DEE/2-MeTHF.

These calculations provide us with two boundary models: (1) isolated dianions wherein the countercations are removed by solvation to the extent that the dianion does not "see" them at all (barrier 2.7 kcal/mol) and (2) an unsolvated, contact ion pair (barrier ca. 9–10 kcal/mol). We would expect the real solvated system to be somewhere in between those extremes. Thus, increasing solvation of the cations should result in a decrease of the barrier in accord with the experimental results (see above). To provide additional support to this conclusion, we have recalculated the transition-state structure for rotation of dilithium **2** complex, while fixing the torsional angle at 64° and adding six molecules of water. The final energy of that system, serving as an approximate model for the solvated transition state, was only 3.6 kcal/mol higher in energy than **2a**$\cdot 6H_2O$. Even though the "corrected" value will be higher, it is still acceptably close to the experimental values. More importantly, these calculations demonstrate that the transition state for rotation in 1,2′-biindenide is more strongly stabilized by solvation than the minimum energy structure, providing a rationale for the NMR results indicating that increased cation solvation lowers the barrier for rotation in that system.

Experimental Section

1,2′-Biindene was synthesized from commercially available 1-indanone according to standard procedures.[22]

2,2′-Biindene was synthesized according to an earlier published procedure.[23]

The biindenide salts were prepared by addition of *n*-butyllithium (1.0 M in hexane) to the corresponding biindene in ethereal solution at −78 °C. The solid material was prepared in hexane solution with 1 equiv of TMEDA added. The crystals were filtered under an argon atmosphere and dried in vacuum.

The solvents used in order of decreasing solvation ability were: THF/*N*,*N*,*N*′,*N*′-tetramethylpyrimidinone (DMPU) or THF/DMEU; THF; 2-MeTHF; and DEE. In some cases, a mixture of ethers was used to increase the solubility of the salt. The solid materials were isolated as TMEDA complexes.

Solution NMR spectra were obtained on Bruker ACP 250 and AM 500 spectrometers, using cyclohexane as internal reference and converted to the δ scale using the ^{13}C NMR chemical shift of cyclohexane, 27.7 ppm.

The assignment of the ^{1}H NMR resonances of the dilithium 1,2′-biindenide was done by double-quantum filtered COSY in combination with NOE difference experiments. The ^{13}C resonances were assigned by C,H-correlated methods. The nonprotonated carbons were assigned by the COLOC pulse sequence optimized for a coupling constant of 18 Hz.

The phase-sensitive HOESY experiments[21b] were performed at room temperature using a mixing time of 2 s.

Solid-state CP/MAS NMR spectra were obtained using a Bruker MSL 100 NMR spectrometer. The samples were rotated at 3 kHz, the repetition time was 2.5 s, and the contact time was 1 ms. The methylene carbon of adamantane was used as external reference at 38.3 ppm relative to TMS.

The ^{13}C CP/MAS spectra were assigned based on similarities to the shifts obtained in solution. Protonated and nonprotonated carbons were distinguished based on the differences in cross–polarization rates.[24]

The activation parameters were derived from the NMR data according to earlier described procedures.[25] In the fast-exchange region the exchange rate was calculated according to $k = \pi\delta\nu^2/(2(W^* - W_0))$; in the slow-exchange region the exchange was calculated according to $k = \pi(W^* - W_o)$.

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Registry No. 1, 87632-29-9; **2**, 137895-40-0.

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Kinetics of Alkylhalocarbene Rearrangements: Modulation by Fluorine Substituents

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Abstract: Rate constants were measured by laser flash photolytic methods for hydrogen and carbon 1,2-migrations in four different alkylchlorocarbenes and in the analogous alkylfluorocarbenes. The carbenes, products, and rate constants (s^{-1}) were as follows: phenoxymethylchlorocarbene to (*Z*)- and (*E*)-1-chloro-2-phenoxyethene ($Z/E \sim 4/1$), $k = 3.6 \times 10^7$; phenoxymethylfluorocarbene to (*Z*)-1-fluoro-2-phenoxyethene ($Z/E > 10/1$), $k = 1.3 \times 10^7$; neopentylchlorocarbene to (*Z*)- and (*E*)-1-*tert*-butyl-2-chloroethene ($Z/E = 1/12$), $k = 1.4 \times 10^7$; neopentylfluorocarbene to (*Z*)- and (*E*)-1-*tert*-butyl-2-fluoroethene ($Z/E = 1/2.5$), $k = 2.6 \times 10^6$; cyclobutylchlorocarbene to 1-chlorocyclopentene (C migration) and chloromethylenecyclobutane (H migration), $k_c = 4.6 \times 10^7$, $k_H = 2.1 \times 10^7$; cyclobutylfluorocarbene to 1-fluorocyclopentene (C migration) and fluoromethylenecyclobutane (H migration), $k_c = 1.8 \times 10^6$, $k_H = 5.3 \times 10^5$; cyclopropylchlorocarbene to 1-chlorocyclobutene, $k = 9 \times 10^5$; cyclopropylfluorocarbene to 1-fluorocyclobutene, $k = 1.4 \times 10^5$. Activation energies for several of these processes were in the range of 2–4 kcal/mol, with $A \sim 10^8$–10^9 s^{-1}.

Hydride and carbon 1,2-shifts are fundamental intramolecular carbene reactions.[1] The simultaneous availability of nanosecond laser flash photolytic (LFP) equipment, appropriate (diazirine) precursors,[2] and Platz's ylide kinetic methodology[3] permits us to determine kinetic parameters for these processes. Although alkyl and dialkylcarbenes often rearrange too quickly for nanosecond

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studies,[4] alkylchlorocarbenes, stabilized by the chlorine–carbene interaction, exhibit appropriate longevity, and their rearrangements have been intensively examined.

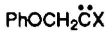
Examples include H 1,2-migrations in methylchlorocarbene,[5] benzylchlorocarbene,[6] and other alkylchlorocarbenes,[7] as well as C 1,2-migrations in cyclopropylchlorocarbene,[7,8] cyclobutylchlorocarbene,[9] and *tert*-butylchlorocarbene.[10] The reported rate constants for H 1,2-migrations are in the 10^6–10^8-s^{-1} range, with $E_a \leq 2.4$ kcal/mol (i-C_3H_7CCl) to $\sim$5 kcal/mol (MeCCl).[5b] Corresponding data for C 1,2-migrations include $k \sim (10^5$–$5) \times 10^7$ s^{-1}, with a low E_a ($\sim$3 kcal/mol) for the ring expansion of cyclopropylchlorocarbene.[8b,11] Large negative activation entropies are found to play major roles in these reactions.[5b,8b,10]

The carbene 1,2-rearrangements have recently garnered much theoretical attention.[12] Evenseck and Houk presented high-level ab initio calculated activation energies for the paradigmatic H 1,2-migration $CH_3CX \rightarrow CH_2{=}CHX$, describing a strong dependence of E_a on X, with E_a = 0.6, 11.5, 19, or 27 kcal/mol, when X = H, Cl, F, or OMe (*trans*-Me–C–OMe), respectively.[12a] Although the stabilizing and selectivity enhancing effects of the fluorine for chlorine substitution are precedented theoretically[13] and well-recognized in the *intermolecular* chemistry of CX_2,[14] comparable experimental results are absent for *intramolecular* carbene reactions.

Here, we report the first rate constants and activation parameters for alkylfluorocarbene H and C 1,2-migrations. Comparisons with analogous alkylchlorocarbenes reveal appropriate structure/reactivity trends, but F/Cl substitutions in RCX afford *significantly smaller changes in* E_a than might have been expected, based on theoretical considerations.[12a] The disparity between calculated and experimental results is important and suggests that additional scrutiny must be directed at these seemingly simple rearrangements.

Results and Discussion

Products. We studied four pairs of alkylhalocarbenes, **1–4**, where X = Cl or F. The carbene precursors were halodiazirines **5**. Chlorodiazirines, **5**-Cl, were prepared by Graham oxidations of the corresponding alkylamidinium salts,[15–18] whereas fluorodiazirines, **5**-F, were provided by $Bu_4N^+F^-$ exchange reactions[19] on *bromo*diazirines, **5**-Br; the latter were obtained by Graham oxidations with NaOBr.[15] Nonvolatile diazirines were purified by silica gel chromatography (pentane eluent); volatile diazirines were extracted into decane and then distilled (0.5–1 mmHg) into pentane or other solvents. All diazirines 5-X (X = F, Cl, Br) exhibited appropriate UV spectra, with two to three absorptions in the 330–380-nm range.[15] A table of these UV absorptions

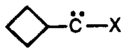


$PhOCH_2\ddot{C}X$

1

$Me_3CCH_2\ddot{C}X$

2



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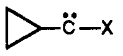

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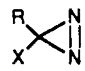

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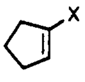
appears in the Experimental Section, where other properties of the new fluorodiazirines are also described.

Pentane or isooctane solutions of the diazirines ($A_{340-350} \sim 1.0$) were photolyzed at 20 °C with a 200-W focused Osram XE UV lamp ($\lambda > 320$ nm) until the diazirines were destroyed. Carbenes **1–4** thus generated afforded (Z)- and (E)-**6** (from **1**), (Z)- and (E)-**7** (from **2**), **8** and **9** (from **3**), and **10** (from **4**). These were characterized by GC, ^{1}H (and ^{19}F) NMR spectroscopy, and elemental analysis or mass spectrometry (M^+).

PhOCH=CHX **6** Me$_3$CCH=CHX **7**



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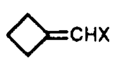

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10

In the chlorocarbene series, the rearrangements of **1**,[16] **3**,[9] and **4**,[8] their products, and distributions have been described. Carbene **2**-Cl gave the known[20] alkene isomers **7**-Cl, with a Z/E distribution of 1/12. The products derived from the fluorocarbenes were analogous to those of the corresponding alkylchlorocarbenes. Thus, H 1,2-shift in carbene **1**-F gave >90% of (Z)-**6**-F,[21] whereas the same process in neopentylfluorocarbene (**2**-F) gave (Z)- and (E)-**7** in a ratio of 1/2.5. Competitive C and H 1,2-rearrangements were observed with cyclobutylfluorocarbene (**3**-F), affording fluorocyclopentene, **8**-F,[22] and fluoromethylenecyclobutane, **9**-F, in a distribution of 3.4/1 at 23 °C. Only the ring expansion product, **10**-F, was obtained, in near quantitative yield, from cyclopropylfluorocarbene. Its NMR spectra were consistent with those of other fluorocyclobutenes.[23]

It is important to be certain that the rearrangements of carbenes **1–4** to products **6–10** under our reaction conditions are quantitative or nearly so, because the pyridine ylide kinetic method[3] that we employ to determine the rate constants for these rearrangements (see below) actually affords rate constants that are sums of all those processes that "destroy" the carbenes in the *absence* of added pyridine. We therefore carefully examined NMR spectra and GC traces of the crude reaction products from the photolyses of the diazirine precursors.

Importantly, there was no evidence of azine or carbene dimer formation in the reactions of carbenes **1–3**. Azines and dimers are the usual unwanted side products of the intermolecular carbene–diazirine or carbene–carbene reactions that occur when the rates of carbene intramolecular rearrangements are too low ($<10^6$ s^{-1}) and/or the concentrations of carbene or diazirine are

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too high. The absence of these products following the photolysis of pentane or isoctane solutions of the appropriate diazirine precursors (conditions described above) is suggestive evidence that the intramolecular rearrangements of carbenes **1**–**3** to products **6**–**9** are effectively quantitative.

Examinations of the crude product mixtures support this conclusion. Thus, NMR product studies of carbenes **1**-Cl and **1**-F showed only alkenes **6** as products (yields >90%). From **1**-Cl, we obtained (*Z*)-**6** and (*E*)-**6** (X = Cl) in a 4/1 ratio (lit.[16] ratio 81/19) based on intergration of the corresponding vinyl proton (=CHCl) doublets at δ 5.85 (*Z* isomer, $J = 4$ Hz) and δ 6.38 (*E* isomer, $J = 11$ Hz). From **1**-F, we obtained only (>90%) (*Z*)-**6** (X = F). The spectroscopic properties of this alkene (and the other new fluoroalkenes) are described in detail in the Experimental Section. The preference for the *Z*-alkenes as products of the hydride 1,2-shifts of carbenes such as **1**-Cl and **1**-F has been discussed by Tomioka.[16]

With carbene **2**-Cl, only alkenes *Z*- and *E*-**7** (X = Cl) were observed by NMR in the crude photolysis product mixtures. Here, the *E*/*Z* ratio was 12:1 based on capillary GC or the corresponding Me_3CCH= vinyl signals at δ 5.67 (*Z* isomer, J = 8 Hz) and δ 5.89 (*E* isomer, J = 13.7 Hz). The fluorocarbene analogue, **2**-F, was produced by photolysis of the diazirine ($A_{350} = 1.2$) in $CDCl_3$. Both ^1H and ^{19}F NMR revealed only products *Z*- and *E*-**7** (X = F), with an *E*/*Z* ratio of 2.5:1. The appropriate NMR signals are described in the Experimental Section.

The conversions of chlorocarbenes **3**-Cl and **4**-Cl to chloroalkenes **8** and **9** (from **3**) and **10** (from **4**) have been discussed previously,[8,9] but the analogous fluorocarbene reactions will be described here. The photolysis at 23 °C of cyclobutylfluorodiazirine ($A_{356} = 1.4$) in $CDCl_3$ afforded *only* alkenes **8** and **9** (X = F). The **8** (~C) to **9** (~H) ratio was 3.36, as determined by capillary GC on SE-30 at 0 °C, or 3.28 from integration of the appropriate vinyl proton signals (see the Experimental Section) in the NMR spectrum of the crude product. In the photolytic generation of **3**-F in isooctane, the ratio of **8**/**9** varied with reaction temperature, ranging from 5.39 at −27 °C to 2.97 at 40 °C. This is discussed more fully below. Additionally, LFP studies of the formation of the pyridinium ylide derived from carbene **3**-F and pyridine in pentane showed excellent first-order behavior for the growth of the ylide, indicating that competitive intermolecular carbene dimerization is unimportant under the LFP conditions.

Finally, photolysis of cyclopropylfluorodiazirine ($A_{358} = 0.97$) in $CDCl_3$ at 25 °C gave a near quantitative yield (>90%) of 1-fluorocyclobutene, identified by its NMR spectra (see the Experimental Section and ref 23). However, under LFP conditions, the divergence of the ylide growth from first-order behavior signaled the probable intervention of competing carbene dimerization. The rearrangement of **4**-F to **10**-F is the slowest of all the intramolecular reactions we consider here (see below), and it is expected to be most sensitive to intermolecular diversion at low [pyridine].

A series of LFP experiments in isooctane, carried out with decreasing concentrations of cyclopropylfluorodiazirine, indicated that the desired first-order ylide formation behavior could be obtained with $A_{358} = 0.033$ for the diazirine. A similar procedure to circumvent unwanted intermolecular carbene reactions has been employed with *tert*-butylchlorocarbene, where intramolecular reactions are also slow.[10] No LFP evidence was observed for intermolecular complications in the reactions of carbenes **1**-Cl, **1**-F, **2**-Cl, or **2**-F.

Kinetics. Absolute rate constants were determined for the rearrangements of carbenes **1**–**4** (X = Cl, F) using the pyridine ylide method.[3] LFP irradiation[8a] at ~20 °C of pentane or isooctane solutions of diazirines **5** ($A_{340-350}$ was usually 0.5–1.0) in the presence of 0.1–3.0 mM pyridine[24] gave rise, in each case, to ylides with $\lambda \sim$ 360–410 nm, λ_{max} = 375–380 nm. The observed rate constants for transient growth were linear with [pyridine], affording $k \sim 10^8$–10^{10} M^{-1} s^{-1} for the generation of the various ylides. The *y* intercepts of these correlations, at [pyridine] = 0, were taken as the rate constants for the carbene rearrangements.[3]

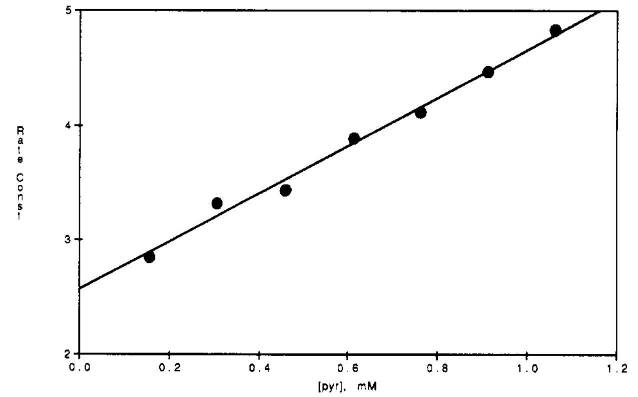

Figure 1. Pseudo-first-order rate constants ($10^{-6}k_f$ (s^{-1})) for pyridinium ylide formation from carbene **2**-F and pyridine vs [pyridine] (mM) in isooctane at 20.5 °C. The *y* intercept, k_H for the rearrangement of carbene **2**-F, is 2.57×10^6 s^{-1}, and the second-order rate constant for pyridinium ylide formation, computed from the slope of the correlation ($r = 0.995$), is 2.09×10^9 M^{-1} s^{-1}.

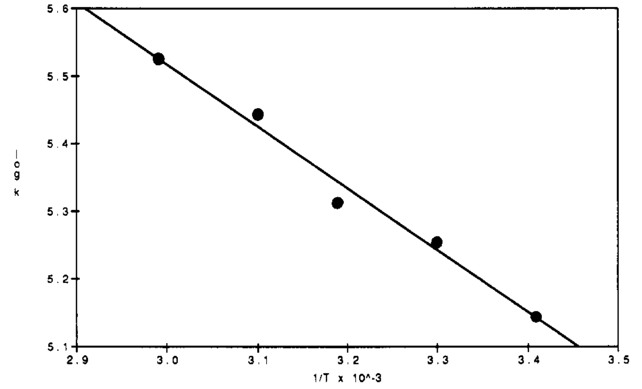

Figure 2. Logarithms of the rate constants at temperatures between 293.5 and 334 K for the rearrangement of carbene **4**-F plotted vs $1/T$ (K^{-1}). The intercept, log *A*, is 8.26, and the activation energy, computed from the slope of the correlation ($r = 0.992$), is 4.2 kcal/mol.

Table I. Temperature Dependence of the Reactions of Carbene **2**-F[a]

temp (K)	$10^{-6}k_t$ (s^{-1})[b]	k_8/k_9[c]	$10^{-6}k_c$ (s^{-1})[d]	$10^{-6}k_H$ (s^{-1})[e]
246	0.94 ± 0.06	5.39	0.79	0.15
262	1.33 ± 0.03	5.01	1.11	0.221
278	1.81 ± 0.08	4.48	1.48	0.330
296	2.31 ± 0.05	3.36	1.78	0.530
313	3.02 ± 0.02	2.97	2.26	0.760

[a] Reactions were carried out in isooctane solution. [b] Total rate constant for carbene rearrangement by LFP. Errors are uncertainties in the *y* intercepts of the least-squares linear correlations between k_f for ylide formation from **2**-F and [pyridine]; see Figure 1 for an example of this type of correlation. [c] Product distributions of **8** and **9** determined by capillary GC on separate stationary photolytic runs. [d] Rate constant for the rearrangement of **2**-F to **8**-F. [e] Rate constant for the rearrangement of **2**-F to **9**-F.

An example of this methodology appears in Figure 1, where the observed pseudo-first-order rate constants for the formation of the pyridinium ylide derived from neopentylfluorocarbene (**2**-F) and pyridine are plotted against [pyridine]. The second-order rate constant for ylide formation, given by the slope of the least-squares linear correlation ($r = 0.995$), is $(2.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. The *y* intercept, $(2.6 \pm 0.1) \times 10^6$ s^{-1}, is taken as the rate constant for the rearrangement of **2**-F to (*Z*)- and (*E*)-**7**-F (see above).

In the cases of carbenes **3**-Cl and **3**-F, the total rearrangement rate constants, determined by the ylide method, were partitioned into rate constants for C 1,2-shift (to **8**) and H 1,2-shift (to **9**) using product distribution ratios obtained by capillary GC analysis. This procedure has been described for carbene **3**-Cl.[9] Table I displays the analogous total rearrangement rate constants, product

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[24] The pyridine concentration range was higher for **3**-Cl; see ref 9.

Table II. Kinetics of Carbene Rearrangements[a]

R (in RCX)	X	1,2 rearr type	$10^{-6}k$ (s^{-1})[b]	E_a (kcal/mol)[c]	log A (s^{-1})[d]	ΔS^* (eu)
$PhOCH_2$ (**1**)	Cl	H	36[e]			
$PhOCH_2$ (**1**)	F	H	13[e]			
Me_3CCH_2 (**2**)	Cl	H	14			
Me_3CCH_2 (**2**)	F	H	2.6	3.3	8.9	−19.8
c-C_4H_7 (**3**)	Cl	C	46[f]			
c-C_4H_7 (**3**)	Cl	H	21[f]			
c-C_4H_7 (**3**)	F	C	1.8[g]	2.3	8.0	−23.9
c-C_4H_7 (**3**)	F	H	0.53[g]	3.8	8.5	−21.6
c-C_3H_5 (**4**)	Cl	C	0.90[h]	3.0[i]	8.2	−22.9
c-C_3H_5 (**4**)	F	C	0.14[g]	4.2	8.3	−22.5

[a] See text for conditions. [b] Estimated errors are ±15%. [c] Estimated errors are ±0.5 kcal/mol. [d] Estimated errors are ±5%. [e] At −32 °C. [f] Reference 9 at 21 °C. [g] At 23 °C. [h] Reference 8a, by direct observation of **4**-Cl. [i] Reference 8b.

distributions, and (dissected) C and H 1,2-shift rate constants for the rearrangements of carbene **3**-F in isooctane at five different temperatures. We estimate the errors in the dissected rate constants at 10–15%.

In the cases of carbenes **2**-F, **3**-F, **4**-Cl,[8b] and **4**-F, activation parameters for the rearrangements were determined from rate constants measured at five different temperatures over a 40–60 °C range. A typical example of the Arrhenius analysis, applied to the kinetic data for carbene **4**-F, appears in Figure 2. Table II collects rearrangement rate constants, activation energies, preexponential factors, and (for convenience) the corresponding entropies of activation for all of the carbenes in the present study.

The dependence of the rate constants on the structure of the carbenic R groups can be understood in conventional terms. Thus, the hydride shifts in $PhOCH_2CX$ (**1**) are very rapid, and presumably driven by the phenoxy substituent at the migration origin that mitigates the accumulation of positive charge at this center in the corresponding rearrangement transition state.[25]

Hydride shifts in the oxahalocarbenes, **1**, are therefore faster than comparable processes in either the neopentylhalocarbenes, **2**, or the cyclobutylhalocarbenes, **3**.[26] Also, as previously noted,[9] C 1,2-shifts are much faster in cyclobutylhalocarbenes **3**-Cl and **3**-F than in the analogous cyclopropylhalocarbenes, **4**, probably reflecting the anticipated greater stabilization of the latter.

Most importantly, in each of the five Cl/F comparisons of Table II, the rate constants for H or C 1,2-shifts are greater for RCCl than RCF, in keeping with theoretical ideas.[12a] However, the differences in RCCl/RCF rate constants (factors ranging from ~3 (H 1,2-shift in **1**) to ~40 (H 1,2-shift in **3**)) as well as the absolute (2–4 kcal/mol) and differential activation energies (~1–2 kcal/mol) *are considerably smaller than might have been expected*, based on the calculated E_a's and the CH_3CCl/CH_3CF H 1,2-shift ΔE_a of 7.5 kcal/mol.[12a] Some of the difference between experimental and calculated results must be due to the reduced absolute and differential activation energies for the *R*CX studied here, as opposed to (the calculated) *CH_3*CX.[27]

Moreover, we observe low preexponential factors (large negative entropies of activation) in the RCF rearrangements, just as in the rearrangements of MeCCl[5b] or **4**-Cl.[8b] The importance of unfavorable entropies of activation in these rearrangements may indicate divergence between the variational and conventional minimum energy reaction transition states,[28] with possible consequences for the agreement between experimental and calculated data. It is also conceivable that tunneling reduces the anticipated activation energies, particularly for H 1,2-migrations. Experimental tests of this latter possibility are in progress.

Table III. UV Absorptions (nm) of Alkylhalodiazirines[a]

R in diazirine **5**	X in diazirine **5**: Br	Cl	F
$PhOCH_2$	334	332	318
	350	348	332
			348
c-C_4H_7	348	348	332
	366	366	348
			364
Me_3CCH_2	346	344	330
	354	354	344
	362	362	362
c-C_3H_5	348	348	342
	358	358	358
	380	380	378

[a] Hewlett-Packard Model 8451A spectrometer; isopentane or pentane solutions.

Experimental Section

General Methods. NMR spectra were determined with a Varian XL-200 spectrometer operated at 200 MHz for protons and at 188 MHz for fluorine. Chemical shifts are reported (ppm) relative to Me_4Si for ^1H and Cl_3CF for ^{19}F nuclei, respectively. UV spectra were determined with a Hewlett-Packard Model 8451A spectrometer. LFP studies were carried out with our previously described installation.[29] Preparative GC used Varian Models 90-P or 1700 instruments; capillary GC employed a Varian Model 3700 flame-ionization instrument. Mass spectra were determined with a Finnigan MAT 8230 instrument. Microanalyses were performed by Robertson Laboratory, Madison, NJ.

Amidinium Salts. Amidinium salts in the cyclopropyl[8a] and cyclobutyl[9,17] series are well-known. Neopentylamidinium chloride (Anal. C, H, N) is discussed above.[15] Phenoxyacetamidinium chloride is not well described in the literature. Phenoxyacetonitrile[30] (8.2 g, 62 mmol) was stirred in 50 mL of methanol with 0.10 g (1.8 mmol) of NaOMe at 25 °C for 8 h, after which time NMR indicated that ~50% of the nitrile has been converted to the imino ester.[31] Then, 3.4 g (64 mmol) of NH_4Cl was added and the solution was stirred for an additional 2 h. The volume of the solution was reduced by evaporation to ~20 mL, 50 mL of ether was added, and the white precipitate was filtered. The 4.5 g (24.1 mmol) of dried phenoxyacetamidinium chloride, mp 100–103 °C, was obtained in 39% overall yield.

Anal. Calcd. for $C_8H_{11}N_2OCl$: C, 51.5; H, 5.94; N, 15.0. Found: C, 51.0; H, 6.15; N, 15.3.

Bromodiazirines. All bromodiazirines were prepared by the Graham oxidation[15] of the appropriate amidinium salts using freshly prepared NaOBr solution. As an example, we describe the synthesis of 3-bromo-3-cyclobutyldiazirine. Cyclobutylamidinium chloride[17] (1.34 g, 10 mmol) and LiBr (4.35 g, 50 mmol) were dissolved in 50 mL of DMSO, and 100 mL of pentane was added. To this stirred mixture was slowly added 100 mmol of NaOBr solution (prepared from 16 g of Br_2 and 8 g of NaOH in 100 mL of water) while the temperature was maintained at 30–35 °C. Stirring was continued for an additional 1 h after addition of the NaOBr, and then 100 mL of water was added. The pentane layer was separated, dried over $CaCl_2$, reduced to ~20 mL by rotoevaporation at 25 °C, and then purified by passage through a small silica gel column, followed by additional elution with 100 mL of pentane.

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(25) Kirmse, W.; Buschoff, M. *Chem. Ber.* **1967**, *100*, 1491.

(26) The hydride shifts in **3** are "slow" for a *secondary* alkyl-substituted carbene;[9] the comparable rearrangements in *i*-PrCCl or *i*-PrCF are $>10^8$ s^{-1} [5b,7] or $\sim 7 \times 10^7$ s^{-1} (our work), respectively. The slowdown could be due to a stabilizing interaction between the cyclobutyl C–C bonds and the carbenic p orbital.[17]

(27) This contribution should not be too large; the experimental E_a for H 1,2-shift in CH_3CCl itself is only ~5 kcal/mol,[5b] less than half of the calculated[12a] value.

(28) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919. Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(29) Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Ławrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

(30) McManus, J. M.; Herbst, R. M. *J. Org. Chem.* 1959, *24*, 1464.

(31) Schaefer, F. C.; Peters, G. A. *J. Org. Chem.* **1961**, *26*, 412.

The UV spectrum of the cyclobutylbromodiazirine thus obtained is summarized in Table III, together with the spectra of all the other alkylhalodiazirines employed in the present study.

Fluorodiazirines. The bromodiazirines were not further characterized but were immediately converted to the corresponding fluorodiazirines by exchange with tetra-*n*-butylammonium fluoride (TBAF).[19] The general procedure is as follows. To the pentane solution of 3-bromo-3-alkyldiazirine (above) was added 50 mL of DMF that had been dried over 4A molecular sieves. The pentane was then removed on the rotary evaporator to afford a solution of bromodiazirine in DMF. Meanwhile, 10 g of TBAF·xH$_2$O (Aldrich) was dehydrated. It was dissolved in 100 mL of 4/1 benzene/acetonitrile, and the solvent was stripped under vacuum (oil pump) on the rotary evaporator. This operation was repeated twice. Then 50 mL of dry DMF was added, followed by reduction of the DMF volume to ~30 mL. The TBAF/DMF solution was then mixed with the bromodiazirine/DMF solution, and the whole was stirred at 25 °C for 20 h.

Depending on its volatility, the fluorodiazirine product was isolated in one of two ways. For volatile fluorodiazirines (R = cyclopropyl, cyclobutyl) 50 mL of decane and 200 mL of brine was added to the DMF solution, followed by thorough mixing. The decane phase was separated, washed with 0.1 N HCl (2 × 50 mL), 0.1 N NaOH (2 × 50 mL), and brine (3 × 50 mL), and then dried over CaH$_2$. The diazirine was then distilled (25 °C/0.5 mmHg) out of the decane into the desired solvent (e.g., pentane, isooctane, or CDCl$_3$) which was cooled to 77 K.

For heavier fluorodiazirines (R = neopentyl, phenoxymethyl), the fluorodiazirine/DMF product solution (see above) was partitioned between 300 mL of ice water and 100 mL of isopentane. The isopentane phase was separated, washed with water (3 × 100 mL), dried over CaCl$_2$, and reduced to the desired volume.

UV maxima of the fluorodiazirines appear in Table III. Proton NMR data for the 3-alkyl-3-fluorodiazirines follow. R = cyclopropyl (δ, CDCl$_3$): 0.40–0.50, 0.65–0.75 (m's, 2 H each, methylene protons); 1.4–1.6 (m, 1 H, CH proton). R = cyclobutyl (CDCl$_3$): 1.85, 1.95, and 2.05 (m's, 2 H each, methylene protons); 2.90 (m, 1 H, CH proton). R = neopentyl (CDCl$_3$): 1.08 (s, 9 H, Me$_3$C); 1.71 (d, $J_{\rm HF}$ = 17 Hz, 2 H, CH$_2$). R = PhOCH$_2$ (CD$_3$CN): 4.49 (d, $J_{\rm HF}$ = 9 Hz, 2 H, CH$_2$); 6.8–7.5 (m, 5 H, phenyl).

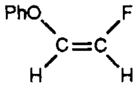
^{19}F NMR spectra were obtained for three of the new diazirines. Chemical shifts (solvents as above, δ relative to CFCl$_3$): R = cyclopropyl, −140.2 ppm (s); R = neopentyl, −133.4 (t, $J_{\rm HF}$ = 17 Hz); R = phenoxymethyl, −148.5 (t, $J_{\rm HF}$ = 9 Hz).

Chlorodiazirines. The cyclopropyl,[8a] cyclobutyl,[9,17] and phenoxymethyl[16] examples are known. All chlorodiazirines were prepared by Graham oxidation of the appropriate amidinium salts with "pool chlorine", an aqueous OCl$^-$ preparation that is ~12% in oxidant. The preparation of 3-chloro-3-neopentyldiazirine is presented as an example. A solution of 3 g (19.9 mmol) of neopentylamidinium chloride and 8 g (188 mmol) of LiCl in 150 mL of DMSO was placed in a 1-L, three-neck reaction flask that was fitted with a dropping funnel, a thermometer, and a mechanical stirrer. Pentane (100 mL) was added to the flask, stirring was initiated, and 100 mL of pool chlorine (saturated with NaCl) was then added via the dropping funnel at such a rate that the reaction temperature remained at ~30 °C during the addition. Stirring was continued for an additional 1 h after addition had been completed. The reaction solution was then diluted with 300 mL of cold water and transferred to a separatory funnel. The pentane phase was isolated, washed with water (3 × 200 mL), dried over CaCl$_2$, and reduced in volume as desired. The UV spectrum of the diazirine appears in Table III. The NMR spectrum (CDCl$_3$) showed singlets at δ 1.06 and 1.85 for the Me$_3$C and CH$_2$ protons, respectively.

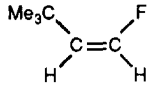
The more volatile cyclopropyl and cyclobutylchlorodiazirines were extracted into decane, rather than pentane, and treated as their fluorodiazirine analogues (see above).

Products. Pentane, isooctane, or CDCl$_3$ solutions of the chloro- or fluorodiazirines were irradiated at ~20 °C (λ > 320 nm) with a 200-W focused Osram XE UV lamp until the diazirines were destroyed. The products were either isolated by GC on SE-30 and characterized spectroscopically, or, if very volatile, they were examined by NMR methods in situ. Products (*Z*)- and (*E*)-**7**-Cl, **8**-Cl, **9**-Cl, and **10**-Cl have been described.[8,9,20] Alkenes (*Z*)- and (*E*)-1-chloro-2-phenoxyethene[16] showed δ (DMSO-d_6) (*Z* isomer) 5.85 (d, J = 4 Hz, ClCH=), 7.22 (d, J = 4 Hz, PhOCH=), 7.05–7.45 (m, PhO), (*E* isomer) 6.38 (d, J = 11 Hz, ClCH=), 7.01 (d, J = 11 Hz, PhOCH=), and 7.05–7.45 (m, PhO).

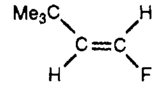
The analogous fluoroalkene products are new, and their NMR properties are described here with reference to formulas **6–10**.



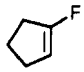
(*Z*)-**6**



(*Z*)-**7**



(*E*)-**7**



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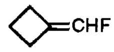

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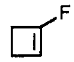

10

(*Z*)-**6**: ^{1}H NMR (DMSO-d_6) vinyl protons, δ 6.72 (dd, $J_{\rm HF}$ = 75 Hz, $J_{\rm HH}$ = 2.4 Hz, =CHF) and 6.54 (dd, $J_{\rm HF}$ = 26 Hz, $J_{\rm HH}$ = 2.4 Hz, PhOC*H*=); phenyl protons, 7.2–7.4 (m, 5 H); ^{19}F NMR (DMSO-d_6) 155.8 ppm upfield from CCl$_3$F (dd, $J_{\rm HF}$ = 75, 26 Hz).

(*Z*)-**7**: ^{1}H NMR (CDCl$_3$) vinyl protons, δ 6.23 (dd, $J_{\rm HF}$ = 85 Hz, $J_{\rm HH}$ = 5.4 Hz, =CHF) and 4.55 (dd, $J_{\rm HF}$ = 50 Hz, $J_{\rm HH}$ = 6 Hz, Me$_3$CCH=); Me$_3$C was obscured by pentane; ^{19}F NMR (CDCl$_3$) 130.4 ppm upfield from CCl$_3$F (dd, $J_{\rm HF}$ = 85, 50 Hz).

(*E*)-**7**: ^{1}H NMR (CDCl$_3$) vinyl protons, δ 6.46 (dd, $J_{\rm HF}$ = 86 Hz, $J_{\rm HH}$ = 11 Hz, =CHF) and 5.42 (dd, $J_{\rm HF}$ = 23 Hz, $J_{\rm HH}$ = 11 Hz, Me$_3$CCH=); Me$_3$C was obscured by pentane; ^{19}F NMR (CDCl$_3$) 141.7 ppm upfield from CCl$_3$F (dd, $J_{\rm HF}$ = 86, 23 Hz).

8: ^{1}H NMR (CDCl$_3$) δ 4.8–4.9 (m, 1 H, =CH), 1.9–2.2 (m's, 6 H, methylenes); ^{19}F NMR (CDCl$_3$) "singlet" 125.3 ppm unfield from CCl$_3$F. The very small HF coupling has been previously noted.[22]

9: ^{1}H NMR (CDCl$_3$) δ 6.15 (dm, $J_{\rm HF}$ = 85 Hz, 1 H, =CHF), 2.2–2.6 (m's, 6 H, methylenes); ^{19}F NMR (CDCl$_3$) 146.4 ppm upfield from CCl$_3$F (d, $J_{\rm HF}$ = 85 Hz).

10: ^{1}H NMR (CDCl$_3$) δ 4.74 (d, $J_{\rm HF}$ = 8.8 Hz, 1 H, =CH), 2.73 ("quintet", $J_{\rm HF}$ ~ 3 Hz, $J_{\rm HH}$ ~ 3 Hz, 2 H, CH$_2$CF), 1.98 (dm, $J_{\rm HF}$ = 16 Hz, $J_{\rm HH}$ ~ 3, 1 Hz, CH_2CH); ^{19}F NMR (CDCl$_3$) m at 84.5 ppm upfield from CCl$_3$F.

As further substantiation of the structures of the fluoroalkenes, we obtained GC–MS parent ions for (*Z*)-**7** and (*E*)-**7** (*m*/*e* 102, M$^+$, each isomer), **8** and **9** (*m*/*e* 86, M$^+$, each isomer), and **10** (*m*/*e* at 72, M$^+$). An appropriate elemental analysis (C, H) was obtained for (*Z*)-**6**.

The yields and purities of these products are discussed in detail in the Results and Discussion. The yields quoted for the reactions of carbenes **3**-Cl, **3**-F, **4**-Cl, and **4**-F are absolute, relative to their diazirine precursors, and were obtained by NMR integration vs CHCl$_3$ or CH$_2$Cl$_2$ internal standards. For the rearrangements of carbenes **1**-Cl, **1**-F, **2**-Cl, and **2**-F yields are not absolute, but GC, ^{1}H, and (where applicable) ^{19}F NMR spectroscopy demonstrated the absence of any but the indicated products. In particular, NMR supplied no evidence for the formation of polymer, azine, or carbene dimers.

Kinetics. Kinetic methodology and results are extensively described above, illustrated by Figures 1 and 2, and summarized in Tables I and II.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. 1 (X = Cl), 104678-23-1; **1** (X = F), 137720-23-1; **2** (X = Cl), 137742-09-7; **2** (X = F), 137720-24-2; **3** (X = Cl), 71946-84-4; **3** (X = F), 137720-25-3; **4** (X = F), 120159-08-2; (*Z*)-**6**, 137720-26-4; (*Z*)-**7**, 6418-03-7; (*E*)-**7**, 5063-68-3; **8**, 27415-42-5; **9**, 137720-27-5; **10**, 53661-90-8.