432. *Interaction of Boron Trichloride and Amides or Oximes, and Allied Reactions.*

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Boron halides (Cl, Br) and titanium tetrachloride form with amides 1 : 1 complexes, which are hydrolysed readily. The pyrolysis of the complexes is described. Benzophenone oxime underwent the Beckmann rearrangement when treated with boron trichloride.

As well as forming hydrochlorides, amides form complexes with a number of inorganic halides. Thus copper^{II} (2 : 1),[1] cadmium^{II} (2 : 1),[1] and mercury^{II} (1 : 1) [1] chloride, boron trifluoride (1 : 1),[2,3,4] titanium^{IV} (2 : 1),[5] cobalt^{II} (1 : 1),[1] and nickel^{II} (1 : 1) [1] chloride complexes have been prepared (ratios in parentheses refer to mol. ligand : mol. halide). Reactions of primary amides with aluminium trichloride [6] and phosphorus pentachloride [7,8] (see also ref. 9) have also been studied and the ultimate products were corresponding nitriles, although intermediates, $R\cdot CCl{:}N\cdot PCl_2$ [7] and $R\cdot CO\cdot N{:}PCl_3$,[8] have been described. Data on parachors [4] and infrared [2,10] and nuclear magnetic resonance [10] spectra are available. The boron trifluoride–*NN*-dimethylformamide complex was hydrolysed readily; [2] pyrolysis of the corresponding formamide complex gave carbon monoxide and hydrogen cyanide. The boron trifluoride–acetamide complex reacted as an acetylating agent with alcohols and amines (primary and secondary).[11, 12]

Table 1.

Complex	M. p.	Complex	M. p.
$Me\cdot CO\cdot NH_2,BCl_3$	75·5—76·5°	$H\cdot CO\cdot NHMe,BCl_3$	(Viscous liquid)
$Me\cdot CO\cdot NHMe,BCl_3$	88—90	$H\cdot CO\cdot NMe_2,BCl_3$	119—122°
$Me\cdot CO\cdot NMe_2,BCl_3$	99—101	$Ph\cdot CO\cdot NH_2,BCl_3$	95
$Me\cdot CO\cdot NHPh,BCl_3$	130	$Me\cdot CO\cdot NH_2,BBr_3$	98—99
$Me\cdot CO\cdot NH\cdot C_6H_4\cdot OMe\text{-}p,BCl_3$	103—104	$Me\cdot CO\cdot NHMe,BBr_3$	104—106
		$Me\cdot CO\cdot NMe_2,BBr_3$	110—114
$Et\cdot CO\cdot NH_2,BCl_3$	(n_D^{20} 1·4980, d_4^{20} 1·5469)	$Me\cdot CO\cdot NHMe,TiCl_4$	(softens at ~130°) (m. p. $>200°$)

In the present work, various unsubstituted and *N*-substituted amides were shown (Table 1) to form moderately stable 1 : 1 complexes with boron halides (Cl, Br) and titanium tetrachloride.

Reactions between the halides and such a variety of amides were carried out in order (1) to determine whether complex formation was general; (2) to study the structure of the complexes (see following paper [10]); and (3) to study selected chemical reactions (particularly pyrolyses) of the boron trichloride complexes, because the trichloride has proved [13] such a versatile reagent with most classes of organic compound.

All the complexes were readily hydrolysed by cold water, unlike amine–boron trichloride adducts.[14] They were also reactive with alcohols (but not as acylating agents); thus the benzamide–boron trichloride complex with butan-1-ol afforded hydrogen chloride,

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[1] André, *Compt. rend.*, 1886, **102**, 115.

[2] Muetterties and Rochow, *J. Amer. Chem. Soc.*, 1953, **75**, 490.

[3] Bowlus and Nieuwland, *ibid.*, 1931, **53**, 3835.

[4] Sugden and Waloff, *J.*, 1932, 1492.

[5] Dermer and Fernelius, *Z. anorg. Chem.*, 1934, **221**, 83.

[6] Norris and Klemka, *J. Amer. Chem. Soc.*, 1940, **62**, 1432.

[7] Wallach, *Annalen*, 1877, **184**, 1.

[8] Kirsanov, *Bull. Acad. Sci. U.S.S.R.*, 1954, 551.

[9] von Braun and Heymons, *Ber.*, 1930, **63**, 502, and earlier references cited therein.

[10] Gerrard, Lappert, Pyszora, and Wallis, following paper.

[11] Sowa and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 5052.

[12] *Idem, ibid.*, 1937, **59**, 1202.

[13] Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1081.

[14] *Idem, J.*, 1951, 1020; *Chem. and Ind.*, 1952, 53.

benzamide hydrochloride, and tri-n-butyl borate. It seems probable that pyrolysis of primary amide–boron trichloride proceeds as follows:

$$\underset{\text{(I)}}{R{\cdot}CO{\cdot}NH_2,BCl_3} \xrightarrow{-\,HCl} \underset{\text{(II)}}{R{\cdot}CO{\cdot}NH{\cdot}BCl_2} \xrightarrow{-\,HCl} \underset{\text{(III)}}{R{\cdot}CO{\cdot}N{:}BCl} \longrightarrow RCN + \tfrac{1}{3}(BOCl)_3$$

$$\longrightarrow [\tfrac{1}{3}B_2O_3 + \tfrac{1}{3}BCl_3] \longrightarrow \underset{\text{(IV)}}{RCN,BCl_3}$$

A compound of type (II) was isolated from acetamide, and analogous compounds $R{\cdot}CO{\cdot}NR'{\cdot}BCl_2$ (V) were obtained from *N*-methylformamide and acetanilide. Neither chemical reactions nor infrared spectra indicated whether in these the boron atom was attached to oxygen or nitrogen. In the propionamide experiment, the complex (IV) was isolated and benzonitrile was obtained from benzamide–boron trichloride.

Continuing the study [13] of reactions of boron trichloride with different classes of organic compound, we examined the boron trichloride–benzophenone oxime system. In common with many other inorganic halides,[15] the trichloride was shown to be an effective reagent for the Beckmann rearrangement of oxime to amide (to give in this case benzanilide, after hydrolysis).

EXPERIMENTAL

General Procedures.—All the amides, except *NN*-dimethylacetamide [16] [b. p. 64—65°/15 mm., n_D^{20} 1·4380, d_4^{20} 0·4458 (Found: N, 16·1. Calc. for C_4H_9ON: N, 16·1%)], *NN*-diphenylacetamide [17] [m. p. 102° (Found: N, 6·2. Calc. for $C_{12}H_{11}N$: N, 6·3%)], and *p*-methoxyacetanilide [18] [m. p. 130—132° (Found: N, 8·4. Calc. for $C_9H_{11}O_2N$: N, 8·4%)], were commercial samples purified by standard methods. Benzophenone oxime, m. p. 146—147° (Found: N, 7·0. Calc. for $C_{13}H_{11}ON$: N, 7·1%), was prepared by Beckmann's method.[19] Hydrocarbon solvents were dried over sodium, and methylene chloride over phosphoric oxide. Boron halides and titanium tetrachloride were redistilled before use. Chlorine, bromine, and boron were analysed acidimetrically as hydrogen halide (Methyl Red) and boric acid (phenolphthalein, in presence of mannitol) formed by cold-water hydrolysis of samples in enclosed systems. Nitrogen was estimated by the Kjeldahl procedure. M. p.s were determined in sealed capillary tubes.

TABLE 2.

Complex	Solvent	Yield (%)	Found (%) N	Hal	B	Required (%) N	Hal	B
$Me{\cdot}CO{\cdot}NH_2,BCl_3$ *	CH_2Cl_2	99	7·8	60·1	6·30	7·95	60·4	6·14
$Me{\cdot}CO{\cdot}NHMe,BCl_3$ †	CH_2Cl_2 ‡	95	7·4	54·8	5·58	7·4	55·9	5·68
$Me{\cdot}CO{\cdot}NMe_2,BCl_3$ †	n-C_5H_{12}	98	6·9	51·7	5·28	6·9	51·2	5·30
$Me{\cdot}CO{\cdot}NHPh,BCl_3$ *	CH_2Cl_2	72	5·6	41·9	4·32	5·6	42·2	4·29
$Me{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$-*p*,$BCl_3$ †	CH_2Cl_2 ‡	84	5·1	36·4	3·85	5·0	37·7	3·83
$Me{\cdot}CO{\cdot}NPh_2,BCl_3$ †	CH_2Cl_2 ‡	97	4·2	32·8	3·42	4·3	32·4	3·29
$Et{\cdot}CO{\cdot}NH_2,BCl_3$ *	CH_2Cl_2	100	7·5	54·7	5·92	7·4	55·9	5·68
$H{\cdot}CO{\cdot}NHMe,BCl_3$ †	CH_2Cl_2 ‡	100	8·2	58·2	6·23	7·95	60·4	6·14
$H{\cdot}CO{\cdot}NMe_2,BCl_3$ *	CH_2Cl_2 ‡	91	7·3	54·8	5·81	7·4	55·9	5·68
$Ph{\cdot}CO{\cdot}NH_2,BCl_3$ *	CH_2Cl_2 ‡	93	5·9	44·6	4·60	5·9	44·7	4·54
$Me{\cdot}CO{\cdot}NH_2,BBr_3$ *	C_6H_6	79	4·7	75·4	3·74	4·5	77·4	3·56
$Me{\cdot}CO{\cdot}NHMe,BBr_3$ †	C_6H_6	60	4·2	73·4	4·34	4·3	74·1	4·21
$Me{\cdot}CO{\cdot}NMe_2,BBr_3$ *	n-C_5H_{12}	81	4·0	69·6	3·31	4·15	71·0	3·20
$Me{\cdot}CO{\cdot}NHMe,TiCl_4$ *	C_6H_6	82	5·5	51·7	—	5·3	54·0	—

* Addition of amide to halide. † Addition of halide to amide. ‡ Pptn. completed by addition of n-pentane.

Preparation of Boron Halide and Titanium Tetrachloride Complexes.—The complexes were obtained by addition of the amide (1 mol.) in an inert solvent to the halide (1 mol.) in the same

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[15] Beckmann and Bark, *J. prakt. Chem.*, 1923, **105**, 327.

[16] Aschan, *Ber.*, 1898, **31**, 2344.

[17] Kaufmann and Luterbacher, *ibid.*, 1909, **42**, 3483.

[18] Reverdin and Bucky, *ibid.*, 1906, **39**, 2679.

[19] Beckmann, *ibid.*, 1886, **19**, 988.

solvent at −78°. The order of addition was reversed, and the amide was in suspension in cases where the amide had sparing solubility in the chosen solvent. The reactions, which were exothermal, were carried out on approximately 0·05 molar scale. The solid *complexes* were purified by filtration, washing with n-pentane, and freeing from solvent at 20°/0·1—15 mm. The liquid complexes were isolated as residues after removal of volatile matter at 20°/0·1 mm.; details are shown in Table 2.

Hydrolysis and Alcoholysis of Certain of the Complexes.—That all the complexes were hydrolysed by cold water to produce hydrogen halide and boric acid was evident from the analytical results. This was checked for the benzamide–boron trichloride complex by treating it (4·19 g.) with cold water (30 ml.) and then extracting the mixture with chloroform (2 × 20 ml.). The chloroform solution was washed with water and, after drying ($MgSO_4$), afforded benzamide (1·90 g., 89%), m. p. 130° (from aqueous ethanol) (Found: N, 11·5. Calc. for C_7H_7ON: N, 11·5%).

Butan-1-ol (4·58 g.) in n-pentane (15 ml.) was slowly added to the complex (4·91 g.) suspended in n-pentane (15 ml.); an exothermal reaction, with evolution of hydrogen chloride, took place. The mixture was heated under reflux for 1 hr.; and 1·36 g. (91%) of hydrogen chloride were trapped in potassium hydroxide absorption tubes. Benzamide hydrochloride (3·27 g., 100%), m. p. 95—96° (Found: N, 9·0; Cl, 23·1. Calc. for C_7H_8ONCl: N, 8·9; Cl, 22·5%), was separated by filtration and washing (n-pentane). The combined filtrate afforded tri-n-butyl borate (4·41 g., 93%), b. p. 116—117°/15 mm., n_D^{21} 1·4087 (Found: B, 4·75. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%). Yields are based on: $Ph{\cdot}CO{\cdot}NH_2,BCl_3 + 3C_4H_9{\cdot}OH \longrightarrow Ph{\cdot}CO{\cdot}NH_2,HCl + 2HCl + B(OC_4H_9)_3$.

Pyrolysis of Amide Complexes.—(a) *Acetamide.* The complex (6·91 g.) was heated under reflux at 100°/15 mm. for 10 hr. and the evolved hydrogen chloride (1·43 g., 100%) was absorbed in alkali. The yellow *compound* (II) (R = Me) (5·40 g., 98%) (Found: N, 10·2; Cl, 49·5; B, 8·4. $C_2H_4ONCl_2B$ requires N, 10·0; Cl, 50·6; B, 7·75%) was obtained as a residual glass.

(b) N-*Methylformamide.* The complex (16·42 g.) was heated for 17 hr. at 110° and treated as in (a), to give hydrogen chloride (3·01 g., 100%) and the yellow solid *compound* (V) (R = H, R′ = Me) (13·13 g., 100%) (Found: N, 10·3; Cl, 49·0; B, 7·93. $C_2H_4ONCl_2B$ requires N, 10·0; Cl, 50·6; B, 7·75%).

(c) *Acetanilide.* The complex (7·74 g.) when heated for 6 hr. at 120°/15 mm. and treated as in (a) afforded hydrogen chloride (1·06 g., 100%) and *compound* (V) (R = Me, R′ = Ph) (6·63 g., 100%) as a yellow glass (Found: N, 6·5; Cl, 35·2; B, 4·62. $C_8H_8ONCl_2B$ requires N, 6·4; Cl, 32·3; B, 4·92%).

(d) NN-*Dimethylacetamide.* The complex was unchanged (analysis and infrared spectrum) after 6 hr. at 120°/15 mm.

(e) *Propionamide.* The complex (14·65 g.) in toluene (40 ml.) was heated under reflux for 12 hr. Hydrogen chloride (5·12 g., 91%) was evolved. Matter volatile at 110° was removed from the residue by distillation to leave a black solid (9·57 g.) (Found: N, 10·8; Cl, 22·3; B, 9·34%). Boron trichloride (6·00 g.) in n-pentane (50 ml.) was added to the distillate to give the propionitrile–boron trichloride complex [20] (0·98 g., 11%), m. p. 136—138° (authentic infrared spectrum, C≡N band at 2326 cm.$^{-1}$) (Found: N, 8·2; Cl, 61·4; B, 6·43. Calc. for $C_3H_5NCl_3B$: N, 8·1; Cl, 61·8; B, 6·28%).

(f) *Benzamide.* The complex (12·50 g.) in toluene (40 ml.) was treated as in (e). Hydrogen chloride (3·39 g., 88%) was evolved and a solid (9·13 g.) was obtained, which when extracted with n-pentane afforded the soluble benzonitrile (1·54 g., 43%) (authentic infrared spectrum, C≡N band at 2223 cm.$^{-1}$), n_D^{20} 1·5243. The insoluble portion (7·25 g.) (Found: N, 8·03; Cl, 11·4; B, 8·21%) was a white solid.

Yields in (a), (b), and (c) are based on an equation, $R{\cdot}CO{\cdot}NHR',BCl_3 \longrightarrow HCl + R{\cdot}CO{\cdot}NR'{\cdot}BCl_2$; and in (e) and (f) on: $3R{\cdot}CO{\cdot}NH_2,BCl_3 \longrightarrow 2RCN + 6HCl + (RCN,BCl_3 + B_2O_3)$.

Interaction of Benzophenone Oxime and Boron Trichloride.—The trichloride (4·60 g., 1·5 mol.) in methylene chloride (20 ml.) at −78° was added dropwise to the oxime (5·07 g., 1 mol.) in the same solvent (20 ml.) at −78°. The solvent was partially removed at 20°/20 mm. and addition of n-pentane (50 ml.) resulted in precipitation of a yellow solid (8·01 g.) (Found: N, 4·1; Cl,

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[20] Gerrard, Lappert, and Wallis, *J.*, in the press; Gerrard, Lappert, Pyszora, and Wallis, *J.*, in the press.

35·6; B, 4·32%). A portion (2·12 g.) of this was hydrolysed with cold water (20 ml.) to give benzanilide (1·08 g., 81%), m. p. 163° (from ethanol) (Found: N, 7·0. Calc. for $C_{13}H_{11}ON$: N, 7·1%) (authentic infrared spectrum).

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