

The Addition of Dimethyl Sulfoxide Anion to Olefins and the Pyrolysis of Sulfoxides¹

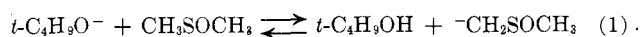
CHEVES WALLING AND LASZLO BOLLYKY²

Department of Chemistry, Columbia University, New York, New York 10027

Received April 28, 1964

Base-catalyzed additions of aryl-conjugated olefins, styrene, and 1,1-diphenylethylene to dimethyl sulfoxide occur rapidly at room temperature and give the corresponding methyl 3-arylpropyl sulfoxides in almost quantitative yield. The reaction fails with aliphatic olefins, but occurs with molecules such as allylbenzene which presumably isomerize before addition. The resulting sulfoxides decompose thermally below 200°, giving quantitative yields of 3-arylpropenes with no double bond isomerization. The kinetics of sulfoxide decomposition in diglyme solution have been studied briefly. Decompositions are first order with half-lives (for aliphatic sulfoxides) of 10–30 hr. at 145°, and the reaction should be of general synthetic value.

The marked enhancement of the basic properties of alkali metal alkoxides in dimethyl sulfoxide and facilitation of carbanion-type processes in this medium has been the subject of a number of recent papers.^{3–9} Among the reactions observed is that of the dimethyl sulfoxide anion itself, produced by an equilibration such as is shown in eq. 1.



The addition of this anion to benzophenone has been found by Chaykovsky and Corey⁸ and by ourselves⁹ to yield a mixture of products including 1,1-diphenylethylene, diphenylmethane, and 1,1-diphenylcyclopropane.

We have shown that 1,1-diphenylethylene is an intermediate in the formation of the other products, since they are obtained by heating dimethyl sulfoxide anion in dimethyl sulfoxide with diphenylethylene alone. However, a major additional product of this reaction proved to be 3,3-diphenylpropene. This paper reports a study of the nature and scope of this new and synthetically interesting process.

Reaction of Dimethyl Sulfoxide Anion with Olefins.

—Addition of 1,1-diphenylethylene to a solution of dimethyl sulfoxide anion in dimethyl sulfoxide under nitrogen at room temperature leads immediately to the brownish red color characteristic of a benzylic carbanion. Quenching of the system with water followed by distillation gives an almost quantitative yield of 3,3-diphenylpropene; identified by analysis and infrared and n.m.r. spectra, uncontaminated by isomers. Less than one equivalent of dimethyl sulfoxide anion is required for the reaction in the presence of excess dimethyl sulfoxide, and significant yields of hydrocarbon by-products are obtained only at higher temperatures. Results of experiments on which these conclusions are based are shown in Table I.

(1) Taken from the Ph.D. Thesis of L. Bollyky, Columbia University, 1963. Partial support of this work by the National Science Foundation is gratefully acknowledged.

(2) American Cyanamid Co. Fellow, 1962–1963.

(3) D. J. Cram, B. Kickborn, C. A. Kingsbury, and P. Haberfeld, *J. Am. Chem. Soc.*, **83**, 3678 (1961).

(4) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, **83**, 3731 (1961).

(5) G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962); G. A. Russell and H. D. Becker, *ibid.*, **85**, 3406 (1963).

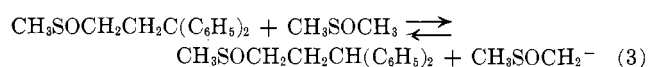
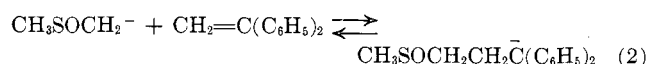
(6) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *ibid.*, **85**, 2739 (1963).

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

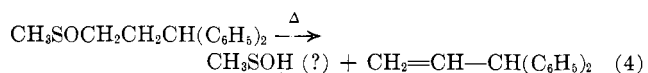
(8) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

(9) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

We find that the over-all formation of the 3,3-diphenylpropene is actually a two-step process: a base-catalyzed addition of dimethyl sulfoxide to the diphenylethylene *via* the equilibria shown in eq. 2 and 3

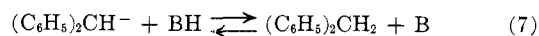
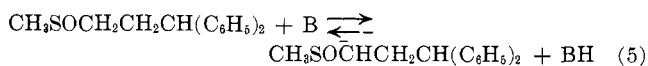


and a pyrolysis of the resulting sulfoxide during distillation (eq. 4). The intermediate sulfoxide, m.p. 70–



71°, was isolated from the quenched reaction system, and its pyrolysis (which occurs rapidly below 200°) is discussed further in the next section.

Formation of diphenylmethane is presumably from the intermediate sulfoxide, *via* a reverse Michael addition (eq. 5–7) where B represents one of the other basic

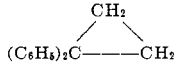


species in the system. Reaction is negligible at room temperature and is apparently an equilibrium process at 70°, since treatment of diphenylethylene with dimethyl sulfoxide anion and periodic sampling of the system showed that diphenylmethane yield reached 8% in 7 hr. and increased no further after as much as 50 hr. of heating, the balance of the product being 3,3-diphenylpropene. Assuming that the product ratio is determined by the equilibrium in eq. 6, the result corresponds to an equilibrium constant, $K = 0.007$.

This base-catalyzed addition of dimethyl sulfoxide and pyrolysis of the resulting sulfoxides were attempted with several additional olefins, as shown in Table II. With styrene, formation of a 2:1 product which pyrolyzed to 3,5-diphenyl-1-pentene was a complication, but could be minimized by slow addition of styrene dissolved in dimethyl sulfoxide. With allylbenzene and 3,3-diphenyl-1-propene, addition was presumably preceded by the isomerization of the double bonds into conjugation with the aromatic systems which is known to occur rapidly in basic solution,^{4,10} since the reaction

(10) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962).

TABLE I
 BASE-CATALYZED ADDITION OF DIMETHYL SULFOXIDE TO 1,1-DIPHENYLETHYLENE

Temp., °C.	Time, hr.	Base ^a	Yield, %		
			(C ₆ H ₅) ₂ CH ₂ CH=CH ₂	(C ₆ H ₅) ₂ CH ₂	
25	0.3	1.0	96 ^b		
25	3.5	0.25	96	Trace	
70	61	1.0	91	7.5	1.2
80	42	1.2	79, 76 ^b	15.1	5.5
82	12	0	0 ^c		

^a Moles of dimethyl sulfoxide anion/mole of olefin. ^b Distilled product was isolated; other analyses were by g.l.c. ^c 97% of starting material was recovered.

 TABLE II
 ADDITION OF DIMETHYL SULFOXIDE TO OTHER OLEFINS

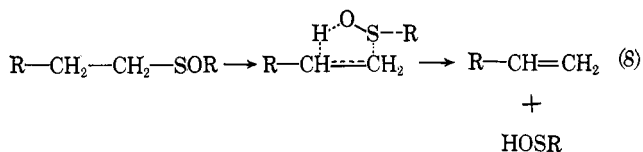
Olefin	Temp., °C.	Time, hr.	Base ^a	Products (%)
C ₆ H ₅ CH=CH ₂	43	0.5	1.0	C ₆ H ₅ CH ₂ CH=CH ₂ (62) C ₆ H ₅ CH ₂ CH ₂ CHC ₆ H ₅ CH=CH ₂ (28)
C ₆ H ₅ CH=CH ₂	25	0.3	0.22	C ₆ H ₅ CH ₂ CH=CH ₂ (71) C ₆ H ₅ CH ₂ CH ₂ CHC ₆ H ₅ CH=CH ₂ (19)
C ₆ H ₅ CH=CH ₂	25 ^b	0.3	2.2	C ₆ H ₅ CH ₂ CH=CH ₂ (88) C ₆ H ₅ CH ₂ CH ₂ CHC ₆ H ₅ CH=CH ₂ (2)
C ₆ H ₅ CH ₂ CH=CH ₂	25	0.5	1.0	C ₆ H ₅ CH ₂ C(CH ₃)=CH ₂ (92)
(C ₆ H ₅) ₂ CHCH=CH ₂	70	2.5	1.0	(C ₆ H ₅) ₂ CHC(CH ₃)=CH ₂ (30) (C ₆ H ₅) ₂ CH ₂ (50)
Cyclohexene	25		1.0	Starting material
CH ₂ CH=CHCOCH ₃	25		1.0	Polymeric product

^a Moles/mole of olefin. ^b Slow addition of dilute styrene to basic solution.

might be expected to involve the formation of a resonance-stabilized anion and no addition was observed with a simple aliphatic olefin, cyclohexene. The experiment with 3,3-diphenylpropene was carried out at 70° and yielded a relatively large amount (50%) of diphenylmethane, indicating that here the equilibrium corresponding to eq. 6 lies considerably farther to the right.

Successful addition might also be anticipated with carbonyl-conjugated and similarly activated olefins. Although a single experiment using 3-penten-2-one yielded only high-boiling polymeric products, this extension is probably worth further study.

Pyrolysis of Sulfoxides.—Although they have received little attention, two convenient methods are available for the direct conversion of sulfoxides to olefins: base-catalyzed β -elimination and simple pyrolysis. The former has been studied recently by Wallace, Hofmann, and Schriesheim⁶ who reported a 90% yield of propylene on heating diisopropyl sulfoxide with potassium *t*-butoxide in dimethyl sulfoxide for 17 hr. at 55°. The thermal elimination requires a somewhat higher temperature but is potentially a cleaner reaction. The only examples which have been studied in any detail are those of the stereoisomeric 1,2-diphenyl-1-propyl phenyl sulfoxides. Here Kingsbury and Cram¹¹ observed a stereospecific *cis* elimination at 80°, and a less stereospecific process at higher temperatures. The



(11) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

low temperature reaction they considered an Ei elimination analogous to the Cope pyrolysis of amine oxides.

Cram's reactions involve bond breaking at two benzylic carbons and the formation of a phenyl-conjugated olefin. Our own results on pyrolysis of dimethyl sulfoxide addition products indicated that essentially aliphatic sulfoxides also decompose smoothly but require somewhat higher temperatures for the elimination. In order to characterize the decompositions more completely we have made a brief kinetic study of the thermal elimination reaction of three sulfoxides in diglyme (dimethyl ether of diethyl glycol) solution. Experiments were carried out in sealed ampoules and followed by measuring olefin formation. Results are summarized in Table III, and indicate first-order decompositions with half-lives of 10–30 hr. at 145°. In the case of methyl 3-phenylpropyl sulfoxide, studied in the most detail, the first-order rate constant showed only a small decrease with tenfold increase in initial concentration and a temperature dependence corresponding to an activation energy of 31.6 ± 3 kcal. Results indicate that variation in decomposition rate with structure parallels the number of β -hydrogens available for transfer with perhaps some facilitation of transfer of tertiary hydrogen in the branched-chain sulfoxide. At 165° the pure sulfoxides all decompose smoothly to olefin in high yield. The other presumed products, alkane sulfenic acids, evidently undergo extensive decomposition and disproportionation, since no significant yield of any identifiable nonhydrocarbon product could be obtained from any of the systems.

Summary.—Our results indicate that the base-catalyzed addition of dimethyl sulfoxide occurs readily to a variety of aryl-conjugated olefins to yield the corresponding sulfoxides, and that these (and sulfoxides in general) pyrolyze smoothly to olefins. From the

TABLE III

THERMAL ELIMINATION REACTIONS OF SULFOXIDES ^a		
Sulfoxide	[Molar]	k , sec. ⁻¹ × 10 ⁶
C ₆ H ₅ CH ₂ CH ₂ CH ₂ SOCH ₃	0.056	6.87 ± 0.35
	0.098	6.75 ± 0.35
	0.56	6.02 ± 0.3
	0.56	0.261 ^b
C ₆ H ₅ CH ₂ CH(CH ₃)CH ₂ SOCH ₃	0.069	4.70 ± 0.25
(<i>n</i> -C ₁₂ H ₂₅) ₂ SO	0.072	18.3 ± 0.95

^a In diglyme at 145° unless noted. ^b At 136°.

synthetic point of view the reaction provides a simple synthesis of methyl 3-arylpropyl sulfoxides and of 3-arylpropenes which might be extended to other olefins yielding resonance-stabilized carbanions providing carbanionic polymerization can be avoided. On the other hand, it illustrates an additional complication which may arise when unsaturated molecules are employed in base-catalyzed reactions in dimethyl sulfoxide solution. The pyrolysis reaction appears quite general and provides an alternative to the number of better known olefin syntheses *via* thermal Ei processes.

Experimental

Reagents were commercial materials unless noted, freshly distilled before use. Dimethyl sulfoxide was distilled from CaH₂ under reduced pressure and contained not more than 0.001% water by Karl Fischer titration. **Di-*n*-dodecyl sulfoxide** was prepared by treating 1 g. of dodecyl sulfide in 15 ml. of *t*-butyl alcohol with 0.35 ml. of 30% H₂O₂ in 10 ml. of *t*-butyl alcohol and stirring for 60 hr. at room temperature. The product was recrystallized from ether with m.p. 88.5–89°, yield 97.5%. The preparations of other sulfoxides are described below.

Addition of Dimethyl Sulfoxide to 1,1-Diphenylethylene.—The dimethyl sulfoxide anion was prepared by dissolving 1 mole of sodium hydride in 400 ml. of dimethyl sulfoxide. One equivalent of 1,1-diphenylethylene was added at 25°; the mixture was quenched with water, extracted with ether, and dried; and the methyl 3,3-diphenylpropyl sulfoxide was recrystallized from 3:1 ether-hexane. The product, m.p. 70–71°, had an infrared spectrum showing aromatic absorption and a strong sulfoxide band at 9.6 μ. N.m.r. spectra showed ten aromatic protons, singlet at τ 2.70; one benzylic proton, multiplet at τ 5.90; and seven methyl and methylenic protons in a broad multiplet at τ 7.60.

Anal. Calcd. for C₁₆H₁₈SO: C, 74.85; H, 6.42; S, 12.49. Found: C, 74.41; H, 6.75; S, 12.30.

When the crude sulfoxide from a similar experiment was distilled under reduced pressure at 150–200°, 3,3-diphenyl-1-propene, characterized as described earlier,⁹ was obtained in a 96% over-all yield. Other experiments listed in Table I were carried out similarly, except that, when gas-liquid chromatography (g.l.c.) was used for analysis, the extracted sulfoxide solution was injected directly into the g.l.c. instrument and underwent immediate pyrolysis in the injector block which was maintained at 250°. The identifications of diphenylmethane and 1,1-diphenylcyclopropane were made as in our previous paper.⁹

Addition to styrene was carried out in the same manner under conditions shown in Table II. The intermediate methyl 3-phenylpropyl sulfoxide, m.p. 43–44°, had the expected infrared and n.m.r. spectra.

Anal. Calcd. for C₁₀H₁₂SO: C, 65.89; H, 7.74; S, 17.59. Found: C, 65.90; H, 7.64; S, 17.65.

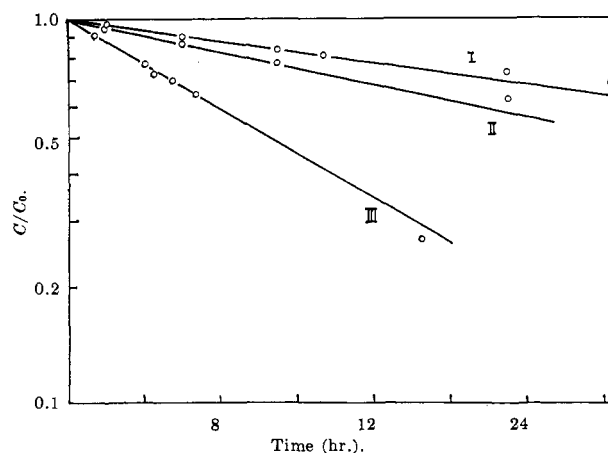


Fig. 1.—Thermal decomposition of sulfoxides at 145°: I, C₆H₅CH₂CH(CH₃)CH₂SOCH₃, C₀ = 0.069 M; II, C₆H₅CH₂CH₂CH₂SOCH₃, C₀ = 0.056 M; III, (C₁₂H₂₅)₂SO, C₀ = 0.072 M.

Pyrolysis of the crude sulfoxide gave allylbenzene, identified by infrared and n.m.r. spectra and g.l.c. retention time, and a small amount of 3,5-diphenyl-1-pentene, identified by infrared spectrum (terminal olefinic absorption at 11.1 μ) and n.m.r. spectrum.

Anal. Calcd. for C₁₀H₁₀: C, 91.48; H, 8.16. Found: C, 91.69; H, 8.19.

Addition to allylbenzene was carried out in the same manner under the conditions indicated. The methyl 3-phenyl-2-methylpropyl sulfoxide, m.p. 80.5–81°, had the expected infrared and n.m.r. spectra.

Anal. Calcd. for C₁₁H₁₆SO: C, 67.30; H, 8.22; S, 16.34. Found: C, 67.50; H, 8.32; S, 16.46.

Pyrolysis gave 3-phenyl-2-methylpropene in 92% yield, identified by infrared and n.m.r. spectra and index of refraction, n^{25}_D 1.5072, lit. n^{25}_D 1.5075.¹²

Reaction with 3,3-Diphenylpropene.—The reaction at 70° for 2.5 hr. gave, on distillation, 50% diphenylmethane and 30% 3,3-diphenyl-2-methylpropene, identified by infrared and n.m.r. spectra and analysis.

Anal. Calcd. for C₁₆H₁₆: C, 91.81; H, 8.19. Found: C, 91.86; H, 8.12.

The intermediate sulfoxide was isolated from another experiment as a white solid, m.p. 130.5–131°, but was not further characterized.

Kinetic Experiments.—The sulfoxides used were recrystallized material, part of the same samples submitted for elementary analysis. Standard solutions in dry diglyme containing tetralin as an internal standard for g.l.c. analysis were prepared in a drybox; aliquots were transferred to clean ampoules, degassed and sealed. Decompositions were carried out in constant temperature oil baths ($\pm 0.015^\circ$) and four–eight samples were taken for each run. After the reaction tubes were cooled, the contents were transferred to test tubes containing water and *n*-hexane. After stoppering and shaking, the aqueous layer was frozen, the top layer was decanted, and the extraction was repeated. G.l.c. analysis of blanks before and after extraction (silicone column at 160°) showed no change in the ratio of olefin to internal standard. Some typical first-order rate plots are shown in Fig. 1. In some cases a decrease in rate constant with conversion was observed, as also noted by Kingsbury and Cram,¹¹ and initial rates were used in calculating the constants of Table III.

(12) K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **71**, 2019 (1949).