shifts given in Table XI for the compounds examined in this work are similar in direction and magnitude to those observed by Gerrard et al (6), and insofar as the argument presented by these authors is valid the results obtained in the present work can be regarded as supporting the view that co-ordination occurs through the oxygen atom.

References - Pt. IV

1. Kemmitt, Milner and Sharp
J. Chem. Soc. 1963, 111.

2. H. H. Bosshard and H. Zollinger
Helv. Chim. Acta 1959, 42, 1659.

3. Landesman and William.
J. Amer. Chem. Soc. 1961, 2663.

4. H. Meerwein, P. Laasch, R. Mersch, and J. Spille.
Ber., 1956, 89, 224.

5. W. Gerrard, M.F. Lappert and J. W. Wallis.
J. Chem. Soc. 1960, 2178, 2141.

6. K. Hoesch, Ber. 1915, 48, 1122.

7, H. Stephen, J. Chem. Soc. 1925, 127, 1874.

8. A. Hantzch, Ber. 1931, 64, 670.

9. Beiltein org. chemic Band II p.245.

10. Wallach, Annalen 1882, 214, 193.

11. Von Braun, Jostes and Heymons.
Ber. 1927, 60, 92.

12. Farbenfabriken Bayer A.G.
Brit. 1954, 595, 704.

13. J. E. Gordon and G. C. Turrell.
J. Org. Chem, 1959, 24, 269.

14. idem. J. Chem. Phys. 1959, 30, 895.

15. W. Gerrard, M. F. Lappert and J. W. Wallace
J. Chem. Soc. 1960, 2182.

16. I. R. Beattie & T. Gilson, J. Chem. Soc. 1964, 2294.

17. K. F. Purcell and R. S. Drago J. Amer. Chem. Soc. 1966, 88, 919.

18. N. Sheppard and D. M. Simpson Quat. Revs. 1952.

19. G. Herzberg, "I.R. and Raman spectra of polyatomic Molecules". 1945, p. 173.

20. Bourguel and Daure. Bull. Soc. Chim., 1930, 47, 1349.

21. Meister and Cleveland J. Chem. Phys. 1944, 12, 393.

22. Klages, Ruhnan and Hauser Annalen 1959, 626, 60.

23. M. F. Lappert. Proc. Chem. Soc. 1957, 121.

24. Menschutkin, Chem. Zentr. 1906, 11, 1720.

25. idem J. Russ. Phys. Chem. Ges. 1910, 42, 1310.

26. Bertrand. Bull. Soc. Chim. 1880, 33, 403.

27. Cullinance, Chard, and Leyshon. J. Chem. Soc. 1952, 4106.

28. Meerwein and Maier - Huser J. Prakt. Chem. 1932, 134, 51.

29. Nespital, Z. Phys. Chem. 1932, 16B, 153.

30. K. Wade, Ph.D. Thesis University of Nottingham 1957.

31. R. C. Aggarwal & P. P. Singh Z. Anorg. Chem. 1964, 332, 103.

32. R. B. Penland, S. Mizushima, C. Curran and J. V. Quaglino J. Amer. Chem. Soc. 1957, 79, 1575.