558. *Studies with Boron Trichloride and Organic Sulphides. Part I. The Preparation and Properties of Di-*n*-butyl Sulphide–Boron Trichloride.*

By M. F. LAPPERT.

Addition of boron trichloride (whether 1 mol. or an excess) to di-*n*-butyl sulphide (1 mol.) afforded a liquid molecular complex, which decomposed only very slowly at high temperature to give boron trichloride and di-*n*-butyl sulphide. There was apparently no tendency for C–S fission, by contrast to the ready C–O fission in ether–boron trichloride systems. On hydrolysis the complex gave di-*n*-butyl sulphide, hydrogen chloride, and boric acid, whereas pyridine displaced di-*n*-butyl sulphide and gave pyridine–boron trichloride. *n*-Butanol (1 mol.) and the sulphide complex (1 mol.) gave a tri-*n*-butylsulphonium complex, $Bu^n_3SBCl_4$, (0·5 mol.) as a solid, the formula of which was shown by its reaction with pyridine and by hydrolysis whereupon tri-*n*-butylsulphonium chloride was obtained, and this with boron trichloride produced again the sulphonium–boron complex. The latter was also instantly formed by the action of tri-*n*-butylsulphonium chloride on di-*n*-butyl sulphide–boron trichloride, whereas the addition of diethyl ether to the sulphide complex afforded di-*n*-butyl sulphide, triethyl borate, and a di-*n*-butylethylsulphonium complex, $Bu^n_2EtSBCl_4$.

A WELL-KNOWN property of dialkyl sulphides is their ability to form addition compounds. For example, several complexes of di-*n*-butyl sulphide with platinous salts have been recorded by Löndahl (*J. pr. Chem.*, 1888, **38**, 512). Phillips, Hunter, and Sutton (*J.*, 1945, 146) have described a complex, di*iso*butyl sulphide–boron trichloride, prepared by the interaction of excess of the trichloride with the sulphide in ligroin. The compound could not be isolated in a pure state and was described as thermally unstable, but a pure specimen of a corresponding diethyl sulphide complex was obtained and was required for physicochemical measurements.

The addition of di-*n*-butyl sulphide (1 mol.) to boron trichloride (whether 1 or 2 mols.) gave at once a quantitative yield of a molecular complex, Bu^n_2S,BCl_3. This was a colourless viscous liquid which was not decomposed to any considerable extent when heated at 215° for 32 hr., 75% of the complex being recovered on distillation. There was no indication of *n*-butyl chloride having been formed, but some di-*n*-butyl sulphide and boron trichloride were obtained. Pyridine hydrochloride had no catalytic effect on the reaction.

The complex was readily hydrolysed, and addition of pyridine (1 mol.) at low temperature to the complex (1 mol.) gave a high yield of pyridine–boron trichloride, which has previously been prepared by Gerrard and Lappert (*J.*, 1951, 1020; *Chem. and Ind.*, 1952, 53) and di-*n*-butyl sulphide.

$$Bu^n_2S,BCl_3 + 3H_2O \longrightarrow Bu^n_2S + H_3BO_3 + 3HCl$$

$$Bu^n_2S,BCl_3 + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + Bu^n_2S$$

It is of interest to compare the reactivity of the two boron trichloride complexes towards hydrolysis and alcoholysis. While these reactions are now shown to go to completion at 20° for the di-*n*-butyl sulphide complex, this is not so with the pyridine complex, for which several hours' heating is required (Lappert, *J.*, 1953, 667).

The addition of *n*-butyl alcohol (1 mol.) to di-*n*-butyl sulphide–boron trichloride (1 mol.) afforded hydrogen chloride (1 mol.) at 20°. Crystallisation commenced after some days and was complete after about 3 weeks. The crystals were those of a new co-ordination compound, Bu^n_3S,BCl_4, the other products being tri-*n*-butyl borate, tri-*n*-butyl sulphide, and boron trioxide :

$$2Bu^n_2S,BCl_3 + 2Bu^nOH \longrightarrow Bu^n_3S,BCl_4 + 2HCl + Bu^nO{\cdot}BO$$
$$3Bu^nO{\cdot}BO \longrightarrow (Bu^nO)_3B + B_2O_3$$

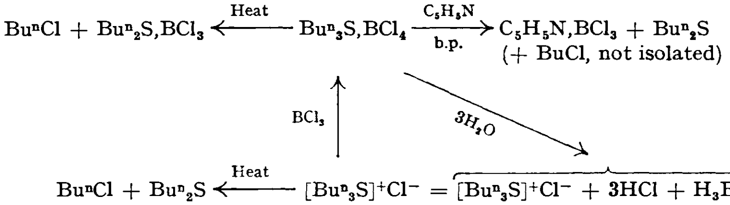
The addition of *n*-butyl alcohol (2 or 3 mols.) to di-*n*-butyl sulphide–boron trichloride (1 mol.) was less complex and proceeded as follows (at 20°) :

$$2Bu^nOH + Bu^n_2S,BCl_3 \longrightarrow 2HCl + Bu^n_2S + (Bu^nO)_2BCl$$

Further decomposition to trialkyl borate followed, and then the reaction :

$$3Bu^nOH + Bu^n_2S,BCl_3 \longrightarrow 3HCl + Bu^n_2S + (Bu^nO)_3B$$

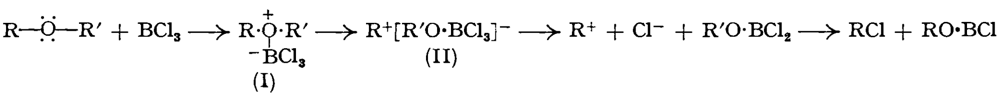
The evidence for considering the tri-*n*-butylsulphonium complex to have the formula Bu^n_3S,BCl_4 is summarised in the reactions illustrated below. However, two alternative structural possibilities, $[Bu^n_3S]^+[BCl_4]^-$ and $[Bu^n_3S,BCl_3]^+Cl^-$, cannot be distinguished by these experiments although the former is considered the more probable.



When shaken with cold water for some hours the sulphonium complex dissolved, and titration with sodium hydroxide revealed only 0·75 equivalent of chloride as hydrochloric acid, whereas all the boron was present as boric acid. When this solution was saturated with solid sodium hydroxide crude tri-*n*-butylsulphonium chloride separated as a yellow oil which was reconverted into its boron complex by addition of boron trichloride. On distillation tri-*n*-butylsulphonium chloride decomposed to *n*-butyl chloride and di-*n*-butyl sulphide, whereas heating of the sulphonium–boron complex gave *n*-butyl chloride and di-*n*-butyl sulphide–boron trichloride. The sulphonium–boron complex was soluble in cold pyridine but without reaction, but when the solution was boiled pyridine–boron trichloride and di-*n*-butyl sulphide were obtained. This may have been due to the decomposition of the sulphonium–boron complex by heat and subsequent reaction of pyridine with the di-*n*-butyl sulphide–boron trichloride thus formed. Tri-*n*-butylsulphonium chloride quickly displaced the di-*n*-butyl sulphide from its boron trichloride complex.

Fission of C–S *and* C–O *Bonds in Ethers and Sulphides.*—Gerrard and Lappert (*J.*, 1952, 1486) have shown that the C–O bond in aliphatic ethers was broken with great ease (*e.g.*, at −80°) by reaction with boron trichloride ($ROR' + BCl_3 \longrightarrow RCl + R'O{\cdot}BCl_2$) and that the reaction appeared to be of S_N1 type. Other examples of ether fission are well established. Resistance to fission of a C–S bond in dialkyl sulphides by a variety of reagents is, however, considerable (Tarbell and Harnish, *Chem. Reviews*, 1951, **49**, 1). In the present experiments C–S fission did not occur.

The following mechanism of ether fission by boron trichloride was suggested :



$$R{-}\ddot{O}{-}R' + BCl_3 \longrightarrow \underset{(I)}{R{\cdot}\underset{^-BCl_3}{\overset{+}{O}}{\cdot}R'} \longrightarrow \underset{(II)}{R^+[R'O{\cdot}BCl_3]^-} \longrightarrow R^+ + Cl^- + R'O{\cdot}BCl_2 \longrightarrow RCl + RO{\cdot}BCl_2$$

The difference between the S and the O systems appears to be in stage (I). Whereas the di-*n*-butyl sulphide–boron trichloride probably has a structure analogous to (I), the ether complex has only transient existence and very rapidly rearranges to (II). This view is taken in the light of the work of Greenwood, Martin, and Emeléus (*J.*, 1950, 3030) with the boron trifluoride–diethyl ether complex, the structure of which was shown to be $Et^+[EtO·BF_3]^-$.

EXPERIMENTAL

Interaction of Di-n-*Butyl Sulphide and Boron Trichloride.*—(*a*) Di-*n*-butyl sulphide (4·19 g., 1 mol.) was added during 30 min. to boron trichloride (3·38 g., 1 mol.) at −80°. A yellow, viscous liquid was obtained which fumed (hydrogen chloride) only slightly in air. The mixture was kept at 20°/20 mm. for 30 min., but no condensate appeared in a trap at −80°. Distillation of 7·52 g. afforded crude *di*-n-*butyl sulphide–boron trichloride* (6·40 g., 85%), b. p. 78—85°/0·5 mm. (Found: Cl, 38·3; B, 3·9. $C_8H_{18},SBCl_3$ requires Cl, 40·4; B, 4·1%), which, purified by redistillation, had b. p. 83°/0·5 mm., n_D^{21} 1·4960 (Found: Cl, 39·8; B, 4·0%). From the first distillation, a dark residue (0·46 g.) remained and di-*n*-butyl sulphide (0·34 g.), n_D^{20} 1·4534, was collected in the trap at −80°.

(*b*) Di-*n*-butyl sulphide (4·21 g., 1 mol.) was added during 35 min. to boron trichloride (6·70 g., 2 mols.) at −80° (final wt. 10·82 g.), but copious fuming, due to boron trichloride, was evident. The whole was left at −10°/20 mm. for 15 min. (loss in wt., 3·30 g. Calc.: loss in weight due to 1 mol. of boron trichloride, 3·35 g.) and then afforded di-*n*-butyl sulphide–boron trichloride, b. p. 88—94°/0·4 mm. (6·5 g., 86%), and a residue (0·45 g.). The complex, when redistilled, had b. p. 80°/0·4 mm., n_D^{20} 1·4953, $d_4^{17.5}$ 1·145 (Found: Cl, 39·9; B, 4·05%).

The di-*n*-butyl sulphide–boron trichloride complex did not crystallise, even at 0° during several weeks.

Hydrolysis of Di-n-*Butyl Sulphide–Boron Trichloride.*—The complex (1·50 g.) was shaken with water (20 c.c.), then extracted with ether. The ethereal solution was washed with aqueous sodium carbonate and water, and dried ($MgSO_4$). On evaporation and distillation, di-*n*-butyl sulphide (0·75 g., 91%), b. p. 74°/10 mm., n_D^{21} 1·4532, was obtained.

A sample (0·2904 g.) was hydrolysed in an enclosed system (to avoid escape of hydrogen chloride evolved). Direct titration with carbonate-free 0·0765N-sodium hydroxide (methyl-red) required 42·6 c.c. On addition of phenolphthalein and mannitol a further 14 c.c. of the hydroxide solution were required for neutralisation. The two titrations thus represent respectively 0·119 g. of HCl (checked by a Volhard estimation) and 0·068 g. of H_3BO_3 (corresponding to Cl, 39·9; B, 4·1%).

Effect of Heat on Di-n-*Butyl Sulphide–Boron Trichloride.*—The complex (4·88 g.) was heated at 215° for 32 hr. under a condenser attached to a potassium hydroxide absorption tube. Some darkening was observed and boron trichloride (0·45 g., 21%) was trapped (Found: Cl, 0·408 g.; B, 0·0413 g.). The remainder (4·41 g.) had a black sediment and afforded on distillation unchanged di-*n*-butyl sulphide–boron trichloride (3·71 g., 76%), b. p. 78—84°/0·4 mm., n_D^{25} 1·4914 (Found: Cl, 38·0; B, 3·8%), di-*n*-butyl sulphide (collected at −80°) (0·43 g., 16%), n_D^{25} 1·4510, and a black residue (0·23 g.).

Di-*n*-butyl sulphide–boron trichloride (5·34 g.) was heated at 100° for 24 hr. in the presence of anhydrous pyridine hydrochloride (0·154 g.) under the same conditions as above. After evacuation (20 mm.) the residue (5·43 g.) was distilled, affording the unchanged complex (4·8 g.), b. p. 88°/0·5 mm., n_D^{20} 1·4950 (Found: Cl, 38·2; B, 4·0%).

Interaction of Pyridine (1 *Mol.*) *and Di*-n-*Butyl Sulphide–Boron Trichloride* (1 *Mol.*).—Pyridine (0·61 g., 1 mol.) in *n*-pentane (5 c.c.) was added to the complex (2·00 g., 1 mol.) at −10°. The addition was vigorous and a white precipitate was formed instantly. The mixture was set aside for 15 min. and the precipitated pyridine–boron trichloride (1·354 g., 91%), m. p. 114° (Found: Cl, 53·8. Calc. for $C_5H_5NCl_3B$: Cl, 54·2%), was filtered off. The filtrate, after removal of the solvent under vacuum, yielded di-*n*-butyl sulphide (0·96 g., 87%), b. p. 74°/14 mm., n_D^{20} 1·4536.

Addition of n-*Butyl Alcohol* (1, 2, *and* 3 *Mols. severally*) *to the Complex* (1 *Mol.*).—*n*-Butyl alcohol (1·10 g., 1 mol.) was added to di-*n*-butyl sulphide–boron trichloride (3·90 g., 1 mol.) at 15°. The reaction was vigorous and hydrogen chloride was instantly evolved and absorbed by potassium hydroxide. The mixture was left for 15 hr. at 15°, whereafter analysis of the contents of the absorption tube showed that hydrogen chloride (0·531 g., 98%) had evolved. Next day crystallisation had begun and 21 days were allowed for its completion. Pentane was then added and the mixture filtered, yielding solid *tri*-n-*butylsulphonium chloride*–

boron trichloride (1·98 g.) (Found : C, 40·3; H, 7·6; S, 8·9; Cl, 40·3; B, 3·1. $C_{12}H_{27}SCl_4B$ requires C, 40·5; H, 7·7; S, 9·0; Cl, 39·9; B, 3·05%). The filtrate, after evaporation, fumed slightly (Found : Cl, 3·3; B, 5·5%) and afforded di-*n*-butyl sulphide (1·2 g.) contaminated with a little tri-*n*-butyl borate (b. p. 68—70°/10 mm., n_D^{19} 1·4500) (Found : B, 0·85%), tri-*n*-butyl borate (0·43 g.), b. p. 68°/0·2 mm., n_D^{19} 1·4200 (Found : B, 4·6. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%), and a residue (0·62 g.), smelling of butyl alcohol and containing boron.

In a second experiment *n*-butyl alcohol (4·74 g., 1 mol.) was added to the di-*n*-butyl sulphide complex (17·3 g., 1 mol.). The mixture was set aside for 8 weeks, whereafter tri-*n*-butylsulphonium chloride–boron trichloride (11·70 g., 100%) (Found: Cl, 39·9; B, 3·0%) was filtered off. The filtrate, on fractionation, afforded di-*n*-butyl sulphide (4·32 g., 90%), b. p. 82—86°/22 mm., n_D^{20} 1·4532, tri-*n*-butyl borate (1·82 g., 72%), b. p. 120—124°/24 mm. (redistilled: b. p. 117°/15 mm., n_D^{20} 1·4112. Found: B, 4·8%), and a residue of boron trioxide (0·72 g., 94%). Yields in this experiment are calculated on the reaction: $2Bu^n_2S,BCl_3 + 2Bu^nOH \longrightarrow 2HCl + Bu^n_3SCl,BCl_3 + Bu^nO{\cdot}BO$; $3Bu^nO{\cdot}BO \longrightarrow B_2O_3 + (RO)_3B$.

n-Butyl alcohol (2·94 g., 2 mols.) was added to di-*n*-butyl sulphide–boron trichloride (5·23 g., 1 mol.) at 15°. After 14 days there was no crystallisation; the absorption tubes had trapped hydrogen chloride (1·46 g., 100%). The residue (6·72 g.) was heated at 80°/0·5 mm. and a condensate (6·2 g.) (Found: Cl, 8·0; B, 3·0%) was collected at −80°. There remained what appeared to be a mixture (0·38 g.) of the complex and boron trioxide (Found: Cl, 7·6; B, 6·9%). The condensate was difficult to fractionate; the first portion (4·55 g.), b. p. 72—100°/12 mm., n_D^{15} 1·4398 (Found : Cl, 4·6; B, 2·3%), was probably a mixture of di-*n*-butyl sulphide (49%), tri-*n*-butyl borate (42%), and the complex (9·0%); the second was pure tri-*n*-butyl borate (1·1 g.), b. p. 104—106°/10 mm., n_D^{15} 1·4168 (Found : B, 4·7%); a distillation residue (0·23 g.) remained.

n-Butyl alcohol (2·22 g., 3 mols.) was added to di-*n*-butyl sulphide–boron trichloride (2·62 g., 1 mol.) at 15°. After 20 hr., the absorption tubes had trapped hydrogen chloride (1·06 g., 98%). Quantitative fractionation, again difficult, gave fractions : I (1·30 g.), b. p. 68—72°/10 mm., n_D^{20} 1·4538 (Found: B, 0·3%); II (1·12 g.), b. p. 72—101°/10 mm., n_D^{20} 1·4200 (Found : B, 4·0%); and III (1·24 g.), b. p. 104—106°/10 mm., n_D^{20} 1·4133 (Found: B, 4·6%). Fractions I and III were apparently fairly good specimens of di-*n*-butyl sulphide and tri-*n*-butyl borate respectively, and the middle fraction was a mixture with a large preponderance of the latter.

Hydrolysis of Tri-n-*Butylsulphonium Chloride–Boron Trichloride.*—Water (20 c.c.) was added to the complex (0·1540 g.). There was no immediate reaction and in order to dissolve the crystals mechanical shaking for about 2 hr. was required. No oil (*n*-butyl chloride or di-*n*-butyl sulphide) was formed. Titration with carbonate-free 0·102N-sodium hydroxide required 12·6 c.c. (methyl-red), and a further 4·75 c.c. after addition of mannitol and phenolphthalein (*i.e.*, 0·0472 g. of HCl and 0·0271 g. of H_3BO_3. Calc. : H_3BO_3, 0·0268 g.; $\frac{3}{4}$Cl as HCl, 0·0475 g.). Nitric acid and standard silver nitrate solution were added and chlorine ion was estimated by the Volhard method (Found : Cl, 40·1%).

The complex (4·00 g.) gave a clear solution in warm 3N-sodium hydroxide (10 c.c.), and this was saturated with solid sodium hydroxide, a light brown oil separating as upper layer. This was insoluble in ether and *n*-pentane, but was soluble in methylene dichloride. The solvent layer was dried (K_2CO_3) and the solvent removed at 0·01 mm. A viscous oil, crude *tri*-n-*butylsulphonium chloride* (2·54 g., 95%) [Found : Cl (Volhard, cold), 12·9. $C_{12}H_{27}SCl$ requires Cl, 14·9%], n_D^{20} 1·5036, not volatile at 25°/0·005 mm., remained. The % yield is based on the reaction : $Bu^n_2S,BCl_3,Bu^nCl + 3H_2O \longrightarrow Bu^n_2S,Bu^nCl + 3HCl + H_3BO_3$.

Effect of Heat on Tri-n-*Butylsulphonium Chloride–Boron Trichloride.*—The complex (2·87 g.) was heated at 180°/0·3 mm. for 2 hr. A yellow liquid (di-*n*-butyl sulphide–boron trichloride) (1·78 g., 84%) (redistilled : b. p. 83—84°/0·5 mm., n_D^{20} 1·4975. Found : Cl, 40·3; B, 4·07%) gradually distilled, leaving a carbonaceous residue (0·20 g.). In a trap at −80° a clear liquid (0·88 g.) was collected which on distillation afforded *n*-butyl chloride (0·66 g., 89%), b. p. 77—79°, n_D^{17} 1·4051, d_4^{26} 0·885 [Found : Cl (sealed tube), 38·1. Calc. for C_4H_9Cl : Cl, 38·4%], and a residue (0·19 g.) of di-*n*-butyl sulphide, n_D^{20} 1·4520. Yields are based on the reaction : $Bu^n_2S,BCl_3,Bu^nCl \longrightarrow Bu^n_2S,BCl_3 + Bu^nCl$).

Interaction of Pyridine and Tri-n-*Butylsulphonium Chloride–Boron Trichloride.*—Pyridine (0·50 g.) was poured on tri-*n*-butylsulphonium chloride–boron trichloride (0·520 g.) at 20°. The solid dissolved and the solution was set aside at 20° for 2 hr., then placed in a vacuum (0·01 mm.). A crystalline residue (0·524 g.) of unchanged complex (Found : Total Cl, 39·4; B, 3·1%) remained.

To the complex (2·35 g.), pyridine (4·00 g.) was added and the solution was heated at 90° under reflux for 2 hr., a slight flocculent precipitate being formed. The mixture was cooled and placed at 25 mm., but no volatile matter was removed (*i.e.*, no free *n*-butyl chloride). The precipitate (0·036 g.) was filtered off and washed with pyridine (3 g.). The filtrate was then evacuated (0·2 mm.). Solid pyridine–boron trichloride (1·30 g., 100%) remained. The condensate collected in a trap at −80° was washed with dilute hydrochloric acid (to remove pyridine) and extracted with ether, and the ethereal layer was dried (K_2CO_3). After removal of the solvent, di-*n*-butyl sulphide (0·94 g., 97%), b. p. 71—80°/17 mm., n_D^{24} 1·4518, was distilled. The pyridine–boron trichloride residue from the primary distillation, recrystallised from chloroform–*n*-pentane, had m. p. 114° (Found : Cl, 53·7; C_5H_5N, 40·2. Calc. for C_5H_5N,Cl_3B : Cl, 54·2; C_5H_5N, 40·3%). % Yields are based on the reaction : $Bu^n{}_3SCl,BCl_3 + C_5H_5N \longrightarrow C_5H_5NBCl_3 + Bu^n{}_2S + Bu^nCl$.

Effect of Heat on Tri-n-*Butylsulphonium Chloride.*—Distillation of tri-*n*-butylsulphonium chloride (2·00 g.) was attempted at 20 mm. At 100°, decomposition took place, di-*n*-butyl sulphide (0·96 g., 79%), b. p. 72—75°/17 mm., n_D^{21} 1·4507, distilled, and a dark residue (0·15 g.) remained. In a trap at −80° *n*-butyl chloride (0·62 g., 80%), n_D^{20} 1·4030, was collected; distilled, it had b. p. 75—79°, n_D^{21} 1·4000 [Found : Cl (sealed tube), 38·0%]. % Yields are based on the reaction : $Bu^n{}_3SCl \longrightarrow Bu^n{}_2S + Bu^nCl$).

Interaction of Boron Trichloride (1 *Mol.*) *and Tri*-n-*Butylsulphonium Chloride* (1 *Mol.*).—Tri-*n*-butylsulphonium chloride (2·97 g., 1 mol.) in methylene dichloride (10 c.c.) was added to boron trichloride (2·90 g., >1 mol.) at −80°, and the mixture was left for 10 hr. at 20°, then placed in a vacuum, initially by using a water-pump and finally at 0·01 mm. A solid residue, tri-*n*-butylsulphonium chloride–boron trichloride (4·48 g., 100%) [Found: Cl (methyl-red), 29·5, (Volhard), 39·4; B, 3·1%] remained.

Interaction of Diethyl Ether and Di-n-*Butyl Sulphide–Boron Trichloride.*—Diethyl ether (1·78 g., >1 mol.) was added to di-*n*-butyl sulphide (4·19 g., 1 mol.) at −80°. After 12 hr. at 20°, distillation afforded di-*n*-butyl sulphide (1·11 g., 96%), b. p. 60°/9 mm., n_D^{20} 1·4529, and triethyl borate (1·13 g., 98%) was collected at −80°, (b. p. 115—117°/760 mm., n_D^{20} 1·3737) (Found : B, 7·5. Calc. for $C_6H_{15}O_3B$: B, 7·4%). The residual liquid (2·64 g., 100%) was non-volatile, even at 180°/0·1 mm., was water-soluble, and appeared to be *di*-n-*butylethylsulphonium chloride–boron trichloride* [Found : Cl (methyl-red titration), 31·5; Total Cl, 42·6; B, 3·24. $C_{10}H_{23}Cl_4SB$ requires $\frac{3}{4}$Cl, 32·3; Total Cl, 43·4; B, 3·30%]. The % yields are based on the reaction: $2Bu^n{}_2S,BCl_3 + 3(Et)_2O \longrightarrow Bu^n{}_2S + (EtO)_3B + EtBu^n{}_2SCl,BCl_3 + 2EtCl$ (not isolated).

Interaction of Tri-n-*Butylsulphonium Chloride and Pyridine–Boron Trichloride.*—Pyridine–boron trichloride (1·51 g., 1 mol.) in methylene dichloride (4 c.c.) was added to tri-*n*-butylsulphonium chloride (1·84 g., 1 mol.), and the mixture kept at 20° for 12 hr., then the solvent was removed. Water was added and the solid pyridine–boron trichloride, m. p. 114° (1·39 g., 92%), was recovered. Water was removed from the filtrate by evacuation over concentrated sulphuric acid, and tri-*n*-butylsulphonium chloride (1·63 g., 89%) was recovered as a viscous oil.

Addition of Tri-n-*Butylsulphonium Chloride* (1 *Mol.*) *to Di*-n-*Butyl Sulphide–Boron Trichloride* (1 *Mol.*).—Di-*n*-butyl sulphide–boron trichloride (1·65 g., 1 mol.) was added to tri-*n*-butylsulphonium chloride (1·49 g., 1 mol.) at 15°. There was instantaneous formation of solid and, after addition of pentane, tri-*n*-butylsulphonium chloride–boron trichloride (2·10 g., 91%) [Found: Cl, (methyl red) 29·5, (total) 39·5; B, 3·0%] was filtered off. The filtrate on distillation afforded di-*n*-butyl sulphide (0·90 g., 98%), b. p. 68—70°/12 mm., n_D^{22} 1·4530.

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THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD,
LONDON, N.7.

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