

Scheme I



products. Support for such ideas may be found in the photochemical solvolysis experiments described by Zimmerman¹¹ and in the work of Beugelmans,¹² who

has reported photochemical rearrangements, solvolyses, and eliminations, which also appear to involve carbonium ion intermediates.

On the other hand, our work on halides can be rationalized via triplet diradical intermediates, for example, as in Scheme I. A similar process can be imagined for the $1 \rightarrow 2$ conversion via triplet intermediates, but with a 1,4-chlorine shift, rather than a 1,2 or 1,3 shift.



Further exploratory and mechanistic work on such rearrangements is in process or planned.

(11) H. E. Zimmerman and V. R. Sandel, J. Amer. Chem. Soc., 85, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, 85, 922 (1963).
(12) (a) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (b) H. C. de Marcheville and R. Beugelmans, *ibid.*, 6331 (1968); (c) R. Beugelmans and H. C. de Marcheville, *Chem. Commun.*, 241 (1969).

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Additions and Corrections

Radical Additions of Cl-CCl₃ to *cis*-Cyclooctane [J. Am. Chem. Soc., 89, 3205 (1967)]. By JAMES G. TRAYNHAM and THOMAS M. COUVILLON, Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803.

The correct symmetry number for BrCCl₈ was used for the calculations summarized on page 3308, although the number itself is erroneously printed.

Addition of Electronegatively Substituted Azides to Allenes [J. Am. Chem. Soc., 90, 2131 (1968)]. By R. F. BLEIHOLDER and H. SHECHTER, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

On page 2133, paragraphs 1 and 2, and page 2134, paragraphs 1 and 2, the unusual nmr spectra of N-(1,2-3-trimethyl-2-butenylidene)benzenesulfonamide (XVII) and N-(1,2,3-trimethyl-2-butenylidene)-p-toluenesulfonamide (XIX) were discussed on the basis of hindered rotation of their α -methyl groups or syn-anti isomerism of the arylsulfonimino groups. Reevaluation of the nmr spectra of XVII and XIX reveals that the absorptions of the methyl groups in the τ 7.8–7.9 and the 7.4 regions are singlets. The interpretation that the nmr results from a barrier to rotation of one of the methyl groups in XVII and XIX is untenable in that the nonequivalent protons should thus constitute an A₂X group with a minimum of 5 lines and J_{AX} quite large. The nmr spectra of XVII and XIX are interpretable however in that in solution the sulfonimines exist as equilibrium mixtures of syn and anti isomers. Confirmation of the latter conclusion is derived from observations that in various solvents the singlets for the α -methyl groups in XVII and XIX occur in ratios of less than 2:1. The long-range deshielding, the rapid syn-anti isomerization upon heating, and the crystallization of single geometric isomers from syn and anti mixtures of XVII and XIX, respectively, in solution parallel the behavior reported previously for N-(3b,4,-5,6,6,6a-hexachlorodecahydro-2,5,7-metheno-3H-cyclopenta[a]pentalen-3-ylidene)-p-toluenesulfonamide [R. J. Stedman, A. C. Swift, and J. R. E. Hoover, Tetrahedron Lett., 2525 (1965); R. J. Stedman, private communication]. We wish also to acknowledge communication with M. Raban on this subject.

Temperature Effect on Sulfur Dioxide Vapor Luminescence [J. Am. Chem. Soc., 90, 2972 (1968)]. By H. D. METTEE, Department of Chemistry, University of Texas at Austin, Austin, Texas 78712.

Reactions 1, 2, and 3 between SO and O_3 do not require the third body M as shown. The bimolecular