obtained. The ethanol-insoluble part (34 g) was cyano copper (I) complex **2**, containing no halogen. An analytical sample of **1** was obtained by recrystallization several times from benzene or from acetonitrile–diethyl ether mixture. The ethanol-insoluble part **2** was sufficiently pure for analysis. It is slightly soluble in hot acetonitrile. Analytical data and physical properties of **1** and **2** are given in Table I. Total yield of the complexes (**1** plus **2**) was practically quantitative based on Cu(I) ion. The complexes **1** and **2** were identified as bromotris(*t*-butyl isocyanide)copper(I) and cyano(*t*-butyl isocyanide)copper(I), respectively, by the elemental analysis, infrared spectra (Table I), and mixture melting point test with the authentic complexes prepared by known methods[21] (see also Chart I).

A mixture of 5.0 g (50 mmoles) of cuprous chloride, 40 ml (1 mole) of hydrogen cyanide, and 24 ml (250 mmoles) of isobutene was heated at 100° for 5 hr. Similar work-up gave 2.6 g of the insoluble complex **2**, and ethanol-soluble solids. Recrystallization of the latter solids from acetonitrile–diethyl ether gave 2.8 g of a mixture of chloro copper(I) complexes. Because of the instability in solution, pure tris(*t*-butyl isocyanide) complex, $[(CH_3)_3CNC]_3CuCl$, could not be obtained. Analysis suggested that it is contaminated with probably bis(isocyanide) complex. Repeated recrystallization of the impure chloro isocyanide complex from a hot mixture of acetonitrile–ether gave a small amount of cyanobis(*t*-butyl isocyanide)copper(I), $[(CH_3)_3CNC]_2CuCN$, mp 173–175°, which did not show a melting point depression with an authentic sample.

Anal. Calcd for $CuC_{11}H_{19}N_3$: C, 51.64; H, 7.09; Cu, 24.84; N, 16.43. Found: C, 51.59; H, 7.29; Cu, 24.87; N, 16.18.

A mixture of 19.0 g (0.1 mole) of cuprous iodide, 20 ml (0.5 mole) of hydrogen cyanide, and 47 ml (0.5 mole) of isobutene was heated at 100° for 5 hr. The residual product after freeing from unchanged reactants was soluble in cold ethanol. Iodobis(*t*-butyl isocyanide)copper(I) seems to constitute the major component, although the analytical results were unsatisfactory, since repeated crystallization from ethanol or ethanol–ether mixture resulted in steady decrease in isocyanide ligands. Finally a small amount of the complex **2** was obtained.

Similarly a mixture of cuprous cyanide, hydrogen cyanide, and isobutene was heated up to 100° for 5 hr. Cuprous cyanide was remained unchanged.

B. With Solvents.—A mixture of 3.6 g (25 mmoles) of cuprous bromide, 10 ml (250 mmoles) of hydrogen cyanide, 24 ml (250 mmoles) of isobutene, and 20 ml of water was heated at 50° for 24 hr in a glass ampoule. The reaction mixture after being freed from the unchanged reactants was filtered to isolate 2.8 g of an isoluble complex which was identified as **2**. About 10 g of *t*-butyl alcohol was obtained from an ether extract of the filtrate and 0.15 g of *t*-butylamine hydrogen bromide from the aqueous filtrate. Gas chromatographic analysis of the above *t*-butyl alcohol fraction indicated presence of *t*-butyl bromide in 4–5% of the butyl alcohol.

Similarly the reaction was carried out in various solvents. The results are summarized in Table II.

Formation of Cyano(*t*-butyl isocyanide)copper(I) (2).—Suspension of 1.0 g of bromotris(*t*-butyl isocyanide)copper(I) (**1**) in 30 ml of water was boiled for 2 hr to give 0.37 g (84% yield) of colorless crystals, mp 196–198° (from acetonitrile). The benzene solution of **1** was refluxed overnight to give a small amount of the same product. The infrared spectrum and mixture melting point test revealed it to be cyano(*t*-butyl isocyanide)copper(I) (**2**). The authentic sample was prepared from cyanobis(*t*-butyl isocyanide)copper(I) by repeated recrystallization from a chloroform–ether mixture.

Alkylation with Olefins Other Than Isobutene.—In general, a mixture of an olefin, hydrogen cyanide, and cuprous bromide in a mole ratio of 4:4:1 was heated at 100° for 5 hr. Cuprous complexes were not isolated; instead they were decomposed similarly by aqueous potassium cyanide to release the isocyanide ligands. Table III summarized physical properties, yield, and analytical data of the *t*-alkyl isocyanide thus obtained.

Modified Passerini Reaction of Complex 1.—Complex **1** (4 g, 10.2 mmoles) was dissolved in a mixture of 40 ml of acetone and 10 ml of 6 *N* hydrobromic acid. The solution was stirred at room temperature for 30 min and then heated at 40° for 2 hr. Usual work-up with diethyl ether gave 3.62 g of colorless crystals which were recrystallized from *n*-hexane and sublimed to give analytical sample **6** as platelets, mp 96–97°.

Anal. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.40; H, 10.69; N, 8.95.

Compound **6** was identified as N-*t*-butyl-2-methyl-2-hydroxypropionamide by synthesis; *viz*, α-bromoisobutyronitrile prepared according to a known method[25] was subjected to Ritter reaction to give N-*t*-butyl-2-methyl-2-bromopropionamide,[26] mp 87–88°. This was hydrolyzed to **6**. Alternatively **6** can be made by aminolysis of the corresponding hydroxy ester (Chart I).

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(25) C. L. Stevens, *J. Am. Chem. Soc.*, **70**, 167 (1948).

(26) J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).

Aralkyl Hydrodisulfides.[1] VII. The Reaction with Trisubstituted Phosphites

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Received May 11, 1966

Benzyl hydrodisulfide, $C_6H_5CH_2SSH$, is attacked competitively both on sulfenyl and sulfhydryl sulfur atoms by triethyl phosphite, $(EtO)_3P$, and gives triethyl phosphorothionate, $(EtO)_3PS$, α-toluenethiol, dibenzyl disulfide, hydrogen sulfide, and toluene. The reactions of triethyl phosphite with benzhydryl or triphenylmethyl hydrodisulfide and of triphenyl phosphite with benzyl or benzhydryl hydrodisulfide occur only on sulfhydryl sulfur atom yielding the corresponding trisubstituted phosphorothionate and thiol. As for the reaction with tertiary phosphine, steric hindrance is concluded here to predominate over other factors. By using benzyl and benzhydryl hydrodisulfides-^{35}S sulfenyl sulfur of which is specifically labeled, activity measurement of the products with triphenyl phosphite confirms the mechanism of sulfhydryl sulfur attack.

Previous work[3] has shown that aralkyl hydrodisulfide, when attacked by tertiary phosphine on the sulfenyl sulfur atom, gives phosphine sulfide, hydrogen sulfide, the corresponding disulfide, and hydrocarbon, and that, when attacked on the sulfhydryl sulfur atom, it yields phosphine sulfide and thiol. These mechanisms were further confirmed in our previous paper[4] by using aralkyl hydrodisulfides labeled with ^{35}S.

In the present work aralkyl hydrodisulfide (benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) was allowed to react with trisubstituted (triethyl or triphenyl) phosphite. It seems interesting to compare the variety and amounts of the present reaction products to those with the phosphine, to determine whether the phosphites behave similarly.

For further confirmation of the mechanism, benzyl and benzhydryl hydrodisulfides, the sulfenyl sulfur atoms of which were labeled with ^{35}S, were allowed to

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(1) Part VI: S. Kawamura, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **31**, 1985 (1966).

(2) Author to whom inquiries should be addressed.

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

(4) T. Nakabayashi, S. Kawamura, T. Kitao, and J. Tsurugi, *ibid.*, **31**, 861 (1966).

react with the triphenyl phosphite as in the reaction[4] with phosphines.

Results and Discussion

The interactions of aralkyl hydrodisulfides with triethyl phosphite at room temperature and with triphenyl phosphite at 60° were carried out in an atmosphere of nitrogen. To bring both reactions to completion, 20 hr is sufficient. The variety and amounts of the products are summarized in Table I. Table I indicates that, with the exception of expt 1, the aralkyl hydrodisulfides react with the phosphites to give the corresponding thiol and O,O,O-trisubstituted phosphorothionate, the latter of which is analogous to tertiary phosphine sulfide. The distribution and amounts of the products indicated in expt 2–6 suggest that the phosphite attacks predominantly the sulfhydryl sulfur, as do phosphines.[3] The distribution and amounts of the products of expt 1 suggest competitive attacks on both the sulfenyl and sulfhydryl sulfur atoms. However, prior to proposing the analogous mechanism, the reactions of trisubstituted phosphite with other organic sulfur compounds should be considered briefly.

Table I

Reactions of Aralkyl Hydrodisulfides with Tertiary Phosphites for 20 Hr

Reactants, mmoles		Products, mmoles					
Expt	R in RSSH	R′ in P(OR′)$_3$	(R′O)$_3$-PS	RSH	RS$_2$R	H$_2$S	RH
1	$C_6H_5CH_2$, 10	C_2H_5, 12	9.5	3.7	1.2	2.7	1.4[a]
2	$(C_6H_5)_2CH$, 10	C_2H_5, 12	9.4	10.0	...	...	...
3	$(C_6H_5)_3C$, 10	C_2H_5, 12	9.9	10.0	...	...	...
4	$C_6H_5CH_2$, 10	C_6H_5, 12	9.8	9.9	...	...	...
5	$(C_6H_5)_2CH$, 10	C_6H_5, 12	9.7	9.8	...	...	...

[a] Toluene, in this case, was estimated by gas chromatography.

The reactions of trialkyl phosphites with thiols and disulfides reported by Walling and Rabinowitz[5] are summarized to be a free-radical process induced by light or a radical initiator. However, independent occurrence of competitive Arbuzov-type process such as

$$RSSR + P(OR')_3 \longrightarrow RS\overset{+}{P}(OR')_3RS^- \longrightarrow RSPO(OR')_2 + RSR' \quad (1)$$

was observed by the same authors[5] in the presence of 0.5 mole % of hydroquinone and at higher temperatures. Harvey, *et al.*,[6] also reported that eq 1 was applicable to the reaction between trialkyl phosphite and symmetrical or unsymmetrical disulfide under similar conditions. In eq 1 the intermediate cleaves at an alkoxy linkage to yield S-substituted O,O-dialkyl phosphorothiolate and RSR′. However, in the case

$$RSSR + P(OR')_3 \longrightarrow RS\overset{+}{P}(OR')_3RS^- \longrightarrow SP(OR')_3 + RSR \quad (2)$$

of dibenzoyl disulfide,[6] cleavage at C–S linkage of the intermediate gives O,O,O-trialkyl phosphorothionate and RSR. When one of the R groups is replaced by H, eq 2 can be applied to the results of expt 2–6 in Table I. We confirmed that the addition of 2 mole % of hydroquinone had no effect on the variety or amounts of products from benzyl hydrodisulfide and triphenyl phosphite. This finding eliminates even an independent competitive occurrence of a free-radical chain process.

Applicability of eq 2 to expt 2–6, and especially analogy with the reaction of phosphine, supports the nucleophilic attack of phosphite on sulfhydryl sulfur of the hydrodisulfide. The sequence can be written as shown below by replacing PR′$_3$ in the sequence reported in our previous paper[3] with P(OR′)$_3$. When sequence A is adapted, by analogy with the phosphine, nucleophilic attack on alternative sulfenyl sulfur atom should give hydrogen sulfide, the corresponding disulfide, hydrocarbon, and O,O,O-trisubstituted phosphorothionate. The result of expt 1 indicates competitive attacks on both sulfenyl and sulfhydryl sulfur atoms. As mentioned in our previous paper,[3] two equivalent sequences can be applied to sulfenyl sulfur attack of the phosphine. Also for the present reaction with phosphites equivalent sequences B and C can be written as shown. To verify the step B-3, dibenzyl tetrasulfide[7] and an equimolar amount of triethyl phosphite in ether were kept standing for 20 hr at room temperature, and found to give dibenzyl disulfide and O,O,O-triethyl phosphorothionate.

$$RSSH + P(OR')_3 \longrightarrow [RS]^-\left[\begin{array}{l} SH \\ | \\ P(OR')_3 \end{array}\right]^+ \longrightarrow RSH + SP(OR')_3 \quad (A)$$

$$RSSH + P(OR')_3 \longrightarrow [R]^-\left[\begin{array}{l} SSH \\ | \\ P(OR')_3 \end{array}\right]^+ \longrightarrow RH + (R'O)_3\overset{+}{P}SS^- \quad (B\text{-}1)$$

$$(R'O)_3\overset{+}{P}SS^- + 2RSSH \longrightarrow H_2S + (R'O)_3PS + RS_4R \quad (B\text{-}2)$$

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

$$RSSH + P(OR')_3 \longrightarrow \left[\begin{array}{l} R\text{—}S \\ \quad\ | \\ \quad\ P(OR')_3 \end{array}\right]^+ [SH]^- \quad (C\text{-}1)$$

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

$$RS\overset{+}{P}(OR')_3 + RSSH \longrightarrow RH + SP(OR')_3 + RSS^+ \quad (C\text{-}3)$$

$$RSS^- + RSS^+ \longrightarrow RSSSSR \xrightarrow[(B\text{-}3)]{2(R'O)_3P} RS_2R \quad (C\text{-}4)$$

The next problem to be solved is to elucidate the reason for competitive attacks on both sulfur atoms occurring only in the reaction of benzyl hydrodisulfide with triethyl phosphite and for only sulfhydryl sulfur attack occurring in other reactions. As stated in our previous papers[1,3,8] the factors that determine which sulfur atom is attacked by a nucleophile are thiophilicity of a nucleophile and steric hindrance of both substrate and nucleophile. Our previous paper[3] clearly indicates that the tertiary phosphine attacks competitively both sulfenyl and sulfhydryl sulfur atoms of benzyl and benzhydryl hydrodisulfides, but attacks only sulfhydryl sulfur of triphenylmethyl hydrodisulfide because of steric hindrance of the substrate. The results in Table I indicate that the sterically less

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(5) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959).

(6) R. G. Harvey, H. I. Jacobson, and E. V. Jensen, *ibid.*, **85**, 1618 (1963). Reference literature on Arbuzov-type reactions was cited therein.

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

(8) S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *ibid.*, **30**, 2711 (1965).

hindered triethyl phosphite can attack sulfenyl sulfur atom of also sterically less hindered benzyl hydrodisulfide. In the reaction of trisubstituted phosphite, steric factor may be considered to predominate over thiophilicity.

In this respect, it is interesting that triphenylmethyl hydrodisulfide reacted only sluggishly with triphenyl phosphite even at 60°, and that vigorous evolution of hydrogen sulfide was observed after 5 hr. This suggests that bulky groups of both the substrate and nucleophile block nucleophilic reaction and that homolitic decomposition of triphenylmethyl hydrodisulfide may initiate the evolution of hydrogen sulfide.

Reaction with ^{35}S-Labeled Aralkyl Hydrodisulfides.—Benzyl and benzhydryl hydrodisulfides, the sulfenyl sulfurs of which were specifically labeled with ^{35}S, were allowed to react with triphenyl phosphite at 60° for 20 hr. The conditions were quite the same as for nonlabeled compounds. The results are shown in Table II. As stated in our previous paper,[4] tracer studies concern only the activities of sulfur compounds separated in radiochemically pure state. Therefore, Table II indicates only specific activities of radiochemically pure reaction products and those of the corresponding radiochemically standard compounds for comparison. The latter compounds were prepared from the same radioactive species (thiourea-^{35}S) as were the aralkyl hydrodisulfides. The conclusion derived from tracer studies will be correct, unless scrambling of labeling occurs between the material and products and also between the labeled products and nonactive products throughout the reaction or separation of the products. The exchange between sulfhydryl sulfur in the starting aralkyl hydrodisulfide and sulfur in the aryl-substituted alkanethiol produced was already shown not to occur in the reaction[4] with triphenylphosphine. The exchange reaction between sulfur atom of triphenyl phosphorothionate and that of α-diphenylmethanethiol-^{35}S was found to occur to a very minor extent under the reaction conditions. Specific activities of the aryl-substituted alkanethiols indicated in Table II clearly confirmed the sequence A, which means that all the sulfur atoms in arylsubstituted alkanethiol stem from the sulfenyl sulfur-^{35}S of the aralkyl hydrodisulfide-^{35}S. Although the specific activities of the triphenylphosphorothionate in Table II seemingly contradict sequence A to a minor extent, they probably result from isotope exchange either between the phosphorothionate and the thiol-^{35}S or between phosphorothionate and the hydrodisulfide-^{35}S. The former exchange reaction was already mentioned above.

TABLE II

SPECIFIC ACTIVITIES OF THE REACTION PRODUCTS OF ARALKYL HYDRODISULFIDES-^{35}S (10 MMOLES) WITH TRIPHENYL PHOSPHITES (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	$B/A \times 100$[b]
For Benzyl Series				
$(C_6H_5O)_3PS$	$(C_6H_5O)_3PS$	8,792	189	2.2 (2.3)[c]
$C_6H_5CH_2SH$	$(C_6H_5CH_2)_2S_2$	28,464	27,935	98.1
For Benzhydryl Series				
$(C_6H_5O)_3PS$	$(C_6H_5O)_3PS$	9,310	191	2.1 (1.9)[c]
$(C_6H_5)_2CHSH$	$[(C_6H_5)_2CH]_2S_2$	14,540	14,620	101

[a] The specific activities of the standards fluctuate because of the different time periods of counting. [b] $B/A \times 100$ indicates the per cent distribution of radioactive sulfur to total sulfur in the products. [c] Figures in parentheses represent the values obtained by double dilution method. See the Experimental Section.

Discussion in Connection with Analogous Reactions.—This item seems interesting at the present time when the mechanisms of nucleophilic attack of trisubstituted phosphite on hydrodisulfide have been made clear. In the reaction of hydroperoxide with trivalent phosphorous compounds, Denney, *et al.*,[9] proposed the mechanisms such as

$$\mathrm{ROOH} + \mathrm{PR'_3} \longrightarrow [\mathrm{RO}]^- [\mathrm{R'_3P{-}OH}]^+ \longrightarrow \mathrm{ROH} + \mathrm{R'_3P{=}O} \quad (3)$$

and disagreed with the mechanism by Walling[5] such as

$$\mathrm{ROOH} + \mathrm{PR'_3} \longrightarrow [\mathrm{R{-}O{-}PR'_3}]^+ [\mathrm{OH}]^- \longrightarrow \mathrm{ROH} + \mathrm{OPR'_3} \quad (4)$$

because Denney observed no isotopic exchange between the intermediate and $H_2{}^{18}O$ used as a solvent. The present paper also supports eq 3 and eliminates eq 4, because the intermediate indicated in eq 4 must give complex variety of the products by analogy with the hydrodisulfides. To explain attack on hydroxy oxygen, steric hindrance was suggested by Denney, and supported by the present paper, because the oxygen atom is less bulky than sulfur and hence more susceptible to steric hindrance of the groups R, which are *trans*-9-decalyl and cumyl, respectively, in Denney's work.

As reported in our previous papers,[1,3,8] in the absence of steric hindrance, sulfenyl sulfur of hydrodisulfide is preferably attacked by even weaker nucleophiles, and sulfhydryl sulfur by stronger nucleophiles in competition with sulfenyl one. This means that the sulfenyl sulfur is more susceptible than the sulfhydryl one. In the presence of steric hindrance this preference is disturbed as in the present paper.

The susceptibility of the sulfur compounds to nucleophilic attack with triethyl phosphite falls in the order RSSH, dibenzoyl disulfide > unsymmetrical disulfide including alkyl alkenyl disulfide[10] > symmetrical disulfide, by referring the present and other papers.[5,6,10] This susceptibility may depend on the rate forming the intermediate indicated in eq 1 or A.

Experimental Section

Materials and Authentic Specimens for the Reactions with Nonradioactive Hydrodisulfides.—Benzyl,[7] benzhydryl,[7] and triphenylmethyl[11] hydrodisulfides were prepared and purified

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

[10] C. G. Moore and B. R. Trego, *J. Chem. Soc.*, 4205 (1962).

[11] T. Nakabayashi, J. Tsurugi, and T. Yabuta, *J. Org. Chem.*, **29**, 1236 (1964).

before use by the methods reported elsewhere. Commercial triethyl and triphenyl phosphites were purified before use by fractional distillation, bp 154–155° (760 mm) and 198–201° (5 mm), respectively. Authentic triethyl[12] or triphenyl[13] phosphorothionate, dibenzyl[3] or dibenzhydryl[3] disulfide, and 2-nitrophenyl triphenylmethyl disulfide[3] were prepared by the method in the literature.

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. Toluene and triethyl phosphorothionate were identified and estimated by gas chromatography in a stream of nitrogen using a column packed with commercial silicon oil DC 550 (Hitachi). Hydrogen sulfide evolved during the reaction was determined by the method[3] reported already.

Procedure for Benzyl Hydrodisulfide with Trisubstituted Phosphites.—Benzyl hydrodisulfide (10 mmoles, 1.5627 g) in 5 ml of ether was placed into a flask described elsewhere.[3] A solution of trisubstituted phosphites (12 mmoles, 1.9940 g for triethyl and 3.7235 g for triphenyl phosphites) in ether was added dropwise to the ethereal solution of hydrodisulfide in a stream of nitrogen. The mixture was kept in a gentle stream of nitrogen for 20 hr (at room temperature for triethyl or at 60° for triphenyl phosphite) to complete the reaction. In the reaction at 60° ether soon escaped from the reaction flask through the condenser by a nitrogen stream.

A.—For triethyl phosphite, the contents of the flask, which contains triethyl phosphorothionate, α-toluenethiol, dibenzyl disulfide, toluene, and unchanged triethyl phosphite, were diluted with ether to 25 ml. To an aliquot (2 ml) of the solution were added benzene and enough elemental sulfur to conuert the excess phosphite into phosphorothionate. In preliminary experiments we found that triethyl phosphite reacts with elemental sulfur at room temperature yielding phosphorothionate which is inert to iodine. Thus, the thiol can be titrated with ethanolic iodine. The solution was kept at room temperature for 2–3 hr after the addition of sulfur, and then titrated. Gas chromatography (at 150°) of other two aliquots (each 10 μl) allowed identification and estimation of toluene and triethyl phosphorothionate. The remaining portion of the ethereal solution, after evaporation of the solvent, gave an oily material, which was dissolved in benzene. The benzene solution was treated with a 10% aqueous potassium hydroxide solution to separate the thiol from the benzene layer and then treated with an ethereal solution of mercuric chloride to remove unchanged triethyl phosphite. After the double salt of mercuric chloride–triethyl phosphite was separated, the benzene layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent and triethyl phosphorothionate under reduced pressure, the solids were weighed, recrystallized from ethanol, and identified as dibenzyl disulfide. For further identification of the thiol the aqueous layer containing potassium thiolate was acidified with 6 *N* hydrochloric acid. The resulting oil was extracted with benzene. To the benzene solution was added an ethanolic iodine solution for conversion to the disulfide. The benzene solution was washed with an aqueous solution of sodium thiosulfate to remove excess iodine, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the solvent, white crystals were recrystallized from a mixture of benzene and ethanol, and found to be dibenzyl disulfide.

B.—When triphenyl phosphite was used, the reaction mixture was diluted with ether to 50 ml. An aliquot (5 ml) of the solution was directly titrated with a kerosene solution of cupric oleate.[14] Contrary to triethyl phosphite, triphenyl phosphite does not react with elementary sulfur at room temperature. Therefore, titration of the thiol with iodine is not applicable in this case. However, we found that the cupric oleate solution can titrate the thiol successfully even in the presence of triphenyl phosphite, but not in the presence of triethyl phosphite. For identification of α-toluenethiol, an aliquot (10 ml) of the ethereal solution was pipetted. The solvent was replaced with benzene. The benzene solution was treated with aqueous potassium hydroxide. The aqueous solution was acidified and extracted with benzene. The benzene solution was treated as described in A and gave dibenzyl disulfide. For estimation of triphenyl phosphorothionate, the remaining portion (35 ml) of the solution was treated with an ethereal solution of mercuric chloride to remove the thiol and unchanged phosphite. The solvent of the filterate was replaced with benzene. The benzene solution was washed with water, dried over anhydrous sodium sulfate, passed through a column packed with silica gel, and eluted with benzene. After evaporating the solvent, the eluate gave white solids which were collected, weighed, recrystallized from ethanol, and found to be triphenyl phosphorothionate.

Procedure for Benzhydryl Hydrodisulfide with Trisubstituted Phosphites.—Benzhydryl hydrodisulfide (10 mmoles, 2.3269 g) was allowed to react with trisubstituted phosphites (12 mmoles) under the same conditions as described for the benzyl compound. Throughout the reaction no evolution of hydrogen sulfide was observed.

A.—For the products with triethyl phosphite, the contents of the flask were diluted with ether to 25 ml. Gas chromatographic analysis of two aliquots (each 10 μl) of the solution indicated the presence of and allowed the determination of the amount of triethyl phosphorothionate. To determine the amount of α-diphenylmethanethiol, another aliquot (5 ml) of the solution was titrated with an ethanolic iodine solution as for the procedure for benzyl hydrodisulfide A. For identification of the thiol the remaining portion of the solution was oxidized with an ethanolic iodine solution. The white crystals which separated from the solution were collected, recrystallized from a benzene–ethanol mixture, and identified as dibenzhydryl disulfide.

B.—When triphenyl phosphite was used, the contents of the flask were diluted with ether to 50 ml. An aliquot (5 ml) of the solution was titrated with cupric oleate as for benzyl hydrodisulfide (B). Another aliquot (10 ml) was oxidized with ethanolic iodine. White crystals which separated were collected, recrystallized, and found to be dibenzhydryl disulfide. From the remaining aliquot, triphenyl phosphorothionate was isolated, weighed, recrystallized, and identified by the procedure for benzyl hydrodisulfide (B).

Procedure for Triphenylmethyl Hydrodisulfide with Trisubstituted Phosphites.—Triphenylmethyl hydrodisulfide (10 mmoles, 3.0847 g) and triethyl phosphite (12 mmoles) both in ether were allowed to stand for 20 hr at room temperature. No hydrogen sulfide was detected. Triethyl phosphorothionate was identified and estimated by gas chromatography. Triphenylmethanethiol was titrated with cupric oleate and identified as 2-nitrophenyl triphenylmethyl disulfide as described in previous paper.[3]

Triphenylmethyl hydrodisulfide (10 mmoles) and triphenyl phosphite (12 mmoles) both in ether were heated at 60°. An aliquot was pipetted at given time intervals and was checked for the thiol produced by aqueous lead acetate solution. Formation of the thiol was not observed during the first 5 hr. Thereafter, vigorous evolution of hydrogen sulfide was observed.

Materials and Authentic Specimens for the Reaction with Radioactive Hydrodisulfides.—Benzyl and benzhydryl hydrodisulfides-^{35}S, of which the sulfenyl sulfur atom was labeled, were prepared *via* the sequence cited below, where R signifies benzyl and benzhydryl groups. Details of the sequence and the specificity of labeling sulfenyl sulfur atom were already reported in previous paper.[4] Triphenyl phosphorothionate-^{35}S, mp 53–54°, as a standard specimen for counting analysis, was prepared by the literature method[5] modified as follows. α-Toluenethiol-^{35}S (3.1 g), triphenyl phosphite (7.8 g), and azobisisobutyronitrile (0.04 g) were placed in a flask equipped with a nitrogen inlet tube, a condenser, and a thermometer. The mixture was kept at 60° for 2 hr under a stream of nitrogen and then allowed to stand overnight at room temperature. Solids (6.5 g) obtained were filtered, recrystallized from ethanol, mp 53–54°, and identified by mixture melting point (53–54°) with an authentic specimen. Dibenzyl and dibenzhydryl disulfides-^{35}S (mp 69–70° and 150–151°, respectively) as standard specimens for counting analysis were prepared by the same method as described elsewhere.[4]

$$\text{thiourea-}^{35}\text{S} \xrightarrow{\text{RBr}} \text{R}^{35}\text{SC(NH}_2\text{)}{=}\overset{+}{\text{N}}\text{H}_2\text{Br}^- \longrightarrow$$

$$\text{R}^{35}\text{SH} \xrightarrow{\text{CH}_3\text{COCl}} \text{R}^{35}\text{SSCOCH}_3 \longrightarrow \text{R}^{35}\text{SSH}$$

Isotopic Exchange of Triphenyl Phosphorothionate with Diphenylmethanethiol-^{35}S in the Presence of Triphenyl Phosphite.—Triphenyl phosphorothionate was examined to determine whether or not its sulfur atom exchanges with that of thiol.

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(12) T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Am. Chem. Soc.*, **67**, 1662 (1945).

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A mixture containing triphenyl phosphorothionate (7.5 mmoles, 2.5677 g), α-diphenylmethanethiol-^{35}S (7.5 mmoles, 1.5023 g), and triphenyl phosphite (1.5 mmoles, 0.4654 g) was kept in a gentle stream of nitrogen for 20 hr at 60°. The mixture was then treated by the same procedure as described for nonradioactive compound and gave benzene solution containing triphenyl phosphorothionate which was free from other compound. Since crystals of the phosphorothionate did not separate for a few days and were expected to have low activity, a double-dilution method was utilized. The benzene solution was diluted with ethanol to 20 ml. To each of two aliquots (2 ml) of the solution was added a known amount (a or a', $a < a'$) of the nonactive triphenyl phosphorothionate. The added crystals dissolved on heating. White crystals of triphenyl phosphorothionate which were isolated by cooling from each aliquot were collected, recrystallized from ethanol, and assayed for radioactivities. The specific activity (S) of the phosphorothionate to be determined is given by the equation

$$S = \frac{bb'(a' - a)}{a'b' - ab}$$

where b and b' represent specific activities resulted from dilution. The results are indicated in Table III.

Table III showed that, under the condition mentioned above, sulfur atom of triphenyl phosphorothionate exchanges with that of α-diphenolmethanethiol-^{35}S to a minor extent (0.8%).

TABLE III

ISOTOPIC EXCHANGE OF TRIPHENYL PHOSPHOROTHIONATE WITH α-DIPHENYLMETHANETHIOL-^{35}S IN THE PRESENCE OF TRIPHENYL PHOSPHITE

$(C_6H_5O)_3PS$ added as a diluent, mg	383.8 (a'), 152.8 (a)
Specific activity of diluted $(C_6H_5O)_3PS$, cpm/mg	18 (b'), 26 (b)
Specific activity (S) of $(C_6H_5O)_3PS$, cpm/mg	37
Specific activity (A) of standard $(C_6H_5O)_3PS$, cpm/mg	4557
$S/A \times 100$, %	0.8

Procedure for Aralkyl Hydrodisulfides-^{35}S, $(C_6H_5)_2CH^{35}SSH$ $C_6H_5CH_2{}^{35}SSH$, with Triphenyl Phosphite.—Benzyl and benzhydryl hydrodisulfides-^{35}S (10 mmoles) were allowed to react with triphenyl phosphite (12 mmoles) under the same conditions as described for the nonactive compounds. Radioactive thiols (after conversion to the corresponding disulfides) and triphenyl phosphorothionate were isolated and identified by the procedures described for the nonactive compounds. The radioactive compounds were recrystallized to constant activities and subjected to counting analysis. The specific activity of triphenyl phosphorothionate was determined also by the double-dilution method because of its low radioactivity (see Table II).

Counting Analysis of the Active Products.—Activities were counted with a Packard Tri-Carb liquid scintillation spectrometer Model 314 using POPOP as a scintillator and toluene as a solvent.

The Synthesis of *cis*- and *trans*-δ-Pinenes *via* Hydroboration of Verbenene

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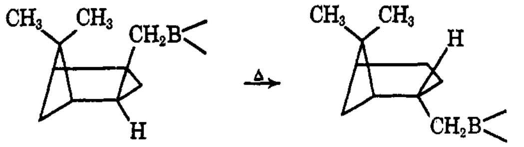
Received June 15, 1966

Bromination of β-pinene with N-bromosuccinimide produces myrtenyl bromide as the major product. α-Pinene reacts under similar conditions to give verbenyl bromide, contaminated with some myrtenyl bromide. Dehydrobromination of either myrtenyl bromide or verbenyl bromide gives verbenene in high yield. The hydroboration of verbenene with bis(3-methyl-2-butyl)borane proceeds selectively at the *exo*-cyclic double bond. Protonolysis of the intermediate organoborane with propionic acid yields *cis*-δ-pinene. Alternatively, hydroboration of verbenene with dicyclohexylborane followed by isomerization and protonolysis affords *trans*-δ-pinene.

In connection with a study on elimination reactions in the pinane series, the *cis*- and *trans*-δ-pinenes were required as reference compounds. *cis*-δ-Pinene has been previously synthesized by thermal decomposition of the xanthates derived from iso- and neoisoverbanol.[1] These alcohols, however, are not readily accessible. The *trans* olefin has been isolated by repeated distillations from a mixture of α-pinene and *trans*-δ-pinene obtained by elimination from pinocampheyl tosylate with sodium ethoxide.[1] It appeared to us, however, that the selective hydroboration of verbenene followed by protonolysis might offer a convenient synthesis of the *cis*- and *trans*-δ-pinenes.

Recent investigations on the hydroboration of β-pinene with diborane revealed that the *cis* addition of the boron-hydrogen bond moiety proceeds from the side away of the *gem*-dimethyl group to produce the less stable of the two possible myrtanylboranes.[2,3] The product, when heated *in situ* with propionic acid, a reaction which proceeds with retention of configuration, was converted into *cis*-pinene.[3] Under the influence of heat, the initially formed organoborane isomerized to the *trans* derivative,[2] which gave *trans*-pinane on protonolysis.[3]



Provided that the *exo*-cyclic double bond of verbenene could be selectively converted into the organoborane, the combination of a hydroboration–protonolysis or a hydroboration–isomerization–protonolysis sequence would result in the formation of *cis*- and *trans*-δ-pinenes, respectively.

Verbenene has previously been synthesized by dehydration of verbenol, obtained from the autooxidation of α-pinene.[4,5] This route, however, gives low yields of the diene and involves tedious isolation procedures. Allylic brominations of olefins with N-bromosuccinimide (NBS) followed by dehydrobromination have been widely used for the preparation of dienes.[6] Thus, the readily accessible pinenes appeared to offer the logical substrates for the preparation of verbenene. Treatment of (−)-β-pinene (100% excess) with NBS in carbon tetrachloride yielded, among the higher boiling components, a monobromide (51%), which by gas

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