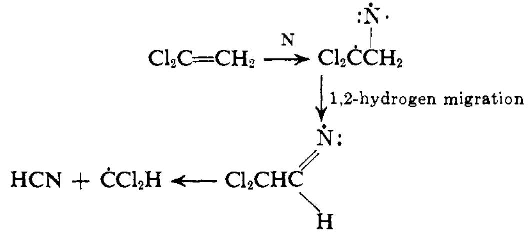
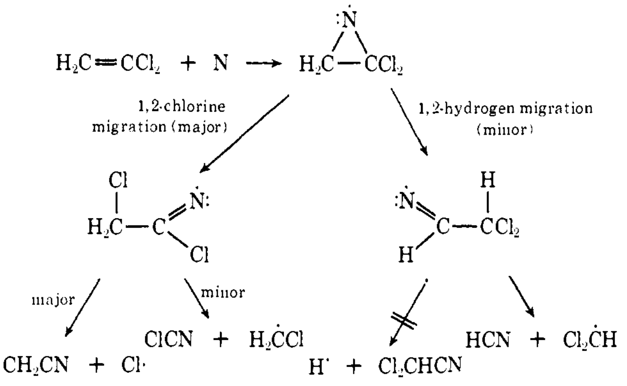
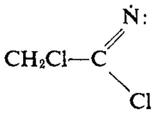
Scheme I. Minor Reaction Pathway



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 $\cdot\mathrm{CH_2Cl}$ from

Scheme II. Major Reaction Pathway

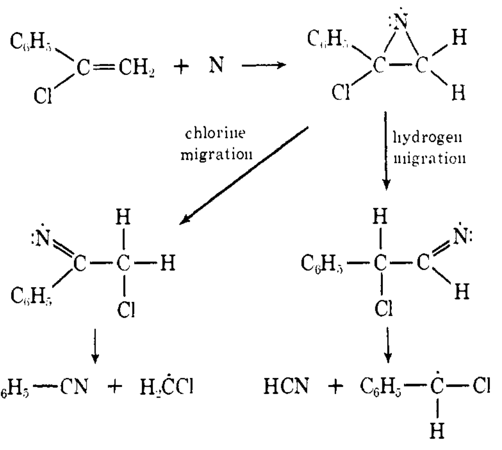




accounts for the high yield of $\mathrm{ClCH_2{-}CN}$.

Direct competition of bromine *vs.* chlorine migration in $\mathrm{H_2C{=}C(Cl)Br}$ shows that bromine migrates twice as readily as chlorine. But the relative percentage of $\mathrm{BrCH_2{-}CN}$ (the product of halogen rearrangement) from the reaction of 1,1-dibromoethylene is smaller than the relative percentage of $\mathrm{ClCH_2{-}CN}$ from the 1,1-dichloroethylene reaction. These results, along with the increase in HCN yield in the series $\mathrm{H_2C{=}CCl_2}$, $\mathrm{H_2C{=}C(Cl)Br}$, $\mathrm{H_2C{=}CBr_2}$, 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: $\mathrm{Br_2\dot{C}R > Br(Cl)\dot{C}R > Cl_2\dot{C}R}$.

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] ($\mathrm{RC({=}\dot{N}{:})R' \rightarrow R\cdot + R'CN}$ or $\mathrm{R'\cdot + RCN}$) can be predicted from the relative bond energies[7] for R–X: $\mathrm{Br\cdot > Cl\cdot > \dot{C}Cl_3 > CH_2Cl > \dot{C}N, C_6H_5\cdot}$, or $\mathrm{H\cdot}$. Some products derived from the radicals produced by cleavage of the ketimino radicals have been isolated.

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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,