Aralkyl Hydrodisulfides. IV. The Reaction of Benzyl Hydrodisulfide with Several Nucleophiles

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Benzyl hydrodisulfide was allowed to react with various anions, such as hydroxide, sulfite, cyanide, and thiolate ions, in a nitrogen stream at room temperature. Hydrogen sulfide, dibenzyl disulfide, and dibenzyl polysulfides or free sulfur were produced from the reactions with hydroxide and sulfite ions, whereas thiols as well as the products cited above were produced from the reactions with cyanide and thiolate ions. It is postulated from these results that less nucleophilic reagents, hydroxide and sulfite ions, preferably attack the α-toluenesulfenyl sulfur atom, while stronger nucleophiles, cyanide and thiolate ions, attack both electrophilic centers, α-toluenesulfenyl and sulfhydryl sulfur atoms in benzyl hydrodisulfide, but still attack mainly the inner sulfenyl sulfur.

In the previous paper[1] the reaction of organic hydrodisulfide with triphenyl- or triethylphosphine was examined. There it was reported that triphenylmethyl hydrodisulfide gives tertiary phosphine sulfide and triphenylmethanethiol, both of which are sulfur analogs of the reaction products of hydroperoxide with tertiary phosphine,[2] and that benzyl or benzhydryl hydrodisulfide gives hydrogen sulfide, the corresponding diaralkyl disulfide, and hydrocarbon, besides tertiary phosphine sulfide and thiol. The formation of these products was explained by assuming that both sulfur atoms of the hydrodisulfide are attacked by the phosphine. Attack on sulfenyl sulfur atom by the phosphine gives hydrogen sulfide, diaralkyl disulfide, hydrocarbon, and tertiary phosphine sulfide; attack on sulfhydryl sulfur atom leads to the thiols and phosphine sulfide. Triphenylmethyl hydrodisulfide is attacked by the phosphine on sulfhydryl sulfur atom only because the alternative sulfenyl sulfur is sterically hindered. Detailed investigation using O^{18}, however, revealed that triphenylphosphine exclusively attacks the outer hydroxyl oxygen of hydroperoxide.[3] Therefore, we considered that each sulfur atom of the hydrodisulfide has a different susceptibility toward nucleophiles from that of the corresponding oxygen atoms of the hydroperoxide.

Nucleophilic scissions of the O–O bond of hydroperoxides have been studied by many investigators. The initial step of the reaction seems to be a proton abstraction by base from the hydroxyl group or α-carbon atom depending on the structure of hydroperoxides.[4,5] Nucleophilic scission of the S–S bond of organic sulfur compounds, especially of organic disulfides, has also been studied. It has been pointed out that the order of nucleophilicity toward sulfur atom is not always consistent with what is determined toward carbon.[6] The nucleophilic order of many nucleophiles for the S–S bond, the so-called thiophilic order which was reviewed and extended by Parker and Kharasch[7,8] and further revised by Pryor,[9] is shown

$$(C_2H_5O)_3P > R^-, HS^-, C_2H_5S^- > C_6H_5S^- > (C_6H_5)_3P, CN^- > SO_3^{-2} > OH^- > 2,4\text{-}(NO_2)_2C_6H_3S^- > N_3^- > SCN^-, I^-, C_6H_5NH_2$$

above, although it is only semiquantitative in nature. However, since hydrodisulfides can be considered to be a special type of unsymmetrical disulfides, the sulfur atoms in the hydrodisulfide may respond differently from those in other disulfides. In the present paper, the reaction of benzyl hydrodisulfide with thiolate, cyanide, sulfite, and hydroxide ions was examined in order to study hydrodisulfide group as an electrophilic center.

Results and Discussion

Possible Reaction Sequences Presumed for Present Reaction.—Four behaviors are possible when the hydrodisulfide group is attacked by a nucleophile: (1) removal of proton attached to outer sulfhydryl group, (2) attack on the outer sulfhydryl sulfur atom, (3) attack on the inner aralkylsulfenyl sulfur atom, and (4) removal of a proton attached to the α-carbon atom.

It is well known that the proton attached to a sulfhydryl group of a thiol is labile, and the thiol is easily converted to its salts by alkali or heavy metal ions. This may also be the case in the hydrodisulfides. Tertiary alkyl hydroperoxides, such as cumene hydroperoxide, which bear no hydrogen on the α-carbon, give only the sodium salt in the presence of a large excess of sodium hydroxide. The hydroperoxide suffers, however, further decomposition to give alcohol and oxygen in the presence of an adequate amount (20%) of sodium hydroxide.[5] When a proton is

$$\text{ROOH} \xrightarrow{\text{excess NaOH}} \text{ROONa}$$

$$\text{ROOH} \xrightarrow{20\%\ \text{NaOH}} \text{ROO}^- \xrightarrow{\text{ROOH}} \text{ROH} + O_2$$

abstracted first from the sulfhydryl group of hydrodisulfide by nucleophile N (as a base), aralkyl disulfide ion will be formed. This disulfide ion may further decompose to thiolate ion and elemental sulfur *via* (1a). A seemingly related example of such a decomposition

$$\text{RSSH} + \text{N}^- \longrightarrow \text{RSS}^- + \text{HN} \quad (1)$$

$$\text{RSS}^- \longrightarrow \text{RS}^- + {}^1/{}_8S_8 \quad (1a)$$

$$\text{RSS}^- + \text{RSSH} \longrightarrow \text{RS}^- + \text{RSH} + {}^1/{}_4S_8 \quad (1b)$$

$$\text{RSS}^- + \text{RSSH} \longrightarrow \text{RSSSR} + \text{SH}^- \quad (1c)$$

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

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

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

[4] M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

[5] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 121.

[6] L. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[7] A. J. Parker and N. Kharasch, *ibid.*, **82**, 3071 (1960).

[8] A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

[9] W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 89.

has been reported by Swan in the hydrolysis of cystine.[10] From the structural viewpoint, 2-amino-2-carboxyethyl disulfide ion formed from cystine is, however, not an adequate example to discuss the nucleophilic decomposition of benzyl hydrodisulfide, and specific reaction sequences such as (1) still remain to be examined. The basic disulfide ion may also induce the decomposition of another hydrodisulfide molecule *via* (1b), which is similar to the reaction of hydroperoxide with base mentioned above.[5] Another possible course is attack of the disulfide ion on another hydrodisulfide molecule to produce trisulfide and hydrosulfide ion as in eq. 1c, just as benzyl disulfide ion attacks acetyl benzyl disulfide to give dibenzyl trisulfide.[11] Hydrodisulfides may be viewed as unusual dialkyl disulfides, wherein one alkyl group is replaced by a hydrogen. Disulfides may display the following behavior when they are attacked by nucleophile. Generally the mercaptide group which has lower thiophilicity is more easily displaced, and when the thiophilicity of N^- is much less than those of RS^- and $R'S^-$, no reaction takes place.[8] The thiophilicities of RS^- and SH^- are of the same magnitudes and therefore either path may occur in the present reaction. If the nucleophile attacks the outer sulfhydryl sulfur, the thiol will be formed and a successive reaction may then follow, as shown below. Reaction 2a, however, would occur when, in turn, thiolate ion attacks the inner sulfenyl sulfur, contrary to the case when the nucleophile attacks preferentially the outer sulfhydryl sulfur, as in (2). In the case when the nucleophile preferentially attacks the inner aralkylsulfenyl sulfur, the intermediate could react successively with another hydrodisulfide molecule and thus produce an aralkyl disulfide or trisulfide. As the final case to be considered, if the nucleophile abstracts a proton attached to the α-carbon atom, thiobenzaldehyde and consequently its high-melting trimer[12] will be produced according to the following sequence. Secondary alkyl hydroperoxides are attacked preferentially on the labile hydrogen attached to α-carbon and give the carbonyl-containing product when allowed to react with base. Hydrogen atom attached to α-carbon of benzyl group is less acidic and hence the reactions suggested for benzyl hydrodisulfide required experimental study.

$$\begin{aligned} RSSR' + N^- &\rightleftharpoons RSN + R'S^- \\ &\rightleftharpoons R'SN + RS^- \end{aligned}$$

$$\underset{\substack{\uparrow \\ N^-}}{RSSH} \longrightarrow RS^- + NSH \qquad (2)$$

$$RSSH + RS^- \longrightarrow RSSR + SH^- \qquad (2a)$$

$$\underset{\substack{\uparrow \\ N^-}}{RSSH} \longrightarrow [RSN] + SH^- \qquad (3)$$

$$\begin{aligned} RSSH + [RSN] &\longrightarrow RSSR + NSH \qquad (3a) \\ &\text{or} \\ &\longrightarrow RSSSR + NH \qquad (3b) \end{aligned}$$

$$C_6H_5CH_2SSH + N^- \longrightarrow C_6H_5\bar{C}HSSH + NH \qquad (4)$$

$$C_6H_5\bar{C}HSSH \longrightarrow C_6H_5CHS + SH^- \qquad (4a)$$

$$3C_6H_5CHS \longrightarrow (C_6H_5CHS)_3 \qquad (4b)$$

When a concentrated aqueous solution of a nucleophile was added to a solution of benzyl hydrodisulfide in dioxane, in a nitrogen stream, the solution immediately became yellow or dark orange and hydrogen sulfide was evolved. Little hydrogen sulfide evolved from strongly basic solutions (*viz.*, hydroxide and thiolate ion solutions). Basicities are in the order $OH^- > RS^- \gg CN^- > SO_3^{-2}$. After 10 or 15 min., the color faded. When the solution was neutralized with dilute hydrochloric acid, after being kept overnight, additional hydrogen sulfide evolved. More hydrogen sulfide evolved when the strongly basic solution was neutralized. Table I summarizes the results. The smaller amount of hydrogen sulfide evolved from the reaction with 1.5 moles of potassium hydroxide and 1.5 moles of cyanide implies that some complicated successive reactions were taking place, and that hydrogen sulfide was consumed from the basic reaction system. When 0.5 mole of nucleophile was used, nearly 0.5 mole of hydrogen sulfide was evolved, but dibenzyl disulfide, one of the products, did not crystallize, probably because of the presence of other impurities, and the subsequent treatment was difficult. Apparently, an induced decomposition predominates in this case, as also in the reaction of hydroperoxides with alkali. Therefore, it seems preferable to carry out the reaction with 1 mole of the hydrodisulfide to each mole of nucleophile. All products for the 1:1 reactions are shown in Table II.

TABLE I

MOLE OF HYDROGEN SULFIDE EVOLVED IN RELATION TO MOLES OF NUCLEOPHILES ADDED/MOLE OF BENZYL HYDRODISULFIDE

	H_2S evolved, mole	
Nucleophile, moles	Immediately after reaction started	When reaction mixture was neutralized
KOH, 1.5	Trace	0.29
KOH, 1.0	Trace	0.45
KOH, 0.5	Trace	0.50
KCN, 1.5	0.04	0.04
KCN, 1.0	0.09	0.10
KCN, 0.5	0.44	Trace

When 1 mole of benzyl hydrodisulfide reacted with an equivalent amount of hydroxide ion, 0.5 mole each of hydrogen sulfide, free sulfur,[13] and dibenzyl disulfide was detected. The finding that neither thiobenzaldehyde nor its trimer was found eliminates the assumed

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[10] J. M. Swan, *Nature*, **179**, 965 (1957).

[11] B. Milligan, B. Saville, and J. M. Swan, *J. Chem. Soc.*, 4629 (1961).

[12] E. Baumann and E. Fromm [*Ber.*, **24**, 1436 (1891)] report m.p. 167°.

[13] When the solvent was removed under reduced pressure from the reaction mixture and an appropriate amount of alcohol was added to the residue, free sulfur precipitated. All free sulfur could not be collected in this way. A small amount of sulfur may be bound in the form of polysulfidic sulfur of dibenzyl polysulfides. At present such sulfur cannot be estimated separately from free sulfur. The polysulfidic sulfur is called "combined sulfur" throughout this paper. Two sulfur components were estimated together from the following desulfurization reaction by triphenylphosphine.[14,15]

$$RSS_nSR \text{ (or free S)} + n(C_6H_5)_3P \longrightarrow RSSR + n(C_6H_5)_3PS$$

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

[15] 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).

TABLE II

THE PRODUCTS FROM THE REACTIONS OF $C_6H_5CH_2SSH$ WITH NUCLEOPHILES (1:1 IN MOLES)[a]

Nucleophile	Thiols, mole	H_2S, mole	Free sultur, g.-atom	Combined sulfur, g.-atom	Disulfide, mole	n[b] in $(C_6H_5CH_2)_2S_r$	SCN^-, g.-ion	$S_2O_3^{-2}$, g.-ion	Material balance H	S	$C_6H_5CH_2$
$C_6H_5S^-$	0.358 {0.257[c] 0.101[d]	0.734		0.277	0.687[e]	2.403			91	92	87[f]
CN^-	0.328	0.185		0.064	0.296	2.218	0.697		70	93	91
SO_3^{-2}	0	0.453		0.174	0.443	2.393		0.306	91	91	89
OH^-	0	0.449	0.474		0.493				90	95	99
$5OH^-$	0	0.408	0.343		0.493				82	87	99

[a] Experiments were carried out in the scale of 0.0192 mole but the amounts of products were recalculated to a 1-mole scale for convenience of discussion. [b] $n = 2$ represents pure disulfide, $n = 3$ represents apparent trisulfide; actually, it must be composed of disulfide, trisulfide, and higher polysulfides. [c] The amount of benzenethiol. [d] The amount of α-toluenethiol. [e] In this case, it is probably the mixture of dibenzyl, benzyl phenyl, and diphenyl disulfide. [f] The sum of both groups, phenyl and benzyl.

reaction sequence 4. Furthermore, since no α-toluenethiol was detected, the assumed sequence 2 is also excluded. Preliminary experiments showed that α-toluenethiol is stable enough to be detectable under the reaction condition studied, although, since dioxane is a solvent which is fairly easily autoxidized, if any peroxide is present in the reaction system, α-toluenethiol may be easily oxidized to dibenzyl disulfide. Further, if any peroxide was present in the system, the full 0.5 mole of hydrogen sulfide would not be evolved since benzyl hydrodisulfide is more easily oxidized than α-toluenethiol and must give dibenzyl tetrasulfide. For these reasons, the reaction sequence 2 cannot be the main reaction path, and the remaining possibility is sequence 1 and/or 3.

Table II indicates that the addition of a large excess of potassium hydroxide did not yield the potassium salt of the hydrodisulfide, but rather the similar products of those of the equimolar reaction. This result therefore eliminates assumed sequence 1, and the formation of the reaction products with hydroxide ion can be explained by a route involving nucleophilic attack on the inner sulfenyl sulfur, namely reaction sequence 3. The intermediate α-toluenesulfenic acid is considered to be unstable, by analogy with other sulfenic acids.[16] The interaction of the acid with another molecule of hydrodisulfide could give dibenzyl disulfide as the main product ($R = C_6H_5CH_2$). At

$$\mathrm{RSSH + OH^- \longrightarrow RSOH + SH^-}$$
$$\mathrm{RSSH + RSOH \longrightarrow RSSR + (HSOH)}$$
$$\mathrm{(HSOH) \longrightarrow {}^1/_8S_8 + H_2O}$$

first glance, it seems strange that hydroxide ion which is considered to be most basic among the nucleophiles used here abstracts no proton. However, Edwards and Pearson[17,18] postulated that the major factors determining nucleophilic reactivity are basicity and polarizability of nucleophiles, and that polarizability becomes more important for nucleophilic attack on oxygen and bivalent sulfur atoms as a substrate. Polarizability will be of greater importance in the case of sulfur, which has a more complicated electronic structure than oxygen. Therefore, it appears reasonable to consider that, when hydrodisulfide is attacked by a nucleophile, S–S bond fission occurs preferentially, as in the reaction of hydrodisulfide with tertiary phosphine.[1]

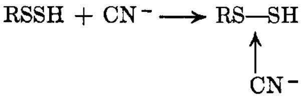
The reaction of benzyl hydrodisulfide with sulfite ion was found to exhibit the same characteristic feature as that with hydroxide ion. In this case, however, thiosulfate ion was formed in place of free sulfur, and the "combined sulfur" in Table II represents the net sulfur content as polysulfidic sulfur of dibenzyl polysulfides.[13] Also in this case, reaction 2 is implausible

$$\mathrm{RSSH + SO_3^{-2} \longrightarrow RSSO_3^- + SH^-}$$
$$\mathrm{RSSH + RSSO_3^- \longrightarrow RSSR + HS_2O_3^-}$$
$$\mathrm{(R = C_6H_5CH_2)}$$

since no thiol was found. The following reactions (reaction 1) are also implausible because reaction 5 is improbable at a low temperature.[19]

$$\mathrm{RSSH + SO_3^{-2} \longrightarrow RSS^- + HSO_3^-}$$
$$\mathrm{RSS^- + RSSH \longrightarrow RSSSR + SH^-}$$
$$\mathrm{RSSSR + SO_3^{-2} \longrightarrow RSSR + S_2O_3^{-2}} \qquad (5)$$
$$\mathrm{(R = C_6H_5CH_2)}$$

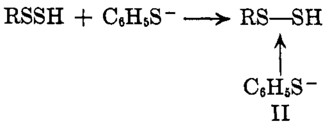
Contrary to the above two nucleophiles, cyanide and thiolate ions seem to attack hydrodisulfide on both sulfur atoms, since α-toluenethiol was formed, as well as hydrogen sulfide, the disulfide, and polysulfides. As stated above, the formation of α-toluenethiol can be explained by assumed sequence 2. The main reaction paths, therefore, may be written as follows



$$\mathrm{RSSH + CN^- \longrightarrow \underset{\substack{\uparrow\\ CN^-}}{RS{-}SH}}$$

I

$$\mathrm{I \longrightarrow RSCN + SH^-}$$
$$\mathrm{RSSH + RSCN \longrightarrow RSSR + HSCN} \qquad (6)$$
$$\mathrm{I \longrightarrow RS^- + HSCN}$$



$$\mathrm{RSSH + C_6H_5S^- \longrightarrow \underset{\substack{\uparrow\\ C_6H_5S^-}}{RS{-}SH}}$$

II

$$\mathrm{II \longrightarrow RSSC_6H_5 + SH^-}$$
$$\mathrm{II \longrightarrow RS^- + C_6H_5SSH}$$

($R = C_6H_5CH_2$). Step 6 seems to be reasonable, since benzyl disulfide was obtained when authentic benzyl thiocyanate was allowed to react with an equimolar amount of benzyl hydrodisulfide. This is presumed from the result that benzyl disulfide and hydrogen sulfide were the main products when benzyl

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[16] N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 327 (1947).

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

[18] J. O. Edwards and R. G. Pearson, *ibid.*, **76**, 1540 (1954).

[19] E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1531 (1947).

hydrodisulfide was treated with sodium α-toluenethiolate.

In view of the above over-all reactions, it is concluded that, as far as these four nucleophiles are concerned, less nucleophilic reagents, such as hydroxide ion and sulfite ion, preferably attack the inner α-toluenesulfenyl sulfur atom in benzyl hydrodisulfide, and while stronger nucleophiles such as cyanide ion and thiolate ion attack both electrophilic centers, the attack is mainly on the inner sulfur atom. The questions still remain as to why these nucleophiles preferably attack the inner aralkylsulfenyl sulfur and why hydrosulfide ion is easily displaced in spite of the fact that the hydrosulfide ion itself is a very strong nucleophile as seen in the thiophilic order cited above. Parker and Kharasch[8] pointed out as a general rule that more nucleophilic N displaces another less nucleophilic X in a substrate SX, although the reaction is somewhat reversible. Solvation of SH^- may be important. At present, these points are not clear.

$$N + SX \longrightarrow SN + X$$

However, two significant similarities are observed between the reactions of hydrodisulfide with tertiary phosphine[1] and with inorganic nucleophiles. First, in the absence of steric hindrance, the less nucleophilic reagent attacks the inner sulfenyl sulfur, whereas the more nucleophilic one attacks both the inner and outer sulfur atoms. Secondly, attack on the outer sulfur atom yields the thiol and the other sulfur-containing products, whereas attack on the inner sulfur atom yields hydrogen sulfide, diaralkyl disulfide, and other products.

Experimental

Materials.—Benzyl hydrodisulfide was prepared by the previous method.[20] Benzyl thiocyanate was prepared by the condensation of benzyl chloride with potassium thiocyanate.[21] Other substances, potassium salts used as reagent nucleophiles, benzene- and α-toluenethiol, and dioxane were the commercial products.

The Reaction of Benzyl Hydrodisulfide with Nucleophiles.—Benzyl hydrodisulfide (3 g., 0.0192 *M*) in 20–60 ml. of dioxane was placed into a three-necked flask equipped with a dropping funnel, a thermometer, and gas inlet and outlet tubes. Nitrogen was bubbled into the solution for 30 min. An equimolar amount of nucleophile (potassium hydroxide, sulfite, or cyanide) dissolved in 10–30 ml. of water was then introduced into the hydrodisulfide solution from a dropping funnel under continuous bubbling of nitrogen at room temperature. In the case of potassium benzenethiolate, it was prepared with an equimolar amount of benzenethiol and aqueous potassium hydroxide, and used as a nucleophile. The solution became yellow or dark orange, and from a weakly basic solution (*e.g.*, with sulfite) most of the hydrogen sulfide was evolved and absorbed in aqueous iodine solution. The color almost faded after 10 or 15 min. The solution was kept overnight, then 4 *N* hydrochloric acid was added until the solution became weakly acidic. Additional hydrogen sulfide evolved at this time. (Qualitative gas chromatographic analysis was made after the neutralization.) After addition of about 200 ml. of water, the solution was extracted with about 100 ml. of benzene and dried over anhydrous sodium sulfate. The thiols were determined by using this benzene solution. An aliquot of the benzene solution was desulfurized with an excess of triphenylphosphine. Thus, the total sulfur content, which consists of free sulfur and combined sulfur was estimated. Then thiols in the remaining portion of the solution were converted to the disulfide by adding alcoholic iodine solution. After the solvent was removed from the solution, under reduced pressure, below 40°, oil or in many cases white crystals were obtained. In the case of the reaction of dibenzyl hydrodisulfide with potassium hydroxide, when alcohol was added to the residual oil or crystals, free sulfur precipitated and the oil crystallized. Benzyl disulfide, containing a small amount of polysulfides, obtained in this way, had m.p. 66–69°, m.m.p. 67–70° with authentic benzyl disulfide. After recrystallization from alcohol, the product melted at 69–70°.[22] The residual oil or crystals were desulfurized with sodium sulfite in a benzene–water mixture, in a nitrogen stream at 90°. The resulting dibenzyl disulfide was collected and weighed. The disulfide formed from α-toluenethiol was subtracted from this value. The products obtained are listed in Table II, where the molar amounts of all compounds are conveniently calculated for those which would be obtained when 1 mole of the hydrodisulfide and the respective nucleophiles were employed.

The Reactions of Benzyl Hydrodisulfide with Sodium α-Toluenethiolate and with Benzyl Thiocyanate.—To 3.1 g. of benzyl hydrodisulfide in dioxane was added an aqueous solution of an equimolar amount of sodium α-toluenethiolate, under a nitrogen stream at room temperature, and then was kept overnight. After neutralization and addition of water, the reaction mixture was extracted with ether, and ether was removed. White crystals that formed were collected, m.p. 69–70°, 4.2 g. (86%). Similarly, 2.5 g. of benzyl hydrodisulfide and 2.5 g. of benzyl thiocyanate were allowed to react under a nitrogen stream at room temperature. Dibenzyl disulfide obtained melted at 67–69°.

Estimation of the Reaction Products.—Hydrogen sulfide, evolved from the reaction of 0.005 *M* benzyl hydrodisulfide and the potassium salts, was absorbed in 0.05 *M* aqueous iodine solution. Then the excess of iodine was titrated with 0.05 *M* sodium thiosulfate solution. Thiols were estimated by gas chromatographic analysis. An aliquot (0.05 or 0.1 ml.) of a benzene extract was injected into a column (5-mm. diameter, 1 m. in length) which was packed with Celite impregnated with high-vacuum silicon grease (30%), with hydrogen gas as carrier (59 cc./min.), at 108°. Under these conditions, the retention times for benzene- and α-toluenethiol were 10 and 18 min., respectively. The contents of the thiols in the solution were calculated in comparison with authentic thiols. The amount of dibenzyl disulfide was determined by weighing the crystals obtained by removal of solvent from the benzene extract and further by extraction of free sulfur and combined sulfur[13] with sodium sulfite. The total sulfur, which consists of free sulfur and combined sulfur, was estimated together by desulfurization of an aliquot of the extract with triphenylphosphine. Thiocyanate ion in the aqueous solution remaining after benzene extraction was evaluated by photometric determination of the colored solution formed with ferric chloride, in comparison with standard potassium thiocyanate solution. Small deviations resulting from cyanide ion present were neglected. Thiosulfate ion was estimated as follows. Coexisting sulfite ion was removed by addition of strontium nitrate. A 0.05 *M* iodine solution then was added to the aqueous solution and excess iodine was titrated with standard sodium thiosulfate solution.

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

(21) H. B. Footner and S. Smiles, *J. Chem. Soc.*, **127**, 2887 (1925).

(22) *Cf.* dibenzyl monosulfide, 48.5°; disulfide, 70°; trisulfide, 48°; tetrasulfide, 53.5–54°; pentasulfide, 57.5–58.5°.[20] Crystals obtained from the reaction of benzyl hydrodisulfide with benzenethiolate melted in the range *ca.* 35–60°; *cf.* diphenyl disulfide, 40°.