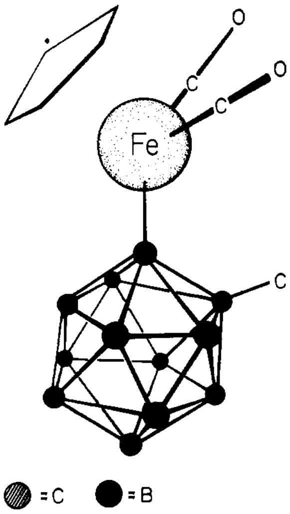

Figure 1. Proposed structure of 1-(π-C_5H_5)Fe$(CO)_2$-2-(CH_3)-(σ-1,2-$B_{10}C_2H_{10}$) (I). H atoms of BH units not shown.

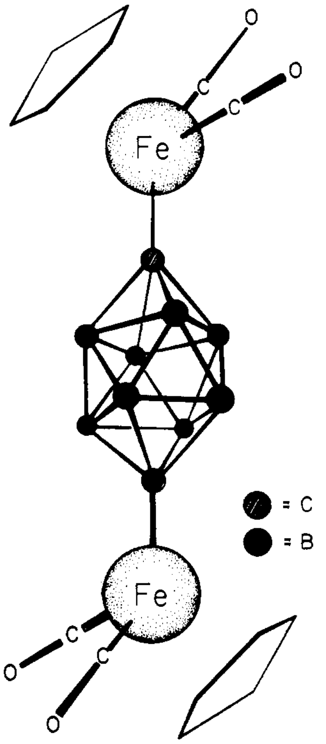

Figure 2. Proposed structure of 1,10-[(π-C_5H_5)Fe$(CO)_2$]$_2$-1,10-(σ-$B_8C_2H_8$) (II). H atoms of BH units not shown.

Reaction of 1,10-$B_8C_2H_{10}$[7] with 2 moles of *n*-butyllithium gives 1,10-Li_2-$B_8C_2H_8$.[8] Treatment of this dianion with (π-C_5H_5)Fe$(CO)_2$I in diethyl ether solvent gave a 71% yield of dark yellow crystalline 1,10-[(π-C_5H_5)Fe$(CO)_2$]$_2$-1,10-(σ-$B_8C_2H_8$) (II). Purification of II was achieved by column chromatography using silica gel and 20% benzene–hexane as the eluent followed by recrystallization from benzene–heptane (mp 203.0–204.0°). *Anal.* Calcd for $B_8C_{16}H_{18}Fe_2O_4$: B, 18.31; C, 40.68; H, 3.81; Fe, 23.65. Found: B, 18.82; C, 40.53; H, 3.88; Fe, 24.67. The parent peak in the mass spectrum calculated for the $(^{11}B_8{}^{12}C_{16}{}^{1}H_{18}{}^{56}Fe_2{}^{16}O_4)^+$ ion: *m/e* 474 (found 474).

The proposed structure of II is presented in Figure 2. The 60-Mcps ^{1}H nmr spectrum consisted of a sharp singlet at τ 5.0 (relative to TMS) which was assigned to the cyclopentadienyl protons. Infrared absorptions in the carbonyl stretching region of II gave two bands observed at 2038 (s) and 1991 (s) cm^{-1}. The electronic spectrum of II was determined in cyclohexane solution [λ_{max} mμ (ϵ): 290 sh (12,500) and 360 (2200)].

Preliminary evidence suggests that similar σ-bonded manganese complexes can be prepared Further work is in progress and will be reported elsewhere.

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(7) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 90, 869 (1968).

(8) Unpublished results.

Photodifluoramination of Allene. A Novel Substitution Pathway[1]

Sir:

Continuing our study of the photochemistry of tetrafluorohydrazine,[2] we irradiated (2537 Å, room temperature) mixtures of allene and N_2F_4 in the gas phase. Two types of carbon-containing products were isolated (70% yield), one resulting from an addition process with the elements of NF_3 added to the allenic substrate ($C_3H_4NF_3$) and the other product arising from a substitution process where an NF_2 moiety has replaced a hydrogen atom ($C_3H_3NF_2$). The data collected in Table I show the addition and substitution products to be, respectively, 3-difluoramino-2-fluoropropene (I) and 3-difluoraminopropyne (II).[3]

Formation of these compounds was not unexpected since previous work[4] indicated that photolysis of N_2F_4 leads to atomic fluorine which may add to a carbon–carbon double bond or abstract hydrogen atoms from alkanes.

Compound II thus appeared to arise simply by allenic hydrogen abstraction followed by combination of NF_2 with the resulting delocalized propargyl radical.[5,6]

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(1) We gratefully acknowledge support of this work by National Science Foundation Grant GP 8083.

(2) C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

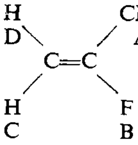
(3) These products differ from those obtained in the thermal reaction of allene and N_2F_4; see G. N. Sausen and A. L. Logathetis, *J. Org. Chem.*, 32, 2261 (1967). The thermal process at 25° is negligibly slow relative to the photochemical reaction.

(4) (a) C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964); (b) C. L. Bumgardner and E. L. Lawton, *ibid.*, 3059 (1968).

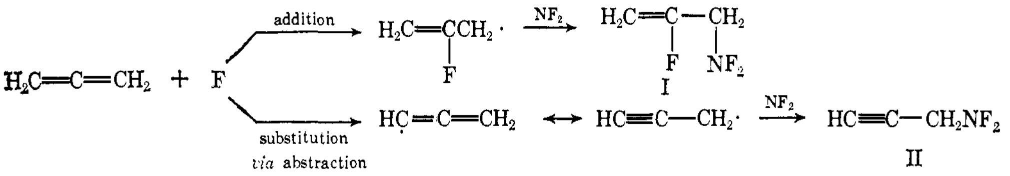
(5) Allene does not isomerize to propyne under the reaction conditions. Photolysis of N_2F_4 with propyne also affords II as well as 1,1-difluoro-2-(N-fluorimino)propane, but no I.

(6) Photochlorination of allene with *t*-butyl hypochlorite gives propargyl chloride: M. C. Caserio and R. E. Pratt, *Tetrahedron Lett.*, 91 (1967).

Table I. Characterization of Photolysis Products

Compound[a]	Nmr[b]		Ir, μ	m/e
	ϕ	δ		
 I	A, −55 B, 99.2	A, 4.08 (t in d) C, 4.92 (m) D, 4.67 (d in d)	5.94 (C=C) 9.14 (CF) 11.45 (NF), 12.0 (NF)	39 ($C_3^+H_3$) 45 ($C_2^+H_2F$) 59 ($C_3^+H_4F$) 111 (parent)
$HC{\equiv}CCH_2NF_2$ A B II	B, −54.5	A, 2.73 (t) B, 4.48 (t in d)	3.00 (C≡CH) 10.95 (NF), 12.05 (NF)	39 ($C_3^+H_3$) 51 (C_3^+HN) 71 ($C_3^+H_2NF$)

[a] Satisfactory analyses obtained. [b] Spectra were run as approximately 5% by volume solutions in $CDCl_3$ at room temperature. ^{19}F chemical shifts (ϕ) are in parts per million relative to $CFCl_3$ as an external reference, and ^1H chemical shifts (δ) are in parts per million downfield relative to TMS as both an external and internal reference. The ratios of signal areas were in agreement with assigned structures.



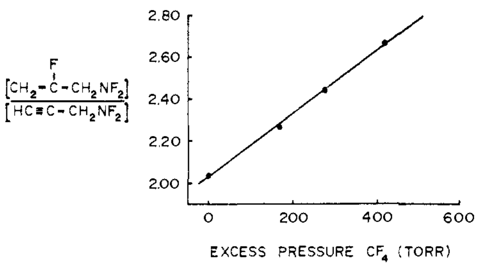
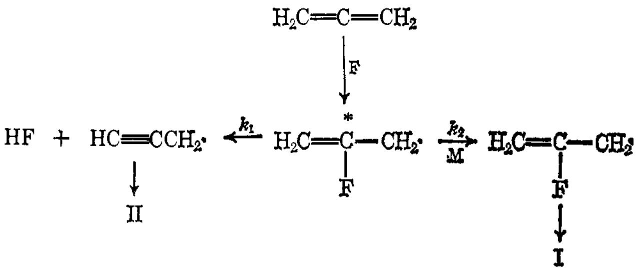


Figure 1. Pressure dependence of product ratio.

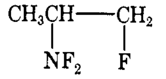
The ratio of I/II however was found to depend on the total pressure of the system, a finding not accommodated by the above reaction scheme.

Figure 1 displays the quantitative relationship between the product ratio and pressure when inert carbon tetrafluoride was used to pressurize the system. These data indicate that I and II have a common precursor, very likely a vibrationally excited 2-fluoropropene radical. This "hot" intermediate may undergo collisional deactivation with inert body M to yield ultimately I or lose HF unimolecularly to give a propargyl radical which then furnishes II. This scheme does correctly predict the linear relation shown in Figure 1 and is novel in that over-all substitution occurs *via* addition–elimination instead of by simple hydrogen abstraction.[7]

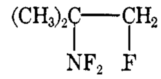


$$I/II = k_2(M)/k_{-1}$$

An alternative scheme involving addition of $^*NF_2$ to allene is unattractive for the following reasons: (1) the main products from photolysis of N_2F_4 with propylene and isobutylene are the adducts III and IV, re

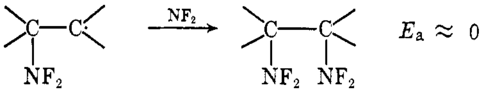


III



IV

The orientation indicates that F, not NF_2, leads the attack on the unsaturated substrates. (2) If NF_2 added first to allene, some bis-NF_2 adduct (or products derived from it)[3] would be expected, as NF_2 is an efficient radical trap.[9] Such products are not observed



in the room-temperature photolytic reactions of N_2F_4 with allene or with olefins.[8] (3) Predissociation has been observed in the ultraviolet spectrum of NF_2.[10]

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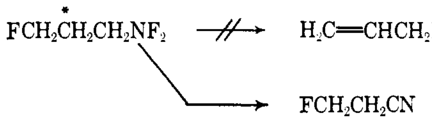
[7] Formation of excited I could also account for the results in Figure 1 but this intermediate would be expected to lose HF from the CN atoms rather than from the CC atoms; *e.g.*



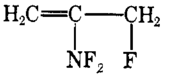
See ref 2 and 4b.

[8] C. L. Bumgardner and K. G. McDaniel, to be published.

[9] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, *A*, 105 (1967).

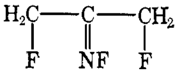
[10] P. L. Goodfriend and H. P. Woods, *J. Mol. Spectrosc.*, **13**, 63 1964).

Interestingly, only one addition product was isolated from the allene reaction although a search was made for the isomer of I with F on the terminal carbon atom (V).[11] On the basis of previous observations V



$H_2C{=}C(NF_2){-}CH_2F$

V



$FH_2C{-}C({=}NF){-}CH_2F$

VI

would be expected to rearrange to VI which should be stable and isolatable under the experimental conditions.[4a] However, no evidence for V or VI was obtained. Substituted allenes are currently under investigation.

[11] CF_3 radicals attack the terminal carbon of allene: H. G. Meunier and P. I. Abell, *J. Phys Chem.*, **71**, 1430 (1967). For addition of Br to allene see E. I. Heiba and W. O. Haag, *J. Org. Chem.*, **31**, 3814 (1966).

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Stereospecific Hydroxyalkylation of Chloromethyl Phenyl Sulfoxide

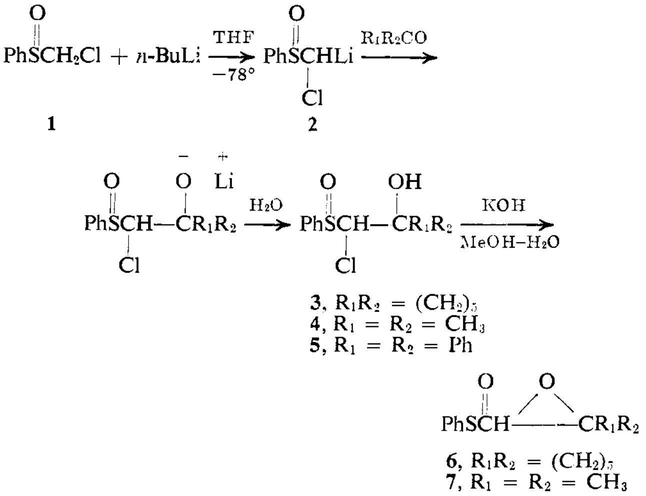
Sir:

The generation and synthetic applications of α-sulfinyl carbanions have been actively investigated since the initial reports of Corey and Chaykovsky regarding the preparation and synthetic utility of methylsulfinyl carbanion.[1] The stereochemical preference of such carbanions has been studied to a considerable extent and a number of interesting results have been reported in this area. For instance, the unequal rate of exchange of the methylene hydrogens of a number of benzyl alkyl and benzyl aryl sulfoxides[2–6] in D_2O–NaOD was suggested by Wolfe and Rauk[3] to be due to preferred abstraction of the hydrogen bisecting the internal oxygen–sulfur–lone pair angle. Molecular orbital calculations by Wolfe and coworkers[7] on the hypothetical carbanion $^{-}CH_2S(O)H$ and on methylsulfinyl carbanion also indicated a marked stability of the carbanion in such a conformation.

We have been investigating the metalation of sulfoxides and sulfones bearing heteroatoms in the α position, *i.e.*, $RSOCH_2X$ and RSO_2CH_2X, and report preliminary results derived from such a study of chloromethyl phenyl sulfoxide (**1**) that are of synthetic utility and of unusual stereochemical specificity.

Addition of *n*-butyllithium to a 0.3 *M* solution of chloromethyl phenyl sulfoxide[8] in tetrahydrofuran at −78° produced an immediate bright yellow solution containing the lithio derivative **2** which was stable for at least 2 hr at −78°. Decomposition occurred rapidly above −20° with the solution becoming turbid and the color changing to dark brown.[9]

Reaction of a solution of **2** with cyclohexanone, acetone, or benzophenone for 10 min at −78° followed by 30 min at −20° yielded after hydrolysis the adducts **3**, **4**, and **5** in 79, 75, and 68% yields, respectively.[10]



3, $R_1R_2 = (CH_2)_5$
4, $R_1 = R_2 = CH_3$
5, $R_1 = R_2 = Ph$

6, $R_1R_2 = (CH_2)_5$
7, $R_1 = R_2 = CH_3$

Each of these compounds appeared to be a *single* isomer as judged by sharp melting points and tlc behavior in various solvents. In addition, the nmr spectrum of each adduct taken in $CDCl_3$ and in either acetone-d_6 or acetonitrile-d_3 showed only one methine proton as a sharp singlet; the positions in $CDCl_3$ were 4.31, 4.32, and 5.36 ppm downfield from TMS for the adducts **3**, **4**, and **5** respectively.

The nmr spectrum of the acetone adduct **4** in $CDCl_3$ showed, in addition to the singlet at δ 4.32, another singlet at δ 1.58 which was attributed to the two methyl groups. In acetone-d_6 the singlet for the methine proton shifted to δ 4.52, but the methyl groups gave rise to two singlets at δ 1.44 and 1.48. Examination by nmr of the total crude product from each reaction failed to reveal the presence of any trace of isomeric products.[11]

Treatment of the adducts **3** and **4** with dilute methanolic KOH at room temperature for 10 min gave the epoxy sulfoxides **6** and **7** in greater than 90% yield. α-Epoxy sulfoxides have to our knowledge not been reported, and an investigation of their properties is under way. The ease of intramolecular displacement of chloride ion from the adducts contrasts with the great difficulty in displacing chloride ion from chloromethyl phenyl sulfoxide by external nucleophiles.[8]

Oxidation of the sulfoxide adducts **3**–**5** with *m*-chloroperbenzoic acid gave the corresponding sulfones (yield >85%) which were identical with the adducts obtained by reaction of the lithium derivative of chloro-

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[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

[2] A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *ibid.*, **87**, 5498 (1965).

[3] S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

[4] E. Bullock, J. M. W. Scott, and P. D. Golding, *ibid.*, 168 (1967).

[5] M. Nishio, *ibid.*, 562 (1968).

[6] R. R. Fraser and F. Schuber, private communication.

[7] S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

[8] M. Hojo and Z. Yoshida, *ibid.*, **90**, 4496 (1968). Contrary to the report of these authors we have found that chloromethyl phenyl sulfoxide is obtained in greater than 70% yield by oxidation of chloromethyl phenyl sulfide with *m*-chloroperbenzoic acid. Chloromethyl phenyl sulfoxide was obtained as colorless needles, mp 35–36°; lit. mp 28–29° (F. G. Bordwell and W. T. Branner Jr., *ibid.*, **86**, 4645 (1964).

[9] The possible decomposition of **2** by α elimination to form either phenylsulfinylcarbene or chlorocarbene is being investigated.

[10] All new compounds reported herein gave correct elemental analysis.

[11] It is estimated that 2% of an isomeric adduct would have been readily detected.