2. The compound was readily resolved through the strychnine salt.

3. The active forms did not racemize under the ordinary conditions which might be expected to effect racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION AND PROPERTIES OF CERTAIN SULFOXIDES AND SULFONES

BY R. L. SHRINER, H. C. STRUCK AND W. J. JORISON

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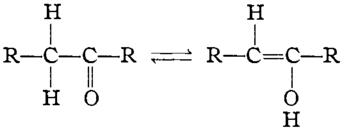
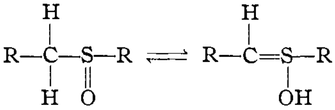
Although the enolization of a methylene group adjacent to a carbonyl group has been thoroughly studied, not much information is available on the behavior of compounds containing other linkages adjacent to a methylene group. The purpose of the present investigation was to study the influence exerted on a methylene group by the sulfoxide and sulfone linkages.

Using the customary notation, a comparison of the following formulas would indicate a similarity in chemical behavior; *i. e.*, under the proper conditions the sulfoxide might be expected to tautomerize in the same manner as the ketone



$$R\text{—}CH_2\text{—}C(=O)\text{—}R \rightleftharpoons R\text{—}CH{=}C(OH)\text{—}R$$



$$R\text{—}CH_2\text{—}S(=O)\text{—}R \rightleftharpoons R\text{—}CH{=}S(OH)\text{—}R$$

However, it has been known for some time that the chemical behavior of the sulfoxide linkage does not parallel that of the carbonyl.[1] Moreover, the electronic structures of sulfur–oxygen compounds, as formulated on the Lewis–Langmuir octet theory of valence, do not parallel exactly the electronic structure for carbon–oxygen.[2] The recent work of Sugden, who has found a considerable difference in the parachors of the carbonyl and the sulfoxide[3] groups, and the resolution by Phillips[4] of the sulfinic esters and sulfoxides, have furnished good evidence of the dis-

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[1] For example, the Grignard reagent does not add to the sulfoxide linkage as it does to the carbonyl linkage. Courtot, "Le Magnesium en Chimie organique," Rigot and Co., **1926**, pp. 125, 225, ff.

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, **1923**, pp. 95, 100.

[3] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924); **127**, 1525, 1868 (1925).

[4] Phillips, *ibid.*, **127**, 2552 (1925); **129**, 2079 (1926).

similarity between these two groupings. The behavior of compounds containing the sulfone group adjacent to a methylene group has been studied in two instances. Michael and Comey[5] and Tröger and Lux[6] have prepared and studied benzene sulfonyl acetic ester, and Schroeder and Herzberg[7] have alkylated the esters of methionic acid. Although many of the simple sulfones of the type RSO_2R are described in the literature, practically no data are available on their properties and especially on the behavior of sulfones with different radicals.

Accordingly, a series of sulfoxides and sulfones was prepared, and their behavior toward reagents which would indicate the influence exerted by these groupings on the adjacent methylene groups studied. The compounds prepared are listed in Table I. They were made by modifications of general methods given in the literature which resulted in increased yields, and hence made larger quantities available for their study. The details of their preparation are given in the experimental part. Table I also lists the effect of various reagents on these sulfoxides and sulfones and summarizes the data obtained.

TABLE I

PROPERTIES OF SULFOXIDES AND SULFONES

Compound	Solubility in 10% NaOH	Solubility in 10% Na_2CO_3	Color with $FeCl_3$	Re-action metallic Na	Salt formation with sodium ethylate	Alkylation with MeI and NaOEt
Sulfoxides						
(1) $C_6H_5SOC_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(2) $C_6H_5SOCH_2C_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(3) $C_6H_5CH_2SOCH_2C_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
(4) $C_6H_5SOCH_2SOC_6H_5$	Insol.	Insol.	−	−	−	Not alkylated
Sulfones						
(5) $C_6H_5SO_2CH_2C_6H_5$	Insol.	Insol.	−	+	+	Not alkylated
(6) $C_6H_5CH_2SO_2CH_2C_6H_5$	Sl. sol.	Insol.	−	+	+	Not alkylated
(7) $C_6H_5SO_2CH_2SO_2C_6H_5$	Sol.	Insol.	−	+	+	Gives mono and dimethyl alkylations

Theoretical Discussion

The Sulfoxides.—It will be noted that none of the methylene hydrogens in any of the sulfoxides (2, 3, 4) was activated. Diphenyl sulfoxide (1) was prepared and used as a control in order to guard against addition compounds. In each case the result was negative, even compound (4), which possessed a methylene group between two sulfoxide linkages, showed no tendency to alkylate and was recovered unchanged from the attempted alkylations. All of these compounds were insoluble in aqueous sodium and potassium hydroxides, and their benzene solutions did not

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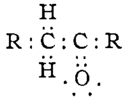
[5] Michael and Comey, *Am. Chem. J.*, **5**, 116 (1883).

[6] Tröger and Lux, *Arch. Pharm.*, **247**, 618 (1909).

[7] Schroeder and Herzberg, *Ber.*, **38**, 3391 (1905).

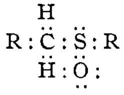
react with metallic sodium. Alcoholic solutions of these sulfoxides did not give any color with ferric chloride. The behavior of these sulfoxides is in sharp contrast to that of the corresponding ketones.

These results furnish further evidence that the nature of the sulfoxide linkage differs from that of the carbonyl. It is of interest in this connection to consider the following electronic formulas



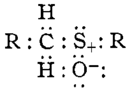
$$\begin{array}{c}\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\mathrm{C}:\mathrm{R}\\ \ddot{\mathrm{H}}\;.\underset{..}{\ddot{\mathrm{O}}}.\end{array}$$

I



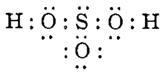
$$\begin{array}{c}\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\ddot{\mathrm{S}}:\mathrm{R}\\ \ddot{\mathrm{H}}:\underset{..}{\ddot{\mathrm{O}}}:\end{array}$$

II



$$\begin{array}{c}\mathrm{H}\\ \mathrm{R}:\ddot{\mathrm{C}}:\ddot{\mathrm{S}}_{+}:\mathrm{R}\\ \ddot{\mathrm{H}}:\underset{..}{\ddot{\mathrm{O}}}^{-}:\end{array}$$

III



$$\begin{array}{c}\mathrm{H}:\underset{..}{\ddot{\mathrm{O}}}:\ddot{\mathrm{S}}:\underset{..}{\ddot{\mathrm{O}}}:\mathrm{H}\\ :\underset{..}{\ddot{\mathrm{O}}}:\end{array}$$

IV

Formulas II and III are the only ones possible which are consistent with the postulates of the octet theory[2] and Phillips'[4] resolution of the sulfoxides. Formula II is analogous to that given to sulfurous acid (IV) by Latimer and Rodebush[8] and used by them to explain the weakly acidic nature of sulfurous acid. Formula III is given by Sugden,[3] in which the sulfur–oxygen linkage is classed as a semi-polar linkage, *i. e.*, a pair of electrons and an electrostatic charge.[9] Formulas II and III are essentially the same, the chief difference being one of notation. Latimer and Rodebush consider that the disproportionation of the electrostatic charges (caused by the fact that the oxygen is held to the sulfur atom by sharing only one pair of electrons, neither of which came from the oxygen atom) is understood as the natural result of writing Formula II. Sugden indicates this electrostatic effect at the sulfur–oxygen linkage in giving Formula[10] III.

In either case both Formulas II and III indicate a different condition of the oxygen atom from (I). It seems probable that it is the unshared pair of electrons on the sulfur atom which prevents the hydrogen atoms from ionizing. Latimer and Rodebush[8] explain the weakly acidic properties of sulfurous acid (IV) as due to the presence of an unshared pair of electrons on the sulfur atom. This mobile pair of electrons prevents the pulling in of the electrons shared between the oxygen and hydrogen in

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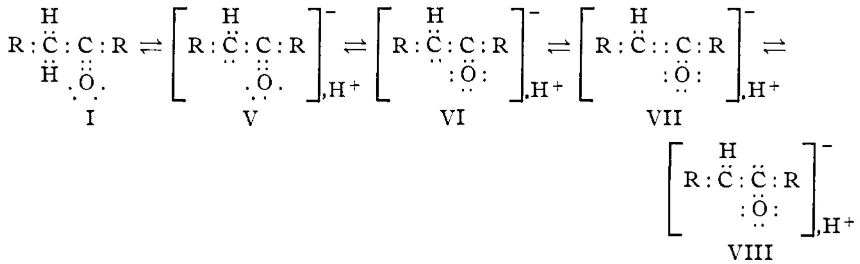
[8] Latimer and Rodebush, THIS JOURNAL, **42**, 1425 (1920).

[9] The disproportionation of the electrostatic charges can be shown by making use of the formula for the calculation of residual atomic charge. [See Langmuir, *Science*, **54**, 59 (1921); Carothers, THIS JOURNAL, **46**, 2228 (1924)]. Residual charge $= e - (S - V_0)$ where e is electrons in shell of the atom in free state; S is electrons in shell of the atom in the compound and V_0 is valence. For the sulfur in a sulfoxide we obtain: Res. charge $= 6 - (8 - 3) = +1$. For the oxygen, Res. charge $= 6 - (8 - 1) = -1$. This, of course, is the fundamental basis for Sugden's formula.

[10] It is to be emphasized that Sugden's method of indicating the semi-polar double bond is a separate and distinct notation. The presence of the plus and minus signs does *not* indicate *unit* charges as in the case with H^+, Cl^- where there is the complete transference of an electron. It also has nothing in common with the use of plus and minus signs used by Fry, Lowry, Ingold and others to denote an alternating polarity.

the case of sulfurous acid and it seems probable that the same explanation will hold for the sulfoxide (II or III) where the unshared pair prevents the pulling in of the electrons between carbon and hydrogen.

Further support for this explanation may be obtained by considering the process of enolization of a ketone. In terms of the electron theory enolization may be regarded as a change from the non-polar form of (I) to the polar forms of (V, VI, VII, VIII), this transformation being due to the pull exerted by the oxygen atom on the electrons. These stages in the enolization of a carbonyl compound may be indicated as follows



$$\underset{\text{I}}{\mathrm{R}:\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{C}}}}:\underset{\cdot\ddot{\mathrm{O}}\cdot}{\mathrm{C}}:\mathrm{R}} \rightleftharpoons \underset{\text{V}}{\left[\mathrm{R}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\underset{\cdot\ddot{\mathrm{O}}\cdot}{\mathrm{C}}:\mathrm{R}\right]^-,\mathrm{H}^+} \rightleftharpoons \underset{\text{VI}}{\left[\mathrm{R}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}:\mathrm{R}\right]^-.\mathrm{H}^+} \rightleftharpoons \underset{\text{VII}}{\left[\mathrm{R}:\overset{\mathrm{H}}{\mathrm{C}}::\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}:\mathrm{R}\right]^-.\mathrm{H}^+} \rightleftharpoons \underset{\text{VIII}}{\left[\mathrm{R}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\underset{:\ddot{\mathrm{O}}:}{\ddot{\mathrm{C}}}:\mathrm{R}\right]^-,\mathrm{H}^+}$$

All four of the above polar forms are undoubtedly in equilibrium with each other and the electrostatic charges change from carbon to oxygen according to solvents and reagents.

Now it is well known that only one of the hydrogens is tautomeric at a time; *i. e.*, only one can be replaced by sodium and the second one does not ionize off or does so only to a very, very slight extent. The anions (V, VI, VII and VIII) would have to dissociate again and they exhibit no such tendency. Now these anions resemble, in one respect at least, the normal structure for the sulfoxides; *i. e.*, there is present in (V, VI and VIII) an unshared pair of mobile electrons which act to prevent any further ionization of the second hydrogen atom of the adjacent carbon. Hence, in the sulfoxides which also possess an unshared pair of electrons (Formulas II, III), the ionizing tendency should resemble the secondary ionization of (V, VI, VII, VIII); *i. e.*, they should not undergo enolization. This is in agreement with the experimental data. It also receives confirmation from the data obtained on the corresponding sulfones.

The Sulfones.—By reference to Table I it will be noted that the methylene hydrogens of the sulfones were activated in each case, the greatest activity being exhibited by Compound 7, which was readily soluble in sodium hydroxide and easily alkylated. The behavior of the sulfones is in sharp contrast to the behavior of the sulfoxides, which exhibited no such tendency. Dibenzoylmethane, which is the carbonyl compound analogous to methylene diphenyldisulfone, undergoes enolization[11] and may be alkylated but it is not soluble in aqueous alkalies. This behavior

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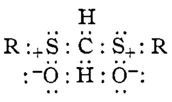
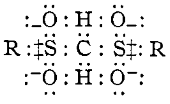
[11] Claisen, *Ann.*, **277**, 184 (1893); **291**, 25 (1896).

constitutes still further evidence of the difference between the carbon–oxygen linkage and the sulfur–oxygen linkage. It is of interest to compare in this connection the electronic formulas for the sulfoxides, sulfones and carbonyl compounds



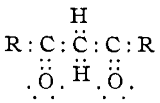
$$\begin{array}{ccccc} & & \mathrm{H} & & \\ \mathrm{R}: & {}_{+}\ddot{\mathrm{S}}: & \ddot{\mathrm{C}}: & \ddot{\mathrm{S}}_{+}: & \mathrm{R} \\ & :^{-}\ddot{\mathrm{O}}: & \mathrm{H}: & \ddot{\mathrm{O}}^{-}: & \end{array}$$

IX



$$\begin{array}{ccccc} & :_{-}\ddot{\mathrm{O}}: & \mathrm{H}: & \ddot{\mathrm{O}}_{-}: & \\ \mathrm{R}: & \ddagger\ddot{\mathrm{S}}: & \ddot{\mathrm{C}}: & \ddot{\mathrm{S}}\ddagger: & \mathrm{R} \\ & :^{-}\ddot{\mathrm{O}}: & \mathrm{H}: & \ddot{\mathrm{O}}^{-}: & \end{array}$$

X

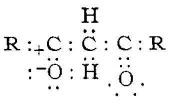


$$\begin{array}{ccccc} & & \mathrm{H} & & \\ \mathrm{R}: & \mathrm{C}: & \ddot{\mathrm{C}}: & \mathrm{C}: & \mathrm{R} \\ & .\ddot{\mathrm{O}}. & \mathrm{H} & .\ddot{\mathrm{O}}. & \end{array}$$

XI

The first two formulas make use of the semi-polar linkage developed by Sugden as the result of the calculation of the parachors for sulfoxides and sulfones.[3] It has already been pointed out that the failure of the hydrogen of the methylene group in the sulfoxide (IX) to ionize was probably due to the presence of the unshared pair of electrons on the sulfur atom. The sulfone (X) contains no unshared pairs of electrons on its sulfur atoms. Each sulfur atom in the above sulfone has two semi-polar linkages, which results in the sulfur being doubly positive.[12] This resultant residual positive charge on the sulfur atom causes a distortion or pull on the electrons in the octet about the carbon of the methylene group which pulls in one pair of electrons and thus renders one of the hydrogens active. Since (X) has two sulfone groups, one on each side of the methylene group, the hydrogens in the latter group should be activated very readily. Compound 5 having only one sulfone group and a phenyl group about the methylene group should give rise to active hydrogens less readily and in dibenzyl sulfone (6) the distorting effect caused by the sulfonyl group is distributed among two methylene groups and hence this compound is the least active of the three.

The diketone (XI) contains a non-polar double bond on each of the carbons of the carbonyl group. The enolization of this substance is due to its transformation under the influence of reagents into one of the active forms of the double bond between carbon and oxygen.[13] If we suppose this conversion to result in the momentary production of the form shown, then it is evident that one carbonyl carbon carries a residual atomic charge of plus one and hence exerts a pull on the electrons of the octet about the methylene carbon atom with resultant activation of the hydrogen. Since the carbon in the above diketone carries a residual charge of only plus one, while the sulfur atoms in the disulfone (X) have a residual charge of plus two, it is now clear that the methylene hydrogens in (X) should be more active than those in (XI). This is in agreement with the experimental facts.

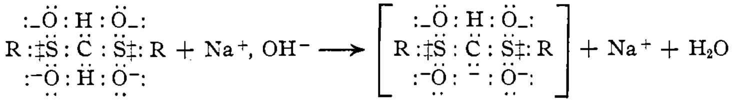


$$\begin{array}{ccccc} & & \mathrm{H} & & \\ \mathrm{R}: & {}_{+}\mathrm{C}: & \ddot{\mathrm{C}}: & \mathrm{C}: & \mathrm{R} \\ & :^{-}\ddot{\mathrm{O}}: & \mathrm{H} & .\ddot{\mathrm{O}}. & \end{array}$$

[12] *Cf.* Ref. 9. The approximate residual charge calculated from the formula $e - (S - V_c)$, for the sulfur atom is $6 - (8 - 4) = +2$. This does not mean that there are two *unit* charges on the sulfur atom. See Ref. 10.

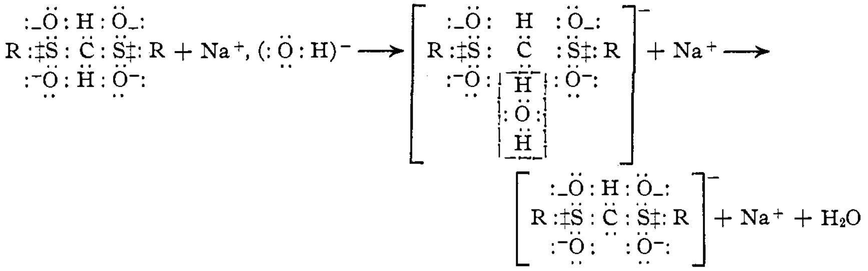
[13] Carothers, This Journal, **46**, 2229 (1924).

The conversion of the sulfone (X) into a salt under the influence of alkalies is of considerable theoretical interest since it is the first case in which the position of one of the residual negative charges is unquestionably on the methylene carbon atom.



It is obviously impossible to write any other electronic formula without violating the postulates of the octet theory. This, of course, does not mean that the sodium is attached to the carbon atom. This compound is an excellent example of the redistribution of electrostatic charges about the molecule in accordance with the reagents acting upon it. The second point of theoretical interest is that in the case of this sulfone the sodium salt is *not* formed as the result of a primary transformation to a true *enol* form,[14] with ionization of the enolic form, and finally combination of the hydrogen ion with the hydroxyl ion.

Since no true enol form exists, the formation of the sodium salt probably takes place by a combination of the sulfone with hydroxyl ion by means of a "bivalent" hydrogen[15] of the methylene group and subsequent elimination of a molecule of water. The following equation represents this type of transformation



Experimental

Preparation of Diphenyl Sulfoxide.—One hundred grams of benzene and 33 g. (0.28 mole) of thionyl chloride were placed in a 500-cc. round-bottomed flask. The

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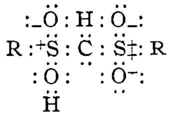
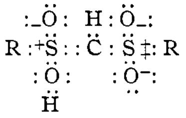
[14] The possibility of an enol form of either of the following forms is extremely improbable



A



B

Form (A) leaves an unshared pair of electrons on the central carbon and (B) puts ten electrons in the valence shell of sulfur.

[15] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, **1923**, p. 109.

mixture was immersed in an ice-salt bath and 60 g. of anhydrous aluminum chloride added in 0.5-g. portions over a period of two hours. Then 40 g. of benzene was added and the solution refluxed on a steam cone until no further hydrochloric acid gas was evolved.

After about one hour the contents were poured slowly on 600 g. of cracked ice which had been slightly acidified with dilute hydrochloric acid. A vigorous reaction took place and the yellow oil which separated was removed and washed four times with 50-cc. portions of distilled water. The excess benzene was driven off by distillation and the reddish-brown oil that remained solidified upon cooling. The diphenyl sulfoxide was extracted with (70–90°) petroleum ether. Ten to fifteen extractions were necessary to completely remove the sulfoxide. It was a white crystalline substance, m. p. 70–71°, which agreed with the value given by previous investigators;[16] yield, 28.9 g. or 51%.

Anal. (Parr Bomb) Subs., 0.5158: $BaSO_4$, 0.5912. Calcd. for $C_{12}H_{10}SO$: S, 15.84. Found: S, 15.72.

Preparation of Dibenzyl Sulfide.[17]—One hundred and sixteen g. (0.56 mole) of benzyl chloride was dissolved in 300 cc. of 95% alcohol. The solution was then heated on the steam cone and 35 g. of sodium sulfide, which had been dissolved in 100 to 125 cc. of distilled water, was added. The mixture was stirred continuously and heated on the steam-bath for three days. The greater portion of the alcohol was distilled and the contents were then poured on 700 g. of cracked ice. The yellowish-brown oil which separated was removed and vacuum distilled to remove water and excess benzyl chloride. The distillation was accomplished by heating until the temperature of the vapors reached 134°, or until the distillate in the receiving flask began to solidify. The residual oil was then placed in the ice box until it solidified and was recrystallized from 70% alcohol; m. p. 49°; yield, 48 g. or 83%.

Preparation of Dibenzyl Sulfoxide.—Thirty grams of dibenzyl sulfide was dissolved in 250 cc. of acetone. The solution was filtered to remove undissolved substances. Then 15 g. of 30% hydrogen peroxide was added, the solution thoroughly shaken and allowed to stand at room temperature for forty-eight hours. The acetone was distilled and the oily residue cooled. It solidified to a white crystalline solid which was purified by recrystallization from petroleum ether;[18] m. p. 132–133°; yield, 22 g. or 75%.

Anal. Subs., 0.5463: $BaSO_4$, 0.5519. Calcd. for $C_{14}H_{14}SO$: S, 13.91. Found: S, 13.93.

Preparation of Benzyl Phenyl Sulfide.—Twelve grams (0.52 mole) of metallic sodium was dissolved in 300 cc. of absolute alcohol in a 1-liter three-necked flask fitted with a reflux condenser and a mechanical stirrer. Then 57 g. of thiophenol was added in a slow but steady stream. Next 68.8 g. of benzyl chloride was added drop by drop over a period of one and one-half hours and the mixture refluxed on a steam-bath for two hours. The alcohol was practically all distilled and while the solution was still hot it was poured on 400 g. of cracked ice. The impure sulfide was filtered and washed twice with 50-cc. portions of distilled water to remove any traces of sodium chloride. The sulfide was a white, crystalline compound;[19] m. p. 40–41°; yield, 61 g. or 60%.

Preparation of Benzyl Phenyl Sulfoxide.—Fifty-two grams of the sulfide was dissolved in 250 cc. of acetone. The solution was filtered to remove any undissolved substances. Then 40 g. of 30% hydrogen peroxide was added, the mixture thoroughly

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[16] Hinsberg, *Ber.*, **43**, 289 (1910); Colby and McLaughlin, *ibid.*, **20**, 195 (1887); Krafft and Lyons, *ibid.*, **29**, 441 (1896); Rosenheim and Singer, *ibid.*, **37**, 2154 (1904).

[17] Märcker, *Ann.*, **136**, 90 (1865).

[18] Fromm and Flaschen, *ibid.*, **394**, 310 (1912).

[19] Carlson, *Ber.*, **40**, 4194 (1907); Fromm, *ibid.*, **41**, 3403 (1908).

shaken and allowed to stand at room temperature for seventy-two hours. The acetone was evaporated and the oil which remained solidified immediately upon slight cooling. The sulfoxide was recrystallized from 60% alcohol; m. p. 122–123°; yield, 40 g.

Anal. Subs., 0.4709: $BaSO_4$, 0.5105. Calcd. for $C_{13}H_{12}SO$: S, 14.81. Found: S, 14.86.

Preparation of Methylene Diphenyl Disulfide.—This intermediate was prepared by modifying methods previously given by Otto and Tröger,[20] Baumann[21] and Fromm.[22] Twenty-three grams (1 mole) of metallic sodium was dissolved in 400 cc. of absolute alcohol. The mechanical stirrer was started and 110 g. (1 mole) of thiophenol was added in a slow but steady stream. Then 86.9 g. (0.5 mole) of methylene bromide was run in drop by drop. The addition of the methylene bromide took one hour. The mixture was refluxed, with stirring, on a steam-bath for two and one-half hours. The hot contents were immediately poured on 1000 g. of cracked ice. The solid product which separated was filtered and recrystallized from 95% alcohol. It was a white, crystalline powder; m. p. 35–36°; yield, 112 g. or 96.5%.

Anal. Subs., 0.3144: $BaSO_4$, 0.6294. Calcd. for $C_{13}H_{12}S_2$: S, 27.54. Found: S, 27.48.

Preparation of Methylene Diphenyl Disulfoxide.—Fifty grams of methylene diphenyl disulfide was dissolved in 400 cc. of acetone and filtered to remove any undissolved substances. Then 58 g. of 30% hydrogen peroxide was added. The mixture was allowed to stand at room temperature for forty-eight hours and heated for six hours at 37.5°. The acetone was distilled and the oil which remained behind was placed in the ice box overnight. The water was decanted and the solid disulfoxide was recrystallized five times from alcohol; m. p. 188–189°; yield, 30 g. or 52%.

Anal. Subs., 0.5004: $BaSO_4$, 0.8836. Calcd. for $C_{13}H_{12}S_2O_2$: S, 24.25. Found: S, 24.21.

Preparation of Phenyl Benzyl Sulfone.—Phenyl benzyl sulfone was prepared by the method given by Otto.[23] A mixture of 178 g. (1 mole) of sodium benzene sulfinate and 127 g. (1 mole) of benzyl chloride in 500 cc. of absolute alcohol was refluxed for seven to eight hours. The sulfinate did not dissolve completely, but this did not interfere with the reaction. The hot reaction mixture was poured into 1000 cc. of ice water. The crude product was filtered and dried. It was recrystallized from alcohol; m. p. 146–146.5°; yield, 120 g. (52%).

Anal. Subs., 0.5330: $BaSO_4$, 0.5363. Calcd. for $C_{13}H_{12}O_2S$: S, 13.78. Found: S, 13.80.

Preparation of Dibenzyl Sulfone.—Twenty-five grams (0.11 mole) of dibenzyl sulfide was dissolved in 130 cc. of glacial acetic acid, and 32 g. of CrO_3 added over the period of an hour. The reaction was started by the application of heat, but, once started, it proceeded smoothly. After the CrO_3 was added, the mixture was refluxed gently for fifteen minutes. The hot solution was poured directly on 500 g. of crushed ice. The precipitate was filtered and washed with ice water. Recrystallization three times from 95% alcohol gave white needles; m. p. 149.5–150°. This melting point agrees with that of Vogt and Henniger,[24] who prepared it by the action of benzyl chloride on potassium sulfite; yield, 7 g. or 23.7%.

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[20] Otto and Tröger, *Ber.*, **25**, 3429 (1892).

[21] Baumann, *ibid.*, **19**, 2806 (1886).

[22] Fromm, *Ann.*, **253**, 161 (1889).

[23] Otto, *Ber.*, **21**, 1696 (1888).

[24] Vogt and Henniger, *Ann.*, **165**, 375 (1873).

Anal. Subs., 0.5255: $BaSO_4$, 0.4979. Calcd. for $C_{14}H_{14}O_2S$: S, 13.00. Found: S, 13.00.

Preparation of Methylene Diphenyl Disulfone.—A modification of the methods of Otto and Tröger[20] and Fromm[22] was used; 18 g. (0.077 mole) of crude methylene diphenyl disulfide was dissolved in 80–100 cc. of glacial acetic acid and 42 g. of CrO_3 was added slowly over a period of one and one-half hours. The flask was warmed at first, but later the reaction proceeded smoothly without further heating. After the reaction had stopped, the hot mixture was poured on 1000 g. of crushed ice. The crude methylene diphenyl disulfone was filtered by suction and washed with ice water. Recrystallization twice from water gave white needles; yield, 4.2 g. (18% of the theoretical); m. p. 118–119°.

Anal. Subs., 0.4888: $BaSO_4$, 0.7640. Calcd. for $C_{13}H_{12}O_4S_2$: S, 21.62. Found: S, 21.48.

Properties of Sulfoxides

I. **Solubility in Alkali.**—The solubilities of the above four sulfoxides in 5 and 10% sodium and potassium hydroxides were tested. None of the compounds dissolved.

II. **Metallic Sodium.**—A solution of 0.5 g. of each of the above sulfoxides in dry benzene was treated with 0.1 g. of sliced sodium. No reaction took place in the cold.

III. **Ferric Chloride.**—Addition of ferric chloride to alcohol solutions of these sulfoxides caused no deepening of the yellow color as compared with a blank alcohol solution.

IV. **Attempted Alkylations.**—All three of the above sulfoxides were treated with sodium ethylate in absolute alcohol and methyl iodide added. A typical experiment is as follows.

Attempt to Alkylate Methylene Diphenyl Disulfoxide.—Eighty-seven hundredths gram of metallic sodium was dissolved in 100 cc. of absolute alcohol and 10 g. of methylene diphenyl disulfoxide was added. The solution was heated to dissolve the disulfoxide and 17 g. of methyl iodide was added slowly over a period of fifteen minutes with vigorous shaking. The mixture was then refluxed on a steam-bath for three hours and the hot contents poured on 200 g. of cracked ice. The reddish-brown solid upon recrystallization was found to be the original compound; m. p. 188–189°.

Properties of Sulfones

I. **Solubility in Dilute Alkalies.**—The solubilities of the three sulfones in 10% sodium and potassium hydroxides were tested. It was found that methylene diphenyl disulfone dissolved readily, phenyl benzyl sulfone only partially and dibenzyl sulfone not at all. All of the sulfones were completely insoluble in 6 *N* hydrochloric acid and this reagent was used to precipitate the first two compounds above from their alkaline solutions. All of the sulfones were insoluble in 5 and 10% sodium carbonate solution.

II. **Metallic Sodium.**—A solution of 0.5 g. of each of the above sulfones in dry benzene was treated with 0.1 g. of sliced sodium. Hydrogen was liberated very slowly and the sodium became coated with the salt after about half an hour.

III. **Ferric Chloride.**—Addition of dilute ferric chloride to alcohol solutions of these sulfones caused no deepening of the yellow color as compared with a blank alcohol solution.

IV. Alkylations.—The alkylation of phenyl benzyl sulfone and dibenzyl sulfone was attempted using the same procedure outlined above. Both compounds failed to alkylate and were recovered almost quantitatively from the reaction mixture unchanged.

Alkylation of Methylene Diphenyl Disulfone

(a) **With One Equivalent of Methyl Iodide.**—To a solution of 0.23 g. (0.01 mole) of sodium in 300 cc. of absolute alcohol was added 3 g. (0.01 mole) of methylene diphenyl disulfone. Next, 1 cc. (slight excess) of methyl iodide was added and the mixture refluxed for two and one-half hours; 150–200 cc. of alcohol was distilled from the mixture and the residue poured on crushed ice. The precipitate was filtered by suction and washed with ice water. Four recrystallizations from alcohol gave white needles: yield, 1 g. (47.6%); m. p. 100–101°; mixed melting point with original disulfone (m. p. 118–119°), 80–86°; mixed melting point with disubstitution product (m. p. 181–182°), 94–98°.

Anal. Subs., 0.2821: $BaSO_4$, 0.4151. Calcd. for $C_{14}H_{14}O_4S_2$: S, 20.64. Found: S, 20.22.

(b) **With Two Equivalents of Methyl Iodide.**—To a solution of 0.46 g. (0.02 mole) of sodium in 300 cc. of absolute alcohol was added 3 g. (0.01 mole) of methylene diphenyl disulfone. Next, 2.5 cc. (slight excess) of methyl iodide was added and the mixture refluxed for two and one-quarter hours; 150 cc. of alcohol was distilled from the flask and the residue poured on crushed ice. The product was filtered by suction and washed with ice water. Three recrystallizations from alcohol gave white needles: m. p. 181–182°; mixed melting point with original disulfone (m. p. 118–119°), 101–105°.

Anal. Subs., 0.4672: $BaSO_4$, 0.6723. Calcd. for $C_{15}H_{16}O_4S_2$: S, 19.75. Found: S, 19.76.

Summary

1. The preparation and enolization tendency of certain sulfoxides have been studied. It was found that the sulfoxides do not tautomerize into enolic forms under the conditions used.

2. Phenyl benzyl sulfone, dibenzyl sulfone and methylene diphenyl disulfone were prepared and their properties studied.

3. The hydrogen of the methylene group in methylene diphenyl disulfone was most active and the hydrogen in dibenzyl sulfone least active.

4. In each case the sulfone group activated the hydrogens to a much greater extent than the sulfoxide group.

5. Some of the theoretical aspects of the behavior of these compounds are discussed.

URBANA, ILLINOIS