# **150.** *Interaction of Boron Trihalides with Aryl Phosphates and Phosphorochloridates.*

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Aryl phosphates form complexes with boron halides, $(RO)_3P{=}O,BX_3$ [R = Ph, *m*- or *p*-Me·$C_6H_4$, *p*-Cl·$C_6H_4$, 2,4-$Cl_2C_6H_3$; X = Cl, Br, or (except for the last two) F]. The good thermal stability is in marked contrast with the instability of the complexes when R = alkyl and X = Cl. There are no marked substitution effects, except that the acceptor power is $BBr_3 > BCl_3 > BF_3$, in accord with infrared spectroscopic data which point to the structure $(RO)_3P{=}\overset{\delta+}{O}{-}\overset{\delta-}{B}X_3$. The complexes, $(RO)_2P(O)Cl,BCl_3$ and $RO{\cdot}P(O)Cl_2,BCl_3$, are less stable, and for them infrared data do not support P=O co-ordination to boron.

Correlations with boron trihalide–triphenyl phosphite systems are discussed.

INVESTIGATIONS into the mutual replacement of an alkoxyl or aryloxyl group attached to one non-metal, and halogen attached to another have shown that in alkoxysilane–phosphorus halide,[1] alkoxysilane–boron trichloride,[2] and triphenyl phosphite–boron trihalide [3] systems mixtures of halogeno-esters are with certain exceptions primarily produced, the non-metals remaining in separate compounds. Thus triphenyl phosphite [3] and boron trichloride at temperatures above about −10°, form diphenyl phosphorochloridite, phenyl phosphorodichloridite, and phosphorus trichloride in proportions depending upon the relative amounts of reactants and the conditions. Phenyl dichloroborinate and diphenyl chloroboronate were formed as intermediates which afforded triphenyl borate by redistribution during distillation. There was always a drift towards phosphorus trichloride and triphenyl borate, which did not interact even at 80°. In marked contrast, triethyl phosphate gave a complex,[4] $(EtO)_3P{=}O,BCl_3$, at −80°, which slowly evolved ethyl chloride at room temperature, the evolution being completed at higher temperatures, and at no stage were there chloro-esters analogous to those in the phenyl phosphite system. Finally, boron phosphate was obtained.

It is now reported that aryl phosphates form complexes, $(RO)_3P{=}O,BX_3$ [R = Ph, *m*- or *p*-Me·$C_6H_4$, *p*-Cl·$C_6H_4$, 2,4-$Cl_2C_6H_3$; X = Cl, Br, or (except for the last two) F] (cf. Table 1). The complexes were easily hydrolysed, the fate of the $BX_3$ part being the same as that of the trihalide if alone. Thermal behaviour of the complexes was very different from that of those in which R is alkyl and X = Cl.[4] Thus at 100° the complex $(PhO)_3P{=}O,BCl_3$ was unchanged for 5 hr.; at 200° (3 hr.) there was a small loss in weight, but little change in content of easily hydrolysed chlorine. At higher temperatures there was decomposition, rather than dissociation. Similar remarks apply to the complexes where R = *m*-Me·$C_6H_4$ or 2,4-$Cl_2C_6H_3$ and X = Cl. When R = Ph and X = F or Br, there was little change at 300° (about 3 hr.). However, when heated at 0·2 mm. the complex $(PhO)_3P{=}O,BCl_3$ gave triphenyl phosphate in 89% yield. Butan-1-ol caused ready fission of the co-ordinative bond in this complex or the *m*-tolyl analogue, the triaryl phosphate, hydrogen chloride, and tributyl borate being formed.

Effects of substituent were not marked but in general the order of acceptor power was $BBr_3 > BCl_3 > BF_3$,[5] notably since the chloroaryl phosphates did not form complexes with boron trifluoride. This order was also supported by infrared spectroscopy.

*Infrared Spectra.*—In the spectra of the complexes, the band at 1296—1312 cm.$^{-1}$

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[1] Fertig and Gerrard, *Chem. and Ind.*, 1956, 83; Fertig, Gerrard, and Herbst, *J.*, 1957, 1488; Currell and Gerrard, *Chem. and Ind.*, 1958, 1289.

[2] Gerrard and Strickson, *ibid.*, 1958, 860.

[3] Frazer, Gerrard, and Patel, *ibid.*, 1959, 90, 728.

[4] Gerrard and Griffey, *ibid.*, 1959, 55.

[5] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, 2173.

assigned to the P=O absorption in a triaryl phosphate,[6] and the band at 959—970 cm.$^{-1}$ assigned to the (P–O)–C absorption [7] were not present. Instead there was a new band at 1027—1050 cm.$^{-1}$. The frequency, 1182 cm.$^{-1}$, assigned to P=O in triphenylphosphine oxide was shifted to 1073 cm.$^{-1}$ when the complex with boron trichloride was formed. Further, the P=O frequency, 1258 cm.$^{-1}$, for tri-isobutyl phosphate was shifted to 1133 cm.$^{-1}$ in the boron trichloride complex.[8]

TABLE 1. 1 : 1 *Boron trihalide–triaryl phosphate complexes*, $(RO)_3PO,BX_3$.

| No. | R in $(RO)_3PO$ | Weight (g.) | $CH_2Cl_2$ (c.c.) | $BX_3$ X | Yield of complex g. | Yield of complex % | M. p. |
|---|---|---|---|---|---|---|---|
| 1 | Ph .............. | 16·78 | 30 | Cl | 22·5 | 98·5 | 86—90° |
| 2 | *m*-Me·$C_6H_4$ ... | 11·05 | None | ,, | 14·25 | 96·7 | liq. |
| 3 | *p*-Me·$C_6H_4$ ... | 10·00 | 15 | ,, | 12·98 | 98·5 | 125—130 |
| 4 | *p*-Cl·$C_6H_4$ [a] ... | 8·59 | 30 | ,, | 10·74 | 98·2 | 90—94 |
| 5 | 2,4-$Cl_2C_6H_3$ [a] | 9·11 | 30 | ,, | 10·55 | 95·0 | 86—90 |
| 6 | Ph [b] ........... | 7·68 | 30 | Br | 13·35 | 98·2 | 86—90 |
| 7 | *m*-Me·$C_6H_4$ ... | 11·00 | None | ,, | 17·50 | 97·6 | liq. |
| 8 | *p*-Me·$C_6H_4$ ... | 7·50 | 15 | ,, | 12·40 | 98·4 | 131—135 |
| 9 | *p*-Cl·$C_6H_4$ [b] ... | 6·86 | 25 | ,, | 10·75 | 98·9 | 95—104 |
| 10 | 2,4-$Cl_2C_6H_3$ [b] ... | 6·38 | 20 | ,, | 9·23 | 98·2 | 98—104 |
| 11 | Ph [b] ........... | 16·31 | 30 | F | 19·42 | 98·6 | 85—88 |
| 12 | *m*-Me·$C_6H_4$ ... | 18·42 | None | ,, | 21·75 | 99·7 | liq. |
| 13 | *p*-Me·$C_6H_4$ ... | 9·21 | 20 | ,, | 10·6 | 97·2 | liq. |

[a] Added to boron trichloride in n-pentane (20 c.c.). [b] Dissolved in chloroform and precipitated by pentane.

| | Found (% | | | | | Required (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | C | H | Hal | P | B | C | H | Hal | P | B |
| 1 | 48·4 | 3·9 | 23·4 | 6·7 | 3·0 | 48·5 | 3·9 | 24·0 | 7·0 | 2·4 |
| 2 | — | — | 20·9 | 6·0 | 2·7 | — | — | 21·9 | 6·4 | 2·2 |
| 3 | — | — | 21·3 | 6·2 | 2·2 | — | — | 21·9 | 6·4 | 2·2 |
| 4 | 39·4 | 2·9 | 19·7 | 5·3 | 2·0 | 39·5 | 2·2 | 19·4 [c] | 5·7 | 2·0 |
| 5 | 32·45 | 2·1 | 17·0 [c] | 4·4 | 1·8 | 33·2 | 1·4 | 16·4 [c] | 4·8 | 1·7 |
| 6 | — | — | 41·8 | 5·3 | 2·0 | — | — | 41·6 | 5·4 | 1·9 |
| 7 | 41·2 | 4·45 | 38·1 | 4·7 | 1·75 | 40·7 | 3·4 | 38·7 | 5·0 | 1·75 |
| 8 | — | — | 38·7 | 4·8 | 1·7 | — | — | 38·7 | 5·0 | 1·75 |
| 9 | 32·5 | 1·9 | 35·5 | 4·4 | 1·7 | 31·8 | 1·8 | 35·3 [c] | 4·6 | 1·6 |
| 10 | — | — | 30·3 [c] | 3·9 | 1·3 | — | — | 30·6 [c] | 4·0 | 1·4 |
| 11 | 54·3 | 5·2 | 13·8 | 7·8 | 2·9 | 54·8 | 3·8 | 14·5 | 7·9 | 2·75 |
| 12 | 57·2 | 5·9 | 12·1 | 7·1 | 2·5 | 57·7 | 4·8 | 13·1 | 7·1 | 2·5 |
| 13 | — | — | 12·5 | 6·9 | 2·3 | — | — | 13·1 | 7·1 | 2·5 |

[c] Easily hydrolysable.

The magnitude of these shifts was 109 and 125 cm.$^{-1}$ respectively. If the P=O band in the aryl phosphate complex had moved to a lower frequency by about the same amount it would appear in the region of the P–(O–C) absorption band at 1240—1190 cm.$^{-1}$. In fact, in the complexes the intensity of this band had increased.

The new band at 1027—1050 cm.$^{-1}$ in the complexes is probably due to the shift of (P–O)–C absorption (980 cm.$^{-1}$) to higher frequencies.

The formula suggested for the complexes is $(RO)_3\overset{\delta+}{P}{=}O{-}\overset{\delta-}{B}X_3$.

Sheldon and Tyree [9] reported the spectra of phosphoryl halides, triphenylphosphine oxide, and their addition compounds with metal halides such as tin and titanium tetrachloride and tetrabromide and ferrous bromide. From the shift of P=O band they suggested that oxygen serves as donor and this produces a shift of 90—55 cm.$^{-1}$ to lower frequency. For the phosphoryl halide–boron trihalide complexes there was a shift of

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[6] Meyrick and Thompson, *J.*, 1950, 225; Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853; Bellamy and Beecher, *J.*, 1952, 475.

[7] *Idem, J.*, 1953, 728.

[8] Gerrard and Griffey, unpublished work.

[9] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775; 1959, **81**, 2290.

12—18 cm.$^{-1}$ to higher frequency. This suggests that halogen serves as donor, giving the ionic structure $POX_2^+BX_4^-$ as suggested by Greenwood and Wade [10] for the $GaCl_3,POCl_3$ complex.

The spectra of the complexes of boron trichloride and a diaryl phosphorochloridate or an aryl phosphorodichloridate were difficult to interpret, but there was some indication of a P=O band shift to higher frequency, and this suggests that chloride ion might be donor.

## EXPERIMENTAL

*Triaryl Phosphate–Boron Trihalide Complexes.*—The triaryl phosphate (1 mol.), usually in methylene dichloride, was slowly added to boron trichloride (1 mol.) at −80°. Volatile matter was removed at about 23°/15 mm., and the *complex* washed with pentane and held at about 23°/0·2 mm. for 2 hr. The phosphate was added to the tribromide (1 mol.) in n-pentane (*ca.* 20 c.c.) at *ca.* −30°, and to the trifluoride (1 mol.) in ether at −80°. Results are recorded in Table 1.

The triphenyl phosphate–boron trichloride complex (4·95 g.) retained its weight and easily hydrolysable chlorine at 100° for 5 hr. and almost entirely at 200° for 3 hr. When the temperature was raised under reduced pressure, triphenyl phosphate (3·25 g., 89·3%), b. p. 170—174°/0·2 mm., m. p. 40°, and a residue (0·11 g.) were obtained. Addition of butan-1-ol (2·16 g., 3 mol.) to the same complex (4·3 g., 1 mol.) at −80°, the mixture then being allowed to warm to 24°, led to evolution of hydrogen chloride (1·55 mol.) (the remainder at 15 mm.) and the isolation of tributyl borate (1·52 g., 67·8%), b. p. 112°/15 mm., $n_D^{20}$ 1·4100 (Found: B, 4·80. Calc. for $C_{12}H_{27}O_3B$: B, 4·72%), and triphenyl phosphate (2·07 g., 65·3%), b. p. 162°/0·05 mm., m. p. 44°. There was a residue (0·95 g.). On addition of excess of water to the same complex (7·9 g.) in ether (30 c.c.) and evaporation of the ethereal layer triphenyl phosphate (5·7 g., 98·2%) was obtained.

The tri-*m*-tolyl phosphate–boron trichloride complex lost little weight or easily hydrolysable chlorine at 300° in 3 hr.; but mixed with butan-1-ol (3 mol.), at −80°, and warmed to 20° it gave hydrogen chloride (96·6%), tributyl borate (73%), b. p. 115°/18 mm., $n_D^{20}$ 1·4105 (Found: B, 4·35%), and tri-*m*-tolyl phosphate (81·7%), b. p. 158—162° 0·1 mm. Similarly hydrogen chloride, tributyl borate (85%), b. p. 108—112°/20 mm., $n_D^{20}$ 1·4098 (Found: B, 4·65%), and tri-*p*-chlorophenyl phosphate (71%), m. p. 85—88°, b. p. 160—170°/0·1 mm., were obtained from the corresponding complex. The boron trichloride complex with 2,4-dichlorophenyl phosphate was stable up to 300°. The triphenyl phosphate–boron tribromide complex was rather less stable; the corresponding boron trifluoride complex lost weight and ionisable fluorine very slowly at 300°.

*Interaction of Phenyl Phosphorodichloridate and Boron Trichloride.*—The dichloridate (5·4 g., 1 mol.) in n-pentane (30 c.c.) was added to boron trichloride (3·3 g.) at −80°. *Phenyl phosphorodichloridate–boron trichloride complex* (7·97 g., 95%), m. p. 35—42° (Found: Cl, 53·7; P, 8·8; B, 3·24. $C_6H_5O_2Cl_5PB$ requires Cl, 54·0; P, 9·4; B, 3·30%), was filtered off at 22° and kept at 22°/0·2 mm. for 1 hr. On being slowly heated to 300°, the complex (4·06 g.) afforded phosphoryl chloride–boron trichloride complex (1·23 g., 73·5%) (Found: Cl, 77·8; B, 3·83%), m. p. 68—71°, boron trichloride (1·0 g., 69%), and diphenyl phosphorochloridate (1·03 g., 61·9%), b. p. 150—156°/0·5 mm. (Found: Cl, 13·6. Calc. for $C_{12}H_{10}O_3ClP$: Cl, 13·0%). Heated under reduced pressure, however, the complex (14·38 g.) gave phenyl phosphorodichloridate (9·5 g., 94·1%), b. p. 58—64°/0·1 mm., $n_D^{24}$ 1·5228 (Found: Cl, 32·8. Calc. for $C_6H_5O_2Cl_2P$: Cl, 33·8%).

p-*Chlorophenyl phosphorodichloridate–boron trichloride complex* (9·01 g., 97%), m. p. 46—50° (Found: C, 20·7; H, 1·7; easily hydrolysable Cl, 48·8; P, 7·8; B, 2·9. $C_6H_4O_2Cl_6PB$ requires C, 19·9; H, 1·1; e.h. Cl, 48·9; P, 8·8; B, 3·0%), was similarly obtained from the dichloridate (6·28 g.) in n-pentane. It (4·04 g.) gave phosphoryl chloride–boron trichloride complex (1·34 g., 88·7%), m. p. 67—68° (Found: Cl, 78·8; B, 3·9%), boron trichloride (0·42 g., 64·6%), and di-*p*-chlorophenyl phosphorochloridate (0·9 g., 47·9%), b. p. 168—172°/0·2 mm. (Found: Cl, 10·3%), when slowly heated to 300° at atmospheric pressure. There was a residue (0·72 g.).

*Interaction of Diphenyl Phosphorochloridate with Boron Trichloride.*—The chloridate (4·58 g., 1 mol.), suspended in n-pentane (20 c.c.), was added slowly to boron trichloride (2·36 g.) at −80°, and the *complex* (6·47 g., 98·3%), m. p. 54—64° (Found: Cl, 35·1; P, 8·9; B, 2·9.

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[10] Greenwood and Wade, *J.*, 1957, 1517.

$C_{12}H_{10}O_3Cl_4BP$ requires Cl, 36·7; P, 8·0; B, 2·8%), was filtered off, washed with n-pentane, and kept at 24°/0·5 mm. for 2 hr. At 100° the complex lost no weight, but as the temperature was raised to 300° the phosphoryl chloride—boron trichloride complex (99·7%), m. p. 66—68° (Found: Cl, 76·2; B, 4·17. Calc. for $OCl_6PB$: Cl, 78·6; B, 3·99%), sublimed; a residue afforded an unidentified mixture on distillation. However, when the complex (10·4 g.) was heated under reduced pressure, the original chloridate (6·54 g., 90%), b. p. 132—136°/0·2 mm., $n_D^{24}$ 1·5492 (Found: Cl, 13·5. Calc. for $C_{12}H_{10}O_3ClP$: Cl, 13·0%), and boron trichloride (2·61 g., 82·5%) were obtained.

*Di-*p*-chlorophenyl phosphorochloridate–boron trichloride complex* (70·7%), m. p. 49—55° (Found: easily hydrolysable Cl, 31·8; P, 6·9; B, 2·3. $C_{12}H_8O_3Cl_6PB$ requires easily hydrolysable Cl, 31·2; P, 6·8; B, 2·4%), was similarly obtained, and on being heated slowly to 300° it afforded phosphoryl chloride–boron trichloride complex (98·5%), m. p. 68° (Found: Cl, 78·7; B, 3·83%), boron trichloride (28%), and tri-*p*-chlorophenyl phosphate (56·6%), m. p. 90—95°, b. p. 180—200°/0·4 mm.

*Phosphoryl Halide–Boron Trihalide Complexes.*—Phosphoryl chloride (6·71 g., 1 mol.) in n-pentane (30 c.c.) was added dropwise to boron trichloride (5·33 g., 1 mol.) at −80°. The white complex (8·32 g., 70%), m. p. 72—73° (Found: Cl, 78·5; P, 11·1; B, 4·3. Calc. for $OCl_6PB$: Cl, 78·6; P, 11·5; B, 4·0%), was filtered off at 24° and kept at 24°/20 mm. for 1 hr. On being heated to 100°, the complex (3·32 g.) gave sublimed complex (2·01 g., 60·5%), m. p. 70—71° (Found: Cl, 77·8; B, 3·9%), boron trichloride (0·44 g., 30·6%), and phosphoryl chloride (0·65 g., 34·6%) (Found: Cl, 66·4%).

The white *phosphoryl bromide–boron tribromide complex* (7·13 g., 95·2%) m. p. 150—154° (Found: Br, 88·8; P, 5·7; B, 2·2. $OBr_6PB$ requires Br, 89·4; P, 5·8; B, 2·0%), was obtained by addition of phosphoryl bromide (4·01 g., 1 mol.) in n-pentane (25 c.c.) and of methylene dichloride (5 c.c.) to boron tribromide (3·67 g., 1·05 mol.) in pentane (15 c.c.) at −80°. The

TABLE 2. *Infrared spectra.*

| | | Frequency (cm.$^{-1}$) | | | Shifts (cm.$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | Compounds | P=O | P–(O–C) | (P–O)–C | P=O | P–(O–C) | (P–O)–C |
| 1 | $(PhO)_3PO$ | 1297 | 1188; 1160 | 959·7 | — | — | — |
| 2 | ,, ,$BF_3$ | 1190—1149 | 1179; 1159 | 1033 | 107—148 | 9, 1 | −73·3 |
| 3 | ,, ,$BCl_3$ | 1190—1149 | 1175; 1153 | 1043 | 107—148 | 13, 7 | −83·3 |
| 4 | ,, ,$BBr_3$ | 1190—1149 | 1172; 1152 | 1050 | 107—148 | 16, 8 | −90·3 |
| 5 | $(m\text{-}Me{\cdot}C_6H_4{\cdot}O)_3PO$ | 1299 | 1190; 1139 | 969·1 | — | — | — |
| 6 | ,, ,$BF_3$ | 1190—1136 | 1183; 1161 | 1029 | 109—163 | 7, −22 | −59·9 |
| 7 | ,, ,$BCl_2$ | 1190—1124 | 1179; 1140 | 1045 | 109—151 | 11, −1 | −75·9 |
| 8 | ,, ,$BBr_3$ | 1190—1124 | 1190; 1140 | 1049 | 109—151 | 0 −1 | −79·9 |
| 9 | $(p\text{-}Me{\cdot}C_6H_4{\cdot}O)_3PO$ | 1295 | 1190; 1164 | 970·9 | — | — | — |
| 10 | ,, ,$BF_3$ | 1205—1163 | 1190; 1166 | 1031 | 90—132 | −2 | −60·1 |
| 11 | ,, ,$BCl_3$ | 1190—1149 | 1182; 1160 | 1037 | 105—146 | 8, 4 | −66·1 |
| 12 | ,, ,$BBr_3$ | 1190—1149 | 1182; 1159 | 1040 | 105—146 | 8, 5 | −69·1 |
| 13 | $(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_3PO$ | 1302 | 1215; 1190 | 969·1 | — | — | — |
| 14 | $(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_3PO,BCl_3$ | 1190—1149 | 1188; 1160 | 1033 | 112—153 | 27, 30 | −63·9 |
| 15 | ,, ,$BBr_3$ | 1190—1149 | 1181; 1159 | 1036 | 112—153 | 34, 31 | −66·9 |
| 16 | $(2,4\text{-}Cl_2C_6H_3{\cdot}O)_3PO$ | 1312 | 1217 | 970·0 | — | — | — |
| 17 | ,, ,$BCl_3$ | 1205—1163 | 1189 | 1027 | 107—149 | 28 | −57 |
| 18 | ,, ,$BBr_3$ | 1220—1163 | 1218; 1166 | 1035 | 92—149 | 5, 51 | −65 |
| 19 | $(PhO)_2POCl$ | 1300 | 1179; 1157 | 966·4 | — | — | — |
| 20 | ,, ,$BCl_3$ | 1337 | 1179; 1144 | 970·9<br>930·1 | −37 | 0, 13 | −4·5<br>36·3 |
| 21 | $(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_2POCl$ | 1304 | 1185; 1160 | 970·9 | — | — | — |
| 22 | ,, ,$BCl_3$ | 1342 | 1188; 1160 | 1035 | −38 | −3, 0 | −64·1 |
| 23 | $PhO{\cdot}POCl_2$ | 1302 | 1181; 1160 | 946·9 | — | — | — |
| 24 | ,, ,$BCl_3$ | 1342 | 1172; 1156 | 990·1 | −40 | 9, 4 | −43·2 |
| 25 | $p\text{-}Cl{\cdot}C_6H_4{\cdot}O{\cdot}POCl_2$ | 1305 | 1188; 1161 | 950·6 | — | — | — |
| 26 | ,, ,$BCl_3$ | 1348 | 1182; 1157 | 982·0 | −48 | 6, 4 | −31·4 |
| 27 | $POCl_3$ | 1299 | — | — | — | — | — |
| 28 | ,, ,$BCl_3$ | 1311 | — | — | −12 | — | — |
| 29 | $POBr_3$ | 1271 | — | — | — | — | — |
| 30 | ,, ,$BBr_3$ | 1289 | — | — | −18 | — | — |
| 31 | $(Ph)_3PO$ | 1182 | — | — | — | — | — |
| 32 | ,, ,$BCl_3$ | 1073 | — | — | 109 | — | — |
| 33 | $(Bu^iO)_3PO$ | 1258 | — | 1025 | — | — | — |
| 34 | ,, ,$BCl_3$ | 1133 | — | 1057 | 125 | — | −32 |

complex was filtered off at 20°, washed with pentane, and kept at 20°/0·1 mm. for 1 hr. It (4·3 g.) was stable at 100° for 1 hr., but on being heated to 200° gave sublimed complex (2·82 g., 65·6%) (Found: Br, 88·2; B, 2·3%), boron tribromide (0·35 g., 17·5%), and a residue of phosphoryl bromide (0·8 g., 34·9%) (Found: Br, 85·3%).

*Triphenylphosphine Oxide–Boron Trichloride Complex.*—Triphenylphosphine oxide (2·37 g., 1 mol.) in methylene dichloride (20 c.c.) was added dropwise to boron trichloride (1·2 g., 1·2 mols.) at −80°. The white *complex* (3·2 g., 94·9%), m. p. 207—208° (Found: Cl, 26·2; B, 2·8; P, 7·8. $C_{18}H_{15}OCl_3BP$ requires Cl, 26·9; B, 2·7; P, 7·9%), was filtered off at 20°, washed with pentane, and kept at 20°/0·1 mm. for 3 hr.

*Infrared Spectra.*—The spectra of the compounds listed in Table 2 were measured on a Grubb–Parsons double-beam spectrometer with a sodium chloride prism. The spectra of the solids were measured in chloroform solutions and of the liquids in capillary fillings; some solids were examined in Nujol suspension.

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