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Reaction of Dibenzyl Disulfide and Analogues with Na_2S_x-NaOH[1) Supplementary Data for Mechanism for Reaction of *p*-Nitrotoluene with Na_2S_x[2)

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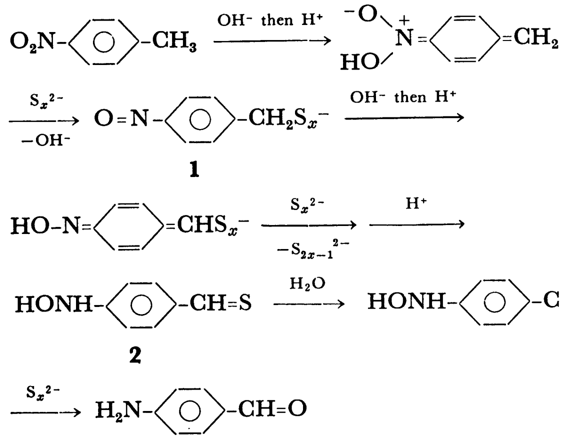
Synopsis. Reaction of dibenzyl disulfide with aquoethanolic NaOH gave benzaldehyde and α-toluenethiol. On the other hand, the reaction of dibenzyl disulfide with Na_2S_x in the presence of NaOH gave preferentially benzaldehyde alone. These facts are explained by the further reaction of α-toluenethiol with Na_2S_x giving benzaldehyde and support our mechanism proposed previously for the reaction of *p*-nitrotoluene with Na_2S_x.

In the previous article,[2) we reported the mechanism for the reaction of *p*-nitrotoluene with Na_2S_x. The mechanism involves a benzyl polysulfide derivative as one of the intermediates to give *p*-aminobenzaldehyde.



(1)

Among steps in this mechanism, there is no literature on the step for the formation of thioaldehyde (**2**) from benzyl polysulfide derivative (**1**) and, in the reaction path, there may be dibenzyl polysulfide derivatives produced from **1**. It has been reported that, for example, dithiodiacetic acid[3,4) or its ester[5) which has electron-withdrawing groups on the α-carbon to the dithio group decomposes by OH^- to give thioaldehyde and thiol, but the reaction of dibenzyl disulfide with OH^- is unknown. Hence dibenzyl disulfide and bis(*p*-nitrobenzyl) disulfide were selected as model compounds, and they were allowed to react with NaOH or Na_2S_x–NaOH. Further, the reaction of α-toluenethiol with Na_2S_x–NaOH was also examined.

TABLE 1. YIELDS OF PRODUCTS FROM A REACTION OF DIBENZYL DISULFIDE WITH NaOH OR Na_2S_x-NaOH IN H_2O-EtOH (2:1) BY REFLUXING FOR 1 h

Products	Yield (%)	
	with NaOH[a)	with Na_2S_x-NaOH[b)
PhCHO	24.0	49.0
$PhCH_2SH$	24.4	trace
PhCOOH	3.1	4.5
$PhCH_2OH$	3.3	0.8

a) $[NaOH]_0 = 0.74$ M. b) $[NaOH]_0 = 0.70$ M, $[Na_2S \cdot 9H_2O]_0 = 0.17$ M, $[S]_0 = 0.65$ M; A mixture of Na_2S and S can form Na_2S_x (x= 1—5), its initial concentration being *ca.* 0.17 M as Na_2S_4.

Results and Discussion

Reaction with NaOH. The reaction of dibenzyl disulfide with aquoethanolic NaOH gave benzaldehyde, α-toluenethiol and a small amount of benzoic acid and benzyl alcohol. Yields of products are listed in Table 1.

$$PhCH_2SSCH_2Ph \xrightarrow{NaOH} PhCHO + PhCH_2SH + PhCOOH + PhCH_2OH \quad (2)$$

This type of reaction is expected from the alkaline decomposition of dithiodiacetic acid[3,4) or its ester[5) which gives $HSCH_2COOH$ and OHCCOOH.

Benzoic acid and benzyl alcohol appearing in Eq. 2 may be the products of Cannizzaro reaction of benzaldehyde.

Reaction with Na_2S_x–NaOH. The reaction of dibenzyl disulfide with aquoethanolic Na_2S_x, which was prepared from Na_2S and S *in situ* (see Experimental Section), in the presence of NaOH gave benzaldehyde and a small amount of benzoic acid and benzyl alcohol along with a trace amount of α-toluenethiol (Table 1). The yield of benzaldehyde (49%) in the reaction of dibenzyl disulfide with Na_2S_x–NaOH is nearly equal to the sum of yields of benzaldehyde (24%) and α-toluenethiol (24%) in the reaction with NaOH. Hence, the produced α-toluenethiolate ion may react further with Na_2S_x to give benzyl polysulfide ion, and then deprotonation occurs to facilitate the S–S bond fission as observed with other disulfide compounds such as dibenzyl disulfide (Eq. 3).

$$PhCH_2S^- \xrightarrow[-S^{2-}]{S_{x+1}^{2-}} PhCH_2S\text{-}S_x^- \xrightarrow{OH^-} Ph\overset{-}{C}H\text{-}S\text{-}S_x^- \quad (3a)$$

$$Ph\overset{-}{C}HS\text{-}S_x^- \xrightarrow{-S_x^{2-}} PhCH{=}S \xrightarrow{H_2O} PhCH{=}O \quad (3b)$$

Thiobenzaldehyde is easily hydrolyzed as reported previously by King[6) (Eq. 3b).

The reaction of *α-toluenethiol* with aquoethanolic Na_2S_x in the presence of NaOH gave mainly benzaldehyde, but no reaction occurred with NaOH. This fact supports the above mechanism, *i.e.*, polysulfide ion is necessary for the oxidation of thiol to the corresponding aldehyde.

In the reaction of *bis(p-nitrobenzyl) disulfide*, *p*-aminobenzaldehyde was identified by means of NMR as one of the products, which suggests that the analogous mechanism involving S–S cleavage followed by the hydrolysis of thioaldehyde would operate.

These results suggest that the benzyl polysulfide derivatives or dibenzyl polysulfide derivatives, if produced during the reaction of *p*-nitrotoluene with Na_2S_x, should be easily converted into benzaldehyde derivatives by NaOH and Na_2S_x, so that the results support our mechanism previously postulated.

Experimental

Melting points were measured by a Yanagimoto micro melting point apparatus and were not corrected. NMR spectra were recorded on a Hitachi R-24B NMR spectrometer using Me_4Si as an internal standard. The GLC analysis was performed with a Yanagimoto G 180 gas chromatograph with a flame ionization detector.

Materials. Dibenzyl disulfide was prepared by the method of Minoura;[7] mp 69—70 °C (lit,[7] 71 °C); NMR ($CDCl_3$): δ 3.59 (s, 4H, CH_2), 7.24 (s, 10H, ArH). Bis(*p*-nitrobenzyl) disulfide was prepared according to Price;[8] mp 124.5—126 °C (lit,[8] 126.5 °C); NMR ($CDCl_3$): δ 3.69 (s, 4H, CH_2), 7.4 (d, 4H, ArH, $J=9$ Hz), 8.2 (d, 4H, ArH, $J=9$ Hz).

Reaction of Dibenzyl Disulfide with NaOH. A hot solution (14 ml) of NaOH (0.65 g, 16 mmol) was poured into a 100 ml round-bottomed flask containing a hot ethanolic solution (7 ml) of dibenzyl disulfide (1.00 g, 4.1 mmol). The mixture was heated under reflux for 1 h. Most of the products were extracted with diethyl ether from the alkaline solution and then the aqueous solution was acidified with dil. H_2SO_4. The acidic solution was also extracted with diethyl ether and the extract containing benzoic acid was esterified by diazomethane. Both extracts from alkaline and acidic solutions were analyzed by GLC, using two sorts of columns (2.5 mm × 1 m), PEG 20 M and Silicone OV 17, at 100—250 °C. Biphenyl was used as an internal standard.

Reaction of Dibenzyl Disulfide with Na_2S_x–NaOH. The analogous reaction of dibenzyl disulfide was done with a mixture of dibenzyl disulfide (1.00 g, 4.1 mmol), $Na_2S_x \cdot 9H_2O$ (0.83 g, 3.5 mmol), S (0.39 g, 1.2×10^{-2} g atom) and NaOH (0.65 g, 16 mmol). The products and their yields were listed in Table 1. All products were identified by comparison of GLC peaks with those authentic specimens.

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