Thermal Reactions of Dibenzyl Disulfide and Dibenzyl Sulfide with Metals: A New Route to *trans*-Stilbene and Dibenzyl

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Abstract—A procedure was developed for preparing stilbene by thermal desulfuring of dibenzyl disulfide and dibenzyl sulfide with metals (Fe, Zn). The major product of the similar reaction of dibenzyl disulfide with copper is dibenzyl.

Thermal decomposition of dibenzyl sulfide I and dibenzyl disulfide II is fairly well studied [1]. The primary products of thermolysis of these compounds at temperatures above 185°C were stilbene and hydrogen sulfide [2-4]; their further reaction gave tetraphenylthiophene and 2-phenylbenzothiophene. The identified by-products of these reactions were toluene and pentaphenylcyclopentadiene [3], erroneously identified earlier as 1,2,3,4-tetraphenylbutane [2]. Stilbene is also one of the products of thermal reactions of I and II with sulfur [4, 5]. When the reaction of II with sulfur was performed at 150°C with distillation of the forming stilbene in a vacuum, its yield reached 31%. Stilbene was obtained in 17% yield in the reaction of disulfide II with potassium tert-butylate in DMF at 80°C [6].

With the aim to develop a convenient procedure for preparing stilbene, we studied the thermal reactions of readily available compounds I and II [7] with some metals (activated Fe, Zn, Cu powders) in 1:4 molar ratio.

The reaction of **II** with iron powder was performed at 200–215°C for 15 h in a continuous argon flow. Longer heating was not appropriate because of tarring of the reaction mixture. The reaction was accompanied by evolution of H_2S and sublimation of the forming *trans*-stilbene. From the residue, we isolated an additional crop of stilbene by vacuum distillation. The total yield of stilbene was ~50% (see table). Heating of **II** with zinc dust under similar conditions gave *trans*-stilbene in 40% yield (see table). The reactions of **II** with Fe and Zn are described by the following equation:

$$PhCH_2SSCH_2Ph + M \xrightarrow{\Delta} PhCH=CHPh + MS + H_2S,$$

$$\mathbf{II}$$

$$M = Fe, Zn.$$

Heating of **II** with copper powder was accompanied by gradual darkening of the mixture, followed by fast sintering at $200-215^{\circ}$ C. No hydrogen sulfide evolved, and the yield of *trans*-stilbene did not exceed 10% (see table). In the reaction mixture, we identified by GLC the degradation products: toluene, phenylmethanethiol, dibenzyl, and sulfide **I**. When the reaction of **II** with copper was performed at a lower temperature (130-140°C), no stilbene was obtained. The major reaction product was sulfide **I** (see table).

Heating of dibenzyl sulfide I with iron powder at 200-215°C for 20 h gave a mixture of trans-stilbene (15%), dibenzyl (5%), and unchanged I (GLC data). The reaction was accompanied by evolution of hydrogen sulfide and formation of iron sulfide. At a higher temperature (230-235°C), the content of trans-stilbene in the reaction mixture increased to 40% (see table). On heating of I with zinc dust at 210–220°C for 32 h, a mixture containing 50% unchanged I, 36% stilbene, 4% II, and 2% dibenzyl was formed. After appropriate work-up, the yield of trans-stilbene was 32% (see table). At the reaction temperature was increased to 240-250°C, the yield of *trans*-stilbene was as high as 46%. A product of secondary transformation of stilbene, tetraphenylthiophene, was also detected (yield 3%). The process can be described by the equation

$$\begin{array}{c} 2PhCH_2SCH_2Ph + M \xrightarrow{\Delta} 2PhCH=CHPh + MS + H_2S, \\ \mathbf{I} \end{array}$$

$$M = Fe, Zn.$$

Dibenzyl sulfide **I** did not noticeably react with copper powder at $160-165^{\circ}C$ (5 h). At the temperature increased to $205-215^{\circ}C$ and time, to 8 h, the conversion of **I** appreciably grew, but the yield of the reaction products remained poor (see table).

Reagent	Metal	T, °C	τ, h	Reagent conversion, %	Stilbene yield, %	Other reaction products (yield, %) ^a
II	Fe	210-215	15	94	48	R_2S (9)
	Zn	210-220	18	95	38	$R_2S(12)$
11	Cu	210-215	0.5	100	7	RH (4), RSH (2), R_2 (39), R_2 S (28)
II	Cu	130–140	5	56	-	R_2 (5), R_2S (23)
Ι	Fe	200-215	20	70	15	$R_{2}^{-}(5)$
Ι	Fe	230-235	20	88	40	$\bar{R_2}$ (10)
Ι	Zn	210-220	32	58	32	\bar{R}_{2} (1), $\bar{R}_{2}S_{2}$ (2)
Ι	Zn	240-250	35	90	46	$\overline{R}_{2}(2), \overline{R}_{2}\overline{S}_{2}(5)$, tetraphenylthiophene (3)
Ι	Cu	160-165	5	13	_	RSH (5), R_{2} (2)
Ι	Cu	205–215	8	56	2	RH (1), RSH (8), R_2 (7), R_2S_2 (4)

Products of thermal reactions of dibenzyl sulfide I and dibenzyl disulfide II with metals

^a R = PhCH₂.

EXPERIMENTAL

To monitor the reaction progress and analyze the products, we used TLC (Silufol UV-254 plates, eluent hexane–benzene, 10 : 1) and GLC (Tsvet-500 chromatograph, thermal conductivity detector, 3×2000 -mm stainless steel column, liquid phase 5% XE-60 on Chromaton N-AW-HMDS, 0.25–0.315 mm; linear heating from 40 to 220°C at a rate of 12 deg min⁻¹; carrier gas He). All the reactions were performed under Ar.

Dibenzyl disulfide **II** was prepared according to [8], mp 71°C. Dibenzyl sulfide **I** was of analytically pure grade. Iron, zinc, and copper powders were activated according to [9].

Thermal reaction of dibenzyl disulfide II with iron. A mixture of 4.93 g of disulfide II and 4.48 g of iron powder was stirred for 15 h at 210-215°C. Hydrogen sulfide evolved [reaction with a Pb(OAc)₂ solution], and the forming stilbene sublimed and deposited on cold walls of the reactor. The reaction was stopped because of extensive tarring of the reaction mixture. The sublimed trans-stilbene after recrystallization from ethanol [yield 1.3 g (36%)] had mp 122-123°C (published data [10]: mp 123-124°C). The remaining mixture was treated with hot benzene. The dark yellow residue after removing the solvent was distilled in a vacuum. A fraction (1.1 g) distilling in the range 160-230°C (12-15 mm Hg) was collected; according to GLC, it contained 40% transstilbene, 35% dibenzyl sulfide I, and 25% dibenzyl disulfide II, which was consistent with the results of its elemental analysis. Found, %: C 80.32; H 6.91; S 11.99. Calculated, %: C 81.86; H 6.39; S 11.75. From this mixture, we isolated 0.43 g of trans-stilbene. Total yield of *trans*-stilbene 1.73 g (48%). Treatment of the inorganic residue with dilute HCl results in evolution of H_2S , suggesting the presence of iron sulfide.

Reaction of dibenzyl disulfide II with zinc. A mixture of 4.18 g of **II** and 4.4 g of zinc dust was heated at $210-220^{\circ}$ C for 18 h. This was accompanied by evolution of H₂S and sublimation of stilbene. The yield of stilbene after recrystallization from ethanol was 1.16 g (38%). The remaining reaction mixture, according to TLC, contained a minor amount of stilbene, dibenzyl disulfide **II**, dibenzyl sulfide **I**, elemental sulfur, and tars.

Desulfuring of dibenzyl disulfide II with copper. *a*. A mixture of 4.3 g of disulfide **II** and 4.4 g of copper powder was heated to 200°C. The mixture gradually darkened, and at $210-215^{\circ}$ C its rapid sintering started. No hydrogen sulfide evolved. The mixture was kept at $210-215^{\circ}$ C for an additional 15 min, cooled, and treated with benzene. The insoluble residue was filtered off, the benzene solution was evaporated, and the residue (2.4 g) was analyzed by GLC. The mixture of reaction products contained 5% toluene, 3% phenylmethanethiol, 8% stilbene, 39% dibenzyl, and 45% dibenzyl sulfide **I**.

b. The same amounts of reactants were kept at $130-140^{\circ}$ C for 15 h. The mixture was worked up as in procedure *a*. The residue after removal of benzene was vacuum-distilled, and a broad fraction distilling in the range $130-190^{\circ}$ C (7–8 mm Hg) was isolated in the amount of 2.95 g. According to GLC and elemental analysis, it consisted of 65% disulfide **II**, 30% sulfide **I**, and 5% dibenzyl. Found, %: C 72.29; H 5.80; S 19.67. Calculated, %: C 72.53; H 6.06; S 21.41.

Reaction of dibenzyl sulfide I with iron. a. A

mixture of 2.7 g of sulfide **I** and 2.8 g of iron powder was heated at 200–215°C for 20 h. Hydrogen sulfide evolved. After cooling, the dark yellow mixture was treated with benzene. The benzene solution was evaporated, and the residue was vacuum-distilled. A fraction distilling at 183–187°C (15 mm Hg) was collected (0.96 g); according to GLC and elemental analysis, it contained 80% dibenzyl sulfide **I**, 15% stilbene, and 5% dibenzyl. Found, %: C 81.49; H 7.35; S 11.91. Calculated, %: C 81.42; H 6.61; S 11.97.

b. A mixture of 5.4 g of dibenzyl sulfide **I** and 5.6 g of iron powder was stirred at $230-235^{\circ}$ C for 20 h. The mixture gradually became dark and viscous, and hydrogen sulfide evolved. The mixture was worked up as in procedure *a*. In vacuum distillation, a fraction distilling at $130-150^{\circ}$ C (5–7 mm Hg) was collected (1.3 g); according to GLC and elemental analysis, it contained 50% dibenzyl sulfide **I**, 40% stilbene, and 10% dibenzyl. Found, %: C 86.18; H 6.91; S 7.40. Calculated, %: C 85.81; H 6.71; S 7.48.

Reaction of dibenzyl sulfide I with zinc. A mixture of 8.6 g of sulfide I and 10.4 g of zinc dust was stirred at $240-250^{\circ}$ C for 35 h. The sublimed stilbene (1.3 g) was separated, and the remaining mixture was worked up as in the reaction with Fe. In vacuum distillation, we collected fractions distilling at $125-140^{\circ}$ C (8 mm Hg) and $170-176^{\circ}$ C (5 mm Hg), from which we isolated 2.0 g of stilbene, 0.5 g of dibenzyl disulfide II, 0.3 g of elemental sulfur, and 0.3 g of tetraphenylthiophene. The latter compound was identified by elemental analysis and IR spectroscopy.

Desulfuring of dibenzyl sulfide I with copper. *a*. A mixture of 4.3 g of sulfide I and 5.1 g of copper powder was heated at $160-165^{\circ}$ C for 5 h, cooled, and worked up as in the previous examples. Vacuum distillation gave 3.8 g (87%) of unchanged sulfide I, 0.1 g (2%) of dibenzyl, and 0.2 g (5%) of phenylmethanethiol. b. The same amounts of the reactants were heated at $205-215^{\circ}$ C for 8 h; the resulting mixture was worked up as in procedure *a*. In vacuum distillation (8 mm Hg), we collected the fractions distilling at 130-160 and $160-165^{\circ}$ C. By GLC, we identified (yield, %) dibenzyl (7), phenylmethanethiol (8), stilbene (2), dibenzyl disulfide (4), and unchanged dibenzyl sulfide (44).

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