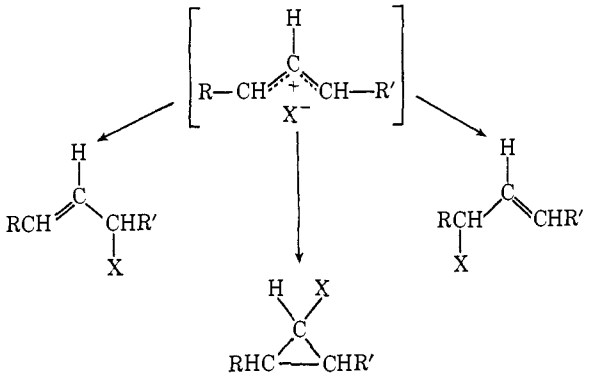
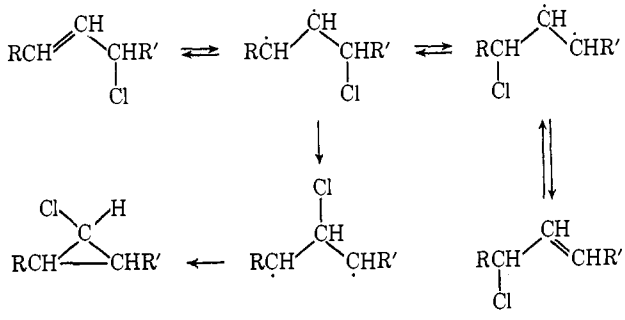
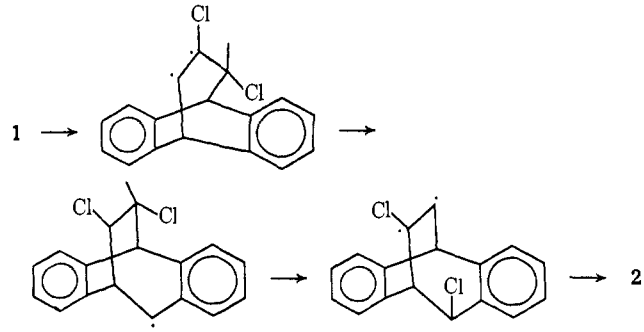


Scheme I



products. Support for such ideas may be found in the photochemical solvolysis experiments described by Zimmerman[11] 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** → **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).

Stanley J. Cristol, George A. Lee
Department of Chemistry, University of Colorado
Boulder, Colorado 80302
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Additions and Corrections

Radical Additions of Cl–CCl_3 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 $BrCCl_3$ 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 non-equivalent protons should thus constitute an A_2X 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

character was explicitly mentioned by Halstead and Thrush (ref 1). This error has no effect on the implications of the "temperature quenching" of the triplet SO_2 in the optical excitation experiment.

Nuclear Magnetic Resonance Studies of *ortho*-Substituted Phenols in Dimethyl Sulfoxide Solutions. Electronic Effects of *ortho* Substituents [*J. Am. Chem. Soc.*, **91**, 379 (1969)]. By M. THOMAS TRIBBLE and JAMES G. TRAYNHAM, Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803.

In Table I, three $\Delta\delta_o$ entries should be changed to the following: *t*-Pen, −0.23; OEt, −0.57; SOMe, 1.27. These changes do not change eq 5.

In Figure 2, the vertical axis should be labeled $\Delta\delta_p$, and the point labels I and $CH{=}CHCO_2Me$ should be interchanged.

Stereochemical Nonrigidity in Phosphorus Trifluoride Substituents of Trifluoromethylcobalt Tetracarbonyl [*J. Am. Chem. Soc.*, **91**, 526 (1969)]. By CARL A. UDOVICH and RONALD J. CLARK, Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

There is a typographical error in the column headings of Table I. The last three headings read J_{FF_C}, $J_{P_PF_C}$, J_{FF_P}, but should read J_{PF_C}, $J_{F_PF_C}$, J_{PF_P}.

Kinetics and Mechanism of the Reaction of the Thianthrene Cation Radical with Water [*J. Am. Chem. Soc.*, **91**, 1872 (1969)]. By HENRY J. SHINE and YUZURU MURATA, Department of Chemistry, Texas Technological College, Lubbock, Texas 79490.

On page 1873, the concentrations listed in the lines of text immediately under eq 7 should read as follows: $[\mathbf{1}]_0$ was 2.12, 2.10, and 1.06×10^{-4} *M*, $[Th]_0$ was 1.03×10^{-3} *M*.

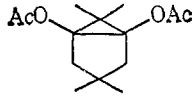
The Base-Catalyzed Fragmentation of a Peroxide, 2-*t*-Butylperoxy-2-methylpropanoic Acid [*J. Am. Chem. Soc.*, **91**, 3610 (1969)]. By WILLIAM H. RICHARDSON and RONALD S. SMITH, Department of Chemistry, San Diego State College, San Diego, California 92115.

On page 3615, column 2, line 14, the analysis should read: *Anal.* Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.86; H, 49.3.

***vic*-Cyclopropanediols from Lithium in Ammonia Reductions of Cyclic β-Diketones** [*J. Am. Chem. Soc.*, **91**, 3677 (1969)]. By WILLIAM REUSCH and D. B. PRIDDY, Department of Chemistry, Michigan State University, East Lansing, Michigan 48823.

The hydroxyl protons were omitted in the nmr spectrum of 2,2,4,4,6,6-hexamethyl-1,5-dihydroxybicyclo-[3.1.0]hexan-3-one (VI). These appear as a singlet at δ 5.98 (pyridine solution). In DMSO-d_6 the nmr of sublimed VI consists of sharp singlets at δ 0.92 (3 H), 1.00 (6 H), 1.11 (3 H), 1.18 (6 H), and 4.70 (2 H). Material recrystallized from wet ether is apparently a hydrate, since the δ 4.70 signal doubles in area.

The structure of compound X should be



Book Reviews

Organic Functional Group Preparations. By STANLEY R. SANDLER and WOLF KARO. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. 1968. xi + 578 pp. 15.5 × 23.5 cm. $18.50.

At the present status of the art of preparative organic chemistry, both the grand strategists and the ordinary practitioners eventually reach the point where the ingeniously devised synthesis or the seemingly straightforward preparation needs to be implemented in the laboratory. As yet there is no machine, no computer, no magic to help the chemist here, and he relies primarily on analogies in deciding how to execute a particular transformation. Even if he has learned that a certain "name reaction" has a good chance of giving him the desired transformation, he still has to decide precisely which experimental conditions to employ. The volume under review intends to offer advice at this stage.

The authors have arranged their material by functional groups, *e.g.*, hydroxy compounds, ethers, esters, carboxylic acids, amines, nitro compounds, and in each chapter they show how such groups have been produced from precursor functions attached to a variety of residues. In selecting examples for inclusion, the authors have looked for wide applicability, high yields, simplicity, and safety. The primary methods chosen are accompanied by experimental details; methods judged useful but less general are cited as references.

The present work is certainly not the only one of its type. The Fieser and Fieser "Reagents" books fill a similar need; "Organic Reactions" is a related series, and so is the Foerst Series, "Newer Methods of Preparative Organic Chemistry," to mention just a few. In my opinion, however, all of these serve purposes not identical with the one Sandler and Karo addressed themselves to. Perhaps the best way to describe and to appreciate this book is to call it a "Portable Houben-Weyl" because in conception, lay-out, and wealth of material, it reminds me of that famous compendium. The authors' viewpoint essentially excludes the interface of organic and biological chemistry: The reader will find no help in such undertakings as peptide synthesis, phosphoric acid esters, nucleosides, or the manipulation of steroids or carbohydrates, but in the territory covered, the job is well done.

Hans Heymann

Research Department, CIBA Pharmaceutical Company
Summit, New Jersey 07901