TABLE II

Salt	Yield of I, g
"Control" (no added salt)	0.37
LiCl	0.48
$LiClO_4$	0.44
NaCl	0.29
$NaClO_4$	0.37

A solution of 2.6 g (0.01 mole) of trinitrobenzyl chloride in 25 ml of THF and 15 ml of cyclohexene was prepared. To this solution was added 10 ml of methanol containing 0.56 g (0.01 mole) of potassium hydroxide, at once and with thorough mixing. A crystalline product appeared in the mixture within 1 min. The mixture was allowed to stand at ambient temperature for 1 hr, then filtered, and the filter cake was washed with methanol and water and dried. It weighed 0.81 g, 35.5% of theoretical yield. Recrystallized from nitrobenzene it formed light yellow needles, mp 316° dec.

A "control" reaction using 15 ml of methanol instead of cyclohexene was carried out simultaneously. The yield of crystalline product was 0.8 g, 35.5% of the theoretical.

2,2',4,4',6,6'-Hexanitrobibenzyl (III). From TNT and Sodium Hypochlorite.—A solution of 10 g of TNT in 50 ml of THF and 100 ml of methanol was prepared in a 500-ml wide-mouth erlenmeyer flask equipped with a mechanical stirrer and a 125-ml dropping funnel. A solution prepared by adding 35 ml of "Clorox" to 65 ml of water containing 0.5 g of sodium hydroxide was placed in the dropping funnel and added, with rapid stirring, during 5–10 min, to the TNT solution. The mixture turned dark red-brown and a crystalline product appeared after about 1 min. Formation of the crystalline product was heavy by the end of the addition of the hypochlorite solution and the temperature of the reaction mixture had risen to 35°. The mixture was allowed to stand for 15 min, then filtered with suction, and the filter cake was washed thoroughly with methanol and dried. It weighed 7.9 g, 79% of the theoretical yield. The material was recrystallized by dissolving it in hot acetone with Darco and Celite, filtering the hot solution, adding water to the cloud point, and chilling. It formed faintly yellow needles which melted at 218–220° and the melting point was not depressed on admixture with an authentic sample of III prepared by the nitration of bibenzyl, *vide supra*. X-Ray powder diffraction patterns of the two samples, however, were not superimposable The product formed in the TNT–hypochlorite reaction was a metastable polymorph of the product obtained by the nitration of bibenzyl. This metastable polymorph transformed into the stable form at ambient temperature when placed under 1-nitropropane, a solvent in which it was slightly soluble. When the stable polymorph was heated a solid–solid transition at 105° produced the metastable polymorph.[28]

2,2',4,6,6'-Pentanitrobibenzyl.—A solution of 0.52 g (0.002 mole) of 2,6-dinitrobenzyl bromide and 0.45 g (0.002 mole) of TNT in 10 ml of THF and 5 ml of methanol was prepared. To this solution was added 10 ml of water containing 0.08 g (0.002 mole) of sodium hydroxide, at once and with rapid stirring. The reaction mixture immediately became dark red-brown in color and precipitation of a crystalline product began within 2 min. The mixture was allowed to stand at ambient temperature for 2 hr, then filtered, and the filter cake was washed thoroughly with methanol and dried. It weighed 0.69 g, 86.5% of the theoretical yield. Recrystallized from methyl ethyl ketone–water it formed colorless needles, mp 155–156°. *Anal.* Calcd for $C_{14}H_9N_5O_{10}$: C, 41.50; H, 2.21; N, 17.21; mol wt, 407. Found: C, 41.71, 41.30; H, 2.64, 2.20; N, 17.34, 17.16; mol wt, 395, 400 (acetonitrile solution).

2,4,4',6-Tetranitrobibenzyl.—This compound was prepared from TNT, 4-nitrobenzyl bromide, and sodium hydroxide in the same manner as the pentanitrobibenzyl, above. The reaction produced a 73.6% yield of crude crystalline product. Recrystallized from methyl ethyl ketone–methanol it formed very faintly yellow needles, mp 179–180°. *Anal.* Calcd for $C_{14}H_{10}N_4O_8$: C, 46.40; H, 2.76; N, 15.45; mol wt, 362. Found: C, 46.46, 46.34; H, 2.95, 2.68; N, 15.16, 15.17; mol wt, 365, 357 (acetonitrile solution).

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[28] Dr. J. M. Rosen of these laboratories determined the transition temperature and carried out the transformation of the metastable form into the stable form under solvent.

Aralkyl Hydrodisulfides.[1] V. The Reaction of ^{35}S-Labeled Aralkyl Hydrodisulfides with Triphenylphosphine

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Benzyl or benzhydryl hydrodisulfides-^{35}S ($C_6H_5CH_2{}^{35}SSH$, $(C_6H_5)_2CH{}^{35}SSH$), the sulfenyl sulfur atom of which is labeled with radioactive sulfur, were prepared and allowed to react with triphenylphosphine. Radioactivities of the products, triphenylphosphine sulfide, hydrogen sulfide, aryl-substituted alkanethiol, and diaralkyl disulfide, were measured and compared with those of the corresponding radioactive standard compounds. These data showed that benzyl or benzhydryl hydrodisulfides are attacked by triphenylphosphine both on the sulfenyl and sulfhydryl sulfur atoms. Thus, the mechanisms suggested in a preceding paper are confirmed. The proportions and significance of reaction at sulfenyl and sulfhydryl sulfur atoms are discussed on the basis of the activities of the products.

Hydroperoxides are well known to be attacked on the hydroxy oxygen by triphenylphosphine,[2] to give alcohols and triphenylphosphine oxide.[2,3] A preceding paper[4] reported that triphenylmethyl hydrodisulfide reacts with tertiary phosphine to give the phosphine sulfide and triphenylmethanethiol similarly as hydroperoxides, while benzyl hydrodisulfide and benzhydryl hydrodisulfide give the phosphine sulfide, hydrogen sulfide, the corresponding thiol, disulfide, and hydrocarbon. On the basis of these results, the mechanisms by which hydrodisulfides react with tertiary phosphine were suggested,[4] involving nucleophilic attack of the phosphine on sulfenyl sulfur to yield the phosphine sulfide, hydrogen sulfide, diaralkyl disulfide, and hydrocarbon and competitive attack on sulfhydryl sulfur

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[1] Part IV: S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **30**, 2711 (1965).

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

[3] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[4] J. Tsurugi, T. Nakabayashi, and T. Ishihara, *J. Org. Chem.*, **30**, 2707 (1965).

to yield the phosphine sulfide and the thiol. These mechanisms would be decisively established, if hydrodisulfide labeled with ^{35}S at either sulfenyl or sulfhydryl sulfur atom was allowed to react with the phosphine. In this paper the sulfenyl sulfur atoms of the above hydrodisulfides were labeled with ^{35}S for convenience of the preparation. The above conclusions will be correct, unless scrambling of labeling occurs between the material and the products and also between the labeled products and nonactive products throughout the reaction or separation of the products. Actually no isotopic exchange was observed, as described below.

Because nucleophilic attack of the phosphine on radioactive sulfenyl sulfur yields radioactive phosphine sulfide and diaralkyl disulfide, the measurements of specific activities of the products, especially those of the phosphine sulfide, will not only confirm the mechanisms reported already, but also establish the proportion of attack on sulfenyl sulfur to the over-all reaction.

Results and Discussion

Preparation of Labeled Compounds and Specificity of Labeling Aralkyl Hydrodisulfides.—The sequences (1 and 2) of the reactions employed in the syntheses of benzyl and benzhydryl hydrodisulfides-^{35}S labeled at sulfenyl sulfur atom are shown. In the present study, the specific activities of sulfur compounds were measured by means of the liquid scintillation spectrometer. The specific activities of the radiochemically pure reaction products were compared with those of radiochemically standard compounds. The latter were prepared from the same radioactive species as were the aralkyl hydrodisulfides. Dibenzyl disulfide-^{35}S, an intermediate in the preparation of benzyl hydrodisulfide-^{35}S, as seen in sequence 1, was used as the standard substance for counting analysis. Triphenylphosphine sulfide-^{35}S, for use as standard, was prepared from the original ^{35}S indicated in sequence 1. Since the activities of the original ^{35}S was reduced by one-half by diluting with sodium sulfide for the further syntheses of sequence 1, the specific activity of the triphenylphosphine sulfide should be twice those of the other labeled compounds. For convenience of comparison, the half-value of specific activity of the phosphine sulfide-^{35}S thus obtained was used as standard for counting analysis. In the benzhydryl series, dibenzhydryl disulfide-^{35}S as standard for counting analysis was prepared from the α-diphenylmethanethiol-^{35}S indicated in sequence 2. Triphenylphosphine sulfide-^{35}S was prepared from ^{35}S obtained by oxidizing the original thiourea-^{35}S. To prove that the radioactive label in aralkyl hydrodisulfides was only in the desired position, the hydrodisulfides-^{35}S were oxidized to the corresponding diaralkyl tetrasulfides, which were then desulfurated[5] to the diaralkyl disulfides. The specific activities of the latter were compared with those of the standards: for dibenzyl disulfide, standard, 5260 cpm/mg, and desulfurated product, 5330 cpm/mg; for dibenzhydryl disulfide, standard, 3797 cpm/mg, and desulfurated product, 3821 cpm/mg. These results clearly indicate the following sequence and therefore assure the specificity of labeling.

For synthesis of labeled benzyl hydrodisulfide

$$^{35}S \xrightarrow{Na_2S} Na_2{}^{35}S_2 \xrightarrow{2C_6H_5CH_2Cl} C_6H_5CH_2{}^{35}S_2CH_2C_6H_5 \xrightarrow{LiAlH_4}$$
$$C_6H_5CH_2{}^{35}SH \xrightarrow{CH_3COSCl} C_6H_5CH_2{}^{35}SSCOCH_3 \xrightarrow[HCl]{C_2H_5OH}$$
$$C_6H_5CH_2{}^{35}SSH \quad (1)$$

For synthesis of labeled benzhydryl hydrodisulfide

$$(NH_2)_2C{=}^{35}S \xrightarrow{(C_6H_5)_2CHBr} (C_6H_5)_2CH^{35}SC(NH_2){=}\overset{+}{N}H_2Br^- \xrightarrow[\text{then HCl}]{NaOH}$$
$$(C_6H_5)_2CH^{35}SH \xrightarrow{CH_3COSCl} (C_6H_5)_2CH^{35}SSCOCH_3 \xrightarrow[HCl]{C_2H_5OH}$$
$$(C_6H_5)_2CH^{35}SSH \quad (2)$$

$$2R^{35}SSH \xrightarrow{\text{oxidation}} R^{35}SSS^{35}SR \xrightarrow{\text{desulfuration}} R^{35}S^{35}SR$$

The Reaction Products.—Triphenylphosphine, dissolved in ether, was added dropwise, in a stream of nitrogen at room temperature, to an ethereal solution of labeled aralkyl hydrodisulfide (benzyl or benzhydryl hydrodisulfide-^{35}S). The variety and amounts of the reaction products from nonradioactive materials under the same conditions were previously reported.[4] However, the present study concerns only the activities of sulfur compounds separated in radiochemically pure state. The procedures of separation are mentioned briefly. The hydrogen sulfide evolved during the reaction was absorbed in ethanolic iodine solution, and thereby oxidized to elemental sulfur, which was then converted to triphenylphosphine sulfide, which is a convenient product of sulfur for counting analysis. Aryl-substituted alkanethiols were separated from the reaction mixture by vacuum distillation or by extraction with aqueous sodium hydroxide and oxidized with iodine to the easily isolable diaralkyl disulfides, which adapt well to counting. Triphenylphosphine sulfide and diaralkyl disulfides were separated from the reaction mixture as crystals, identified and subjected to counting as such. The specific activities of the products are listed in Table I.

TABLE I

SPECIFIC ACTIVITIES OF THE REACTION PRODUCTS OF ARALKYL HYDRODISULFIDES-^{35}S (10 MMOLES) WITH TRIPHENYLPHOSPHINE (12 MMOLES)

Products	Chemical forms for counting analysis	Specific activities[a] (*A*) of standards, cpm/mg	Specific activities (*B*) of the products or those derived from the products, cpm/mg	*B*/*A* × 100[b]
For Benzyl Series				
$(C_6H_5)_3PS$	$(C_6H_5)_3PS$	2395	594	24.8
$(C_6H_5CH_2)_2S_2$	$(C_6H_5CH_2)_2S_2$	6080	5940	97.7
$C_6H_5CH_2SH$	$(C_6H_5CH_2)_2S_2$	5260	5180	98.5
H_2S	$(C_6H_5)_3PS$	5250	0	0
For Benzhydryl Series				
$(C_6H_5)_3PS$	$(C_6H_5)_3PS$	2615	131	5.0
$(C_6H_5)_2CHSH$	$[(C_6H_5)_2CH]_2S_2$	3797	3856	102

[a] The specific activities of the same standard compounds fluctuate because of the different time periods of counting. [b] *B*/*A* × 100 indicates the per cent distribution of radioactive sulfur to total sulfur in the products.

The results in Table I clearly indicate that all the sulfur atoms in aryl-substituted alkanethiol and diaralkyl disulfides stem from the sulfenyl sulfur-^{35}S of the aralkyl hydrodisulfides-^{35}S and that hydrogen

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(5) S. Ikeda and Y. Minoura, *Nippon Kagaku Zasshi*, **75**, 260 (1954); *Chem. Abstr.*, **51**, 11278*a* (1957).

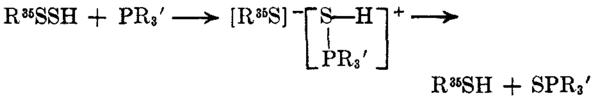
sulfide arises from the sulfhydryl group of the same compounds. In view of this, the exchange reaction between sulfhydryl sulfur in the starting aralkyl hydrodisulfide and sulfur in aryl-substituted alkanethiol-^{35}S produced in the reaction is concluded not to occur. If exchange occurred, hydrogen sulfide would be labeled to some extent, whereas the results showed no activity in the hydrogen sulfide.

Mechanisms.—It seems necessary to cite briefly the results and mechanisms reported in our previous paper,[4] where nonradioactive aralkyl hydrodisulfides were allowed to react with triphenylphosphine under the same conditions. The variety and amounts of the products in that study are cited in Table II. Our preceding paper also reported that nucleophilic attack of phosphine on sulfhydryl sulfur yields phosphine sulfide and aryl-substituted alkanethiol, while the same attack on sulfenyl sulfur gives phosphine sulfide, hydrogen sulfide, diaralkyl disulfides and hydrocarbon. In the present study, using aralkyl hydrodisulfides specifically labeled at sulfenyl sulfur atom, the mechanisms proposed in the previous paper are written, using symbol ^{35}S, as follows.

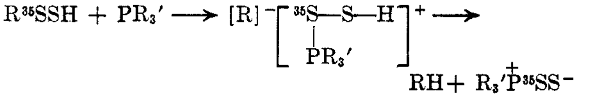
TABLE II

Reactants, mmoles		Products, mmoles				
RSSH	$(C_6H_5)_3P$	$(C_6H_5)_3PS$	RSH	RS_2R	H_2S	RH
10 (R = $C_6H_5CH_2$–)	12	9.8	0.2	2.8	3.7	2.8
10 (R = $(C_6H_5)_2CH$–)	12	10.4	8.9		0.1	[a]

[a] Qualitatively observed.



$$\mathrm{R^{35}SSH + PR_3' \longrightarrow [R^{35}S]^{-}\left[\begin{array}{l} \mathrm{S{-}H} \\ \;| \\ \mathrm{PR_3'} \end{array}\right]^{+} \longrightarrow R^{35}SH + SPR_3'} \qquad \text{(A)}$$



$$\mathrm{R^{35}SSH + PR_3' \longrightarrow [R]^{-}\left[\begin{array}{l} \mathrm{^{35}S{-}S{-}H} \\ \;| \\ \mathrm{PR_3'} \end{array}\right]^{+} \longrightarrow RH + R_3'\overset{+}{P}{}^{35}SS^{-}} \qquad \text{(B-1)}$$

$$\mathrm{R_3'{}^{+}P^{35}SS^{-} + 2\ R^{35}SSH \longrightarrow H_2S + R_3'P^{35}S + R^{35}SSS^{35}SR} \qquad \text{(B-2)}$$

$$\mathrm{R^{35}SSS^{35}SR + 2\ PR_3' \longrightarrow R^{35}S^{35}SR + 2SPR_3'} \qquad \text{(B-3)}$$

or

$$\mathrm{R^{35}SSH + PR'_3 \longrightarrow [R{-}^{35}S{-}PR_3']^{+}[SH]^{-}} \qquad \text{(C-1)}$$

$$\mathrm{HS^{-} + R^{35}SSH \longrightarrow H_2S + R^{35}SS^{-}} \qquad \text{(C-2)}$$

$$\mathrm{R^{35}SPR_3'{}^{+} + R^{35}SSH \longrightarrow RH + {}^{35}SPR_3' + R^{35}SS^{+}} \qquad \text{(C-3)}$$

$$\mathrm{R^{35}SS^{-} + R^{35}SS^{+} \longrightarrow R^{35}SSS^{35}SR} \qquad \text{(C-4)}$$

$$\mathrm{R^{35}SSS^{35}SR + 2PR_3' \longrightarrow R^{35}S^{35}SR + 2SPR_3'} \qquad \text{(C-5)}$$

The results indicating that the sulfur atom of the thiols arises solely from sulfenyl sulfur can be interpreted by sequence A. The facts indicating that hydrogen sulfide arises only from sulfhydryl group (–SH) and diaralkyl disulfides from sulfenyl group ($R^{35}S$–) can also be explained by either sequence B or C. From the point of view of the variety and amounts of the products, sequence B is equivalent to C, as discussed in the previous paper. Although it cannot be decided whether sequence B or C is appropriate, the present tracer study unquestionably confirms the mechanisms of nucleophilic attack both on sulfenyl and sulfhydryl sulfur atoms.

Distribution of ^{35}S in triphenylphosphine sulfide permits a more detailed discussion concerning the relative contributions of sequence A and B (or C) to the reaction. Supposing the equations A and B (or C) take place in a 1:1 ratio, the distribution of ^{35}S in phosphine sulfide will be one-fourth, because the other two molecules of aralkyl hydrodisulfide are consumed by the succeeding equations in sequence B or C. Table I indicates that in the reaction of benzyl hydrodisulfide with the phosphine the resulting phosphine sulfide contains just about one-fourth distribution of radioactivity of the standard compound. This means that the resulting phosphine sulfide inherits one-fourth of its radioactivity from the original benzyl hydrodisulfide-^{35}S, which coincides with the contribution of sequence A and B (or C) in a 1:1 ratio. This presumption must lead to the production of each 0.25 mole of α-toluenethiol, hydrogen sulfide, dibenzyl disulfide, and toluene for consumption of 1 mole of benzyl hydrodisulfide. However, the results in Table II, cited from our previous paper, indicate excessive hydrogen sulfide and a much lesser amount of the thiol than one-fourth value, and contrast with the above presumption. In our previous paper this discrepancy was erroneously attributed to the inaccurate experimental procedures. However, in the present study, the discrepancy may be explained by following subsidiary step B-2a or C-2a, which occurs at the later stage of the reaction, where the concentration of α-toluenethiol increases at the expense of benzyl hydrodisulfide. Equation B-2a or C-2a seems probable for the following reason. When 10 mmoles of benzyl hydrodisulfide was allowed to react with 12 mmoles of triphenylphosphine in the presence of 10 mmoles of α-toluenethiol, 4.2 mmoles of hydrogen sulfide was obtained, compared with the yield of 3.7 mmoles in the absence of the thiol.

$$\mathrm{R_3'\overset{+}{P}{}^{35}SS^{-} + 2R^{35}SH \longrightarrow H_2S + R_3'P^{35}S + R^{35}S^{35}SR} \qquad \text{(B-2a)}$$

or

$$\mathrm{HS^{-} + R^{35}SH \longrightarrow H_2S + R^{35}S^{-}} \qquad \text{(C-2a)}$$

In the case of benzhydryl hydrodisulfide the results indicate that sequence A occurs to a major extent and B or C to a minor extent. Therefore, the concentration of the intermediate $\mathrm{R_3'\overset{+}{P}{}^{35}SS^{-}}$ or HS^{-} may be low, and hence eq B-2a or C-2a exerts little influence on the products.

Experimental Section

Radioactive elemental sulfur and thiourea-^{35}S were purchased from Japan Radioisotope Association. Activities of the samples were counted with a Packard Tri-Carb liquid scintillation spectrometer, Model 314, using POPOP as a scintillator.

A. Materials and Standard Specimens for Counting Analysis in the Reaction of Benzyl Hydrodisulfide-^{35}S.—Radioactive sulfur (1 mcurie) in benzene was diluted with 10 g of inactive sulfur in 100 ml of benzene. The crystals (7 g) obtained were used as starting material.

Triphenylphosphine sulfide-^{35}S as a standard specimen for counting analysis was prepared from triphenylphosphine and the radioactive sulfur according to the method of Bartlett, *et al.*,[6] and recrystallized from benzene–methanol (1:9 v/v) mixture, mp 159–161°.

Dibenzyl disulfide-^{35}S was prepared by the ordinary method.[7] To 33.6 g of benzyl chloride in ethanol was added, dropwise, the ethanolic solution of sodium disulfide-^{35}S obtained from 48 g

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(6) P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 109 (1961).

(7) M. T. Bogert and A. Stull, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1956, p 220.

of crystalline sodium sulfide and 6.4 g of sulfur-^{35}S. White crystals (25.4 g, 77%) separated and were filtered, recrystallized from ethanol, and found to be dibenzyl disulfide-^{35}S, mp 69–70°; they were also used as a standard specimen for counting analysis.

α-Toluenethiol-^{35}S was prepared by reducing dibenzyl disulfide-^{35}S with lithium aluminum hydride[8] in dry ether: bp 194–196°, yield 84%.

Benzyl hydrodisulfide-^{35}S, bp 65–70° (0.01 mm), was prepared by the method of Tsurugi and Nakabayashi,[9] using α-toluenethiol-^{35}S.

B. Materials and Standard Specimens for Counting Analysis in the Reaction of Benzhydryl Hydrodisulfide-^{35}S.—Radioactive thiourea (5 mcuries) was diluted with 60 g of inactive thiourea.

Triphenylphosphine sulfide-^{35}S as a standard specimen was prepared by the same method as described in A. Radioactive sulfur, in this case, was obtained by the decomposition[10] of thiourea-^{35}S with lead dioxide in the presence of acetic acid.

α-Diphenylmethanethiol-^{35}S.—Benzhydryl bromide (37 g) and thiourea-^{35}S were placed in a 500-ml flask equipped with a dropping funnel, a condenser, a stirrer, and a gas inlet tube. The mixture was refluxed for 3 hr, and then cooled to room temperature. To the mixture was added 7 g of sodium hydroxide in water under a stream of nitrogen. The contents of the flask were poured into a large amount of water and acidified with 6 *N* hydrochloric acid and extracted with two 100-ml portions of benzene. After evaporating the solvent, the oily residue was distilled under vacuum, bp 98–99° (0.03 mm), to yield 22.4 g (75%).

Dibenzhydryl disulfide-^{35}S, mp 150–151°, as a standard specimen for counting analysis, was prepared by oxidation of α-diphenylmethanethiol-^{35}S with ethanolic iodine and recrystallized from a mixture of benzene and ethanol.

C. Location of Label in Benzyl and Benzhydryl Hydrodisulfides-^{35}S.—Benzyl and benzhydryl hydrodisulfides-^{35}S prepared as described in sections A and B were oxidized with ethanolic iodine to the corresponding tetrasulfides-^{35}S. The resulting dibenzyl and dibenzhydryl tetrasulfides-^{35}S (mp 53–54° and 72–73°, respectively) were desulfurated[11] to dibenzyl and dibenzhydryl disulfides-^{35}S (mp 70° and 150–151°, respectively). The specific activities of the resulting disulfides-^{35}S were the same as those of the corresponding standard specimens.

D. Isotopic Exchange of Triphenylphosphine Sulfide-^{35}S with Several Sulfur-Containing Compounds.—Triphenylphosphine sulfide was examined to determine whether or not its sulfur atom exchanges with those of sulfur compounds which were expected to be present in the reactions studied. To about 20 ml of benzene–ethanol solutions containing 0.2 g of triphenylphosphine sulfide-^{35}S there was added equimolar amounts of each compound (or mixtures of compounds) cited in Table III. The mixture was kept for 1 week at room temperature under an atmosphere of nitrogen. A small portion of the precipitates obtained after evaporation of the solvents was recrystallized from benzene–ethanol mixture. The results are indicated in Table III. Besides checking exchange reaction under conditions similar to those during the reaction or separation of the products, the exchange reaction of triphenylphosphine sulfide under more vigorous conditions was examined. Triphenylphosphine sulfide-^{35}S was refluxed under bubbling nitrogen with sodium sulfide in ethanol for 2 hr, 1 day, and 1 week. The phosphine sulfide, obtained by the similar procedure to the above, showed the same specific activities within experimental error. Similarly, triphenylphosphine sulfide and an equivalent of radioactive sulfur were kept in ethanol–carbon disulfide mixture for 2 hr at room temperature under a nitrogen atmosphere. The resulting phosphine sulfide indicated no activity. This was true even in the presence of potassium hydroxide and hydrochloric acid.

TABLE III

ISOTOPIC EXCHANGE OF TRIPHENYLPHOSPHINE SULFIDE WITH SULFUR COMPOUNDS

	Specific activity of starting $(C_6H_5)_3PS$, cpm/mg	Specific activity of treated $(C_6H_5)_3PS$, cpm/mg
$C_6H_5CH_2SH$	369	373
$C_6H_5CH_2SK$, KOH	369	381
$(C_6H_5CH_2)_2S_2$	369	377
$(C_6H_5CH_2)_2S_2$, KOH	369	368

E. The Reaction of Benzyl Hydrodisulfide-^{35}S with Triphenylphosphine.—A given amount (10 mmoles, 1.5627 g) of benzyl hydrodisulfide-^{35}S in 10 ml of ether was placed in a three-necked flask equipped with a reflux condenser, a dropping funnel, and a nitrogen inlet tube, each of which was fitted with a stopcock. In a stream of nitrogen, a solution of triphenylphosphine (12 mmoles, 3.1474 g) in ether was added dropwise, under magnetic stirring, at room temperature. Hydrogen sulfide was swept out by nitrogen and absorbed in ethanolic iodine solution. The sulfur released was filtered and allowed to react with triphenylphosphine to give triphenylphosphine sulfide, and the latter was subjected to counting analysis. The reaction mixture in ether was kept overnight at room temperature, under nitrogen, to complete the reaction. White crystals separated from the ethereal solution, were collected and, after recrystallization from a benzene–ethanol (1:9 v/v) mixture, had mp 159–161° and were identified as triphenylphosphine sulfide and subjected to counting analysis. This compound separated nearly completely from the solution owing to its low solubility in ether. The solvent of the filtrate was replaced with benzene. The benzene solution contained thiol, disulfide, and unchanged triphenylphosphine. The solution was treated with a 10% aqueous potassium hydroxide solution to separate thiol from the benzene layer and then treated with an aqueous solution of mercuric chloride to remove unchanged triphenylphosphine. After the double salt of triphenylphosphine mercuric chloride was separated, the benzene solution was washed with water and dried over anhydrous sodium sulfate. After evaporating the solvent under reduced pressure, the solids were recrystallized from ethanol. The product had mp 70–71°, was shown to be dibenzyl disulfide, and was subjected to counting analysis. The water extract containing the potassium thiolate described above was acidified with 6 *N* hydrochloric acid to give the thiol. The resulting oil was extracted with benzene. To this solution was added ethanolic iodine solution to oxidize thiol to disulfide. The solution was washed with an aqueous solution of sodium thiosulfate to remove excess of iodine and washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, white solids were obtained, recrystallized from ethanol, and found to be dibenzyl disulfide, mp 70–71°; they were subjected to counting analysis.

F. Reaction of Benzhydryl Hydrodisulfide-^{35}S with Triphenylphosphine.—As for the benzyl hydrodisulfide-^{35}S, triphenylphosphine (12 mmoles, 3.1474 g) was added to benzhydryl hydrodisulfide-^{35}S (10 mmoles, 2.3236 g). Triphenylphosphine sulfide-^{35}S separated from the reaction mixture, was filtered by the same method as described in section E, identified, and subjected to counting analysis. After the solvent of the filtrate was evaporated, the residue was distilled under vacuum, bp 98–100° (0.03 mm), and oxidized with ethanolic iodine. The solids obtained were recrystallized from a benzene–ethanol (1:1 v/v) mixture, found to be dibenzhydryl disulfide, mp 150–151°, and subjected to counting analysis. Hydrogen sulfide as well as dibenzhydryl disulfide, both of which might be produced in the reaction mixture to small extent, were neither identified nor subjected to counting analysis in the present work.

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(8) R. C. Arnold, A. P. Lien, and R. M. Alm, *J. Am. Chem. Soc.*, **72**, 731 (1950).

(9) J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

(10) E. Mulder and J. A. R. Smit, *Chem. Ber.*, **7**, 1637 (1874).

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