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The Generation of CF and an Investigation of the Products of Its Reaction with Alkenes

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Abstract: The reaction of arc generated carbon atoms with CF_4 at 77 K in the presence of alkene trapping agents results in the formation of fluorocyclopropanes and 1,1-difluoroalkanes. The fluorocyclopropanes are postulated to arise by addition of CF to the double bond generating a cyclopropyl radical which abstracts H. CF adds stereospecifically to olefins and gives both cis and trans fluorocyclopropanes with the trans generally predominating. The 1,1-difluoroalkanes are postulated to be the result of a $^3CF_2$ reaction. In the presence of oxygen, the CF is oxidized to CO_2, and the $^3CF_2$ gives carbonyl fluoride.

Although monovalent carbon intermediates are quite common when coordinated to metal complexes,[1] little is known about the chemistry of free methylidynes.[2] There have been spectral,[3] theoretical,[4] and kinetic[5] studies of fluoromethylidyne, CF, but no reports of the products of the reactions of this interesting species. In this paper, we report evidence for the formation of CF in the reaction of atomic carbon with fluorocarbons and give details of its reaction with alkenes.

The intermediacy of CF in the reactions of atomic carbon was postulated by Blaxell, MacKay, and Wolfgang who reacted nucleogenic carbon-11 atoms with fluorocarbons and observed organic products which were thought to contain a single fluorine atom.[6] Finn, Ache, and Wolf[7] reported high yields of $^{11}CO_2$ when ^{11}C was reacted with fluorocarbons and O_2 and proposed that an intermediate, perhaps CF, was oxidized to CO_2. The intermediacy of CF in these systems is reasonable as the abstraction in eq 1 is exothermic by 28 kcal/mol for $C(^1D)$ and only slightly endothermic by 2 kcal/mol for $C(^3P)$.[8]

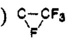
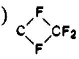
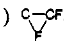
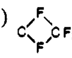
$$C + CF_4 \rightarrow CF + CF_3 \qquad (1)$$

In order to determine if the reaction in eq 1 is kinetically favorable, we have carried out ab initio molecular orbital studies of the reaction of atomic carbon with CF_4. We have also examined the reaction experimentally by reacting arc generated carbon atoms with CF_4 in both the presence and absence of olefinic trapping agents.

Results and Discussion

Molecular Orbital Calculations. In these calculations, which utilized the GAUSSIAN 82 program,[9] geometries were optimized by using the 3-21G basis set at the single configurational level with the restricted Hartree–Fock formulism for closed shell systems and the unrestricted formulism for open-shell systems. Single point calculations were made at the 6-31G* level and at the MP2/6-31G level in order to estimate relative energies at the MP2/6-31G* level by using the additivity approximation.[10]

Table I. Relative Energies (kcal/mol) of Various Species on the C_2F_4 Potential Energy Surface

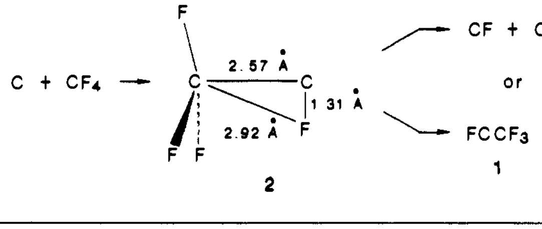
molecule	electrnc state	6-31G	MP2/ 6-31G	6-31G*	[MP2/ 6-31G*]^a
(**1**) $C + CF_4$	^3P, $^1A_1$	0	0	0	0
(**2**) $C + CF_4$	^1D, $^1A_1$				30.0^b
(**3**) $CF + CF_3$	$^2\pi$, $^2A_1$	14.9	3.7	16.2	5.0
(**4**) $2(CF_2)$	$^1A_1$	11.9	−20.5	4.8	−27.6
(**5**) $FCCF_3$	$^1A'$	−23.0	−52.7	−27.8	−57.5
(**6**) $FCCF_3$	$^3A''$	−37.9	−52.7	−34.8	−49.6
(**7**) $F_2C{=}CF_2$	^1A_g	−58.4	−97.0	−55.6	−94.2
(**8**) F_2CCF_2	$^3A_1$	−22.6	−41.4	−14.0	−32.8
(**9**) 	$^1A'$	123.7	80.5	131.4	88.2
(**10**) 	$^1A_1$	89.4	35.5	97.2	43.3
(**11**) 	$^3A''$	18.3	4.8	18.5	5.0
(**12**) 	$^3B_2$	65.3	31.4	72.0	38.1

^{a}Additivity approximation; ref 10. ^{b}Taken from experimental $C(^3P) - C(^1D)$ splitting. Moore, C. E. *Natl. Bur. Stand. Circ.* (*U.S.*) **1949**, 1, no. 467.

The reactions considered in these calculations were the fluorine abstraction to give CF (eq 1), concerted formation of two molecules of CF_2 (eq 2), and insertion into the C–F bond to generate tetrafluoroethanylidene, **1**. The calculated energies, relative to $C(^3P) + CF_4$, are shown in Table I.

$$C + CF_4 \rightarrow 2CF_2 \qquad (2)$$

These calculations indicate that $C(^3P)$ will react with carbon via the transition structure **2**, which lies 5 kcal/mol above $C(^3P) + CF_4$ at the [UMP2/6-31G*] level. Removal of two fluorines by $C(^3P)$ to give either $2CF_2$ or C_2F_4 is calculated to have a barrier of 38.1 kcal/mol (entry 12, Table I). A treatment of the reaction



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[4] Gutsev, G. L.; Zyubina, T. S. *Chem. Phys.* **1984**, *83*, 89.

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[9] Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople; J. A. GAUSSIAN 82; Carnegie-Mellon University.

[10] McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497. McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 762.

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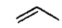
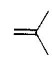
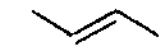
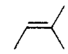
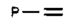
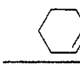
Table II. Yields of Fluorocyclopropanes and 1,1-Difluoroalkanes in the Reaction of C + CF_4 + Alkenes

reactants[a]		product yields (mmol × 10^3)[b]	
alkene	C mmol[c]	fluorocyclopropane	1,1-difluoroalkane
	8.36	6.84	1.28
	13.10	cis 8.79, trans 6.2	1.23
	8.40	2.95	2.78
	2.88	cis 0.87, trans 1.14	0.27
	5.79	cis 2.28, trans 2.30	1.97
	1.76	2.34	0.44
	3.27	cis 0.95, trans 1.60	0.30
	1.55	cis 0.77, trans 0.94	*d*
	1.62	syn 1.96, anti 3.86	1.10

[a] In all cases 15 mmol each of alkene and CF_4 were cocondensed with carbon. [b] Although CHF_3 is detected among the products it is difficult to quantitate due to its volatility under the reaction conditions. [c] This is the amount of carbon lost from the graphite electrodes. Since some carbon is physically removed, the actual amount of carbon vaporized is less. [d] No 3-phenyl-1,1-difluoropropane could be detected. Perhaps the HCF_2 polymerizes the styrene.

between CF_4 and $C(^1D)$ is more complex in that this state of carbon has both open and closed shell components and is not well treated by a single configurational method. Thus, we have evaluated the reactivity of $C(^1D)$ by separately considering both open and closed shell reaction paths.[11] When this is done, the closed shell singlet is calculated to form tetrafluoroethylene directly with a barrier of 13.3 kcal/mol. In order to evaluate the open shell singlet surface, we have assumed that the energy of open shell **2**, with its widely separated unpaired spins, is only slightly higher than that of triplet **2**. Since $C(^1D)$ is 30 kcal higher in energy than $C(^3P)$, this assumption leads to the conclusion that $C(^1D)$ will react with CF_4 to form **2** with little or no barrier. Thus, the calculations predict that the lowest energy process for both singlet and triplet carbon will be the formation of **2**. However, an examination of the geometry of **2** does not allow us to determine if it will proceed directly to CF + CF_3 or collapse to tetrafluoroethanylidene, **1**. In good agreement with experimental heats of reaction,[8] fluorine abstraction by $C(^3P)$ is calculated to be endothermic by 5 kcal/mol while abstraction by $C(^1D)$ is exothermic by 25 kcal/mol. Dixon has calculated that carbene **1** has a singlet ground state with a singlet–triplet splitting of 9.2 kcal/mol.[12] A splitting of 7.9 kcal is calculated in the present work.

Reaction of Arc Generated Carbon Atoms with CF_4. In order to examine this reaction experimentally, we have generated atomic carbon in a carbon arc and cocondensed it with CF_4 at 77 K.[13] Reaction of carbon with CF_4 alone generates no volatile products. Extraction of the reactor bottom with acetone yields a polymer with an IR absorbance at 1215 cm^{-1}. It is interesting that this IR band is the same position as that reported for $(CF)_n$.[14]

The lack of volatile products in the C + CF_4 reaction induced us to follow the lead of Wolfgang and co-workers[6] and add alkenes to trap any intermediates that may be present. Since the products of the reaction of atomic carbon with alkenes themselves are generally well understood,[13] we have focused our attention on products containing fluorine. Two common products always observed are fluorocyclopropanes and 1,1-difluoroalkanes (eq 3 whose yields are shown in Table II. In no case could tetrafluoroethylene or adducts of carbene **1** be detected among the products.

Table III. ^{19}F Chemical Shifts and Coupling Constants for the Fluorocyclopropanes

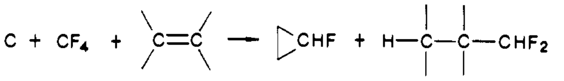
fluorocyclopropane	δF^a (ppm)	J_{H1-F} (Hz)	J_{Hcis-F} (Hz)	$J_{Htrans-F}$ (Hz)
fluorocyclopropane	−212.6	65.28	21.59	10.14
trans-2-methylfluorocyclopropane	−208.0	64.62	21.98, 21.65	9.96
cis-2-methylfluorocyclopropane	−229.0	65.9	20.0	11.17, 10.93
2,2-dimethylfluorocyclopropane	−218.0	65.25	21.12	9.50
trans,cis-2,3-dimethylfluorocyclopropane	−203.5	63.36	22.0	
cis,cis-2,3-dimethylfluorocyclopropane	−242.5	67.77		7.64
cis,trans-2,3-dimethylfluorocyclopropane	−224.9	65.10	21.35	*b*
trans-2,2,3-trimethylfluorocyclopropane	−215.4	65.23	22.98	
cis-2,2,3-trimethylfluorocyclopropane	−232.6	65.99		11.85
trans-2-ethylfluorocyclopropane	−208.1	65.0	21.80, 21.45	10.5
cis-2-ethylfluorocyclopropane	−228.6	64.0	21.52	10.45, 10.10
syn-7-fluorobicyclo[4.1.0]heptane	−205.5	64.55	22.54	
anti-7-fluorobicyclo[4.1.0]heptane	−234.5	67.63		9.07
trans-2-phenylfluorocyclopropane	−203.0	64.2	19.15, 18.6	8.0
cis-2-phenylfluorocyclopropane	−223.0	65.75	18.0	7.75, 7.4

[a] Chemical shifts are relative to $CFCl_3$. [b] Coupling could not be resolved.

Table IV. ^{19}F Chemical Shifts and Coupling Constants for $RCHF_2$

R	δF^a (ppm)	$^2J_{H-F}$ (Hz)	$^3J_{H-F}$ (Hz)
ethyl	−118.3	56.65	17.40
n-propyl	−116.9	56.75	17.42
isobutyl	−116.8	57.13	17.20
sec-butyl	−123.9	56.69	14.76
3-methyl-2-butyl	−119.0	55.32	12.33
n-butyl	−116.6	56.65	17.40
cyclohexyl	−124.2	56.8	13.0

[a] Chemical shifts are relative to $CFCl_3$.


(3)

Spectral Characterization of Fluorine Containing Products. The structures of the fluorine containing products were deduced from their ^{19}F NMR spectral data. The stereochemistry of the fluorocyclopropanes can be determined from their F–H couplings and ^{19}F chemical shifts.[15] The vicinal protons trans to the F in fluorocyclopropanes couple with J_{H-F} = 8–12 Hz while cis protons have J_{H-F} = 18–23 Hz. Fluorines cis to alkyl groups in fluorocyclopropanes always resonate at higher fields than trans fluorines. Of the 15 fluorocyclopropanes identified in this study, the ^1H spectra of fluorocyclopropane,[16] and the ^{19}F spectra of 2,2-dimethylfluorocyclopropane,[17] *cis*- and *trans*-2,2,3-trimethylfluorocyclopropane,[15] *cis*- and *trans*-2-phenylfluorocyclopropane,[15] and *syn*- and *anti*-7-fluorobicyclo[4.1.0]heptane[15] have appeared

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[11] Ahmed, S. N.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 3942. Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 5191.

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[14] This IR absorbance is identical with that reported for $(CF)_n$ by Lagow, R. J.; Shimp, L. A.; Lam, D. K.; Baddour, R. F. *Inorg. Chem.* **1972**, *11*, 2568.

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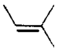
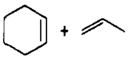
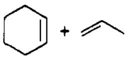
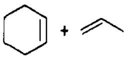
[16] Scherr, P. A.; Oliver, J. P. *J. Mol. Spectrosc.* **1969**, *31*, 109.

[17] Oliver, J. P.; Rao, U. V.; Emerson, M. T. *Tetrahedron Lett.* **1964**, 3419.

Table V. Cis–Trans Ratios of Fluorocyclopropanes Formed in the Reactions of C + CF_4 and CHF with Alkenes

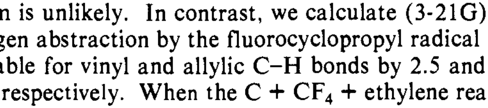
	cis–trans ratios in product fluorocyclopropanes		
alkene substrate (s)	C + CF_4	CTF (gas)[a]	CHF (soln)[b]
	0.76	1.09	
	0.99	1.0	
	0.59	1.0	1.1
	0.51		1.0
 (1:1)	0.23		
 (1:1.5)	0		
 (1:2)	0		

[a] Generated by the reaction of energetic tritium atoms with difluoromethane.[20] [b] From the photolysis of fluorodiiodomethane.[21]

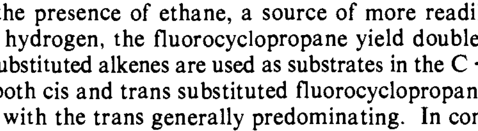
in the literature. We have synthesized *cis*- and *trans*-2-ethylfluorocyclopropane and *cis,cis*-, *trans,cis*-, and *cis,trans*-2,3-dimethylfluorocyclopropane.[17] In all cases the spectra of our products are similar to those of the authentic sample. We have also synthesized all the 1,1-difluoroalkanes[18] with the exception of 2,3-dimethyl-1,1-difluorobutane and have observed similar ^{19}F spectra to our products and those reported in the literature.[19] The ^{19}F spectral data of products are listed in Tables III and IV.

In order to further characterize the fluorine containing products, they were separated by gas chromatography, and their structures were confirmed by mass spectrometry. While the fluorocyclopropanes show a parent ion in their mass spectrum, the 1,1-difluoroalkanes generally exhibit a peak corresponding to the loss of HF from the parent. Mass spectra and retention times of the authentic samples are identical with those of our products.

The Mechanism of Formation of the Fluorocyclopropanes. Since the fluorocyclopropane products represent the addition of both a carbon and a fluorine to the olefinic trapping agent, it is reasonable to assume the involvement of CF in the mechanism of their formation. If CF were formed initially, addition to a double bond would give a fluorocyclopropyl radical. Subsequent hydrogen abstraction generates the fluorocyclopropane as shown in eq 4. Alternatively, the CF could abstract hydrogen to generate HCF which then adds to the alkene (eq 5). However, an examination



(4)



(5)

of the enthalpy of the hydrogen abstraction in eq 5 reveals that the process is endothermic for both vinyl ($\Delta H = +37$ kcal/mol) and allylic C–H bonds ($\Delta H = 10$ kcal/mol). Hence, this mechanism is unlikely. In contrast, we calculate (3-21G) that the hydrogen abstraction by the fluorocyclopropyl radical in eq 4 is favorable for vinyl and allylic C–H bonds by 2.5 and 26.4 kcal/mol, respectively. When the C + CF_4 + ethylene reaction is run in the presence of ethane, a source of more readily abstractable hydrogen, the fluorocyclopropane yield doubles.

When substituted alkenes are used as substrates in the C + CF_4 reaction, both cis and trans substituted fluorocyclopropanes are generated with the trans generally predominating. In contrast, when CHF is reacted with alkenes in the gas phase[20] or in solution,[21] the cis:trans ratios in the product cyclopropanes are invariably close to unity. Table V compares cis/trans ratios from reaction of fluoromethylene with alkenes to those observed in the present study. These data indicate that the reactivity of fluoromethylene is different from that observed here and provide evidence that the intermediate in our system is not HCF but CF.

Scheme I

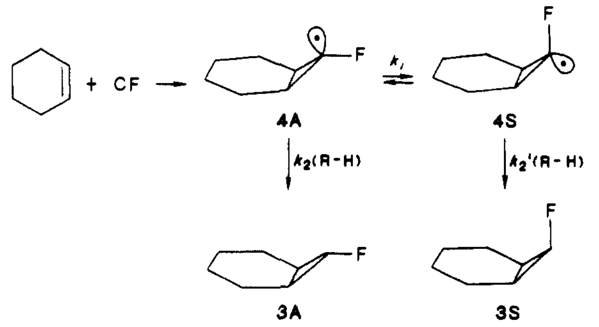
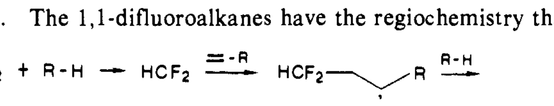
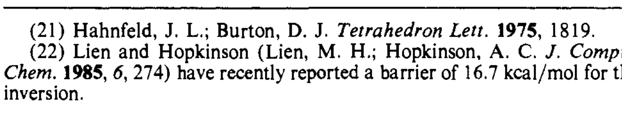


Table V demonstrates that, when propene is added to the C + CF_4 + cyclohexene system, the syn:anti ratio in 7-fluorobicyclo[4.1.0]heptane (**3-S** and **3-A**) decreases from 0.51 to 0. We feel that this result is consistant with the mechanism in Scheme I involving initial addition of CF to cyclohexene to give the anti radical **4-A**. Radical **4-A** can either invert to the syn radical **4-S** or abstract a hydrogen. Since propene is expected to be more mobile on the low-temperature matrix than cyclohexene and hence a better hydrogen donor, the ratio $k_2[R-H]:k_i$ is expected to increase as propene is added to the matrix resulting in an increase in **3-A**. Since we calculate ([UMP2/6-31G*]) a barrier of 13.7 kcal/mol for inversion of the fluorocyclopropyl radical,[22] the interconversion of syn and anti radicals is possible if these species are formed with a moderate amount of excess energy on the matrix. A variation of the **3-S**:**3-A** ratio as a function of hydrogen doner concentration would not be anticipated if CF were to first abstract hydrogen to give CHF.

The Stereochemistry of CF Additions. The use of *E*- and *Z*-2-butene as substrates allows an evaluation of the stereochemistry about the alkene C–C bond during addition of CF. If CF were to add as a radical, one might expect the open shell intermediate **5** to have sufficient lifetime to permit rotation about the C–C bond and consequently nonstereospecific formation of the fluorocyclopropyl radical. However, the stereospecific formation of *trans-cis*- and *cis,cis*-2,3-dimethylfluorocyclopropane from (*Z*)-2-butene and only *cis,trans*-2,3-dimethylfluorocyclopropane from (*E*)-2-butene rules out an open shell intermediate such as **5** in which there is free rotation about the C–C bond.



The Mechanism of Formation of 1,1-Difluoroalkanes. Although the presence of 1,1-difluoroalkanes in the C + CF_4 reaction appears to be indicative of the intermediacy of CF_2, no products in which CF_2 has added to the alkene to give a difluorocyclopropane are ever observed. Instead, the results are best accommodated by invoking a CF_2 which abstracts a hydrogen to generate CHF_2 which then adds to the alkene in a radical manner as shown in eq 6. The 1,1-difluoroalkanes have the regiochemistry that is



(6)

expected for addition of CHF_2 to a substituted alkene to give the

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(18) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574.

(19) Weigert, F. J. *J. Org. Chem.* **1980**, *45*, 3476.

(20) Tang, Y.-N.; Rowland, F. S. *J. Am. Chem. Soc.* **1967**, *89*, 6420.

(21) Hahnfeld, J. L.; Burton, D. J. *Tetrahedron Lett.* **1975**, 1819.

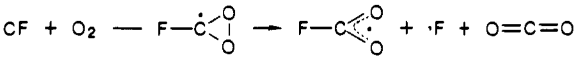
(22) Lien and Hopkinson (Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274) have recently reported a barrier of 16.7 kcal/mol for this inversion.

most stable free radical. Since hydrogen abstractions by carbenes are characteristic of triplet states, we feel that reactive form of CF_2 in this system is the excited triplet state. However, the reaction shown in eq 2 in which either $C(^3P)$ or $C(^1D)$ reacts with CF_4 to give exclusively $^3CF_2$ is endothermic. As an alternative to the reaction in eq 2, we postulate that the $^3CF_2$ arises by reaction of carbon with the CF_3 (eq 7). A simple test of this postulate

$$C + CF_3 \rightarrow CF + {}^3CF_2 \qquad (7)$$

is the substitution of a fluorocarbon which will not yield CF_3 upon fluorine abstraction by carbon. Accordingly, atomic carbon was condensed with perfluoroisobutane in the presence of ethylene and propene. This reaction resulted in the formation of fluorocyclopropanes but no 1,1-difluoroalkanes.

Reaction of C with CF_4 in the Presence of O_2. The reaction of nucleogenic carbon-11 atoms with CF_4 has been reported to generate $^{11}CO_2$.[7] This is in contrast to the reaction of carbon atoms with oxygen alone which yields CO.[13] When arc generated carbon atoms are cocondensed with CF_4 containing 5% oxygen, carbon dioxide and carbonyl fluoride are formed in a 1.1:1 ratio. The carbon dioxide, which has also been reported in the ^{11}C system,[7] may be rationalized by addition of CF to O_2 followed by ring opening to a fluorocarboxy radical which loses a fluorine atom (eq 8). The formation of carbonyl fluoride in the reaction between $^3CF_2$ and O_2 has been reported and is thought to be a reaction characteristic of $^3CF_2$.[23]



(8)

Conclusions. These investigations demonstrate that the reaction of carbon with fluorocarbons is a convenient way to generate CF which reacts with alkenes by stereospecific addition to give fluorocyclopropyl radicals.

Experimental Section

Physical Measurements. The ^{19}F NMR spectra were recorded on a Bruker AM 400 spectrometer at 376.4 mHz. Gas chromatography–mass spectrometry data were obtained with a Finnigan 9500 chromatograph interfaced to a Finnigan 3300 mass spectrometer with an Incos data system. Fluorocyclopropanes and 1,1-difluoroalkanes were analyzed by gas chromatography on 6 ft porapak Q (80/100 mesh) and 3% OV-101 (80/100 mesh Supelcoport) glass columns.

Carbon Atom Reactions. The carbon atom reactor is modeled after that reported by Skell, Wescott, Goldstein, and Engel.[24] Carbon is vaporized by striking an intermittent arc between two graphite rods attached to water cooled brass electrodes and condensed on the walls of the reactor at 77 K with reactants under vacuum.

Reaction of Carbon Vapor with Tetrafluoromethane. Tetrafluoromethane (25 mmol) was introduced into the reactor through the vacuum line at a flow rate of 0.12 mmol/s and cocondensed on the walls of the reactor at 77 K with carbon vapor (4.0 mmol). After the reaction, the volatiles were pumped through traps at 113 and 77 K. No products were found in the 113 K trap. The infrared spectrum of the 77 K trap showed only CF_4. The nonvolatile residue in the reactor bottom was dissolved in acetone and filtered, and the acetone removed under vacuum. The solid residue showed an IR absorbance at 1215 cm^{-1} and was not further characterized.

Reaction of Carbon Vapor with Tetrafluoromethane in the Presence of Alkenes. In a typical reaction, CF_4 (15 mmol) and alkene (15 mmol) were allowed to mix for half an hour in the vacuum line. The gas mixture was allowed to condense with carbon vapor as above. After the reaction, the volatile products were pumped from the reactor and transferred to an NMR tube with $CDCl_3$ as solvent. The ^{19}F spectra are listed in Tables III and IV. The yields in Table II were determined by integration of NMR peaks using trifluorotoluene as internal standard. The products were also analyzed by gas chromatography, and their structures were confirmed by mass spectrometry.

Reaction of Carbon Vapor with Tetrafluoromethane in the Presence of Cyclohexene and Propene. CF_4 (25.0 mmol), cyclohexene (12.5 mmol), and different amounts of propene were mixed in the vacuum line and condensed at 77 K with carbon vapor. The ratio of the *syn*- and *anti*-7-fluorobicyclo[4.1.0]heptanes was determined by ^{19}F NMR and is shown in Table V.

Reaction of Carbon Vapor with Tetrafluoromethane and Oxygen. The reaction was carried out as described above with the condensation of CF_4 (80 mmol), O_2 (4 mmol), and carbon vapor (12.06 mmol). Analysis of the volatile products revealed the presence of $CF_2{=}O$ (1.18 mmol) and CO_2 (1.37 mmol).

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Registry No. C, 7440-44-0; CF_4, 75-73-0; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}C(CH_3)_2$, 115-11-7; (*E*)-$CH_3CH{=}CH{-}CH_3$, 624-64-6; $PhCH{=}CH_2$, 100-42-5; $CH_2{=}CHCH_3$, 115-07-1; $CH_3CH_2CH{=}CH_2$, 106-98-9; (*Z*)-$CH_3CH{=}CHCH_3$, 590-18-1; $CH_3CH{=}C(CH_3)_2$, 513-35-9; $(CH_3)_3CCHF_2$, 53731-22-9; $F_2CHCH(CH_3)CH_2CH_3$, 66688-67-3; $F_2CHCH_2CH_2CH_3$, 2358-38-5; $F_2CHCH_2CH_2CH_2CH_3$, 62127-40-6; $F_2C{=}O$, 353-50-4; $F_2CHCH_2CH(CH_3)CH(CH_3)_2$, 103835-63-8; CO_2, 124-38-9; CF, 3889-75-6; $^3CF_2$, 2154-59-8; cyclohexene, 110-83-8; fluorocyclopropane, 1959-79-1; 2,2-dimethylfluorocyclopropane, 1891-97-0; *cis-trans*-2,3-dimethylfluorocyclopropane, 50422-75-8; *cis-cis*-2,3-dimethylfluorocyclopropane, 50422-79-2; *trans-cis*-2,3-dimethylfluorocyclopropane, 50422-78-1; *cis*-2-phenylfluorocyclopropane, 22140-51-8; *trans*-2-phenylfluorocyclopropane, 22140-50-7; 1,1-difluoropropane, 430-61-5; *cis*-2-methylfluorocyclopropane, 50422-73-6; *trans*-2-methylfluorocyclopropane, 50422-72-5; *cis*-2-ethylfluorocyclopropane, 50422-77-0; *trans*-2-ethylfluorocyclopropane, 50422-76-9; *cis*-2,2,3-trimethylfluorocyclopropane, 22140-49-4; *trans*-2,2,3-trimethylfluorocyclopropane, 22140-48-3; 7-fluorobicyclo[4.1.0]heptane (isomer 1), 16646-97-2; 7-fluorobicyclo[4.1.0]heptane (isomer 2), 16646-98-3; (difluoromethyl)cyclohexane, 329-29-3.

Supplementary Material Available: Mass spectrometry data for fluorocyclopropanes (Table I) and 1,1-difluoroalkanes (Table II) (2 pages). Ordering information can be found on any current masthead page.

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[24] Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.