

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEHIGH UNIVERSITY, BETHLEHEM, PENNA.]

Cycloaddition Reactions of Sulfenes¹

BY IRVING J. BOROWITZ

RECEIVED OCTOBER 28, 1963

The reactions of morpholine enamines with methanesulfonyl chloride and triethylamine to give four-membered cyclic β -aminosulfones such as IV are reported. A similar reaction involving ketene diethylacetal is also discussed. It is proposed that these reactions involve the intermediacy of sulfene I. Evidence eliminating an alternate mechanistic possibility is presented. The rearrangement of IV to a mixture of enamines is presented.

Recently the chemistry of sulfenes $\text{H}_2\text{C}=\text{SO}_2$ (I) and $\text{R}_2\text{C}=\text{SO}_2$ (II) has received renewed attention. Sulfenes have been implicated as intermediates in the irradiation of unsaturated sulfoxides,² the rearrangement of phenylmethanesulfonyl chloride with tertiary amines to give an oxythiono derivative,³ and in the reactions of enamines^{1b,4} and ketene acetals⁵ with methanesulfonyl chloride and triethylamine to give four-membered ring sulfones. The concept of a sulfonyl halide being converted to a sulfene by the action of base, a process akin to the formation of ketenes from carboxylic acid chlorides,⁶ appears in several early papers.^{7,7a}

In other relevant work, Staudinger and Pfenniger^{8a} found that the reaction of diphenyldiazomethane with sulfur dioxide in inert solvent gives tetraphenylethylene sulfone, and when the sulfur dioxide is in excess, benzophenone. The authors postulated that these reactions involved initial formation of diphenyl sulfene. Similar syntheses of symmetrical dialkyldiarylethylene sulfones were later reported.^{8b}

The reaction of diazomethane with sulfur dioxide to give ethylene sulfone was conceived of as proceeding through the intermediacy of sulfene I which then reacts further with diazomethane.⁹

The reaction of 1-N-morpholinocyclohexene (III) in dioxane at room temperature overnight with one equivalent of methanesulfonyl chloride and one equivalent of triethylamine led to a 54% yield of the four-membered sulfone IV. The structure of IV follows from evidence already published.^{1b} A similar reaction with 1-N-morpholinocyclopentene gave a 77% yield of V, while 1-N-morpholinopropene gave a 71% yield of VI. Full details for these reactions and the structural proof of IV are given in the Experimental section.

The formation of these four-membered sulfones can be visualized as occurring *via* the reaction of methanesulfonyl chloride with triethylamine to form sulfene I, which then undergoes cycloaddition reactions with the enamines to give the observed products (Fig. 2). The formation of four-membered sulfones might then

serve as a diagnostic test for the intermediacy of sulfenes in various reactions.

Alternatively, the formation of products such as IV need not involve sulfenes. Thus the reaction of III with methanesulfonyl chloride might proceed to give the immonium salt VIIa as does the reaction of 1-N-pyrrolidinocyclohexene with *p*-toluenesulfonyl chloride to give the corresponding immonium salt.¹⁰ Proton abstraction from VIIa with triethylamine could then lead to VIII which cyclizes to IV (Fig. 3).¹¹

The latter possibility seemed unlikely since only a poor yield of 2-methylsulfonylcyclohexanone (IX) was obtained from the reaction of excess III with methanesulfonyl chloride in the absence of triethylamine.¹² This pathway was eliminated from further consideration by the following experiments. Reaction of morpholine with IX in toluene containing a trace of *p*-toluenesulfonic acid led to a mixture of enamines (X, XI) which contained mainly the isomer XI. Treatment of the enamine mixture with 1.1 equivalents of hydrogen bromide in dry dioxane gave the immonium bromide VIIb. Conversion to VIIb was complete as evidenced by the disappearance of the enamine absorption band in the infrared at 6.15 μ . Addition of triethylamine to the solution containing VIIb led to a 62% regeneration of the original enamine mixture as indicated by infrared and n.m.r. spectra. No IV was found.

The regenerated enamine mixture was converted to the 2,4-dinitrophenylhydrazone of IX and was identical with a genuine sample. The elimination of the next most likely mechanism enhances the postulate that sulfene is involved in the formation of the four-membered sulfones.

It was found that if methanesulfonyl chloride and triethylamine were allowed to react in dioxane for 1 hr. at room temperature and then III was added, the yield of IV was lowered to 5.6%. Thus methanesulfonyl chloride and triethylamine react irreversibly to give a species which can initially react with III. After 1 hr., however, this species has presumably been mainly converted to another one which no longer reacts with III. In view of these facts, the reaction of methanesulfonyl chloride with triethylamine was investigated. A rapid reaction occurred when these reagents were mixed in various solvents to give a water-soluble mixture of triethylamine hydrochloride and what may have been a polymeric form of sulfene: $(\text{CH}_2\text{SO}_2)_n$.¹³

(10) (a) G. Stork, Abstracts of the XVth National Organic Symposium, Seattle, Wash., June, 1959, p. 52. *cf.* H. K. Landesman, Ph.D. Thesis, Columbia University, New York, 1958; (b) For further reactions of enamines with arylsulfonyl chlorides, see M. E. Kuehne, *J. Org. Chem.*, **28**, 2124 (1963).

(11) J. Szmuszkovicz in "Advances in Organic Chemistry, Methods and Results," ed. by R. Raphael, E. C. Taylor, and H. Wynberg, Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1963, p. 69. See also W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3231 (1963).

(12) No IV was isolated in this reaction. The reaction of excess 1-N-pyrrolidinocyclohexene with methanesulfonyl chloride and triethylamine led to poor yields of IX. See Experimental section for details.

(13) Triethylamine hydrochloride may catalyze the polymerization of sulfene. The dimerization of ketenes by tertiary amine salts may serve as an analogy; *cf.* ref. 6, p. 126.

(1) (a) Work done at the Department of Chemistry, Columbia University, New York 27, N. Y. (b) Part of this work has appeared in preliminary form: G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962).

(2) (a) E. Henmo, P. de Mayo, A. B. M. A. Sattar, and A. Stoessl, *Proc. Chem. Soc.*, 238 (1961); (b) J. F. King, P. De Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963).

(3) J. F. King and T. Durst, *Tetrahedron Letters*, No. 9, 585 (1963).

(4) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

(5) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 3030 (1962).

(6) W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. 3, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 124.

(7) (a) T. Zincke and R. Brune, *Ber.*, **41**, 902 (1908); (b) E. Wedekind and D. Schenk, *ibid.*, **44**, 198 (1911); (c) E. Wedekind, D. Schenk, and R. Stüsser, *ibid.*, **56**, 633 (1923); (d) E. Wedekind and R. Stüsser, *ibid.*, **56**, 1557 (1923).

(7a) NOTE ADDED IN PROOF.—The existence of sulfenes as intermediates in the alcoholyses of phenylmethanesulfonyl chloride and methanesulfonyl chloride has now been demonstrated; *cf.* J. F. King and T. Durst, *J. Am. Chem. Soc.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

(8) (a) H. Staudinger and F. Pfenniger, *Ber.*, **49**, 1941 (1916); (b) C. von Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942).

(9) G. Hesse, E. Reichold and S. Majumdar, *ibid.*, **90**, 2106 (1957).

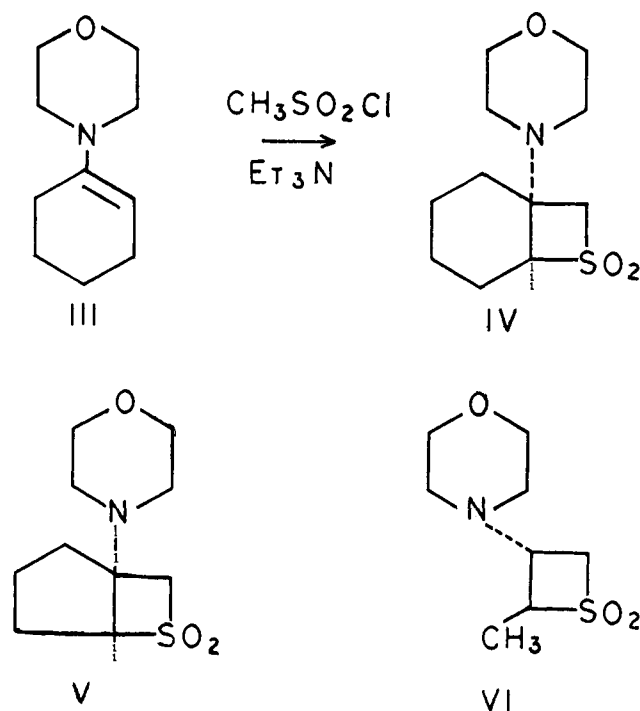


Figure 1.

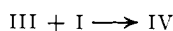
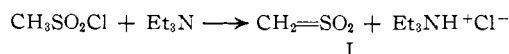


Figure 2.

The reaction of methanesulfonyl chloride and triethylamine in the presence of 1,1-diethoxyethylene (ketene diethyl acetal) gave 3,3-diethoxythietane 1,1-dioxide (XII) in 35% yield.¹⁴ No adduct was formed in the presence of cyclohexene, ethoxyacetylene, or anthracene. Thus thietane dioxide formation occurs only in the presence of olefins with strongly electron-donating substituents.

Since 2-methylsulfonylcyclohexanone (IX) was not formed directly from III in satisfactory yield, it was of interest that IV could be converted to IX. Thermal rearrangement of IV, in the absence of solvent, gave a mixture containing the enamines X, XI, and a ketone. This mixture was converted to essentially X and XI upon treatment with morpholine in the presence of *p*-toluenesulfonic acid. The enamine mixture could be hydrolyzed to IX, as identified by its 2,4-dinitrophenylhydrazone, in 50% yield (Fig. 5).

The rearrangement of IV to X and XI is analogous to the more facile thermal rearrangements of β -aminocyclobutanones to β -amino- α,β -unsaturated ketones.¹⁵ One such example is the conversion of 2,2-dimethyl-3-morpholinocyclobutanone to 4-methyl-N-morpholino-1-butene-3-one.^{15b}

Thus the reactions of enamines with methanesulfonyl chloride and tertiary amines are similar to those of enamines and ketenes. The further chemistry of sulfenes is being investigated.

Experimental

Melting points are corrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were recorded on Baird Model B and Perkin-Elmer Infracord infrared spectrophotometers. Vapor phase chromatograms were

(14) This reaction has also been observed by W. E. Truce and co-workers (*cf. ref. 5*), who kindly acknowledged our similar finding in their paper.

(15) (a) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **26**, 4775 (1961)

(b) G. A. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., *ibid.*, **26**, 4776 (1961); (c) R. H. Hasek and J. C. Martin, *ibid.*, **28**, 1468 (1963).

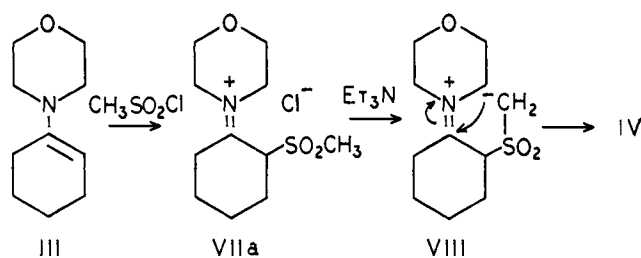


Figure 3.

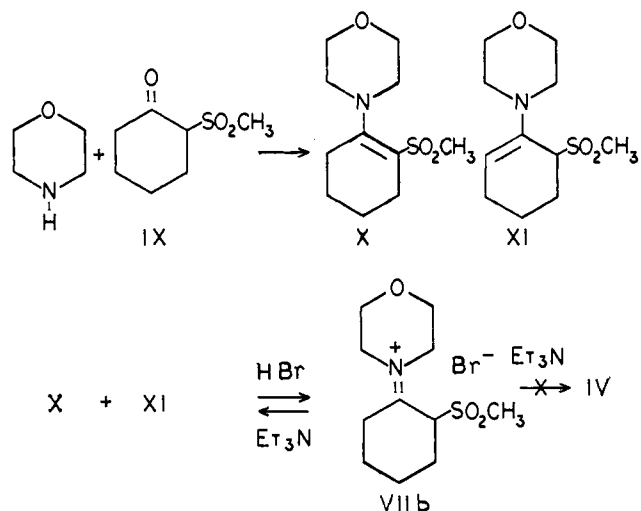


Figure 4.

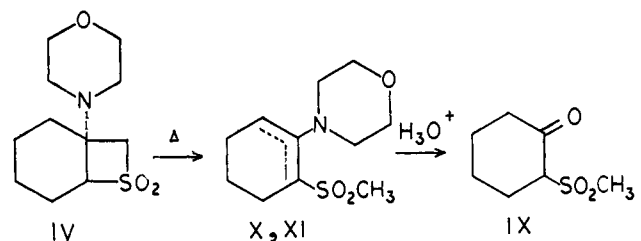


Figure 5.

recorded on Wilkens Aerograph Hy-Fi and A-90-P chromatographs. N.m.r. spectra were recorded on a Varian A-60 spectrometer. Tetramethylsilane (τ 10) was used as an internal reference unless otherwise indicated.

Reaction of 1-N-Morpholinocyclohexene with Methanesulfonyl Chloride and Triethylamine.—Freshly distilled methanesulfonyl chloride (0.10 mole) was added dropwise over 45 min. to a magnetically stirred mixture of 1-N-morpholinocyclohexene (16.7 g., 0.10 mole) and triethylamine (13.7 ml., 10.0 g., 0.10 mole) in freshly distilled dioxane. The triethylamine had been distilled from calcium hydride at a b.p. of 88–89°. The mixture was stirred under nitrogen at room temperature for 15 hr. during which time a light yellow precipitate had formed. It was kept at room temperature for 4 days without stirring and then poured into ice and water (200 ml.) and extracted with ether. A white solid, which was insoluble in both aqueous and ether phases, was filtered off. It was shown to be the cyclic sulfone IV (13.2 g., 0.054 mole, 54% yield, m.p. 139–140°). It was soluble in concentrated HCl and was reprecipitated at pH 12 upon addition of dilute NaOH. After two recrystallizations from methanol it was obtained as prisms, m.p. 139–140°. The infrared spectrum (CH₂Cl₂ or CHCl₃) contains strong peaks at 7.60 (sym. stretch) and 8.58 μ (asym. stretch) indicative of a sulfone and 8.97 μ for the ether group in the morpholine moiety. The n.m.r. (CHCl₃) in τ p.p.m. values shows: τ_a 6.1 (center of AB quartet with *J* 12.5 c.p.s. for 2 nonequivalent H of -CH₂SO₂-); τ_b 5.6 (broad multiplet for tertiary H of CH-SO₂-); τ_c 7.45 (center of triplet for 4 H of -CH₂NCH₂-); τ_d 6.3 (center of triplet for 4 H of -CH₂OCH₂-), and τ_e 8.25 (center of broad peak for 8 H of cyclohexane ring). The n.m.r. (aqueous HCl) shows: τ_a 5.1, τ_b 4.5, τ_c 5.5, τ_d 6.2, and τ_e peaks at 6.85, 7.1, 7.3, 7.5, and 7.9 (main peak). Thus in acid the sulfone hydrogens shift downfield from 6.1 and 5.6 τ to 5.1 and 4.5 τ and are now seen separately from the hydrogens next to the morpholine oxygen. The hydrogens next to morpholine nitrogen overlap some cyclohexane ring

methylene hydrogen absorption but are distinct in acid solution since they are shifted from 7.45 to 5.5 τ .

Anal. Calcd. for $C_{11}H_{15}O_3NS$: C, 53.86; H, 7.81. Found: C, 53.56; H, 7.76.

The ether extract was washed with dilute HCl and saturated $NaHCO_3$ and dried over $MgSO_4$. After removal of drying agent and evaporation of the ether, the liquid residue was distilled at b.p. 99–100° to give a yellow semisolid IX (1.2 g., 0.0068 mole, 7% if pure IX) whose infrared spectrum ($CHCl_3$) shows a peak at 5.87 μ ($C=O$) and is very similar to that of genuine IX.

The reaction of methanesulfonyl chloride (1 molar equiv.) with 1-N-pyrrolidinocyclohexene (2 molar equiv.) in toluene or under various other conditions, which, however, always involved extraction with ether from an acidic solution, gave mixtures of cyclohexanone and 2-methylsulfonyl cyclohexanone (IX) which corresponded to a maximum yield of 17% of IX.

The reaction of 1-N-morpholinocyclohexene (1 molar equiv.) with triethylamine (1 molar equiv.) and methanesulfonyl chloride (1 molar equiv.) in dioxane at reflux for 43 hr. yielded 38% of IV in contrast to 54% when the reaction was kept at room temperature.

Reaction of IV with Lithium Aluminum Hydride to Give 1-(1-N-Morpholino)-7-thiabicyclo[4.2.0]octane (XIII).—A solution of IV (3.01 g., 0.0122 mole) in dry tetrahydrofuran (40 ml.) was added dropwise over 0.5 hr. with stirring to a solution of lithium aluminum hydride (1.2 g., 0.0318 mole, 0.127 equiv.) in dry diethyl ether (120 ml.). The addition was accompanied by vigorous reaction. The mixture was refluxed with stirring an additional hour and left at room temperature for 39 hr. Then water (10 ml.) was added cautiously with stirring, followed by 2 N HCl (20 ml.) to leave a final acidic pH. Ether extraction of this acidic solution gave only a very small amount of compound. The aqueous solution was treated with 30% NaOH to pH 12 and extracted with ether. After drying and then distilling the ether, a thick colorless oil (0.7 g.) was obtained; infrared spectrum ($CHCl_3$): 8.9 μ (ether of a morpholine moiety) but no bands at 7.62 or 8.60 μ ($-SO_2-$). To part of this oil, shown to be the cyclic sulfide XIII (0.226 g., 0.00113 mole) in 95% ethanol (2 ml.), a 0.21 M picric acid solution (16.7 ml., 0.0035 mole) was added to give the picrate of XIII (0.483 g., 0.00109 mole, 96% yield, m.p. 160–161°). After recrystallization from 95% ethanol, a m.p. of 165–167° was obtained for the analytical sample as yellow platelets.

Anal. Calcd. for $C_{17}H_{22}O_3N_4S$: C, 46.15; H, 5.01. Found: C, 46.23; H, 4.86.

The Reaction of 1-N-Morpholinocyclopentene with Methanesulfonyl Chloride and Triethylamine.—Methanesulfonyl chloride (12.7 g., 0.11 mole) in dry purified dioxane (20 ml.) was added over 40 min. with stirring under nitrogen to a mixture of 1-N-morpholinocyclopentene (15.3 g., 0.10 mole; infrared in CCl_4 : 6.14 μ) and triethylamine (15.1 ml., 0.11 mole) in dry purified dioxane (20 ml.). A white precipitate formed immediately. The mixture was stirred at room temperature for an additional 43.5 hr. Most of the dioxane was then removed *in vacuo*. Dilute NaOH was added to a pH of 12. An insoluble solid (V, 8.94 g.) was filtered off and after drying melted at 119–120°. The basic aqueous layer was extracted with methylene chloride and yielded a brown semisolid (16.6 g.) which was recrystallized from methanol to give a light brown solid (V, 8.75 g., m.p. 117–120°). This represents a total yield of V of 77% (0.077 mole). The infrared spectra of the two fractions are identical. The analytical sample of V, after two more recrystallizations from methanol, melted at 122–123°. It exhibits infrared peaks ($CHCl_3$) at: 7.64, 8.40, 8.51 (sulfone), and 8.96 μ (morpholino oxygen).

Anal. Calcd. for $C_{10}H_{17}O_3NS$: C, 51.94; H, 7.41. Found: C, 51.97; H, 7.34.

The Reaction of 1-N-Morpholinopropene with Methanesulfonyl Chloride and Triethylamine.—A solution of methanesulfonyl chloride (7.38 g., 0.0645 mole) in dioxane (10 ml.) was added over 0.5 hr. with stirring under nitrogen to a solution of 1-N-morpholinopropene (7.5 g., 0.059 mole; infrared in CCl_4 : 6.16 and 7.3 μ) and triethylamine (8.35 ml., 6.16 g., 0.060 mole) in dry purified dioxane (70 ml.). A cold water bath was used since a slightly exothermic reaction ensued. A white precipitate formed immediately during the addition. The reaction mixture was then stirred for 43.5 hr. at room temperature. Most of the dioxane was removed *in vacuo* and dilute NaOH was added to pH 12. A methylene chloride extract of the basic aqueous solution yielded a semisolid which was distilled from an oil-jacketed flask at bath temperature 130° (0.2 mm.) to give a solid (VI, 10.55 g., 0.052 mole, 87% yield). Since the infrared spectrum ($CHCl_3$) still showed some absorption at 6.16 μ (uncor., enamine), the solid was dissolved in 4 N HCl (30 ml.) and kept at room temperature for 1 hr. The solution was then treated with 30% NaOH to obtain a pH of 12 and extracted with methylene chloride (total volume 200 ml.). This extract yielded a semisolid which was distilled from an oil-jacketed flask at bath temperature 140° and at 0.1 mm. to give a light tan solid VI (8.65 g., 0.0422 mole, 71% yield, m.p. 64–65°). The infrared spectrum ($CHCl_3$)

shows bands at 7.5, 7.65, 8.67, and 9.0 μ . The n.m.r. ($CHCl_3$) revealed: τ 5.63, 5.76, 5.88, 5.97, 6.02, and 6.10 (multiplet

for 3 H of $-CH_2-SO_2-C<$); τ 6.32 (center of triplet for 4 H of $-CH_2-O-CH_2$); τ 7.15, 7.28, 7.42 (triplet for 1 ring H next to nitrogen); τ 7.60 (center of triplet for 4 H of $-CH_2-N-CH_2-$); and τ 8.5 (center of doublet for 3 H of CH_3-C-). An analytical sample of VI, recrystallized from methanol, was obtained, m.p. 107–108°.

Anal. Calcd. for $C_8H_{16}O_3NS$: C, 46.81; H, 7.37. Found: C, 47.12; H, 7.41.

2-Thiomethylcyclohexanone.—The conversion of 2-chlorocyclohexanone with sodium methylmercaptide in ethanol by the procedure of Truce¹⁶ gave 2-thiomethylcyclohexanone (62% yield), b.p. 88–90° (8 mm.), infrared absorption ($CHCl_3$) at 5.89 μ . In a later run the yield was 74%, b.p. 84–86° (6 mm.). The compound gives upon v.p.c. analysis 1 peak at a retention time of 6.92 min. while 2-chlorocyclohexanone gives 1 peak at 4.21 min. on a 5% SE-30 on Chromosorb W column at a column temperature of 147°. The n.m.r. (CCl_4) shows: τ_a 6.96 (doublet); 7.35 (singlet); the areas under the τ_a and τ_b peaks included the α -protons plus partly others; τ_c 8.1 (singlet for $S-CH_3$) and τ_d 7.9–8.4 (broad peak for other hydrogens).

Reaction of 2-Thiomethylcyclohexanone with Perphthalic Acid to Give IX.¹⁷—A 0.198 M perphthalic acid solution (200 ml., 39.6 meq.) was added dropwise with stirring at 0° to 2-thiomethylcyclohexanone (2.20 g., 15.3 mequiv.) in anhydrous ether (20 ml.). The mixture was stirred overnight, treated with solid sodium bisulfite to destroy excess peracid, and washed with saturated sodium bicarbonate. The ether solution was dried over magnesium sulfate, filtered, and evaporated to give a white wax (2.44 g.). Recrystallization from ethyl acetate–cyclohexane yielded in two crops 2-methylsulfonylcyclohexanone (IX, 0.974 g., m.p. 53.5–55.5°, and 0.225 g., m.p. 50–53°; a total of 6.82 mmoles, 45% yield). This compound slowly formed a yellow 2,4-DNP, m.p. 192–194°. The infrared spectrum ($CHCl_3$) of IX shows peaks at 5.87, 7.6, and 8.6 μ . The n.m.r. ($CHCl_3-CCl_4$) exhibits the spectrum: τ 6.32 (triplet for 1 H); τ 7.12 (singlet for 3 H); and other bands at τ 7.6 and 8.1.

Formation of the Morpholine Enamines (X and XI) of 2-Methylsulfonylcyclohexanone (IX).—The sulfone IX (0.574 g., 3.26 mmoles), dry morpholine (1.0 ml., 1.0 g., 11.5 mmoles), and a trace of *p*-toluenesulfonic acid were dissolved in dry toluene (30 ml.). The mixture was refluxed through a Soxhlet thimbleful of Molecular Sieve 4A which had previously been dehydrated at 400° for 0.5 hr. After 4 hr., additional ketosulfone IX (0.324 g., 1.84 mmoles), in the form of a mixture of IX and its enamines, was added. The total mixture was refluxed through fresh sieve for 23 hr. The infrared spectrum (CH_2Cl_2) of an aliquot showed carbonyl absorption at half the intensity of the C–H band. The mixture was refluxed 47 hr. more at which time the infrared spectrum of an aliquot showed only very weak carbonyl absorption at 5.86 μ and enamine absorption of X and XI at 6.15 μ which was nearly as intense as the C–H band. The n.m.r. ($CCl_4-CH_2Cl_2$) of the mixture of enamines X and XI shows: τ 2.85 (0.70 H equivalent to 70% XI); τ 6.38 (triplet including 4 H of CH_2-O); τ 6.84 (triplet for 4 H of CH_2-N of X corresponding to 33% X); τ 7.09 (singlet including 3 H of SO_2CH_3 and 0.7 H of $CH-SO_2-$ from XI); τ 7.40 (triplet for 4 H of CH_2-N of XI corresponding to 67% XI); τ 7.65, 7.85, and 8.35 (4.5 H including nonallylic CH_2 groups of cyclohexene ring). The allylic hydrogens are obscured. Thus the enamine mixture contains about 67–70% of the unconjugated isomer XI.

Formation of the Immonium Salt VIIb and Its Reaction with Triethylamine to Give the Enamines X + XI.—An aliquot containing one half of the above enamine mixture X + XI (0.63 g., 2.55 mmoles) was dissolved in dry dioxane (10 ml.). A solution of HBr (0.24 g., 2.9 mmoles) in dry dioxane was added dropwise at room temperature with stirring. A white precipitate formed which soon coalesced to a light brown gum (VIIb). The residual solution contained no enamine as shown by the absence of the enamine peak at 6.15 μ in the infrared spectrum (CH_2Cl_2) of an aliquot from which the solvent had been evaporated.

After 0.5 hr., triethylamine (1.0 ml., 0.73 g., 7.2 mmoles) in dioxane (3 ml.) was added with stirring to form a white precipitate. The mixture was allowed to stir for 12 hr. The solvent was evaporated and dry ether was added. A tan solid (0.928 g.,

5.09 mmoles if pure $Et_3N^+HBr^-$), which was insoluble in ether and completely soluble in water, was obtained. Its infrared spectrum (CH_2Cl_2) had bands at 4.1 and 4.35 μ , indicating it to contain $(CH_3CH_2)_3N^+HBr^-$, and lacked carbonyl or sulfone peaks. Its

(16) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955).

(17) Prepared by a modification of the procedure of W. E. Truce; *cf.* ref. 16. Use of 30% hydrogen peroxide under the conditions of Truce led to an oil whose infrared spectrum included all of the peaks of IX later obtained by the use of perphthalic acid. However, the oil could not be solidified.

n.m.r. (CH_2Cl_2) had peaks at τ 3.25 (singlet, H), τ 6.85 (quartet, H), and τ 8.60 (triplet, H) which were identical with those obtained with a genuine sample of triethylamine hydrobromide. There were also present, however, peaks at τ 3.65, 5.75, and 6.15. None of the peaks of the four-membered sulfone IV were present.

The ether-soluble portion gave a yellow oil (0.390 g., 62% recovery) which had essentially the same n.m.r. spectrum and an identical infrared spectrum with that of the starting enamine mixture X and XI. No four-membered sulfone IV was found. The oil obtained was converted to the known 2,4-DNP of 2-methylsulfonylcyclohexanone. It was recrystallized from ethanol to give a first crop (0.246 g., 27% yield from the original enamine used, m.p. 187–190° and m.m.p. 187–189 with genuine 2,4-DNP of m.p. 192–194°).

Delayed Addition of 1-N-Morpholinocyclohexene to a Mixture of Methanesulfonyl Chloride and Triethylamine.—Methanesulfonyl chloride (5.5 g., 0.048 mole) in dry dioxane (5 ml.) was added dropwise over 20 min. with stirring under nitrogen to a solution of triethylamine (6.9 ml., 5.0 g., 0.050 mole) in dry dioxane (35 ml.). The resultant mixture was stirred at room temperature for 45 min. The flask was connected to a trap immersed in Dry Ice-acetone. No material indicating volatile sulfene was collected in the trap. At this point 1-N-morpholinocyclohexene (8.0 g., 0.048 mole) was added with stirring. The mixture was stirred for 23 hr. at room temperature. The solvent was removed *in vacuo*. Water was added and the resultant solution was basic. No solid insoluble in water and in ether (as is IV) was found. The solution was acidified and extracted with methylene chloride. The acidic solution was adjusted to basic pH and extracted with methylene chloride. This solution was dried, filtered, and evaporated to give an oil, which when seeded with genuine sulfone IV gave IV (0.198 g., 8.6 mmoles, 5.6% yield), m.p. 136–137° and m.m.p. 139–141° with IV (m.p. 139–141°). The infrared spectrum was identical with that of genuine IV. No more IV was present in the residual oil as shown by the infrared spectrum of the latter.

Reaction of Methanesulfonyl Chloride with Trimethyl- and Triethylamine.—The reaction between methanesulfonyl chloride and triethylamine or trimethylamine (in small excess) in methylene chloride or carbon tetrachloride led to the formation of the corresponding amine hydrochloride and water-soluble compound(s) having possibly polymeric sulfone structures of the type $(\text{CH}_2\text{SO}_2)_n$. The reaction as followed by n.m.r. spectroscopy showed no detectable formation of structures with vinyl hydrogens, *i.e.*, no monomeric sulfene. Similarly, no volatile product(s) were detected. Sulfone structures were suggested by the infrared (7.58, 8.60 μ) spectra of the product mixtures while the $\text{CH}_2\text{-SO}_2\text{-CH}_2$ grouping was suggested by an n.m.r. peak at 6.65 τ .

The Reaction of 1,1-Diethoxyethylene with Methanesulfonyl Chloride and Triethylamine to Give XII.—Methanesulfonyl chloride (9.4 g., 0.082 mole) was added to a stirred mixture at 0° of 1,1-diethoxyethylene (ketene diethyl acetal, b.p. 75–78° at 133 mm., 5.58 g., 0.048 mole) and triethylamine (8.2 g., 0.081 mole) in methylene chloride (150 ml.). The 1,1-diethoxyethylene had been prepared (32 and 41% yields) according to the procedure of McElvain¹⁸ from diethyl bromoacetal and potassium *t*-butoxide. The reaction mixture at hand was stirred for 18 hr. at room temperature. The solution was washed with water, dried, and solvent was evaporated to give solid XII (3.25 g., 0.0167 mole, 29%, m.p. 43.5–46°). In smaller runs yields up to 48% were obtained. The compound was recrystallized three times from cyclohexane to give white prisms, m.p. 48.5–49°. Spectral and analytical evidence identified XII to be 3,3-diethoxythietane-1,1-dioxide. The infrared spectrum (CHCl_3) showed peaks at 7.6 and 8.4 μ (sulfone). The n.m.r. (CH_2Cl_2) showed: τ 5.95 (singlet, 4 H of $-\text{CH}_2\text{-SO}_2\text{-CH}_2-$), τ 6.60 (quartet, 4 H from the methylenes of ethyl groups), and τ 8.80 (triplet, 6 H from the methyls of ethyl groups).

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{O}_6\text{S}$: C, 43.29; H, 7.27. Found: C, 43.52; H, 7.42.

Attempted Reactions of Methanesulfonyl Chloride and Triethylamine with Various Olefinic and Acetylenic Compounds. A. With Cyclohexene.—The addition of methanesulfonyl chloride to a mixture of triethylamine and cyclohexene in methylene chloride led to no reaction involving the olefin. The solid iso-

lated had n.m.r. peaks at 7.35 τ (singlet, probably due to $(\text{CH}_2\text{-SO}_2)_n$ and at 6.8 τ (quartet) and 8.6 τ (triplet) which are typical of $(\text{CH}_2\text{CH}_2)_n^+\text{NHCl}^-$.

b. With Ethoxyacetylene.¹⁹—The addition of methanesulfonyl chloride to a mixture of triethylamine and ethoxyacetylene (1.9 equiv.) led to no reaction involving the acetylene. An infrared spectrum (CH_2Cl_2) of the reaction mixture had significant

peaks at 4.3 (R_2NH) and 4.8 μ (acetylene) and a weak peak at 5.86 μ ($\text{C}=\text{O}$ of ethyl acetate). A washing with 4 *N* HCl converted the peak at 4.8 μ to one at 5.86 μ ; *i.e.*, unreacted ethoxyacetylene was converted to ethyl acetate.

c. With Anthracene.—The addition of methanesulfonyl chloride to a mixture of triethylamine and anthracene led to only a trace of compound other than virtually a quantitative recovery of anthracene from the water-insoluble fraction.

The Rearrangement of IV to Enamines X and XI and Their Conversion to IX.—The four-membered sulfone IV (3.873 g., 15.8 mmoles) was heated under nitrogen for 21 hr. at a bath temperature of 128–137° and now appeared as a black gum. It was distilled from an oil-jacketed flask (b.p. 150° using a mercury diffusion pump) to give a thick light brown oil (1.695 g.). An infrared spectrum (CH_2Cl_2) of the oil showed peaks at 5.9 (slightly weaker than C–H indicating about 50% ketone) and 6.2 μ (weak enamine band). The above oil was dissolved in dry toluene (80 ml.), and morpholine (2 ml., 2 g., 23 mmoles) was added. The solution was refluxed for 36 hr. through Molecular Sieve 4A (dried previously at 425° for 0.5 hr.). Evaporation of the solvent and distillation from an oil-jacketed flask gave a liquid (0.656 g.), which boiled at a bath temperature of 120° (0.1 mm.), and a solid (0.749 g.), which distilled at a bath temperature of 180° (1 mm.). The former gave a 2,4-DNP immediately and the latter only on standing with 2,4-DNPH solution. The infrared spectrum (CH_2Cl_2) of the liquid had a band at 5.89 μ which was as strong as the C–H band. The n.m.r. spectrum contained the expected peaks for the morpholine enamine(s) of 2-methylsulfonylcyclohexanone plus others. The ratio of CH_2N protons/ $\text{CH}_2\text{-SO}_2$ protons was 1.35 (1.33 calcd.). The solid fraction had an infrared spectrum (CH_2Cl_2) showing a weak peak at 5.90 μ and a moderate peak at 6.14 μ . Its n.m.r. spectrum (CH_2Cl_2) was very similar to that of the enamine mixture prepared from genuine IX. By comparing the relative areas of the CH_2N protons for X and XI which were therefore assumed to be present, the mixture appeared to consist of 33% of X and 67% of XI.

In a similar run, IV (1.85 g., 0.0075 mole) was heated without solvent for 15 hr. to leave a black gum which exhibited a weak infrared band (CHCl_3) at 5.88 μ and a very small amount of volatile yellow oil which had a strong infrared band (CHCl_3) at 5.90 μ . Trituration of this mixture with ethanol gave IV (0.34 g., 0.0014 mole, m.p. 132–133°, 18% recovery) as the insoluble fraction. The soluble fraction was treated with 24 ml. of dilute HCl (0.016 equiv. in water-ethanol (1:5)) for 45 min. at room temperature and then neutralized with saturated aqueous sodium bicarbonate. Concentration of the solvents *in vacuo*, addition of water (10 ml.), and extraction with methylene chloride led to an oil (1.05 g.) which was distilled at a bath temperature of 150° (0.04 mm.) to give a yellow semisolid (0.666 g., 0.0038 mole if all IX, or 51% yield from IV) whose infrared spectrum (CHCl_3) was similar to that of genuine IX. Of this semisolid, 0.199 g. (0.0013 mole if IX) gave the yellow 2,4-DNP (0.182 g. of crude, m.p. 145–148°; 0.00051 mole or 45% conversion), which after two recrystallizations from ethanol (0.080 g.) had m.p. 193–194°. The m.m.p. with 2,4-DNPH (m.p. 198°) was 178–190°. The ultraviolet spectrum (EtOH) of this 2,4-DNP had an unusually low λ_{max} 345 m μ .

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_6\text{S}$: C, 43.81; H, 4.53. Found: C, 43.74; H, 4.76.

Acknowledgments.—The author wishes to express his gratitude to Professor Gilbert Stork of Columbia University for suggesting the research problem, discussing its aspects, and providing the research facilities. Support of this research by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

(18) P. R. Johnson, H. M. Barnes, and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 964 (1940).

(19) K. Pfister and Co., Ridgefield, N. Y.