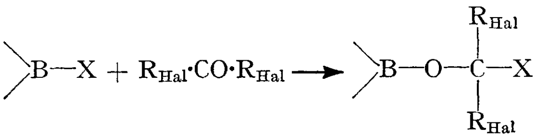
The Synthesis of Perhalogeno-organic Borates from Perhalogenoketones

By **E. W. Abel,* N. Giles, D. J. Walker** and **J. N. Wingfield,** Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Hexafluoroacetone and other polyfluorinated ketones react with boron halides, organoboron halides, and alkylthioboranes to form a wide range of perhalogeno-organic borates and related compounds.

Although boron esters are usually prepared[1,2] from the alcohol and either boric acid or the boron halides, the inaccessibility of perhalogeno-alcohols makes this course unpracticable for perhalogeno-esters. Certain perhalogeno-aldehydes[3] and -ketones,[4,5] however, insert into boron–halogen bonds to form boron esters.

We find[6] that a number of polyfluorinated perhalogenoacetones insert into boron–halogen and boron–sulphur bonds to produce an extensive series of boron esters.



$$>B{-}X + R_{Hal}{\cdot}CO{\cdot}R_{Hal} \longrightarrow >B{-}O{-}C(R_{Hal})_2{-}X$$

[X = Cl, Br, I, and SMe]

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[1] M. F. Lappert, *Chem. Rev.*, 1956, **56**, 959.

[2] H. Steinberg, ' Organoboron Chemistry,' Interscience, New York, 1964.

[3] M. J. Frazer, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1957, 739.

[4] U.S.P. 3,052,710/1962.

[5] G. W. Parshall, *Inorg. Chem.*, 1965, **4**, 52.

[6] E. W. Abel, D. J. Walker, and J. N. Wingfield, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 139.

The reactions proceed under mild conditions, and by variation of reagent proportions it is possible to obtain borates, boronates, and borinates.

$$BCl_3 + 3(CF_3)_2CO \longrightarrow B[OC(CF_3)_2Cl]_3$$
$$BCl_3 + 2(CF_3)_2CO \longrightarrow ClB[OC(CF_3)_2Cl]_2$$
$$BCl_3 + (CF_3)_2CO \longrightarrow Cl_2BOC(CF_3)_2Cl$$

Table 1 illustrates the range of products formed in these types of reaction.

TABLE 1

Interaction of boron compounds and perhalogenoketones

Reactants	Product	Yield (%)	Analysis Calc. (%) C	H	Br	Cl	Found (%) C	H	Br	Cl	B.p. °/mm.	M.p.	n_D^{20}
$BBr_3 + 3(CF_3)_2CO$	$B[OC(CF_3)_2Br]_3$	90	14·4		32·0		14·5		31·9		82/8	43—45	
$BBr_3 + 3(CF_3)CO(CF_2Cl)$	$B[OC(CF_3)(CF_2Cl)Br]_3$	85	13·7		30·0		13·6		29·8		134/7	27—29	
$BBr_3 + 3(CF_2Cl)_2OC$	$B[OC(CF_2Cl)_2Br]_3$	83	12·7		28·3	25·1	12·9		28·5	24·9	115°/ 0·05	23—25	
$BBr_3 + 3(CF_2Cl)CO(CFCl_2)$	$(CF_2Cl)CO(CBrCl_2)$		13·0		28·9	38·5	13·2		28·4	38·3	147		1·4552
$BBr_3 + 3(Cl_3C)_2CO$	No reaction												
$BCl_3 + 3(CF_3)_2CO$	$B[OC(CF_3)_2Cl]_3$	80				17·3				17·5	64/10	35	
$BCl_3 + 3(CF_3)CO(CF_2Cl)$	$B[OC(CF_3)(CF_2Cl]_3$	75	16·2			32·0	16·2			31·8	103/8	24—26	
$BCl_3 + 3(CF_2Cl)_2CO$	$B[OC(CF_2Cl)_2Cl]_3$	62	15·1			44·7	15·2			44·8	91/0·2		1·4127
$BCl_3 + 3(CFCl_2)CO(CF_2Cl)$	$(Cl_3C(CO(CF_2Cl)$		15·5			61·2	15·7			61·2	122		1·4261
$BCl_3 + 3(Cl_3C)_2CO$	No reaction												
$BCl_3 + (CF_3)_2CO$	$Cl_2BOC(CF_3)_2Cl$		12·7			37·6	12·8			37·1	131		
$BCl_3 + 2(CF_3)_2CO$	$ClB[OC(CF_3)_2Cl]_2$		16·0			23·7	16·4			23·4	150		
$BF_3 + 3(CF_3)_2CO$	No reaction												
$BF_3{\cdot}O(C_2H_5)_2 + 3(CF_3)_2CO$	No reaction												
$PhBCl_2 + 2(CF_3)_2CO$	$PhB[OC(CF_3)_2Cl]_2$	94	29·3	1·02			30·2	1·00			78/7		1·3978
$Ph_2BCl + (CF_3)_2CO$	$Ph_2BO(CF_3)_2Cl$	90	49·1	2·73			49·2	2·76					1·4992
$Ph_2BCl + (CF_3)CO(CF_2Cl)$	$Ph_2BOC(CF_3)(CF_2Cl)Cl$	90	47·0	2·60			47·4	2·71					1·5162
$PhBF_2 + 2(CF_3)_2CO$	No reaction												
$B(SMe)_3 + 3(CF_3)_2CO$	$B[OC(CF_3)_2SMe]_3$	90	22·2	1·38			22·3	1·37			85/0·01		1·3808
$PhB(SMe)_2 + 2(CF_3)_2CO$	$Ph[BOC(CF_3)_2SMe]_2$	66	32·7	2·12			33·5	2·17			98/0·35		1·4360
$Ph_2BSMe + (CF_3)_2CO$	$Ph_2BOC(CF_3)_2SMe$	74	49·6	3·36			48·9	3·36			110/0·02		1·5097

Perhalogenoketones do not insert into boron–fluorine bonds, even under vigorous conditions. Efforts to prepare trisperfluoroisopropylborate by a metathetical reaction between the purported[7] caesium 'heptafluoroisopropoxide' and boron trichloride were unsuccessful.

Reactions between polyfluorinated ketones and aluminium halides have been reported[8] to give aluminium fluoride and the corresponding perhalogeno-ketone. With the boron halides, we have found a comparable reaction with 1,1,3-trichloro-1,3,3-trifluoroacetone. No borate insertion product is detectable from the reaction of this with either the boron halides or with trimethylthioborane. Instead a metathetical reaction to form boron trifluoride and a series of new ketones occurs.

$$3(CF_2Cl)(CO(CFCl_2) + BX_3 \longrightarrow 3(CF_2Cl)CO(CCl_2X) + BF_3$$

[X = Cl, Br, I, and SMe]

Substitution is confined exclusively to the fluorine atom of the $CFCl_2$ group in the original ketone. None of the borates reported in Table 1 when heated for a prolonged period showed any tendency to evolve boron trifluoride.

Although organic borates are, in general,[1] prevented from being strong Lewis acids by oxygen-to-boron back-donation, a number of borates with electron-withdrawing groups have been reported[1,2,9] to form co-ordination complexes, as also does the related[10] tris(amino-oxy)-boron, $B[ON(CF_3)_2]_3$. We find the perhalogeno-alkyl borates reported in Table 1 all form complexes with pyridine. Over a period of time, however, these complexes loose ketone and produce the pyridine complex of the corresponding boron halide.

$$\begin{tikzcd} B[OC(CF_3)_2X]_3 + C_5H_5N \arrow[r] & C_5H_5N\rightarrow B[OC(CF_3)_2X]_3 \arrow[dl, "\text{slow}"'] \\ C_5H_5N\rightarrow BX_3 + 3(CF_3)_2CO & \end{tikzcd}$$

All the borates, boronates, and borinates reported in Table 1 are rapidly hydrolysed by water.

The n.m.r. spectra of the compounds reported in Table 1 are in accord with the proposed formulations. Data on these compounds are recorded in Table 2. Borates formed from the ketone $CF_3{\cdot}CO{\cdot}CF_2Cl$ have a particular point of interest, in that borate formation renders the ex-carbonyl carbon atom asymmetric. This, in turn, causes magnetic non-equivalence of the fluorine atoms of the CF_2Cl group. Thus, a combination of this non-equivalence and the presence of the adjacent CF_3 group results in ABX_3 patterns for the F^aF^b resonances. The values of J_{AB} and δ_{AB} depend markedly

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[7] M. E. Redwood and C. J. Willis, *Canad. J. Chem.*, 1967, **45**, 389; F. W. Evans, M. H. Litt, A. M. Weidler-Kubanck, and F. P. Avonda, *J. Org. Chem.*, 1968, **33**, 1837.

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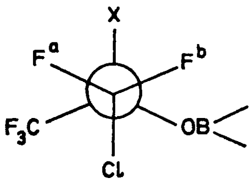

Illustration of the non-equivalence of two fluorine atoms due to asymmetry

upon other groups present in the borates, boronates, and borinates (Table 2).

TABLE 2

N.m.r. data

Compound	^{19}F				^{1}H	
	δCF_3 [a]	δCF_2 [a]	δ_{AB} of CF_AF_B [b]	J_{AB} of CF_AF_B [c]	τ_{CH_3}	$\tau_{C_6H_5}$
$B[OC(CF_3)_2Cl]_3$	78·4					
$B[OC(CF_3)_2Br]_3$	76·4					
$B[OC(CF_3)_2I]_3$	73·3					
$PhB[OC(CF_3)_2Cl]_2$	78·6					2·0—2·8
$Ph_2BOC(CF_3)_2Cl$	78·6					2·0—2·8
$ClB[OC(CF_3)_2Cl]_2$	78·2					
$Cl_2BOC(CF_3)_2Cl$	78·2					
$B[OC(CF_3)_2SMe]_3$	72·8				7·74	
$PhB[OC(CF_3)_2SMe]_2$	72·8				8·22	2·98 and 2·42
$Ph_2BOC(CF_3)_2SMe$	72·2				8·68	3·22 and 2·86
$B[OC(CF_3)(CF_2Cl)Cl]_3$	76·2 [d]	63·7 [d]	0·83	180		
$B[OC(CF_3)(CF_2Cl)Br]_3$	73·7 [d]	60·6 [d]	4·99	184		
$B[OC(CF_3)(CF_2Cl)I]_3$	70·3 [d]	54·7 [d]	9·68	183		
$PhB[OC(CF_3)(CF_2Cl)Cl]_2$	75·4 [d]	63·7 [d]	1·28	180		1·9—2·7
$Ph_2BOC(CF_3)(CF_2Cl)Cl$	76·4 [d]	64·1 [d]				2·0—2·8
$B[OC(CF_2Cl)_2Cl]_3$		0 [e]				
$B[OC(CF_2Cl)_2Br]_3$		58·9 [d]	2·36	180		
$B[OC(CF_2Cl)_2I]_3$		52·8 [d]	7·12	180		
$(CBrCl_2)CO(CF_2Cl)$		57·2				
$(CCl_3)CO(CF_2Cl)$		58·1				
$(MeSCCl_2)CO(CF_2Cl)$		57·8			7·6	

[a] P.p.m. upfield from $CFCl_3$. [b] Calculated in p.p.m. [c] In Hz. [d] Measured from centre of absorption multiplet. [e] δ_{AB} Is so small only one peak is observed.

EXPERIMENTAL

All materials were handled under dry conditions, and gaseous reagents such as hexafluoroacetone were measured with a calibrated gas burette.

Preparation of Tris-[1*-bromo-*1*-*(*chlorodifluoromethyl*)*-*2,2,2*-trifluoroethyl*] *Borate.*—Monochloropentafluoroacetone (16·0 g., 3 mol.) was condensed into a thick-walled glass tube containing boron tribromide (7·32 g., 1 mol.). The tube was evacuated, sealed at *ca.* −150°, and then kept at 70° for 3 days. Subsequent distillation of the resulting colourless liquid gave the *borate* (19·8 g., 85%), m.p. 27—29°, b.p. 134°/7 mm. (Found: C, 13·6; Br, 29·8; Cl, 13·2. $C_9BBr_3Cl_3F_{15}O_3$ requires C, 13·5; Br, 30·2; Cl, 13·3%).

All other borates, boronates and borinates reported in Table 1 were prepared in an analogous manner.

Interaction of Boron Trichloride and $(CF_3)_2CO,CsF$.—Caesium ' heptafluoroisopropoxide '[7] was prepared by the action of hexafluoroacetone (6·65 g.) on caesium fluoride (6 g.) in acetonitrile (10 ml.) in a sealed tube at 25°/50 hr. After removal of solvent under reduced pressure, boron trichloride (1·53 g.) was condensed onto the resulting white solid; the tube was resealed and set aside at 25°/50 hr. Subsequent work-up of the reaction mixture produced mainly boron trichloride and the residual white solid $(CF_3)_2CO,CsF$, together with tris-(1-chloro-2,2,2-trifluoro-1-trifluoromethyl)borate presumably formed by the action of boron trichloride upon hexafluoroacetone. There was no trace of the desired tris(perfluoroisopropyl)borate.

Formation of 1*-Methylthio-*1,1,3*-trichloro-*3,3*-difluoroacetone.*—1,1,3-Trichloro-1,3,3-trifluoroacetone (11·9 g., 3 mol.) and tris(methylthio)borane (3·2 g., 1 mol.) were sealed in a thick-walled glass tube and heated at 70° for 3 days. Boron trifluoride was evolved upon opening of the tube, and fractional distillation of the residual liquid gave the *ketone* (4·53 g., 30%), b.p. 90—91°/15 mm. (Found: C, 19·4; H, 1·1. $C_4H_3Cl_3F_2OS$ requires C, 19·7; H, 1·2%).

From 1,1,3-trichloro-1,3,3-trifluoroacetone and boron trichloride and boron tribromide respectively were formed $CCl_3{\cdot}CO{\cdot}CF_2Cl$ and $CCl_2Br{\cdot}CO{\cdot}CF_2Cl$ in an analogous manner.

Interaction of Pyridine and tris-(1*-bromo-*2,2,2*-trifluoro-*1*-trifluoromethyl*) *Borate.*—Pyridine (1 mol.) in dry ether was added to the borate (1 mol.) in ether. An immediate precipitation of white crystals took place, and after removal of solvent, the white crystalline complex pyridine–tris-(1-bromo-2,2,2-trifluoro-1-trifluoromethyl) borate, m.p 93—96° (Found: C, 20·0; H, 0·9; Br, 29·4. $C_{14}H_5BBr_3F_{18}NO_3$ requires C, 20·3; H, 0·6; Br, 29·4%), was isolated.

All the other borates, boronates, and borinates reported in Table 1 formed complexes with pyridine.

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