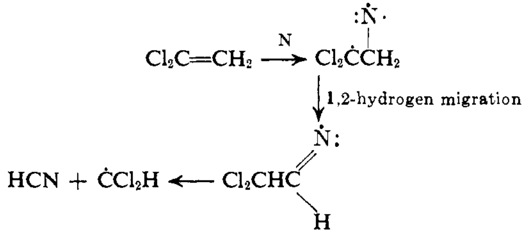
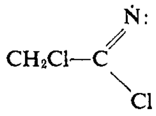
Scheme I. Minor Reaction Pathway

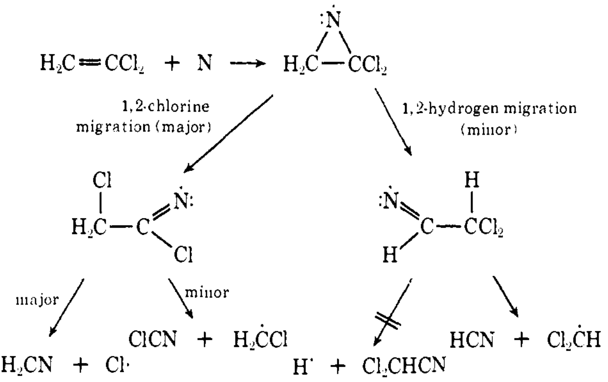


Alternatively, the hypothesis of an intermediate aziridino radical from addition of N(^{4}S) ground-state atoms to carbon–carbon double bonds is attractive; Winkler has reported[5] decomposition of independently generated aziridino radicals to nitrilic products. Opening of the aziridino radical is postulated here to be concerted with a 1,2 migration of a substituent (Scheme II) since stepwise reaction would lead directly into Scheme I through cleavage of the aziridino radical to give the most stable radical. The direction of opening of the nitrogen bridge is determined by the relative migratory aptitudes of the rearranging groups, Cl > H. The preference for loss of Cl· rather than ·CH$_2$Cl from



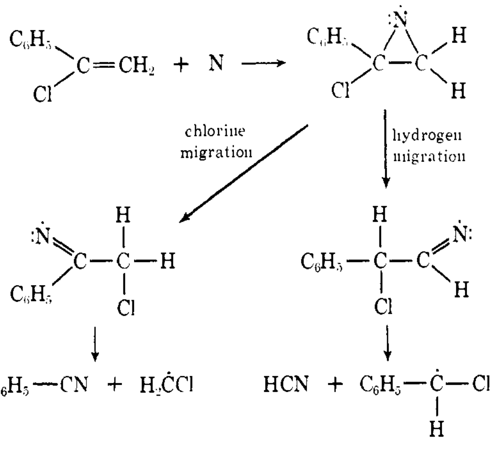
accounts for the high yield of ClCH$_2$–CN.

Scheme II. Major Reaction Pathway



Direct competition of bromine *vs.* chlorine migration in H$_2$C=C(Cl)Br shows that bromine migrates twice as readily as chlorine. But the relative percentage of BrCH$_2$–CN (the product of halogen rearrangement) from the reaction of 1,1-dibromoethylene is smaller than the relative percentage of ClCH$_2$–CN from the 1,1-dichloroethylene reaction. These results, along with the increase in HCN yield in the series H$_2$C=CCl$_2$, H$_2$C=C(Cl)Br, H$_2$C=CBr$_2$, indicate that the reaction includes both Schemes I and II. Product formation from an open 1,1,3 triradical (Scheme I) is favored in the following order: $Br_2\dot{C}R > Br(Cl)CR > Cl_2\dot{C}R$.

The reactions in which carbon–carbon bond cleavage is the dominant process probably involve aziridino intermediates also. For example, the reaction of α-chlorostyrene goes as follows.



The bond of the ketimino radical which is cleaved[6] (RC(=$\dot{N}$:)R′ → R· + R′CN or R′· + RCN) can be predicted from the relative bond energies[7] for R–X: Br· > Cl· > $\dot{C}Cl_3$ > CH$_2$Cl > $\dot{C}N$, C$_6$H$_5$·, or H·. Some products derived from the radicals produced by cleavage of the ketimino radicals have been isolated.

Acknowledgment. The financial support of the Air Force Office of Scientific Research is gratefully acknowledged (Grant No. 4057).

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(5) J. N. S. Jamieson and C. A. Winkler, *J. Phys. Chem.*, **60**, 1542 (1956).

(6) M. L. Poutsma and P. A. Irarbia, *J. Org. Chem.*, **34**, 2848 (1969).

(7) B. deB. Darwent, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **31**, (1970).

(8) National Science Foundation Fellow, 1968–1972.

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Additions and Corrections

Measurement of Optical Anisotropies of Molecules in Solution by Light Scattering at 6328 Å [*J. Amer. Chem. Soc.*, **92**, 455 (1970)]. By W. R. Russo and W. H. Nelson, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881.

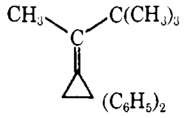
The equation written on page 458 should read

$$\frac{1}{\gamma^2} = \frac{16p(n^2 + 2)^2}{135\lambda^4 R_{\mathrm{ivs}}}$$

and affects conclusions to be drawn from our data. Specifically, the γ^2 values obtained by us for various aromatic molecules are substantially larger than those obtained by means of static field Kerr effect work.

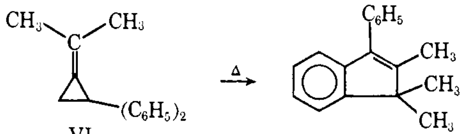
Stereoselective Reactions of 1,2,2-Trimethylpropylidenecarbene with 1,1-Diphenylethylene, Tetramethylallene, and Triethylsilane [*J. Amer. Chem. Soc.*, **92**, 4312 (1970)]. By Melvin S. Newman and Timothy B. Patrick, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

The structure of *cis*-1-(1,2,2-trimethylpropylidene)-2,2-diphenylcyclopropane (V) was assigned because the



V

methyl signal appeared at τ 8.1, the same place as one of the methyl signals in 1-isopropylidene-2,2-diphenylcyclopropane (VI). However, we have been informed [private communication from Michael E. Hendrick and Maitland Jones, Jr., of Princeton University, and by James R. Butler and John C. Gilbert of the University of Texas] that VI readily rearranges on heating to 1-phenyl-2,3,3-trimethylindene (XVI) [compare M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970)]. Pure VI has both methyl signals (multiplet) in the τ 8.1 region while XVI has a methyl signal near τ 8.1, s, 3 H, and 8.7, s, 6 H. Thus the vpc fraction we used to obtain our nmr spectrum must have been composed of a mixture of VI and XVI in such a proportion that there appeared to be methyl groups at τ 8.1 and 8.7.



VI XVI

Therefore, our argument concerning the structure of V (and also the question of the purity of our samples of V) remains unproved. The stereochemical argument for the formation of V is therefore invalid until the structure of V is established. However, the stereochemical argument for the formation of the silane (XII) remains valid.

σ–π Conjugation of Carbon–Metal Bonds. Stereoelectronic and Inductive Effects [*J. Amer. Chem. Soc.*, **92,** 7476 (1970)]. By W. Hanstein, H. J. Berwin, and T. G. Traylor, Chemistry Department, Revelle College, University of California, San Diego, La Jolla, California 92037.

The frequency of VIII should be 23,300 and not 24,300 cm^{-1}.

Conformational Effects of Sulfur, Silicon, Germanium, and Tin on Alkyl Radicals. An Electron Spin Resonance Study of the Barriers to Internal Rotation [*J. Amer. Chem. Soc.*, **93,** 846 (1971)]. By Paul J. Krusic and Jay K. Kochi, Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

A reference to earlier papers by Bauld, *et al.*, was inadvertently omitted [N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *J. Amer. Chem. Soc.*, **89**, 3948 (1967); **91**, 6666 (1969)] in which these authors carried out a similar analysis of β-hfs in their study of cyclopropyl conformations.

An 11-Atom Polyhedral Metallocarborane Formed from 1,6-*closo*-$B_8C_2H_{10}$ by Polyhedral Expansion [*J. Amer. Chem. Soc.*, **93,** 3063 (1971)]. By William J. Evans and M. Frederick Hawthorne, Department of Chemistry, University of California, Los Angeles, California 90024.

On page 3063, the third sentence from the bottom of the second paragraph should read: The 60-MHz ^{1}H nmr spectrum consisted of a sharp singlet of area 5 at τ 4.32 and a broad singlet of area 2 at τ 3.28 which were assigned to the cyclopentadienyl and polyhedral C–H protons, respectively.

The Stereochemistry of Base-Catalyzed β Elimination from 2-Bromobutane [*J. Amer. Chem. Soc.*, **93,** 3683 (1971)]. By Richard A. Bartsch, Department of Chemistry, Washington State University, Pullman, Washington 99163.

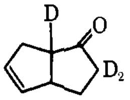
The numerical portion of Table III should read as follows

4.5	61.4	7.2	2.0	1.9	23.0
5.9	60.0	7.2	2.0	1.5	23.4
2.4	30.9	7.0	1.7	5.6	52.4
2.8	30.5	7.0	1.7	3.5	54.5
2.6	54.1	4.5	1.9	1.7	35.2
5.4	51.3	4.5	1.9	2.1	34.8

A Mechanistic Alternative for the Thermal Antara–Antara Cope Rearrangements of Bicyclo[3.2.0]hepta-2,6-dienes and Bicyclo[4.2.0]octa-2,7-dienes [*J. Amer. Chem. Soc.*, **93,** 3969 (1971)]. By John E. Baldwin and Mark S. Kaplan, Department of Chemistry, University of Oregon, Eugene, Oregon 97403.

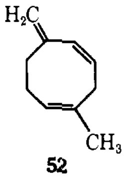
On page 3970, column 2, the sentence beginning on line 14 should read: We interpret the exchange data in terms of product **17**; no change in the fine structure of the olefinic protons was noticeable.

Structure **17** should be



17

Structure **52** should be



52

On page 3976, column 1, line 37 should read: from sodium (15 g) and mercury (585 g) was added in 2 min.