[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Condensation of Sulfoxides with *p*-Toluenesulfonamide and Substituted Acetamides

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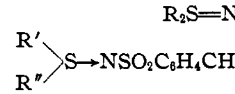
Mann and Pope[2] reported that organic sulfides react with chloramine-T, yielding compounds of a new class which they called "sulfilimines." They formulated the reaction as follows, regarding the sulfur as being connected to the nitrogen of the sulfilimine by a double bond.

$$R_2S + (p)CH_3C_6H_4SO_2\underset{Na}{N}Cl \longrightarrow R_2S{=}NSO_2C_6H_4CH_3 + NaCl$$



$$\begin{matrix}R' \\ R''\end{matrix}\!\!>S\rightarrow NSO_2C_6H_4CH_3 \qquad \text{I}$$

Clarke, Kenyon and Phillips[3] proposed the much more plausible formula, I, in which the sulfur is attached to nitrogen by a coördinate bond; they supported this formula by showing that *m*-carboxyphenyl - methylsulfin - *p* - toluenenesulfonylimine (I, $R' = m\text{-}C_6H_4COOH$, $R'' = CH_3$) could be resolved, similar to unsymmetrical sulfoxides and to sulfinic esters. Since these compounds are known to have coördinate links between sulfur and oxygen, the sulfilimines are assigned structure I with a coördinate link between sulfur and nitrogen.

Sulfilimine formation seems to be a general reaction of sulfides and chloramine-T, although diethyl sulfides with more than two chlorine atoms do not react.[2] The sodium salt of N-chlorobenzenesulfonamide has been used instead of chloramine-T.[4] The sulfilimines are crystalline compounds and their ease of preparation recommends them for the characterization of liquid sulfides, although they have not been used very frequently for this purpose.

In studying the reactions of sulfoxides, we have found that they condense with *p*-toluenesulfonamide in the presence of acetic anhydride or phosphorus pentoxide to yield sulfilimines.

$$R_2S\rightarrow O + (p)CH_3C_6H_4SO_2NH_2 \longrightarrow R_2S\rightarrow NSO_2C_6H_4CH_3 + H_2O$$

Sulfilimines were obtained from *p*-toluenesulfonamide and diethyl, diphenyl and tetramethylene sulfoxides; they were characterized by analysis, and were also prepared from chloramine-T and the corresponding sulfide. The compounds obtained by the two methods were identical. The sulfilimine from diphenyl sulfoxide could not be obtained using acetic anhydride as the condensing agent, but the product was obtained using phosphorus pentoxide in chloroform solution.

Mann[4a] attempted to condense β,β'-dihydroxyethyl sulfoxide with *p*-toluenesulfonamide in various solvents with no dehydrating agent but obtained no product, whereas the corresponding sulfide and chloramine-T gave a hydrated sulfilimine. In our experiments acetic anhydride also failed to bring about condensation when the same conditions were employed which were successful with the sulfoxides mentioned above.

The sulfilimines are unaffected by aqueous alkali, but dissolve in cold hydrochloric acid, presumably due to salt formation. If the acid solution is heated, hydrolysis occurs with the formation of the sulfoxide and the sulfonamide[5]; both

$$(C_6H_5)_2S\rightarrow NSO_2C_6H_4CH_3\text{-}p + H_2O \longrightarrow (C_6H_5)_2S\rightarrow O + H_2NSO_2C_6H_4CH_3\text{-}p$$

fragments were isolated from diphenylsulfin-*p*-toluenesulfonylimine.

Since the sulfoxides condense readily with *p*-toluenesulfonamide, which is the amide of a strong acid, an analogous reaction was investigated using the amides of the chloroacetic acids. A sulfilimine was obtained from trichloroacetamide and tetramethylene sulfoxide (II, $R_2 = (CH_2)_4$)

$$R_2S\rightarrow NCOCCl_3 \qquad \text{II}$$
$$R_2S\rightarrow NCOCHCl_2 \qquad \text{III}$$

and from dichloroacetamide with tetramethylene sulfoxide and with diethyl sulfoxide (III, $R_2 = (C_2H_5)_2$, $R_2 = (CH_2)_4$). No product could be obtained from tetramethylene sulfoxide and monochloroacetamide or benzamide. Sulfilimines of this type derived from carboxylic amides have not been previously described. Petrov[4b] attempted to prepare a sulfilimine by the action of N-chloroacetamide on dibutyl sulfide, but obtained only dibutyl sulfoxide.

These reactions of sulfoxides are analogous to

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[1] Sherman Clarke Fellow, 1940–1941.

[2] Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

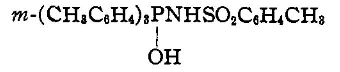
[3] Clarke, Kenyon and Phillips, *ibid.*, 188 (1927).

[4] (a) Mann, *ibid.*, 958 (1932); (b) Petrov, *J. Gen. Chem.* (U. S. S. R.), **9**, 1635 (1939) (*C. A.*, **34**, 3703 (1940)).

[5] *Cf.* Holloway, Kenyon and Phillips, *J. Chem. Soc.*, 3000 (1928).

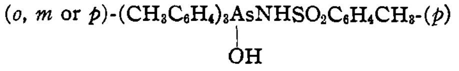
the formation of phosphinimines (IV) from phosphine oxides and p-toluenesulfonamide[6]; more

$o\text{-}(CH_3C_6H_4)_3P\rightarrow NSO_2CH_4CH_3(p)$ IV



$m\text{-}(CH_3C_6H_4)_3\underset{\underset{OH}{|}}{P}NHSO_2C_6H_4CH_3$ V

often, the phosphine oxides yield phosphonium bases such as V. Arsine oxides condense with p-toluenesulfonamide, giving the arsonium base VI, instead of the arsinimine corresponding to IV.[4a]



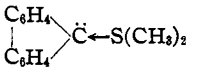
$(o, m \text{ or } p)\text{-}(CH_3C_6H_4)_3\underset{\underset{OH}{|}}{As}NHSO_2C_6H_4CH_3\text{-}(p)$ VI

$(C_6H_5)_3P\rightarrow NCOC_6H_5$ VII

Staudinger and Hauser[7] prepared a benzoylphosphinimine VII by the action of triphenylphosphine on benzoylazide, which is similar to compounds II and III.

Ingold and Jessop[8] obtained an interesting compound by the action of alkali on fluorenyl-9-dimethylsulfonium bromide (VIII) which they regarded as dimethylsulfonium-9-fluorenylidide

VIII



IX

(IX), having an unshared pair of electrons on carbon and a coördinate link between sulfur and carbon. This compound should also be produced by elimination of water from dimethyl sulfoxide and fluorene; attempts to prepare IX and its analog from 2,7-dinitrofluorene[9] by this method have not been successful.

Because these condensation reactions of sulfoxides have a formal similarity to reactions of carbonyl compounds, attempts were made to obtain characteristic carbonyl reactions from a sulfoxide. Tetramethylene sulfoxide was unchanged by treatment with diazomethane under a variety of conditions—a reaction which proceeds very readily with cyclic ketones.[10] Tetramethylene sulfone also gave no reaction with diazomethane. Treatment with benzaldehyde under conditions which form the dibenzal derivatives of cyclic ketones[11] gave no product.

Experimental

Tetrahydrofuran.—One mole of furan[12] was reduced with 4–5 cc. of moist Raney nickel catalyst at 2–4 atm. pressure. After three hours of reducing the yield of tetrahydrofuran, b. p. 65–67°, was 93% of the theoretical. Previous workers[13] have carried out the reduction with Raney nickel at elevated temperatures and pressures.

Tetramethylene Bromide.—The method of Fried and Kleene[14] was used with the modification that the product was isolated by steam distillation of the tarry reaction mixture. The yield of pure tetramethylene bromide, b. p. 62–63° (3 mm.), was 63% of the theoretical.

Tetramethylene Sulfide.[15]—Fifty cubic centimeters of 95% ethanol was heated to reflux in a 3-liter three-necked flask equipped with a stirrer, dropping funnel and an addition tube bearing a condenser and a second dropping funnel. The reagents were added drop by drop with stirring and refluxing as follows: from one dropping funnel 54 g. (0.25 mole) of tetramethylene bromide in 100 cc. of ethanol and from the other a solution of 60 g. (0.25 mole) of sodium sulfide nonahydrate in a mixture of 100 cc. of ethanol and 50 cc. of water. The rate of addition of the two solutions was regulated so that both were completely added at approximately the same time, about three hours being necessary. The mixture was then refluxed for six hours, after which a second addition was made using identical amounts and procedure described above. After refluxing an additional four hours, the reaction mixture was distilled until no sulfide could be detected in the distillate, about 450 cc. being collected. The first 100 cc. of distillate was collected separately and diluted with an equal volume of water; the sulfide layer was separated, washed three times with water, and the washings, together with the aqueous layer, added to the main body of the distillate. An aqueous solution of mercuric chloride was added with stirring to precipitate the remainder of the tetramethylene sulfide in the distillate. The white mercuric chloride complex which separated was collected by filtration and subjected to steam distillation until no more oil distilled. The distillate was added to the sulfide obtained above and extracted with petroleum ether (b. p. 30–40°). The extracts were dried over potassium hydroxide, then over sodium and finally distilled from sodium, yielding 28 g. (64%) of tetramethylene sulfide, b. p. 119–120°, $n^{21}\text{D}$ 1.5037.

Diethyl Sulfide.—One mole (156 g.) of ethyl iodide in 250 cc. of 95% ethanol was stirred and refluxed while 120 g. (0.5 mole) of sodium sulfide nonahydrate in 200 cc. of water was added dropwise as rapidly as possible. After the addition was completed the mixture was refluxed for two hours, then distilled, collecting 200 cc. of distillate. The addition of an equal volume of water caused the diethyl sulfide to separate and it was washed thoroughly with water, taken up in petroleum ether and dried as de-

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(6) Mann and Chaplin, *J. Chem. Soc.*, 527 (1937).

(7) Staudinger and Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

(8) Ingold and Jessop, *J. Chem. Soc.*, 713 (1930).

(9) Hughes and Kuriyan, *ibid.*, 1609 (1935).

(10) Mosettig and Burger, This Journal, **52**, 3456 (1930); Kohler, Tishler, Potter and Thompson, *ibid.*, **61**, 1057 (1939).

(11) Vorländer and Hobohm, *Ber.*, **29**, 1836 (1896).

(12) Prepared according to Wagner and Simmons, *J. Chem. Ed.*, **13**, 265 (1936), and Cloke and Pilgrim, This Journal, **61**, 2667 (1939).

(13) Cloke and Ayers, *ibid.*, **56**, 2144 (1934); Cloke and Pilgrim, ref. 12; Heisig, *ibid.*, **61**, 525 (1939).

(14) Fried and Kleene, *ibid.*, **62**, 3258 (1940).

(15) *Cf.* von Braun and Trumpler, *Ber.*, **43**, 549 (1910); Bost and Conn, *Oil Gas J.*, **32** (3), 17 (1933), and Clarke, *J. Chem. Soc.*, **101**, 1805 (1912).

scribed under the preparation of tetramethylene sulfide. After fractionation[16] the yield of pure product was 35 g. (78%), b. p. 90–92°.

Dimethyl Sulfide.[16]—The same method was used as described for diethyl sulfide except that the sodium sulfide solution was added at room temperature, the heat of reaction being sufficient to cause ebullition. The yield was low (50%) because of loss due to the high volatility of the product, b. p. 37–39°.

Tetramethylene Sulfoxide. Method A.[17]—From 8 g. of tetramethylene sulfide in 25 cc. of acetone and 10.4 g. of 30% hydrogen peroxide was obtained 8.3 g. (88%) of tetramethylene sulfoxide after distillation, b. p. 106–107° (15 mm.). The distillation was accompanied by considerable decomposition, imparting a slight yellow color to the product.

Method B (no solvent).—To 5 g. of tetramethylene sulfide, cooled in an ice-bath, was added dropwise 6.5 g. of 30% hydrogen peroxide (theoretical amount for sulfoxide formation) while stirring. The mixture was then stirred for one hour in the ice-bath, when a homogeneous solution was obtained. After standing overnight (slowly warming to room temperature as the ice melted), the water was removed under diminished pressure and the clear oil distilled. There was little or no decomposition and the yield of pure product was 5.3 g. (90%), b. p. 105–107° (12 mm.), $n^{23}\text{D}$ 1.5198.

Anal. Calcd. for C_4H_8OS: C, 46.1; H, 7.7; S, 30.8. Found: C, 45.6; H, 7.9; S, 30.3.

Diethyl Sulfoxide.—Following essentially procedure A, 15 g. of diethyl sulfide in 50 cc. of acetone and 18.9 g. of 30% hydrogen peroxide yielded 12.5 g. (70%) of diethyl sulfoxide, b. p. 83–85° (12 mm.),

Dimethyl Sulfoxide.—Method A resulted in a 50% yield of dimethyl sulfoxide, b. p. 85–87° (25 mm.).

Diphenyl Sulfoxide.—The procedure of Colby and McLaughlin[18] was used with the exception that the crude product was separated from the reaction mixture by extraction with benzene. After washing with water, the benzene solution was dried, decolorized and petroleum ether (b. p. 60–70°) added to cause crystallization. The yield of crude product, m. p. 65–68°, was 68% of the theoretical. After recrystallization from benzene and petroleum ether the pure sulfoxide melted at 67–69°.

Tetramethylene Sulfone.—To 8.8 g. (0.1 mole) of tetramethylene sulfide was added all at once 22.8 g. of 30% hydrogen peroxide (the theoretical amount for sulfone formation). Heat was liberated and after one hour the solution became homogeneous. The mixture was refluxed for four hours, then the condenser was removed and water distilled off for one hour. The remaining solvent was removed under reduced pressure, leaving 11.7 g. (97%) of colorless tetramethylene sulfone, m. p. 10–10.5°.[19]

Tetramethylenesulfin-*p*-toluenesulfonylimine (I, R'R" = $(CH_2)_4$).—Tetramethylene sulfoxide (0.02 mole, 2.1 g.) and 3.4 g. (0.02 mole) of *p*-toluenesulfonamide were dissolved in 15 cc. of acetic anhydride and heated on the steam-bath for forty-five minutes. The reaction mixture was then cooled and the acetic anhydride hydrolyzed with a slight excess of sodium hydroxide. This was accomplished best by pouring the reaction mixture with stirring into the calculated amount of 25% sodium hydroxide solution containing crushed ice. After standing at room temperature several hours the oil which formed became crystalline and was separated by filtration. The yield of crude sulfilimine was 3.4 g. (66%). The crude product was taken up in hot benzene, decolorized with charcoal and crystallized, yielding 2 g. (39%) of pure sulfilimine, m. p. 134–135°. A mixed melting point with a sample prepared from choramine-T and tetramethylene sulfide by the method of Mann and Pope[2] showed no depression. A small sample of I(R'R" = $(CH_2)_4$) was readily soluble in cold dilute hydrochloric acid; addition of dilute sodium hydroxide solution reprecipitated the sulfilimine as shown by a mixed melting point. When the acidic solution was heated on the steam-bath a few minutes, no sulfilimine was recovered by the addition of base. *p*-Toluenesulfonamide was isolated by cooling the acidic solution and identified by a mixed melting point.

Anal. Calcd. for $C_{11}H_{15}NO_2S_2$: C, 51.3; H, 5.9 Found: C, 51.8; H, 5.6.

When β,β'-dihydroxyethyl sulfoxide and *p*-toluenesulfonamide were treated with acetic anhydride according to the above procedure, alkaline hydrolysis yielded only a trace of an unidentified oil. By acidification of the basic solution, 90% of the starting sulfonamide was recovered.

Diphenylsulfin-*p*-toluenesulfonylimine (I, R'R" = C_6H_5).—Attempts to condense diphenyl sulfoxide with *p*-toluenesulfonamide in the presence of acetic anhydride were unsuccessful, the only product being N-acetyl-*p*-toluenesulfonamide (m. p. 137–139°).[20] The following procedure gave the expected sulfilimine. To 1.7 g. (0.01 mole) of *p*-toluenesulfonamide and 2 g. (0.01 mole) of diphenyl sulfoxide in 10 cc. of dry chloroform was added 1 g. of phosphorus pentoxide. After refluxing for thirty minutes an additional 1 g. of phosphorus pentoxide was added and the mixture was refluxed for thirty minutes longer. The hot chloroform solution was decanted from the sludge present, washed with three 10-cc. portions of 10% sodium hydroxide and then with water. After evaporation of the chloroform, the residue was taken up in benzene and boiled to expel water. Addition of ligroin (b. p. 90–100°) produced 1 g. of crude product, m. p. 105–110°. The sludge from the reaction mixture was heated with a few cc. of 5% NaOH and the precipitate (0.8 g., m. p. 105–110°) collected by suction. This was combined with the crude product above and recrystallized from benzene, yielding 1.1 g., m. p. 108–110°. A mixed melting point with a sample prepared from chloramine-T and diphenyl sulfide showed no depression.

Anal. Calcd. for $C_{17}H_{19}NO_2S_2$: C, 64.2; H, 4.8. Found: C, 64.8; H, 4.7.

A sample of I (R'R" = C_6H_5) was hydrolyzed with a solution of hydrochloric acid. Dilute acid acted very slowly on this sulfilimine but a concentrated solution brought about hydrolysis after thirty minutes by heating on the steam-bath. The oil which formed after sodium

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(16) If a product entirely free from starting iodide is desired, it must be carefully fractionated. Presence of the halide in the sulfide causes precipitation of the sulfonium salt on standing.

(17) Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

(18) Colby and McLaughlin, *Ber.*, **20**, 197 (1887).

(19) *Cf.* Bost and Conn, *Ind. Eng. Chem.*, **23**, 93 (1931).

(20) German Patent 466,519 (*C. A.*, **23**, 1651 (1929)).

hydroxide was added solidified when cooled and was diphenyl sulfoxide as shown by a mixed melting point. By acidification of the alkaline solution *p*-toluenesulfonamide was obtained and identified by means of a mixed melting point.

Diethylsulfin-*p*-toluenesulfonylimine (I, $R'R'' = C_2H_5$).—Diethyl sulfoxide (1 g.) and 1.7 g. of *p*-toluenesulfonamide, condensed by both the acetic anhydride and phosphorus pentoxide methods, gave approximately the same yield (54%) of pure sulfilimine, m. p. 145–146°. A sample of the sulfilimine prepared from diethyl sulfide and chloramine-T did not depress the melting point.

Trichloroacetamide.—To 33 g. (0.2 mole) of trichloroacetic acid and 15 cc. of thionyl chloride in 50 cc. of absolute ether was added 1 cc. of dry pyridine.[21] After refluxing for thirty minutes, the mixture was allowed to stand for one hour and then treated with a rapid stream of dry ammonia. During this treatment it was necessary to add several new portions of absolute ether since the ammonium chloride precipitate is bulky and ether evaporation is rapid. After the mixture was saturated with ammonia (evidenced by the disappearance of ammonium chloride fog), the inorganic precipitate was separated by filtration, the ether solution concentrated and again filtered. The solution was then evaporated to dryness and the residue taken up in benzene, filtered and crystallized, yielding 17.5 g. (54%) of trichloroacetamide, m. p. 139–141°.

Tetramethylenesulfintrichloroacetylimine (II, $R_2 = (CH_2)_4$).—Tetramethylene sulfoxide (0.01 mole, 1 g.) and 1.6 g. (0.01 mole) of trichloroacetamide were condensed in 5 cc. of acetic anhydride, following the procedure given above for the reaction with *p*-toluenesulfonamide. The crude product was recrystallized from benzene and ligroin (90–100°), giving 1.1 g. of pure product, m. p. 116–117°, which was soluble in cold dilute hydrochloric acid. The sulfilimine could be recovered unchanged by the addition of dilute sodium hydroxide to the cold solution. Hydrolysis presumably occurred by heating, since no sulfilimine could be recovered.

Anal. Calcd. for $C_6H_8Cl_3NOS$: C, 29.0; H, 3.3. Found: C, 29.3; H, 3.6. Qualitative tests for sulfur and nitrogen were strongly positive.

The same procedure failed to give a definite product when applied to diethyl and diphenyl sulfoxides.

Tetramethylenesulfindichloroacetylimine (III, $R_2 = (CH_2)_4$).—From 1 g. of tetramethylene sulfoxide and 1.3 g. of dichloroacetamide[22] in 5 cc. of acetic anhydride was obtained 1.1 g. of oil by the procedure outlined above. This was taken up in benzene and boiled to expel water, filtered and cooled to obtain 0.7 g. of crystalline product. After recrystallization from benzene the pure sulfilimine melted at 149–151°.

Anal. Calcd. for $C_6H_9Cl_2NOS$: C, 33.7; H, 4.2. Found: C, 33.6; H, 4.2. Qualitative test for sulfur and nitrogen strongly positive.

Diethylsulfindichloroacetylimine (III, $R = C_2H_5$).—Two grams of diethyl sulfoxide and 2.6 g. of dichloroacetamide in 5 cc. of acetic anhydride were heated on the steam bath for three hours. The mixture was cooled and poured with stirring into 20 cc. of 25% sodium hydroxide containing crushed ice. The oil which separated was extracted with benzene (three 20-cc. portions), and the extracts evaporated to a volume of 20 cc. After decolorizing with charcoal, petroleum ether (b. p. 40–60°) was added, and the crystals which formed were collected and recrystallized from benzene. The yield of pure sulfilimine, m. p. 112–113°, was 0.7 g.

Anal. Calcd. for $C_6H_{11}Cl_2ONS$: C, 33.4; H, 5.1. Found: C, 33.3; H, 5.0. Qualitative test for sulfur was positive; for nitrogen faint.

Attempted condensations using chloroacetamide and tetramethylene sulfoxide failed to yield a definite product. When benzamide was treated with tetramethylene or diethyl sulfoxides in the presence of acetic anhydride, the only product obtained was benzonitrile. This resulted when the reaction mixture was refluxed, no reaction being evident at steam-bath temperature.

Attempted Condensation of Fluorene and Sulfoxides.—When equivalent amounts (0.01 mole) of fluorene and dimethyl or tetramethylene sulfoxide were treated with acetic anhydride by the usual procedure, no reaction took place. The fluorene was recovered practically quantitatively. A similar attempt using 2,7-dinitrofluorene and dimethyl sulfoxide also failed.

Treatment of Tetramethylene Sulfoxide with Diazomethane.—A solution of the sulfoxide in methanol was treated with diazomethane by the method which gives ring expansion of ketones.[10] No reaction took place and 90% of the sulfoxide was recovered unchanged. Attempts to catalyze the reaction with zinc chloride and boron fluoride (using absolute ether as solvent) also resulted in recovery of starting material.

Experiments on Tetramethylene Sulfone.—Diazomethane showed no tendency to react with an alcoholic solution of the sulfone. An attempted aldol condensation with benzaldehyde, using conditions which give the dibenzal derivative of cyclohexanone,[11] failed as did a similar reaction using tetramethylene sulfoxide.

Summary

1. Sulfoxides have been shown to condense with *p*-toluenesulfonamide in the presence of acidic dehydrating agents to yield sulfilimines.

2. Sulfilimines of a new type, derived from dichloro- and trichloroacetamide, have been prepared. No product was obtained from the condensation of dimethyl sulfoxide with fluorene or dinitrofluorene.

3. Tetramethylene sulfoxide has been found not to give reactions which proceed readily with cyclopentanone.

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(21) Fieser and Fieser, THIS JOURNAL, 57, 782 (1935); Norris and Bearse, *ibid.*, 62, 953 (1940).

(22) "Organic Syntheses," Vol. XX, 1940, p. 37.