Aralkyl Hydrodisulfides.[1] VIII. Alkaline Decomposition and Its Competition with Nucleophiles

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By reexamination of the reaction of benzyl hydrodisulfide with potassium hydroxide another mechanism has proved favorable, that involving proton abstraction followed by elimination of the hydrodisulfide ion. When a decreased amount of potassium hydroxide was added to the hydrodisulfide, a mixture of benzyl polysulfides was formed, the formation of which is attributed to hydropolysulfide ion. Nucleophilic attack by cyanide ion appears to proceed competitively with alkaline decomposition in the reaction of benzyl hydrodisulfide with potassium cyanide in aqueous dioxane. The formation of polysulfides in this case is also discussed.

A More Plausible Route for Alkaline Decomposition.—A previous study[2] has confirmed nucleophilic attack on both sulfur atoms of benzyl hydrodisulfide by anions. For the reaction with hydroxide ion, however, it appears that the following sequence also interprets the products, about 0.5 mol each of hydrogen sulfide, dibenzyl disulfide, and sulfur.

$$\mathrm{RSSH + OH^- \longrightarrow RSS^- + H_2O} \qquad (1)$$

$$\mathrm{RSSH + RSS^- \longrightarrow RSSR + HS_2^-} \qquad (1a)$$

$$\mathrm{HS_2^- \xrightarrow{H^+} H_2S + {}^1/_8S_8} \qquad (1b)$$

Proton abstraction (eq 1) was once abandoned because the products and their amounts did not coincide with those from the assumed sequence[2] subsequent to eq 1. Then the nucleophilic attack on sulfenyl sulfur was considered.

$$\mathrm{RSSH + OH^- \longrightarrow [RSOH] + SH^-} \qquad (2a)$$

$$\mathrm{RSSH + [RSOH] \longrightarrow RSSR + [HSOH]} \qquad (2b)$$

$$\mathrm{[HSOH] \longrightarrow H_2O + {}^1/_8S_8} \qquad (2c)$$

The objectives of this paper are to determine if the sequence in eq 1 is preferable to that in eq 2 in the reaction of the hydrodisulfide with alkali and to examine whether or not hydroxide ion in the reaction with the hydrodisulfide is competitive with nucleophiles (RS^-, CN^-, and SO_3^{2-}), since they give definite concentrations of hydroxide ion due to hydrolysis in aqueous solutions.

First, benzyl hydrodisulfide solution was added quickly to aqueous potassium hydroxide and immediately the resulting mixture was neutralized. Such treatment shows that the reaction of benzyl hydrodisulfide with alkali was a fast reaction and that benzyl disulfide was formed even before neutralization (expt 1 and 2 in Table I). Thus, the succeeding step (eq 1a) is faster than that of eq 1 and this fact makes it impossible to recover the potassium salt of the hydrodisulfide, which had been expected to be produced in the previous paper.[2]

TABLE I
THE REACTION OF BENZYL HYDRODISULFIDE (1 MOL) WITH POTASSIUM HYDROXIDE AND SODIUM HYDROSULFIDE IN DIOXANE–WATER (20 ML:10 ML) MIXTURE

		Product, mol or g-atom				
Expt	Reactant	H_2S	RSSR	RS_nR[c]	Polysulfidic sulfur,[d] S_x	Free sulfur
1[a]	5KOH	0.45	0.50			0.43
2[a]	5KOH	0.38	0.45[b]			0.79
3	pH 10 (with KOH)	0.41	0.21	0.30	0.46	
4	pH 13 (with KOH)	0.50	0.29	0.22	0.40	
5	NaSH	1.21	0.35	0.18	0.33	
6	NaS_2H (NaSH + S)	1.44	0.19	0.30	0.60	0.59

[a] The products after quick addition of the reactant and immediate neutralization of the mixture. [b] Extracted before the neutralization. [c] The sum of molarities of polysulfides (n = 3–5). [d] S_x in RSS_xSR.

When the colored aqueous layer in expt 2 was neutralized, its color faded, and at the same time hydrogen sulfide was evolved and free sulfur precipitated. These phenomena show that sulfur had been dissolved in the basic medium, a fact that is well known from other cases.[3] Separate experiments proved that the dioxane–water mixture also dissolves sulfur in the presence of OH^- or SH^- under our experimental conditions and exhibits similar color formation. The absorption maxima resemble well that of the reaction of benzyl hydrodisulfide (Figure 1). Slight dissimilarities seem to result from sulfur chains involving an indefinite number of sulfur atoms.[4–6] All these facts point to the existence of HS_x^-, which was formed from disproportionation of HS_2^- as shown in eq 1a.

When a large amount of potassium hydroxide (at least over 0.5 mol based on the hydrodisulfide) exists in the reaction of the hydrodisulfide, about a half mole each of hydrogen sulfide, the disulfide, and sulfur are produced. Experiments 3 and 4 (Table I) indicate that an insufficient amount of potassium hydroxide produces polysulfidic mixtures at the expense of elemental sulfur. Under these conditions hydroxide was rapidly consumed (eq 1) at earlier stages of the reactions, and the resulting hydrodisulfide ion reacted with remaining benzyl hydrodisulfide to give polysulfides, although the actual paths are not

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[1] Part VII: T. Nakabayashi, J. Tsurugi, S. Kawamura, T. Kitao, M. Ui, and M. Nose, *J. Org. Chem.*, **31**, 4174 (1966).

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

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Table II

Reaction of Benzyl Hydrodisulfide (1 mol) with Cyanide, Thiolate, and Sulfite

			Product, mol or g-atom				
Expt	Reactant	Solvent	H_2S	RSH	RSSR	Polysulfidic sulfur, S_x	SCN^- or $S_2O_3^{2-}$
7[a]	KOH	Dioxane–water	0.45	0	0.49	(0.47)[b]	
8	KCN + KOH	Dioxane–water	0.33	0.24	0.37	Trace[c]	0.61
9	KCN + 0.1KOH	Dioxane–water	0.23	0.31	0.33	Trace[c]	0.66
10[a]	KCN	Dioxane–water	0.19	0.33	0.30	0.06	0.70
11	1.2KCN	Dioxane	0.31	0.08	0.45	Trace[c]	0.51
12	1.2RSNa	Dioxane	0.85	0.12	0.89	0	
13	$1.2Na_2SO_3$	Dioxane	0.44	0.18	0.03	0.53[d]	0.03

[a] Cited from ref 2. [b] Free sulfur. [c] From nmr, RS_3R. [d] Bonded as RS_3R, RS_4R, and RS_5R.

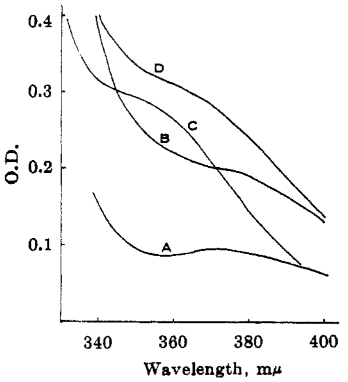

Figure 1.—Ultraviolet spectra of sulfur in dioxane–water. (A) contains KOH, (B) NaSH and KOH, (C) $C_6H_5CH_2SH$ and KOH, (D) benzyl hydrodisulfide and KOH. Each except D contains 10 mg of sulfur. See Experimental Section.

well understood. We therefore offer tentatively the sequence shown in eq 3a–d for the polysulfide formation.

$$HS_2^- \rightleftharpoons HS^-, HS_2^-, HS_3^- \cdots HS_x^- \quad (3a)$$

$$RSSH + HS_x^- \longrightarrow RSS_xH + SH^- \quad (3b)$$

$$RSS_xH \xrightarrow{B} RSS_x^- \quad (3c)$$

$$RSSH + RSS_x^- \longrightarrow RSS_xSR + SH^- \quad (3d)$$

Formation of polysulfide by thio anions, HS^-, HS_2^-, $HS_3^- \cdots HS_x^-$, is clear from the results of expt 5 and 6 (Table I). It is concluded from these data that the attack by hydroxide is faster than the attack by the thio anions.

The results appear in Table I and other facts are thus explained by the assumed sequence 1. The sequence 2 based on the initial sulfenyl sulfur attack, on the contrary, tells us nothing about the polysulfide formation at an insufficient concentration of the hydroxide ion or about the color of the reaction mixture mentioned above. Moreover, from the sequence 2, we can expect the formation of at least detectable amounts of stable oxygen-containing compounds such as RS(O)SR, $RS(O_2)SR$, or RSO_3H by the mutual interaction of the intermediate[7,8] RSOH in eq 2a.

Competition of Alkaline Decomposition with Nucleophilic Attack.—In previous papers,[2,9–12] it was concluded that nucleophilic attack on both sulfur atoms of hydrodisulfides occurs (for example, eq 4, 4a, and 5).

$$RSSH + CN^- \longrightarrow RSCN + SH^- \quad (4)$$

$$RSSH + RSCN \longrightarrow RSSR + HSCN \quad (4a)$$

$$RSSH + CN^- \longrightarrow RS^- + HSCN \quad (5)$$

We have tried to determine whether alkaline hydrolysis of hydrodisulfides was also taking place in such aqueous systems. Addition of alkali to the reaction system with cyanide considerably changed the amounts of products (expt 8 and 9 in Table II). We would like to know the reaction with CN^- alone, and tried to carry out reactions under anhydrous conditions. Under these conditions, the reaction proceeded heterogeneously and gave mainly hydrogen sulfide, dibenzyl disulfide, and thiocyanate ion (Table II, expt 11). In the case of the reaction with α-toluenethiolate, hydrogen sulfide and the disulfide were the main products (Table II, expt 12). Therefore, eq 4 and 4a in expt 11 and eq 6 in expt 12 are major reactions.

$$RSSH + RSNa \longrightarrow RSSR + NaSH \quad (6)$$

Formation of polysulfides is attributed to the competitive alkaline decomposition of the hydrodisulfide. Thio anion HS_x^- formed by the decomposition (in sequence 1), will give polysulfenyl ion as in eq 3c which in turn will react with the hydrodisulfide as in eq 3d.

In view of above results, it is likely that nucleophilic attack on both sulfur atoms occur, besides minor alkaline decomposition.

Treatment of sodium sulfite, under anhydrous conditions (Table II, expt 13), with benzyl hydrodisulfide was a sluggish reaction that yielded a large amount of the dibenzyl polysulfides and an extremely small amount of thiosulfate ion which was different from those in aqueous medium.[2] Thus the reaction under anhydrous conditions seems to be a decomposition similar to that of benzhydryl hydrodisulfide induced by sulfite ion as reported in the previous paper.[11]

Experimental Section

Benzyl hydrodisulfide was prepared and purified before use by a method reported elsewhere.[13] Powdered sodium hydrosulfide was prepared from the treatment of sodium ethoxide with hydrogen sulfide in ethanol and its precipitation from ether. Sodium α-toluenethiolate was prepared from the treatment of α-toluenethiol with metallic sodium in a small amount of ether. Inorganic salts were commercial, extra pure. Dioxane was purified before use by boiling with metallic sodium. Dibenzyl disulfide was identified by mixture melting point

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[11] S. Kawamura, T. Nakabayashi, T. Kitao, and J. Tsurugi, *ibid.*, **31**, 1985 (1966).

[12] T. Nakabayashi, J. Tsurugi, S. Kawamura, T. Kitao, M. Ui, and M. Nose, *ibid.*, **31**, 4174 (1966).

[13] J. Tsurugi and T. Nakabayashi, *ibid.*, **24**, 807 (1959).

when it contained little or no polysulfides (expt 1, 2, 8, 9, 11 and 12). Nuclear magnetic resonance spectra were taken on a JNM 3H-60 spectrometer, with tetramethylsilane as an internal standard. Ultraviolet spectra were recorded on a Shimadzu SV-50 spectrometer. Analytical procedures for other reaction products, hydrogen sulfide, α-toluenethiol, and thioanions were the same as in the previous study.[2]

Ultraviolet Spectra of Basic Mixtures.—Three dioxane–water (20 ml:10 ml) mixtures, containing (A) 1.08 g of potassium hydroxide, (B) 0.54 g of sodium hydrosulfide and 1.08 g of potassium hydroxide, and (C) 1.19 g of α-toluenethiol and 1.08 g of potassium hydroxide, were prepared. To each mixture. 10 mg of sulfur was added. A portion of the upper dioxane-rich layer was pipetted and was subjected to uv analysis (Figure 1), Positions of the maxima and their intensities considerably changed depending on temperature and time. The maximum for the sample prepared from 1 drop of the hydrodisulfide and A was also shown in Figure 1. The mixtures A, B, and C dissolved 0.9, 1.2, and 1.4 g, respectively, of crystalline sulfur at equilibrium (with stirring overnight at room temperature).

Procedure for the Reaction with Potassium Hydroxide.—In a three-necked flask on an ice bath equipped with an equilibrated dropping funnel, a thermometer, and nitrogen gas inlet and outlet tubes, the latter of which was connected with absorbing bottles of hydrogen sulfide, are placed 5 g (90 mmol) of KOH and 10 ml of water. Benzyl hydrodisulfide, 2.92 g (18.7 mmol) in 20 ml of dioxane which was bubbled with nitrogen in advance, was added to the flask from the dropping funnel for 3 min with magnetic stirring under a nitrogen atmosphere. The temperature rose to 32° and the reaction mixture became a deep red. After 2 min it was neutralized with 4 *N* hydrochloric acid until it became weakly acidic. Then the color was discharged and hydrogen sulfide evolved. The neutralized mixture was extracted with benzene. Dibenzyl disulfide and sulfur from the extract were analyzed by the previous method.[2] Another aliquot of benzyl hydrodisulfide, 3 g (19.2 mmol), was allowed to react under identical conditions, but this time organic material was extracted with benzene before neutralization. From the extract, dibenzyl disulfide was obtained, mp and mmp 68.5–71°, and sulfur was found in the aqueous layer after neutralization. The products of these experiments were cited in Table I, expt 1 and 2. The reactions with dilute alkalis at room temperature were carried out under similar conditions, where the hydrodisulfide solution was added to 10 ml of water of pH 10 or pH 13. The reaction at pH 10 was so sluggish that it took 2 days to finish the reaction and the reaction mixture did not become colored. The products, dibenzyl di- and polysulfide mixtures were analyzed by nmr spectra as indicated in the following section, and were listed in Table I, expt 3 and 4.

Analysis of Dibenzyl Di- and Polysulfide Mixtures.—It is known[14] that the nmr signals of methylene protons of dibenzyl polysulfides $C_6H_5CH_2SS_xSCH_2C_6H_5$ are distinguishable from each other even in their mixture. Determination of the amounts of dibenzyl di- and polysulfides were as follows. When the benzene extracts from the reaction mixtures contained α-toluenethiol, (*e.g.*, as in expt 8), the amounts were determined by iodometry[11] and the thiol was oxidized to dibenzyl disulfide. Thus benzene solutions containing only di- and polysulfides were obtained. Then the benzene was removed, and to the residues (oil or crystals), appropriate amounts of carbon tetrachloride were added, to make 10–20% solutions whose nmr spectra were taken with integrals by which amounts of the di-, tri-, tetra-, and pentasulfides were determined. Amounts of polysulfidic sulfur, S_x in RSS_xSR, were calculated from the integral values assigned to the respective polysulfides.

Procedure for the Reaction with Sodium Hydro- or Hydropolysulfide.—The reaction condition and procedure were similar to those of the reaction with potassium hydroxide (at room temperature). Aqueous sodium hydropolysulfide NaS_xH ($x_{av} = 2$) solution was prepared from sodium hydrosulfide and crystalline sulfur. To sulfur (0.62 g, 19.3 mg-atoms) suspended in 10 ml of water and 1.08 g (19.3 mmol) of sodium hydrosulfide, was added 5 ml of dioxane with magnetic stirring under a nitrogen atmosphere. After 5 min, the sulfur dissolved and the solution became colored. To this was added 3 g (19.2 mmol) of the hydrodisulfide in 15 ml of dioxane. Hydrogen sulfide was evolved in both reactions even before neutralization. α-Toluenethiol could not be detected either by usual methods or by nmr spectroscopy. Analytical results are given in Table I, expt 5 and 6.

Procedure for the Reaction under Anhydrous Conditions.—To 1.5 g (23 mmol) of potassium cyanide, 3.35 g (23.1 mmol) of sodium α-toluenethiolate, or 2.42 g (19.2 mmol) of sodium sulfite was added 3 g (19.2 mmol) of benzyl hydrodisulfide in 20 ml of dioxane with vigorous stirring at room temperature under a nitrogen atmosphere, in the same glassware as that used in the foregoing experiments. The reactions proceeded heterogeneously and the reaction mixtures became colored with the evolution of hydrogen sulfide in the case of cyanide and the thiolate. The reaction with sulfite was sluggish but was complete after 1 day. To each reaction mixture was added about 100 ml of benzene, the insoluble material was removed by filtration, and the benzene solution washed with water and dried over magnesium sulfate. The benzene solution was treated as in the previous experiments. Analytical results are cited in Table II, expt 11, 12 and 13.

Procedure for the Reactions with Cyanide in the Presence of Potassium Hydroxide.—The reactions with potassium cyanide in strong basic media were carried out as follows. Using analogous glassware, to benzyl hydrodisulfide (3 g, 19.2 mmol) in 20 ml of dioxane was added 1.25 g (19.2 mmol) of potassium cyanide and 0.108 g (1.92 mmol) or 1.08 g (19.2 mmol) of potassium hydroxide in 10 ml of water with stirring under a nitrogen atmosphere at room temperature. The reaction mixture became red immediately and the color faded after about 10 min. (The reaction mixture with only potassium cyanide was light yellow.[2]) A major portion of hydrogen sulfide was evolved from the reaction mixture containing 1.92 mmol of potassium hydroxide after neutralization and most of hydrogen sulfide from that containing 19.2 mmol after neutralization. Succeeding treatment of the reaction mixtures was the same as that in the previous paper.[2] The amounts of products are shown in Table II, expt 8 and 9.

Registry No.—Benzyl hydrodisulfide, 3492-66-8.

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