29. *Promoters for the Dropwise Condensation of Steam. Part III.*[1] *Preparation of Silicon and Phosphorus Compounds.*

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We have prepared a number of thiosilicates and phosphorothioates of high molecular weight as possible promoters of dropwise condensation.

IN Parts I and II [1] we described the preparation of a number of compounds in which sulphur-containing groups are associated with hydrocarbon residues, for trial as promoters for the dropwise condensation of steam. Here we describe the preparation of a series of analogous compounds in which the surface-active group is a thiosilicate or phosphorothioate residue.

Although the compounds were purified by fractional distillation or recrystallisation, the crude products were very pure. Thus, three fractions of dodecyltrisdodecylthiosilane and the undistilled product were analysed, with no apparent significant increase in purity due to distillation. The original chlorosilanes were the purest obtainable (98%) from the Midland Silicone Company.

The fact that very pure products could be obtained without fractional distillation (provided that the starting materials were of high purity) was very useful in the preparation of thiophosphorus compounds. Many of these were liquids and could not be distilled owing to decomposition. Extra precaution was taken to ensure the complete absence of unchanged thiol in the product.

The dodecylthio-compounds prepared from phosphorus trichloride, phosphorus thiochloride, phosphorus oxychloride, and thiopyrophosphoryl tetrabromide were prepared by treatment of the halides with pure sodium dodecyl sulphide, as in the case of the silicon compounds. An excess (10%) of the sulphide was used. The products could not be purified by fractional distillation, but all volatile impurities were removed at 55°/10^{-4} mm. In the case of tridodecyl phosphorotetrathioate, a trace of tridodecyl phosphorotrithioite was added to the phosphorus thiochloride in order to catalyse the reaction. This was a slight modification of Gottlieb's method [2] where a trace of phosphorus trichloride is added to achieve the same result, *viz.*:

$$PSCl_3 + P(SC_{12}H_{25})_3 = PS(S{\cdot}C_{12}H_{25})_3 + PCl_3$$

OO-Dioctadecyl hydrogen and *OOS*-trioctadecyl phosphorodithioate were prepared by the reaction of 4 and 6 mols. respectively of octadecanol with one of phosphorus pentasulphide. Bisdioctadecyloxyphosphinothioyl sulphide, $(RO)_2P(S){\cdot}S{\cdot}P(S)(OR)_2$, was prepared from octadecanol and thiopyrophosphoryl tetrabromide, $(Br_2PS)_2S$.

The mercuri-iodides of some of the thiophosphorus compounds were prepared by heating the compounds in an ethereal solution of the reagent.

EXPERIMENTAL

Tri(dodecylthio)methylsilane.—A suspension of sodium dodecyl sulphide in ether was prepared by heating under reflux for 6 hr. a mixture of dodecanethiol (15·1 g.) and clean sodium

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[1] Parts I and II, Blackman and Dewar, preceding papers.
[2] Gottlieb, *J. Amer. Chem. Soc.*, 1932, **54**, 1932.

sand (1·73 g.). Trichloromethylsilane (3·4 g.) in dry ether (20 ml.) was added slowly to the stirred suspension. The mixture was stirred for a further 2 hr., then heated on a water-bath for 10 min. The cooled mixture was filtered through a sintered-glass funnel (No. 2 grade) to remove the excess of sulphide, and then the filtrate was washed with several small amounts of water to remove sodium chloride. The ethereal solution was dried (Na_2SO_4) and the *silane* (12·4 g.) was isolated by distillation as a white waxy solid, b. p. 220—240°/10^{-4} mm., m. p. 33—34° (from acetone) (Found: C, 68·9; H, 12·3; S, 14·7. $C_{37}H_{78}S_3Si$ requires C, 68·6; H, 12·2; S, 14·9%).

Di(dodecylthio)dimethylsilane.—Dichlorodimethylsilane (4·7 g.) reacted likewise with sodium dodecyl sulphide [from dodecanethiol (15·8 g.) and sodium sand (1·8 g.)] in ether, to give the *silane* (13·5 g.) as a white microcrystalline solid, b. p. 210°/10^{-2} mm., m. p. 29·5—30° (from acetone) (Found: C, 68·0; H, 12·5; S, 13·6. $C_{26}H_{56}S_2Si$ requires C, 67·7; H, 12·3; S, 13·9%).

(Dodecylthio)trimethylsilane.—Trimethylchlorosilane (7·4 g.) with sodium dodecyl sulphide [from dodecanethiol (14·6 g.) and sodium sand (1·65 g.)] in ether gave the *silane* (14·9 g.), b. p. 210—215°/0·1 mm., n_D^{20} 1·4750 (Found: C, 65·9; H, 12·7; S, 11·5. $C_{15}H_{34}SSi$ requires C, 65·6; H, 12·5; S, 11·7%).

Tetrakisdodecylthiosilane.—Silicon tetrachloride (7·8 g.) in dry ether was added to a stirred suspension of sodium dodecyl sulphide [from dodecanethiol (40 g.) and sodium sand (4·6 g.)] in ether. The mixture was kept at room temperature for one day, and then warmed on a water-bath for 8 hr. Water (100 ml.) was added to the cool mixture, and the ether layer was separated and dried (Na_2SO_4). The ether was removed by distillation and the residue was recrystallised from light petroleum, to give the *silane* (29 g.) in white plates, m. p. 43—44° (Found: C, 68·9; H, 12·2; S, 15·4. $C_{48}H_{100}S_4Si$ requires C, 69·1; H, 12·1; S, 15·4%).

Dodecyltrisethylthiosilane.—Dodecyltrichlorosilane (15 g.) in dry ether was added to a stirred suspension of sodium ethyl sulphide [from ethanethiol (10 g.) and sodium sand (3·7 g.)] in ether. The mixture was stirred for a further 8 hr. and then kept at room temperature for a day. The suspended solids were removed and the *silane* (14·5 g.) was isolated by distillation as a pale straw-coloured liquid, b. p. 188°/2·5 mm., n_D^{20} 1·5133 (Found: C, 57·0; H, 10·7; S, 24·9. $C_{18}H_{40}S_3Si$ requires C, 56·8; H, 10·6; S, 25·3%).

Dodecyltrisdodecylthiosilane.—Dodecyltrichlorosilane (30·4 g.) in ether was added to a stirred suspension of sodium dodecyl sulphide [from dodecanethiol (68 g.) and sodium sand (7·55 g.)] in ether. The mixture was stirred for 6 hr. and kept at room temperature overnight. It was then heated on a water-bath for 2 hr. The cooled mixture was filtered, and the filtrate was washed with several small portions of water. The ether solution was dried (Na_2SO_4) and the *silane* (57 g.) was isolated as a pale straw-coloured oil, b. p. 130—140°/10^{-3} mm., n_D^{20} 1·4825, m. p. *ca.* 12—14° (Found: C, 72·1; H, 12·5; S, 11·8. $C_{48}H_{100}S_3Si$ requires C, 71·9; H, 12·6; S, 12·0%).

Phosphorus Thiochloride.—This was prepared by Booth and Cassidy's method.[3]

Thiopyrophosphoryl Tetrabromide.—This was prepared as a yellow oil, b. p. 50—52°/0·5 mm., by a known method.[4]

Tridodecyl Phosphorotrithioite.—Phosphorus trichloride (8·2 g.) in dry ether was added to a stirred suspension of sodium dodecyl sulphide [from dodecanethiol (40 g.) and sodium sand (4·54 g.)] in ether. The mixture was stirred for a further 2 hr. and then warmed on a water-bath for 10 min., filtered, and washed with several small amounts of water. The ether solution was dried (Na_2SO_4) and evaporated. The product was warmed at 55°/10^{-4} mm. The *product* (23 g.) crystallised from acetone in white plates, m. p. 29·5—30° (Found: C, 68·0; H, 12·0; S, 15·5; P, 4·5. $C_{36}H_{75}S_3P$ requires C, 68·1; H, 11·9; S, 15·1; P, 4·9%).

A solution was prepared by heating under reflux mercuric iodide (5 g.) and ether (100 ml.) for 20 min. About 80 ml. of this were added to a warm ether solution of tridodecyl phosphorotrithioite (5 g.) and the mixture was heated for 20 min., then cooled at 0° for 1 hr. The pale yellow *mercuri-iodide* that separated was collected and washed with ether; it had m. p. 162—163° (Found: I, 23·4; S, 8·4. $C_{36}H_{75}S_3P,HgI_2$ requires I, 23·3; S, 8·8%). Other mercuri-iodides were prepared in the same way.

SSS-*Tridodecyl Phosphorotrithioate.*—Phosphorus oxychloride (5 g.) reacted likewise with sodium dodecyl sulphide [from dodecanethiol (23 g.) and sodium sand (2·62 g.)] in ether, to give the *ester* (11·9 g.) which, crystallised from acetone, had m. p. 26—27° (Found: C, 66·7; H,

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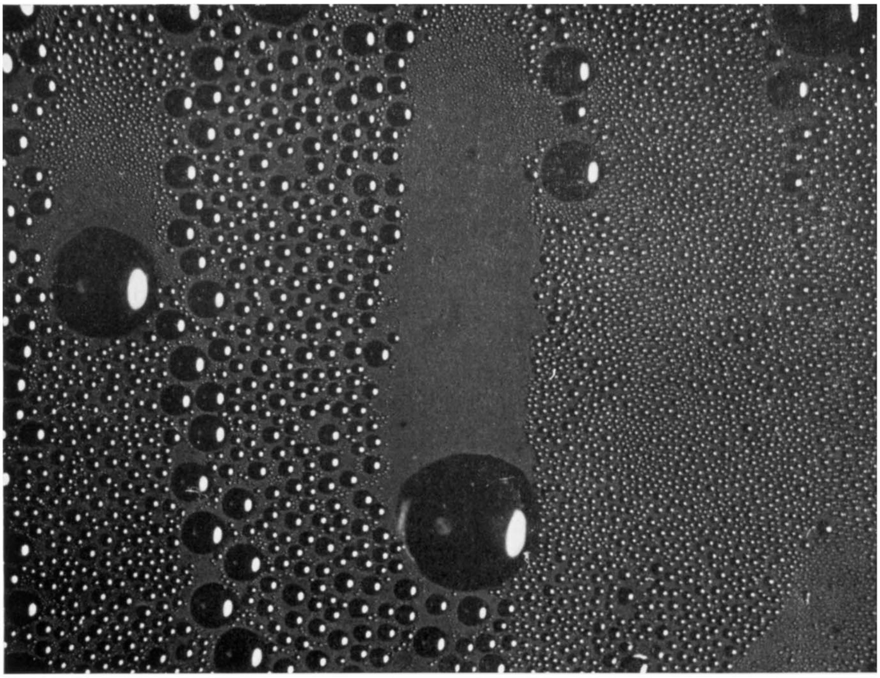
[3] Booth and Cassidy, *J. Amer. Chem. Soc.*, 1940, **62**, 2369.

[4] Mellor, "Inorganic and Theoretical Chemistry," Longmans, London, 1928, Vol. VIII, p. 1077.



" Ideal " dropwise condensation.

11·9; S, 14·5; P, 4·4. $C_{36}H_{75}OS_3P$ requires C, 66·4; H, 11·6; S, 14·8; P, 4·8%). *The mercuri-iodide* had m. p. 162—164° (Found: I, 23·3; S, 8·3. $C_{36}H_{75}OS_3P,HgI_2$ requires I, 22·9; S, 8·7%).

Di(bisdodecylthiophosphinothioyl) Sulphide, $(RS)_2P(S){\cdot}S{\cdot}P(S)(SR)_2$.—Thiopyrophosphoryl tetrabromide (7 g.) with sodium dodecyl sulphide [from dodecanethiol (10·5 g.) and sodium sand (3·08 g.)] in ether gave this *compound* (25 g.), n_D^{20} 1·5020, f. p. *ca.* 5—8° (Found: C, 59·6; H, 10·3; S, 23·0; P, 6·0. $C_{48}H_{100}S_7P_2$ requires C, 59·8; H, 10·5; S, 23·2; P, 6·4%). The *dimercuri-iodide* had m. p. 162—163° (Found: I, 27·3; S, 11·7. $C_{48}H_{100}S_7P_2,2HgI_2$ requires I, 27·1; S, 12·0%).

Tridodecyl Phosphorotetrathioate.—Phosphorus thiochloride (9·0 g.) was added to a stirred ether suspension of sodium dodecyl sulphide [from dodecanethiol (27 g.) and sodium sand (3·08 g.)] to which had been added a trace of tridodecyl phosphorotrithioite (0·01 g.). The *product* (25 g.) was obtained as above as a colourless oil, n_D^{20} 1·5051, f. p. *ca.* 15° (Found: C, 65·0; H, 11·5; S, 18·9; P, 4·3. $C_{36}H_{75}S_4P$ requires C, 64·8; H, 11·4; S, 19·2; P, 4·6%). The *mercuri-iodide* had m. p. 162—163° (Found: I, 22·5; S, 11·0. $C_{36}H_{75}S_4P,HgI_2$ requires I, 22·6; S, 11·4%).

Bisdioctadecyloxyphosphinothioyl Sulphide.—Thiopyrophosphoryl tetrabromide (19·1 g.) and octadecanol (43·2 g.) were heated under reflux in toluene (200 ml.) and pyridine (12·7 g.) for 20 hr. The cool mixture was filtered and the toluene removed under reduced pressure. The solid residue was boiled in acetone with charcoal for 30 min. and the mixture was filtered while hot. The *product* crystallised at 0° (33 g.) and recrystallised from acetone as white plates, m. p. 34—34·5° (Found: C, 70·0; H, 12·1; S, 7·9; P, 4·5. $C_{72}H_{148}O_4S_3P_2$ requires C, 69·9; H, 12·1; S, 7·8; P, 4·9%). The *dimercuri-iodide* had m. p. 150—152° (Found: I, 23·7; S, 4·7. $C_{72}H_{148}O_4S_3P_2,2HgI_2$ requires I, 23·7; S, 4·5%).

OO-*Dioctadecyl Hydrogen Phosphorodithioate.*—Octadecanol (45 g.) and phosphorus pentasulphide (9·25 g.) were heated under reflux in toluene (130 ml.) for 22 hr. The *product* (39 g.), which was isolated as above, crystallised from acetone in white plates, m. p. 54—54·5° (Found: C, 67·8; H, 12·0; S, 9·6; P, 4·6. $C_{36}H_{75}O_2S_2P$ requires C, 68·1; H, 11·9; S, 10·1; P, 4·9%). A mercuri-iodide could not be prepared.

OOS-*Trioctadecyl Phosphorodithioate.*—Octadecanol (32·4 g.) and phosphorus pentasulphide (4·84 g.) reacted likewise in toluene (150 ml.) to give the *compound* (24 g.) which crystallised from acetone in white plates, m. p. 59—60° (Found: C, 72·8; H, 12·5; S, 7·0; P, 3·4. $C_{54}H_{111}O_2S_2P$ requires C, 73·1; H, 12·6; S, 7·2; P, 3·5%). A mercuri-iodide salt could not be prepared.

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[*Received, June* 18*th*, 1956.]