(~7%) and B (~4.5%) were the remaining components of the distillate.

The second fraction was found to contain only 13% of the desired sulfoxylate ester XIV along with some sulfite and several unidentified nonvolatile components. Surprisingly, both volatile A (12%) and B (15%) were present in greater concentration than in the first distillation cut.

Isolation of pure sulfoxylate XIV involved fractional distillation of the 40.8 g. of the first-cut distillate to give 15 g., b.p. 30–35° (0.2 mm.), of about 90% purity. This material, on subsequent refractionation, gave 3.0 g. of essentially pure XIV, b.p. 31.5–32° (0.25 mm.), n^{25}_{D} 1.4692.

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.50; H, 9.15; S, 18.19. Found: C, 54.14; H, 9.10; S, 17.80.

The pure material appeared to be quite unstable; viscosity and index of refraction changed appreciably after only 1 week at −5°. On the basis of g.l.c. analysis the total yield of XIV was roughly 29%.

Isolation of 2,2,4,4-Tetramethyl-3-thionotetrahydrofuran (V).—During the various distillations required to isolate the sulfoxylate XIV from higher boiling by-products, it was observed by g.l.c. that two volatile materials A and B appeared to arise as a result of decomposition attending distillation of the more crude fractions. These materials were concentrated to some extent in the Dry Ice traps of the vacuum system. No attempt was made to isolate and identify[13] the volatile A component, but volatile B was readily obtained as a pink solid in the cold-trap system. Approximately 1.5 g. of this material (~70% purity) was fractionated by preparative g.l.c. affording 0.5 g. of pink crystals, m.p. 31–32°, $\lambda_{\max}^{\text{alc}}$ 233 mμ (ε 4325). The infrared spectrum showed no carbonyl or hydroxyl bands. Bands in the 6–13-μ region were 6.85 (m), 7.30 (w), 7.36 (m), 7.84 (m), 8.21 (m), 8.5 (w), 8.67 (2), 8.85 (s), 9.64 (vs), 10.39 (w), 10.71 (vw), 11.11 (s), and 12.45 (m) μ. The very simple p.m.r. spectrum contained three unsplit resonances at δ = 1.21, 1.33, and 3.87 p.p.m. in a 3:3:1 ratio corresponding to two pairs of methyl groups and a methylene group. Structure XV was assigned on this basis.

Anal. Calcd. for $C_8H_{14}OS$: C, 60.71; H, 8.92; S, 20.23; mol. wt., 158. Found: C, 60.40; H, 8.90; S, 20.13; mol. wt., 158 (mass spectroscopy).

Desulfurization of 2,2,4,4-Tetramethyl-3-thionotetrahydrofuran (XV).—To a slurry of 3.0 g. of Raney nickel in 6 ml. of pentane was added 180 mg. of XV. An immediate discharge of the pink color was observed on mixing. After 20 min., the nickel was removed by centrifugation. Solvent was removed by careful fractionation leaving 120 mg. of a colorless oil. G.l.c. indicated that this mixture contained ~60% of one component. Approximately 50 mg. of the pure compound was collected by g.l.c. Infrared and p.m.r. spectra were identical with those of authentic 2,2,4,4-tetramethyltetrahydrofuran prepared as described below.

2,2,4,4-Tetramethyltetrahydrofuran (XVI).—The method used was essentially that described by Franke[8]; the yield of XVI was, however, relatively low. A solution of 2,2,4-trimethyl-1,3-pentanediol (XIII) in 250 ml. of 10% (by volume) sulfuric acid solution was steam distilled very slowly for 3 hr. A clear oil (6 g.) with a camphor-like odor steam distilled from the reaction. This was taken up in ether and washed with water and the solution was dried. Removal of ether and distillation of the residue gave 1.5 g. of colorless oil, b.p. 118–126°.[14] G.l.c. showed this material to be ~70% XVI. Both infrared and p.m.r. spectra of the pure ether, collected from the g.l.c. column, were compatible with XVI. The p.m.r. spectrum showed two pairs of uncoupled methyl resonances at δ = 1.08 and 1.20 p.p.m. and two unsplit methylene resonances at δ = 1.53 and 3.42 p.p.m.

---

(13) Subsequent findings suggested that volatile A was probably 2,2,4,4-tetramethyltetahydrofuran (XVI), but this was not established.

(14) Franke[8] gives b.p. 120–122°.

Aralkyl Hydrodisulfides.[1] III. The Reaction with Tertiary Phosphines

JITSUO TSURUGI, TAKESHIGE NAKABAYASHI, AND TETSUO ISHIHARA[2]

Department of Chemistry, Radiation Center of Osaka Prefecture, Sakai City, Osaka, Japan

Received September 15, 1964

Triphenylmethyl hydrodisulfide, $(C_6H_5)_3CSSH$, is attacked on the sulfhydryl sulfur atom by tertiary phosphines (triphenyl- or triethylphosphine) and gives the phosphine sulfide and thiol in a manner similar to that reported for hydroperoxides. Benzhydryl or benzyl hydrodisulfide is attacked by the phosphine both on the sulfhydryl and sulfenyl sulfur atoms, in contrast to the results for hydroperoxides. Nucleophilic attack on the sulfenyl sulfur atom yields diaralkyl disulfide, hydrogen sulfide, and hydrocarbon, besides phosphine sulfide. Steric effects in the hydrodisulfide and thiophilicity of the nucleophile are the factors which govern whether the sulfhydryl or sulfenyl sulfur atom is attacked.

In previous papers of this series the free-radical, thermal decomposition of benzhydryl hydrodisulfide[1] and the reaction[3] of benzyl and benzhydryl hydrodisulfides with the free-radical scavengers were reported. Hydrodisulfides, RSSH, which can be considered the thio analogs of hydroperoxides, have not been studied in reference to nucleophilic attack, although hydroperoxides as well as organic polysulfides and some disulfides were reported to be cleaved by nucleophiles, for example, by tertiary phosphines and phosphites. Hydroperoxide is reduced to alcohol by tertiary phosphine, which in turn is oxidized to phosphine oxide.[4,5] In this work, aralkyl hydrodisulfides (RSSH: benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) were allowed to react with tertiary phosphines (R'_3P: triphenyl- or triethylphosphine) in order to examine whether the hydrodisulfide function behaves like hydroperoxide. Since empty d-orbitals of the sulfur atom may be utilized in bond formation by accepting electrons from phosphorus, sulfur is known to be more susceptible to attack by phosphine than is the oxygen atom.[6] In this respect, the nucleophilic reactions of tertiary phosphines with hydrodisulfide seem interesting.

Results and Discussion

In a stream of nitrogen a tertiary phosphine (triphenyl- or triethylphosphine) in ether was added dropwise, at room temperature, to an aralkyl hydrodisulfide (benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) in ether. The reverse addition of the reactants, that is, addition of benzyl hydrodisulfide to triphenyl-

---

(1) Part II: T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **28**, 813 (1963).

(2) Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai City, Osaka, Japan.

(3) T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **28**, 811 (1963).

(4) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

(5) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **82**, 1393 (1960).

(6) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 599 (1959).

phosphine, did not alter the variety and amounts of the products shown in Table I. Table I indicates the products, of which one group consists of only phosphine sulfide, stemming from phosphine, and another group of thiol, diaralkyl disulfide, hydrogen sulfide, and hydrocarbon from the hydrodisulfide. The yield (in moles) of phosphine sulfide was equivalent within experimental error to that of the hydrodisulfide in each experiment. However, the variety and amounts of the products arising from the hydrodisulfide vary depending on the reactants used in the experiment as indicated in Table I. Preliminary study showed that neither the corresponding diaralkyl disulfide [dibenzyl, dibenzhydryl, or bis(triphenylmethyl) disulfide] nor the phenyl-substituted alkanethiol (α-toluene-, α-diphenylmethane- or triphenylmethanethiol) reacted with triphenyl- or triethylphosphine under the same conditions. Therefore, the high reactivity of the hydrodisulfide with the phosphine, as indicated in Table I, appears to be specific for the hydrodisulfides. As to the organic polysulfides, only higher polysulfides than trisulfides, in general, can react with the phosphine[7,8] under the same condition, with exception of dialkenyl or alkenyl alkyl disulfide. Hydroperoxide, when allowed to react with the phosphine, is well known to give alcohol and phosphine oxide[4,5] and to be attacked on the hydroxy oxygen by the nucleophile.[5] Table I indicates that triphenylmethyl hydrodisulfide yields only thiol and phosphine sulfide, which are analogous with the products from hydroperoxide. The other two hydrodisulfides give diaralkyl disulfide, hydrogen sulfide, and hydrocarbon at the expense of thiol. Therefore, the mechanism by which triphenylmethyl hydrodisulfide, at least, reacts with phosphine should be analogous with that of hydroperoxide.[5] Preliminary works also indicated that benzhydryl hydrodisulfide reacted with triphenylphosphine even in the presence of hydroquinone as rapidly as in its absence. The rate was followed by determining evolution of hydrogen sulfide. This result suggests a nonradical mechanism.

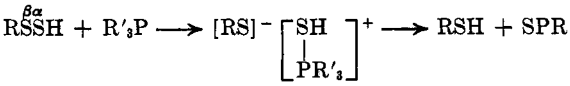
TABLE I

ARALKYL HYDRODISULFIDES AND TERTIARY PHOSPHINES, BOTH IN ETHER AT ROOM TEMPERATURE

Expt. no.	Reactants, mmoles RSSH R	 R'_3P R'	Products, mmoles R'_3PS	 RSH	 RS_2R	 H_2S	 RH
1	$C_6H_5CH_2$, 10	C_6H_5, 12	9.8	0.2	2.8	3.7	2.8
2	$(C_6H_5)_2CH$, 10	C_6H_5, 12	10.4	8.9	...	0.1	*a*
3	$(C_6H_5)_3C$, 10	C_6H_5, 12	9.7	9.9	...	None	...
4	$C_6H_5CH_2$, 10	C_2H_5, 10.5	9.7	3.7	1.7	2.5	1.3
5	$(C_6H_5)_2CH$, 10	C_2H_5, 10.5	9.7	9.1	...	0.1	*a*
6	$(C_6H_5)_3C$, 10	C_2H_5, 10.5	9.8	9.8	...	None	...

[a] Although a quantitative determination was not carried out, the presence of RH was established.

In the following discussion of the reaction mechanism, sulfhydryl sulfur and sulfenyl sulfur atoms are designated as the α- and β-sulfur atoms, respectively, as in RS(β)S(α)H. Equation A, which is based on nucleophilic attack by phosphine on α-sulfur atom, followed by proton transfer, is quite analogous to the mechanism proposed by Denney[5] for hydroperoxide.



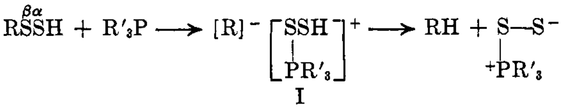
$$\mathrm{R\overset{\beta\alpha}{SS}H + R'_3P \longrightarrow [RS]^- \begin{bmatrix} SH \\ | \\ PR'_3 \end{bmatrix}^+ \longrightarrow RSH + SPR'_3} \qquad (A)$$

In order to explain the formation of diaralkyl disulfide, hydrogen sulfide, and hydrocarbon an alternative mechanism is necessary, which must involve nucleophilic attack on the alternative β-sulfur atom. For nucleophilic attack on the β-sulfur atom it seems reasonable to consider two intermediate ion pairs, such as I and II. Equation B-1 and succeeding ones which result from B-1 will be discussed first. Intermediate I can easily explain the formation of hydrocarbon by simple proton transfer similarly as in A. Moreover, the carbanion R^- in intermediate ion pair I, say, for benzyl hydrodisulfide, is stabilized by the following resonance. When eq. B-1 is accepted, the next problem is the fate of the dipolar intermediate, phosphine disulfide. This intermediate product was already postulated by Bartlett and Meguerian[9] as an intermediate in the reaction of triphenylphosphine with elemental sulfur and may react with another molecule of the phosphine as indicated in eq. 2 and as already reported by the same authors.[9] Alternatively, in the reaction

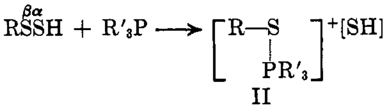
$$R'_3P^+SS^- + R'_3P \longrightarrow 2R'_3PS \qquad (2)$$

of phosphine with hydrodisulfide, the phosphine disulfide may react with hydrodisulfide to give hydrogen sulfide, phosphine sulfide, and diaralkyl tetrasulfide.

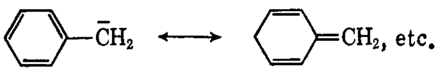
$$R'_3P^+SS^- + 2RSSH \longrightarrow H_2S + R'_3PS + RS_4R \qquad (B\text{-}2)$$



$$\mathrm{R\overset{\beta\alpha}{SS}H + R'_3P \longrightarrow [R]^- \underset{I}{\begin{bmatrix} SSH \\ | \\ PR'_3 \end{bmatrix}^+} \longrightarrow RH + \begin{matrix} S{-}S^- \\ | \\ {}^+PR'_3 \end{matrix}} \qquad (B\text{-}1)$$



$$\mathrm{R\overset{\beta\alpha}{SS}H + R'_3P \longrightarrow \underset{II}{\begin{bmatrix} R{-}S & \\ \ \ | & \\ \ \ PR'_3 & \end{bmatrix}^+}[SH]^-} \qquad (C\text{-}1)$$



In order to decide which mechanism is appropriate, a given amount of benzhydryl hydrodisulfide was allowed to react with the increasing amounts of triphenylphosphine. The results are summarized in Table II.

TABLE II

REACTION OF BENZHYDRYL HYDRODISULFIDE (10 mmoles) AND TRIPHENYLPHOSPHINE, BOTH IN ETHER AT ROOM TEMPERATURE

Reactant, mmoles $(C_6H_5)_3P$	Products, mmoles $(C_6H_5)_3PS$	 $(C_6H_5)_2CHSH$	 $H_2S \times 10^2$	 $(C_6H_5)_2CH_2$
11	10.4	8.8	1.3	*a*
12	10.4	8.8	8.7	*a*
15	10.4	8.9	10.0	*a*
20	10.5	8.8	6.2	*a*

[a] Hydrocarbon was identified by gas chromatography, but quantitative determination was not carried out.

If the reaction of eq. 2 predominates over (B-2), the amount of phosphine sulfide should increase with increasing concentration of starting phosphine. Table II indicates that about an equimolar amount of phos-

---

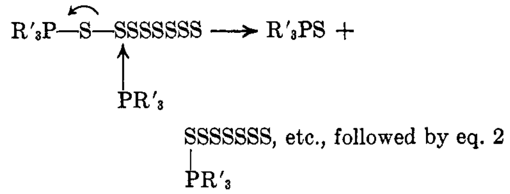
[7] M. B. Evans, G. M. C. Higgins, C. G. Moore, M. Porter, B. Saville, J. F. Smith, B. R. Trego, and A. A. Watson, *Chem. Ind.* (London), 897 (1960).

[8] C. G. Moore and B. R. Trego, *Tetrahedron*, **18**, 205 (1962).

[9] P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

phine sulfide is formed regardless of the starting amount of phosphine, although the amount of hydrogen sulfide fluctuates depending on the initial proportion of phosphine. Moreover, when eq. B-1 is adopted, eq. 2 cannot explain the formation of hydrogen sulfide. In the reaction of triarylphosphine with the sulfur molecule, Bartlett and Meguerian[9] proposed the following reaction sequence. Although the dipolar polysulfides ($R'_3{}^+PS^-_n$) shown in the above equation react with phosphine rapidly, there should be apparently an electrostatic barrier to shift eq. 2 to the right[9] because the dipolar phosphine disulfide (R'_3PSS) reacts with phosphine on the electronegative sulfur atom. In the presence of hydrodisulfide, as in the present study, the intermediate phosphine disulfide may prefer reaction according to eq. B-2 rather than to (2), because of the lower energy barrier. The diaralkyl tetrasulfide produced in (B-2) then reacts with phosphine to give the disulfide and phosphine sulfide, as already reported for the desulfuration of dialkyl or dibenzyl tetrasulfides to the corresponding disulfides in the similar nucleophilic attack by triphenylphosphine.[7,8]

$$R'_3P + S_8 \longrightarrow R'_3P^+SSSSSSSS^-$$



$$RS_4R + 2R'_3P \longrightarrow RS_2R + 2R'_3PS \qquad \text{(B-3)}$$

Equation C-1 and succeeding ones which result from (C-1) will be discussed next. The cation $RS^+PR'_3$ in intermediate II is also stabilized by resonance. The resonance-stabilized intermediate ion II may then react with another molecule of hydrodisulfide as shown.

$$R{-}S{-}\overset{+}{P}{\equiv}R'_3 \longleftrightarrow R{-}\overset{+}{S}{=}P{\equiv}R'_3 \longleftrightarrow \overset{+}{R}S{=}P{\equiv}R'_3$$

$$HS^- + RSSH \longrightarrow H_2S + RSS^- \qquad \text{(C-2)}$$

$$RS\overset{+}{P}R'_3 + RSSH \longrightarrow RH + SPR'_3 + RSS^+ \qquad \text{(C-3)}$$

Thus, hydrogen sulfide is produced from the anion ^-SH. To allow the formation of hydrocarbon, the S-bonded carbon atom of the cation must be attacked by hydride of RSSH as in (C-3), possibly involving $R^+S{=}P{\equiv}R'_3$. The bond between sulfur and phosphorus atoms may be stronger than that between carbon and sulfur, since a similar C–S bond fission by a nucleophile was reported by Challenger and Greenwood.[10]

$$Ph_3\overset{+}{P}{-}SR + RS^- \longrightarrow Ph_3PS + RSR$$

The resulting anion and cation (RSS^- and RSS^+, respectively) from (C-2) and (C-3) combine to give the diaralkyl tetrasulfide, which is desulfurated by phosphine to the diaralkyl disulfide (*cf.* eq. B-3).

For interpreting the reaction products, schemes B and C are quite equivalent, so far as the experimental results indicate, because both give the same proportion of the products, that is, 1 mole of phosphine sulfide and each 0.33 mole of diaralkyl disulfide, hydrogen sulfide, and hydrocarbon for each mole of the reagents. Experimental procedures for determining diaralkyl disulfide and hydrocarbon are not so accurate and tend to give the lower value. As seen in expt. 1 of Table I, the amount of dibenzyl disulfide is equivalent to that of toluene, although the amount of hydrogen sulfide surpasses that of diaralkyl disulfide or toluene. The result of expt. 4 shows approximately the similar situation. Consideration of the experimental errors cited above shows that the amount of thiol indicates roughly the contribution of scheme A to the reaction; that of hydrogen sulfide, or alternatively of diaralkyl disulfide or hydrocarbon, indicates the contribution of scheme B or C. Table I indicates that triphenylmethyl hydrodisulfide reacts with phosphine exclusively on the α(sulfhydryl)-sulfur atom. The attack on β(sulfenyl)-sulfur atom occurs to a minor and to a comparable extent in the reaction of benzhydryl and benzyl hydrodisulfide, respectively. These results show clearly that the steric factor predominates overwhelmingly over other factors in the reaction of triphenylmethyl hydrodisulfide with tertiary phosphine and to a lesser extent in benzhydryl hydrodisulfide. As to benzyl hydrodisulfide attack on the α-sulfur atom contributes to the reaction with triethylphosphine more preferably than that with triphenylphosphine. This means that triethylphosphine attacks the α(sulfhydryl)-sulfur atom of benzyl hydrodisulfide more preferably than does triphenylphosphine. Since triethylphosphine may suffer less steric hindrance than the triphenyl compound, a factor other than steric hindrance is necessary to explain the result. It was reported that triethylphosphine[11] is more basic than the triphenyl compound, and that the affinity of a base for sulfur[12,13] depends on the basicity and polarizability of the atom forming a new bond with sulfur. Since polarizability of both compounds may fall in the same range in the present case, triethylphosphine is considered to be more thiophilic ("S-nucleophilic") than the triphenyl compound. The reason that triethylphosphine attacks the α-sulfur atom in preference to the triphenyl compound may be that the triethyl compound is more thiophilic than the triphenyl compound. In the succeeding paper, in which benzyl hydrodisulfide was allowed to react with various inorganic nucleophiles, the same trend was observed. In this respect, the less nucleophilic reagent, in the absence of steric hindrance, apparently prefers attack on the β(sulfenyl)-sulfur atom of hydrodisulfide. This contrasts with behavior preferred in hydroperoxides.

Experimental

Materials.—Benzyl, benzhydryl, and triphenylmethyl hydrodisulfides, b.p. 65–70° (0.01 mm.), m.p. 32.5–34°, and m.p. 114–116°, respectively, were prepared by the method reported elsewhere.[14,15] Triphenylphosphine,[16] m.p. 78–79°, and triethylphosphine,[17] b.p. 127–128°, were prepared also by the method in the literature. Both the hydrodisulfides and tertiary phosphines were purified immediately before use by recrystallization

---

[10] F. Challenger and D. Greenwood, *J. Chem. Soc.*, 26 (1950).

[11] W. A. Henderson, Jr., and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5791 (1960).

[12] See ref. 6, p. 600.

[13] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[14] J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

[15] T. Nakabayashi, J. Tsurugi, and T. Yabuta, *ibid.*, **29**, 1236 (1964).

[16] J. Dodonow and H. Medox, *Chem. Ber.*, **61**, 907 (1928).

[17] H. Hibbert, *ibid.*, **39**, 161 (1906).

or distillation. The solvents were conventionally purified, dried commercial products.

Identification of the Products.—All of the products which melted above room temperature were identified by mixture melting point with authentic specimens. Toluene and diphenylmethane were identified by gas chromatography (Hitachi KGL-2 Type). The column was packed with commercial Silicon Oil DC 550 (Hitachi), and helium gas was used as carrier. The peak of the chromatogram was compared with that of authentic specimens.

Procedure for Benzyl Hydrodisulfide with *t*-Phosphines.—A given amount (10 mmoles, 1.5627 g.) of benzyl hydrodisulfide in 10 ml. of ether was placed in a three-necked flask equipped with a reflux condenser, dropping funnel, and nitrogen inlet tube, each of which was fitted with a stopcock. In a stream of nitrogen, a solution of *t*-phosphine (12 mmoles, 3.1474 g. for triphenyl-; 10.5 mmoles, 1.2406 g. for triethylphosphine) in ether was added dropwise, with magnetic stirring at room temperature. Hydrogen sulfide was swept out by nitrogen and absorbed in a series of absorbing bottles, two of which contained aqueous iodine solution, and one an aqueous potassium iodide solution. Titration of iodine remaining, with sodium thiosulfate, gave the amount of hydrogen sulfide evolved. The ethereal solution was kept overnight, under nitrogen, at room temperature, to complete the reaction.

A.—The procedure for obtaining the products from triphenylphosphine was as follows. White crystals separated from the solution were collected, weighed, recrystallized from benzene–ethanol (1:9 vol.) mixture, m.p. 159–161°, and confirmed by comparison to be triphenylphosphine sulfide. This compound could be estimated nearly quantitatively owing to its low solubility in ether. The filtrate was diluted with ether to 100 ml. To an aliquot (10 ml.) of the solution were added benzene and then 0.3 g. of elemental sulfur[9] to convert excess phosphine to phosphine sulfide (which is inert to iodine). The thiol in the solution could be titrated with an aqueous iodine solution only in the absence of the phosphine. Titration was carried out by adding excess iodine and by titrating the unreacted iodine with sodium thiosulfate solution. Gas chromatography (at 80°) of another aliquot (10 ml.) indicated the presence of toluene and allowed estimation of the amount. The remaining portion (80 ml.) of the solution was treated with an ethereal solution of mercuric chloride to remove the unchanged phosphine and the thiol. The double salt of triphenylphosphine–mercuric chloride and the mercaptide of α-toluenethiol precipitated. The solvent of the filtrate was replaced with benzene. The benzene solution was dried over anhydrous sodium sulfate, passed through a column of silica gel (Mallinckrodt, 100 mesh), and eluted with benzene. After evaporation of the solvent, the eluate gave white crystals, recrystallized from ethanol, m.p. 70–71°, and shown to be dibenzyl disulfide.

B.—Since triethylphosphine sulfide is more soluble in ether than triphenylphosphine sulfide, the content of the reaction flask was diluted with ether to 100 ml. to dissolve partly crystallized triethylphosphine sulfide. The solution contained phosphine sulfide, the thiol, the disulfide, toluene, and a small amount of unchanged triethylphosphine. Two aliquots (each 10 ml.) of the solution were utilized to titrate the thiol and to determine toluene, respectively, by the same method as for A. The remaining portion (80 ml.) of the solution was treated with ethereal mercuric chloride solution. The solvent of the filtrate was replaced with benzene. The benzene solution was extracted by several washings with hot water. The water extract gave white solids after evaporation of the solvent under reduced pressure. The solids were weighed, recrystallized from ether (m.p. 95°), and identified as triethylphosphine sulfide. The residual benzene solution was treated as for A and gave dibenzyl disulfide.

Procedure for Benzhydryl Hydrodisulfide with Tertiary Phosphines.—As for the benzyl compound, tertiary phosphine (12 mmoles for triphenyl-, 10.5 mmoles for triethylphosphine) was added to benzhydryl hydrodisulfide (10 mmoles, 2.3236 g.). Hydrogen sulfide evolved was determined by the same method as for benzyl hydrodisulfide.

A.—Triphenylphosphine sulfide separated from the reaction mixture owing to its low solubility in ether. The crystals were collected, weighed, and identified. The filtrate was diluted with ether to 100 ml. To determine an amount of α-diphenylmethanethiol, an aliquot (10 ml.) of the solution was titrated by the same method as for benzyl hydrodisulfide. The gas chromatogram (at 250°) of another aliquot (10 ml.) indicated the presence of diphenylmethane. To a residual portion of the solution was added a sufficient amount of ethanolic iodine solution to oxidize the phosphine and the thiol. White crystals obtained by evaporating the solvent were recrystallized from benzene–ethanol mixture (1:1 v./v.), m.p. 150–151°, and identified as dibenzhydryl disulfide. Similarly, α-diphenylmethanethiol was determined by titration and identified as the disulfide. On the other hand, dibenzhydryl disulfide which might be produced in the reaction mixture to a small extent was neither identified nor estimated by the present procedure.

B.—When triethylphosphine was used, the reaction mixture was made up to 100 ml. with benzene to dissolve the phosphine sulfide. Two aliquots (each 10 ml.) of the benzene solution were used to titrate for the thiol and for gas chromatography. The remaining portion was oxidized with ethanolic iodine solution as for A and extracted with hot water. The water extract yielded white solids, which were weighed, recrystallized, and identified as triethylphosphine sulfide, as for the procedure for benzyl hydrodisulfide (B). The benzene solution yielded dibenzhydryl disulfide, which resulted from α-diphenylmethanethiol.

Procedure for Triphenylmethyl Hydrodisulfide with *t*-Phosphines.—As for benzyl and benzhydryl compounds, phosphine (12 mmoles for triphenyl-, 10.5 mmoles for triethylphosphine) was added to 10 mmoles (3.0845 g.) of triphenylmethyl hydrodisulfide. Evolution of hydrogen sulfide was not observed throughout the reaction. Triphenylphosphine sulfide and triethylphosphine sulfide were separated, weighed, and identified by the same procedure as for benzhydryl hydrodisulfide, A and B, respectively. Since triphenylmethanethiol does not consume iodine, the thiol was titrated with a "kerosin" solution of cupric oleate[18] and identified as 2-nitrophenyl triphenylmethyl disulfide. As an authentic specimen the latter compound was prepared from triphenylmethanethiol with 2-nitrobenzenesulfenyl chloride and recrystallized from benzene, m.p. 147–152°.

Anal. Calcd. for $C_{25}H_{19}NO_2S$: S, 14.93. Found: S, 15.2.

---

(18) G. R. Bond, Jr., *Ind. Eng. Chem., Anal. Ed.*, **5**, 257 (1933).