ALKOXYBORON DIFLUORIDES AND DICHLORIDES: PREPARATION, STRUCTURE AND SPECTROSCOPIC PROPERTIES

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Abstract—The alkoxyboron dihalides $ROBX_2$ (X = Cl or F) have been prepared by the reaction of the boron trihalide on the trialkyl borate or on the dialkoxydialkyltin R_3 'Sn(OR)₂. The ¹H, ¹¹B and ¹⁹F (for the fluorides) resonance spectra have been recorded and the chemical shifts are discussed in relation to the structure of these compounds.

Two series of pyridine complexes have been isolated and the ^{11}B shifts of the 1:1 complexes ROBX₂, Py are used to obtain a measure of the acceptor strengths of the dichlorides.

The i.r. spectra have been recorded, particular attention being given to the B-O stretching frequencies.

INTRODUCTION

THE INTERACTION of boron trifluoride with trialkyl borates was originally believed⁽¹⁾ to result in the formation of a complex involving donation from two of the three alkyl-oxygen atoms. LANDESMAN and WILLIAMS⁽²⁾ showed that when triethyl borate was saturated with boron trifluoride only a single ¹¹B resonance line was found, the chemical shift of which indicated the presence of a single type of tetrahedral boron atom. On this evidence structure (I) was proposed for the product, i.e. the trimeric ethoxyboron difluoride; the compound was however, not isolated.



(I)

EXPERIMENTAL

Preparation of alkoxyboron difluorides. By reaction (ii). The tin ester (1.0 mole) was dissolved in petroleum ether $(30-40^\circ)$ and saturated with boron trifluoride gas. Fractional distillation afforded the alkoxyboron difluoride (Table 1) and a residue which, after washing with ethanol and petroleum ether, afforded the pure dialkyltin difluoride.

By reaction (i). The borate was saturated with boron trifluoride at 0° , and fractional distillation afforded the alkoxyboron difluoride (Table 1).

- * Present address: University of Birmingham, Birmingham 15.
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- ⁽¹⁾ P. A. MCCUSKER and M. L. LILZER, J. Am. chem. Soc. 82, 372 (1960).
- ⁽²⁾ H. LANDESMAN and R. E. WILLIAMS, J. Am. chem. Soc. 83, 2663 (1961).

(ROBF ₃) ₃
DIFLUORIDES,
ALKOXYBORON
OF
1Preparation
TABLE

								Anal	ysis			
	Method of	Yield				Foi	pun			Calc.	%	
R	preparation	(%)	B.p.	n_{D}^{20}	U	Η	Ч	[M] ^(a)	C	Η	ц	[M]
A.C.	i	93	86		14.8	3.9	47·2)	(4)000	1			
IMIC	ü	75	86-5		15·2	3.6	47·3)	100 26 7	0.01	9.¢	C·/4	239.4
) - -	• •••	83	82]	25-7	5.4	40-4)	000	7.30	, ,		
ī	ii	55	78	1	25-7	5.4	40.4)	067	0.07	0.0	40.4	5-167
	· 1	62	88–90	1-3685	33-5	6.4	35-0)	010		2	0.00	
14-4	:п	70	91.5	1·3701	33-5	6-4	35-0)	318	33.4	c.0	2.05	323-4
	• ==	86	46/12 mm	1·3842	39-4	7:2	30-8)			t		
) IIG- <i>u</i>	ii	55	45/14 mm	1.3850	39-3	7·2	30-9	4/د	4.66	4·/	1.16	4-coc
(a) De	termined cryoso	onically i	n cycloheyane	neine he	nzil as re	farence c	tandard					
® Dič	d not afford a cl	lear solut	ion in repeated	d attempts			-n mnimi					

Preparation of alkoxyboron dichlorides. By reaction (ii). Boron trichloride (2.0 mole) at -80° was added to the dialkoxy-di-n-butyltin also maintained at -80° . Fractional distillation afforded the alkoxyboron dichloride (Table 2) and a residue of di-n-butyltin dichloride.

The alkoxyboron dichlorides were also prepared from the appropriate trialkylborate and boron trichloride by procedures already described; $(^{3-6})$ the yields are shown in Table 2.

	Method				Found	(%)	Analysis	Calc. (%)
R	of preparation	Yield (%)	B.p.	n_D^{20}	B	CÌ	B	Cl
	(i)	77	58-61	1.3890	9.7	63·1	0.6	63 .9
ме	(ii)	95	58	1.3885	9.7	63·4	9.0	02.8
	(i)	77	77–79		8.5	55.8		
Et	(ii)	91	79	1· 3 949	8∙5	55.8	8.2	20.0
-	(i)	63	50–54/102 mm	1.4031	7·5	49·8		50.4
Pr	(ii)	90	48/75 mm	1.4041	7· 7	4 9·9	7.7	50.4
_	(i)	80	46–52/13 mm	1.4120	7 ∙0	45·4		
Bu	(ii)	7 8	42/13 mm	1.4110	7·2	44·8	7.0	45.8
ClCH₂CH	2 (i)	60	66–68/16 mm	1.4470	6.6	65·7	6.7	66·0

TABLE 2.-PREPARATION OF ALKOXYBORON DICHLORIDES, ROBCl₂

The ¹H and ¹⁹F resonance spectra were obtained on a Perkin-Elmer R.10 (60 Mc/s) NMR spectrometer at 60.0 and 56.4 Mc/s respectively, using 4.6-mm spinning tubes. The ¹¹B resonance spectra were obtained on a Perkin-Elmer (40 Mc/s) NMR spectrometer at 12.83 Mc/s using non-spinning 8-mm tubes.

The i.r. spectra were recorded on Perkin–Elmer 237 (grating) and 137 (KBr) Infracord spectrometers, the calibration of which was checked using primary standards.⁽⁷⁾ Potassium chloride blanks were used for recording the spectra of alkoxyboron dichlorides to prevent halide exchange.

The physical data for the 1:1 alkoxyboron dihalide complexes are shown in Table 3.

RESULTS AND DISCUSSION

In the present work the compounds (I) have been prepared by reaction (i) and also by reaction (ii); the latter is an extension of the reaction of boron trichloride and di-n-butoxy-di-n-butyltin previously described.⁽⁸⁾ The alkoxyboron dichlorides were prepared by reaction (i), first described by WIBERG and SMEDSRUD⁽³⁾ for the preparation of methoxyboron dichloride, and later extended to other alkoxy- and aryoxyboron dichlorides,⁽⁴⁻⁶⁾ and by reaction (ii).

(6) J. D. EDWARDS, W. GERRARD and M. F. LAPPERT, J. chem. Soc. 1470 (1955).

⁽³⁾ E. WIBERG and H. SMEDSRUD, Z. anorg. allg. Chem. 225, 204 (1935).

⁽⁴⁾ W. GERRARD and M. F. LAPPERT, J. chem. Soc. 2545 (1951); *ibid.* 3084 (1955).

⁽⁵⁾ T. COLCLOUGH, W. GERRARD and M. F. LAPPERT, J. chem. Soc. 907 (1955); ibid. 3006 (1956).

⁽⁷⁾ Tables of Wave Numbers for the Calibration of Infrared Spectrometers. Butterworths, London (1961).

⁽⁸⁾ W. GERRARD and R. G. REES, J. chem. Soc. 3510 (1964).

(a) All	koxyboron	difluorides	ROBF.	Py					
						Analysis			
	Yield		Four	nd (%)			Calc	. (%)	
R	(%)	С	н	F	N	С	н	F	N
Me	70	45 ∙6	5.0	24·0	8.8	45 ∙8	5.1	24.2	8.9
Et	60	48.5	5.6	21.5	7.9	48∙6	5.8	22.0	8 ∙1
Pr	47	51-1	6·2	20.0	7.5	51.4	6.4	20.4	7.5
(h) All	coxyboron	dichloride	ROBCL	Pv ^a					

TABLE 3.—PREPARATION OF ALKOXYBORON DIHALIDE PYRIDINE COMPLEXES

(b) Alkoxyboron dichlorides, ROBCl₂, Py

			Ana	lysis	
		Fou	nd (%)	Calc	(%)
		В	Ру	В	Ру
Me	82	5.5	41.9	5.6	41.4
Et	64	5.3	39.6	5.3	38.4
Pr	63	5.0	36-5	4.9	36.1
ClCH ₂ CH ₂ -	90	4·3	33.9	4.4	33.9

^a The complex from BuOBCl₂ could not be isolated in a pure state, as disproportionation into BCl_aPy occurred (cf. LAPPERT⁽¹⁴⁾).

$$(RO)_{3}B + 2BX_{3} \xrightarrow{X = CI} 3 ROBX_{2}$$
$$\xrightarrow{X = F} (ROBX_{2})_{3}$$
(i)

$$3 \operatorname{R'_2Sn}(OR)_2 + 6 \operatorname{BX_3} \longrightarrow 6 \operatorname{ROBX_2} + 3\operatorname{R'_2SnX_2}$$

$$\xrightarrow{X=C} 6 \operatorname{ROBX_2} + 3\operatorname{R'_2SnX_2}$$
(ii)

Both the alkoxyboron dichlorides and difluorides formed two series of pyridine complexes, namely 1:1 and 1:2. Although several 1:1 complexes with the dichlorides have been reported,⁽⁹⁾ the only 2:1 complex previously described was that of the 2-chloroethoxyboron dichloride.⁽⁶⁾ Although the 1:1 complexes were soluble and the ¹¹B chemical shifts have confirmed the structure, the 2:1 pyridine-alkoxyboron dihalide complexes were insoluble, and so the exact structure is uncertain.

The ¹¹B chemical shifts of the alkoxyboron dichlorides and the 1:1 alkoxyboron dichloride-pyridine complexes are shown in Table 4. It is clear from the Δ values (where Δ is the shift in ppm to high field on complex formation, i.e. δ complex – δ ROBCl₂) that complex formation results in the boron becoming tetrahedral. It has recently been demonstrated⁽¹⁰⁾ that, in the case of boron trihalide complexes, the Δ value provides information on both the donor and acceptor properties of the system. Thus, for a given ligand, the acceptor power of the boron halide increases as the Δ value becomes greater. Compared with pyridine-boron trichloride, where the Δ value was +39.6,⁽¹⁰⁾ it is clear that the alkoxyboron dichlorides ($\Delta = +23.5$ to +24.7) are poorer acceptors than boron trichloride.

The ¹¹B shifts of the alkoxyboron difluorides and the 1:1 pyridine complexes are

(*) M. F. LAPPERT, Chem. Rev. 56, 959 (1956).

⁽¹⁰⁾ P. N. GATES, E. J. MCLAUGHLAN and E. F. MOONEY, Spectrochim. Acta 21, 1445 (1965).

R	ROBCl_2	ROBCl_2 , Py δ	$\Delta^{\mathfrak{a}}$
Me	-31.8	-8.3	+23.5
Et	-32.1	-7.4	+24.7
Pr	-31.2	-8.5	+22.7
Bu	-31.2	<u> </u>	
ClCH ₂ CH ₂ -	-32.5	-7.6	+24.6

Table 4.—¹¹B chemical shifts of alkoxyboron dichlorides and the 1:1 pyridine complexes, in ppm from external Me_2O , BF_3

^a Shift to high field on formation of complex, i.e.

 δ complex $- \delta$ ROBX₂ (X = Cl or F).

Table 5.—¹¹B chemical shifts of alkoxyboron difluorides and the 1:1 pyridine complexes, in ppm from external (MeO)₃B

	ROBF ₂	ROBF ₂ Py	
R	δ	δ	Δ^{a}
Me	+18.7	÷19·4	+0.7
Et	+18.6	+19.1	+0.2
Pr	+18.4	+18.0	-0.4
Bu	+18.55		

^a defined as in Table 4.

shown in Table 5, and it is evident that the values for Δ are very small, which here cannot indicate the absence of complex formation since the complexes were isolated (Table 3). Hence, in agreement with the suggestion of LANDESMAN and WILLIAMS,⁽²⁾ the boron atom in the alkoxyboron difluoride must already be tetrahedral (as in I). and on dissociation and formation of the pyridine complex the boron atom returns to essentially the same tetrahedral hybridization.

There has previously been considerable conflicting evidence for the structure of the alkoxyboron difluorides. In 1939 MEERWEIN *et al.*⁽¹¹⁾ and later in 1960 MCCUSKER *et al.*⁽¹⁾ suggested that the alkoxyboron difluorides were but boron trifluoride complexes of the trialkyborates, this, as stated above, was disproved by LANDESMAN and WILLIAMS,⁽²⁾ but the difluoride was not isolated by these authors. ALLEN and SUGDEN⁽¹²⁾ isolated the methoxyboron difluoride (1932) and, from consideration of parachor studies, suggested a dimeric structure with bridging fluorine atoms (II). Later in 1952 GOUBEAU and LUCKE⁽¹³⁾ reinvestigated the same compound and found it to be monomeric above 80° but associated at lower temperatures, and, from Raman studies on

$$\begin{array}{cccc}
\mathbf{RO} & F & F \\
& & B & F & F \\
& & F & F & OR
\end{array}$$
(II)

- ⁽¹¹⁾ H. MEERWEIN, E. BATTONBERG, H. GOLD, E. PFEIL and O. WILLIFANG, J. prakt. Chem. 154, 83 (1939).
- ⁽¹²⁾ E. C. Allen and S. SUGDEN, J. chem. Soc. 760 (1932).
- ⁽¹³⁾ J. GOUBEAU and K. E. LUCKE, Ann. 575, 37 (1952).

molten methoxyboron difluoride, suggested the structure as (III), LAPPERT (1955)⁽¹⁴⁾ stated that n-butoxyboron difluoride was dimeric in cyclohexane.



In the present work it has been shown that the alkoxyboron difluorides, with the exception of the methoxy compound which was insoluble, are trimeric in cyclohexane solution (Table 1). This is in agreement with the observations of MCCUSKER *et al.*,⁽¹⁾ which lead to the structure being postulated as the complex, $(RO)_3B_2BF_3$, which has the same molecular weight as (I).

The ¹⁹F spectra of alkoxyboron difluorides consists of a single line and therefore cyclization involving donation from fluorine, as in (II), cannot occur as in this case two different fluorine resonances would be expected. The ¹⁹F chemical shifts are given in Table 6 and, from the width of the resonance lines, the ¹¹B–¹⁹F coupling must be less than 2 c/s.

TABLE 6.—¹⁹F CHEMICAL SHIFTS OF ALKOXYBORON DIFLUORIDES

R in ROBF ₂	Φª
Ме	+153-25
Et	+149·3
Pr	+148.9
Bu	+148.9
ClCH ₂ CH ₂ -	+147.85

^a ppm from internal CCl₃F.

Further evidence for the formation of the internal co-ordination structure of the alkoxyboron difluoride is obtained from the ¹H resonance chemical shifts of the two series of compounds (Table 7). Donation of the lone pair or electrons of the oxygen atom of dialkyl ethers results in a shift of the α and β methylene (methyl) resonances to low field, e.g. in diethyl ether there are shifts of 0.78 ppm (α CH₂) and 0.25 ppm (β CH₃) to low field on complexing the ether with boron trifluoride. From Table 7 it is evident that the α CH₂ and β CH₃ or CH₂ resonances are to lower field, by 0.2–0.4 ppm, in the diffuorides than in the dichlorides. Although $p\pi$ - $p\pi$ bonding between oxygen and boron exists in the trialkylborates, with the corresponding shifts of the —OCH₂-resonance to low field, we would not expect this type of bonding to be very prominent in the monomeric diffuorides as $p\pi$ - $p\pi$ bonding from fluorine to boron is strong; it is for this reason that boron trichloride. Structure (I) fully accounts for the lower field ¹H resonances in the alkoxyboron diffuorides.

It is also of significance in this respect that the B–O stretching frequency is fairly ⁽¹⁴⁾ M. F. LAPPERT, J. chem. Soc. 748 (1955).

		2	x
R	Group	Cl	F
Ме	OMe	3.96	3.71
Et	O·CH ₂ C·CH ₃	3·47 6·34	3·07 6·04
Pr	$\left\{\begin{array}{l} \mathbf{O} \cdot \mathbf{CH}_2\\ \boldsymbol{\beta} \mathbf{CH}_2\\ \boldsymbol{\omega} \mathbf{CH}_3\end{array}\right.$	3·45 5·87 6·52	3·08 5·49 6·51
Bu	$\left\{\begin{array}{l} \text{O·CH}_2\\ \beta\text{CH}_2\\ \gamma\text{CH}_2\\ \omega\text{CH}_3\end{array}\right.$	3·42 5·7-6·3 6·50	3·01 5·53 5·8–6·35 6·48

TABLE 7.—¹H SHIFTS OF ALKOXYBORON DIHALIDES ROBX₂, IN PPM TO HIGH FIELD OF BENZENE (AS SOLVENT)^a

^a T.M.S. cannot be used as internal standard, as boron compounds containing active *B*-halogen groups readily cleave T.M.S.

constant in position in the alkylborates and their derivatives; it is ithe intensity of the \sim 1340 cm⁻¹ B-O stretching mode which varies. The B-O and B-X stretching bands of the alkoxyboron dichlorides and diffuorides are shown in Table 8. There can be no

Table 8.—B–O and B–X stretching frequencies (cm⁻¹) of alkoxyboron dihalides, $ROBX_2$

		X = Cl			X = F	
R	$v_{(11_{B-0})}$	$v_{asym(^{11}B-01)}$	$v_{sym(^{11}B-Cl)}$	$v_{(11B-0)}$	$v_{asym(^{11}B-F)}$	$v_{\rm sym(^{11}B-F)}$
Me	1339	995	935	1253	1043	998
Et	1332	971	936	1255	1043	960
Pr	1330	975	935	1256	1046	970
Bu	1335	965	933	1256	1043	954

doubt that the lower frequency B–O stretching mode in the alkoxyboron difluorides is due to delocalization of the lone-pair on the alkoxy-oxygen atom thus preventing any $p\pi$ – $p\pi$ B–O bonding; such behaviour would be expected from structure (I). The B–Cl variations are in the general region expected, but the B–F frequencies are slightly lower than expected, more in keeping with the asymmetric B–F stretch of the tetrafluoroborate which occurs at ~1070 cm⁻¹. This however is again in favour of structure (I) as the two fluorine atoms are attached to a tetrahedral boron atom.