# **422.** *Formation of Sulphites, Phosphites, and Phosphates of Alcohols containing an Aryl Group.*

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2-Phenylethanol, 3-phenylpropanol, 1 : 3-diphenylpropan-2-ol, 1-phenylpropan-2-ol, 1 : 2-diphenylethanol, and benzyl alcohol behave as does butan-1-ol in that only sulphite and base hydrochloride are quickly formed at −10° by thionyl chloride and pyridine, whereas 1-phenylethanol, 1-2′-naphthylethanol, and diphenylmethanol give the chloride RCl concurrently, although at −78° only diphenylmethanol still does so. Phosphorus oxychloride and pyridine give base hydrochloride and phosphate with the first four alcohols named, as does butan-1-ol; but the others give chloride RCl and little if any phosphate. Phosphorus trichloride and pyridine give base hydrochloride and phosphite with all the alcohols, as does butan-1-ol.

FOR the purpose of describing alcohol–inorganic non-metallic halide systems it is desirable to compare the behaviour of the alcohol with that of butan-1-ol or of 1-phenylethanol in the same system (Gerrard, *J.*, 1944, 85; 1945, 106; 1946, 741; Gerrard and Woodhead, *J.*, 1951, 519; Gerrard and Lappert, *ibid.*, p. 1020; Gerrard and Phillips, *Chem. and Ind.*, 1952, 540). During the addition of thionyl chloride (0·5 mol.) to an ethereal solution of alcohol (1 mol.) and pyridine (1 mol.) there was rapid reaction, even at −78°, probably by the steps: $ROH,NC_5H_5 + SOCl_2 \longrightarrow RO{\cdot}SOCl + C_5H_5N,HCl$; $ROH,NC_5H_5 + RO{\cdot}SOCl \longrightarrow SO(OR)_2 + C_5H_5N,HCl$. At −10°, but not at −78°, 1-phenylethanol and 1-2′-naphthylethanol gave also chloride, RCl, whereas diphenylmethanol still gave some chloride at −78°. If 1-chloro-1-phenylethane came from the intermediate chlorosulphinate the reaction must have been fast at −10°, for it was competing with the rapid second reaction. Furthermore, when the alcohol is added to thionyl chloride alone, the formation of chloride RCl is so fast at −10° that tangible evidence of the formation of the chlorosulphinate has still to be secured. Although 1 : 2-diphenylethanol and benzyl alcohol both have a phenyl group attached to the alcoholic carbon atom, they gave only the sulphite at −10°.

When phosphorus oxychloride (1 mol.) was added to the alcohol (3 mol.) and pyridine (3 mol.) in ether there were two types of reaction. Alcohols having an aryl group attached to the alcoholic carbon atom (nos. 5—9, see Table 4) gave alkyl chloride, unchanged alcohol, and little or no alkyl phosphate, all the phosphorus tending to be with the base in the precipitate, whereas the other alcohols behaved as does butan-1-ol and cleanly gave trialkyl phosphate and base hydrochloride. It is known (unpublished work) that reaction of this oxychloride in the presence of pyridine is slower than that with thionyl chloride and phosphorus trichloride, and the rate falls off perceptibly for the second and especially the third step. It appears that the formation of alkyl chloride is faster when the reactivity of the alcoholic carbon atom is increased by attachment of an aryl group.

In the phosphorus trichloride systems all the alcohols resembled butan-1-ol in that all chlorine was quickly precipitated as base hydrochloride, and the phosphorus was retained as trialkyl phosphite. The phosphites were readily dealkylated (1 group) by hydrogen chloride, and with compounds containing an aryl group attached to the alcoholic carbon atom (5—9) the process readily went further:

$$P(OR)_3 + HCl \longrightarrow P(OH)(OR)_2 + RCl \longrightarrow P(OH)_2(OR) + RCl \longrightarrow P(OH)_3 + RCl$$

1 : 3-Diphenylpropan-2-ol requires special mention. Not only was there some hindrance to the formation of the phosphite (probably concerning the last step), but the interaction between the phosphite and hydrogen chloride was comparatively slow. There was some evidence for the existence of the compound $P(OR)_3,3HCl$, as though each oxygen atom was being hydrogen-bonded (cf. Gerrard and Whitbread, *J.*, 1952, 914).

## EXPERIMENTAL

Light petroleum had b. p. 40—60°, and ligroin, b. p. 90—120°.

*Interaction with Thionyl Chloride in the Presence of Pyridine.*—A standardised procedure was followed with respect to time of addition, total reaction time, concentration, and temperature.

To a solution of the alcohol (0·05 mole) and pyridine (0·05 mole) in ether (30 ml.) at −10° (or −78°) thionyl chloride (0·025 mole) in ether (15 ml.) was added dropwise (20—30 min.), with shaking. After a total time of 1 hr., the mixture was filtered. The precipitate, after thorough and rapid washing with dry ether, was kept in a vacuum-desiccator until its weight became constant, and analysed without further purification. The filtrate was concentrated to constant weight under reduced pressure at room temperature. Distillation of the residue was attempted. Purification of the sulphite in nearly every case was difficult, owing to limited thermal stability; but the essential points to establish were the fates of chlorine and sulphur and the degree of completion of the reaction. Data are recorded in Table 1, and in the following notes.

TABLE 1.

| | | | Pyridine hydrochloride | | | | | Sulphite dist'd, yield, % |
|---|---|---|---|---|---|---|---|---|
| | | | Wt., g. | Found, % | | Residue, g. | | |
| No. | Alcohol | Temp. | | Cl | $C_5H_5N$ | Found | Calc. | |
| 1 | 2-Phenylethanol | −10° | 5·50 | 30·6 | 67·8 | 7·10 | 7·25 | 89·0 |
| | | −78 | 5·60 | 30·0 | 67·5 | 7·00 | 7·25 | 85·7 |
| 2 | 3-Phenylpropanol | −10 | 5·65 | 29·8 | 67·5 | 7·92 | 7·95 | 90·0 |
| | | −78 | 5·50 | 29·2 | 66·0 | 7·35 | 7·95 | 85·0 |
| 3 | 1 : 3-Diphenylpropan-2-ol | −10 | 5·36 | 30·5 | 67·1 | 11·18 | 11·75 | — |
| | | −78 | 5·33 | 29·3 | 66·0 | 10·95 | 11·75 | — |
| 4 | 1-Phenylpropan-2-ol | −10 | 5·61 | 30·1 | 66·6 | 7·70 | 7·95 | 86·2 |
| | | −78 | 6·09 | 27·5 | 59·0 | 7·35 | 7·95 | 86·6 |
| | (in pentane) | −10 | 5·64 | 30·4 | 67·5 | 7·85 | 7·95 | 92·2 |
| 5 | 1 : 2-Diphenylethanol | −10 | 5·39 | 29·9 | 67·5 | 10·47 | 11·05 | — |
| | | −78 | 5·57 | 30·2 | 67·0 | 10·10 | 11·05 | — |
| 6 | Benzyl alcohol | −10 | 5·50 | 30·3 | 68·4 | 6·36 | 6·55 | 81·0 |
| | | −78 | 5·55 | 30·3 | 67·3 | 6·32 | 6·55 | 87·0 |
| 7 | 1-Phenylethanol | −78 | 5·60 | 29·1 | 64·5 | 6·77 | 7·25 | — |
| 8 | 1-2′-Naphthylethanol | −10 | 3·70 | 29·2 | 67·4 | — | — | — |
| | | −78 | 5·90 | 29·0 | 67·2 | 9·00 | 9·75 | — |
| 9 | Diphenylmethanol | −10 | 3·46 | 28·0 | 39·0 | — | — | — |
| | | −78 | 5·15 | 29·4 | 64·5 | — | — | — |
| | | Calc. : | 5·77 | 30·7 | 68·4 | — | — | — |

(1) Di-(2-phenylethyl) sulphite had b. p. 162—165°/0·5 mm., $n_D^{15}$ 1·5510 (Found: C, 66·7; H, 6·5; S, 10·5. Calc. for $C_{16}H_{18}O_3S$: C, 66·3; H, 6·2; S, 11·0%).

(2) Di-(3-phenylpropyl) sulphite had b. p. 185—190°/0·3 mm., $n_D^{18}$ 1·5423 (Found: $SO_2$, 19·4. Calc. for $C_{18}H_{22}O_3S$: $SO_2$, 20·1%).

(3) The reactions both at −10° and at −78° were not quite complete; a filtrate residue (Found: $SO_2$, 12·2. Calc. for $C_{30}H_{30}O_3S$: $SO_2$, 13·6%) was obtained.

(4) *Di-(1-methyl-2-phenylethyl) sulphite* had b. p. 158—160°/0·1 mm., $n_D^{21·5}$ 1·5351, $d_4^{20}$ 1·1104, $\alpha_D^{16}$ +5·00° ($l = 1$; from ROH, $\alpha_D^{16}$ −10·60°) (Found: C, 68·5; H, 7·0; S, 9·8. $C_{18}H_{22}O_3S$ requires C, 67·9; H, 6·9; S, 10·1%). Hydrolysis by steam-distillation from aqueous potassium hydroxide (20% w/v) afforded the alcohol, b. p. 96°/10 mm., $\alpha_D^{16}$ −9·92° ($l = 1$), thus showing no significant loss in rotatory power in either preparation or hydrolysis of the sulphite.

(5) No alkyl chloride was formed. *Di-(1 : 2-diphenylethyl) sulphite* had m. p. 96—99° (from ligroin) (Found: C, 76·1; H, 5·9; S, 6·45; $SO_2$, 13·6. $C_{28}H_{26}O_3S$ requires C, 76·1; H, 5·9; S, 7·25; $SO_2$, 14·4%).

(6) Dibenzyl sulphite had b. p. 152°/0·4 mm., $n_D^{25}$ 1·5590 (Found: S, 11·9. Calc. for $C_{14}H_{14}O_3S$: S, 12·2%).

(7) The special point with this alcohol is that, whereas 1-chloro-1-phenylethane was formed together with the sulphite at −10° (Gerrard, *J.*, 1944, 90), it is now shown that at −78° base hydrochloride accounted for nearly all halogen, and no alkyl chloride was detected in the filtrate residue, which was kept at 60°/1 mm. for 1 hr. (Found: $SO_2$, 20·9. Calc. for $C_{16}H_{18}O_3S$: $SO_2$, 22·1%). Dry hydrogen chloride was passed into the sulphite (5·72 g.) at −10° for 2·5 hr. From the dried ethereal extract of the mixture after treatment with water, 1-chloro-1-phenylethane (4·53 g., 82%), b. p. 69—71°/10 mm., $n_D^{17}$ 1·5277 (Found: Cl, 25·0. Calc. for $C_8H_9Cl$: Cl, 25·25%), was obtained. The same chloride (4·97 g., 85%) (Found: Cl, 25·15%) was obtained when the sulphite (6·02 g., 1 mol.) was kept with thionyl chloride (1 mol.) for 2 hr. at −10°, sulphur dioxide being evolved, and volatile matter being finally removed at

−10°/0·1 mm. (trap). Furthermore, the same chloride (6·47 g., 92%), b. p. 66—71°/10 mm. (large middle cut, b. p. 67°/9 mm.) (Found: Cl, 25·25%), was obtained when dry hydrogen chloride was passed into the alcohol (6·10 g.) (2 hr. at −10°), water treatment being given before distillation. No unchanged alcohol was detected.

(8) At −10° 1-chloro-1-2′-naphthylethane (2·90 g., 30%), b. p. 95°/0·1 mm., m. p. 62—63° (from light petroleum) (Found: Cl, 17·7. Calc. for $C_{12}H_{11}Cl$: Cl, 18·6%), and the impure alcohol (2·08 g., 24%), b. p. 83°/0·1 mm., m. p. 37—39° (Found: Cl, 3·2%), were obtained. At −78°, however, no alkyl chloride could be detected, and the viscous, golden residue was heated to 40°/0·1 mm. (Found: $SO_2$, 16·3. Calc. for $C_{24}H_{22}O_3S$: $SO_2$, 16·4%).

(9) Alkyl chloride was found both at −10° and at −78°. At −10° the precipitate (5·23 g.) was contaminated with a water-insoluble solid which, when dried, afforded diphenylmethanol (1·77 g., 19·2%), m. p. 66—67°, mixed m. p. 65—67°. From the filtrate were obtained chlorodiphenylmethane (3·55 g., 35·1%), b. p. 88—92°/0·1 mm. (Found: Cl, 16·1. Calc. for $C_{13}H_{11}Cl$: Cl, 17·5%), and bisdiphenylmethyl ether (2·12 g., 24%), b. p. 185°/0·1 mm., m. p. 108—109° (from ligroin) (Found: C, 89·2; H, 6·5. Calc. for $C_{26}H_{22}O$: C, 89·1; H, 6·3%). At −78° the precipitate (6·20 g.) contained this ether (1·05 g.), m. p. 107—109°, mixed m. p. 106—107°. The filtrate residue (Found: $SO_2$, 7·4%) afforded chlorodiphenylmethane (1·11 g., 11%), b. p. 96°/0·2 mm. (Found: Cl, 16·5%), and a tar (7·0 g.).

*Phosphorus Trichloride–Pyridine System.*—To the alcohol (0·10 mole) and pyridine (0·10 mole) in ether phosphorus trichloride (0·034 mole) in ether (10—20 ml.) was added with shaking during 15 min. After a total time of 1 hr., the precipitate was separated. The filtrate was concentrated to constant weight at 15—20°/15 mm., and distillation attempted. The tendency for the phosphite to precipitate with the pyridine hydrochloride at −78° made separation under anhydrous conditions difficult. The results are summarised in Table 2, and in the following notes.

TABLE 2.

| | | | Pyridine hydrochloride | | | Phosphite residue, g. | | |
|---|---|---|---|---|---|---|---|---|
| | | | Wt., | Found, % | | | | Dist'd |
| No. | Alcohol | Temp. | g. | Cl | $C_5H_5N$ | Found | Calc. | yield, % |
| 1 | 2-Phenylethanol | −10° | 11·57 | 29·8 | 67·2 | 13·00 | 13·13 | 80·80 |
| | | −78 | 11·96 | 28·4 | 61·4 | 12·90 | 13·13 | 86·30 |
| 2 | 3-Phenylpropanol | −10 | 11·27 | 30·8 | 68·2 | 14·65 | 14·50 | 85·4 |
| | | −78 | 12·42 | 27·4 | 59·7 | 13·90 | 14·50 | 76·0 |
| 3 | 1 : 3-Diphenylpropan-2-ol | −10 | 11·15 | 30·6 | 68·2 | 22·5 | 22·13 | — |
| 4 | 1-Phenylpropan-2-ol | −10 | 11·30 | 29·2 | 64·5 | 14·80 | 14·50 | 88·3 |
| | | −10 | 11·20 | 30·7 | 67·9 | 14·92 | 14·50 | 85·5 |
| | | −78 | 11·60 | 29·0 | 64·0 | 14·92 | 14·50 | 83·0 |
| 5 | 1 : 2-Diphenylethanol | −10 | 11·35 | 29·6 | 64·2 | 21·60 | 20·70 | D |
| | | −10 | 11·15 | 30·2 | 66·5 | 20·70 | 20·70 | — |
| 6 | Benzyl alcohol | −10 | 11·24 | 30·7 | 68·0 | 12·10 | 11·76 | — |
| | | −10 | 11·33 | 30·0 | 67·8 | 11·70 | 11·76 | 89·3 |
| | | −78 | 11·90 | 28·9 | 63·0 | 11·60 | 11·76 | 76·60 |
| 7 | 1-Phenylethanol | −10 | 11·45 | 29·0 | 64·2 | 13·05 | 13·13 | — |
| | | −78 | 11·85 | 28·4 | 64·8 | 12·60 | 13·13 | — |
| 8 | 1-2′-Naphthylethanol ... | −10 | 11·40 | 30·2 | 68·6 | 18·10 | 18·14 | — |
| 9 | Diphenylmethanol ........ | −10 | 11·40 | 30·0 | 67·0 | 19·80 | 19·30 | — |
| | | Calc.: | 11·55 | 30·7 | 68·4 | — | — | — |

(1) *Tri-2-phenylethyl phosphite* had b. p. 162—171°/0·05 mm., $n_D^{25}$ 1·5550 (Found: P, 8·1. $C_{24}H_{27}O_3P$ requires P, 7·9%). Hydrogen chloride and the phosphite (4·83 g.) at −10° afforded 1-chloro-2-phenylethane (76%), b. p. 75°/10 mm. (Found: Cl, 25·5. Calc. for $C_8H_9Cl$: Cl, 25·25%), and *di-2-phenylethyl hydrogen phosphite* (95·6%), b. p. 147°/0·05 mm., $n_D^{26}$ 1·5429 (Found: P, 10·7. $C_{16}H_{19}O_3P$ requires P, 10·7%).

(2) *Tri-3-phenylpropyl phosphite*, b. p. 195—200°/0·05 mm., $n_D^{18}$ 1·5480 (Found: P, 7·05. $C_{27}H_{33}O_3P$ requires P, 7·1%), with hydrogen chloride gave 1-chloro-3-phenylpropane (72%), b. p. 90°/10 mm. (Found: Cl, 23·1. Calc. for $C_9H_{11}Cl$: Cl, 23·0%), *di-3-phenylpropyl hydrogen phosphite* (85%), b. p. 186°/0·2 mm., $n_D^{14}$ 1·5382 (Found: P, 9·5. $C_{18}H_{23}O_3P$ requires P, 9·8%), and the phosphite (13·2%), b. p. 210°/0·1 mm., $n_D^{21}$ 1·5428. Dealkylation (one group) was more nearly complete at 15°, the yield of hydrogen phosphite then being 91%.

(3) Presumably because the removal of the third chlorine atom was perceptibly slower in this case, precipitation of base hydrochloride was incomplete (85%) after the stated time. After 3 hr. at 15° the precipitate (91·5%) increased to 98% when the volume of solution was reduced to half. After being at 15°/0·1 mm. for 2 hr., the filtrate residue weighed 22·10 g. (Calc. : 22·13 g.) (Found : P, 4·63%). In a further experiment, base hydrochloride (11·15 g., 97%) (Found: Cl, 30·6; $C_5H_5N$, 68·2%) and *tri-*(1-*benzyl-*2-*phenylethyl*) *phosphite* (22·50 g.) (Found : P, 4·71. $C_{45}H_{45}O_3P$ requires P, 4·67%) were obtained after the mixture had been at −10° for 1 hr. and 15° for 16 hr. Decomposition of the phosphite occurred at 120—180°/0·2 mm.; 1 : 3-diphenylpropene, b. p. 88°/0·01 mm., $n_{\rm D}^{19}$ 1·5933, which gave 1 : 2-dibromo-1 : 3-diphenylpropane, m. p. 109—110° (Found : C, 50·6; H, 4·0; Br, 45·1. Calc. for $C_{15}H_{14}Br_2$ : C, 50·9; H, 4·0; Br, 45·1%), was obtained.

Unusual phenomena attended the passage of hydrogen chloride into this phosphite, the unstable compound $P(OR)_3,3HCl$ being precipitated. When hydrogen chloride was passed (2 hr.) into the phosphite (6·25 g.) in ether (10 c.c.) at −10°, the white precipitate weighed 3·80 g. (immediate analysis : Cl, 12·6%), the readily ionisable chlorine decreasing in amount by the time a second specimen could be weighed (Found : Cl, 11·7; P, 4·45. Calc. for $C_{45}H_{45}O_3P,3HCl$ : Cl, 13·75; P, 4·0%). After 5 hr. the material became sticky (Found : Cl, 10·4%), and after several days crystallisation from light petroleum gave *di-*(1-*benzyl-*2-*phenylethyl*) *hydrogen phosphite* as needles, m. p. 77—79° (Found : P, 6·7. $C_{30}H_{31}O_3P$ requires P, 6·6%). The first filtrate residue after being at 70°/0·1 mm. weighed 2·70 g. (Found : Cl, 1·4; P, 4·41%).

(4) *Tri-*(1-*benzylethyl*) *phosphite* had b. p. 181°/0·05 mm., $n_{\rm D}^{19}$ 1·5364 (Found : P, 7·8. $C_{27}H_{33}O_3P$ requires P, 7·1%). The phosphite, $\alpha_{\rm D}^{21}$ +21·12° ($l = 1$) (from ROH, $\alpha_{\rm D}^{16}$ +26·72°), afforded, on hydrolysis with aqueous potassium hydroxide, the alcohol, $\alpha_{\rm D}^{16}$ +26·32°, and with hydrogen chloride gave 2-chloro-1-phenylpropane (64·5%), b. p. 80°/15 mm., $n_{\rm D}^{16}$ 1·5213, $\alpha_{\rm D}^{16}$ −22·60° ($l = 1$), and *di-*(1-*benzylethyl*) *hydrogen phosphite* (92·4%), b. p. 147°/0·02 mm. $n_{\rm D}^{20}$ 1·5291, $\alpha_{\rm D}^{20}$ +21·68° (Found : P, 9·8. $C_{18}H_{23}O_3P$ requires P, 9·8%). Passage of hydrogen chloride into this ester did not give rise to any isolable alkyl chloride, the ester being recovered.

(5) The phosphite residue was obtained as a viscous liquid (21·60 g. Calc. for $C_{42}H_{39}O_3P$ : 20·70 g.) by heating the reagents to 40—50°/0·1 mm. with automatic shaking (1 hr.). After further heating (80°/0·1 mm. for 1 hr.) the phosphite residue had $n_{\rm D}^{26}$ 1·5870 (Found : P, 4·80. Calc. for $C_{42}H_{39}O_3P$: P, 5·0%). Distillation of a portion (4·15 g.) caused vigorous decomposition at 165°/0·0005 mm. to a white solid (2·90 g.) which after two recrystallisation from ligroin gave stilbene, m. p. 122—124° (Found : C, 93·1; H, 6·8. Calc. for $C_{14}H_{12}$ : C, 93·3; H, 6·7%).

(6) The phosphite residue (11·70 g.) afforded fractions : (i) (4·93 g.), b. p. 160—175°/0·08 mm., $n_{\rm D}^{18}$ 1·5680; (ii) (5·0 g.), b. p. 185°/0·02 mm., $n_{\rm D}^{14}$ 1·5749 (Found : C, 71·1; H, 5·8. Calc. for $C_{21}H_{21}O_3P$ : C, 71·6; H, 6·0%).

(7) The phosphite residue, after being heated to 40—60°/0·10 mm. (1 hr.) with automatic shaking, had $n_{\rm D}^{21}$ 1·5440, $d_4^0$ 1·117 (Found : P, 7·82. Calc. for $C_{24}H_{27}O_3P$ : P, 7·87%). Distillation caused decomposition at 120—130°/0·05 mm., affording styrene, b. p. 33—35°/10 mm., $n_{\rm D}^{14}$ 1·5482. A rapid stream of hydrogen chloride was passed into the phosphite residue (5·60 g.) in ether (5 ml.) at −10° for 1 hr. and the excess of gas and ether removed at 15—20 mm. without heating. The product was directly distilled at 0·1 mm. into a trap at −80°. The condensate gave 1-chloro-1-phenylethane (5·60 g., 94% based on 3 groups), b. p. 69°/10 mm., $n_{\rm D}^{16}$ 1·5300 (Found : Cl, 24·5. Calc. for $C_8H_9Cl$ : Cl, 25·3%). The residue was heated to 100—150°/0·1 mm. for 1 hr. whereupon it weighed 1·25 g. (Found : P, 33·0. Calc. for $H_3O_3P$ : P, 37·8%).

(8) Even at −10° the precipitate was contaminated with phosphite. It was quickly removed from the filter, refluxed with fresh ether, and filtered off. After being dried under vacuum the precipitate was still overweight and had to be twice refluxed with ether and again filtered off. The first filtrate on concentration under reduced pressure yielded a yellow-white, semi-solid substance (8·40 g., 92·5%). Volatile matter was removed at 20°/0·4 mm. (4 hr.) with automatic shaking; the residue weighed 8·20 g. (Found : P, 6·24. Calc. for $C_{36}H_{33}O_3P$ : P, 5·70%. Calc. for $C_{24}H_{23}O_3P$ : P, 7·95%). All attempts to recrystallise the product failed. Dry hydrogen chloride was passed through a solution of the phosphite residue (2·75 g.) in ether (10 ml.) for 1 hr. at −10°. Volatile matter was removed at 10—15°/10 mm. and, after treatment with water, distillation afforded 1-chloro-1-2′-naphthylethane (2·20 g., 76·3% based on 3 groups), b. p. 82°/0·03 mm. (Found : Cl, 18·6. Calc. for $C_{12}H_{11}Cl$ : Cl, 18·6%), and a residue (0·25 g.).

(9) The phosphite residue, after 2 hr. at 20—25°/0·1 mm. (with automatic shaking), was obtained as a waxy solid (19·80 g. Calc. for $C_{39}H_{33}O_3P$ : 19·30 g.), m. p. 65—66° (Found : P, 5·21. Calc. for $C_{39}H_{33}O_3P$ : P, 5·35%). The phosphite residue (5·40 g.) was suspended in ether (15 ml.), and hydrogen chloride passed in for 1 hr. at −10°. Volatile matter was removed at 15 mm. The clear solution had separated into two layers. The lower layer of phosphorous acid was heated to 100°/0·1 mm. for 1 hr. (Wt., 0·70 g. Calc. for $H_3O_3P$ : 0·77 g.) (Found : P, 32·5. Calc. : P, 37·8%). The upper layer was redissolved in ether and washed. Chlorodiphenylmethane (5·15 g.; 91·2%, 3 groups), b. p. 88—90°/0·05 mm., $n_D^{20}$ 1·5962 (Found : Cl, 17·3. Calc. for $C_{13}H_{11}Cl$ : Cl, 17·5%), was obtained.

*Phosphorus Oxychloride, Alcohol, and Pyridine.*—The alcohol (1 mol.) was weighed into a reaction vessel designed so that the filtration could be accomplished without exposure to air. Pyridine (1·58 g., 1 mol.) in ether (10 ml.) was added, and phosphorus oxychloride (1·03 g., 0·33 mol.) in ether (10 ml.) was then added at −10° (10 min.). After 23 hr. the precipitate was separated, and the filtrate kept for a further 24 hr. and tested for further precipitation. Results are given in Table 3.

TABLE 3.

| | | Precipitate | | | | |
|---|---|---|---|---|---|---|
| Alcohol no. | Alcohol, g. | Wt., g. | Cl, %, Found | $C_5H_5N$, %, Found | 2nd Ppt., g. | Cl, %, Found |
| 1 | 2·44 | 2·28 | 31·0 | 68·2 | 0·10 | — |
| 2 | 2·72 | 2·30 | 30·4 | 67·0 | 0·10 | — |
| 3 | 4·24 | 1·60 | 30·6 | 67·5 | 0·42 | 30·0 |
| 4 | 2·72 | 1·70 | 29·8 | 66·5 | 0·41 | 30·6 |
| 5 | 3·96 | 4·40 | 14·7 | 40·5 | 0·05 | — |
| 6 | 2·16 | 3·07 | 14·2 | 36·8 | — | — |
| 8 | 3·44 | 3·02 | 14·1 | 38·4 | — | — |
| 9 | 3·68 | 3·90 | 11·9 | 26·4 | — | — |
| Calc. for $C_5H_5N,HCl$ : | | 2·31 | 30·7 | 68·4 | — | — |

Phosphorus oxychloride (0·034 mole) in ether (10 ml.) was added dropwise to a solution of the alcohol (0·10 mole) and pyridine (0·10 mole) in ether (100 ml.) at −10° (10 min.), and the mixture kept at room temperature for the time stated before filtration. The results are summarised in Table 4, and in the notes.

TABLE 4.

| | | | | Analysis of ppt., % | | | Distribution of Cl and P, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Cl | | P | |
| Alcohol no. | Time | ROH, g. | Ppt. g. | Cl | $C_5H_5N$ | P | in ppt. | in filt. | in ppt. | in filt. |
| 1 | 8 days | 12·20 | 10·88 | 30·2 | 67·6 | — | 92·7 | — | — | 100 |
| 2 | 9 ,, | 13·6 | 10·75 | 30·4 | 68·0 | — | 92·2 | — | — | 100 |
| 3 | 24 ,, | 21·2 | 10·44 | 30·5 | 68·2 | — | 90·0 | 7·0 | — | 100 |
| 4 | 21 ,, | 13·6 | 10·85 | 30·2 | 67·5 | — | 92·5 | — | — | 100 |
| 5 | 18 hr. | 19·8 | 14·02 | 19·4 | 47·5 | 7·3 | 75·2 | 23·2 | 97·5 | 2·3 |
| 6 | 16 ,, | 10·8 | 14·82 | 15·6 | 37·2 | 6·5 | 64·0 | 26·0 | 92·0 | 7·6 |
| 7 | 16 ,, | 12·2 | 12·47 | 16·6 | 44·6 | 7·4 | 57·3 | — | 88·0 | 12·0 |
| 8 | 18 ,, | 17·2 | 14·05 | 16·8 | 38·1 | 7·5 | 65·4 | 33·9 | 100 | — |
| 9 | 18 ,, | 18·4 | 19·00 | 15·1 | 30·5 | 5·5 | 79·4 | 20·4 | 100 | — |
| Calc. for $C_5H_5N,HCl$ : | | | 11·55 | 30·7 | 68·4 | 0·0 | — | — | — | — |

(1) Distillation of the filtrate gave *tri-(2-phenylethyl) phosphate* (77% yield), b. p. 192—194°/0·005 mm., $n_D^{24}$ 1·5498, $d_4^{20}$ 1·148 (Found : P, 7·65. $C_{24}H_{27}O_4P$ requires P, 7·56%), and a viscous residue (1·38 g.).

(2) *Tri-(3-phenylpropyl) phosphate* (62%), b. p. 220°/0·001 mm., $n_D^{24}$ 1·5404, $d_4^{20}$ 1·103 (Found : P, 6·72. $C_{27}H_{33}O_4P$ requires P, 6·85%), and a residue (1·76 g.) were obtained.

(3) The washed and dried filtrate residue (85°/0·1 mm.; 1 hr.) weighed 11·25 g. (Calc. for phosphate : 11·33 g.) (Found : Cl, 2·2; P, 4·74. Calc. for $C_{30}H_{30}O_3ClP$ : Cl, 7·0; P, 6·2. Calc. for $C_{45}H_{45}O_4P$ : P, 4·6%). The aqueous washings contained chloride ion (0·016 g.) and pyridine (0·115 g.). In this example, approach to the final precipitation of all chlorine and pyridine was very slow.

(4) The primary filtrate (ppt., 10·45 g.) deposited hydrochloride (0·40 g.) during 6 days at 15° and, on being concentrated, gave more precipitate (0·4 g.) (Found : Cl, 30·5%). The

filtrate residue (80°/0·1 mm.; 1 hr.) weighed 14·85 g. (Calc.: 15·05 g.). After being washed and dried, a viscous residue, $[\alpha]_D^{25}$ $-21{\cdot}60°$ (in $CHCl_3$) (Found: P, 8·0. Calc. for $C_{27}H_{33}O_4P$: P, 6·85%), was obtained. The phosphate (4·40 g.) was heated with aqueous ethanolic potassium hydroxide (50 c.c.; 20%) at 90° for 31 hr., and steamed-distilled (3 hr.) to afford the alcohol (0·80 g.), b. p. 112—114°/23 mm., $n_D^{28}$ 1·5200, $\alpha_D^{32}$ $+21{\cdot}60°$ ($l = 1$) (the original alcohol had $\alpha_D^{16}$ $+26{\cdot}72°$). The extreme slowness of the hydrolysis and the steric course are in accord with similar observations by Gerrard, Green, and Nutkins (*J.*, 1952, 4076). The phosphate decomposed at 120°/0·5 mm.

(5) The washed and dried filtrate residue, b. p. 60°/0·1 mm., weighed 17·7 g. (Found: Cl, 4·75; P, 0·14%). When the primary reaction mixture (half quantities) was stored for 11 days at room temperature, the precipitate weighed 6·27 g. (Found: Cl, 17·8; P, 6·7; $C_5H_5N$, 49·0%) and the filtrate residue (60°/0·1 mm.; 1 hr.) weighed 9·60 g. (Found: Cl, 4·00%; P, nil).

(6) The filtrate was directly distilled; impure benzyl chloride (fractionation tedious) (3·30 g.), b. p. 79—81°/23 mm. [large middle cut, b. p. 71—72°/19 mm., $n_D^{19}$ 1·5384 (Found: Cl, 27·7. Calc. for $C_7H_7Cl$: Cl, 28·0%)], benzyl alcohol (1·55 g.), b. p. 108—109°/23 mm., and a residue (2·85 g.) (Found: P, 2·81%) were obtained.

(7) From the filtrate, volatile matter was removed, first at 15°/20 mm. (residue 12·0 g.), then at 20—80°/0·05 mm. (trap at −80°); the residue (Found: P, 8·52. Calc. for $C_{24}H_{27}O_4P$: P, 7·56%) weighed 1·50 g. The condensate (trap, 10·20 g.) had a wide boiling range and comprised pyridine, 1-chloro-1-phenylethane, and 1-phenylethanol. The speed of the reaction is indicated by the fact that the alcohol (6·1 g.) gave the precipitate (6·08 g.) (Found: Cl, 17·5; P, 8·28; $C_5H_5N$, 46·3%) when the oxychloride was added very slowly (20 min.) and the mixture allowed to warm to 25° (1 hr.).

(8) The filtrate residue (14·5 g.) (80°/0·1 mm.; 1 hr.) gave a solid (10·0 g.), b. p. 65—80°/0·001—0·01 mm., and a gummy residue (4·40 g.). The solid gave 1-chloro-1-2′-naphthylethane (3·55 g.), b. p. 84—88°/0·1 mm., m. p. 65—66° (from light petroleum (Found: Cl, 18·6. Calc. for $C_{12}H_{11}Cl$: Cl, 18·6%), a liquid (3·40 g.), b. p. 94—96°/0·1 mm., m. p. 52—53° (from light petroleum) (Found: Cl, 9·7%), which appeared to be a mixture of the alkyl chloride and 2-naphthylethylene, and a residue of polymeric gum (2·20 g.).

(9) The filtrate residue (12·1 g.) (Found: Cl, 6·1%) gave a fraction (4·70 g.), b. p. 75—78°/0·002 mm., further resolved into impure alkyl chloride, b. p. 86—88°/0·05 mm. (Found: Cl, 15·2%), and diphenylmethyl chloride, b. p. 88—92°/0·05 mm., $n_D^{20}$ 1·5962 (Found: Cl, 17·4. Calc. for $C_{13}H_{11}Cl$: Cl, 17·5%). A viscous residue (6·30 g.) afforded bisdiphenylmethyl ether (5·10 g., 29·1%), b. p. 170°/0·03 mm., m. p. 107—108°, mixed m. p. 107—108°.

*Materials.*—All reagents were carefully purified before use; solvents were dried. 1-Phenylpropan-2-ol was obtained by reduction of the ketone with sodium and ethanol (Pickard and Kenyon, *J.*, 1911, **99**, 58; 1913, **103**, 1943) and was resolved by the method of these workers (*J.*, 1914, **107**, 1115). 1 : 3-Diphenylpropan-2-ol was similarly obtained from the ketone, and 1-2′-naphthylethanol was obtained from the ketone by reduction with aluminium *iso*propoxide (Arcus and Kenyon, *J.*, 1938, 698). 1 : 2-Diphenylethanol was obtained as described by Gerrard and Kenyon (*J.*, 1928, 2564).

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