Inorganica Chimica Acta, 31 (1978) 69–76
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Reactions of Oximes with Covalent Halides. Part III. α-Benzil Monoxime and Acetyl Monoxime with Phenyl Boron Dichloride and Boron Tri-fluoride, -chloride and -bromide

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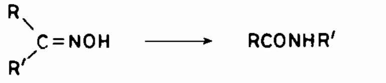
Received February 22, 1978

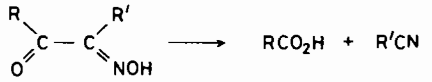
Reaction of boron trifluoride with α-benzil monoxime (bmoH) gave BF_3, bmoH. With boron trichloride and tribromide the oxime gave BX_2(bmo) (X = Cl or Br) and with phenyl boron dichloride it gave PhBCl(bmo). Analogous complexes were obtained from acetyl monoxime (amoH). The complexes BX_2(bmo) were unaffected by water but were hydrolysed by warm alkali; all the other complexes were hydrolysed by water. The adduct BF_3, bmoH underwent Beckmann fragmentation on heating at 120 °C/0.1 mm but at 120°/760 mm the adduct underwent Beckmann rearrangement; the other complexes underwent Beckmann fragmentation on heating. Mass spectrometric studies indicate that the complexes BCl_2(bmo) and BX_2(amo) are dimeric in the vapour state.

Introduction

Oximes may undergo Beckmann rearrangement and Beckmann fragmentation [1]. The rearrangement is shown by several types of oximes and results in the formation of an amide [reaction (1)]. The rearrangement can be effected by a variety of reagents such as protonic acids, non-metal halides and metal salts. The fragmentation is shown by certain types of oximes only *e.g.* α-ketoximes and other α-substituted oximes. The fragmentation involves carbon–carbon bond fission [*e.g.* reaction (2)] and can be effected by reagents such as protonic acis and non-metal halides, as well as by high temperatures. Earlier we reported that the fragmentation of α-benzil monoxime (bmoH) and of β-benzil monoxime can also be effected by using titanium tetrachloride [2] and of the α-isomer by using tin tetrachloride, tetrabromide and tetraiodide [3]. Recently it has been shown that the fragmentation of these and other ketoximes is also induced by reaction with tetrakis-(triphenylphosphine)palladium in the presence of molecular oxygen [4].



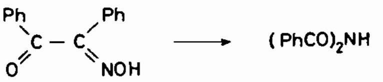
$$RR'C{=}NOH \longrightarrow RCONHR' \qquad (1)$$



$$R{-}CO{-}C(R'){=}NOH \longrightarrow RCO_2H + R'CN \qquad (2)$$

The rearrangement/fragmentation behaviour of α-benzil monoxime has been a subject of intense interest [1, 5]. Suggestions have been made that this oxime in addition to showing fragmentation behaviour may also exhibit Beckmann rearrangement under certain conditions but the validity of these suggestions has been questioned [6, 7].

Here we report on the reactions of phenyl boron dichloride, boron trifluoride, trichloride and tribromide with α-benzil or acetyl monoxime (amoH) and on the properties, structures and decomposition of the complexes derived from these reactions. The study of the decomposition of these complexes provides further examples of Beckmann fragmentation, but significantly, it also indicates that Beckmann rearrangement of α-benzil monoxime to NN-dibenzoylamine [reaction (3)] can be induced by boron trifluoride under certain conditions.



$$Ph{-}CO{-}C(Ph){=}NOH \longrightarrow (PhCO)_2NH \qquad (3)$$

Results and Discussion

When boron trifluoride was passed through a suspension of α-benzil monoxime or of acetyl monoxime in benzene the respective adduct BF_3, moH* was formed. In contrast when boron tri-

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*The abbreviation moH denotes either bmoH or amoH.

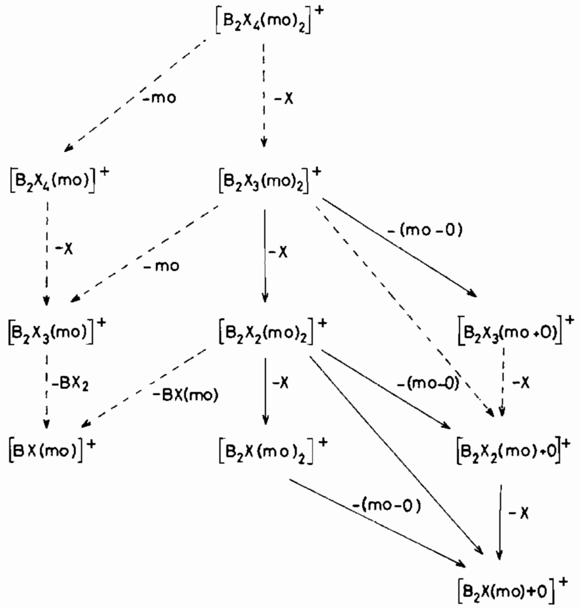
chloride, boron tribromide or phenyl boron dichloride and α-benzil monoxime were mixed in benzene the complexes $BX_2(mo)$ (X = Cl or Br) and PhBCl(mo), which contain the anionic ligand mo^-, resulted.

Both the adducts and the complexes $BX_2(amo)$ (X = Cl or Br) and PhBCl(mo) were readily hydrolysed by water to give the respective oxime. In contrast the complexes $BX_2(bmo)$ (X = Cl or Br) were unaffected by water but could be hydrolysed by treatment with warm aqueous sodium hydroxide.

Structural Considerations

The ligands bmoH and amoH, as well as the respective anionic ligands may coordinate to boron in several ways. Consequently, each of the complexes reported here may have a variety of structures. The insolubility of these complexes in common non-disruptive solvents restricted investigations of their structure to solid state i.r. spectroscopic studies and mass spectrometric studies.

The mass spectra of all the complexes were recorded. The spectra of the adducts, $BBr_2(bmo)$ and PhBCl(mo) showed ions due to species arising from the pyrolysis of the samples prior to ionisation. The complexes $BCl_2(mo)$ and $BBr_2(amo)$ gave well defined spectra (Tables I–III) which indicate that the compounds are dimeric in the vapour state. The complexes $BCl_2(bmo)$ and $BBr_2(amo)$ gave parent ions corresponding to $[B_2X_4(mo)_2]^+$ and their spectra were noted by the presence of several diboron ions which carried most of the ion current. In the spectrum of $BCl_2(amo)$ the ion with highest m/e value corresponded to $[B_2Cl_3(amo)_2]^+$ but again the spectrum showed several other prominent "diboron ions". The presence of at least one organic ligand in each of these ions and the absence of any B_2Cl_n (n = 1–4) fragments free of organic ligand suggests that the organic ligand is involved in bridging the boron atoms and probably precludes any structures with chlorine bridges. The fragmentation pattern of these complexes (Scheme 1) involves loss of X• radicals and to a lesser extent loss of mo• groups. In addition to these reactions bond rupture in the organic ligand also occurs. In all cases elimination of the neutral fragment [mo – O] and formation of ions such as $[B_2X_2(mo) + O]^+$ is observed. The retention of



——→ Process confirmed by presence of metastable peak
– – – – –→ Unconfirmed but possible process

TABLE I. Ion Abundances[a] for Dihalo(monoximato)boron(III).

Ion	$BCl_2(bmo)$		$BCl_2(amo)$		$BBr_2(amo)$	
	m/e	%	m/e	%	m/e	%
$[B_2X_4(mo)_2]^+$	610	10	–	–	538	<1
$[B_2X_3(mo)_2]^+$	575	100	327	100	459	100
$[B_2X_4(mo)]^+$	386	32	262	28	–	–
$[B_2X_3(mo)_2 - RCO]^+$	–	–	–	–	416	1
$[B_2X_3(mo) + O]^+$	–	–	243	16	–	–
$[B_2X_3(mo)]^+$	–	–	227	8	–	–
$[B_2X_2(mo)_2]^+$	540	33	292	40	380	27
$[B_2X(mo)_2]^+$	–	–	257	30	301	16
$[B_2X_2(mo)_2 - RCO]^+$	–	–	–	–	337	5
$[B_2X_2(mo) + O]^+$	332	73	208	42	296	30
$[B_2X(mo) + O]^+$	297	28	173	32	217	18
$[BX_2(mo)]^+$	–	–	–	–	269	2
$[BX(mo)]^+$	270	48	146	16	190	8

[a] Boron-containing species only; all species are corrected for isotopic abundance and the m/e values are given for the ions containing ^{11}B and ^{35}Cl or ^{79}Br.

TABLE II. Metastable Ions in Dihalo(monoximato)boron(III).

Transition		X in BX_2(amo)[a]	m/e Values for transition	m*		Neutral Fragment
				Found[b]	Calcd	
$[B_2X_3(mo)_2]^+$	$\longrightarrow [B_2X_2(mo)_2]^+$	Cl	327 ⟶ 292	260.6	260.7	Cl
$[B_2X_3(mo)_2]^+$	$\longrightarrow [B_2X_2(mo)_2]^+$	Br	459 ⟶ 380	314.5	314.6	Br
$[B_2X_3(mo)_2]^+$	$\longrightarrow [B_2X_2(mo) + O]^+$	Br	459 ⟶ 296	191.0	190.9	Br + (mo – O)
$[B_2X_2(mo)_2]^+$	$\longrightarrow [B_2X(mo)_2]^+$	Cl	292 ⟶ 257	226.1	226.2	Cl
$[B_2X_2(mo)_2]^+$	$\longrightarrow [B_2X_2(mo) + O]^+$	Br	380 ⟶ 296	231.0	230.6	(mo – O)
$[B_2X_2(mo)_2]^+$	$\longrightarrow [B_2X(mo) + O]^+$	Br	380 ⟶ 217	123.9	123.9	Br + (mo – O)
$[B_2X_2(mo) + O]^+$	$\longrightarrow [B_2X(mo) + O]^+$	Br	296 ⟶ 217	159.0	159.1	Br
$[B_2X(mo)_2]^+$	$\longrightarrow [B_2X(mo) + O]^+$	Cl	257 ⟶ 173	116.5	116.4	(mo – O)
$[B_2X(mo)_2]^+$	$\longrightarrow [B_2X(mo) + O]^+$	Br	301 ⟶ 217	156.8	156.4	(mo – O)

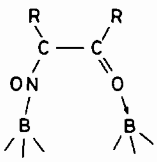
[a] No metastable ions were detected in BCl_2(bmo). [b] Only transitions involving ^{11}B, ^{35}Cl, ^{79}Br are given.

TABLE III. Accurate Mass Measurements on Selected Peaks.

Compound	Nominal Mass	Determined Mass	Ion Assigment	Calculated Mass
BCl_2(bmo)	575	575.0702	$C_{28}H_{20}N_2O_4B_2Cl_3$	575.0728
BCl_2(bmo)	332	332.0228	$C_{14}H_{10}NO_3B_2Cl_2$	332.0224
BCl_2(amo)	327	327.0036	$C_8H_{12}N_2O_4B_2Cl_3$	327.0049
BCl_2(amo)	208	207.9915	$C_4H_6NO_3B_2Cl_2$	207.9911

oxygen in these ions suggests that one or both of the oxygens of the organic ligand could be involved in the bridging. In the case of the complex BBr_2(amo) more extensive fragmentation of the organic ligand occurs. This compound also shows loss of the species $CH_3CO\cdot$ and CH_3CN (Scheme 2).

Selected i.r. data for all the complexes and for the free ligands are given in Table IV. In the case of the complexes BX_2(bmo), the CO stretching frequency appears at a lower frequency than in the free ligand. Similarly the CN stretching frequency is lowered. These observations suggest that both the carbonyl oxygen and the oximino oxygen of the ligand are bonded to boron and indicate dimeric or polymeric structures involving bridges of type I for the BX_2(bmo) complexes in the solid state.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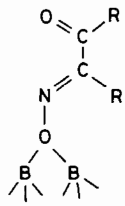
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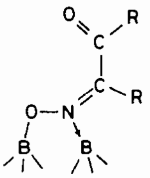

III

In contrast to BX_2(bmo) the CO stretching frequency in the i.r. spectra of BX_2(amo) shifts to higher frequency suggesting that in these complexes the carbonyl group is free. As the complexes BX_2(amo) are dimeric in the vapour state, dimeric or polymeric structures involving bridges of types II or

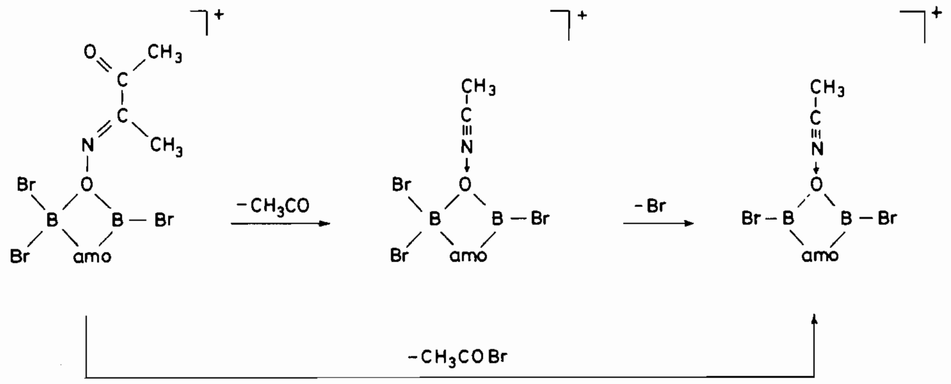


TABLE IV. Selected I.r. Spectroscopic Data[a] on α-Benzil Monoxime, Acetyl Monoxime and their Complexes.

bmoH		BF_3, bmoH	BCl_2(bmo)	BBr_2(bmo)	PhBCl(bmo)	amoH		BF_3, amoH	BCl_2(amo)	BBr_2(amo)	PhBCl(amo)	Assignment
3400s	3490s[b]	3270m				3280s, br	3570s, br[c]	3200s				νOH
3345s	3250s	3170s				3180s, br	3340s, br					
1640s	1675s	1700s	1615s	1612s	1680s	1670s	1698s	1735s	1680s	1680s	1680s	νCO
1645s							1686s					
1620w, sh	1655w, sh	1640m	1600sh	1595s	1650sh	1635sh	1630sh	1645s	1640sh	1630w, sh	1640m	νCN
			1590s		1610s							
1600m	1605m	1600m	1595s	1595s	1600s						1600m	νC=C
1590w	1590w	1590w	1580m	1580m	1580m							
			1500m	1500m	1500m							
			1450m	1450m	1450m							

[a] Solid state unless otherwise stated. [b] In benzene. [c] In carbon tetrachloride. s = strong, br = broad, m = medium, w = weak, sh = shoulder.

III are therefore indicated for these complexes in the solid state. The former type of bridging is more probable because of the presence in their mass spectra of ions such as $[B_2X_n(amo) + O]^+$ and the absence of ions such as $[B_2X_n(amo) + NO]^+$ in which a NO fragment of one of the organic ligands is retained. For the complexes PhBCl(mo) an analogous structure is probable.

The i.r. spectra of the adducts BF_3, bmoH and BF_3, amoH contain strong bands at 1700 and 1735 cm^{-1} respectively assignable to the νCO stretching frequency. The corresponding bands in the free ligands in the solid state and in solution appear lower suggesting that in the complexes the carbonyl group of the ligand is free and that it is the oximino group which is involved in the bonding of the ligand to the boron atom.

Pyrolysis

The adducts were thermally unstable and the products of pyrolysis depended on the conditions. Decomposition of BF_3·amoH occurred also on standing at room temperature to a brown solid (1–2 weeks) but the α-benzil monoxime adduct was stable under these conditions. The adduct BF_3·bmoH on heating at 120 °C/0.1 mm decomposed according to reaction (4). In contrast pyrolysis at 120 °C/760 mm

$$BF_3\cdot bmoH \longrightarrow PhCO_2H + BF_3\cdot PhCN \qquad (4)$$

gave a complex mixture of products, in the form of a sublimate, consisting of BF_3·dbnH (dbnH = NN-dibenzoylamine), dibenzoylamine, benzoic acid and benzamide [reaction (5)]. The nature of these products was established by examining the i.r. spectrum of the mixture and by the isolation and characterisation of hydrolysis products. The dibenzoylamine,

$$\begin{aligned} &BF_3\cdot bmoH \longrightarrow BF_3\cdot dbnH \\ &BF_3\cdot dbnH \longrightarrow dbnH + PhCO_2H + PhCONH_2 \end{aligned} \qquad (5)$$

benzoic acid and benzamide could have arisen from the pyrolysis of BF_3·dbnH, because a separate experiment has shown that this adduct decomposes to give these products.

The difference in the fragmentation behaviour of BF_3·bmoH under different pressure conditions can be explained in terms of Beckmann rearrangement and Beckmann fragmentation processes. When this adduct is heated dissociation occurs [reaction (6)]. Under reduced pressure boron trifluoride is removed

$$BF_3\cdot bmoH \longrightarrow BF_3 + bmoH \qquad (6)$$

and the oxime fragments to give phenyl cyanide and benzoic acid. At 760 mm, the removal of boron trifluoride is not favoured and the reagent remains in the reaction mixture to cause Beckmann rearrangement. The possibility of rearrangement of α-benzil monoxime to NN-dibenzoylamine has been suggested by earlier workers but they were unable to isolate the amine in their experiments [6]. The isolation of NN-dibenzoylamine in this work suggests that α-benzil monoxime can undergo the Beckmann rearrangement under suitable conditions. Several mechanisms have been suggested earlier for such rearrangements [8–10] and the present results can be accounted in a similar fashion.

When $BF_3 \cdot$amoH was heated at 70 °C/0.1 mm it sublimed unchanged but on heating at 100 °C/0.1 mm it decomposed. Several experiments under the latter conditions were carried out but the products of pyrolysis proved difficult to isolate and characterise. However, mass spectrometry indicated the formation of acetic acid and methyl cyanide. On this basis it is assumed that the fragmentation of $BF_3 \cdot$amoH is analogous to the fragmentation of $BF_3 \cdot$bmoH [*cf.* reaction (4)].

The different results obtained at 70 °C and 100 °C can be explained if the rate of decomposition at 100 °C is faster than the rate of sublimation. Decomposition at 100 °C appeared to be rapid (indeed in one experiment the reaction system exploded) whereas sublimation at 70 °C required several hours for completion.

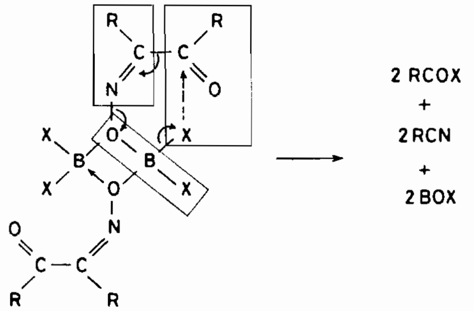
The complexes containing the anionic monoximato ligands were thermally more stable than the adducts. These complexes did not sublime or decompose below ca 140 °C and even at these temperatures prolonged heating was required for complete decomposition to occur. For the complexes BX_2(mo) and PhBCl(mo) the stoichiometry of decomposition [reactions (7) and (8)] has been established by inferring the nature of the products from analysis, from their i.r. spectroscopic and mass spectrometric characteristics, and in some cases from their hydrolytic behaviour. The decomposition involves rupture of B–X and C–C bonds and leads to the formation of RCOX, RCN and BOX (*e.g.* Scheme 3). The species BOX either gives B_2O_3 and BX_3 in the case of the compounds derived from the trihalides or phenylboroxine trimer in the case of the compounds derived from phenyl boron dichloride. In Scheme 3 the compound is assumed to be dimeric containing type II bridges. Analogous schemes could be drawn for structures involving bridges of type III.

$$BX_2(mo) \longrightarrow RCOX + RCN + [BOX] \quad (7)$$

$$(R = Ph \text{ or } Me) \quad [BOX] \searrow \tfrac{1}{3}BX_3 + \tfrac{1}{3}B_2O_3$$

$$PhBCl(mo) \longrightarrow RCOX + RCN + 1/3(BOPh)_3$$

$$(R = Ph \text{ or } Me) \quad (8)$$



Experimental

Reaction of Boron Trifluoride with α-Benzil Monoxime or Acetyl Monoxime

Boron trifluoride was passed through a stirred suspension of the monoxime (*ca.* 5 g) in benzene (200 cm^3). *Trifluoro(monoxime)boron(III)* (see Table V for analysis and yields) was filtered off and dried at 20 °C/0.1 mm.

Reaction or BX_3, (X = Cl or Br) with α-Benzil Monoxime or Acetyl Monoxime

The oxime (*ca.* 5 g, 1 mol equiv.) was added with stirring to a solution of BX_3 (2 mol equiv.) in benzene (*ca.* 100 cm^3) to give dihalo(monoximato)

TABLE V. Analytical Data.

Oxime	Boron Halide	Product Formula	Yield (%)	Found (%)					Requires (%)				
				C	H	B	N	X	C	H	B	N	X
bmoH	BF_3	$BF_3 \cdot$bmoH	70	58.0	3.7	3.4	4.8		57.4	3.6	3.7	4.8	
bmoH	BCl_3	BCl_2bmo	70	55.7	3.2	3.4	4.6	23.3	54.9	3.3	3.5	4.8	23.3
bmoH	BBr_3	BBr_2bmo	46	43.0	2.5	2.9	3.5	40.9	42.6	2.5	2.7	3.5	40.4
bmoH	$PhBCl_2$	PhBClbmo	65	69.4	4.3	3.3	3.8	9.7	69.1	4.3	3.1	4.0	10.2
amoH	BF_3	$BF_3 \cdot$amoH	94	28.5	4.1	6.3	8.1		28.4	4.1	6.4	8.3	
amoH	BCl_3	BCl_2amo	55	26.5	3.6	6.0	7.4	39.5	26.4	3.3	5.9	7.7	39.5
amoH	BBr_3	BBr_2amo	47	16.8	2.2	5.0	4.5	59.2	17.8	2.2	4.0	5.2	59.1
amoH	$PhBCl_2$	PhBClamo	43	53.8	4.9	5.0	6.3	16.3	53.7	4.9	4.8	6.3	15.9

boron(III) (see Table V for analysis and yields). When X = Br the solid product was filtered off and dried at 20 °C/0.1 mm. When X = Cl the product was precipitated by addition of light petroleum (b.p. 40–60 °C, 100 cm^3), was filtered off and dried at 20 °C/0.1 mm.

Reaction of Phenyl Boron Dichloride with α-Benzil Monoxime or Acetyl Monoxime

The oxime (*ca.* 6 g, 1 mol equiv.) was added with stirring to a solution of phenylborondichloride (1.2 mol equiv.) in benzene (200 cm^3). A yellow solution resulted from which on concentration at 20 °C/20 mm *phenylchloro(monoximato)boron(III)* (see Table V for analysis and yields) separated and was filtered off and dried at 20 °C/0.1 mm.

Reaction of Boron Trifluoride with N,N-Dibenzoylamine

Boron trifluoride was passed through a stirred suspension of N,N-dibenzoylamine (1.0 g) in benzene (30 cm^3). *Trifluoro(N,N-dibenzoylamine)boron(III)* (1.2 g, 70%) Found: C, 58.9; H, 3.6; N, 5.3. $C_{14}H_{11}BF_3NO_2$ requires: C, 57.4; H, 3.6; N, 4.8%) was filtered off and dried at 20 °C/20 mm.

Hydrolysis of Dihalo(benzilmonoximato)boron(III)

In water

A suspension of dichloro(benzilmonoximato)boron(III) (1.2 g) in water (50 cm^3) was stirred at 20 °C. After 12h dichloro(benzilmonoximato)boron(III) (1.1 g, 92% recovery) (identified by i.r. spectroscopy) was filtered off and dried at 20 °C/0.1 mm.

Similar recovery of material was found when dibromo(benzilmonoximato)boron(III) was stirred in water at 20 °C.

Using aqueous alkali

A suspension of dichloro(benzilmonoximato)boron(III) (1.0 g) in aqueous sodium hydroxide solution (5%, 50 cm^3) was stirred at 60 °C for 6 h. Dichloro(benzilmonoximato)boron(III) (0.2 g, 20% recovery) (identified by i.r. spectroscopy) was filtered off and dried at 20 °C/1 mm. Addition of hydrochloric acid (5 cm^3) to the filtrate gave α-benzil monoxime (0.6 g, 100%), m.p. 137 °C (lit. [11] 137–138°) (confirmed by i.r. spectroscopy) which was extracted with ether and dried at 20 °C/20 mm.

Similarly dibromo(benzilmonoximato)boron(III) (1.0 g) gave α-benzil monoxime (0.4 g, 70%). No starting material was recovered in this case.

Hydrolysis of Phenylchloro(benzilmonoximato)boron(III)

A suspension of phenylchloro(benzilmonoximato)boron(III) (0.6 g) in water (50 cm^3) was stirred at 20 °C for 12 h. Addition of hydrochloric acid (10 cm^3) to the mixture gave α-benzil monoxime (0.4 g, 90%) m.p. 135–137 °C) (confirmed by i.r. spectroscopy) which was extracted with ether and dried at 20 °C/20 mm.

Hydrolysis of Dihalo(diacetylmonoximato)boron(III)

Dichloro(diacetyl monoximato)boron(III) (0.6 g) was exposed to moist air for 24 h. A yellow gummy solid resulted which on heating at 70 °C/1 mm gave diacetyl monoxime (0.2 g, 60%), m.p. 73 °C (lit. [12] 74–75 °C) (confirmed by i.r. spectroscopy) as a white sublimate.

Similarly, dibromo(diacetylmonoximato)boron(III) (1.6 g) gave diacetylmonoxime (0.3 g, 66%), m.p. 73 °C (confirmed by i.r. spectroscopy).

Hydrolysis of Phenylchloro(diacetylmonoximato)boron(III)

Phenylchloro(diacetylmonoximato)boron(III) (1.1 g) was shaken with 1:1 water and ether (50 cm^3). A white solid (1.0 g) containing diacetyl monoxime (i.r. bands at 3280, 3180 and 1670 cm^{-1}) and triphenyl boroxime (i.r. bands at 1600 and 1350 cm^{-1}) was obtained from the ethereal layer. Attempts to separate the two components by sublimation were not successful.

Pyrolysis of Trifluoro(α-benzilmonoxime)boron(III) at 120 °C/mm

Trifluoro(α-benzilmonoxime)boron(III) (6.0 g) was heated at 120 °C/760 mm for 6 h. A yellow sublimate (5.7 g) (Found: C, 57.3; H, 3.8; N, 5.2%) and a residue (0.1 g) were obtained.

I.r. examination of the sublimate

The i.r. spectrum of the sublimate contained all the bands found in the spectrum of trifluoro(NN-dibenzoylamine)boron(III). In addition there were some other bands which were also present in the spectrum of the sublimate obtained by heating trifluoro(NN-dibenzoylamine)boron(III).

Hydrolysis of the sublimate

A portion of the sublimate (3.8 g) was shaken with water (50 cm^3) and the resultant mixture extracted with diethyl ehter. The aqueous portion was neutralised with aqueous sodium hydroxide and extracted with diethyl ether. The extract on concentration gave benzamide (0.6 g) (Found: C, 69,8; H, 5.6; N, 11.0. Calc. for C_7H_7NO: C, 69.4; 5.8; 11.6%), m.p. 127–130 °C (lit. [13] 132 °C) (confirmed by i.r. spectroscopy). The ethereal extract from the original extraction was shaken with aqueous sodium hydroxide. The solvent was removed from the ethereal portions and the residue was crystallised from benzene to give benzamide (0.4 g) (identified by i.r. spectroscopy) and a colourless filtrate which on concentration at 40 °C/90 mm gave a viscous residue (0.3 g) (benzoyl fluoride?) (ν_{max} 1780, 1725, 1600 cm^{-1} and mass spectrum includes peaks at m/e 124, 123, 122, 105, 103, 96, 77, 76, 51, 50). The aqueous portion was neutralised with aqueous hydrochloric acid and the resultant mixture extracted with diethyl ether. The extract was evaporated, and the residue was heated at 100 °C/0.1 mm. Benzoic acid (1.3 g) (Found: C, 69.0; H, 49. Calc. for $C_7H_6O_2$: C, 69.0; H, 4.9%) (confirmed by i.r. spectroscopy) was obtained as sublimate and dibenzoylamine (0.3 g) (Found: C, 74.6; H, 4.9; N, 5.9. Calc. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.0%), m.p. 142–144 °C (lit. [14] 147–148 °C) (confirmed by i.r. spectroscopy and mass spectrometry) as residue.

Pyrolysis of Trifluoro(α-benzilmonoxime)boron(III) at 120 °C/0.1 mm

Trifluoro(α-benzilmonoxime)boron(III) (3.0 g) was heated at 120 °C/0.1 mm for 6 h. A colourless condensate (1.4 g) consisting of benzonitrile and trifluoro(benzonitrile)boron(III) (identified (i) by comparison with i.r. spectrum of authentic sample of PhCN, BF_3 (ii) by the presence of peaks at m/e 103, 77, 76, 51, 50 in the mass spectrum) was collected at −80 °C, a white solid (1.05 g) (identified by i.r. spectroscopy to consist of mainly benzoic acid) was deposited as sublimate and a black residue (0.2 g) was left behind in the flask.

Pyrolysis of Trifluoro(diacetylmonoxime)boron(III) at 70 °C/0.1 mm

Trifluoro(diacetylmonoxime)boron(III) (4.5 g) was heated slowly at 70 °C/0.1 mm for 6 h. A white sublimate (3.9 g) consisting mainly of trifluoro(diacetylmonoxime)boron(III) (identified by i.r. spectroscopy and elemental analysis), a black residue (0.2 g) and a condensate (0.3 g) were obtained.

Pyrolysis of Trifluoro(diacetylmonoxime)boron(III) at 100 °C/0.1 mm

Trifluoro(diacetylmonoxime)boron(III) (2.6 g) was heated at 100 °C/0.1 mm for 3 h. A black residue (1.0 g) (Found: C, 36.4; H, 4.5; N, 11.7%) and a brown liquid (1.6 g) containing acetonitrile, acetic acid (peaks at m/e 41, 43, 60 in the mass spectrum) and possibly boron trifluoride were obtained.

Pyrolysis of Dihalo(monoximato)boron(III) and Phenylchloro(monoximato)boron(III)

The complexes decomposed when heated under the conditions indicated in Table VI giving a

TABLE VI. Pyrolysis Conditions.

Complex	Wt. (g)	Conditions		Condensate		Residue (g)
		°C/mm	Time (hr)	Yield (g)	Components	
BCl_2bmo	6.0	300/0.1	6	4.0[a]	PhCN, PhCOCl	1.8
BCl_2bmo	5.0	300/760	9	4.1[b,c]	PhCN, PhCOCl BCl_3, PhCN	0.5
BBr_2bmo	2.0	300/760	6	0.8[d]	PhCN, PhCOCl, BCl_3, PhCN	0.7
PhBBrbmo	2.4	140/0.1	6	1.6[e,f]	PhCN, PhCOCl	0.8[g]
BCl_2amo	1.6	160/0.1	20	[h]		1.0[i]
BCl_2amo	3.4	160/760	6	0.5[j]	MeCN, MeCOCl[k]	2.0
BBr_2amo	0.9	160/0.1	8	0.2	MeCN, MeCOBr[l]	0.5
PhBClamo	2.8	140/0.1	6	0.4[m]	MeCN, MeCOCl[k]	1.6[n]

[a] The condensate (2.5 g) was washed with water (20 cm^3) and extracted with diethyl ether (50 cm^3). The ethereal extract contained chlorine (0.27 g) corresponding to benzoyl chloride (1.06 g). [b] Boron trichloride (0.33 g) was collected in sodium hydroxide tubes. [c] Hydrolysis of the condensate (1.1 g) with refluxing aqueous sodium hydroxide (10%, 80 cm^3) gave, after acidification and extraction with diethyl ether, benzoic acid (1.0 g), m.p. 117–120 °C (lit. [13], 121 °C) (confirmed by i.r. spectroscopy). [d] Hydrolysis of the condensate (0.75 g), as in (c), gave benzoic acid (0.55 g) (identified by i.r. spectroscopy). [e] 1:1 mixture of PhCN and PhCOCl (Found: C, 69.8; H, 4.2; Cl, 14.2; N, 5.4. Calc. for 1:1 mixture of PhCN and PhCOCl: C, 69.0; H, 4.1; Cl, 14.6; N, 5.7%) (confirmed by i.r. spectroscopy by comparison with the spectrum of authentic 1:1 mixture of PhCN and PhCOCl). [f] Hydrolysis of the condensate (0.92 g), as in (c), gave benzoic acid (0.95 g) (identified by i.r. spectroscopy). [g] Residue was triphenyl boroxine (Found: C, 68.9; H, 5.0. Calc. for C_6H_5BO: C, 69.0; H, 4.8%) (confirmed by i.r. spectroscopy and mass spectrometry). [h] A sublimate (0.2 g) consisting mainly of BCl_2amo (identified by elemental analysis and i.r. spectroscopy) was also obtained. [i] Residue contained some BCl_2amo (indicated by mass spectrometry). [j] Hydrogen chloride (0.33 g) was collected in sodium hydroxide. [k] Components indicated by presence of peaks at m/e 35, 36, 37, 38, 41, 43 and 60 in the mass spectrum. Peak at m/e 60 due to $CH_3CO_2H^+$ suggesting hydrolysis of the condensate prior to introduction in the mass spectrometer. [l] Components indicated by presence of peaks at m/e 41, 43, 60, 79, 80, 81, 82. [m] A sublimate (0.6 g) consisting mainly of PhBClamo and triphenyl boroxine (bands at 1680, 1600 and 1350 cm^{-1} in i.r. spectrum and peaks at 312, 208 and 104 in the mass spectrum). [n] Residue contained some PhBClamo (indicated by mass spectrometry).

condensate collected at –80 °C, a solid residue and in some cases a sublimate. The products in the condensate, residue and sublimate were inferred by elemental analysis, i.r. spectroscopy, mass spectrometry and in the case of the condensate from its hydrolytic behaviour.

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