The Reaction of Elemental Sulfur with Organic Compounds. II. The Reaction of Dibenzyl Sulfide, Sulfoxide and Sulfone, and Their Related Dibenzyl Compounds[1]

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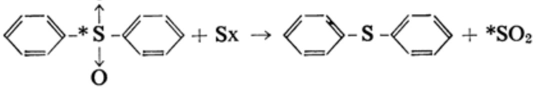
For many years, the reactions of elemental sulfur with organic compounds at elevated temperatures have been a subject of extensive investigation.[2] Aromatization, vulcanization and Wilgerodt reactions are only a few of many well-known applications of these reactions. However, many of the mechanistic features of these reactions are yet to be clarified. For example, even in simple reactions of sulfur with olefins, it is not certain whether the reaction proceeds through the heterolytic or the homolytic pathway. Nor do we know whether the reaction is initiated by the abstraction of hydrogen or by the addition of sulfur to the double bond.[2c]

Many years ago, the reaction of diphenyl sulfone with sulfur was found to give diphenyl sulfide and sulfur dioxide.[3] Recently, we have investigated the mechanism of this reaction using a ^{35}S-labeled compound.[1a] As is illustrated in Eq. 1, the apparent reduction of the S–O bond was found actually to involve the cleavage of the phenyl-S bond and the replacement of the SO_2 group by sulfur to the extent of 70—80%:



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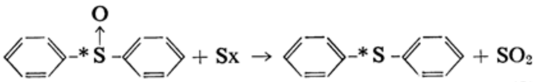

(2)

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1) a) Paper I; S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963); b) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund.

2) a) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York (1962), Chap. 5; b) L. Bateman and C. G. Moore, "Reactions of Sulfur with Olefin," in "Organic Sulfur Compounds," Vol. I, Ed. by N. Kharasch, Pergamon Press, New York (1961); c) S. Oae, *Kagaku* (*Chemistry*), **18**, 779 (1963).

3) F. Kraft and W. Vorster, *Ber.*, **26**, 2813 (1893).

Meanwhile we have found that the corresponding diphenyl sulfoxide is also reduced to diphenyl sulfide. In this case, however, the reaction is a straightforward reduction of the SO group, involving the cleavage of the S–O bond, as is shown in Eq. 2. These different paths were ascribed to the weaker bond strength of the S–O bond in sulfoxide than in sulfone. We now turn our attention to the problem of how the reaction proceeds when a methylene group is inserted between a benzene ring and a sulfur group, i. e., the reaction with a benzylic compound. Here the reaction depends on the relative importance of hydrogen abstraction and of the cleavage of either the C–S or S–O bond, or both.

Therefore, we have investigated the reactions of sulfur with dibenzyl sulfide, sulfoxide, sulfone, ether and ketone, and this paper will present a detailed account of the investigation.

Results and Discussion

The reaction was carried out by heating a mixture of starting compounds and elemental sulfur under a slow stream of nitrogen gas. The evolution of hydrogen sulfide usually started at around 160°C, and the reaction temperature was maintained near 200°C, substantially lower than that used in the reactions of diphenyl sulfoxide and sulfone (∼300°C[1a]). An important though unexpected result was the failure to detect any sulfur dioxide which had been evolved quantitatively in the reactions of diphenyl sulfoxide and sulfone.[1a] In place of sulfur dioxide, a few drops of water were usually observed in all of the oxygen compounds except for dibenzyl ketone. The oily and solid products were separated into pure forms by a combination of gas-, thin-layer-, and column chromatographies and were identified by means of spectroscopic and elemental analyses. The results are shown in Table I and Chart 1.

The Products from Dibenzyl Sulfoxide.—Dibenzyl sulfoxide seems to undergo all the possible reactions conceivable for the compound, i. e., hydrogen abstraction, rearrangement, elimination and cleavage reaction. Therefore, a detailed discussion of the reactions of this compound would be most fruitful, for the reactions of the other compounds can then be discussed by referring to their differences from those of dibenzyl sulfoxide.

As is shown in Table I, the reaction products of dibenzyl sulfoxide were hydrogen sulfide (trapped as lead sulfide) (37.2%), oils (38%), solids (39%) and a small amount of water.

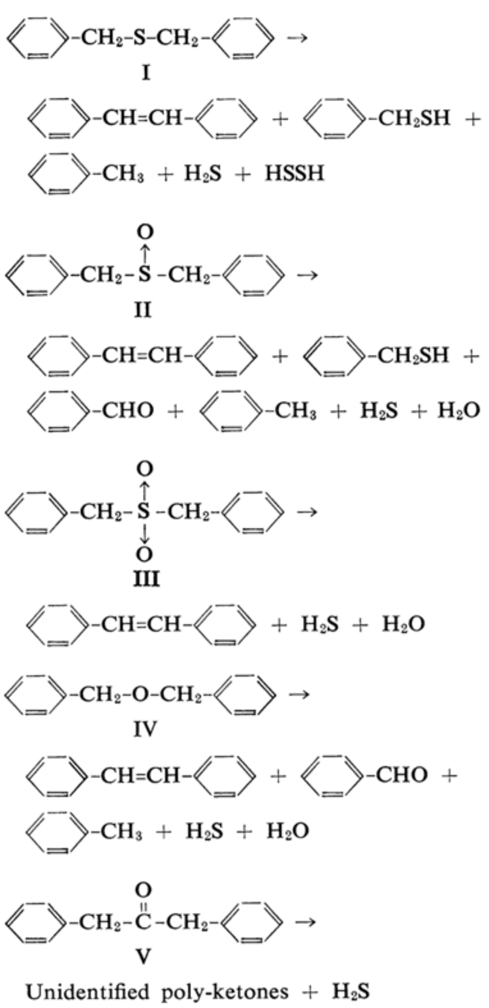
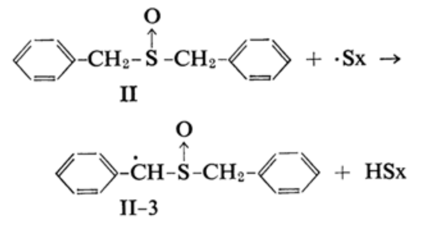


Chart 1. Species of the reaction products.

Since sulfur is known to yield a sulfur free radical at above 150°C, it is reasonable to consider that the initial step of this reaction involves the formation of the sulfoxide free radical, II-3, by the abstraction of benzylic hydrogen by the sulfur free radical, as Eq. 3 illustrates. The radical, II-3, would then undergo a variety of reactions.



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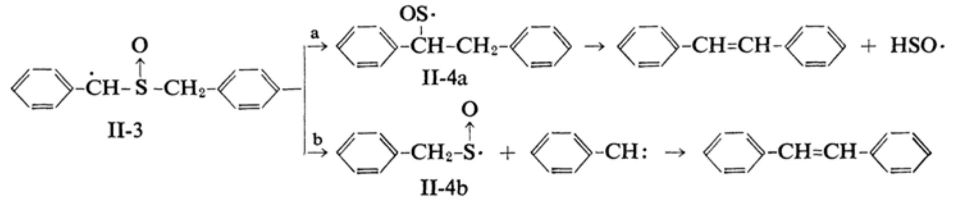
The major portion of the solid product (obtained in a 39% yield) was found to be stilbene. Two possible pathways are conceivable for the formation of stilbene. One is through the rearrangement and elimination of II-3, as is shown in Eq. 4a, and the other is via the

TABLE I. REACTION CONDITIONS AND THE YIELD OF THE PRODUCTS

Compd.	Reaction temp. °C	Reaction time hr.	Weight of the reaction mixture		Yield of the products,[a] mg. and per cent						
			Compd. mg.	Sulfur mg.	PbS	Oils	Solid	H_2S_2	water	SO_2	Residue
$(C_6H_5CH_2)_2S$ (I)	210	6.5	1073	162	472 (39.3)	291[b] (27.2)	375[e] (41.5)	+[g]	–	–	198
$(C_6H_5CH_2)_2SO$ (II)	205	5.0	1157	160	445 (37.2)	442[c] (38)	354[e] (39)	–	+	–	367
$(C_6H_5CH_2)_2SO_2$ (III)	250	7.0	3695	481	1152 (32)	—	1818[e] (68)	–	+	–	1236
$(C_6H_5CH_2)_2O$ (IV)	210	6.0	5940	971	739 (10.2)	3562[d] (60)	775[e] (14.4)	–	+	–	1495
$(C_6H_5CH_2)_2CO$ (V)	230	7.0	4210	640	3477 (72.7)	—	2030[f]	–	–	–	1890

a) Percent yields are shown in the parentheses.
b) Mixture of toluene and benzylmercaptan.
c) Mixture of toluene, benzylmercaptan and benzaldehyde.
d) Mixture of toluene and benzaldehyde.
e) Mainly stilbene.
f) Mainly starting ketone.
g) About 200 mg. containing one drop of toluene and benzylmercaptan.

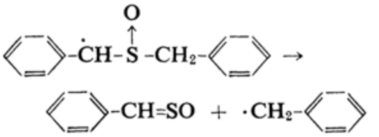


(4)

carbene intermediate, as is illustrated in Eq. 4b. The pathway 4a is a rearrangement involving the C–S bond cleavage of II-3, as in the formation of benzaldehyde, where sulfoxide S–O bond cleavage takes place as is postulated below (Eq. 8). The carbene intermediate leading to stilbene was also postulated in the base-catalyzed carbanion reaction of sulfonyl[4] and sulfonium compounds.[5]

Although there is no conclusive evidence for making any particular choice between these two pathways, we favor the former path, 4a, for the following reasons. A free radical of the Ar–S–O· type has been said to be very stable[6] and has been known to undergo disproportionation to give the corresponding thiolsulfonate.[7] Since the free radical, II-4b, is isoelectronic with Ar–SO·, it would give the thiolsulfonate. However, no such product was detected in the present reaction. Moreover, it also seems difficult for the carbene pathway to account for the reactions of the dibenzyl sulfide and the ether, as will be discussed later.

The oily product (38%) was found to be a mixture of toluene, benzaldehyde and benzyl mercaptan in a ratio of 1:8:13. The formation of toluene can be explained either by the decomposition of II–3 (Eq. 5—6) or by the direct homolysis of the C–S bond of the starting sulfoxide (Eq. 7), although the latter pathway is rather unlikely. The formation of benzaldehyde and benzyl mercaptan can be readily explained by assuming an intramolecular migration of sulfoxide oxygen to the benzylic carbon, followed by the homolytic



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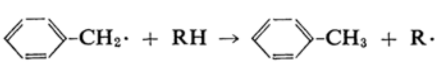

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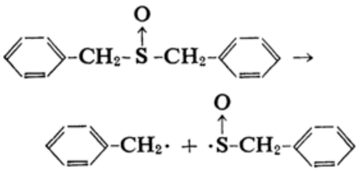

(7)

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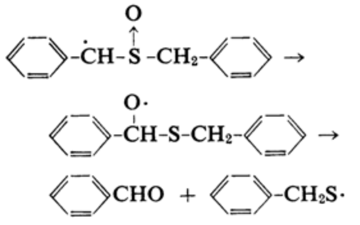
[4] J. F. King and T. Durst, *Tetrahedron Letters*, 585 (1963).

[5] A. W. Johnson, V. J. Hruby and T. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

[6] S. Oae, "3d Orbital Resonance Involving the Sulfur Atom in Organic Sulfides" in "Organic Sulfur Compounds" Vol. IV, Ed. by N. Kharasch, Pergamon Press, New York, in press.

[7] a) R. M. Topping and N. Kharasch, *Chem & Ind.*, **1961**, 178; b) S. Oae and K. Ikura, This Bulletin, **38**, 58 (1965).

cleavage of the C–S bond, as is shown in Eqs. 8 and 9. The relative importance of these reactions (Eqs. 4—9) will be discussed in a later section.



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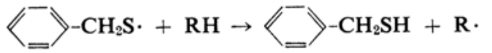

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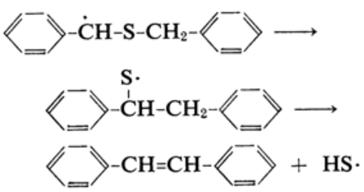
A small amount of water seems to be formed by the reduction with hydrogen sulfide, although it is not clear whether the compound to be reduced is the starting sulfoxide or one of the oxygen-containing intermediates shown in the foregoing equations. Related is the finding by Toland and his co-workers that a carboxylic acid or a nitrile is reduced to a hydrocarbon with hydrogen sulfide.[8]

The yield of the residual solid in the reaction flask was 27.8%, based on the original weight of the reactants. Alumina column chromatography and infrared analyses showed that this was mainly composed of elemental sulfur and the starting sulfoxide, and that there was no detectable amount of the other products which could be expected if species such as $C_6H_5CH_2SO$ and $C_6H_5CH{=}SO$ were the real intermediates.

The Products from the Other Dibenzyl Compounds.—The mechanism of the reactions with the other compounds appear to be essentially similar to those with dibenzyl sulfoxide, i. e., the initial abstraction of hydrogen by a sulfur-free radical, followed by several competing reactions of the resulting free radicals. The relative importance of such competing reactions, however, varies depending on the nature of the dibenzyl compounds.

The products from the reaction with dibenzyl sulfide were hydrogen sulfide (39.3%), hydrogen persulfide, toluene, benzyl mercaptan and stilbene (41.5%). The formation of toluene, in an amount about equal to that of benzyl mercaptan, suggests three pathways; one is the direct splitting of the C–S bond, such as in Eq. 7, while the others are decompositions of the initially-formed free radical, such as in Eqs 5 and 4b. The direct splitting, however, seems unlikely, and the carbene pathway also fails to account for the yield of toluene, which should be smaller than that of benzyl mercaptan since the carbene would readily dimerize to stilbene. The pathway similar to Eq. 5 would, however, predict the formation of benzthioaldehyde. A related reaction to form benzaldehyde was actually observed in the reaction of dibenzyl ether, as will be described below. However, in the reaction of dibenzyl sulfide, infrared and gas chromatographic analyses failed to detect the formation of such thioaldehyde. Probably thioaldehyde, even when formed, was readily reduced to the corresponding mercaptan by hydrogen sulfide.

An interesting observation was the formation of hydrogen persulfide. The reaction leading to this product seems to be unique only to dibenzyl sulfide, since hydrogen persulfide was not detected in the reactions of the other dibenzyl compounds. Probably the following reactions, 10 and 11, are competing in the formation of stilbene:



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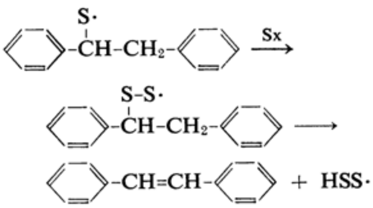

(11)

The products of dibenzyl sulfone were hydrogen sulfide (32%), stilbene (68%) and a small amount of water. Although the reaction was carried out several times, in no case was the evolution of sulfur dioxide detected. This observation seems strange when one recalls the quantitative formation of sulfur dioxide in the reaction of diphenyl sulfone.[1a] In this connection, it is interesting to compare the relative yields of lead sulfide and stilbene obtained from the three dibenzyl sulfur compounds. In the case of both sulfide and the sulfoxide, the yields of the two compounds were nearly the same, while the yield of lead sulfide from the reaction with the sulfone was about half of that of stilbene. The formation of water and no evolution of sulfur dioxide undoubtedly indicate that hydrogen sulfide was used for the reduction of the SO_2 group.

The major products in the case of dibenzyl ether were hydrogen sulfide (10.2%), benzaldehyde, toluene (60%), stilbene (14.4%), and a small amount of water. The formation of

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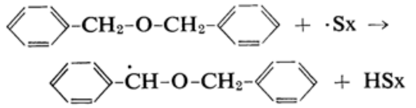
[8] W. G. Toland and R. W. Campbell, *J. Org. Chem.*, **28**, 3124 (1963).

toluene and benzaldehyde can be readily explained by means of Eqs. 12—14, which indicate the initial formation of a free radical, followed by its decomposition. As is illustrated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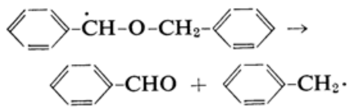
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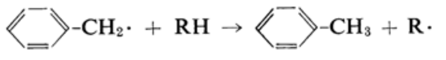
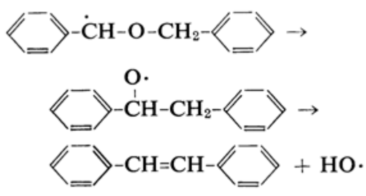

(14)

in Eqs. 7 and 4b, if the reaction is initiated by the direct splitting of the C–O bond or by the decomposition of the initially-formed free radical to give carbene, we might expect the formation of benzyl alcohol. However, the formation of benzyl alcohol was not detected by infrared and gas chromatographic analyses. These observations, together with the formation of a small amount of water, strongly indicate that the reaction to form stilbene proceeds through the pathway shown in Eq. 15: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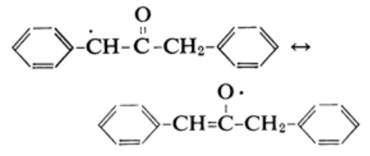
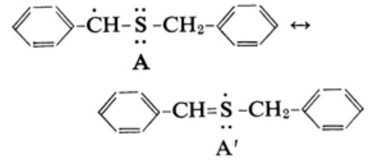
A remarkable feature of the reaction of dibenzyl ketone was the high yield of hydrogen sulfide (72.7%) as compared with the yields of less than 40% for the other compounds. This implies fewer fragmentation products, such as toluene and ketone, than would be expected if reactions of the type shown in Eqs. 5—6 or in Eqs. 12—14 took place. Actually, infrared spectra and alumina column chromatography failed to detect any fragmentation products except for the starting ketone and unidentified polyketones. These observations suggest that the initially-formed free radical is so stable that it undergoes dimerization or polymerization with less fragmentation than in the case of the other compounds.

General Remarks. — As has been described above, all these reactions appear to be initiated by the abstraction of benzylic hydrogen by the sulfur free radical. For the present five dibenzyl compounds, the total yield of stilbene plus fragmentation products (the yield of lead sulfide in the case of dibenzyl ketone) amounts to about 70%: i. e., all the compounds appear to undergo a facile abstraction of hydrogen. This is undoubtedly due to the very active nature of the benzylic hydrogen atom. For compounds having less active hydrogen, the reaction somewhat different from those of the dibenzyl compounds. Our preliminary experiments on the reactions of di-*n*-butyl sulfide, sulfoxide and sulfone indicate that these compounds undergo hydrogen abstraction to a much lesser extent than do the dibenzyl compounds under similar reaction conditions.⁹⁾ Extreme are the cases of the reaction of diphenyl sulfoxide and sulfone,¹ᵃ⁾ as has been described before. The fate of the initially-formed free radical depends on its stability and also on the relative ease of the bond breakings of C–C, C–S, C–O and S–O linkages.

The following resonance stabilization of the initial free radical seems to be responsible for the apparent lack of fragmentation in the reaction with dibenzyl ketone. The dependence of the fragmentation reaction on the stability



of the initial free radical seems also to be manifested in the reactions of dibenzyl sulfide and ether. The free radical of the sulfide (A) can be stabilized by the 3d-orbital resonance of sulfur (A′) as well as by the resonance



stabilization by the phenyl ring, whereas such stabilization is impossible in the ether. This difference seems to be partly responsible for the higher yield of stilbene from the sulfide than from the ether and for the higher yield of fragmentation products from the ether than from the sulfide.

The same view can be derived from the reaction of benzyl cyanide. Recently, Mayer and Scheithauer found that the reaction of benzyl cyanide with sulfur above 175°C gave hydrogen sulfide and *trans*-dicyanostilbene as the major products and a small amount of 1, 2-dicyanodiphenylethane.¹⁰⁾ Although no mechanistic interpretation has been made, the reaction seems to be initiated by the abstraction of benzylic hydrogen by the sulfur free radical, and the initially-formed free radical

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9) Unpublished work of these laboratories.

10) R. Mayer and St. Scheithauer, *J. Prakt. Chem.*, **21**, 214 (1963).

seems to be so stable that it readily dimerizes to give 1,2-dicyanodiphenylethane, which is then transformed to dicyanostilbene.

Although it is not easy to compare the relative ease of the bond breakings of C–C, C–O and C–S bonds from the product analyses, the product distribution can often serve as a measure for the comparison of some particular bonds. A good example is the case of the S–O bond in sulfoxide and sulfone. The formation of benzaldehyde and benzyl mercaptan clearly indicates the S–O bond breaking in dibenzyl sulfoxide, while no such bond breaking was detected in the corresponding sulfone except for the formation of water. In the reactions of di-*n*-butyl sulfoxide and sulfone, the S–O bond breaking in the former compound resulted in the formation of di-*n*-butyl sulfide, while no such reaction was observed with the latter compounds.⁹⁾ The most clear-cut case is the comparison between those of diphenyl sulfoxide and the sulfone.¹⁾ In all these cases, the S–O bonds in the sulfoxides are found to be much weaker than those of the corresponding sulfones and to be readily cleaved, as had been predicted.¹¹⁾

Experimental

The Synthesis of the Starting Compounds.—Dibenzyl sulfide was prepared by the reaction of benzyl chloride with sodium sulfide; m. p. 49°C (lit., 49°C),¹²⁾ recrystallized from 70% aqueous ethanol. Dibenzyl sulfoxide was prepared by the oxidation of the sulfide with hydrogen peroxide in acetic acid, m. p. 136—137°C (lit., 132—133°C),¹²⁾ recrystallized from *n*-hexane. Dibenzyl sulfone was prepared by the chromic acid oxidation of the sulfide in acetic acid, m. p. 150—151°C (lit., 149.5—150°C),¹²⁾ recrystallized from *n*-hexane-benzene.

Dibenzyl ether was prepared by the reaction of benzyl chloride with sodium benzyl alkoxide in dioxane, m. p. 148°C/6 mmHg (lit., 170°C/16 mmHg).¹³⁾

Dibenzyl ketone was prepared by the reaction of benzylcyanide with benzyl magnesium chloride in anhydrous ether, followed by the decomposition of the resulting imino complex with water; m. p. 34—35°C (lit., 35°C),¹⁴⁾ recrystallized from *n*-hexane.

General Procedure for the Reaction with Elemental Sulfur. — The reaction apparatus (Fig. 1) was essentially the same as that employed in the previous reactions of diphenyl sulfoxide and sulfone, but here modified to trap volatile products and hydrogen sulfide.

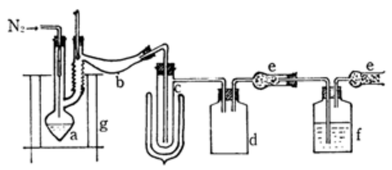

Fig. 1

a, Reaction flask; b, trap for solid or oils; c, trap for volatile oils; d, empty bottle; e, calcium chloride drying tube; f, trap for hydrogen sulfide containing lead acetate.

Equimolecular amounts of the starting compound and sulfur were thoroughly mixed and placed in a Säbel-type flask with a short fractionating column (a) (in Fig. 1). The whole system was first flushed with nitrogen gas at room temperature for about 10 min. The reaction flask was then heated in an air bath (g) under a slow stream of nitrogen. At around 160°C, the evolution of hydrogen sulfide was usually observed. After the temperature had been slowly raised to about 200°C, this temperature was maintained for five to nine hours. The oily or solid product was trapped in (b) (in Fig. 1), the volatile product was trapped in (c) (in Fig. 1), which was cooled in a dry ice-acetone bath (below −50°C), and the hydrogen sulfide was trapped in a vessel as lead sulfide. After the evolution of hydrogen sulfide was no longer observed, the substance which remained in the reaction flask (a) (Fig. 1) was vacuum-distilled. The oily and solid products thus obtained were purified by a combination of gas-liquid and column elution chromatographies and identified by spectroscopy and by elemental analysis. At least three runs were carried out for each compound in order to (test the reproducibility). A typical run with dibenzyl sulfide is described in the next paragraph. Table I gives one representative run for each compound.

The Reaction of Dibenzyl Sulfide. — After the reaction had been completed, the hydrogen sulfide trapped as lead sulfide was filtered, washed with water, dried and weighed; it was found to amount to 472 mg. (39.3%). A volatile product in the trap c, was found to be a mixture of hydrogen persulfide and a very small fraction of benzylmercaptan plus toluene as two immiscible liquids. This mixture was mechanically separated from hydrogen persulfide with a syringe and analyzed by gas chromatography and infrared spectrometry. The gas chromatography was carried out using a high-vacuum silicone column and hydrogen carrier gas, at the column temperature of 88.5°C. The retention times of toluene and benzyl mercaptan were 5.2 and 40 min. respectively, and no other component was detected. The oils in trap b were also found to be a mixture of toluene and benzyl mercaptan by infrared and gas chromatographic analyses; the yield was 291 mg. (27.2%). The hydrogen persulfide was identified by its boiling point 73—74°C (lit., 74.5°C and its ultraviolet spectra (λ_{max}, 261, 268 mμ in EtOH).

After the mixture of toluene and benzyl mercaptan had been removed from the trap b, the brown residue in the reaction flask was vacuum-distilled to give a pale yellow solid, which was found to be

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11) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962), Chapters 3 and 4.

12) R. L. Shriner, H. C. Struck and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060 (1930).

13) G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, **1928**, 2305.

14) H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, *J. Am. Chem. Soc.*, **71**, 3629 (1949).

mainly composed of stilbene. The analysis was first made by alumina thin-layer chromatography, using *n*-hexane as the developing solvent. The chromatogram after iodine coloration showed a main spot of stilbene and three other small faint spots. The alumina elution chromatography was carried out using a *n*-hexane-benzene (7 : 3 v/v) mixture as the developing solvent. Over 90% of the eluted fractions was found to be stilbene on the basis of their having the same melting point and the same infrared spectra as those of authentic stilbene. The fractions corresponding to the small spots on the thin-layer chromatogram were not detected by this column chromatography.

The dark brown residue in the reaction flask amounted to 198 mg., and its infrared spectra were found to be almost identical with those of the starting sulfide. This residue was probably composed of the starting sulfide, elemental sulfur and small amounts of unknown products.

The Reaction of Dibenzyl Sulfoxide.—Three runs were performed. In each case, the attempt to detect SO_2 failed. Hydrogen sulfide was obtained as lead sulfide, as has been described before. The oily product was found to be composed of toluene, benzaldehyde and benzyl mercaptan by infrared spectra and gas chromatography, which was carried out under conditions similar to those described above. The retention times of toluene, benzaldehyde and benzyl mercaptan at 85°C were 5.4, 24.2 and 45.6 min. respectively. The infrared spectra of the oil showed a strong band at 1730 cm^{-1} due to benzaldehyde. The identification of benzaldehyde was also made converting it to the 2,4-dinitrophenylhydrazone m. p. 238—239°C (mixed melting point, 237—239°C). The solid product, m. p. 117—120°C was analyzed by alumina column chromatography to give stilbene as the major fraction and a trace of a yellow solid. Stilbene was identified by the infrared spectra, elemental analysis and a mixed melting point determination with an authentic sample:

Found: C, 92.65; H, 6.85. Calcd.: C, 93.33; H, 6.60%.

The above unknown yellow solid showed the following properties; m. p. 116—119°C.

Found: C, 49.65; H, 4.45%.

A small amount of white crystals gradually adhered on the inner walls of the trap c as the reaction proceeded. This melts near 0°C and is miscible with water. The presence of the O-H band in the infrared spectra of the non-dried oily product (in the trap b) and the indication of water on the gas chromatogram of the same oily product indicated that the product in the trap c was water.

The identification of the black residue in the reaction flask was attempted. The infrared spectrum was very similar to the starting sulfoxide. This residue was probably mainly composed of the starting sulfoxide and elemental sulfur.

The Products of the Other Compounds.—The reaction conditions and the yields of the products are shown in Table I. The analytical methods were essentially the same as those described above.

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