Aralkyl Hydrodisulfides.[1] IX. The Reaction with Tertiary Arsines

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The reaction of triphenylarsine with benzyl or benzhydryl hydrodisulfide and of triethylarsine with benzhydryl hydrodisulfide occurs only on sulfhydryl sulfur atom yielding the corresponding trisubstituted arsine sulfide and thiol. Benzyl hydrodisulfide is attacked competitively on sulfenyl and sulfhydryl sulfur atoms by triethylarsine and gives triethylarsine sulfide, α-toluenethiol, dibenzyl trisulfide, and hydrogen sulfide. The products resulted from sulfenyl sulfur attack by the arsine are different from those by tertiary phosphines or trisubstituted phosphites. The mechanism of sulfenyl sulfur attack by the arsine was confirmed by using benzyl hydrodisulfide, of which the sulfenyl sulfur was labeled with ^{35}S, and compared with that by phosphine or phosphite. A correction was made on the latter mechanism.

Previous works[2–4] have shown that aralkyl hydrodisulfide, when attacked by tertiary phosphine (or trisubstituted phosphite) on the sulfenyl sulfur atom, gives phosphine sulfide (or O,O,O-trisubstituted phosphorothionate), hydrogen sulfide, the corresponding disulfide, and hydrocarbon, and that, when attacked on the sulfhydryl sulfur, it yields phosphine sulfide (or the phosphorothionate) and thiol. In the present work benzyl or benzhydryl hydrodisulfide was allowed to react with tertiary (triethyl or triphenyl)arsine, in order to check whether or not the arsine behaves similarly to the phosphorus compound.

Results and Discussion

In a stream of nitrogen a tertiary arsine in ether was added at room temperature to an aralkyl hydrodisulfide in the same solvent. Although the reaction seemed to proceed at once, the mixture was kept standing for 20 hr under an atmosphere of nitrogen to complete the reaction. The variety and amounts of the products are summarized in Table I. The results in Table I indicate that triphenylarsine yielded the corresponding arsine sulfide and thiol, but triethylarsine gave the same products only when treated with benzhydryl hydrodisulfide.

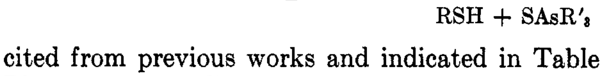
TABLE I

REACTION OF ARALKYL HYDRODISULFIDES WITH TERTIARY ARSINES

Expt	Reactants, mmol				Products, mmol			
no.	R	RSSH	R′	AsR′$_3$	R′$_3$AsS	RSH	RS$_3$R	H$_2$S
1	$C_6H_5CH_2$	10[a]	C_2H_5	11[a]	7.2	9.0	0.5	0.7
2	$(C_6H_5)_2CH$	10[a]	C_2H_5	11[a]	7.0	8.7		
3	$C_6H_5CH_2$	10	C_6H_5	11	7.9	9.8		
4	$(C_6H_5)_2CH$	10	C_6H_5	11	8.9	9.8		

[a] See Experimental Section.

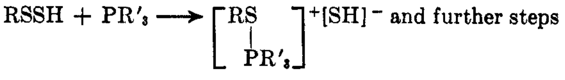
Previous works[2–4] have confirmed that the sulfhydryl sulfur attack by trivalent phosphorus compounds yields the phosphine sulfide (or phosphorothionate) and the thiol. By analogy with the above reaction, the sequence with a tertiary arsine can be written by replacing PR′$_3$ [or P(OR′)$_3$] with AsR′$_3$. However, the variety and amounts of the products in expt 1 are different from those of the reaction with triethylphosphine or triethyl phosphite, which are again



$$\mathrm{RSSH} + \mathrm{AsR'_3} \longrightarrow [\mathrm{RS}]^-\begin{bmatrix}\mathrm{SH}\\ | \\ \mathrm{AsR'_3}\end{bmatrix}^+ \longrightarrow \mathrm{RSH} + \mathrm{SAsR'_3} \qquad (1)$$

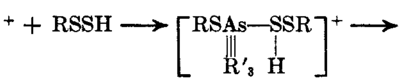
cited from previous works and indicated in Table II. The prominent distinction between expt 1 in Table I and the results in Table II is that arsine yields a small amount each of dibenzyl trisulfide and hydrogen sulfide, an almost quantitative amount of the thiol, no hydrocarbon, and no dibenzyl disulfide. All of our efforts to find toluene in the present products by using gas chromatography or nmr method proved fruitless. From the viewpoint of material balance the nearly quantitative yield of the thiol in expt 1, Table I, may result at least from the expense of toluene in Table II. Nucleophilic attack of arsine on alternative sulfenyl sulfur which is similar to attack of trivalent phosphorus compounds may interpret the formation of the present results. As mentioned in our previous papers[2–4] two quite equivalent sequences (eq 2 and 3) could be applied to sulfenyl sulfur attack

$$\mathrm{RSSH} + \mathrm{PR'_3} \longrightarrow [\mathrm{R}]^-\begin{bmatrix}\mathrm{SSH}\\ | \\ \mathrm{PR'_3}\end{bmatrix}^+ \longrightarrow \mathrm{RH} + \mathrm{R'_3P^+SS^-} \text{ and further steps} \qquad (2)$$



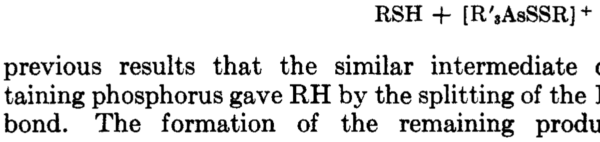
$$\mathrm{RSSH} + \mathrm{PR'_3} \longrightarrow \begin{bmatrix}\mathrm{RS}\\ | \\ \mathrm{PR'_3}\end{bmatrix}^+[\mathrm{SH}]^- \text{ and further steps} \qquad (3)$$

of phosphorus compounds, where R′ signified C_2H_5, C_6H_5, OC_2H_5, and OC_6H_5. The sequence in eq 2 should be abandoned only for the reason that arsine did not give toluene. The similar sequence in eq 4–7 can be adopted for the present case. However, intermediate I should give RSH by the splitting of the S–As bond as indicated in eq 6 in contrast to the previous results that the similar intermediate containing phosphorus gave RH by the splitting of the R–S bond. The formation of the remaining products,



$$\mathrm{RSSH} + \mathrm{AsR'_3} \longrightarrow \begin{bmatrix}\mathrm{RS}\\ | \\ \mathrm{AsR'_3}\end{bmatrix}^+[\mathrm{SH}]^- \qquad (4)$$

$$\mathrm{HS^-} + \mathrm{RSSH} \longrightarrow \mathrm{H_2S} + [\mathrm{RSS}]^- \qquad (5)$$



$$[\mathrm{RSAsR'_3}]^+ + \mathrm{RSSH} \longrightarrow \underset{\mathrm{I}}{\begin{bmatrix}\mathrm{RSAs{-}SSR}\\ \quad|||\quad\; | \\ \quad\mathrm{R'_3}\;\;\mathrm{H}\end{bmatrix}^+} \longrightarrow \mathrm{RSH} + [\mathrm{R'_3AsSSR}]^+ \qquad (6)$$

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Table II

Reaction of Benzyl Hydrodisulfide (RSSH, 10 mmol) with Trivalent Phosphorus Compounds Cited from Previous Works[a,b]

Expt no.	Table	Part no.	Reactants	Products, mmol: Pentavalent P compounds	RSH	RS_2R	H_2S	RH
4	I	III[a]	$(C_2H_5)_3P$	$(C_2H_5)_3PS$, 9.7	3.7	1.7	2.5	1.3
1	I	VII[b]	$(C_2H_5O)_3P$	$(C_2H_5O)_3PS$, 9.5	3.7	1.2	2.7	1.4

[a] See ref 2. [b] See ref 4.

Table III

Specific Activities of the Reaction Products of Benzyl Hydrodisulfide-[^{35}S] with Triethylarsine

Products	Chemical forms for counting analysis	Specific activities (A) of standards, cpm/mg	Specific activities (B) of the products or those derived from the products, cpm/mg	$B/A \times 100$[a]
$(C_2H_5)_3AsS$	$(C_2H_5)_3AsS$	26,254	0	0
$C_6H_5CH_2SH$	$(C_6H_5CH_2)_2S_2$	43,823	41,232	94.1
$(C_6H_5CH_2)_2S_3$	$(C_6H_5CH_2)_2S_2$	43,823	41,476	94.9
H_2S	$(C_6H_5)_3PS$	17,415	0	0

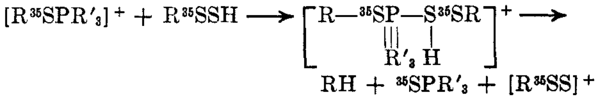
[a] Indicates the per cent distribution of radioactive sulfur to total sulfur in the products.

dibenzyl trisulfide and the arsine sulfide, can be explained by interaction of $[R'_3AsSSR]^+$ (eq 6) and $[RSS]^-$ (eq 5). The sequence in eq 4–7 for the present

$$[R'_3AsSSR]^+ + [RSS]^- \longrightarrow R'_3AsS + RSSSR \qquad (7)$$

reaction will be confirmed by using benzyl hydrodisulfide labeled with ^{35}S.

Reaction with ^{35}S-Labeled Benzyl Hydrodisulfide.—Benzyl hydrodisulfide-[^{35}S] ($C_6H_5CH_2{}^{35}SSH$), the sulfenyl sulfur of which was specifically labeled with ^{35}S, was allowed to react with triethylarsine under the same conditions as for nonlabeled compound. The results are shown in Table III, where specific activities of radiochemically pure products and those of the corresponding standard compounds are indicated. The latter compounds were prepared from the same radioactive species as was the benzyl hydrodisulfide-[^{35}S]. Table III indicates that the sulfur atom of the thiol and sulfur atoms attached to benzyl group of the trisulfide arise from the sulfenyl sulfur, and that triethylarsine sulfide and hydrogen sulfide arise only from the sulfhydryl sulfur of the hydrodisulfide. All of these results can be explained by the sequences given in eq 1 and 4–7 if the symbol RSSH in the above equations was replaced with $R^{35}SSH$. On the contrary, in our previous works[3,4] was observed clearly the distribution of ^{35}S in the phosphine sulfide or phosphorothionate. The activity of the compound must result from R–S bond splitting of the intermediate as indicated in eq 8,



$$[R^{35}SPR'_3]^+ + R^{35}SSH \longrightarrow \left[R\text{—}{}^{35}S\underset{R'_3}{\overset{}{P}}\text{—}\underset{H}{S}{}^{35}SR\right]^+ \longrightarrow RH + {}^{35}SPR'_3 + [R^{35}SS]^+ \qquad (8)$$

which follows steps similar to eq 4 and 5 cited above. Otherwise the activity of the compound cannot be explained. The conclusion of the present paper is that, when the arsine and trivalent phosphorus compound attack the sulfenyl sulfur of the hydrodisulfide, both give a similar intermediate, each which, in turn, leads to the different products as indicated in eq 6 and 8.

Connection with Analogous Reaction.—The next problem to be solved is to elucidate the reason why the arsine gave dibenzyl trisulfide, whereas phosphine or phosphite gave the disulfide. The formation of dibenzyl disulfide was previously[2–4] assumed to result from the recombination of the anion RSS^- and the cation RSS^+, and then desulfuration of the tetrasulfide to the disulfide by the phosphine present in the reaction system. Analogy to the reaction with the arsine makes the previously assumed mechanism doubtful. Therefore, the reaction was reexamined here by using nmr spectroscopy. Triphenylphosphine and about an equimolar amount of benzyl hydrodisulfide, both in carbon tetrachloride, were mixed in an nmr test tube. Immediately after mixing, neither tetrasulfide nor disulfide was detected; only signals of the trisulfide were observed. Only 2 days later, signals of the disulfide appeared together with those of the trisulfide.

A supplementary nmr experiment shows that desulfuration of dibenzyl tetrasulfide to disulfide by triphenylphosphine took 24 hr at room temperature. Another experiment, run under the same conditions as those reported in the previous paper,[2] showed the following result. Within 1 hr after mixing both triphenylphosphine and benzyl hydrodisulfide in ether, the triphenylphosphine sulfide that precipitated was filtered, and the solvent was replaced with carbon tetrachloride. The nmr spectra identified dibenzyl trisulfide but no tetrasulfide or disulfide. All nmr evidence suggests that the precursory product should be the trisulfide, the formation of which can be written as follows by the analogy with the sequence for the arsine. The cation RSS^+ produced in eq 8 interacts again with the phosphine to yield $[R'_3PSSR]^+$, which is quite analogous to the cation $[R'_3AsSSR]^+$ in eq 7. This step and the succeeding ones indicated in eq 9–11 will take the place of those reported in our previous works.[2–4] The results of activity measurements carried out in our previous works[3,4] do not contradict the reaction sequence cited above.

$$RSS^+ + R'_3P \longrightarrow [RSSPR'_3]^+ \qquad (9)$$

$$[RSSPR'_3]^+ + RSS^- \longrightarrow R'_3PS + RSSSR \qquad (10)$$

$$RSSSR + R'_3P \longrightarrow RSSR + R'_3PS \qquad (11)$$

It seems necessary here to summarize the reaction mechanisms of aralkyl hydrodisulfide with the nucleophile, the phosphine, the phosphite, or the arsine. The nucleophilic attack on sulfhydryl sulfur yields phosphine sulfide, phosphorothionate, or arsine sulfide and arylalkanethiol *via* eq 1. The attack on sulfenyl sulfur proceeds *via* eq 4 and 5 and then produces the intermediate I. The intermediate I containing phosphorus splits at the R–S bond (by eq 8) and the succeeding steps are given in eq 9–11. On the other hand the intermediate I containing arsenic splits at the S–As bond by eq 6 and yields the end products *via* eq 7. Desulfuration efficiency by triethylarsine may be inferior to that by the corresponding phosphine or phosphite because dibenzyl trisulfide remains among the other products. Therefore, the arsine can be said to have weaker thiophilicity than phosphine or phosphite. Previous works reported that in the absence of steric hindrance sulfenyl sulfur of hydrodisulfide was preferably attacked by nucleophiles. The present results, on the other hand, indicate the preferential attack on sulfhydryl sulfur by the arsine and suggest that the arsine suffers more steric hindrance than phosphine or phosphite.

Experimental Section

Materials.—Nonlabeled benzyl and benzhydryl hydrodisulfide,[5] and ^{35}S-labeled benzyl hydrodisulfide[3] were prepared and purified by the method reported elsewhere. Triphenyl-[6] and triethylarsines[7] as starting materials, triphenylarsine sulfide[8] and triethylarsine sulfide[9] as authentic materials, and also ^{35}S-labeled triethylarsine sulfide[9] as a standard for counting analysis were prepared by the methods in the literature. Nonlabeled dibenzyl di- and trisulfides[5] and dibenzhydryl disulfide[5] as authentic materials and ^{35}S-labeled dibenzyl disulfide[3] as a radioactive standard were prepared by the method described elsewhere.

Identification and Estimation of the Nonradioactive Reaction Products.—The products and their derivatives which melted above room temperature were identified by mixture melting point with authentic specimens. Hydrogen sulfide evolved during the reaction was determined by the method reported elsewhere.[2] Analysis of the polysulfides mixture was accomplished satisfactorily by using nmr spectroscopy.[1,10] We found in the present research that the nmr technique was also feasible for the products containing thiol in addition to the polysulfide mixture. The nmr spectra of all samples were taken on JNM 3H-60 spectrometer (60 Mc) with tetramethylsilane as the internal standard. τ values of authentic specimens at low concentrations (*ca.* 7%) in carbon tetrachloride were as follows: $C_6H_5CH_2SH$, 8.49 (–SH, triplet) and 6.39 (–CH_2–, doublet); $(C_6H_5CH_2)_2S_2$, 6.49; $(C_6H_5CH_2)_2S_3$, 6.02; $(C_6H_5CH_2)_2S_4$, 5.89; $(C_6H_5CH_2)_2S_5$, 5.85; $(C_6H_5)_2CHSH$, 7.95 (–SH, doublet); and 4.66 (–CH–, doublet).

Chemical shifts of each component in arbitrary concentrations were, of course, slightly different from the above values. For identification, authentic compounds were added to the solution of products and the corresponding peaks were carefully examined. Amounts of the components were determined by comparison of the respective integral values with that of tetrachloroethane (τ *ca.* 5.9) as another internal standard for integral purpose only.

The Reaction of Nonlabeled Aralkyl Hydrodisulfides.—To an ethereal solution of the hydrodisulfide in a flask described elsewhere[2] was added dropwise a solution of the arsine in ether in a stream of nitrogen. For the reaction with triethylarsine, 40 mmol of the hydrodisulfide and 44 mmol of the arsine were used for manipulating convenience, and the results were calculated as described in Table I. Because of easy oxidizability of triethylarsine, its solution was syringed into the flask through a rubber stopper instead of a dropping funnel.[2] The mixture was kept under a gentle stream of nitrogen for 20 hr at room temperature to complete the reaction. Throughout the reaction no evolution of hydrogen sulfide was observed except for the reaction of benzyl hydrodisulfide with triethylarsine. White crystals separated from the solution were collected, weighed, recrystallized from ethanol, and identified as triphenylarsine sulfide, mp and mmp 162°, and triethylarsine sulfide, mp 119°. The arsine sulfides could be estimated nearly quantitatively owing to their low solubility in ether. However, *t*-arsine sulfide has slightly higher solubility and, therefore, gives slightly less yield than *t*-phosphine sulfide.[2,3] Similarly triethylarsine sulfide seems to have slightly higher solubility than triphenylarsine sulfide. The ethereal solution filtered from the arsine sulfide was diluted with ether to 100 ml. The succeeding procedure is described separately for the individual reactions.

A.—For the reaction of hydrodisulfides with triphenylarsine, an aliquot (10 ml) of the solution was titrated with a kerosene solution of cupric oleate,[2,4] which was found in a preliminary experiment to be inert to triphenylarsine. For further identification of the thiol, an ethanolic iodine solution was added to the remaining portion (90 ml) of the ethereal solution. The solution was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, white crystals were recrystallized from the benzene–ethanol mixture and found to be the corresponding disulfide.

B.—For benzhydryl hydrodisulfide with triethylarsine, which was found to interact with cupric oleate, the solvent of an aliquot (50 ml) of the ethereal solution was replaced with carbon tetrachloride. The thiol was determined by nmr spectroscopy from the carbon tetrachloride solution and identified from the remaining portion of ethereal solution by method A.

C.—For benzyl hydrodisulfide with triethylarsine, an aliquot (50 ml) of the ethereal solution was used for nmr spectral identification and determination of α-toluenethiol and dibenzyl trisulfide. The remaining portion of the ethereal solution was used for further identification of the thiol by the method described in A.

Procedure for Benzyl Hydrodisulfide-[^{35}S] with Triethylarsine.—Benzyl hydrodisulfide-[^{35}S] (20 mmol) was allowed to react with triethylarsine (22 mmol) under the same conditions as for the nonradioactive compound. Radioactive thiol (after its conversion into the corresponding disulfide), dibenzyl trisulfide (after desulfuration to the corresponding disulfide by potassium cyanide), and nonradioactive triethylarsine sulfide (as such) were isolated and identified, respectively. Hydrogen sulfide absorbed in iodine solution was released as elementary sulfur and converted into triphenylphosphine sulfide.[3] The products were recrystallized to respective constant activities and subjected to counting analysis by the method reported elsewhere.[3,4]

Reexamination of the Reaction Products of Benzyl Hydrosulfide with Triphenylphosphine.—The products from the reaction of benzyl hydrodisulfide with triphenylphosphine were studied again by the nmr method to find if it can be assumed that dibenzyl tetrasulfide is the intermediate compound leading to dibenzyl disulfide.

The reaction was carried out under the same condition as described in the previous experiment,[2] but, after 1 hr, crystals of triphenylphosphine sulfide that separated from the solution were filtered, and ether was quickly evaporated under reduced pressure. To the oily residue was added an appropriate amount of carbon tetrachloride, and then the nmr spectrum was recorded. In the spectrum, the methylene signal of dibenzyl trisulfide was observed but no signal dibenzyl tetrasulfide appeared. Dibenzyl trisulfide was identified by adding the authentic specimen and by confirmation of no splitting and increase in height of the peak of the trisulfide. When the authentic tetrasulfide was added, another peak corresponding to the tetrasulfide was found in the separated position from the trisulfide.

Registry No.—Triphenylarsine, 603-32-7; triethylarsine, 617-75-4; benzyl hydrodisulfide, 3492-66-8; benzhydryl hydrodisulfide, 3492-67-9; benzyl hydrodisulfide-[^{35}S], 6379-78-8.

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