consistent with this induced decomposition as the predominant decomposition path. Radicals derived from chlorobenzene are relatively unreactive toward the perester in low concentration and no induced decomposition appears in this solvent.

This mechanism of induced decomposition is also supported by the observation of a small (*ca.* 30%) increase in rate of decomposition in chlorobenzene when 0.5 molar styrene is present. Radicals of the benzylic type, similar in structure to cumyl radicals, would be generated from the styrene and, in part, attack the peroxide by this induced path.

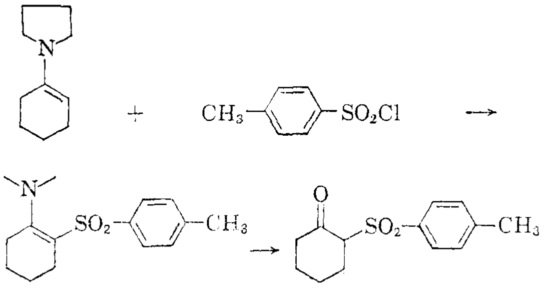
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, B.C., CANADA
RICHARD E. PINCOCK

RECEIVED NOVEMBER 17, 1961

FOUR-MEMBERED SULFONES FROM ENAMINES AND ALIPHATIC SULFONYL HALIDES

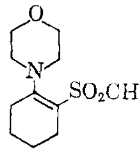
Sir:

Some time ago we reported[1] that enamines such as for instance that from cyclohexanone and pyrrolidine react with aromatic sulfonyl chlorides to produce, after hydrolysis, a β-ketosulfone

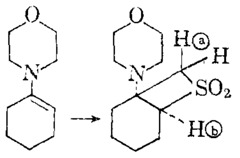


In connection with another problem which required the synthesis of β-ketosulfones we have had occasion to examine the reaction of enamines with aliphatic sulfonyl chlorides.

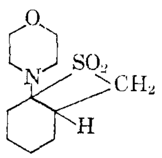
We have found that, in the presence of triethylamine as a proton acceptor, methanesulfonyl chloride reacts with a variety of morpholine enamines to give an interesting new class of compounds, four-membered cyclic aminosulfones. For example, reaction of the morpholine enamine of cyclohexanone (I) in dioxane at room temperature overnight with one equivalent of methanesulfonyl chloride and one equivalent of triethylamine, gives a very good yield of the cyclic sulfone II, m.p. 139–140°.



III



I II

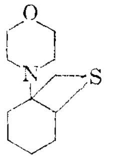


IV

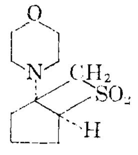
The structure of II follows from its analysis (Calcd. for $C_{11}H_{19}O_3NS$: C, 53.86; H, 7.81. Found: C, 53.56; H, 7.76), its infrared spectrum which shows the presence of the sulfone grouping at 7.62 and 8.60 μ, while the solubility in, and recovery from, dilute acid (as well as the infrared spectrum) exclude the isomeric possibility III. The n.m.r. spectrum is in full agreement with the postulated structure showing (in chloroform) two non-equivalent hydrogens (a) in a typical AB quartet centered at $\tau = 6.1$ with $J = 12.5$ cps., and with the tertiary hydrogen (b) as a broad multiplet centered at $\tau = 5.6$. Absorption from the (a) protons overlapped the absorption of the four hydrogens next to the morpholine oxygen but could be disentangled by putting a positive charge on the nitrogen: solution in aqueous hydrochloric acid moved the protons next to the sulfone about 60 cps. to lower field (5.0 τ for the (a) protons and 4.5 τ for the (b) proton). The CH_2's next to the morpholine nitrogen ($\tau = 7.4$) overlapped some methylene absorption but could be moved to lower field ($\tau = 5.5$) in hydrochloric acid solution.

The orientation of the sulfone with respect to the amino group can, on the basis of the n.m.r. spectrum, only be that shown in II rather than IV. This was confirmed by lithium aluminum hydride reduction[2] of II and acid work up to the amino sulfide V, characterized as its picrate, m.p. 165–167° (Found: C, 46.23; H, 4.86) the alternative arrangement of IV would have produced a sulfide which would have been transformed into an amino or keto mercaptan.

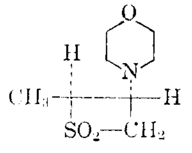
Similar reactions with the morpholine enamine of cyclopentanone gave a 77% yield of the cyclic sulfone VI, m.p. 122–123° (Found: C, 51.97; H, 7.34) while the morpholine enamine of propionaldehyde led in very good yield to the corresponding sulfone VII, m.p. 107–108° (Found: C, 47.12; H, 7.45)



V



VI



VII

Various mechanisms may be written for these reactions. The interesting possibility that the first step involves the formation of an analog of ketene, $CH_2{=}SO_2$, VIII, followed by reaction with the enamine will have to be explored further.

THE CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK
GILBERT STORK
IRVING J. BOROWITZ[3]

RECEIVED NOVEMBER 29, 1961

---

(1) G. Stork, Abstracts of the XVIth National Organic Symposium, Seattle, June, 1959, p. 52; *cf.* H. K. Landesman, Ph.D. thesis, Columbia University, New York, 1956.

(2) *Cf.* P. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

(3) Department of Chemistry, The City College, New York.