827. *Fission of Esters of Carboxylic Acids by Boron Trichloride.*

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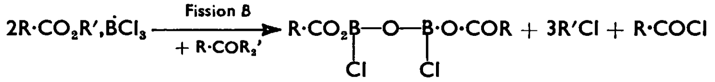
With the exception of ethyl trichloroacetate, which did not undergo fission, all esters $R{\cdot}CO_2R'$ immediately formed a 1 : 1 complex with boron trichloride at $-80°$. Three modes of decomposition were discerned when the complex was heated. When R′ was primary, fission to acyl chloride and alkyl dichloroboronite occurred, accompanied by dissociation to the original compounds when R was $CHCl_2$ or Ph. When R′ was secondary or tertiary and R = Me, boron remained with the acyl part and fission occurred by formation of dichlorodiacetyl diborate and alkyl chloride, predominantly inverted with some loss in optical activity and usually accompanied by olefin, when $R' = Bu^s$ or 1-methylheptyl. Rearrangement to *tert.*-alkyl occurred when R′ = *neo*pentyl or 1 : 2 : 2-trimethylpropyl. Benzyl acetate gave a hydrocarbon polymer. Certain properties of the dichlorodiacetyl diborate are mentioned.

EXTENDING the initial work[1] on the fission of esters by boron trichloride, we sought to discover the influence of the nature of R and R′ in $R{\cdot}CO_2R'$. In all the examples studied fission is preceded by formation of a complex, $R{\cdot}CO_2R',BCl_3$, and three modes of primary decomposition are discernible (1, 2, 3). For simple primary alkyl acetates, fission occurs

(1) $$R{\cdot}CO_2R',BCl_3 \xrightarrow{\text{Dissocn.}} R{\cdot}CO_2R' + BCl_3$$

(2) $$R{\cdot}CO_2R',BCl_3 \xrightarrow{\text{Fission A}} R{\cdot}COCl + R'O{\cdot}BCl_2$$

(3)



$$2R{\cdot}CO_2R',BCl_3 \xrightarrow[+\ R{\cdot}COR_2']{\text{Fission B}} R{\cdot}CO_2\underset{\displaystyle Cl}{B}{-}O{-}\underset{\displaystyle Cl}{B}{\cdot}O{\cdot}COR + 3R'Cl + R{\cdot}COCl$$

(4) $$RO{\cdot}BCl_2 \longrightarrow RCl + [BOCl \longrightarrow BCl_3 + B_2O_3]$$

in accordance with (2), although the system is complicated by partial decomposition (4) of the alkyl dichloroboronite.[2] With *iso*butyl or *neo*pentyl esters, rearrangement led to formation of the tertiary alkyl halide, and when R = Pr or CMe_3, ethyl dichloroboronite was stabilised by the acyl chloride from which separation was difficult. A related phenomenon is the slow separation of acetyl chloride and boron trichloride. Benzyl acetate was peculiar in that the complex vigorously decomposed at 0°, presumably according to scheme (2), but gave a hydrocarbon polymer, a similar but not identical one being formed by the interaction of boron trichloride and benzyl alcohol. Because of the remarkable stability of *o*-nitrophenyl dichloroboronite,[3] the fission of the acetate to acetyl chloride and the dichloroboronite was readily demonstrated. With acetates, substitution of chlorine at the 2-carbon atom of R′ did not alter the primary mode of fission (2), but the dichloroboronite disproportionated[4] to the chloroboronate and trialkyl borate and boron trichloride (5).

(5) $$2RO{\cdot}BCl_2 \longrightarrow (RO)_2BCl + BCl_3;\ 3(RO)_2BCl \longrightarrow 2(RO)_3B + BCl_3.$$

Substitution of chlorine at the 1-carbon atom of R in $R{\cdot}CO_2R'$ caused the complex to dissociate by mechanism (1) as well as to undergo fission by (2). Ethyl dichloroacetate was recovered in 75% yield, and ethyl trichloroacetate did not form a complex. Fission of ethyl benzoate by mechanism (2) was also accompanied by dissociation (1).

With secondary alkyl acetates boron remained almost entirely with the non-volatile part and the stoicheiometry appears to require 3 mols. of ester and 2 of boron trichloride. Analytical evidence points to the formation of a compound provisionally designated

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[1] Frazer and Gerrard, *J.*, 1955, 2959.

[2] Gerrard and Lappert, *J.*, 1951, 1020, 2545; 1955, 3084.

[3] Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

[4] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

" dichlorodiacetyl diborate " (reaction 3). Owing to its low solubility we have not been able to purify it; but on pyrolysis the specimens obtained in different experiments afforded acetyl chloride and boric oxide (reaction 6). With acetic acid (2 mols.) the compound gave hydrogen chloride and tetra-acetyl diborate [5] (reaction 7), and was formed by the interaction of acetic acid (3 mols.) with boron trichloride (2 mols.) as well as by interaction of the latter and acetic anhydride. The fate of R′ was in accordance with known properties

$$(\mathrm{AcO{\cdot}BCl})_2\mathrm{O} \xrightarrow{\text{Heat}} 2\mathrm{AcCl} + \mathrm{B_2O_3} \tag{6}$$

$$(\mathrm{AcO{\cdot}BCl})_2\mathrm{O} + 2\mathrm{AcOH} \longrightarrow [(\mathrm{AcO})_2\mathrm{B}]_2\mathrm{O} + 2\mathrm{HCl} \tag{7}$$

of the dichloroboronites of secondary alcohols in that olefin accompanies the alkyl chloride; the latter had predominantly inverted configuration and was mainly the tertiary alkyl chloride when $\mathrm{R'} = \mathrm{Me_3C{\cdot}CHMe}$. There was insufficient evidence to show whether there was alkyl–oxygen fission, giving primarily the acyl dichloroboronite, which reacted further to afford the dichlorodiacetyl diborate, or whether the fission occurred as in (2), the different sequence of results being due to the known reactivity of a *sec.*-alkyl dichloroboronite, which might react with acetyl chloride in a way leading to formation of the dichlorodiacetyl diborate.

tert.-Butyl acetate behaved similarly to the *sec.*-butyl ester, and even afforded a precipitate of the diborate by addition of boron trichloride to the acetate in *n*-pentane at −10°.

EXPERIMENTAL

General Procedures.—Boron trichloride (1 mol.) was added dropwise to the ester (1 mol.) at −80°, whereupon the solid complex $\mathrm{R{\cdot}CO_2R',BCl_3}$ was immediately formed, as shown by analysis of the solid precipitated from *n*-pentane and by the non-withdrawal of boron trichloride at low pressure. To effect ester fission the complex was heated at the required temperature, volatile matter being condensed at −80°, and the remainder was distilled. Isolation of the individual products of the primary and secondary reactions was difficult because of the following factors: only partial decomposition or disproportionation of the alkyl dichloroboronite, the stabilisation of the latter by acyl chloride, the loose complex formation between acyl chloride and boron trichloride, and in certain examples the appearance of the original ester owing to dissociation as distinct from decomposition of the complex. The acyl chloride and boron trichloride were separated by repeated distillations until the correct analysis (Cl, or Cl and B) was achieved; but the proportions of each constituent in the original mixture were determined by addition of pyridine to obtain the pyridine–acyl chloride compound which reacts with water, and the pyridine–boron trichloride compound which does not. By hydrolysis, proportions of constituents were assessed from the contents of chlorine and boron. The more volatile alkyl chlorides were separated from boron trichloride by fixing the latter as the pyridine complex and distilling the alkyl chloride.

In experiments with esters of secondary and tertiary alcohols, we were led to use different molecular ratios because of the different type of result obtained, and attention was centred on the isolation of dichlorodiacetyl diborate which could not be purified. Different specimens afforded acetyl chloride and boric oxide in almost quantitative yield. Chlorine easily hydrolysed by cold water is indicated by " e.h."

Fission of Primary Alkyl Acetates.—Ethyl acetate (13·25 g.) in *n*-pentane (180 c.c.) gave a precipitate of *ethyl acetate–boron trichloride complex* (28·1 g., 91%), m. p. 43—47° (Found : Cl, 50·9; B, 5·24. $\mathrm{C_4H_8O_2Cl_3B}$ requires Cl, 51·8; B, 5·28%), which was filtered off at 20° and dried at 20°/10 mm. At 82° it decomposed as described.[1] It was vigorously decomposed by water (3 mols.) to ethyl acetate, boric acid, and hydrogen chloride. Similarly *n*-butyl acetate (9·42 g.) in *n*-pentane (40 c.c.) gave a precipitate (17·8 g., 94%) of the complex, m. p. 25—26° (Found : Cl, 44·4; B, 4·43. Calc. for $\mathrm{C_6H_{12}O_2Cl_3B}$: Cl, 45·7; B, 4·64%). To a suspension of the complex (7·77 g., 1 mol.) in *n*-pentane (20 c.c.) pyridine (2·36 g., 1 mol.) in *n*-pentane (20 c.c.) was added at 20°. Pyridine–boron trichloride complex (6·26 g., 97·5%), m. p. 113—114°, was filtered off, and *n*-butyl acetate (3·21 g., 83%), b. p. 122—124°, n_{D}^{22} 1·3925, was recovered. With water the complex was violently hydrolysed to the original ester, hydrogen chloride, and boric

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[5] Gerrard and Wheelans, *Chem. and Ind.*, 1954, 758.

acid. On destructive distillation the complex (17·8 g.) afforded a cold-trap condensate (7·84 g.), *n*-butyl dichloroboronite (7·0 g., 59%), b. p. 34°/12 mm., n_D^{20} 1·4135, d_4^{18} 1·066 (Found : Cl, 42·7; B, 6·82. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 6·99), and a brown solid (2·76 g.) (Found : Cl, 30·8; B, 10·0; OAc, 15·5%). To the condensate (Found : e.h. Cl, 36·4%) aniline was added; *n*-butyl chloride (1·0 g., 15%), b. p. 76°, n_D^{19} 1·3970, was withdrawn at 80°/14 mm., and acetanilide (3·96 g., equiv. to AcCl in 38·4% yield) remained after removal of base hydrochloride with water.

The *o*-nitrophenyl acetate complex (24·8 g.), an orange-red precipitate from methylene dichloride (60 c.c.), decomposed as it melted at about 0°. Volatile matter was removed at 20°/0·5 mm. and trapped at −80°, leaving the bright-red crystalline *o*-nitrophenyl dichloroboronite (18·41 g.), m. p. 63° (Found : Cl, 31·3; B, 5·08. Calc. for $C_6H_4O_3NCl_2B$: Cl, 32·3; B, 4·93%), which (5·29 g., 1 mol.) in benzene (40 c.c.) gave with pyridine (1·90 g., 1 mol.) the pink voluminous precipitate of the base–dichloroboronite complex (7·18 g. Calc., 7·19 g.), m. p. 160° (Found : Cl, 23·5; B, 3·70; C_5H_5N, 26·3. Calc. for $C_{11}H_9O_3N_2Cl_2B$: Cl, 23·7; B, 3·62; C_5H_5N, 26·4%). With aniline the trapped volatile matter afforded acetanilide (9·99 g., 89%), m. p. 114°.

The complex from 2-chloroethyl acetate (9·82 g.) had m. p. 40—50° and decomposed at 87°, giving a distillate (4·94 g.), b. p. 48—51° (Found : e.h. Cl, 53·3; B, 1·44%; equiv. to BCl_3, 0·80 g., and AcCl, 3·98 g.), which afforded acetyl chloride (3·2 g.), b. p. 52° (Found : Cl, 45·5. Calc. for C_2H_3OCl : Cl, 45·2%). The condensate in the trap also contained boron trichloride (0·41 g.) and acetyl chloride (0·17 g.). The residue (12·6 g.) from the primary distillation comprised dichloroboronite, chloroboronate, and undecomposed complex. To further the disproportionation to trialkyl borate, the residue was heated at 160°/10 mm. for 2 hr. The trap (−80°) contained boron trichloride (1·71 g.) and acetyl chloride (1·41 g.), and the residue gave a mixture (3·93 g.) of chloroboronate and borate, b. p. 75—77°/0·6 mm. (Found : e.h. Cl, 14·9; B, 4·82%), and tri-2-chloroethyl borate (1·28 g.), b. p. 92°/0·5 mm. (Found : B, 4·36. Calc. for $C_6H_{12}O_3Cl_3B$: B, 4·34%).

The somewhat soluble 2 : 2 : 2-*trichloroethyl acetate–boron trichloride complex* (21·4 g., 78%), m. p. 19° (Found : e.h. Cl, 34·9; B, 3·32. $C_4H_5O_2Cl_6B$ requires e.h. Cl, 34·6; B, 3·51%), was precipitated as a white solid from *n*-pentane (250 c.c.) by the acetate (17·15 g.). At 25° it slowly decomposed (2·5 hr.), affording at 30 mm. a condensate (4·01 g.) which yielded boron trichloride (1·02 g.) and acetyl chloride (2·80 g.) (Found : Cl, 45·3%), and as residue (9·25 g.) (Found : e.h. Cl, 19·5; B, 3·22%) a mixture of the dichloroboronite and chloroboronate, which (8·6 g.) on being heated under reflux for 3 hr. at 150°/40 mm. gave a condensate (0·43 g.) at −80° and tris-2 : 2 : 2-trichloroethyl borate (5·86 g.), b. p. 134—136°/0·4 mm., m. p. 89° (Found : C, 15·9; H, 2·2; Cl, 69·7; B, 2·51. Calc. for $C_6H_6O_3Cl_9B$: C, 15·8; H, 1·3; Cl, 69·9; B, 2·38%).

The complex from *n*-octyl acetate (12·9 g.) gave no trap-condensate at 15°/30 mm. (45 min.) or at 50°/30 mm. (15 min.), but did so slowly at 80°/30 mm., and more rapidly at 90°/30 mm. The residue afforded *n*-octyl chloride (8·9 g.), b. p. 65—69°/18 mm. (Found : Cl, 23·7. Calc. for $C_8H_{17}Cl$: Cl, 23·9%), and a residue (4·68 g.). The condensate (8·0 g.) (Found : Cl, 52·7; B, 2·23%) comprised boron trichloride (1·95 g.) [separated as pyridine–boron trichloride complex (Found : Cl, 53·9. Calc. for $C_5H_5NCl_3B$: Cl, 54·2%)] and acetyl chloride (5·4 g.) (Found : Cl, 45·7%).

Benzyl acetate (10·0 g.) gave a complex which decomposed vigorously at 0°. Acetyl chloride (Found : Cl, 44·8%) and boron trichloride (Found : Cl, 90·0; B, 9·45. Calc. for Cl_3B : Cl, 90·8; B, 9·20%) were obtained by distillation in amounts equivalent to quantitative decomposition of the complex. Instead of the expected benzyl chloride, however, the residue (7·32 g.), which was not volatile at 200°/0·2 mm., afforded boric acid (2·1 g.) and a polymer (Found : C, 91·5; H, 6·8%; *M*, 2330, by cryoscopy in benzene), the latter being extracted by benzene. Benzyl chloride was not obtained on interaction of benzyl alcohol (3·97 g., 1 mol.) and boron trichloride (1 mol.). Hydrogen chloride continued to be evolved beyond the 1 mol. stage as the temperature was raised from −80° to 15°, and after 2 days a brown glass (2·04 g.), m. p. 58—60° (Found : C, 91·8; H, 6·7%), was obtained from the benzene extract of the residue. Although benzyl chloride is itself converted into a rubbery substance by boron trichloride at 20°, the process is slow and the product is insoluble in benzene.

*iso*Butyl acetate (6·94 g.) afforded the complex (m. p. 36°) which decomposed vigorously at 98° and gave hydrogen chloride (0·835 g.), a condensate (8·29 g.), and a charred residue (3·67 g.) (Found : Cl, 19·0; AcO, 7·9%). Pyridine (6·3 g.) was added to the condensate at −80°, and a mixture (3·66 g.) of *tert.*-butyl chloride (75%, by hydrolysis with cold 3N-nitric acid) and *iso*butyl chloride (25%, by total chlorine content) (Found : Cl, 38·2. Calc. for C_4H_9Cl :

Cl, 38·3%) was withdrawn at low pressure, leaving a mixture of pyridine–acetyl chloride compound (equiv. to AcCl, 4·07 g., by determination of e.h. Cl) and pyridine–boron trichloride complex (1·14 g., equiv. to BCl_3, 0·68 g.) (insoluble in water). The complex from *neo*pentyl acetate (9·61 g.) behaved very similarly, affording a mixture (5·03 g.), b. p. 82—90°, of (mainly) *tert.*-amyl chloride (Found : e.h. Cl, by 3N-nitric acid at 20°, 31·5%) and *neo*pentyl chloride (Found : total Cl, 32·9. Calc. for $C_5H_{11}Cl$: Cl, 33·2%).

Fission of Ethyl Esters of Other Acids.—The complex from the *n*-butyrate (9·00 g.) melted at 10°, but during 30 min. at 110° afforded no condensate. The distillate (16·55 g.), b. p. 89—94°, comprised ethyl dichloroboronite (7·86 g.) and *n*-butyryl chloride (7·05 g.), the proportions being computed from the determination of e.h. chlorine (42·6%), boron (4·06%), and butyric acid, but the condensate at −80° weighed only 0·06 g. The dichloroboronite was remarkably stable in the presence of butyryl chloride, and it was only after long heating under reflux that a pure specimen (Found : Cl, 33·4. Calc. for C_4H_7OCl : Cl, 33·3%) of butyryl chloride (anilide, m. p. 90°) was obtained.

The complex from the trimethylacetate (12·70 g.) was heated at 120° to effect steady decomposition. Protracted distillations (b. p. 78—102°) and analyses showed the presence of ethyl dichloroboronite (11·10 g., 89·6%) and trimethylacetyl chloride (10·64 g., 94%). A specimen (2·52 g.) of trimethylacetyl chloride, b. p. 101—102° (Found : e.h. Cl, 28·8. Calc. for C_5H_9OCl : Cl, 29·4%) (anilide, m. p. 129°), was eventually obtained. There was no condensate in the trap.

The complex from the dichloroacetate (8·12 g.) melted with decomposition and dissociation at 40—45°. The condensate (5·38 g.) (Found : e.h. Cl, 78·6; B, 8·4%) at −80° comprised boron trichloride (4·68 g.) [pyridine–boron trichloride complex (4·52 g.), m. p. 115° (Found : Cl, 53·8%)] and ethyl chloride (0·70 g.), and the residue afforded a mixture (7·36 g.) (Found : e.h. Cl, 4·7%) of dichloroacetyl chloride (1·43 g.) (anilide, m. p. 119—120°) and ethyl dichloroacetate (5·93 g.). The latter was separated in part (2·6 g.), b. p. 146—148°, n_D^{20} 1·4380 (Found : Cl, 45·6. Calc. for $C_4H_6O_2Cl_2$: Cl, 45·2%), by protracted fractionation.

Ethyl trichloroacetate (15·50 g.) gave a mobile liquid which was evidently not a complex. On distillation ethyl trichloroacetate (88·5% recovery), b. p. 62°/16 mm. (Found : Cl, 55·2. Calc. for $C_4H_5O_2Cl_3$: Cl, 55·6%), a condensate of boron trichloride (97·5% recovery) (Found : e.h. Cl, 89·0; B, 9·0%), and a black liquid residue (1·16 g.) (Found : e.h. Cl, 0; B, 5·36%) were obtained. Of the 6·70 g. of boron trichloride used in a second experiment, 6·07 g. were removed in 2·5 hr. at −80°/0·3 mm.

The benzoate (11·90 g.) gave a complex [no trap-condensate at 20°/20 mm.] which melted at 40°, decomposed at 60°/20 mm., giving a condensate (8·89 g.) (Found : e.h. Cl, 72·0; B, 8·44%) comprising ethyl dichloroboronite (1·90 g.), b. p. 36°/140 mm. (Found : e.h. Cl, 56·5; B, 8·10. Calc. for $C_2H_5OCl_2B$: Cl, 55·9; B, 8·54%), and boron trichloride (5·3 g.). At *ca.* 98°/20 mm. a mixture (10·62 g.) (Found : e.h. Cl, 10·9%) of benzoyl chloride (4·5 g., separated as anilide, m. p. 162°) and ethyl benzoate (4·2 g.), b. p. 105°/24 mm. (Found : equiv., 150. Calc. : equiv., 150·2), remained.

Fission of n-*Butyl Formate.*—The formate (5·45 g.) formed a complex which liquefied at *ca.* 15°. It was warmed from 40° to 65° under an upright condenser kept at 9° : hydrogen chloride (1·50 g.), carbon monoxide (1046 c.c. at N.T.P., 87%) and a trap-condensate (2·52 g.) (Found : e.h. Cl, 52·5%) of *n*-butyl chloride and boron trichloride (1·46 g.) [pyridine complex, m. p. 114° (Found : Cl, 53·4; C_5N_5N, 41·0%)] were obtained. The remainder afforded *n*-butyl chloride (2·8 g.), b. p. 76° (Found : Cl, 38·2%), and a black solid (2·17 g.) (Found : Cl, 11·3; B, 15·4%). When the decomposition was carried out at 50—55°/40 mm. impure *n*-butyl dichloroboronite (3·35 g.), b. p. 51°/40 mm. (Found : Cl, 47·1. Calc. for $C_4H_9OCl_2B$: Cl, 45·8%), was isolated and hydrogen chloride (1·92 g.) was absorbed in alkali after passing the cold trap.

Fission of Acetates of Secondary Alcohols.—*sec.*-Butyl acetate (6·63 g.) gave the complex which melted below 0°, but no trap-condensate was formed at 20° (2 hr.) or at 20°/50 mm. At 50°/50 mm. there was a condensate (6·38 g.) and a residue (6·05 g.) (Found : e.h. Cl, 38·3; B, 9·03; AcO, 32·6%) containing 88·5% of the boron in the system. The condensate comprised *sec.*-butyl chloride (4·0 g.) (isolated after treatment with pyridine), b. p. 66—67° (Found : Cl, 38·0%), acetyl chloride (2·1 g.), and boron trichloride (0·2 g.), estimated by means of pyridine–acetyl chloride and pyridine–boron trichloride complexes. When a 2 : 1 molar ratio of ester (14·13 g.) and boron trichloride was used, the mixture was entirely liquid at 20° and distillation afforded acetyl chloride (2·53 g.), *sec.*-butyl chloride (3·97 g.), but-2-ene (1·05 g.) [converted into 2 : 3-dibromobutane (Found : C, 22·4; H, 4·0; Br, 73·8. Calc. for $C_4H_8Br_2$: C, 22·2; H, 3·71; Br, 74·1%)], hydrogen chloride (0·65 g.), *sec.*-butyl acetate (3·52 g.), and a solid (6·06 g.)

(Found : e.h. Cl, 28·7; B, 9·3; AcO, 53·5%). When the primary liquid [ester (17·24 g., 2 mols.) and boron trichloride (8·70 g., 1 mol.)] was allowed to remain at 21° for 22 hr. instead of being distilled, crystals of *dichlorodiacetyl diborate* separated (4·63 g.), were filtered off, and were washed with *n*-pentane (Found: Cl, 31·2; B, 9·09; AcO, 51·2. $C_4H_6O_5Cl_2B_2$ requires Cl, 31·3; B, 9·55; AcO, 52·1%). This compound (3·26 g., 1 mol.), mixed with acetic acid (1·73 g., 2 mols.) in methylene dichloride (30 c.c.) at 20°, evolved hydrogen chloride (0·89 g., 1·7 mol.), and on removal of the solvent (finally at 60°/16 mm.) tetra-acetyl diborate (3·82 g., 97%) (Found : B, 7·75; AcO, 85·6. Calc. for $C_8H_{12}O_9B_2$: B, 7·90; AcO, 86·3%) remained. The dichloro-compound (9·17 g.) began to decompose about 150° and gave acetyl chloride (5·59 g.), b. p. 50—52° (Found : Cl, 45·2%), whereas all the boron remained as impure oxide in a coke-like residue (2·94 g.) (Found : B, 28·0%). There was no melting.

When 3 mols. of ester (19·95 g.) were used with 2 mols. of boron trichloride (13·41 g.) the liquid slowly deposited crystals at 23°. After 5 days the condensate at −80° weighed 3·14 g., increasing to 3·29 g. during the next 2 days. The effluent comprised butene (1·0 g.) and hydrogen chloride (0·776 g.); further volatilisation of the condensate afforded a residue (1·98 g.) which was added to the condensate obtained as follows. From the main residue volatile matter was removed at 23°/20 mm., finally at 65°/20 mm., affording a condensate (13·64 g., total, 15·62 g.) (Found : e.h. Cl, 10·7; total Cl, 36·8%) comprising acetyl chloride (3·5 g.) (converted into the anilide) and *sec.*-butyl chloride (7·5 g.), b. p. 68° (Found : Cl, 37·6%) (isolated after treatment with aniline), and a solid residue (12·94 g. Calc. for dichlorodiacetyl diborate : 12·98 g.) (Found : Cl, 31·2; B, 9·06; AcO, 51·2%). From an acetate having α_D^{21} −6·46° (*l* 1 dm.) (ROH, α_D^{27} −3·28°), *sec.*-butyl chloride having α_D^{25} +4·89° (*l* 1 dm.), n_D^{20} 1·3955, d_4^{20} 0·865, was obtained.

Similarly *iso*propyl acetate (16·3 g., 3 mols.) and boron trichloride (12·47 g., 2 mols.) also gave the diacetyl diborate (9·65 g.) (Found : Cl, 31·7; B, 8·72; AcO, 50·9%); *iso*propyl chloride (7·08 g.), b. p. 36° (Found : Cl, 44·5. Calc. for C_3H_7Cl : Cl, 45·2%) was isolated; and acetyl chloride (3·4 g.) and boron trichloride (0·32 g.) were present in the volatile part.

(−)-1-Methylheptyl acetate (10·60 g., 3 mols.), α_D^{20} −5·87° (from ROH, α_D^{20} −7·99°; *l* 1 dm.), and boron trichloride (4·81 g., 2 mols.) in *n*-pentane (30 c.c.) afforded dichlorodiacetyl diborate (3·47 g.) (Found : Cl, 31·5; B, 9·02; AcO, 52·1%) which was filtered off after the mixture had been warmed at 60° for 20 hr. Distillation of the filtrate afforded acetyl chloride (0·76 g.) (as anilide, 1·31 g.), octene (0·75 g.) (as octene dibromide, 1·40 g.), b. p. 107°/12 mm., and (+)-1-methylheptyl chloride (6·46 g.), b. p. 66°/15 mm., α_D^{22} +21·92° (*l* 1 dm.) n_D^{20} 1·4270 (Found : Cl, 23·7. Calc. for $C_8H_{17}Cl$: Cl, 23·9%).

(−)-1 : 2 : 2-Trimethylpropyl acetate (9·87 g., 3 mols.) (α_D^{20} −6·20°, *l* 1 dm.) and boron trichloride (2 mols.) gave the diborate (5·20 g.) (Found : Cl, 31·7; B, 8·94; AcO, 48·0%), an optically inactive mixture (7·2 g.), b. p. 110—112° (almost entirely *tert.*-chloride), a little 1 : 2 : 2-trimethylpropyl chloride (Found : e.h. Cl, by 3N-nitric acid at 20°, 28·3; total Cl, 29·6. Calc. for $C_6H_{13}Cl$: Cl, 29·5%), and acetyl chloride (1·13 g.).

Fission of tert.-*Butyl Acetate*.—Several experiments under different conditions and with different proportions of reagents indicated a general similarity with the *sec.*-butyl acetate systems. With 3 mols. of acetate (9·31 g.) and 2 mols. of the trichloride, the complex began to decompose at about −25°. After 14 hr. at 20°, volatile matter was withdrawn at 40°/30 mm., leaving the diacetyl diborate (6·78 g.). The condensate (8·33 g.) comprised acetyl chloride, removed by water, and *tert.*-butyl chloride (5·45 g.), b. p. 50—52° (Found : Cl, 38·7. Calc. for C_4H_9Cl : Cl, 38·3%). Dropwise addition of the acetate (5·16 g., 3 mols.) in *n*-pentane to boron trichloride (3·47 g., 2 mols.) in *n*-pentane (20 c.c.) at −10° immediately precipitated white crystals of dichlorodiacetyl diborate (3·45 g., 100%) (Found : Cl, 31·3; B, 8·99; AcO, 52·4%) which were filtered off, washed with *n*-pentane, and dried at 20 mm. With aniline the filtrate afforded acetanilide (1·16 g.), m. p. 114°.

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