Aralkyl Hydrodisulfides. I. The Reaction with 2,2-Diphenyl-1-picrylhydrazyl and with Benzoquinone

TAKESHIGE NAKABAYASHI AND JITSUO TSURUGI

Department of Applied Chemistry, University of Osaka Prefecture, Sakai City, Osaka, Japan

Addition of an aralkyl hydrodisulfide, RSSH (R, benzyl or benzhydryl), in benzene to 2,2-diphenyl-1-picrylhydrazyl in benzene at room temperature and the reverse-order addition of the reactants gave the hydrazine and diaralkyl tetrasulfide, both in nearly quantative yields. Addition of benzoquinone to the RSSH, both in benzene at room temperature, also gave hydroquinone and the diaralkyl tetrasulfide in good yields. Both reactions were compared with those of thiol with the hydrazyl and with the quinone, respectively.

Introduction

Alkyl hydrodisulfides which were prepared by Böhme and Zinner[1] and shown to have a linear sulfur linkage by the same authors, have received little attention. However, the present authors prepared two aralkyl hydrodisulfides, benzyl and benzhydryl hydrodisulfides, and used them for synthetic purposes.[2,3] In the present series, chemical behavior of the aralkyl hydrodisulfide will be studied in comparison with that of thiol and disulfide on one hand and with that of hydroperoxide on the other hand. The physico-chemical studies of the reaction of thiol with 2,2-diphenyl-1-picrylhydrazyl (DPPH) were reported in the literatures,[4-6] where 2,2-diphenyl-1-picrylhydrazine (DPPH₂) was isolated as the only identified product. The addition reaction of thiol to quinone[7-9] and the oxidation reaction of thiol to the disulfide with reduction of the substituted quinone to the hydroquinone[7] were reported by several investigators. Here, by allowing the hydrodisulfide, benzyl, or benzhydryl hydrodisulfide, to react with DPPH or benzoquinone, striking differences in oxidizability and products were observed between thiol and the hydrodisulfide.

Experimental

Materials.—Benzyl and benzhydryl hydrodisulfides, b.p. 65–70°/0.01 mm. and m.p. 32.5–34°, respectively, were prepared by the method reported,[2] and purified directly before use by distillation or recrystallization.[2] The DPPH, m.p. 127–129°, and benzoquinone were obtained from commercial products after two recrystallizations from an ether–chloroform (2:1) mixture and benzene, respectively. Benzene as a solvent was purified and dried as usual.

Procedure A.—The identification of all the products described here was conducted by mixed melting point with an authentic specimen.

To a solution of 2.0 mmoles of the hydrodisulfide in 10 ml. of benzene was added dropwise at room temperature a solution of an equimolar amount of DPPH in 60 ml. of benzene. The purple color of the DPPH turned to bright red soon after it was mixed under swirling with the hydrodisulfide solution. The reverse-order addition of the reactants, namely, addition of the hydrodisulfide solution to the DPPH solution was also carried out at room temperature. The purple color turned gradually to bright red as in titration. The bright red solution in both cases was kept standing overnight. After the solvent was evaporated under diminished pressure, a sufficient volume of benzene just to dissolve the residue and then a fivefold volume of petroleum ether was added. Bright red crystals separated, were filtered, recrystallized from a chloroform–ethanol (1:2) mixture m.p. 168–169°, and identified as DPPH₂. The solvent of the filtrate was replaced by benzene. The benzene solution was passed through a column filled with silica gel (Mallincrodt, 100 mesh) and eluted with benzene. The eluate yielded fractions which after evaporation of the solvent gave pale yellow solids, a yellow oil, and a small amount of unidentified product which contained sulfur and nitrogen. The pale yellow solid gave crystals from a petroleum ether solution; it was recrystallized from ethanol, and identified as benzyl or benzhydryl tetrasulfide. Benzyl tetrasulfide[10] has a melting point of 53–54°; benzhydryl tetrasulfide[10] has two forms, white pillars, m.p. 72–73°, and yellow needles, m.p. 83°. White pillars or a mixture of pillars and needles were obtained from the eluate on treating the benzhydryl compound. Recrystallization carried out over 30° converted the pillars completely to needles.[10] The desulfurization method of Farmer and Shipley[11] to produce disulfide from polysulfides was modified and applied to the oily product. This was suspended in a mixture of water and dioxane (2:1 vol.). The suspended oil was desulfurated with an excess of sodium sulfite under a stream of nitrogen at 80–90° for 3 hr., and poured into a large volume of water to separate the desulfurated products, which were found to be the aralkyl disulfides, benzyl and benzhydryl disulfides, m.p. 70° and 150–151°, respectively.[2]

B.—To a solution of 10 mmoles of the hydrodisulfide in 5 ml. of benzene was added dropwise a solution of 5 mmoles of benzoquinone in 15 ml. of benzene at room temperature. Black crystals with metal-like brightness separated soon after the addition, and turned gradually to white crystals. The crystals, m.p. 168–170°, were filtered, and found to be hydroquinone. The filtrate after chromatography through a silica gel column gave pale yellow solids and a yellow oil as described in procedure A. The solids were identified as benzyl or benzhydryl tetrasulfide while the oil was desulfurated to give the disulfide as described in procedure A.

Results and Discussion

The Reaction with DPPH.—The products which resulted from the addition of the aralkyl hydrodisulfide to DPPH and the reverse-order addition of the reactants are summarized in Table I. Both reagents were dissolved in benzene and were added slowly to each other at room temperature.

The characteristic features of the reaction are that the tetrasulfide is obtained as a free radical dimer and that the yields of both DPPH₂ and tetrasulfide are nearly quantitative, as compared with the reaction of DPPH with thiol. Thiol was reported to react with DPPH by the following mechanism.[4]

$$RSH + DPPH \longrightarrow RS\cdot + DPPH_2 \qquad (1)$$

$$RS\cdot + DPPH \longrightarrow DPPH\text{—}SR \qquad (2)$$
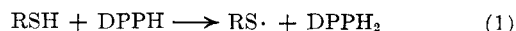
One mole of thiol must consume two moles of DPPH, according to the above sequence. This was true[5] when

(1) H. Böhme and G. Zinner, *Ann.*, **585**, 142 (1954).
(2) J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).
(3) T. Nakabayashi and J. Tsurugi, *ibid.*, **26**, 2482 (1961).
(4) K. Russel, *J. Phys. Chem.*, **58**, 437 (1954).
(5) A. G. Brook, R. J. Anderson, and J. T. van Patot, *Can. J. Chem.*, **36**, 159 (1958).
(6) A. H. Ewald, *Trans. Faraday Soc.*, **55**, 792 (1959).
(7) J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939).
(8) M. Schubert, *ibid.*, **69**, 712 (1947).
(9) A. Blackhall and R. H. Thomson, *J. Chem. Soc.*, 1138 (1953).
(10) J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **25**, 1744 (1960).
(11) E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1531 (1947).

TABLE I

HYDRODISULFIDE (2 MMOLES) AND DPPH (2 MMOLES) BOTH
IN BENZENE AT ROOM TEMPERATURE

Run no.	Addition of	Products in mmole	
		DPPH$_2$	Tetrasulfide[a]
1	DPPH to C$_6$H$_5$CH$_2$SSH	1.84	0.94 (0)
2	C$_6$H$_5$CH$_2$SSH to DPPH	1.77	0.84 (0)
3	DPPH to (C$_6$H$_5$)$_2$CHSSH	1.99	0.93 (0.53)
4	(C$_6$H$_5$)$_2$CHSSH to DPPH	1.91	0.89 (0.44)

[a] This indicates the sum of tetrasulfide obtained as such and that of disulfide by the desulfurization method, the latter written in parentheses. See Experimental. In the case of the benzhydryl compound, benzhydryl disulfide results either from tetrasulfide which cannot crystallize or from the other benzhydryl polysulfides which may be disproportionation products from the tetrasulfide.

thiophenol was added to DPPH both in concentrated solutions. However, when DPPH was added to thiophenol both in dilute solutions, the molar ratio changed[5] to approximately 1.0. To interpret this, equation 3 was proposed in place of equation 2.

$$2RS \cdot \longrightarrow RSSR \qquad (3)$$

Thus it was concluded[5,6] that the over-all stoichiometric ratio depends on the relative importance of equations 2 and 3, which depend on concentrations of species present in the reaction mixture. The isolation of the free radical dimer, disulfide, was not successful.[4-6]

In the present study the equimolar consumption of DPPH and hydrodisulfides as well as the nearly stoimetric yields of DPPH$_2$ and tetrasulfides regardless of the order of addition of the reactants, indicate that equation 5 prevails over equation 6 after the dehydrogenation reaction, equation 4, occurs.

$$RSSH + DPPH \longrightarrow RSS \cdot + DPPH_2 \qquad (4)$$

$$2RSS \cdot \longrightarrow RSSSSR \qquad (5)$$

$$RSS \cdot + DPPH \longrightarrow DPPH-SSR \qquad (6)$$

A trace of the unidentified product containing sulfur and nitrogen which was found in the reaction of hydrodisulfide with DPPH except in experiment 3 suggests that equation 6 occurs only to a minor degree. Such a cleanness of the reaction as observed in the present study has never been reported in the reactions of DPPH with hydroxylamine,[5] alkyl amines,[5] phenols,[12] olefins,[13] and hydroaromatic compounds.[13] In those reactions neither is the yield of DPPH$_2$ quantitative nor is the fate of dehydrogenated products clear, except in the reaction with ammonia.[5] From the point of view cited above, the hydrodisulfide may be a unique compound which reacts with DPPH stoichiometrically and gives the well-identified products in nearly quantitative yields. To explain such a cleanness, it is necessary to consider the high rate of dehydrogenation of hydrodisulfide by DPPH. A comparative reaction of the corresponding thiol (α-toluene- or α-diphenylmethanethiol) with DPPH indicated the far slower decoloration of DPPH than that of hydrodisulfide. When the DPPH solution is added to the hydrodisulfide solution, the only free radical species is RSS·. Therefore, the formation of the tetrasulfide can be explained reasonably. The better yields of the oxidation and reduction prod-

(12) J. S. Hogg, D. H. Lohmann, and K. E. Russel, Can. J. Chem., 39, 1588 (1961).
(13) E. A. Braude, A. G. Brook, and R. P. Linstead, J. Chem. Soc., 3574 (1954).

ucts are reported in Table I on the addition of DPPH to hydrodisulfide than on the alternative addition. However, when the hydrodisulfide solution was added to the DPPH solution, DPPH is abundant in the system. The reason why the recombination of DPPH and RSS· does not occur even under these conditions is obscure at the present time, while a similar recombination appears to occur in the reaction with thiol. Neither steric hindrance nor the greater stability of RSS· than RS· can explain the recombination of RSS· with each other.
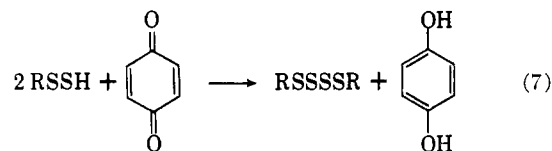
The Reaction with Benzoquinone.—Addition of benzoquinone in benzene to twofold moles of aralkyl hydrodisulfide in benzene at room temperature gave the products cited in Table II.

TABLE II

PRODUCTS OF THE HYDRODISULFIDE WITH BENZOQUINONE

| Reactants in mmoles		Products in mmoles	
Hydrodisulfide	Benzoquinone	Hydroquinone	Tetrasulfide[a]
C$_6$H$_5$CH$_2$SSH, 10	5	3.61	4.00 (0.54)
(C$_6$H$_5$)$_2$CHSSH, 10	5	4.21	4.55 (1.25)

[a] See footnote a of Table I.

Table II indicates that benzoquinone oxidizes the hydrodisulfide to the tetrasulfide and at the same time is reduced to hydroquinone.

$$2 RSSH + \text{(benzoquinone)} \longrightarrow RSSSSR + \text{(hydroquinone)} \qquad (7)$$

Both the oxidation and reduction products are obtained in good yields, especially in the reaction with benzhydryl disulfide. The addition product cannot be isolated here, while thiol was reported to add to quinone according to equation 8.[7]


$$\text{(quinone)} + HSR \longrightarrow \text{(substituted hydroquinone)} \qquad (8)$$
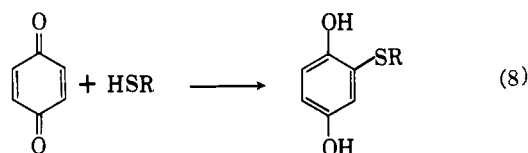
The substituted hydroquinone thus formed reacts further with excess benzoquinone to give substituted quinone and hydroquinone.

$$\text{(substituted hydroquinone)} + \text{(quinone)} \longrightarrow \text{(substituted quinone)} + \text{(hydroquinone)} \qquad (9)$$
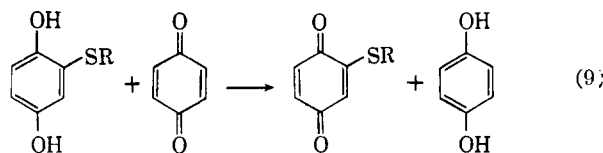
Repetition of the reaction of types 8 and 9 yields di-, tri-, and tetramercaptoquinone.[8] A tetrasubstituted quinone, duroquinone, alone was reported to yield a substituted hydroquinone in slightly alkaline medium.[7] But isolation of the disulfide was unsuccessful.[7] Therefore, the hydrodisulfide can be said to be unique with respect both to the better yields, and clear-cut fates of the oxidation and reduction products as compared with those of thiol.

The dehydrogenation reaction of hydroaromatic hydrocarbons by quinone was reported to proceed by the polar mechanism as

$$RH_2 + Q \longrightarrow RH^+ + QH^- \longrightarrow R + QH_2 \qquad (10)$$
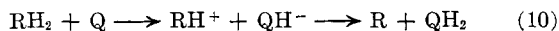
where RH_2 and R represent dihydroaromatic and aromatic hydrocarbons, respectively, and Q and QH_2 quinone and hydroquinone, respectively.[14]

On the other hand, inhibition of free radical polymerization by quinone is well known and interpreted by a free radical mechanism,[15] although the actual mecha-

nism is complex and obscure. The reaction of some hydrogen-donating compounds with quinone was reported to proceed by a radical mechanism,[16] the proof for which is initiation by sunlight and formation of coupling products, for example

$$2(C_6H_5)_2CH_2 + 2Q \longrightarrow (C_6H_5)_2CH\text{-}CH(C_6H_5)_2 + 2QH$$

where $2QH$ represents quinhydrone. In the present study it is difficult to decide whether the reaction proceeds by a free radical or polar mechanism, because of the high rate of the reaction. A comparative reaction of the corresponding thiol with benzoquinone indicates a far slower change to red. The red color suggests the addition of thiol to the quinone.

(14) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548, 3564 (1954); E. A. Braude, A. G. Brook, and R. P. Linstead, *ibid.*, 3569 (1954).

(15) C. Walling, "Free Radicals in Solution." John Wiley and Sons, Inc., New York, N. Y., 1957, p. 166.

(16) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944).

Aralkyl Hydrodisulfides. II. The Thermal Decomposition of Benzhydryl Hydrodisulfide

Takeshige Nakabayashi and Jitsuo Tsurugi

The Department of Applied Chemistry, University of Osaka Prefecture, Sakai City, Osaka, Japan

Decomposition of benzhydryl hydrodisulfide (RSSH) at 120° in the dark gave hydrogen sulfide, diphenylmethanethiol (RSH), and dibenzhydryl tetrasulfide (R_2S_4), and indicated a stoichiometric relation between the products and the starting material. The kinetics of decomposition of RSSH in biphenyl showed that formation of hydrogen sulfide and decomposition of RSSH are at an identical first-order rate. Light was found to increase the rate. Temperature dependence of rate of hydrogen sulfide formation in a temperature range from 100° to 150° gave the equation, rate of RSSH decomposition $= 1.01 \times 10^6 \exp(-20.0 \text{ Kcal.}/RT)$. A simple, consecutive, free radical mechanism was proposed in which homolytic dissociation of the S—S bond of RSSH was concluded to be the slowest step. The mechanism of decomposition of the hydrodisulfide was compared with that of hydroperoxide or disulfide.

In the previous paper[1] of this series two aralkyl hydrodisulfides, benzyl and benzhydryl compounds, were allowed to react with 2,2-diphenyl-1-picrylhydrazyl or benzoquinone. The characteristic features of the reaction as compared with those of thiol and of other hydrogen-donating compounds were the high rate of dehydrogenation of the aralkyl hydrodisulfide by diphenylpicrylhydrazyl or benzoquinone and the formation of the diaralkyl tetrasulfide. It appears interesting to examine whether hydrodisulfide, the thio analog of hydroperoxide, behaves like the hydroperoxides, although an organic disulfide, the thio analog of a peroxide, is known to be much more stable than a peroxide. Among the alkyl and aralkyl hydrodisulfides so far prepared benzhydryl hydrodisulfide could be obtained in the crystalline state[2] and was chosen here as a representative of the hydrodisulfides.

Since hydroperoxides are known to decompose homolytically with heat or light,[3] the thermal decomposition of benzhydryl hydrodisulfide is examined in the present paper. The determination of the decomposition products in the absence of solvent as well as kinetic studies is reported and compared with that of hydroperoxides or dibenzhydryl disulfide. The analytical methods utilized here are specific and therefore will be described in detail.

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

(2) J. Tsurugi and T. Nakabayashi, *ibid.*, **24**, 807 (1959).

(3) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954, p. 88.

Experimental

Materials.—Benzhydryl hydrodisulfide was prepared by the method reported,[2] and recrystallized two times from petroleum ether (b.p. 40–60°) directly before use. This compound (m.p. 32.5–34°) was titrated by an ethanolic iodine solution,[2] and a purity of 99.5% was sufficient to obtain reproducible results. All the solvents used here were purified or dried from commercial products by conventional procedures.

Total Decomposition of Benzhydryl Hydrodisulfide.—A given amount (1.1618 g., 5 mmoles) of the hydrodisulfide was placed in a two-necked quartz flask with a condenser and a gas inlet tube, each of which had stop cock. Air in the flask was replaced with nitrogen by using three cycles of evacuation through the condenser and nitrogen streaming through the inlet tube. The flask, condenser, and inlet tube were wrapped with aluminum foil to be protected from light. Then the flask was heated at a given temperature.

(1) A gentle stream of nitrogen was passed through the inlet tube into the flask and then bubbled through the condenser into a series of three absorbing bottles, two of which contained an aqueous 0.1 N iodine solution and one of which an aqueous potassium iodide solution. The hydrogen sulfide evolved was swept by the nitrogen stream and absorbed in the bottles. Titration of an excess of iodine with sodium thiosulfate gave the amount of hydrogen sulfide evolved.

(2) After the reaction was completed, the contents of the flask were dissolved in benzene and the flask filled to 100 ml. An aliquot (20 ml.) of the solution after addition of ethanol was titrated with an aqueous iodine solution. The titration method with iodine which will appear below was always carried out by adding an excess of iodine and, if necessary, the solution allowed to stand for several hours and then the excess of iodine titrated with a sodium thiosulfate solution. After several washings with water and evaporation of the solvents, this aliquot gave a mixture of a viscous yellow oil and a crystalline benzhydryl disulfide. The latter was recrystallized from a solvent mixture of benzene–