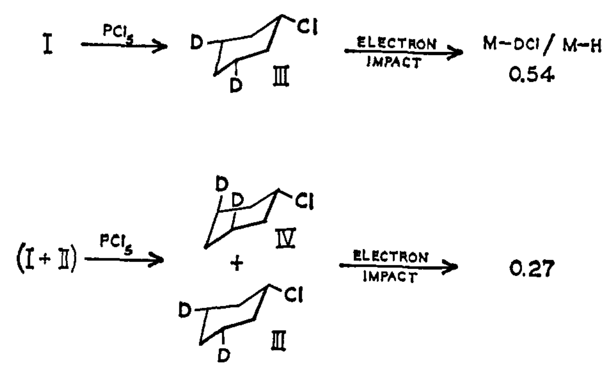
Scheme II[a]



[a] See footnote *a* in Scheme I.

nonstereospecific. Cleavage of the carbon–carbon bond adjacent to the hydroxyl group, that is, α cleavage, as a prerequisite for 1,3 elimination is the only plausible mechanism to account for the lack of stereospecificity. This type of bond cleavage is well documented in the mass spectrometry of alcohols,[11] and further it neatly explains the low 1,3 elimination encountered in acyclic alcohols.[1] That is, while α cleavage can precede the formation of an $M - 18$ ion in ring compounds, it must necessarily preempt such an ion in open-chain counterparts.[12]

Since we have previously demonstrated that the 1,4 elimination in both cyclohexanol and cyclohexyl chloride takes place with high stereospecificity,[4] it is now clear that, whereas unrearranged alcohols show a specific preference for a C-4 hydrogen independent of hydrocarbon structure, the related chlorides may precede directly by both 1,3 and 1,4 elimination according to the structural restrictions imposed by the hydrocarbon grouping. An attractive hypothesis to account for this behavior invokes the variation in bond length encountered in bonds to oxygen and chlorine.[13] In alcohols the shorter radius for bonding would restrict abstractable hydrogens to closer approach than in the case of chlorides, namely from carbon atoms further away along the σ framework. Since the C-4 as well as the C-3 hydrogen distances to the eliminated hydroxyl group in a cyclohexane ring are almost identical with those in an open-chain molecule (by inspection of Dreiding models), it would follow from this argument that hydrogens inaccessible in the acyclic alcohols, namely C-3, should also be inaccessible in cyclohexanol. In the case of chlorides the structure of the hydrocarbon moiety may be expected to play an important role in the choice of abstraction site, since both C-3 and C-4 hydrogens are available for abstraction. Indeed, the entropy of activation in the acyclic chlorides would favor the closure of the smaller ring, that is, hydrogen abstraction from C-3.

In support of this over-all hypothesis it is noteworthy that deuteration studies on acyclic mercaptans[14] show elimination ($X = SH$, eq 1) from both C-4 and C-3 while data on 1-fluorohexane ($X = F$, eq 1) demonstrate competitive hydrogen loss from C-5 and C-4.[15]

Further significance for these findings rests in their probable extension to the mass spectrometry of substituted cyclohexanols. Reports have recently appeared describing a large bias against *cis* isomers, for water elimination, from the epimers of both 4- and 3-*t*-butylcyclohexanol.[16,17] These differences have been ascribed to the availability of tertiary hydrogens in the *trans* isomers. In addition, the 4 substituent is at least an order of magnitude more effective in promoting the isomer difference. The present work strongly suggests that α cleavage precedes the elimination of the tertiary hydrogen in the 3-*t*-butylcyclohexanol isomers, thereby explaining, at least in part, the otherwise mysterious specificity change between the 3 and 4 substituents.

Acknowledgment. We are grateful for support of this research to the National Institute of General Medical Sciences (GM-16638-01).

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[11] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Publishing Co., San Francisco, Calif., 1967, Chapter 2.

[12] Water loss can be observed from an α-cleaved ion from acyclic alcohols if it is not the molecular ion. Such experiments have been carried out. See ref 1 and M. Kraft and G. Spiteller, *Monatsh. Chem.*, **99**, 1839 (1968).

[13] In all cases known oxygen forms stable bonds with shorter bond length than those for chlorine. It is reasonable that this should also be so for the ions of interest here. See L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapters 7 and 12.

[14] A. M. Duffield, W. Carpenter, and C. Djerassi, *Chem. Commun.*, 109 (1967).

[15] W. Carpenter, A. M. Duffield, and C. Djerassi, *ibid.*, 1022 (1967).

[16] C. E. Brion and L. D. Hall, *J. Amer. Chem. Soc.*, **88**, 3661 (1966).

[17] L. Dolejš and V. Hanuš, *Collection Czech. Chem. Commun.*, **33**, 332 (1968). See also M. M. Green, R. J. Cook, W. Rayle, E. Walton, and M. F. Grostic, *J. Chem. Soc.*, *D*, 81 (1969).

[18] National Science Foundation Summer Fellow, 1968.

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Reactions of Energetic Fluorine-18 Atoms with Fluoromethanes. Formation of $CH^{18}F$ and $CF^{18}F$

Sir:

Energetic ^{18}F atoms from nuclear recoil react with hydrocarbons and fluorocarbons by both of the substitution pathways shown in (1) and (2),[1-5] using difluoromethane as the example. The experiments reported here have been designed to permit estimation of the energy deposition in such reactions through the observation of secondary decomposition products,[6] in analogy with similar experiments in recoil tritium systems.[7-10] The results, summarized in Table I, have

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[1] N. Colebourne and R. Wolfgang, *J. Chem. Phys.*, **38**, 2782 (1963).

[2] N. Colebourne, J. F. T. Todd, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 149.

[3] J. F. J. Todd, N. Colebourne, and R. Wolfgang, *J. Phys. Chem.*, **71**, 2875 (1967).

[4] Y.-N. Tang and F. S. Rowland, *ibid.*, **71**, 4576 (1967).

[5] L. Spicer, J. F. J. Todd, and R. Wolfgang, *J. Am. Chem. Soc.*, **90**, 2425 (1968).

[6] Decomposition of monofluorocyclanes following ^{18}F-for-H substitution reactions in cyclanes is reported in ref 4.

[7] Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 626 (1966).

[8] Y.-N. Tang and F. S. Rowland, *ibid.*, **89**, 6420 (1967).

[9] E. K. C. Lee and F. S. Rowland, *ibid.*, **85**, 897 (1963).

[10] R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

Table I. Relative Yields of Labeled Carbenes and Parent Molecules from ^{18}F Reactions with Fluoromethanes

	Carbene yield[a]		
	$CH^{18}F$	$CF^{18}F$ *vs.*	
Target molecule	*vs.* $CH_2F^{18}F$	$CHF_2{}^{18}F$	$CF_3{}^{18}F$
CH_2F_2	3.0	3	...
CHF_3	...	5.2	(1.1)[b]
CF_4	...	...	1.1

[a] Observed carbene + olefin yields have been increased by $^4/_3$ for $CF_3{}^{18}F$; by $^3/_2$ for $CHF_2{}^{11}F$; and by 2 for $CH_2F^{18}F$ to correct for loss of ^{18}F in the form of $H^{18}F$ or $F^{18}F$. [b] $CF^{18}F$ can come from decomposition of either molecule. If one assumes the same $CF^{18}F/CF_3{}^{18}F$ ratio as found for CF_4 and subtracts this yield (1.1) from the total, the remaining $CF^{18}F$ then corresponds to 5.2 times the observed yield of $CHF_2{}^{18}F$.

$$^{18}F + CH_2F_2 \longrightarrow CH_2F^{18}F + F \qquad (1)$$

$$^{18}F + CH_2F_2 \longrightarrow CHF_2{}^{18}F + H \qquad (2)$$

consistently shown that both $CH^{18}F$ and $CF^{18}F$ are formed in appreciable yields from the reactions of ^{18}F with CH_2F_2 or CHF_3, while $CF^{18}F$ is formed from ^{18}F reactions with CF_4. These fluorocarbenes are among the anticipated secondary products based on the known elimination of HF in other fluorocarbon decompositions[7,8,11,12] and have been identified through their reactions with olefin scavengers to form the corresponding mono- or difluorocyclopropanes. The relative yields of the carbenes from excited $CH_2F^{18}F^*$ or $CHF_2{}^{18}F^*$ indicate that >80% of these molecules undergo decomposition at pressures of from 1 to 3 atm. The yield of $CF^{18}F$ from $CF_3{}^{18}F^*$, for which the loss of F_2 or 2F is >8 eV endothermic, indicates about 50% decomposition of the excited molecule.[13]

Energetic ^{18}F atoms have been formed by either of the nuclear reactions $^{19}F(\gamma,n)^{18}F$ or $^{19}F(n,2n)^{18}F$ occurring with the fluorine atoms of the target fluoromethane.[1-3,14] The radioactive ^{18}F-labeled products were analyzed by the usual procedures of radio gas chromatography.[15] Samples contained from 1 to 3 atm of the fluoromethane, about 10–20 cm of the various olefins, and 5 cm of O_2.

Our measured relative yields of $CH_2F^{18}F$, $CHF_2{}^{18}F$, and $CF_3{}^{18}F$ are in good agreement with those reported by Spicer, *et al.*[5] However, as indicated in Table I, the previously unreported fluorocyclopropanes are found in even larger yields in the olefin-scavenged systems. For $CH^{18}F$, the fluorocyclopropanes correspond to the stereospecific addition products, indicating that the reactant carbenes are in the singlet electronic state, and that the reactions do not impart sufficient excitation energy for isomerization or decomposition of the fluorocyclopropanes in subsequent reactions, in close analogy with the comparable reactions of CTF.[7,8] Ethylene is essentially unreactive toward $CF^{18}F$ and no difluorocarbene product was found in this system;[16] the reactivities of substituted olefins are greater toward $CF^{18}F$, and the appropriate product was found in increasing yields with propylene, and the butenes.[17] Present experiments suggest that $CF^{18}F$ is fully scavenged by isobutylene, while percentage decompositions estimated from experiments with propylene or 2-butene scavengers may be only lower limits.

Estimates of the total hot yield from ^{18}F reactions with gas-phase CH_2F_2 cannot be clearly established at present. Earlier experiments indicated a total hot yield of 10.0%, composed of two direct products, $CH_2F^{18}F$ and $CHF_2{}^{18}F$, as well as three kinds of radical appearing as the iodides in the presence of $C_2H_4 + I_2$ as scavenger.[18] Such experiments would not detect as hot products the $H^{18}F$ emitted from excited $CH_2F^{18}F$ or $CHF_2{}^{18}F$, estimated as about 4 and 1%, respectively. In addition, the fate of $CH^{18}F$ or $CF^{18}F$ in C_2H_4–I_2 scavenger is not clear, and this yield may or may not already be included in the total yield estimates through measurement of the iodides of the radicals $CH_2{}^{18}F$, $CHF^{18}F$, and $CF_2{}^{18}F$.[17,18] Instead of a total hot yield of 10.0%, we estimate a minimum value of 15%, with an uncertain additional yield of as much as another 6%. Such changes will already have material effect upon the quantitative interpretation of steric effects in such reactions, but cannot be usefully analyzed until the uncertainty is reduced.

The difluoromethane decomposition observed for ^{18}F-for-F substitution in CH_2F_2 is greater than that for energetic T-for-H in the same molecule.[8] Since these atomic replacements are essentially thermoneutral (except for small isotope effects), an increase in percentage decomposition directly reflects a higher median energy deposition in the hot ^{18}F reactions. While chemical differences in the reactions of ^{18}F and T must certainly be considered, reactions with ^{18}F may proceed with reasonable cross sections to higher energies than for tritium, because the correspondingly lower velocity for ^{18}F permits more time for the molecular readjustments required for successful completion of the substitution process.[3]

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(11) E. Tschuikow-Roux and J. E. Marte, *J. Chem. Phys.*, **42**, 2049 (1965).

(12) Assuming equivalence of fluorine atoms in each molecule, the carbene should contain 50 and 67% of the ^{18}F from $CH_2F^{18}F$ and $CHF_2{}^{18}F$, respectively.

(13) B. Musgrave and and coworkers also have evidence for the formation of $CF^{18}F$ as a product of ^{18}F reactions in fluorocarbon systems (private communication).

(14) The (n,2n) reaction has been produced with 14-MeV neutrons from a neutron generator.

(15) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

(16) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965).

(17) Our present experimental arrangement, using the $(n,2n)^{18}F$ reaction, requires a sample temperature of 9° making I_2 an ineffective scavenger because of its low vapor pressure.

(18) L. Spicer and R. Wolfgang, *J. Am. Chem. Soc.*, **90**, 2426 (1968).

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The Brønsted Acidity of B_6H_{10}. A New Anion, $B_6H_9{}^-$

Sir:

The Brønsted acidity of bridge hydrogens in polyhedral boranes was first demonstrated in decaborane(14)[1] and more recently in pentaborane-

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(1) W. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, pp 184–194; R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.* **81**, 3554 (1959); M. F. Hawthorne and J. J. Miller, *ibid.*, **80**, 754 (1958); J. J. Miller and M. F. Hawthorne, *ibid.*, **81**, 4501 (1959).