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 $CHF_2{}^{18}F$.

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

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

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

^{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]

Yi-Noo Tang, Thomas Smail, F. S. Rowland
Department of Chemistry,[19] *University of California*
Irvine, California 92664

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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.

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(19) This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126 with the University of California, Irvine.

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).

(9).[2-4] Such behavior has now been observed in hexaborane(10) also.

We wish to report the preparation of the new anion nonahydrohexaborate(−1), $B_6H_9^-$, through the following general reaction

$$B_6H_{10} + MB \longrightarrow MB_6H_9 + HB$$
$$MB = LiCH_3, NaH, KH$$

In a typical reaction, potassium hydride reacts with hexaborane(10) in an ether solvent at low temperature to liberate 1 mole of hydrogen per mole of B_6H_{10}. The resulting salt, KB_6H_9, is isolated as a crystalline solid which decomposes slowly at room temperature in a dry inert atmosphere. *Anal.* Calcd for KB_6H_9: B, 56.8; H, 8.03. Found: B, 57.4; H, 7.93.

The $B_6H_9^-$ anion appears to be significantly more stable, thermally, than its analog $B_5H_8^-$,[2-4] which is derived from B_5H_9. The boron-11 nmr spectrum of KB_6H_9 in THF persists for approximately 1 day at 30°, while the spectrum of KB_5H_8 under similar conditions is markedly deteriorated after several minutes.[4]

The boron-11 nmr spectrum of KB_6H_9 in THF is essentially independent of temperature in the range studied (−80 to 30°) with respect to appearance, chemical shifts, and coupling constants; it consists of two symmetrical doublets in an area ratio of 1:5, qualitatively identical with hexaborane(10). The smaller doublet (δ 48.3 ppm with respect to $BF_3 \cdot OEt_2$, J = 134 Hz) is assigned to the apical boron in the framework. The doublet at lower field (δ −9.5 ppm, J = 100 Hz) is assigned to basal borons which are apparently magnetically equivalent. The chemical shifts and coupling constants of the anion are significantly different from those of the parent compound.[5]

The reaction of $B_6H_9^-$ with DCl at low temperature regenerated hexaborane(10) in high yields (*ca.* 90%). The entering deuterium was found only in the bridge position as shown by the infrared spectrum. A band at 1137 cm^{-1} was observed which does not occur in the spectrum of hexaborane(10) of normal isotopic composition.[6] It is assigned to the B–D–B stretch. The isotope shift ($\nu_{B-H-B}/\nu_{B-D-B} = 1.30$) is in excellent agreement with the shift observed for the bridge system in pentaborane(9).[7] This result, plus the fact that the boron-11 nmr spectrum of the ion closely resembles that of the parent compound, indicates that the framework of the ion is the same as that of hexaborane(10), a pentagonal pyramid.

Deprotonation of B_6H_{10} takes place with loss of a bridge hydrogen. Reaction of CH_3Li with hexaborane(10) containing deuterium in terminal positions[8] on basal borons yielded only CH_4; no CH_3D was observed in the mass spectrum. The boron-11 nmr spectrum of the resulting ion showed that the apical boron had retained its hydrogen. Therefore the proton which was removed must have come from the bridge position.

For the boron hydrides B_5H_9, B_6H_{10}, and $B_{10}H_{14}$, the experimental evidence shows that bridge hydrogens are more acidic with respect to deprotonation reactions than terminal hydrogens. It was of interest to determine the relative acid strengths of the series since it had been predicted that acid character increases as the polyhedral boron framework increases in size.[9] We have confirmed this order for the series cited above. From boron-11 nmr, the following acid–base reactions appear complete.

$$LiB_5H_8 + B_6H_{10} \longrightarrow B_5H_9 + LiB_6H_9 \qquad (1)$$

$$LiB_6H_9 + B_{10}H_{14} \longrightarrow B_6H_{10} + LiB_{10}H_{13} \qquad (2)$$

The first reaction was run in ethyl ether at −60°. The nmr spectrum recorded at −30° showed no trace of reactants. The second reaction, also in ethyl ether, proceeded below −78° as evidenced by the appearance of the bright yellow color characteristic of $B_{10}H_{13}^-$ in solution. The nmr spectrum at −10° showed only resonances attributable to B_6H_{10} and $LiB_{10}H_{13}$.

Recent theoretical calculations of the ground-state charge distribution of diborane(6)[10-14] and the higher boron hydrides[11] indicate that the bridge hydrogens are more positive than terminal hydrogens.

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H. D. Johnson, II, S. G. Shore
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

N. L. Mock, J. C. Carter
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213

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Separation of the Cyclization and Rearrangement Processes of Lanosterol Biosynthesis. Enzymic Conversion of 20,21-Dehydro-2,3-oxidosqualene to a Dehydroprotosterol

Sir:

Structure **1**, a cation or its functional equivalent having an enzymic or nonenzymic leaving group attached to C-20, is presumed to be the first tetracyclic intermediate in the enzymic cyclization of 2,3-oxidosqualene[1-3] and the starting point for the multi-

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