alkylation of the anion of **14** proceeds well with **2** to give a 52% yield of the transfer alkylated product **16**, reaction with **4** led only to oxidative dimers. Trienoate **15** shows a remarkable selectivity depending on the choice of bromomalonate. Thus, reaction of the trienolate derived from **15** with **1** generated only the product of 1,6 addition, **17**, in 56% isolated yield as a 2:1 mixture of the fumarate and maleate, respectively, whereas, the similar reaction with **4** generated a 38% isolated yield of the 1,8 product **18** as a 2:1 mixture of maleate and fumarate.

Synthetically the attributes of the cyclic malonate **4** make it the preferred transfer alkylating agent. It is a highly crystalline solid, mp 85–86°, that is easily prepared and purified by recrystallization from isopropyl alcohol. Furthermore, dissolution of the products of transfer alkylation with **4** in trifluoroacetic acid at 25° followed by removal of the solvent *in vacuo* effects selective hydrolysis to the malonic acid which may be decarboxylated by warming in DMSO. Thus, utilizing this sequence, a sample of the fumarate isomer of **8** was converted to **1** in 82% yield.

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Synthesis with Nitrogen Atoms

Sir:

Reaction of atomic nitrogen with organic compounds in the gas phase is characterized by extensive breaking of carbon–carbon bonds.[1] The usual products from olefins are HCN and small amounts of hydrocarbons. The course of these reactions can be very complex, with possible involvement of excited molecular nitrogen, atomic nitrogen, atomic hydrogen, and other radicals resulting from fragmentation of primary products.

One anticipates a simpler chemistry in the condensed phase. Little work has been published on the reactions of atomic nitrogen in solution and at low temperatures.[2] We report here that in the condensed phase some *gem*-dihalo olefins react with nitrogen atoms with minor production of HCN and with the major product being halogenated nitrile; carbon–carbon bond cleavage is not the major reaction.

"Active" nitrogen, which is mainly ground-state (quartet) atomic nitrogen, was generated by pumping molecular nitrogen, from which oxygen was removed over copper at 500°, through a 2450-MHz microwave discharge. The flow rate of nitrogen atoms was measured calorimetrically by catalyzed recombination of the atoms on copper oxide coated copper washers.[3] Reaction with substrate was accomplished by bubbling the atomic nitrogen stream through liquid olefin cooled to a few degrees above its melting point. Most reaction takes place in the condensed phase, since reaction flames[1] are not seen before the nitrogen reaches substrate, and the yellow nitrogen afterglow is extinguished after the substrate. The molar ratio of halo olefins to atomic nitrogen was greater than 90:1. The yields of nitrogenous products account for 70–95% of the atomic nitrogen reaching the substrate (see Table I).

Reaction of vinylidene halides with nitrogen atoms occurs in high yield to produce haloacetonitriles. These reactions do not involve cleavage of the carbon–carbon double bond as a major reaction. With substrates which do not have a *gem*-dihalo group, cleavage

$$H_2C{=}CX_2 + N \longrightarrow X{-}CH_2{-}CN$$

$$H_2C{=}CRX + N \longrightarrow HCN,\ RCN,\ \text{etc.}$$

of the double bond predominates, producing either HCN or other nitriles (C_6H_5–CN, Cl_3C–CN, NC–CN, etc). These observations can be explained readily.

Free radicals have been reported[4] to add preferentially to the CH_2 end of 1,1-dichloroethylene. Such an addition of nitrogen atoms would be expected to give HCN as the major nitrogen-containing product (Scheme I), but in fact, $ClCH_2CN$ is the largest product. The preferred formation of $ClCH_2$–CN requires another reaction route, probably other than addition at the nonmethylene carbon since there is no instance of preferred Markovnikov-type addition of radicals.[4]

Table I. Relative Percentages of Nitrogenous Products[a]

Substrate	Reaction temp, °C	HCN	$ClCH_2$–CN	ClCN	$BrCH_2$–CN	Other nitriles
$H_2C{=}CCl_2$	−126	7.5	91.8	0.7		*b*
$H_2C{=}C(Cl)Br$	−96	10.1	29.3	4.2	56.4	BrCN (trace)
$H_2C{=}CBr_2$	−78	47.3			52.7	BrCN (trace)
$H_2C{=}C(CN)Cl$	−73	36.5	Trace			$(CN)_2$ (63.5%); $CH_2(CN)_2$ (trace)
$H_2C{=}C(CCl_3)Cl$	−78	49.6	28.6			Cl_3C–CN (21.8%)[c]
$H_2C{=}C(C_6H_5)Cl$	−23	51.8		0.6		C_6H_5–CN (47.6%)[d]
cis-ClCH=CHCl	−78	90.7	8.6	0.7		*b*

[a] Products were identified by comparison of vpc retention times with authentic samples, and by infrared and nmr spectroscopy and mass spectroscopy. [b] No Cl_2CH–CN detected. [c] No Cl_3C–CHCl–CN or Cl_3C–CH_2–CN detected. [d] No C_6H_5–CH_2–CN detected.

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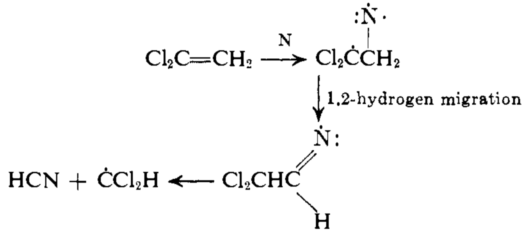
(1) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968.

(2) N. N. Lichtin and C. T. Chen, *J. Amer. Chem. Soc.*, **93**, 5922 (1971).

(3) For the principles of this method, see: B. Bak and J. Rastrup-Andersen, *Acta Chem. Scand.*, **16**, 111 (1962); E. M. Levy and C. A. Winkler, *Can. J. Chem.*, **40**, 686 (1962); J. E. Morgan and H. I. Schiff, *ibid.*, **41**, 903 (1963). The accuracy of the calorimetric method has been verified by the "titration" of atomic nitrogen with nitric oxide. Details of this method will be published elsewhere.

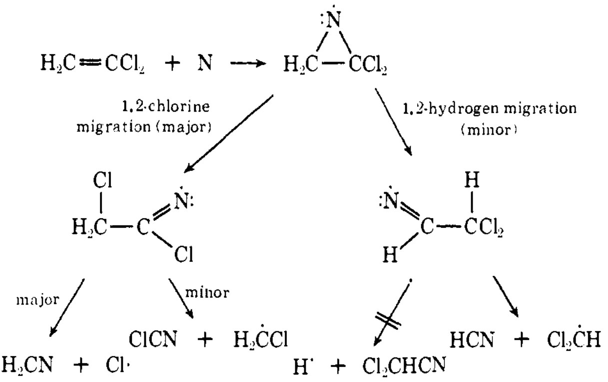
(4) For addition of various radicals to haloethylenes, see: R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953) ($CF_3\cdot$); J. E. Francis and L. C. Leitch, *Can. J. Chem.*, **35**, 500 (1957) ($Br\cdot$); and J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **84**, 3148 (1962), and F. S. Dainton and B. E. Fleischfressen, *Trans. Faraday Soc.*, **62**, 1838 (1966) ($Cl\cdot$).

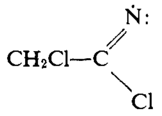
Scheme I. Minor Reaction Pathway



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

Scheme II. Major Reaction Pathway

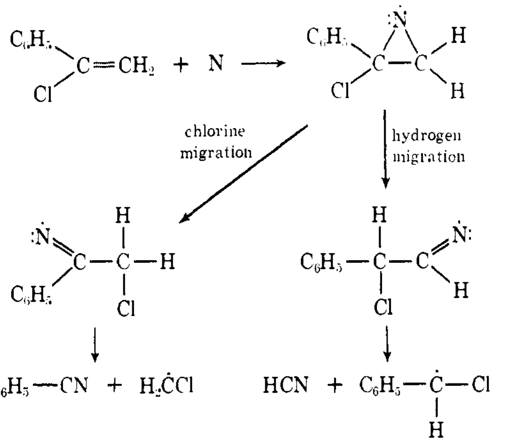




accounts for the high yield of ClCH$_2$–CN.

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)$\dot{C}$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] (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.

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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).

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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

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

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,