188. *Organic Sulphur Compounds. Part XXXII. The Action of Triphenylphosphine on Organic Disulphides.*

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Tables I and II illustrate the different behaviour of certain disulphides towards triphenylphosphine. Diphenyl disulphide forms with triphenylphosphine an addition product which is easily hydrolysed. Table III illustrates the similarity between some reactions of disulphides and of halogens.

WHEREAS the disulphides listed in Table I are stable towards triphenylphosphine when heated in benzene solution, those listed in Table II undergo reaction affording the corresponding monosulphides and triphenylphosphine sulphide :

$$PPh_3\ (I.) + R{\cdot}S{\cdot}SR \longrightarrow PPh_3(SR)_2\ (II.)\dagger \longrightarrow PPh_3S\ (III.) + R{\cdot}SR$$

According to Pauling (" Fortschritte der Chemie Organischer Naturstoffe ", Vol. 3, p. 207, Vienna, 1939), phosphorus can form five covalent bonds. It is noteworthy that (III) is formed from (I) and (VII) even at 30° in carbon tetrachloride.

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* This experiment was carried out by (Miss) Askar.

† This is to be regarded as including the form $\overset{+}{P}Ph_3{\cdot}SR(SR)^-$.

Diphenyl disulphide and (I) in boiling benzene form a product which when treated with water yields triphenylphosphine oxide and phenylthiol :

$$\mathrm{PPh_3 + Ph{\cdot}S{\cdot}SPh\ (IV.) \longrightarrow PPh_3(SPh)_2 \xrightarrow{H_2O} PPh_3O\ (V.) + 2Ph{\cdot}SH}$$

It seems that the reaction takes place even at room temperature, for if a benzene solution of triphenylphosphine containing diphenyl disulphide is shaken with water, the latter turns acid.

The stability of the disulphides listed in Table I towards triphenylphosphine in boiling benzene may be due to the fact that they do not form free radicals in boiling benzene : $\mathrm{R{\cdot}S{\cdot}SR \rightleftarrows 2RS{\cdot}}$. It is possible that the formation of (II) proceeds by the action of (I) on free radicals and not on undissociated disulphides (cf. Part XXXI, preceding paper).

In boiling benzene (VIII) and (IX) do not form the equilibrium $\mathrm{R{\cdot}S{\cdot}SR \rightleftarrows S + R{\cdot}SR}$. This is proved by the fact that no phenyl *iso*thiocyanate is formed when the heating is carried out in the presence of phenyl *iso*cyanide; (III) and the monosulphide are therefore not formed from (I) and the disulphide in boiling benzene according to $\mathrm{R{\cdot}S{\cdot}SR \rightleftarrows R{\cdot}SR + S \xrightarrow{PPh_3} (III)}$.

TABLE I.

Disulphides stable towards triphenylphosphine in boiling benzene : Diethyl (VI), dibenzyl, *oo′*-dinitrodiphenyl, *pp′*-dinitrodiphenyl, dibenzhydryl, dibenzthiazólyl, di-9-fluorenyl, diantipyryl.

TABLE II.

Disulphides which react with triphenylphosphine in boiling benzene : Bisthio-α-naphthoyl $(\alpha\text{-}\mathrm{C_{10}H_7{\cdot}CS{\cdot}S{\cdot})_2}$ (VII), dibenzoyl (VIII), tetramethylthiuram, $\mathrm{(NMe_2{\cdot}CS{\cdot}S{\cdot})_2}$ (IX), bis-*p*-dimethylaniline $\mathrm{(NMe_2{\cdot}C_6H_4{\cdot}S{\cdot})_2}$ (X).

TABLE III.

Similarities in the action of certain organic disulphides with those of free halogens :

$$\mathrm{Ph{\cdot}S{\cdot}SPh\ (or\ I_2) + (Ar_3C{\cdot})_2 \longrightarrow 2CAr_3{\cdot}SPh\ (or\ 2CAr_3I)}\ ^{1,2}$$

$$\mathrm{Ph{\cdot}S{\cdot}SPh\ (or\ I_2) + 2Ar{\cdot}\dot{C}(ONa)Ar' \longrightarrow 2Ar{\cdot}COAr' + 2SPhNa\ (or\ 2NaI)}\ ^{3,4}$$

$$[\alpha\text{-}\mathrm{C_{10}H_7{\cdot}CS{\cdot}S{\cdot}]_2\ (or\ Br_2) + 2Ag \longrightarrow} \alpha\text{-}\mathrm{C_{10}H_7{\cdot}CS{\cdot}SAg\ (or\ 2AgBr)}\ ^{3}$$

$$\mathrm{Ph{\cdot}S{\cdot}SPh\ (or\ Br_2) + Ar_2CN_2 \longrightarrow N_2 + CAr_2(SPh)_2\ (or\ CAr_2Br_2)}\ ^{5,6}$$

$$\mathrm{Ph{\cdot}S{\cdot}SPh\ (or\ Cl_2) + PPh_3 \longrightarrow PPh_3(SPh)_2\ (or\ PPh_3Cl_2)}\ ^{7}$$

[1] Schönberg *et al.*, *Ber.*, 1933, **66**, 242. [2] Gomberg, *Ber.*, 1900, **33**, 3158. [3] Schönberg *et al.*, *Ber.*, 1933, **66**, 1932. [4] Schlenk and Weickel, *Ber.*, 1911, **44**, 1185. [5] Staudinger and Gaule, *Ber.*, 1916, **49**, 1956. [6] Schönberg *et al.*, *Ber.*, 1929, **62**, 440; 1930, **63**, 3102. [7] Cf. Schönberg, *Ber.*, 1935, **68**, 163.

EXPERIMENTAL.

The benzene used was thiophen-free and dried over metallic sodium. When the solutions of the reactants were heated under reflux, the condenser was fitted with a calcium chloride tube and the reagents were protected from direct sunlight. All reaction products were identified by m. p. and mixed m. p. determinations.

Purification of Triphenylphosphine.—A solution of triphenylphosphine (10 g.) in benzene (50 c.c.) was shaken twice with concentrated hydrochloric acid (50 c.c.). The acid layer was separated and distilled water was added until further addition no longer produced a deposit. The mixture was kept for several hours in the dark in a closed vessel, then filtered, and the residue was washed until the washing water was neutral to litmus. Triphenylphosphine was dried in a vacuum over potassium hydroxide and then over phosphoric oxide.

Reaction of Disulphides listed in Table II with Triphenylphosphine.—(*a*) The phosphine (1 mol., 2·62 g.) and (IX) (1 mol.) in benzene (30 c.c.) were heated under reflux for 8 hours. The solution was then allowed to cool, and the benzene driven off in a vacuum. The residue consisted of almost colourless and of yellow crystals. It was powdered and boiled for 15 minutes with distilled water (200 c.c.); the yellow solution was filtered while hot, and on cooling, the filtrate deposited yellow crystals which, recrystallised from dilute alcohol, were proved to be tetramethylthiuram monosulphide (2·1 g.). The triphenylphosphine sulphide (III) did not dissolve in the water and was obtained in nearly theoretical yield.

(*b*) Similarly, (VIII) (2·5 g.) and (I) (2·39 g.) in benzene (50 c.c.) yielded after 12 hours (III) (2·3 g.) and dibenzoyl sulphide (1 g.); also (I) (1 mol., 2·1 g.) and (X) (1 mol.) in benzene (50 c.c.) yielded after 10 hours (III) (1·2 g.) and bis-*p*-dimethylaniline sulphide, $\mathrm{(NMe_2{\cdot}C_6H_4)_2S}$ (1·2 g.).

(*c*) The phosphine (I) (1 mol., 1·31 g.) and (VII) 1 mol.) in carbon tetrachloride (75 c.c.) were kept for 8 days in a closed vessel at about 30°. The solvent was distilled off in a vacuum, and the residue extracted with light petroleum. The remainder was crystallised from carbon tetrachloride, giving triphenylphosphine sulphide (1·10 g.).

Triphenylphosphine and Diphenyl Disulphide.—(*a*) The phosphine (1 mol., 2·4 g.) and the disulphide (1 mol.) in benzene (80 c.c.) were heated under reflux for 14 hours. The solution was then allowed to cool and extracted with 8% sodium hydroxide solution (20 c.c.) for 15 minutes in a separating funnel.

The alkaline aqueous layer was separated, washed with benzene (10 c.c.), and then separated again. Benzoyl chloride (2 c.c.) was added, and the mixture shaken vigorously in a closed vessel. An oil which separated out was isolated and on standing for 3 days it crystallised; the solid was filtered off, washed thoroughly with distilled water, dried, and recrystallised from alcohol. Colourless crystals, m. p. 56°, were obtained and proved to be phenyl thiobenzoate (0·64 g.). The benzene layer was washed with distilled water, dried (Na_2SO_4), filtered, and the benzene driven off; the remaining oil solidified on standing. This solid was heated at 100° for about 30 minutes to dehydrate the hydrate of triphenylphosphine oxide and then crystallised twice from light petroleum (b. p. 80—100°); the oxide (1 g.) separated out.

(*b*) Triphenylphosphine (1 mol., 2·62 g.), diphenyl disulphide (2·18 g.), benzene (35 c.c.), and distilled water (20 c.c.) were heated under reflux for 14 hours, then allowed to cool; the aqueous layer was separated from the benzene layer, which was shaken with concentrated aqueous ammonia, the extract being added to the aqueous layer, which was then filtered and allowed to react with the oxygen of the air, the disulphide (0·55 g.) being recovered. The remaining benzene layer was evaporated to dryness. A brown oil was obtained which solidified on standing and from which triphenylphosphine oxide (1·4 g.) was obtained and identified as above.

(*c*) In one of three similar flasks, each fitted with a stopper, were placed benzene (30 c.c.), triphenylphosphine (1 mol., 2·6 g.), diphenyl disulphide (1 mol.), and distilled water (95 c.c.), previously boiled to free it from carbon dioxide; after one hour's shaking in the dark, the aqueous layer was acid to litmus. At the same time two parallel experiments were done exactly as above, one without the phosphine and the other without the disulphide. In both cases the aqueous layer was neutral to litmus before and after one hour's shaking.

Inactive Disulphides.—The lack of reaction between these disulphides (Table I) and triphenylphosphine was investigated by 10 hours' boiling in benzene solution; in the case of (VI) the experiment was performed at about 98° in a sealed tube.

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