Methylsulfinyl Carbanion (CH_3-SO-CH_2^-). Formation and Applications to Organic Synthesis

E. J. Corey and Michael Chaykovsky

Contribution from the Converse Laboratory of Harvard University, Cambridge, Massachusetts 02138. Received October 16, 1964

A detailed account is given of the generation of the conjugate base of dimethyl sulfoxide (methylsulfinyl carbanion). The chemical properties and utility of this reagent are illustrated by a number of synthetic applications. For example, a new synthetic route to ketones is described.

At the inception of this study little was known about the chemical reactivity of carbanions substituted by a single alkylsulfinyl (R-$\overset{|}{S}$→O) group, although the evidence at hand indicated that the interaction of this function with adjacent negative charge produces appreciable stabilization, intermediate in degree between that associated with nitro, carbonyl, sulfonyl, etc., on the one hand, and hydrogen (*vs.* alkyl) on the other.[1] Furthermore, despite the great utility of reactive carbanions in synthesis, to our knowledge there had been no significant investigation of the α-sulfinyl carbanion class. This paper reports the details of our initial research in this area which has been concerned with the anion derived from the parent compound, dimethyl sulfoxide. A number of the results described here have been reported in a preliminary note.[2] The study of the conjugate base of dimethyl sulfoxide, the methylsulfinyl carbanion, was in part suggested by the ready availability of dimethyl sulfoxide and its growing importance as a highly effective medium for reactions of anionic species,[3] including strong bases such as *t*-butoxide ion.

It was found at the outset that sodium methylsulfinyl carbanion can be generated conveniently by heating finely powdered sodium hydride in an excess of dry dimethyl sulfoxide under nitrogen at about 70–75°. Completion of the reaction is easily seen from the cessation of hydrogen evolution and the disappearance of sodium hydride. By this procedure even fairly concentrated solutions (*e.g.*, 3 *M*) of the carbanion can be prepared easily. Sodium amide can also be used to generate the sodium salt. Lithium methylsulfinyl carbanion can be obtained in dimethyl sulfoxide or in

tetrahydrofuran solution using *n*-butyllithium (Foote Mineral Co.) as base.

The methylsulfinyl carbanion reacts rapidly with oxygen, carbon dioxide, and water, and consequently its formation and reactions should be conducted with rigorous exclusion of these substances. As anticipated the anion is strongly basic, a fact which is indicated by many of its reactions. The anion interacts with triphenylmethane to produce instantaneously a deep red solution of triphenyl carbanion. A number of experiments were performed to ascertain the approximate extent of this proton abstraction from triphenylmethane. These were conducted using concentrations of reactants which are typically in the range of preparative work with these anions. To a solution of triphenylmethane an equivalent amount of sodium methylsulfinyl carbanion was added, and after attainment of equilibrium the anions present were deuterated by rapid mixing with D_2O or D_2O-DCl. The triphenylmethane so formed was isolated and analyzed by n.m.r. spectroscopy to determine the relative amounts of triphenylmethane and triphenylmethane-d_1. Consideration of the results in terms of an ionic equilibrium constant, although not strictly correct because of ion association at the concentrations involved, clearly indicates that the methylsulfinyl carbanion is considerably more basic than the trityl anion. In 2:1 tetrahydrofuran–dimethyl sulfoxide as solvent, the methylsulfinyl carbanion appeared to be roughly 10^2 or 10^3 times more basic than the trityl anion. These figures differ from our preliminary estimate[2] of *ca.* 20. When the deuteration experiments were conducted by addition of D_2O or D_2O-DCl to the solution of the anions, as were our early runs, values of 20–30 were obtained. However, inverse addition, which is undoubtedly a more reliable procedure, and which was used in later runs, gave higher values of relative basicity (see Experimental). This discrepancy, which is somewhat surprising, indicates that a more detailed study of anion neutralization in dimethyl sulfoxide solutions should be made.[4] It seems probable from our results that proton transfers occur extremely rapidly.

As expected for the methylsulfinyl carbanion formulation (I) of the base from dimethyl sulfoxide, this nucleophilic reagent adds to nonenolizable ketones and aldehydes to form β-hydroxy sulfoxides. Thus at
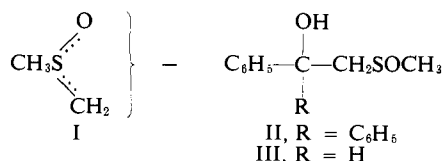
(1) See, for example, (a) H. H. Szmant in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York 22, N. Y., 1961, pp., 154–169; (b) A. Schöberl and A. Wagner in "Methoden der Organischen Chemie," Vol. IX, 4th Ed., Houben-Weyl, Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 211; (c) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

(3) See (a) N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957); (b) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959); (c) L. Friedman and H. Schechter, *J. Org. Chem.*, **25**, 877 (1960); (d) R. A. Smiley and C. Arnold, *ibid.*, **25**, 257 (1960); (e) A. S. Bailey, *J. Chem. Soc.*, 4710 (1960); (f) H. E. Zaugg, *et al.*, *J. Am. Chem. Soc.*, **82**, 2895, 2903 (1960); (g) D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960); (h) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (i) A. Schreisheim, *et al.*, *Tetrahedron Letters*, No. 17, 1005 (1964), and previous publications given therein; (j) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3032 (1963); (k) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

(4) Measurements of the relative acidities of dimethyl sulfoxide and triphenylmethane in dimethyl sulfoxide alone as solvent have been made recently by two groups using a spectrophotometric determination of trityl anion: see (a) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963); (b) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964). Both groups found triphenylmethane to be more acidic than dimethyl sulfoxide by *ca.* 10^4. This figure refers to dilute solutions (on the order of 0.02 *M*: personal communication from Dr. E. C. Steiner), and the discrepancy between this result and ours (for *ca.* 0.3 *M* solutions) could be due to concentration (ion-association) effects as well as to the difference in solvent composition and measurement technique.
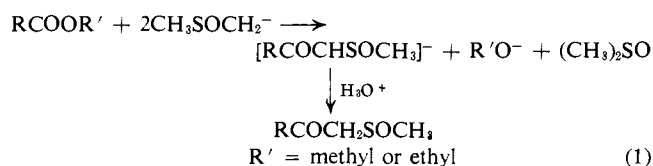
25° in dimethyl sulfoxide as solvent, benzophenone afforded II and benzaldehyde gave III (as a mixture of

$$
\underset{\substack{\text{I}}}{\begin{array}{c} O \\ \diagup \\ CH_3S \\ \diagdown \\ CH_2 \end{array}} \Bigg\} \quad - \quad \underset{\substack{\text{II, } R = C_6H_5 \\ \text{III, } R = H}}{\begin{array}{c} OH \\ | \\ C_6H_5\!-\!\overset{|}{C}\!-\!CH_2SOCH_3 \\ | \\ R \end{array}}
$$

diastereoisomers). In the case of readily enolizable and relatively acidic ketones, e.g., desoxybenzoin, enolate formation occurs exclusively and the starting carbonyl compound can be recovered after treatment with I by acidification. Intermediate cases are common. Treatment of cyclohexanone, for example, with sodium methylsulfinyl carbanion in dimethyl sulfoxide followed by acidification and isolation resulted in 17% yield of the corresponding β-hydroxy sulfoxide and 80% recovery of starting ketone. The relative extent of proton transfer and carbonyl addition depends to a considerable extent on reaction conditions. With the lithium salt of I in tetrahydrofuran and cyclohexanone, a 45% yield of β-hydroxy sulfoxide can be obtained along with 51% of unchanged cyclohexanone.[5] Other examples can be found in the Experimental section.

Benzalaniline reacted readily with I at 25° in a manner analogous to benzaldehyde and gave a mixture of diastereomeric β-anilino sulfoxides.

Aromatic esters and aliphatic esters which do not undergo facile proton transfer react with 2 equiv. of the methylsulfinyl carbanion to form anions of β-keto sulfoxides[6] according to the equation

$$RCOOR' + 2CH_3SOCH_2^- \longrightarrow$$
$$[RCOCHSOCH_3]^- + R'O^- + (CH_3)_2SO$$
$$\downarrow H_3O^+$$
$$RCOCH_2SOCH_3$$
$$R' = \text{methyl or ethyl} \qquad (1)$$

As reported previously these β-keto sulfoxides are valuable synthetic intermediates which permit among other things a simple, economical, and efficient synthesis of ketones[6b] since the methylsulfinyl group is readily replaced by hydrogen using aluminum amalgam–water–tetrahydrofuran. The efficiency of this latter process is illustrated by the data in Table I. The diketone undecane-2,10-dione is readily available from dimethyl azelate by this method. The hydrogenolysis of β-keto sulfoxides by aluminum amalgam appears to be very general and to be paralleled in the cases of β-keto sulfones and β-keto sulfonamides (see Experimental). The great practical value of this reaction when combined with other well-known methods of ring formation and/or chain development has been outlined in our earlier reports.[6b,7] This reductive cleavage permits the temporary utilization of an activating group such as sulfinyl or sulfonyl followed by an operation such as carbon–carbon bond formation

(5) Under more drastic conditions further transformation products result from the reaction of I with aldehydes and ketones: see (a) C. Walling and L. Bollyky, J. Org. Chem., 28, 256 (1963); (b) E. J. Corey and M. Chaykovsky, ibid., 28, 254 (1963).

(6) This reaction was discovered independently in these laboratories and by G. A. Russell and co-workers; see (a) H.-D. Becker, G. J. Mikol, and G. A. Russell, J. Am. Chem. Soc., 85, 3410 (1963); H.-D. Becker and G. A. Russell, J. Org. Chem., 28, 1896 (1963); (b) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 86, 1639 (1964).

(7) E. J. Corey and M. Chaykovsky, ibid., 86, 1640 (1964).

Table I. Conversion of Esters (RCOOC$_2$H$_5$) to β-Keto Sulfoxides (RCOCH$_2$SOCH$_2$) and Methyl Ketones (RCOCH$_3$)

R	Yield, %	
	β-Keto sulfoxide	Methyl ketone
Phenyl	79	>98
Anisyl	>98	>98
α-Naphthyl	>98	89
α-Furyl	71	70
Cyclohexyl	98	98
n-Pentyl	70	>98
n-Heptadecyl	<98	>98

and then removal of the superfluous group in the final stage.

In those cases for which proton transfer from the α-carbon of an ester or lactone is very favorable relative to carbonyl addition, e.g., because of high acidity of the ester or because of strong steric hindrance to carbonyl addition, the proton transfer reaction can dominate. In the recent synthesis of caryophyllene the cyclization process described by eq. 2 was observed as the major reaction under the influence of the reagent I in dimethyl sulfoxide solution.[8] Indeed the methylsulfinyl carbanion was the only one of many basic reagents
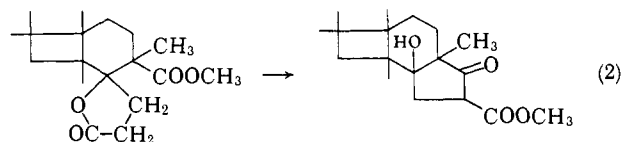
studied which effected this transformation satisfactorily.

Halides, even those which are relatively inert, react rapidly with methylsulfinyl carbanion in dimethyl sulfoxide. Chlorobenzene reacted at room temperature with an excess of sodium methylsulfinyl carbanion (6.7 equiv.) with spontaneous evolution of heat to yield methyl benzyl sulfoxide; when a smaller excess (2.5 equiv.) of the anion was employed, considerable amounts of methyl benzhydryl sulfoxide resulted. A benzyne intermediate may be involved in such reactions.

Treatment of benzyl chloride with I produced stilbene as the major product (together with an oily mixture of sulfoxides). With benzhydryl chloride a nearly quantitative yield of tetraphenylethylene was obtained. It is apparent from our results that the interaction of organic halogen compounds with the methylsulfinyl carbanion deserves further study.

The application of the methylsulfinyl carbanion to the formation of phosphonium ylides ("Wittig reagent") from phosphonium salts has already been described.[2,8,9] In our opinion this technique deserves wide usage because of the advantages of convenience, excellent efficiency of reaction, and, often, ease of isolation of pure product. The generation of oxosulfonium[10] and sulfonium ylides[11] using I has also been reported; these reactions are discussed in detail in an accompanying paper.[12]

(8) E. J. Corey, R. B. Mitra, and H. Uda, ibid., 86, 485 (1964).

(9) R. Greenwald, M. Chaykovsky, and E. J. Corey, J. Org. Chem., 28, 1128 (1963).
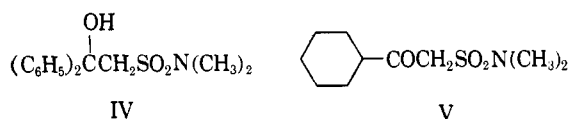
(10) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84, 867 (1962).

(11) E. J. Corey and M. Chaykovsky, ibid., 84, 3782 (1962).

(12) E. J. Corey and M. Chaykovsky, ibid., 87, 1353 (1965).

Several recent notes[4a,4b,13] have discussed the applicability of the methylsulfinyl carbanion as an analytical reagent for the study of weak acids in dimethyl sulfoxide solution, and it is apparent that this is an area worthy of considerable extension.

Further research on the formation and chemistry of substituted sulfinyl carbanions and of some related reactive carbanions is planned. Mention should be made at this point, however, of some interesting results which have been obtained from comparative studies of the methylsulfinyl carbanion and two other anions: (1) the methylsulfonyl carbanion and (2) the dimethylaminosulfonyl carbanion. As expected, the methylsulfonylcarbonyl is much less basic than the methylsulfinyl carbanion. Consequently, the methylsulfonyl carbanion can be generated and applied to syntheses in dimethyl sulfoxide solution using, for example, methylsulfinyl carbanion or sodium hydride as base. Thus the chemistry of α-sulfonyl carbanions, already studied in more traditional media,[14] can now be examined in a solvent *par excellence*. The dimethylaminosulfonyl carbanion, on the other hand, is much more strongly basic than the methylsulfinyl carbanion and therefore cannot be made or used in dimethyl sulfoxide solution. This strongly basic anion can be obtained in tetrahydrofuran, however, by the action of stronger bases such as *n*-butyllithium on N,N-dimethylmethanesulfonamide. The dimethylaminosulfonyl carbanion reacts with benzophenone to give the β-hydroxysulfonamide IV in 85% yield. Similarly a β-hydroxysulfonamide

$$
\underset{\text{IV}}{\overset{\overset{\displaystyle OH}{\underset{|}{}}}{(C_6H_5)_2CCH_2SO_2N(CH_3)_2}} \qquad \underset{\text{V}}{\langle\bigcirc\rangle-COCH_2SO_2N(CH_3)_2}
$$

was obtained from cyclohexanone in 77% yield. The reaction of lithium dimethylaminosulfonyl carbanion with ethyl cyclohexanecarboxylate afforded the β-ketosulfonamide V in 96.6% yield, reduction of which with aluminum amalgam gave methyl cyclohexyl ketone (yield >98%). Clearly, the dimethylaminosulfonyl carbanion is another promising synthetic reagent.

Experimental[15]

Methylsulfinyl Carbanion. General Method of Preparation. A weighed amount of sodium hydride (50% mineral oil dispersion; Metal Hydrides, Inc.) is placed in a three-necked, round-bottomed flask and washed three times with light petroleum ether, by swirling, allowing the hydride to settle, and decanting the liquid portion in order to remove the mineral oil. The flask is immediately fitted with a mechanical stirrer, a reflux condenser, and a rubber cap through which reagents can be introduced *via* hypodermic syringe (a pressure-compensated dropping funnel may also be used). A three-way stopcock, connected to the top of the reflux

(13) G. G. Price and M. C. Whiting, *Chem. Ind.* (London), 775 (1963). These workers have also introduced the term "dimsylsodium" for sodium methylsulfinyl carbanion.
(14) See, for example, L. Field, *et al., J. Am. Chem. Soc.*, **81**, 2572 (1959), and earlier papers.
(15) Melting points, determined using a Kofler hot stage, are corrected; boiling points are uncorrected. N.m.r. spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard. Microanalyses were performed by the Scandanavian Microanalytical Laboratories, Herlev, Denmark.

condenser, is connected to a water aspirator and a source of dry nitrogen. The system is evacuated until the last traces of petroleum ether are removed from the sodium hydride and is then placed under nitrogen by evacuating and filling with nitrogen several times. The aspirator hose is removed and this arm of the stopcock is connected to a mercury-sealed U-tube, to which the system is opened. Dimethyl sulfoxide (distilled from calcium hydride, b.p. 64° at 4 mm.) is introduced *via* hypodermic syringe or dropping funnel and the mixture is heated with stirring to 70–75° until the evolution of hydrogen ceases. A mixture of 0.05 mole of sodium hydride and 20 to 30 ml. of dimethyl sulfoxide requires about 45 min. for complete reaction and yields a somewhat cloudy, pale yellow-grey solution of the sodium salt. The solution can be assayed by titration with formanilide using triphenylmethane as indicator.[4,13]

Powdered sodium amide reacts with dimethyl sulfoxide to generate the sodium salt under the same conditions, with the evolution of ammonia, and is comparable to sodium hydride in its reactivity. Commercial samples of lithium hydride were found to react about one-fifth to one-tenth as fast as sodium hydride under these conditions, and the longer reaction time resulted in extensive decomposition of the sulfinyl carbanion. Although sodium hydride reacts more rapidly with dimethyl sulfoxide at temperatures above 70–75°, extensive decomposition also occurs, especially above 80°.

Reaction of Methylsulfinyl Carbanion with Benzophenone. A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.05 mole of sodium hydride and 20 ml. of dimethyl sulfoxide. To this solution, with stirring at room temperature, was added 4.55 g. (0.025 mole) of benzophenone in 10 ml. of dimethyl sulfoxide over a 3-min. period. The reaction mixture became warm and was then allowed to stir at room temperature for 2 hr., and this was followed by the addition of 50 ml. of cold water and extraction of the precipitated solid with chloroform. The combined extracts were washed three times with water, dried over anhydrous sodium sulfate, and evaporated to yield a white solid which was recrystallized from 45 ml. of ethyl acetate to give 5.6 g. (86.2%) of the hydroxy sulfoxide adduct as colorless prisms, m.p. 144–146°. Recrystallization twice again gave the analytical sample, m.p. 148–148.5°.

Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.21; H, 6.19; S, 12.32. Found: C, 69.03; H, 6.12; S, 12.13.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.9 (m), 3.27 (m), 6.23 (w), 6.68 (m), 6.88 (m), 7.0 (m), 7.1 (m), 9.4 (s), and 9.8 (s) μ. The n.m.r. spectrum (CDCl₃) showed signals at τ 7.45 (three protons) and 6.45 (two protons). A phenyl multiplet appeared at τ 2.5–2.8.

Reaction of Methylsulfinyl Carbanion with Benzaldehyde. A solution of sodium methylsulfinyl carbanion, prepared under nitrogen from 0.05 mole of sodium hydride and 30 ml. of dimethyl sulfoxide, was cooled in a water bath at 15° during the addition, with stirring of 4.76 g. (0.045 mole) of benzaldehyde over a period of 1 min. After stirring at room temperature for 1 hr., 60 ml. of water was added and the mixture was extracted with chloroform. The combined extracts were washed four times with water, once with saturated

salt solution, dried over anhydrous sodium sulfate, and evaporated to yield 4.1 g. (49.6%) of a viscous yellow oil which solidified upon scratching with a glass rod. Recrystallization from ethyl acetate gave colorless needles of the hydroxy sulfoxide adduct as a mixture of diastereoisomers, m.p. 78–123°.

Anal. Calcd. for $C_9H_{12}O_2S$: C, 58.67; H, 6.56; S, 17.41. Found: C, 58.53; H, 6.60; S, 17.37.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.9 (m), 3.27 (m) 6.22 (w), 6.68 (m), 6.85 (m), 7.0 (m), 7.1 (m), 9.45 (s), and 9.7 (s) μ. The n.m.r. spectrum (CDCl$_3$) showed methyl signals at τ 7.48 and 7.40 (*ca.* 2:1; one from each isomer).

Reaction of Methylsulfinyl Carbanion with Camphor. A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.05 mole of sodium hydride and 20 ml. of dimethyl sulfoxide. A solution of 3.8 g. (0.025 mole) of camphor in 10 ml. of dimethyl sulfoxide was added with stirring and the reaction mixture became warm. After stirring at room temperature for 4 hr., 50 ml. of water was added and the mixture was extracted with ether. The ethereal extracts were washed three times with water, dried over anhydrous sodium sulfate, and evaporated to yield a semisolid mass which was taken up in 15 ml. of petroleum ether (90–120°) and cooled to yield 1.6 g. (27.8%) of the hydroxy sulfoxide adduct as a mixture of diastereoisomers, m.p. 88–125°. Recrystallization twice again from petroleum ether gave colorless needles, m.p. 94–130°.

Anal. Calcd. for $C_{12}H_{22}O$ S: C, 62.55; H, 9.63; S, 13.92. Found: C, 62.41; H, 9.66; S, 13.76.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.85 (m), 3.32 (s), 6.85 (m), 7.0 (m), 7.1 (m), 7.18 (m), 9.32 (s), 9.5 (m), and 9.88 (s) μ.

Evaporation of the mother liquor yielded 2.5 g. (66%) of unchanged camphor.

Reaction of Methylsulfinyl Carbanion with Cyclohexanone. A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.052 mole of sodium hydride and 40 ml. of dimethyl sulfoxide. With stirring at room temperature, 4.9 g. (0.05 mole) of cyclohexanone was added neat by syringe over a period of 3 min. After stirring for 1 hr. the mixture was poured into 100 ml. of cold water and extracted with chloroform; the extracts were washed three times with water, dried over anhydrous sodium sulfate, and evaporated to leave a pale yellow oil. The oil was extracted with two 50-ml. portions of pentane and the combined extracts were evaporated to leave 3.9 g. (79.6% recovery) of unchanged cyclohexanone. The pentane-insoluble portion crystallized when scratched with a glass rod. Recrystallization from ethyl acetate-isopropyl ether gave 1.5 g. (17%) of the β-hydroxy sulfoxide as white crystals, m.p. 56–59°. Another recrystallization gave the analytical sample, m.p. 59.5–60°.

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.50; H, 9.15; S, 18.19. Found: C, 54.20; H, 8.95; S, 18.24.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.85 (m), 3.35 (s), 6.95 (m), 7.00 (m), 7.07 (m), 8.03 (m), 8.45 (m), 9.37 (s), 9.78 (s), 10.18 (m) and 10.60 (m) μ. The n.m.r. spectrum (CDCl$_3$) showed a multiplet at τ 8.1–8.65 (ten protons), a singlet at 7.32 (three protons), a pair of doublets centered at 7.12 ($J =$ 13 c.p.s.), and a singlet at 6.21 (one proton).

In another experiment lithium methylsulfinyl carbanion was prepared by adding 0.05 mole of n-butyllithium in 31 ml. of hexane to a stirred solution of 4.7 g. (0.06 mole) of dry dimethyl sulfoxide in 35 ml. of dry tetrahydrofuran under nitrogen. The lithium salt precipitated as a fine white solid. A solution of 4.9 g. (0.05 mole) of cyclohexanone in 10 ml. of tetrahydrofuran was added at room temperature over a period of 3 min. to give a pale yellow solution. After stirring for 30 min. the tetrahydrofuran was evaporated at the water aspirator to leave a pale yellow oil which was dissolved in 100 ml. of chloroform, washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was processed as described above to yield 2.5 g. (51% recovery) of unchanged cyclohexanone and 4.0 g. (45%) of the hydroxy sulfoxide.

Reaction of Methylsulfinyl Carbanion with Cycloheptanone. Lithium methylsulfinyl carbanion was prepared by adding 0.094 mole of n-butyllithium in 58 ml. of hexane to a stirred solution of 8.1 g. (0.11 mole) of dry dimethyl sulfoxide in 60 ml. of dry tetrahydrofuran under nitrogen. Cycloheptanone (10.5 g., 0.094 mole) was added neat at room temperature over a period of 5 min. After stirring for 30 min. the mixture was processed as described above to yield 3.7 g. (35%) of unchanged cycloheptanone and 11.5 g. (64%) of the β-hydroxy sulfoxide as a viscous colorless oil. Distillation at 140° (0.15 mm.) gave the analytical sample.

Anal. Calcd. for $C_9H_{18}O_2S$: C, 56.80; H, 9.54; S, 16.85. Found: C, 56.76; H, 9.62; S, 16.79.

The infrared spectrum showed $\lambda_{max}^{CCl_4}$ 2.88 (m), 3.38 (s), 6.80 (m), 7.04 (m), 9.45 (s), 9.80 (s), 10.39 (m), and 10.65 (m) μ. The n.m.r. spectrum (CCl$_4$) showed multiplets at τ 8.05–9.0 (twelve protons), a singlet at 7.35 (three protons), a peak at 7.10 (two protons), and a peak at 5.65 (one proton).

Reaction of Methylsulfinyl Carbanion with Benzalaniline. A solution of methylsulfinyl carbanion was prepared under nitrogen from 0.02 mole of sodium hydride and 20 ml. of dimethyl sulfoxide. With stirring, a solution of 2.72 g. (0.015 mole) of benzalaniline in 10 ml. of dimethyl sulfoxide was added, with slight external cooling of the reaction flask in a water bath. After stirring for 5 min. the mixture was poured into 150 ml. of cold water. A paste separated which crystallized after cooling the mixture in an ice bath. The solid was crushed, filtered, and dried to yield 3.5 g. (92%) of the β-anilino sulfoxide as an almost white crystalline solid. Recrystallization from ethyl acetate gave colorless needles, m.p. 153–172°. Recrystallization again gave the analytical sample, m.p. 181–184°.

Anal. Calcd. for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.46; H, 6.53; N, 5.35; S, 12.33.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.88 (m), 3.25 (s), 6.20 (s), 6.62 (s), 6.85 (m), 7.00 (w), 7.08 (w), 7.58 (m), 7.90 (m), and 9.70 (s) μ. The n.m.r. spectrum (CDCl$_3$) showed a singlet at τ 7.34 (three protons), a multiplet centered at 6.80 (two protons), broad signals at 4.6–5.6 (two protons), and multiplets at 2.25–3.40 (ten protons).

Reaction of Methylsulfinyl Carbanion with Triphenylmethane. Method A. A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from

0.05 mole of sodium hydride and 50.0 ml. of dimethyl sulfoxide. Titration of 10.0 ml. of this solution in 25 ml. of distilled water to the phenolphthalein end point with 1 N hydrochloric acid showed the exact amount of base present to be 0.0101 mole. Another 10.0-ml. portion of the carbanion solution was added to a stirred solution of 2.468 g. (0.0101 mole) of triphenylmethane in 20 ml. of dry tetrahydrofuran under nitrogen. The deep red reaction mixture was allowed to equilibrate for 15 min. at 25° followed by the addition of 4.0 ml. of deuterium oxide. The triphenylmethane was then isolated by adding 30 ml. of water and extracting with ether. The ether extracts were washed twice with water, dried over anhydrous sodium sulfate, and evaporated to yield 2.45 g. of white crystalline solid, which was dissolved in petroleum ether (b.p. 40–60°) and filtered through alumina. The product thus obtained was recrystallized from absolute ethanol to give long colorless needles, m.p. 95–95.5°. Deuterium combustion analysis showed that the product contained 46.2% of deuteriotriphenylmethane. Quantitative n.m.r. analysis, using a weighed amount of pure iodoform as internal standard ($CDCl_3$ solvent), gave a value of 48.3% deuteriotriphenylmethane. (Triphenylmethane and iodoform give n.m.r. signals at τ 4.48 and 5.06, respectively.) In another similar run, in which the reaction mixture was allowed to equilibrate for 5 hr., the isolated triphenylmethane was shown by quantitative n.m.r. analysis to contain 43.5% deuteriotriphenylmethane.

Assuming that under equilibrium conditions approximately 45% of the triphenylmethane is converted into triphenyl carbanion, an "equilibrium constant" of 21 for the reaction can be calculated for the change

$$CH_3\overset{\overset{O}{\|}}{-S}-\bar{C}H_2 + (C_6H_5)_3CH \rightleftharpoons (C_6H_5)_3\bar{C} + CH_3\overset{\overset{O}{\|}}{-S}-CH_3$$
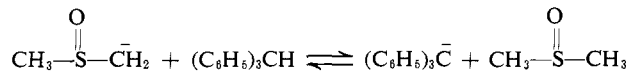
In control experiments it was demonstrated that no deuterium was lost from triphenylmethane-d_1 by the purification procedure used above.

In a third run, the same quantities as described above were used, except that 0.5 g. of phosphorus pentachloride was dissolved in the deuterium oxide (to form DCl) prior to its addition to the equilibrium mixture. The equilibrium constant (25°) for this run, calculated as above, was found to be approximately 28.

Method B. A solution of methylsulfinyl carbanion was prepared by dissolving sodium hydride in dry dimethyl sulfoxide. The solution was titrated by dropwise addition of a sample to a solution of formanilide in dry dimethyl sulfoxide, using triphenylmethane as indicator (the value thus obtained for the concentration of the carbanion was only 92.6% of the value obtained by titrating the total base in water, with hydrochloric acid, as described above). The carbanion solution (6 ml., 5.0 mmoles) was added to a solution of 1.221 g. (5.0 mmoles) of triphenylmethane in 26 ml. of dry tetrahydrofuran and 7 ml. of dimethyl sulfoxide. After 15 min. at 25° the red solution was added dropwise with rapid stirring to 100 ml. of deuterium oxide (in which 50 mg. of phosphorus pentachloride had been dissolved). The triphenylmethane was isolated and purified as described above. The equilibrium constant was found by n.m.r. analysis to be approximately 900.

In another run 6.0 ml. of the carbanion solution (5.0 mmoles) was added to a solution of 1.221 g. (5.0 mmoles) of triphenylmethane in 25 ml. of dry dimethyl sulfoxide. After 15 min. at 25° the solution was added dropwise to 100 ml. of deuterium oxide. The triphenylmethane was isolated and the equilibrium constant found by n.m.r. analysis to be approximately 200.

Reaction of Methylsulfinyl Carbanion with Chlorobenzene. A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.20 mole of sodium hydride and 60 ml. of dimethyl sulfoxide. After adding 3.36 g. (0.03 mole) of chlorobenzene, with stirring, heat was gradually evolved and the reaction mixture reached a maximum temperature of about 60° after 15 min. The red-brown mixture was stirred at room temperature for 3 hr. and then poured into 200 ml. of cold water and the products were extracted with benzene. The combined extracts were washed once with water, once with saturated salt solution, dried over anhydrous sodium sulfate, and evaporated to yield a yellow oil which crystallized to an oily solid after scratching with a glass rod. The product was triturated with 10 ml. of cold ether and filtered to yield 1.9 g. (41%) of benzyl methyl sulfoxide, m.p. 52–55°. Recrystallization from petroleum ether (b.p. 90–120°) gave cottony white needles, m.p. 55–56° (lit.[16] m.p. 54°). The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.3 (s), 6.23 (w), 6.68 (m), 6.88 (m), 7.0 (m), 7.1 (m), 8.05 (m), 9.3 (s), and 9.6 (s) μ.

The ether filtrate was evaporated to yield 1.2 g. of yellow oil which was chromatographed on 70 g. of grade V Woelm alumina to yield 0.33 g. of yellow oil (eluted with 50% benzene–pentane) containing phenyl peaks but no sulfoxide peak in its infrared spectrum. The following fractions (eluted with benzene and benzene–ether mixtures) contained yellow oils having phenyl and sulfoxide infrared peaks. The oils were not further investigated.

In another run, using 0.05 mole of the carbanion and 0.02 mole of chlorobenzene, 8.7% of benzhydryl methyl sulfoxide, m.p. 115–116°, was isolated in addition to yellow oils.

Anal. Calcd. for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found: C, 72.93; H, 6.13; S, 13.92.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.3 (m), 6.25 (w), 6.68 (m), 6.88 (m), 7.05 (w), 7.1 (w), 9.45 (s), and 9.65 (s) μ. The n.m.r. spectrum ($CDCl_3$) showed signals at τ 2.7 (phenyl), 5.28 (–CH), and 7.72 (–CH$_3$) in the expected integral ratio 10:1:3.

Reaction of Methylsulfinyl Carbanion with Benzyl Chloride. A mixture of 0.12 mole of sodium hydride, 28.1 g. (0.36 mole) of dimethyl sulfoxide, and 50 ml. of dry tetrahydrofuran was refluxed under nitrogen until the evolution of hydrogen had ceased (4 hr.). The reaction mixture was cooled in an ice bath and stirred during the addition of 12.6 g. (0.1 mole) of benzyl chloride in 20 ml. of dry tetrahydrofuran over a 5-min. period. The purple reaction mixture was stirred at ice-bath temperature for 30 min. and then at room temperature for 3 hr., followed by the addition of 75 ml. of cold water and extraction with ether. The combined ether extracts were washed three times with water, dried over anhydrous sodium sulfate, and evap-

(16) S. Hunig and O. Boes, *Ann.*, 579, 23 (1953).

orated to yield 11.7 g. of a mixture of oil and solid. The mixture was chromatographed on 200 g. of Merck alumina to yield 3.8 g. (42.2%) of white crystalline solid (eluted with benzene) which was recrystallized from 95% ethanol to give white plates, m.p. 127–128°, identified as *trans*-stilbene (mixture melting point and infrared spectrum). Flushing the column with 500 ml. of methanol yielded 7.5 g. of yellow oil which showed a sulfoxide peak in its infrared spectrum.

A mixture of 3.7 g. of the yellow oil, 6 ml. of 30% hydrogen peroxide, and 15 ml. of glacial acetic acid was allowed to stand at room temperature for 4 days. Water (50 ml.) was added and the product extracted with ether. The combined extracts were washed three times with water and then with 10% aqueous potassium carbonate until free from acetic acid, dried over anhydrous sodium sulfate, and evaporated to yield 3.3 g. of yellow oil which crystallized to an oily solid when scratched with a glass rod. The product was taken up in 8 ml. of hot 95% ethanol and cooled to yield 0.9 g. of a crystalline mixture of sulfones, m.p. 90–115°. Recrystallization twice again from 95% ethanol gave white needles, m.p. 115–127°. The solid was not further characterized.

Anal. Found: C, 68.94; H, 62.24; S, 12.32.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.25 (w), 6.22 (w), 6.68 (m), 6.88 (m), 7.63 (s), and 8.78 (s) μ.

Reaction of Methylsulfinyl Carbanion with Benzhydryl Chloride. A solution of methylsulfinyl carbanion was prepared under nitrogen from 0.042 mole of sodium hydride and 25 ml. of dimethyl sulfoxide. Dry tetrahydrofuran (40 ml.) was added and the mixture cooled in a salt–ice bath. With stirring a solution of 8.08 g. (0.04 mole) of freshly distilled benzhydryl chloride in 20 ml. of dry tetrahydrofuran was added over a period of 20 min. Stirring was continued at salt–ice temperature for 30 min. and then at room temperature for 2 hr. The mixture was poured into 200 ml. of cold water and the precipitated solid filtered to yield 6.5 g. (98%) of pale yellow tetraphenylethylene, m.p. 210–220°. Recrystallization from benzene–ethanol gave colorless prisms, m.p. 221–222° (lit.[17] m.p. 221°).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.91; H, 6.06.

Reaction of Esters with Methylsulfinyl Carbanion. Preparation of β-Keto Sulfoxides. General Procedure. A 1.5 to 2 M solution of methylsulfinyl carbanion in dimethyl sulfoxide is prepared under nitrogen in the usual manner from sodium hydride and dry dimethyl sulfoxide. An equal volume of dry tetrahydrofuran is added and the solution is cooled in an ice bath during the addition, with stirring, of the ester (0.5 equiv. based on 1 equiv. of carbanion; neat if liquid or dissolved in dry tetrahydrofuran if solid) over a period of several minutes. The ice bath is removed, stirring is continued for 30 min., and the reaction mixture is then poured into three times its volume of water, acidified with aqueous hydrochloric acid to a pH of about 3–4 (pH paper), and thoroughly extracted with chloroform. The combined extracts are washed three times with water, dried over anhydrous sodium sulfate, and evaporated to yield the β-keto sulfoxide as a white or

(17) H. Biltz, *Ann.*, **296**, 230 (1897).

pale yellow crystalline solid. The crude product is triturated with cold ether or isopropyl ether and filtered to give the product in a good state of purity.

ω-(Methylsulfinyl)acetophenone. Methylsulfinyl carbanion (0.07 mole) and 5.25 g. (0.035 mole) of ethyl benzoate yielded 5.0 g. (78.6%) of the β-keto sulfoxide as a white crystalline solid. The analytical sample, recrystallized from ethyl acetate as colorless needles, had m.p. 86–86.5°.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.31; H, 5.53; S, 17.60. Found: C, 59.24; H, 5.56; S, 17.44.

ω-(Methylsulfinyl)-p-methoxyacetophenone. Methylsulfinyl carbanion (0.07 mole) and 5.8 g. (0.035 mole) of p-methoxyacetophenone yielded 7.42 g. (quantitative yield) of the β-keto sulfoxide as a white crystalline solid. The analytical sample, recrystallized from ethyl acetate as colorless needles, had a double melting point, at 96° and 104–105°.

Anal. Calcd. for $C_{10}H_{12}O_3S$: C, 56.60; H, 5.72; S, 15.11. Found: C, 56.52; H, 5.74; S, 14.99.

ω-(Methylsulfinyl)-α-acetonaphthone. Methylsulfinyl carbanion (0.05 mole) and 5.0 g. (0.025 mole) of ethyl α-naphthoate yielded 5.8 g. (quantitative yield) of the β-keto sulfoxide as a pale yellow oil which crystallized upon standing overnight in a cold room. A sample, recrystallized from ethyl acetate–isopropyl ether as colorless plates, had m.p. 111–113° dec. (with prior softening at 100°).

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.20; S, 13.80. Found: C, 67.16; H, 5.18; S, 13.85.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.36 (s), 6.65 (m), 7.25 (m), 7.82 (s), 8.07 (m), 9.46 (s), and 10.62 (m) μ. The n.m.r. spectrum (CDCl₃) showed a singlet at τ 7.3 (three protons), a pair of doublets at 5.42 and 5.72 ($J = 15$ c.p.s.; two protons), and multiplets in the region 2.0–2.75 (seven protons).

ω-(Methylsulfinyl)-α-acetofurone. Methylsulfinyl carbanion (0.08 mole) and 5.04 g. (0.04 mole) of methyl α-furoate yielded 4.9 g. (71.3%) of the β-keto sulfoxide as a pale yellow crystalline solid. A sample recrystallized from ethyl acetate as colorless needles had m.p. 84.5–85°.

Anal. Calcd. for $C_7H_8O_3S$: C, 48.82; H, 4.68; S, 18.62. Found: C, 48.60; H, 4.79; S, 18.74.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.38 (m), 6.04 (s), 6.42 (m), 6.85 (s), 7.72 (m), 9.23 (m), 9.44 (s), 9.66 (m), and 9.84 (s) μ. The n.m.r. spectrum (CDCl₃) showed a singlet at τ 7.23 (three protons), a pair of doublets for the methylene group at 5.62 and 5.88 with very small outer peaks and the larger center peaks only slightly separate ($J = 14$ c.p.s.; two protons), a quartet at 3.42 (one proton), and multiplets at 2.36 and 2.66 (total of two protons).

Methylsulfinylmethyl n-Pentyl Ketone. Methylsulfinyl carbanion (0.1 mole) and 7.2 g. (0.05 mole) of ethyl caproate yielded the crude β-keto sulfoxide as a pasty crystalline mass. The material was dissolved in 20 ml. of hot isopropyl ether, 30 ml. of petroleum ether (b.p. 40–60°) was added, and the solution cooled to −15°. Filtration yielded 6.2 g. (70.5%) of white plates, m.p. 40–44°. A sample recrystallized again from isopropyl ether had m.p. 45–46.5°.

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.50; H, 9.15; S, 18.19. Found: C, 54.29; H, 8.97; S, 18.31.

The infrared spectrum showed $\lambda_{max}^{CCl_4}$ 3.35 (s), 5.80 (s), 6.80 (m), 7.10 (m), 7.24 (m), 9.20 (s), and 9.55 (s) μ. The n.m.r. spectrum (CCl_4) showed multiplets in the region τ 8.2–9.3 (nine protons), a sharp singlet at 7.42 in the midst of smaller multiplets (total of five protons), and a pair of doublets at 6.15 and 6.43 (J = 14 c.p.s.; two protons).

Methylsulfinylmethyl Cyclohexyl Ketone. Methylsulfinyl carbanion (0.08 mole) and 6.24 g. (0.04 mole) of ethyl cyclohexanecarboxylate yielded 7.4 g. (98.5%) of the β-keto sulfoxide as a white crystalline solid. A sample recrystallized from isopropyl ether as colorless plates had m.p. 62–63°.

Anal. Calcd. for $C_9H_{16}O_2S$: C, 57.40; H, 8.57; S, 17.04. Found: C, 57.22; H, 8.44; S, 17.17.

The infrared spectrum showed $\lambda_{max}^{CCl_4}$ 3.38 (s), 5.83 (s), 6.88 (m), 9.28 (s), 9.48 (s), 9.95 (m), and 10.30 (m) μ. The n.m.r. spectrum (CCl_4) showed multiplets in the region τ 7.9–8.9 (ten protons), a multiplet centered at 7.5 (one proton), a singlet at 7.39 (three protons), and a singlet at 6.14 (two protons).

Methylsulfinylmethyl n-Heptadecyl Ketone. Methylsulfinyl carbanion (0.04 mole) and 5.97 g. (0.02 mole) of methyl stearate yielded 6.9 g. (quantitative yield) of the β-keto sulfoxide as a white crystalline solid. The analytical sample, recrystallized from ethyl acetate as small white feathery needles, had m.p. 98.5–99°.

Anal. Calcd. for $C_{20}H_{40}O_2S$: C, 69.70; H, 11.70; S, 9.30. Found: C, 69.79; H, 11.80; S, 9.40.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.40 (s), 5.82 (s), 6.80 (m), 7.10 (w), 7.28 (w), 7.68 (w), and a broad peak at 9.65 (s) μ. The n.m.r. spectrum ($CDCl_3$) showed a large peak at τ 8.75 (33 protons), a sharp singlet at 7.34, overlapping with a multiplet centered at 7.45 (total of five protons), and a peak at 6.29 (two protons).

1,11-Bis(methylsulfinyl)undecane-2,10-dione. Methylsulfinyl carbanion (0.07 mole) and 3.78 g. (0.0175 mole) of dimethyl azelate yielded a pale yellow solid which was dissolved in 20 ml. of hot 95% ethanol, cooled, and filtered to give 4.4 g. (81.6%) of a white powdery solid, m.p. 115–125°. The analytical sample was recrystallized twice from methanol–ethyl acetate and had m.p. 129–133°.

Anal. Calcd. for $C_{13}H_{24}O_4S_2$: C, 50.62; H, 7.84; S, 20.79. Found: C, 51.15; H, 7.96; S, 20.03.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.41 (m), 5.83 (s), 6.84 (w), 7.12 (w), 7.32 (w), 7.68 (w), 9.35 (m), and 9.65 (s) μ. The n.m.r. spectrum ($CDCl_3$) showed, in addition to multiplets in the region τ 8.2–8.9, a sharp singlet at 7.32 with overlapping multiplets centered at approximately 7.45 (total of ten protons) and a pair of doublets at 6.13 and 6.40 (J = ~13 c.p.s.; four protons) with very small outer peaks and the center peaks only slightly separated.

Methylsulfonylmethyl Cyclohexyl Ketone. A solution of methylsulfonyl carbanion was prepared in dimethyl sulfoxide by heating a mixture of 0.06 mole of sodium hydride, 11.3 g. (0.12 mole) of dimethyl sulfone, and 40 ml. of dry dimethyl sulfoxide at 70°, with stirring under nitrogen, until the evolution of hydrogen ceased (*ca.* 45 min.). Dry tetrahydrofuran (40 ml.) was added and the solution cooled in an ice bath during the addition of 4.68 g. (0.03 mole) of ethyl cyclohexane-

carboxylate in 10 ml. of dry tetrahydrofuran over a period of 5 min. The bath was removed, stirring was continued for 30 min., and the mixture was poured into 250 ml. of cold water and extracted thoroughly with chloroform. The combined extracts were washed three times with water, dried over anhydrous sodium sulfate, and evaporated to yield 6.4 g. of white crystalline solid containing the desired β-keto sulfone and some dimethyl sulfone. The latter was removed by triturating the material with 50 ml. of water, filtering, and drying to give 5.9 g. (96.4%) of the keto sulfone as a white crystalline solid. The analytical sample was recrystallized from isopropyl ether and had m.p. 80.5–81°.

Anal. Calcd. for $C_9H_{16}O_3S$: C, 52.91; H, 7.90; S, 15.70. Found: C, 52.78; H, 7.95; S, 15.55.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.44 (s), 5.86 (s), 6.92 (m), 7.60 (s), 8.66 (s), and 10.33 (s) μ. The n.m.r. spectrum ($CDCl_3$) showed multiplets in the region τ 7.9–8.9 (ten protons), a multiplet centered at 7.5 (one proton), a singlet at 6.95 (three protons), and a singlet at 5.91 (two protons).

Reduction of β-Keto Sulfoxides, β-Keto Sulfones, and β-Keto Sulfonamides with Aluminum Amalgam. Preparation of Ketones. General Procedure. The compound to be reduced, dissolved in 10% aqueous tetrahydrofuran (60 ml./g. of compound), is placed in a reaction vessel equipped with a stirrer. Aluminum amalgam (10 g.-atoms of aluminum/mole of compound) is then freshly prepared as follows. Aluminum foil is cut into strips approximately 10 cm. × 1 cm. and immersed, all at once, into a 2% aqueous solution of mercuric chloride for 15 sec. The strips are rinsed with absolute alcohol and then with ether and cut immediately with scissors, into pieces approximately 1 cm. square, directly into the reaction vessel. For the reduction of the conjugated aromatic compounds the reaction vessel should be cooled to 0° prior to the addition of the amalgam and stirring then continued for 10 min. at this temperature for completion of the reduction. Longer reaction times and/or higher temperatures lead to pinacol formation by further reduction of the ketone formed. With the nonconjugated compounds, the reaction mixture is heated at 65° for 60–90 min. after addition of the amalgam. The reaction mixture is then filtered and the filtered solids are washed with tetrahydrofuran. The filtrate is concentrated to remove most of the tetrahydrofuran, ether is added, and the ether phase is separated from the water, dried over anhydrous sodium sulfate, and evaporated to leave the ketone, usually in a high state of purity.

Acetophenone. ω-(Methylsulfinyl)acetophenone (0.5 g., 2.75 mmoles) yielded 330 mg. (quantitative yield) of acetophenone as an almost colorless liquid. The infrared spectrum was identical with that of an authentic sample. The 2,4-dinitrophenylhydrazone (ethylene dichloride) had m.p. 242–244° (lit.[18] m.p. 238–240°, from ethanol), undepressed upon mixture with an authentic sample of the same melting point.

p-Methoxyacetophenone. ω-(Methylsulfinyl)-p-methoxyacetophenone (583 mg., 2.75 mmoles) yielded 412 mg. (quantitative yield) of p-methoxyacetophenone

(18) "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

as a colorless oil. Recrystallization from petroleum ether (b.p. 40–60°) gave white plates, m.p. 37.5–38.5° (lit.[19] m.p. 36–37.5°). The infrared spectrum was identical with that of an authentic sample.

α-Acetonaphthone. ω-(Methylsulfinyl)-α-acetonaphthone (6.38 mg., 2.75 mmoles) yielded 455 mg. (89%) of the crude α-acetonaphthone as a pale yellow oil. The semicarbazone (95% ethanol) had m.p. 205–209° (lit.[20] m.p. 205°).

α-Acetofurone. ω-(Methylsulfinyl)-α-acetofurone (1.0 g., 5.81 mmoles) yielded the crude α-acetofurone as a yellow liquid. Rapid evaporative distillation at 100° (30 mm.) gave 450 mg. (70.5%) of the pure product as an almost colorless liquid. The 2,4-dinitrophenylhydrazone (methanol) had m.p. 217–220° (lit.[18] m.p. 220°).

Methyl n-Pentyl Ketone. Methylsulfinylmethyl *n*-pentyl ketone (1.0 g., 5.68 mmoles) yielded 0.65 g. (quantitative yield) of methyl *n*-pentyl ketone as a colorless liquid. The infrared spectrum was identical with that of an authentic sample. The 2,4-dinitrophenylhydrazone (95% ethanol) had m.p. 73–74° (lit.[18] m.p. 74°), undepressed upon admixture with an authentic sample.

Methyl Cyclohexyl Ketone. Methylsulfinylmethyl cyclohexyl ketone (1.0 g., 5.32 mmoles) yielded 660 mg. (98.5%) of methyl cyclohexyl ketone as a colorless liquid. The semicarbazone (methanol) had m.p. 172–174° (lit.[21] m.p. 174–175°).

Methylsulfonylmethyl cyclohexyl ketone and dimethylaminosulfonylmethyl cyclohexyl ketone in the same manner yielded methyl cyclohexyl ketone in yields greater than 98%.

Methyl n-Heptadecyl Ketone. Methylsulfinylmethyl *n*-heptadecyl ketone (1.0 g., 2.91 mmoles) yielded 820 mg. (quantitative yield) of methyl *n*-heptadecyl ketone as a white crystalline solid, m.p. 52–55°. Recrystallization from 95% ethanol afforded colorless plates, m.p. 54.5–55.5° (lit.[22] m.p. 55°).

Undecane-2,10-dione. 1,11-Bis(methylsulfinyl)undecane-2,10-dione (1.0 g., 3.25 mmoles) yielded 600 mg. (quantitative yield) of undecane-2,10-dione as a white solid, m.p. 55–58°. Recrystallization from petroleum ether (b.p. 60–75°) raised the melting point to 61° (lit.[23] m.p. 64°).

Cyclohexanone. α-Methylsulfonylcyclohexanone (437 mg., 2.48 mmoles; obtained from Dr. W. E. Truce[24]) yielded cyclohexanone as a colorless liquid which was converted into its 2,4-dinitrophenylhydrazone (614 mg., 89%), m.p. (from 95% ethanol) 160.5–161.5° (lit.[18] m.p. 160°; 162°).

N,N-Dimethylmethanesulfonamide. A solution of 100 g. (2.22 moles) of dimethylamine in 500 ml. of benzene was cooled in a salt–ice bath during the addition, with stirring, of 125 g. (1.1 moles) of methanesulfonyl chloride over a period of 30 min. After stirring for 1 hr. longer at room temperature the mix-

ture was washed with three 100-ml. portions of water, then with saturated salt solution, dried over anhydrous potassium carbonate, and evaporated to leave the sulfonamide as a pale yellow crystalline solid. Recrystallization from 300 ml. of carbon tetrachloride yielded 95 g. (70.4%) of large colorless prisms, m.p. 49–50° (lit.[25] m.p. 50°).

Preparation of Lithium Dimethylaminosulfonyl Carbanion. Reaction with Benzophenone. To a stirred solution of 3.93 g. (0.032 mole) of N,N-dimethylmethanesulfonamide in 25 ml. of dry tetrahydrofuran, under nitrogen, was added a solution of 0.03 mole of *n*-butyllithium in hexane (17.3 ml.), with slight external cooling in a water bath. A white precipitate of the lithium salt of the sulfonamide formed immediately. A solution of 5.45 g. (0.03 mole) of benzophenone in 15 ml. of dry tetrahydrofuran was added with stirring, and after 30 min. the reaction mixture was poured into 100 ml. of cold water and extracted with chloroform. The combined extracts were washed with water, then with saturated salt solution, dried over anhydrous sodium sulfate, and evaporated to yield 9.2 g. (quantitative yield) of the β-hydroxysulfonamide IV as a white solid. Recrystallization from carbon tetrachloride gave 7.8 g. (85.3%) of colorless prisms with double melting point 98° and 105.5–106.5°. The sodium salt of N,N-dimethylmethanesulfonamide can also be prepared using sodium hydride in refluxing tetrahydrofuran, but the reaction requires over 30 hr. for completion. Sodium methylsulfinyl carbanion in dimethyl sulfoxide did not react with N,N-dimethylmethanesulfonamide to form the conjugate base.

Anal. Calcd. for $C_{16}H_{19}NO_3S$: C, 62.92; H, 6.27; N, 4.59; S, 10.50. Found: C, 62.76; H, 6.21; N, 4.53; S, 10.52.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.80 (m), 3.29 (m), 6.68 (m), 6.88 (m), 7.50 (s), 8.74 (s), 9.42 (m), 10.00 (m), 10.20 (m), and 10.35 (m) μ. The n.m.r. spectrum (CDCl₃) showed a singlet at τ 7.40 (six protons), a singlet at 6.06 (two protons), a singlet at 4.86 (one proton), and multiplets centered at 2.50 (ten protons).

The β-hydroxysulfonamide (1.76 g., 5.77 mmoles) was dehydrated by heating under nitrogen at 230° for 30 min. The cooled residue was recrystallized from ethyl acetate to yield 1.40 g. (84.5%) of the corresponding α,β-unsaturated sulfonamide as long, cottony, white needles, m.p. 141–142.5°.

Anal. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.86; H, 5.96; N, 4.87; S, 11.15. Found: C, 66.64; H, 5.94; N, 4.96; S, 11.43.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.28 (m), 6.25 (m), 6.34 (m) 6.68 (m), 6.90 (m), 7.48 (s), 8.62 (s), 8.80 (s), and 10.37 (s) μ. The n.m.r. spectrum (CDCl₃) showed a singlet at τ 7.33 (six protons), a singlet at 3.31 (one proton), and multiplets centered at 2.65 (ten protons).

Reaction of Lithium Dimethylaminosulfonyl Carbanion with Cyclohexanone. Following the same procedure as described above, the carbanion (0.03 mole) and 2.94 g. (0.03 mole) of cyclohexanone, in tetrahydrofuran, yielded a crystalline β-hydroxysulfonamide. Recrystallization from 30 ml. of carbon tetrachloride gave 5.1 g. (77%) of colorless prisms, m.p. 88.5–89°.

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Anal. Calcd. for $C_9H_{19}NO_3S$: C, 48.84; H, 8.66; N, 6.33; S, 14.49. Found: C, 48.65; H, 8.58; N, 6.20; S, 14.38.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 2.74 (m), 3.37 (s), 6.82 (m), 7.50 (s), 7.84 (m), 8.46 (s), 8.72 (s), 9.40 (m), 10.10 (s), and 10.35 (m) μ. The n.m.r. spectrum (CDCl₃) showed multiplets centered at τ 8.40 (ten protons), a singlet at 7.10 (six protons), a singlet at 6.93 (two protons), and a singlet at 6.50 (one proton).

Dimethylaminosulfonylmethyl Cyclohexyl Ketone. Lithium dimethylaminosulfonyl carbanion was prepared under nitrogen in 50 ml. of dry tetrahydrofuran from 7.4 g. (0.06 mole) of N,N-dimethylmethanesulfonamide and 0.06 mole of *n*-butyllithium in hexane (38 ml.). The mixture was cooled in an ice bath during the addition, with stirring, of 4.68 g. (0.03 mole) of ethyl cyclohexanecarboxylate in 10 ml. of dry tetrahydrofuran. The ice bath was removed and after 30 min. most of the tetrahydrofuran was removed at the water aspirator. The residue was diluted with 75 ml. of water and acidified with dilute hydrochloric acid to pH 3–4 (pH paper); the white precipitate of the β-ketosulfonamide V was filtered, washed with water, and dried (6.75 g., 96.6%). A sample was recrystallized from ethyl acetate to give colorless needles, m.p. 94°.

Anal. Calcd. for $C_{10}H_{19}NO_3S$: C, 51.48; H, 8.21; N, 6.00; S, 13.74. Found: C, 51.44; H, 8.27; N, 5.96; S, 13.67.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 3.45 (s), 5.87 (s), 6.93 (m), 7.46 (s), 8.66 (s), and 10.28 (s) μ. The n.m.r. spectrum (CDCl₃) showed multiplets in the region τ 8.0–8.9 (ten protons), a multiplet centered at 7.3 (one proton), a singlet at 7.12 (six protons), and a singlet at 5.98 (two protons).

Dimethyloxosulfonium Methylide ($(CH_3)_2SOCH_2$) and Dimethylsulfonium Methylide ($(CH_3)_2SCH_2$). Formation and Application to Organic Synthesis
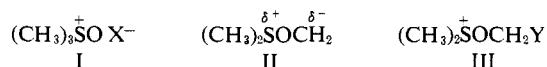
E. J. Corey and Michael Chaykovsky

Contribution from the Converse Laboratory of Harvard University, Cambridge, Massachusetts 02138. Received October 16, 1964

The generation of dimethyloxosulfonium methylide (II) and dimethylsulfonium methylide (XIII) as reactive intermediates is described. Both ylides are nucleophiles and both function to transfer methylene to certain electrophilic unsaturated linkages, including C=O, C=N, C=S, and in certain cases C=C. The less reactive oxosulfonium ylide interacts with the carbonyl function of aromatic and nonconjugated aldehydes and ketones to form oxiranes and with α,β-unsaturated ketones which are Michael receptors to form cyclopropyl ketones. The sulfonium ylide reacts with the same substrates to give oxiranes exclusively even with the α,β-unsaturated carbonyl systems. These reactions are quite general and, therefore, of considerable practical value. The stereochemistry of carbonyl addition to cyclohexanones varies depending on the ylide; the oxosulfonium ylide reacts by equatorial addition (i.e., of methylene) and the sulfonium ylide shows a preference for axial addition. A number of other reactions of these ylides are described including "over-all methylene insertion," and a differential comparison of their chemical properties is made.

This investigation originated from the idea that a moderately stable ylide (II) might result from deprotonation of the recently discovered[1,2] trimethyloxosulfonium[3] ion (I) and that this ylide might possess useful chemical properties. In particular, the reaction of the ylide II with carbonyl compounds, especially ketones, was of interest in connection with certain synthetic problems being studied in these laboratories and other investigations of carbanions stabilized by sulfur-containing functions. It was considered that II might function in a manner comparable to diazomethane, for example, to convert cyclic ketones to homo analogs by ring expansion or oxiranes by methylene transfer. Alternatively II might react in the manner of "Wittig" reagents. From the facile exchange of hydrogen in I with hydroxylic media[4,5] and from the similarity of

$$(CH_3)_3\overset{+}{S}O \ X^- \qquad (CH_3)_2\overset{\delta+}{S}O\overset{\delta-}{C}H_2 \qquad (CH_3)_3\overset{+}{S}OCH_2Y$$
$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$

certain of the molecular orbitals of II with those of the highly stable sulfone function, the possibility of generating the ylide II, at least as a transient, metastable reagent, seemed good. In the first section of this article the details of our study of the generation and

(3) In this paper the compounds having the functional group of type $R_1R_2R_3\overset{+}{S}O$ as in I will be referred to as oxosulfonium derivatives rather than sulfoxonium[1,2] derivatives. The former term seems preferable, especially in view of possible confusion of the word sulfoxonium with the related word sulfonium for compounds of the type $R_1R_2R_3S^+$, which are also discussed in this paper.

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