730. *The Chemistry of Certain Acyloxyboron Compounds and Boron Chelates.*

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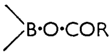
Eight acyloxyboron compounds have been obtained, four methods being used. The compounds hydrolysed readily and some decomposed with elimination of carboxylic anhydride.

The present paper relates to the preparation, characterisation, and selected reactions of acyloxyboron compounds of types (I) and (II) (R = Me or CF_3), and to certain new ethoxycarbonyl-substituted boron esters. Existence of only one compound of type (I) has previously been established with certainty, namely, acetyl diethylboronite,[1] $Et_2B\cdot OAc$, prepared from triethylboron and acetic acid. The so-called " acyl borates " had been thought to be triacyl borates,[2] $(R\cdot CO\cdot O)_3B$, but recent evidence [3] confirms an earlier suggestion [4] that they are tetra-acyl diborates, $[(R\cdot CO\cdot O)_2B]_2O$. The only other acyloxyboron compounds hitherto reported [5, 6] are of type (II) $(AcO\cdot BY)_2O$ (Y = Cl or Bu^n). Certain trifluoroacetoxyboron compounds of indefinite compositon have been mentioned in a recent patent.[7]

(I) 

 (II)

$$R\cdot CO\cdot O\cdot \overset{|}{B}\cdot O\cdot \overset{|}{B}\cdot O\cdot COR$$

Tristrifluoroacetyl borate, $(CF_3\cdot CO\cdot O)_3B$, diacetyl phenylboronate, $(AcO)_2BPh$, and acyl di-*n*-butylboronites, $R\cdot CO\cdot O\cdot BBu^n_2$, were each obtained from the appropriate boron chloride and carboxylic acid by elimination of hydrogen chloride. Under similar conditions boron trichloride and acetic acid gave the diborate,[5] whereas with phenylboron dichloride and trifluoroacetic acid dephenylation (reaction 1) was observed (for other dephenylations see ref. 8). Similar dephenylation occurred when diphenylboron chloride was treated with acetic acid $[Cl\cdot BPh_2 + 2AcOH \longrightarrow (AcO)_2B\cdot Ph + HCl + C_6H_6]$. With the *n*-butoxyboron chlorides and acetic acid, the products isolated are presumed to have been formed by decomposition of intermediate *n*-butoxyboron acetates (reactions 2 and 3).

$$Cl_2B\cdot Ph + 3CF_3\cdot CO_2H \longrightarrow (CF_3\cdot CO\cdot O)_3B + C_6H_6 + 2HCl \quad . \; . \; . \; . \; . \quad (1)$$

$$3Cl_2B\cdot OBu^n + 6AcOH \xrightarrow{-6HCl} 3[(AcO)_2B\cdot OBu^n] \longrightarrow [(AcO)_2B]_2O + B(OBu^n)_3 + Ac_2O \quad . \; . \quad (2)$$

$$6Cl\cdot B(OBu^n)_2 + 6AcOH \xrightarrow{-6HCl} 6[AcO\cdot B(OBu^n)_2] \longrightarrow [(AcO)_2B]_2O + 4B(OBu^n)_3 + Ac_2O \quad . \quad (3)$$

Bistrifluoroacetyl phenylboronate, $(CF_3\cdot CO\cdot O)_2BPh$, and trifluoroacetyl diphenylboronite, $CF_3\cdot CO\cdot O\cdot BPh_2$, were obtained from the phenylboron chlorides and sodium trifluoroacetate with elimination of sodium chloride.

The compound $[(CF_3\cdot CO\cdot O)BBu^n]_2O$ was obtained from di-*n*-butylboronous anhydride $(Bu^n_2B)_2O$ (1 mol.), and trifluoroacetic acid (2 mols.) by elimination of *n*-butane (2 mols.). Tetrakistrifluoroacetyl diborate $[(CF_3\cdot CO\cdot O)_2B]_2O$ was prepared from tristrifluoroacetyl borate by sublimation *in vacuo*, trifluoroacetic anhydride being the other product.

It was necessary to develop a technique for estimating acetic acid and boric acid, in some cases in presence of hydrogen peroxide [used to oxidise $Bu^n\cdot B(OH)_2$ and $Bu^n_2B\cdot OH$ to boric acid]. By potentiometric titration it was established that a mixture of boric acid, hydrogen peroxide, and mannitol has pH 6·8 (in the absence of hydrogen peroxide,

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[1] Meerwein and Sönke, *J. prakt. Chem.*, 1937, **147**, 251.

[2] Pictet and Geleznoff, *Ber.*, 1903, **36**, 2219.

[3] Gerrard and Wheelans, *Chem. and Ind.*, 1954, 758; Gerrard and Mooney, *ibid.*, 1958, 227; Hayter, Laubengayer, and Thomson, *J. Amer. Chem. Soc.*, 1957, **79**, 4243.

[4] Dimroth, *Annalen*, 1926, **446**, 97.

[5] Gerrard and Wheelans, *J.*, 1956, 4296.

[6] Gerrard, Lappert, and Shafferman, *J.*, 1957, 3828.

[7] Muetterties, U.S.P. 2,782,233/1957.

[8] Abel, Gerrard, and Lappert, *J.*, 1957, 5051; *J.*, 1958, 1451.

pH 8·2) and the procedure now recommended for analysing a mixture of a carboxylic acid and boric acid is to titrate in the presence of hydrogen peroxide to Bromothymol Blue (pH 6·0—7·6) with sodium hydroxide, first in the absence ($R{\cdot}CO_2H$), then in the presence [$B(OH)_3$], of mannitol. We also regard this method as the best available for estimating boron in alkylboronic acids, $R{\cdot}B(OH)_2$, dialkylboronous acids, $R_2B{\cdot}OH$, and their derivatives.

All the acyloxyboron compounds were hydrolysed by cold water to the carboxylic acid and boric, boronic, or boronous acids. This was established for acetyl di-*n*-butylboronite by isolation of acetic acid and di-*n*-butylboronous anhydride (formed by dehydration of $HO{\cdot}BBu^n{}_2$) and for the other compounds by analysis.

Replacement of acyloxy- by alkoxy-groups has been made use of for preparing orthoborates from tetra-acetyl diborate, and such replacement has now been further demonstrated by converting trifluoroacetyl di-*n*-butylboronite into (+)-1-methylheptyl di-*n*-butylboronite by reaction with (+)-octan-2-ol.

The acyloxyboron compounds may be regarded as mixed anhydrides of carboxylic and boric or substituted boric acids and thus redistribution might be expected; such a reaction involving tristrifluoroacetyl borate has been mentioned above. The only other compounds which showed a similar tendency were acetyl di-*n*-butylboronite (which, however, it was possible to distil without change in analysis) and diacetyl phenylboronate; in these compounds the presence of acetic anhydride was detected spectroscopically [9] and in one case by gas–liquid chromatography.

Reaction of acetyl di-*n*-butylboronite with either of the two carboxylic acids resulted in the elimination (as *n*-butane) of only one butyl group.

In view of the fact that acyloxyboron compounds are frequently chelated as a result of co-ordination of the carbonyl-oxygen atom with the boron atom,[9] certain potentially chelated ethoxycarbonyl-substituted boron esters were prepared. These were the esters $EtO_2C{\cdot}CH{:}CMe{\cdot}O{\cdot}BR_2$ (R = Bu and Ph), and $EtO_2C{\cdot}CHMe{\cdot}O{\cdot}BBu^n{}_2$, obtained from the appropriate chloride, R_2BCl, and ethyl acetoacetate or ethyl lactate, hydrogen chloride being eliminated.

With regard to substitution of a hydrocarbon radical by an acyloxy-group (*e.g.*, reaction 1), it appears that: (1) dearylation is easier than dealkylation, (2) the propensity for dearylation increases with the number of aryl groups attached to boron, and (3) dearylation is encouraged by increasing acid strength, $CF_3{\cdot}CO_2H > AcOH$.

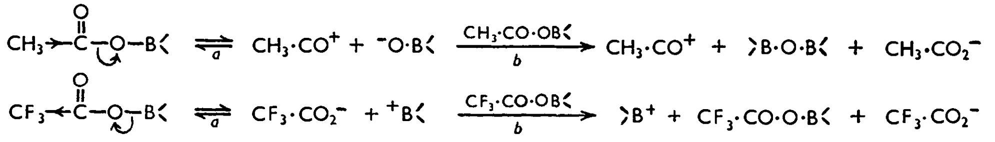
Three types of disproportionation in acyloxyboron compounds have been noted [(4), (5), (6)] and this tendency is greater when R = Me than when R = CF_3: [9]

$$2(R{\cdot}CO{\cdot}O)_3B \longrightarrow [(R{\cdot}CO{\cdot}O)_2B]_2O + (R{\cdot}CO)_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$3(R{\cdot}CO{\cdot}O)_2B{\cdot}R' \longrightarrow (R'BO)_3 + 3(R{\cdot}CO)_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$2R{\cdot}CO{\cdot}O{\cdot}BR_2' \longrightarrow (R'_2B)_2O + (R{\cdot}CO)_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

The greater stability of the trifluoroacetates than of the acetates has also been noted with mixed carboxylic acid anhydrides,[10, 11] and the present results may be explained by postulating reversible dissociations similar to those put forward for the mixed anhydrides,[11, 12] with subsequent competing reactions [(*a*) and (*b*)].



$$CH_3{\rightarrow}C({=}O){-}O{-}B{<} \underset{a}{\rightleftharpoons} CH_3{\cdot}CO^+ + {}^-O{\cdot}B{<} \xrightarrow[b]{CH_3\cdot CO\cdot OB<} CH_3{\cdot}CO^+ + {>}B{\cdot}O{\cdot}B{<} + CH_3{\cdot}CO_2^-$$

$$CF_3{\leftarrow}C({=}O){-}O{-}B{<} \underset{a}{\rightleftharpoons} CF_3{\cdot}CO_2^- + {}^+B{<} \xrightarrow[b]{CF_3\cdot CO\cdot OB<} {>}B^+ + CF_3{\cdot}CO{\cdot}O{\cdot}B{<} + CF_3{\cdot}CO_2^-$$

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[9] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, following paper.

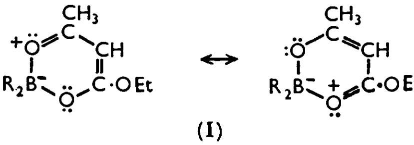
[10] Emmons, McCallum, and Ferris, *J. Amer. Chem. Soc.*, 1953, **75**, 6047; Randles, Tatlow, and Tedder, *J.*, 1954, 436.

[11] Bourne, Stacey, Tatlow, and Worral, *J.*, 1954, 2006.

[12] Emery and Gold, *J.*, 1950, 1443, 1447.

The optical activity data on the alcoholysis of trifluoroacetyl di-*n*-butylboronite show that alkyl–oxygen fission is not involved.

It has been shown that 1-ethoxycarbonylethyl di-*n*-butylboronite is not chelated, whereas chelation occurs with 2-ethoxycarbonyl-1-methylvinyl di-*n*-butyl- and diphenylboronite;[9] this is also borne out by their chemical behaviour. Thus 1-ethoxycarbonylethyl di-*n*-butylboronite was readily oxidised and hydrolysed by air as in general are esters of type $RO\cdot BBu^n_2$,[6] whereas the corresponding vinyl compound was much more stable and the vinyl diphenylboronite (see ref. 13 for behaviour of esters $RO\cdot BPh_2$) did not react perceptibly (98% recovered) with water or 3N-hydrochloric acid during five hours. It also did not co-ordinate with pyridine (see ref. 14 for ester–amine co-ordination). Similar hydrolytic stability has been observed to a smaller extent with 2-aminoethyl diphenylboronite and this has been explained as due to chelation by means of nitrogen–boron co-ordination.[15] That chelation by itself is not sufficient to account for the stability of our compounds can be realised by noting that amine complexes of boronites are still easily hydrolysed[14] and so also are the chelated[9] acyloxyboron compounds. We attribute our results as due to structures[9] (I), the aromatic character of the ring largely contributing to the stability (see also ref. 17).



(I)

EXPERIMENTAL

General Techniques and Preparations.—Phenylboron dichloride and diphenylboron chloride were prepared by Abel, Dandegaonker, Gerrard, and Lappert's method.[16] Refractive indices were measured on an Abbé-type refractometer. M. p.s were taken in sealed capillary tubes. The determination of the acetate radical in the presence of boron has been described above; for a typical run about 0·3 g. of sample was titrated in the presence of 100-vol. hydrogen peroxide (10 c.c.; 15 minutes' standing; Bromothymol Blue). Chlorine and the trifluoroacetate group were estimated acidimetrically (Methyl Red) as the acids formed on hydrolysis. Because of the great ease of hydrolysis of the acyloxyboron compounds, manipulations were carried out in a dry-box and for the di-*n*-butylboron carboxylates in a nitrogen-filled dry-box, to avoid oxidation. Rotatory powers are recorded for $l = 10$ cm.

Preparation of Acyloxyboron Compounds by the Elimination of Hydrogen Chloride.—These reactions were carried out on an approximately 0·05 molar scale. The exact amount of carboxylic acid in *n*-pentane (10 c.c.) was added dropwise with shaking to the appropriate chloride in *n*-pentane (10 c.c.) at 20°. Considerable heat was evolved, and hydrogen chloride was formed. All matter volatile at 20°/20 mm. was removed, to leave the acyloxyboron derivative. The results are shown in the Table.

	Yield †		M. p.		Found (%)			Required (%)		
Product	(%)	B. p./mm.	(decomp.) *	n_D^{20}	B	AcO	$CF_3\cdot CO_2$	B	AcO	$CF_3\cdot CO_2$
$(CF_3\cdot CO\cdot O)_3B$	100	—	88°	—	3·1	—	94·7	3·1	—	96·9
$(AcO)_2BPh$	90	—	172—174	—	5·4	56·5	—	5·3	57·3	—
$CF_3\cdot CO\cdot O\cdot BBu^n_2$...	98	79°/22	—	1·3800	4·6	—	47·5	4·6	—	47·5
$AcO\cdot BBu^n_2$	83	88—94°/16	49—52	1·4372	6·0	31·6	—	5·9	32·1	—

* Owing to disproportionation. † For liquids the yields are based on the distilled product.

Sublimation of Tristrifluoroacetyl Borate.—Sublimation of trifluoroacetyl borate (5·95 g.) at 100° at 10^{-4} mm. yielded *tetrakistrifluoroacetyl diborate* (4·00 g., 96%), m. p. 113—120°

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[13] Abel, Gerrard, and Lappert, *J.*, 1957, 112, 3833.
[14] Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.
[15] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 2491.
[16] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.
[17] Gerrard, Lappert, and Shafferman, *Chem. and Ind.*, 1958, 722.

(decomp.) (Found: B, 4·6; $CF_3{\cdot}CO_2$, 93·0. $C_8O_9F_{12}B_2$ requires B, 4·4; $CF_3{\cdot}CO_2$, 92·3%). A condensate of trifluoroacetic anhydride (1·57 g., 88%), b. p. 39° (also identified by its infrared spectrum), was trapped at −180°. The diborate and also tristrifluoroacetyl borate could not be purified by recrystallisation owing to their insolubility in solvents such as benzene, nitromethane, ether, and methylene iodide.

Preparation of Diacetyl Phenylboronate by Dephenylation.—Acetic acid (0·93 g., 2 mol.) was added dropwise with shaking to diphenylboron chloride (1·54 g., 1 mol.) at 20°. There was considerable heat of reaction and evolution of hydrogen chloride. All matter volatile at 20°/10 mm. was removed to leave diacetyl phenylboronate (1·36 g., 88%), m. p. 172° (Found: B, 5·4; OAc, 56·6%), as the sole residue. Benzene, b. p. 80° (0·60 g., 100%), identified by its infrared spectrum, was trapped at −80°.

Interaction of Trifluoroacetic Acid with Phenylboron Dichloride.—The acid (8·27 g., 2 mol.) was slowly added with shaking to the dichloride (5·75 g., 1 mol.) at 20°. Hydrogen chloride was evolved and heat of reaction noted. Benzene (1·71 g., 92%), b. p. 80° (also identified by its infrared spectrum), was removed at 20°/20 mm. and collected at −80°. Removal of all volatile matter from the *n*-pentane washings of the residue afforded unchanged phenylboron dichloride (1·57 g.) (Found: Cl, 44·3; B, 6·7. Calc. for $C_6H_5Cl_2B$: Cl, 44·6; B, 6·9%). Sublimation of the final residue at 100°/0·02 mm. yielded tetrakistrifluoroacetyl diborate (4·14 g., 76%) (Found: B, 4·3; $CF_3{\cdot}CO_2$, 91·1%).

Interaction of Acetic Acid with the n-*Butoxyboron Chlorides.*—(*a*) Acetic acid (3·22 g., 2 mol.) in *n*-pentane (10 c.c.) was added dropwise with shaking to *n*-butyl dichloroboronite (4·15 g., 1 mol.) in *n*-pentane (10 c.c.) at 20°. There was considerable heat of reaction and evolution of hydrogen chloride. Solvent and all other matter volatile at 20°/20 mm. were removed. Acetic anhydride (0·81 g., 89%) (Found: equiv., 48·0. Calc. for $C_4H_6O_3$: equiv. 51·0) was removed at 20°/0·11 mm. and collected at −80°. Removal of all matter volatile at 20°/20 mm. from the *n*-pentane washings of the residue afforded tri-*n*-butyl borate (1·31 g., 80%) (Found: B, 4·5. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%), also identified by its infrared spectrum. The final residue was tetra-acetyl diborate (2·08 g., 85%), m. p. 149° (Found: B, 7·9; OAc, 85·5. Calc. for $C_8H_{12}O_9B_2$: B, 7·9; OAc, 86·3%). A trace (∼5%) of *n*-butyl acetate was detected in the acetic anhydride by gas–liquid chromatography.

(*b*) This reaction was carried out as described in (*a*). Acetic acid (2·19 g., 1 mol.) and di-*n*-butyl chloroboronate (7·02 g., 1 mol.) afforded tetra-acetyl diborate (1·43 g., 86%) (Found: B, 7·7; OAc, 85·5%), tri-*n*-butyl borate (5·00 g., 89%) (Found: B, 4·6%), and acetic anhydride (0·55 g., 72%) (Found: equiv., 46·9).

Preparation of Bistrifluoroacetyl Phenylboronate and Trifluoroacetyl Diphenylboronite.—(*a*) Phenylboron dichloride (3·05 g., 1 mol.) in ether (20 c.c.) was slowly added with shaking to anhydrous sodium trifluoroacetate (5·22 g., 2 mol.) in ether (20 c.c.) at 20°. Considerable heat of reaction was noted. After shaking (2 hr.), filtration afforded a precipitate of sodium chloride (2·04 g., 91%). Removal of all matter volatile at 20°/20 mm. and subsequent washing with *n*-pentane afforded *bistrifluoroacetyl phenylboronate* (5·06 g., 84%), m. p. 104—108° (decomp.) (Found: B, 3·4; $CF_3{\cdot}CO_2$, 69·8. $C_{10}H_5O_4F_6B$ requires B, 3·5; $CF_3{\cdot}CO_2$, 72·0%].

(*b*) *Trifluoroacetyl diphenylboronite* (7·58 g., 93%), m. p. 85—93° (decomp.) (Found: B, 3·9; $CF_3{\cdot}CO_2$, 39·4. $C_{14}H_{10}O_2F_3B$ requires B, 3·9; $CF_3{\cdot}CO_2$, 40·7%), was prepared as described in (*a*), by the addition of diphenylboron chloride (5·84 g., 1 mol.) to sodium trifluoroacetate (3·97 g., 1 mol.). Attempted recrystallisation of this product and also of the one from (*a*) did not improve their purity.

Preparation of n-*Butyltrifluoroacetoxyboronous Anhydride.*—A mixture of trifluoroacetic acid (5·19 g., 4 mol.) and di-*n*-butylboronous anhydride (3·02 g., 1 mol.) was heated under reflux (6 hr.) at 90—110°. A condensate of *n*-butane (1·17 g., 89·1%) (characterised by gas–liquid chromatography by comparison with an authentic sample), b. p. −1°, was trapped at −80°. Excess of trifluoroacetic acid (2·56 g., 98·5%) (Found: equiv., 113. Calc. for $C_2HO_2F_3$: equiv., 114) was removed at 20°/0·05 mm. and collected at −80°. A crystalline residue of n-*butyltrifluoroacetoxyboronous anhydride* (3·59 g., 83·6%), after recrystallisation (benzene–chloroform), had m. p. 85—88° (Found: B, 5·7; $CF_3{\cdot}CO_2$, 58·4. $C_{12}H_{18}O_5F_6B_2$ requires B, 5·7; $CF_3{\cdot}CO_2$, 59·9%).

Hydrolysis of Acetyl Di-n-*butylboronite.*—Water (0·40 g., 1 mol.) in dry ether (30 c.c.) was added slowly with shaking to acetyl di-*n*-butylboronite (4·11 g., 1 mol.) at 20°. Solvent was removed at 20°/40 mm., and acetic acid (1·16 g., 88%) (Found: equiv., 58·9. Calc. for

$C_2H_4O_2$: equiv., 60·0) was subsequently removed at 20°/3 mm. and collected at −80°. Distillation of the residue afforded di-*n*-butylboronous anhydride (2·61 g., 88%), b. p. 98°/0·11 mm., n_D^{20} 1·4263 (Found: B, 8·0. Calc. for $C_{16}H_{36}OB_2$: B, 8·1%).

*Interaction of Octan-2-ol with Trifluoroacetyl Di-*n*-butylboronite.*—(+)-Octan-2-ol (2·55 g.; α_D^{20} +4·83°) in *n*-pentane (15 c.c.) was added dropwise to trifluoroacetyl di-*n*-butylboronite (4·66 g.) at 20°. Considerable heat of mixing was noted and all matter volatile at 20°/20 mm. was subsequently removed. Distillation of the residue afforded a forerun (0·81 g.) and (+)-1-methylheptyl di-*n*-butylboronite (3·98 g., 80%), b. p. 115—120°/0·4 mm., n_D^{20} 1·4275, α_D^{20} +7·84° (Found: B, 4·4. Calc. for $C_{16}H_{35}OB$: B, 4·3%). This ester had nearly the same rotatory power and sign as when prepared from the alcohol and di-*n*-butylboron chloride.[6]

Preparation of Ethoxycarbonyl-substituted Boron Esters.—(a) *2-Ethoxycarbonyl-1-methylvinyl di-*n*-butylboronite* (1·54 g., 82%), b. p. 72°/0·01 mm., n_D^{20} 1·4582 (Found: C, 65·6; H, 11·0. $C_{14}H_{27}O_3B$ requires C, 66·2; H, 10·7%), was prepared by the dropwise addition of ethyl acetoacetate (0·97 g., 1 mol.) in pentane (10 c.c.) to di-*n*-butylboron chloride (1·20 g., 1 mol.) in *n*-pentane (20 c.c.), removal of matter volatile at 20°/20 mm., and distillation.

(b) The *diphenylboronite* (3·53 g., 99%), m. p. 74—75° (Found: C, 72·5; H, 6·6. $C_{18}H_{19}O_3B$ requires C, 73·5; H, 6·5%), was prepared as in (a) from diphenylboron chloride (2·54 g., 1 mol.) and ethyl acetoacetate (1·59 g., 1 mol.).

(c) *1-Ethoxycarbonylethyl di-*n*-butylboronite* (6·70 g., 93%), b. p. 127°/21 mm. (Found: B, 4·7. $C_{13}H_{27}O_3B$ requires B, 4·5%), was prepared as in (a) from di-*n*-butylboron chloride (4·80 g., 1 mol.) and ethyl lactate (3·47 g., 1 mol.).

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