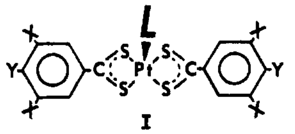
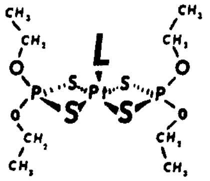
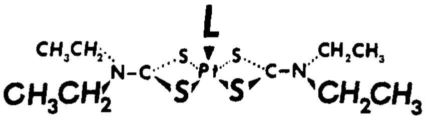
observed. In II, rearrangement through a trigonal-bipyramidal structure equilibrates the ethyl groups. A weakly associated solvent molecule could be liberated in this process to account for the positive $\Delta S^{\ddagger}$ The ability of phosphine to catalyze phosphine exchange and the observation of what may be six-coordinate species precipitating from solution when excess Ph_2PCH_3 is added to Ia and Ib further support the hypothesis that the low-energy configuration in these complexes is a solvated PtS_4L square pyramid.



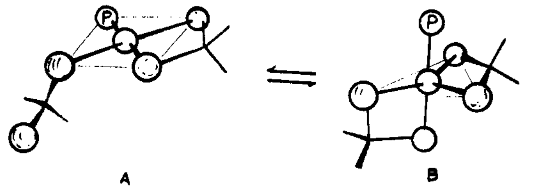
I



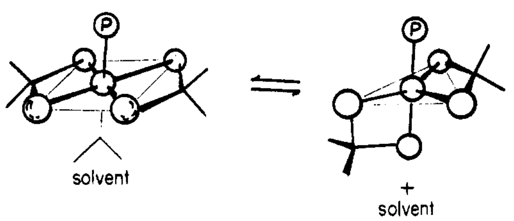
II



III



(1)



(2)

Acknowledgment. This work was supported in part by a grant from the National Science Foundation, GP-7889, and a grant from the donors of the Petroleum Research Fund as administered by the American Chemical Society.

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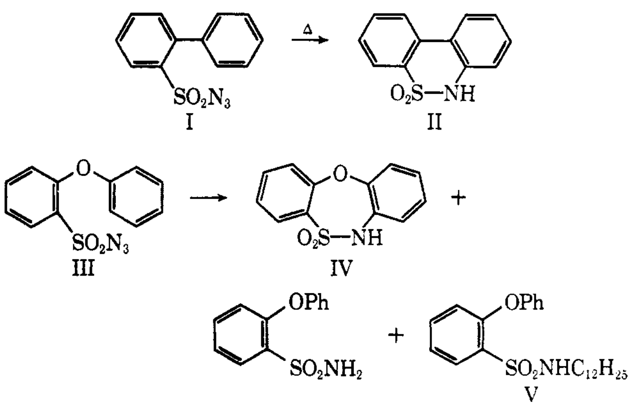
Received October 25, 1968

Intramolecular Cyclizations of Sulfonyl Nitrenes

Sir:

Unlike the aryl nitrenes, sulfonyl nitrenes undergo intermolecular aromatic substitution reactions to give sulfonylaniline derivatives.[1] Aryl nitrenes are known to undergo intramolecular ring closures to five- and six-membered heterocycles readily,[1,2] but no reports of the corresponding cyclizations of sulfonyl nitrenes have appeared. We now wish to report examples of such cyclizations, some of which exhibit unusual features.

Thermolysis of biphenyl-2-sulfonyl azide (I),[3] mp 60-61°, in *n*-dodecane or in the absence of solvent at 150° gave 6H-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (II), mp 200-202° (lit.[4] mp 196°) (38-70% yield). No biphenyl-2-sulfonamide, mp 121-122°, was detected.



The mechanism of this substitution reaction is under study to determine whether or not it proceeds *via* the formation of an aziridine intermediate.[5]

2-Phenoxybenzenesulfonyl azide (III), mp 79-80°, in *n*-dodecane at 135° for 30 hr gave IV (15%), mp 140-141°. Such a cyclization of a nitrene to a seven-membered ring appears to be unprecedented. 2-Phenoxybenzenesulfonamide (4%), mp 113-114° (hydrogen-abstraction product), and N-dodecyldiphenyl ether 2-sulfonamide (11%; V) (probably an unresolved mixture of positional isomers), bp 208° (0.2 mm) (C-H insertion product), were also formed in the thermolysis. In contrast, no internuclear aromatic cyclization was observed when diphenyl sulfide 2-sulfonyl azide (VI) was heated either alone or in dodecane. Instead, cyclization occurred at divalent sulfur to give VII (10%), mp 191-193°. This, too, appears to be a novel intramolecular cyclization of a nitrene and is understandable in terms of an attack by electrophilic singlet nitrene at the electron-rich sulfur atom resulting in expansion of its valence shell, though a concerted attack by sulfur at the azide and elimination of nitrogen cannot be discounted. Three other products were also formed: VIII (19%), mp 112.5°, IX (5%), as a yellow gum, and X[6] (4%), mp 155-156.6°. That VII was formed and not the desired

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(1) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

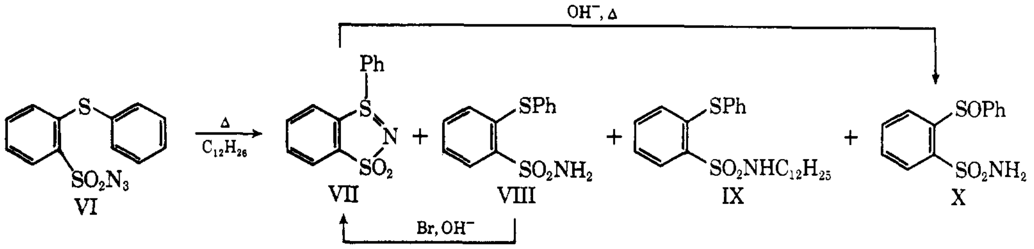
(2) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962); P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, *ibid.*, **75**, 6335 (1953); G. Smolinsky, *ibid.*, **82**, 4717 (1960); **83**, 2489 (1961).

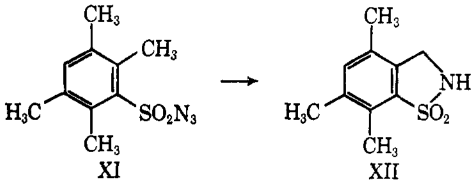
(3) Satisfactory analyses and infrared, nmr, and mass spectral data were obtained for all the new compounds reported.

(4) F. Ullman and C. Grosse, *Ber.*, **43**, 2694 (1910).

(5) R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).

(6) Probably formed during the chromatography on alumina; also formed by basic hydrolysis of VII.





internuclear cyclization product was confirmed by the absence of an NH band in the infrared, by its methylation with dimethyl sulfate to give N,N-dimethyl-2-benzenesulfinylbenzenesulfonamide (82%), mp 120–122°, and by its synthesis from VIII with bromine and alkali. In one thermolysis only, some diphenylene disulfide (3%), mp 156.5–158° (lit.[7] mp 154°), was also obtained.

Thermolysis of diphenyl sulfone-2-sulfonyl azide, mp 99.5–100°, similarly did not yield the cyclic sulfonamide. In dodecane at 150°, the products formed were diphenyl sulfone (27%),[8] mp 125°, and diphenyl sulfone-2-sulfonamide (9%). In Freon E-4 at 150°, the products were diphenylene sulfone (1.3%),[8] mp 230°, and diphenyl sulfone-2-sulfonamide (1.5%), together with tars.

An attempt to effect intramolecular cyclization of a side-chain sulfonyl nitrene failed: thermolysis of α-toluenesulfonyl azide, mp 53.5–54°, in dodecane gave α-toluenesulfonamide (26.5%), mp 103.5–104.5°, and N-dodecyl-α-toluenesulfonamide (41.8%), mp 99–101°. Photolysis or copper-catalyzed[10] decomposition of the azide with or without solvent also did not lead to cyclization, and it would appear as though geometrical restrictions do not permit the formation of the required aziridine intermediate[5] in this case. On the other hand, intramolecular insertion into an aliphatic side chain has been achieved: XI, mp 68.5°, was decomposed in dodecane at 150° to give a 10–15% yield of XII, mp 229.5–230°. No durene-3-sulfonamide was isolated.

The results can be explained if it is assumed that the species undergoing intramolecular aromatic substitution, attack upon divalent sulfur, and C–H insertion is the singlet sulfonyl nitrene, while that undergoing hydrogen abstraction from aliphatic hydrocarbons is the triplet. When the internuclear distance is large or the rotational conformation does not permit easy addition of the nitrene to the aromatic nucleus, it can either insert into a C–H bond, attack sulfur (to form a five-membered ring as is usually favored in nitrene cyclizations), or drop to the triplet ground state and undergo hydrogen abstraction.

Acknowledgment. This research was supported by a grant from the Warner-Lambert Research Institute, whom we thank.

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[7] E. D. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).

[8] The formation of these products suggests the elimination of azide and SO_2 to give the aryl radical, which would have a parallel in the cleavage of sulfonyl chlorides.[9]

[9] F. A. Drahowzal in "Organic Sulfur Compounds," N. Kharasch, Ed., Vol. 1, Pergamon Press, New York, N. Y., 1961, p 372.

[10] H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1951 (1967).

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Received November 4, 1968

The Photochemistry of Aliphatic Azo Compounds. The Role of Triplets and Singlets in Their Photochemistry

Sir:

The gas-phase quantum yields of decomposition, Φ(dec), of azo compounds have long been known to be pressure sensitive and have been explained in terms of the mechanism[1]

$$\text{azo} \underset{+\text{M}}{\overset{h\nu}{\rightleftharpoons}} \text{azo}^* \longrightarrow \text{products}$$

However, this simple scheme is not adequate; if it were it can readily be shown that azo compounds should not photolyze in solution, while they do so.[2] In agreement with this Wu and Rice[3] have recently observed curvature in the plot of 1/Φ(dec) *vs.* [M] for perfluoroazomethane. Moreover we have observed *cis–trans* isomerization of azomethane in solution using both polar and nonpolar solvents.[2] By analogy with other *cis–trans* systems we might expect that this isomerization proceeds *via* the triplet.[4] We have car-

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[1] H. Cerfontain and K. I. Kutscke, *Can. J. Chem.*, **36**, 344 (1958); W. C. Worsham and O. K. Rice, *J. Chem. Phys.*, **46**, 2021 (1967), and references therein.

[2] R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964); S. Kodama, S. Fujita, J. Takeishi, and O. Toyama, *Bull. Chem. Soc. Japan*, **39**, 1009 (1966).

[3] E.-C. Wu and O. K. Rice, *J. Phys. Chem.*, **72**, 542 (1968).

[4] Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964); R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).