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Fluorinated Carbenes

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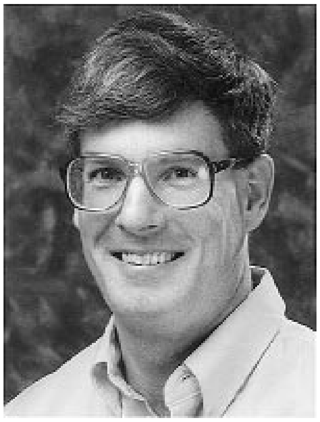
Contents

I. Introduction

Replacement of hydrogen by fluorine can have some dramatic effects on the structure, stability, and reactivity of organic molecules.[1−4] This is especially true for reactive intermediates such as carbenes. While it is well known that fluorine is the most electronegative element, the idea that fluorine can donate electron density to a π system using one of its lone pairs is not as well appreciated. For instance, fluorine can act as a slightly activating ortho−para director in electrophilic aromatic substitution.[3] Because of this π-donating ability, attachment of fluorine directly onto the divalent carbon of a carbene stabilizes the singlet state relative to the triplet.[5,6] This interaction can be expressed in resonance

Dana Lyn S. Brahms was born on July 28, 1969 in Honolulu, HI, and was recently married there to John C. Brahms. She received a Bachelor of Arts degree in chemistry and mathematics from Claremont McKenna College in 1991, where she did undergraduate research with Professor Kersey Black. Ms. Brahms is currently pursuing a Ph.D. in physical-organic chemistry under the direction of Professor Dailey at the University of Pennsylvania. Her research involves the investigation of halocarbenes with the use of low-temperature matrix isolation techniques. Ms. Brahms is an avid figure skater and also enjoys roller blading and swimming.



Bill Dailey was born in 1957 in Elmira, NY, but spent most of his early life in Simsbury, CT. He received his B.S. from the University of Connecticut in 1979 and the Ph.D. from Dartmouth College in 1983 where he studied with Dave Lemal in the area of fluorine-containing strained-ring and annulene chemistry. After two wonderful and productive years of postdoctoral study in the laboratory of Ken Wiberg at Yale University where he investigated the fundamental properties of [1.1.1]propellane and learned the art of low-temperature matrix isolation, Bill accepted a position as Assistant Professor at the University of Pennsylvania. He is currently an Associate Professor and Undergraduate Chair of Chemistry. Current research interests in the Dailey group include the study of reactive intermediates, strained-ring chemistry, fluorocarbon synthesis, and mechanistic studies using a combination of experimental and computational techniques. Bill is an avid backyard gardener and fruit grower and maintains a large collection of rare fruit tree varieties trained in various espalier forms. He also enjoys playing his 5-string banjo which is sometimes less appreciated by his wife, Betsy, and their two daughters, Katherine, 9, and Jennifer, 6.

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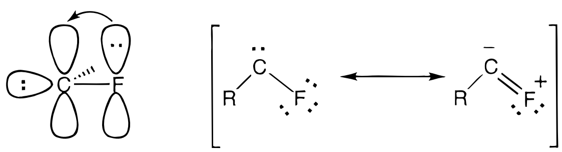
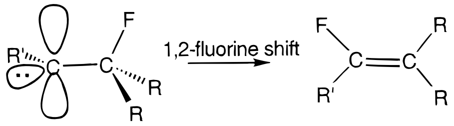


When fluorine atoms are attached to the carbon adjacent to a carbene center, the strength and the electron deficient nature of the C−F bond serve to inhibit 1,2-fluorine atom migration to form an alkene.[7,8] Thus, fluorine directly attached to a carbene center will thermodynamically stabilize the carbene, while fluorine substitution on the carbon atom adjacent to the carbene carbon will kinetically stabilize the carbene by inhibiting 1,2 rearrangements. The increased thermodynamic and kinetic stability imparted by fluorine has been exploited to investigate carbenes for which information on the hydrocarbon counterparts is difficult to obtain.



Since the reactivity and structure of a carbene depends strongly on its spin state,[9−12] this paper will be organized according to the ground state multiplicity of the fluorinated carbene. An exhaustive listing of the literature pertaining to all carbenes containing fluorine substituents has not been attempted. Rather, this paper will focus on carbenes that contain fluorine either directly attached to the carbene carbon or in close proximity to it. There are several excellent earlier reviews of fluorocarbenes.[13−17] In addition, there are many reviews available that include work on fluorine-containing carbenes.[9−12,18−25]

II. Singlet Carbenes

A. Fluoromethylenes

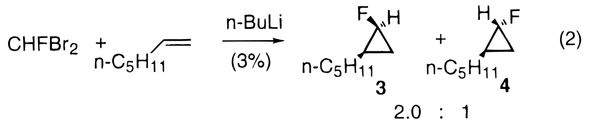
The first class of carbenes considered in this paper are the fluoromethylenes (CFX), carbenes with at least one fluorine substituent directly bonded to the carbene center.

1. Fluorocarbene

Several methods have been developed for the generation of fluorocarbene (**1**). In general, these methods are not as efficient or convenient as preparations for other halo- and dihalocarbenes. If the researcher's goal is the preparation of a monofluorocyclopropane, other methods may in fact be more convenient. Much work has been reported on the dehalogenation of 1-bromo-1-fluorocyclopropanes or 1-chloro-1-fluorocyclopropanes.[16] These compounds can be prepared by the reaction of alkenes with bromofluorocarbene and chlorofluorocarbene, respectively, generally in high yields.

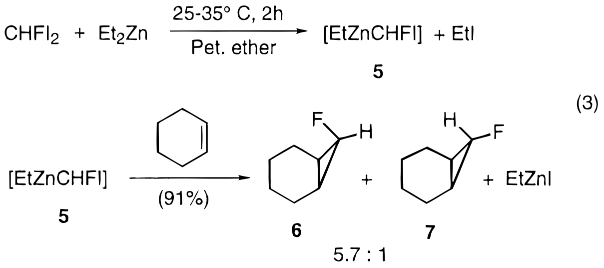
Schlosser and Heinz produced fluorocarbene (**1**) from the reaction of dibromofluoromethane with *n*-butyllithium at low temperature and trapped the carbene with various alkenes.[26] The reaction proceeds by metal−halogen exchange to give the bromofluoromethyl anion (**2**), which loses bromide to generate fluorocarbene (eq 1). The addition of **1** to

$$\mathrm{CHFBr_2} \xrightarrow{n\text{-BuLi}} n\text{-BuBr} + \underset{\mathbf{2}}{\left[{}^{-}\mathrm{CHFBr}\right]} \xrightarrow{-\mathrm{Br}^{-}} \underset{\mathbf{1}}{\left[:\mathrm{CHF}\right]} \qquad (1)$$



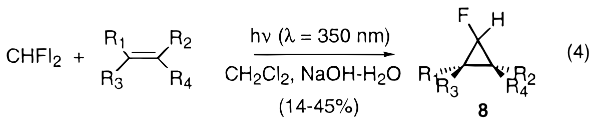
alkenes occurred stereospecifically, with retention of alkene configuration, and stereoselectively, favoring the syn mode of addition over the anti mode (eq 2).[26,27] The alkenes employed in this study were cyclohexene, 2,3-dimethyl-2-butene, heptene, *trans*-4-octene, *cis*-4-octene, and hexene. In the case of heptene the syn adduct **3** was formed in a 2.0:1 ratio to the anti adduct **4**. Cyclohexene, *cis*-4-octene, and hexene showed similar selectivities. However, the yields in these cyclopropanations were low, ranging from 10% for 2,3-dimethyl-2-butene to 2% for *trans*-4-octene.

The reaction of fluorodiiodomethane with diethylzinc in the presence of cyclohexene produced a 91% yield of 7-fluoronorcarane (**6** and **7**) with an endo/exo isomer ratio of 5.7 (eq 3).[28] The reaction was



postulated to proceed through an organozinc carbenoid intermediate (**5**). While the use of the pyrophoric diethylzinc reagent makes this procedure less attractive on a large scale,[29] it has been used to prepare fluorocyclopropylamines in fair to good yield and moderate to excellent cis-selectivity.[30,31] Copper has been used in place of diethylzinc to accomplish the same transformation,[32] but much longer reaction times were required.

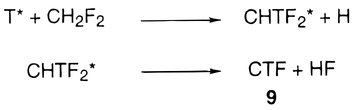
Irradiation ($\lambda > 280$ nm) of dibromofluoromethane in the presence of cyclohexene also afforded **6** and **7** but in low yield.[33] In a related reaction, photolysis ($\lambda = 350$ nm) of fluorodiiodomethane in the presence of various olefins provided synthetically useful preparations of monofluorocyclopropanes **8** (eq 4).[29] 2,3-Dimethyl-2-butene was cyclopropanated in 45% yield, 2-methyl-2-butene (syn/anti ratio = 1.1) and *trans*-4-methyl-2-pentene in 37% yield, *cis*-4-methyl-2-pentene in 36% yield (0.8 syn/anti ratio), cyclohexene in 40% yield (1.0 syn/anti ratio), and 2-methylpentene and hexene in 14% yield (1.2 syn/anti ratio). In



addition, the cyclopropanations were stereospecific, as shown by the reactions with *cis*- and *trans*-4-methyl-2-pentene.

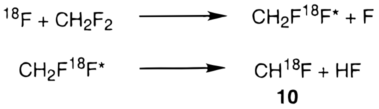
Tang and Rowland produced tritiated fluorocarbene, CTF (**9**), by the unimolecular decomposition of excited CHTFX* formed by energetic tritium atom reactions with polyhalomethanes such as CH_2F_2, CH_2FCl, and CHF_3 (Scheme 1).[34,35]

Scheme 1

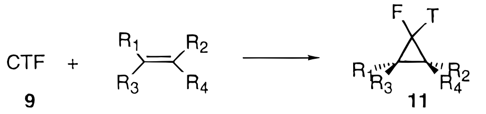


Tang, Smail, and Rowland also prepared fluorine-18-labeled fluorocarbene (**10**), $CH^{18}F$, by the reaction of CH_2F_2 or CHF_3 with energetic ^{18}F atoms from nuclear recoil (Scheme 2).[36,37]

Scheme 2

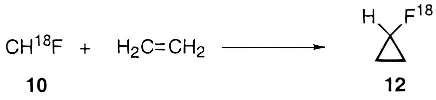


The tritiated fluorocarbene (CTF) produced by Tang and Rowland was shown to react with various alkenes in the gas phase to form the corresponding fluorocyclopropanes (eq 5).[35] The alkenes used in this study included ethene, propene, butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. In all cases for which two isomers were possible, equal yields of both the syn and anti product were observed, and the addition to *cis*- and *trans*-2-butenes took place with complete stereospecificity. The reactivity of CTF toward the alkenes increased with increasing alkyl substitution, with 2,3-dimethyl-2-butene being six times more reactive than ethene. No CH insertion products were observed.



(5)

$CH^{18}F$ also readily reacted with ethene to form the corresponding ^{18}F-labeled cyclopropane (**12**) as well as with HCl to form the direct insertion product $CH_2{}^{18}FCl$ (**13**) (eqs 6 and 7).[37]



(6)

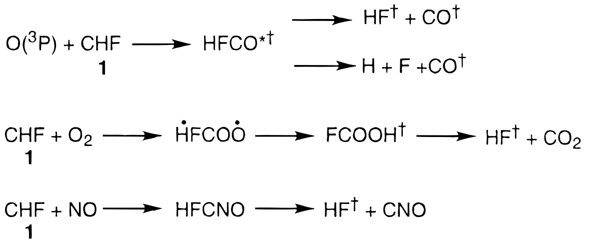
$$\underset{\mathbf{10}}{CH^{18}F} + HCl \longrightarrow \underset{\mathbf{13}}{CH_2{}^{18}FCl} \qquad (7)$$

Samxonov and Petrov studied the addition of excited CHF molecules to ethene forming excited monofluorocyclopropanes.[38] These adducts then either isomerized to a mixture of monofluoropropenes or were stabilized by collisions, with the ratio of fluorocyclopropene to fluoropropene increasing with increasing ethene pressure.

De Zarate et al. examined the removal rates of CHF by collision with various alkenes including ethene, propene, butene, 2-methylpropene, and 1,3-butadiene, as well as with nitric oxide, argon, and difluoromethane.[39-41] The removal processes were found to be second order, and the rate constants increased with increasing double bond substitution.

Fluoromethylene reacted with O_2,[42] NO,[43] and $O(^3P)$,[44] generating vibrationally excited HF molecules. These reactions were believed to occur by the four-centered elimination processes shown in Scheme 3, with * indicating electronic excitation and † indicating vibrational excitation.

Scheme 3



Hancock and Ketley reported a similar reaction of CHF with NO but negligible bimolecular reaction between CHF and O_2 in their kinetic studies involving the use of time-resolved laser-induced fluorescence to monitor the rates of CHF removal in the presence of added gases.[45] Hancock et al. also reported the reaction of ground state CHF and O and N atoms.[46] In the reaction with ground state O atoms, vacuum-UV emission was observed and assigned to the CO (A^1) state. In the reaction with N atoms, $CN(B^2\Sigma^+)$ luminescence was observed. By use of time-resolved fourier transform infrared emission, the reaction of $O(^3P)$ with ground state CHF was further studied and both HF and CO emissions were clearly identified.[47,48] Tsai and McFadden studied the rate constants for the reaction of CHF with atomic hydrogen, nitrogen, and oxygen using a gas flow system with photoionization mass spectrometry detection.[49]

Other methods of CHF generation include the following: the argon resonance photoionization of argon$-CH_2F_2$ samples during condensation at 15 K,[50] the multiple-photon dissociation of CH_2FCl or CH_2F_2 in laser-induced fluorescence studies[39-41,45,46,51-53] and time-resolved Fourier-transform infrared emission studies,[47,48] the reaction of halomethanes with the microwave discharge products of CF_4,[54-63] the high pressure reaction of fluorine atoms with organic iodides,[64,65] organosulfur, or other hydrogen-bearing compounds,[66,67] the reaction of F with dimethyl sulfide in the presence of excess F_2,[68] the reaction of vibrationally excited singlet methylene with HF,[69] the electron-impact dissociation of CHF_3,[70] and the dissociation of CH_2F_2 and CH_2FCl in a radiofrequency discharge.[49]

Much effort has been spent on determining the structure of fluorocarbene. From their rotational analysis, Merer and Travis determined that the ground state singlet structure of fluoromethylene had a C−F bond length of 1.31 Å and a ∠HCF bond angle of 101.8°.[71] These values were based on an assumed

C−H bond length of 1.12 Å. More recent work has allowed the determination of the singlet and triplet structure of fluoromethylene.[55,56] On the basis of an analysis of the laser excitation spectrum, Suzuki and co-workers determined that the singlet had a molecular geometry with C−F = 1.305 Å, C−H = 1.138 Å, and ∠HCF = 104.1°. For the triplet, the structural parameters were determined to be C−F = 1.308 Å, C−H = 1.063 Å, and ∠HCF = 123.8°.

Since the reactivity and selectivity of a carbene is in part guided by its ground state multiplicity and on the energy difference between the singlet and triplet states, there has been much emphasis placed on determining this energy difference and the effect that substitution has on this value. Murray et al. determined the upper boundary of the singlet−triplet energy gap as 14.7 ± 0.2 kcal/mol by photoelectron spectroscopy with the singlet as the ground state.[72] More recently, Gilles et al. estimated an energy difference of 14.9 ± 0.4 kcal/mol based on negative ion photoelectron spectroscopic results and ab initio calculations simulating the Franck−Condon envelope for the triplet state.[73] Many calculations have been reported for singlet and triplet fluorocarbene.[6,74−107] While the structural parameters are well reproduced at many levels of theory, the accurate determination of the energy difference between the singlet and triplet states has been a challenge to computational chemists. However, if large basis sets and extensive electron correlation are included, calculations can reproduce the experimental value for the singlet−triplet gap almost within experimental error.[108,109]

Early estimates of the heat of formation of monofluoromethylene ranged from 25 to 39 kcal/mol.[37,110,111] More recently, Pritchard, Nilsson, and Kirtman reported a value of 39 ± 3 kcal/mol[112] based on the result that the reaction (eq 8)

$$CFH_2 + C_2H_5 \longrightarrow \underset{1}{CHF} + C_2H_6 \qquad (8)$$

occurs and must then be exothermic, whereas the reaction (eq 9)

$$CFH_2 + CFH_2 \longrightarrow \underset{1}{CHF} + CFH_3 \qquad (9)$$

does not take place and was considered to be endothermic. Thus, assuming that $\Delta H_f°(CFH_2) = -7.6 \pm 7$ kcal/mol, the heat of formation of monofluoromethylene was assigned limits of ≤38.8 ± 2.0 and ≥41.6 ± 6.0 kcal/mol. Lias, Karpas, and Liebman reported a value of 26 ± 3 kcal/mol.[113] Their results are based on the occurrence or nonoccurrence of acid−base reactions of the type (eq 10)

$$CFH_2^+ + B \longrightarrow BH^+ + \underset{1}{CHF} \qquad (10)$$

examined for a series of bases. CFH_2^+ was shown to transfer a proton to C_2H_5CN (proton affinity = 192.6 kcal/mol) but not to $(CH_3)_2O$ (proton affinity = 192.1 kcal/mol), which yielded an estimate of 193 kcal/mol for the proton affinity of CFH. Using this value and $\Delta H_f°(CFH_2^+) = 199$ kcal/mol,[114] $\Delta H_f°(CHF) = 26 \pm 3$ kcal/mol was obtained. On the basis of ab initio calculations at the MP4SDTQ/6-311++G(2df,p) level, Rodriquez and Hopkinson estimated that the heat of formation of singlet monofluoromethylene was 33.9 kcal/mol.[92] Recently, Born, Ingemann, and Nibbering derived $\Delta H_f°(CHF) = 37.52 \pm 18$ kcal/mol from the C−H bond dissociation energies of the CH_2F radical.[115]

In 1966, Merer and Travis reported a transient absorption spectrum belonging to CHF, produced by the flash photolysis of dibromofluoromethane.[71] Similarly, Gordon and Lin produced CHF by the photolysis of $CHFCl_2$[42] or $CHFBr_2$ in a Suprasil tube.[43,44,111] This reaction presumably occurs through the successive photodetachments of 2 Cl or Br atoms (eqs 11 and 12).

$$CHFCl_2 \xrightarrow{\lambda \geq 165\ \text{nm}} \underset{1}{[\,CHF\,]} + 2\,Cl \qquad (11)$$

$$CHFBr_2 \xrightarrow{\lambda \geq 200\ \text{nm}} \underset{1}{[\,CHF\,]} + 2\,Br \qquad (12)$$

Other similar preparations based on the gas phase photolysis of $CHFCl_2$[116] and $CHFBr_2$[117] subsequently followed. The UV/vis absorption spectrum for singlet fluorocarbene occurs between 410 and 540 nm.[50,71,118] Calculations at the CIS/DZ+P level predicted a λ_{max} value of 477 nm.[119]

Jacox and Milligan first reported the infrared spectrum of CHF and isotopically labeled CDF and $C^{13}HF$ produced by the vacuum-UV photolysis of methyl fluoride in argon and nitrogen matrices.[118] Since this time, numerous infrared spectroscopic studies have been reported for fluoromethylene.[57,72,92,93] The three fundamental vibrations occur at 2645, 1403, and 1182 cm^{-1}.[59,60,71,118,120]

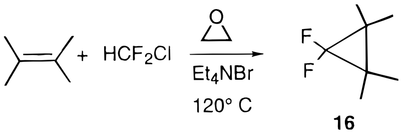
2. Difluorocarbene

Many methods have been developed for the generation of difluorocarbene (**14**).[15−17] The choice of method depends on whether difluorocarbene is needed for spectroscopic study or chemical reaction. Because there are two fluorine atoms interacting with the carbene center, difluorocarbene is more highly stabilized and less reactive than other halo, and dihalocarbenes. While electron-rich substrates react easily with difluorocarbene under mild conditions, less nucleophilic substrates do not. This has led to the development of higher temperature methods for difluorocarbene generation.

Dehydrohalogenation of chlorodifluoromethane[121] or bromodifluoromethane[122] using alkoxides or alkyllithium has been used to generate difluorocarbene in the presence of alkenes. However, these methods generally give poor yields of difluorocyclopropanes. On the basis of mechanistic studies, the dehydrohalogenation reaction was postulated to proceed directly to difluorocarbene by concerted loss of proton and chloride or bromide ion (eq 13).[122,123] The generally low yields of cyclopropanes obtained in these reactions are due to the facile addition of strong base to difluorocarbene.

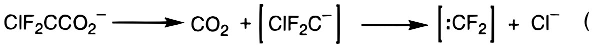
$$HCF_2Cl \xrightarrow{HO^-} \underset{\mathbf{15}}{[\,{}^-CF_2Cl\,]} \longrightarrow \underset{\mathbf{14}}{[\,:CF_2\,]} + Cl^- \qquad (13)$$

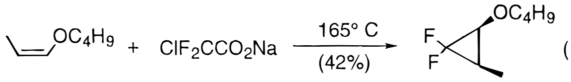
If reaction between difluorocarbene and base is minimized by conducting the process under conditions where only a low concentration of base is present (refer to Scheme 7), the dehalogenation method can give excellent yields of difluorocyclopropanes with electron-rich alkenes (eq 14).[124]



16
(100%)
(14)

Thermolysis of sodium chlorodifluoroacetate was established as the first method of difluorocarbene transfer to several alkenes.[125] Yields are generally modest, but the reaction is easy to perform (eq 16).[126,127] The reaction proceeds by loss of carbon dioxide and loss of chloride ion (eq 15). This method was used to cyclopropanate unsaturated ketones in $\Delta^{4,6}$- and $\Delta^{1,4,6}$-3-ketosteroids.[128–130] Other metal salts of chlorodifluoroacetate besides sodium may perform better in certain cases.[131]

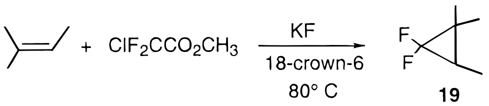

$$\underset{\mathbf{17}}{ClF_2CCO_2^-} \longrightarrow CO_2 + \underset{\mathbf{15}}{\left[ClF_2C^-\right]} \longrightarrow \underset{\mathbf{14}}{\left[:CF_2\right]} + Cl^- \quad (15)$$



18
(16)

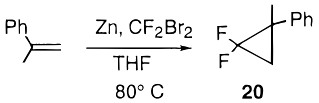
Early kinetic studies in aqueous solutions indicated that the decomposition produces difluorocarbene by a concerted loss of carbon dioxide and chloride ion.[132] However, there is evidence that decarboxylation in nonhydroxylic solvents produces chlorodifluoromethyl anion (**15**) with a finite lifetime.[133] The chlorodifluoromethyl anion has been observed in the gas phase.[134]

In a closely related reaction, treatment of methyl chlorodifluoroacetate with LiCl or KF/18-crown-6 at 80 °C produced good yields of difluorocyclopropanes with electron-rich alkenes (eq 17).[126,135] Modest to poor yields of cyclopropane are obtained with less electron-rich alkenes. For instance, 2,3-dimethyl-2-butene gives an 85% yield of adduct, while cyclohexene yields only 15% of cyclopropane under similar conditions.



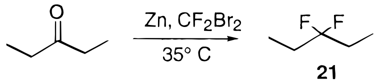
19
(38%)
(17)

Dolbier and co-workers reported a room-temperature reaction, similar to the Simmons–Smith reaction, between dibromodifluoromethane and zinc in THF as a method of forming difluorocyclopropanes from alkenes (eq 18).[136] Yields of difluorocyclopropanes can be excellent with electron-rich alkenes but tend to be poor with less reactive substrates. A relatively unencumbered difluorocarbenoid or free difluorocarbene was suggested as the reactive species, based on a comparison of the relative reactivity of difluorocarbene generated in this manner with that produced by other methods. Some of the other alkenes and yields reported included 2,3-dimethyl-2-butene (96%), phenylcyclopentene (84%), 2-methyl-2-butene (40%), cyclopentadiene (21%), and cyclohexene (7%).



20
(71%)
(18)

Similar conditions using dibromodifluoromethane and zinc reportedly convert carbonyl compounds into *gem*-difluoro compounds in low to moderate yield (eq 19).[137] The authors suggest that difluorocarbene reacts with the carbonyl compound to form a carbonyl ylide **22** that breaks down to give the *gem*-difluoro compound (eq 20).



21
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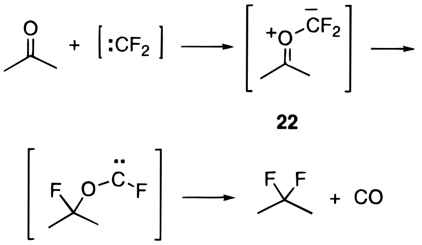
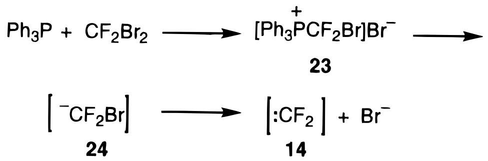
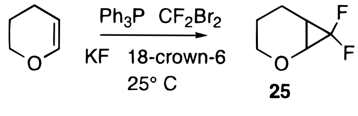
(19)



22
(20)

Another method that uses dibromodifluoromethane to generate difluorocarbene was developed by Burton and Naae.[138] They found that phosphonium salt **23,** formed from dibromodifluoromethane and triphenylphosphine, could transfer difluorocarbene to alkenes when treated with cesium fluoride in a dry ether solvent at room temperature (eq 21). In this manner, electron-rich alkenes were converted to *gem*-difluorocyclopropanes in good yields. Mechanistic studies suggest that (bromodifluoromethyl)triphenylphosphonium bromide (**23**) is converted directly to difluorocarbene (**14**), effectively bypassing the bromodifluoromethyl anion (**24**).[139] The use of potassium fluoride and a catalytic amount of 18-crown-6 has been reported to increase the yields of products (eq 22).[127] This and the previously described $CBr_2F_2/Zn/THF$ procedure are very mild methods for the generation of difluorocyclopropanes, especially those that are thermally unstable. They are the methods of


$$Ph_3P + CF_2Br_2 \longrightarrow \underset{\mathbf{23}}{[Ph_3\overset{+}{P}CF_2Br]Br^-} \longrightarrow$$
$$\underset{\mathbf{24}}{\left[{}^-CF_2Br\right]} \longrightarrow \underset{\mathbf{14}}{\left[:CF_2\right]} + Br^- \quad (21)$$

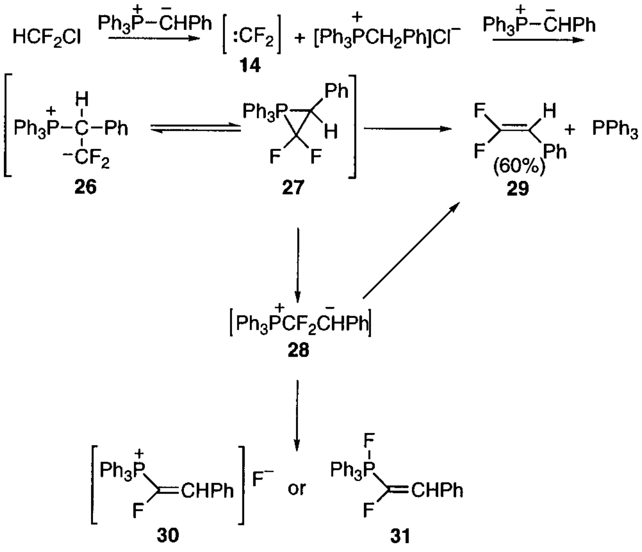


25
(85%)
(22)

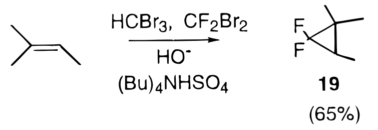
choice for the formation of *gem*-difluorocyclopropanes from electron-rich alkenes.

Wheaton and Burton developed a method for difluoromethylene generation that has been used in the synthesis of 1,1-difluoroalkenes.[140] In this reaction, a primary or secondary ylide dehydrochlorinates chlorodifluoromethane, producing **14**. A second equivalent of the ylide traps carbene **14**, and the decomposition of the intermediate affords difluoroalkene (Scheme 4). Steam distillation of the product mixtures, from the reactions of ylides containing carbanion-stabilizing groups, resulted in the identification of *gem*-hydrofluoroolefins in addition to the difluoroolefins. This was explained by the formation of vinylphosphonium salts or vinylphosphoranes that hydrolyzed during the distillation. Moderate to excellent alkene yields were obtained ranging from 12 to 80% (isolated yield). However, ylides containing highly electron-withdrawing substituents reacted very poorly.

Scheme 4



Jonczyk and co-workers[141,142] reported a different method of preparing *gem*-difluorocyclopropanes from dibromodifluoromethane. Phase transfer reaction conditions using 60% KOH solution, bromoform, and dibromodifluoromethane allowed the formation of difluorocyclopropanes in modest to good yield from electron-rich alkenes (eq 23). Remarkably, only small amounts of dibromocarbene adducts were obtained in competition with the difluorocarbene adducts. The authors propose the following mechanism to account for this reaction (eq 24). In particular, the reaction of tribromomethyl anion with dibromodifluoromethane to produce tetrabromomethane and bromodifluoromethyl anion (**24**) is implied to be faster than its fragmentation to dibromocarbene.

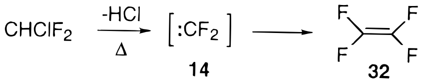


(23)

$$HCBr_3 + HO^- \rightleftharpoons {}^-CBr_3 \xrightarrow{CF_2Br_2}$$
$$CBr_4 + \underset{\mathbf{24}}{\left[{}^-CF_2Br\right]} \longrightarrow \underset{\mathbf{14}}{\left[:CF_2\right]} + Br^- \qquad (24)$$

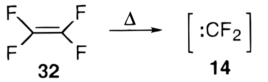
Other methods for the conversion of dibromodifluoromethane to difluorocarbene include reaction with lead[143] and electrochemical reduction.[144] Neither has any synthetic advantage over the other methods.

The formation of difluorocarbene from the thermolysis of fluorinated compounds is an important industrial reaction.[4,13] The thermolysis of chlorodifluoromethane at temperatures above 700 °C is used to prepare tetrafluoroethene (eq 25).



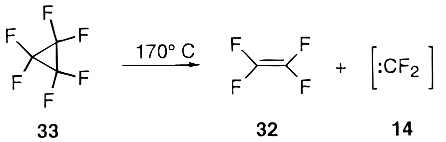
(25)

Pyrolysis of tetrafluoroethene, or poly(tetrafluoroethene) also leads to production of difluorocarbene[4,13] (eq 26).

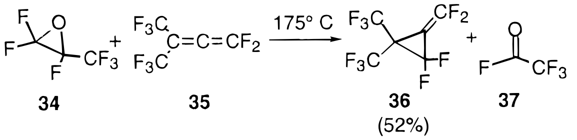


(26)

Milder thermal sources of difluorocarbene are strained ring fluorocarbons containing three-membered rings. Perfluorocyclopropane (**33**), when heated above 165 °C,[145−147] or hexafluoropropylene oxide (**34**),[148] when heated above 150 °C,[149] have both been used as difluorocarbene sources (eq 27). These conditions permit reaction between less reactive alkenes and difluorocarbene to form difluorocyclopropanes (eq 28). Hexafluoropropylene oxide is especially useful because of its commercial availability. In addition, the volatile byproduct, trifluoroacetyl fluoride (**37**), can easily be removed from the reaction mixture.

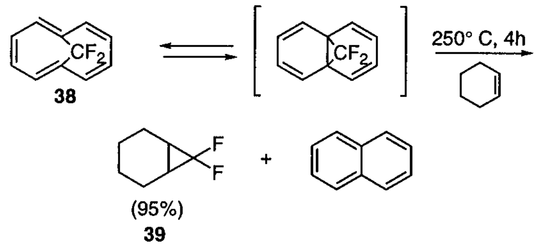


(27)



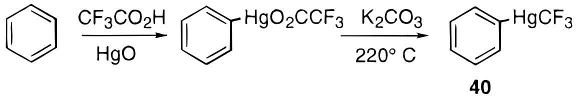
(28)

Another thermal source for difluorocarbene is 11,11-difluoromethano[10]annulene.[150] The pyrolysis of **38** at 450 °C gave a near-quantitative yield of naphthalene. In the presence of cyclohexene, 7,7-difluoronorcarane (**39**) was formed in 95% yield at 250 °C (eq 29).



(29)

Various organometallic reagents have been used as sources of difluorocarbene. This category includes organomercury, organotin, organocadmium, organosilicon, and organophosphorous compounds. The use of these compounds as sources of fluorocarbenes has been reviewed,[16,17] so only a brief discussion will be given here. Probably the most commonly used source of difluorocarbene in this category is $PhHgCF_3$ (**40**), which was developed by Seyferth and co-workers.[151] While the initially reported synthesis is quite tedious, Knunyants and co-workers reported a relatively convenient two-step preparation of **40** starting with benzene, trifluoroacetic acid, and mercuric oxide (eq 30).[152] Additionally, Burton and Kesling have developed a convenient alternative "in situ" method that does not require isolation and purification of **40** (eq 31).[16] However, experimental details have not yet been published.

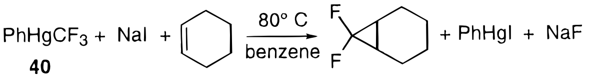


(30)

40
(70% overall yield)

$$PhHgCl + KF + \underset{\mathbf{23}}{[Ph_3\overset{+}{P}CF_2Br]Br^-} \longrightarrow \underset{\substack{\mathbf{40}\\(40\%)}}{PhHgCF_3} + KCl + Ph_3PF_2 \quad (31)$$

Although $PhHgCF_3$ is not a thermal source of difluorocarbene, it can transfer difluorocarbene under the appropriate conditions. When treated with sodium iodide at 80 °C, **40** transferred difluorocarbene to alkenes forming difluorocyclopropanes in good yields (eq 32).[151,153,154] Even electron-deficient alkenes produced difluorocyclopropanes in modest yields using this reagent. For instance, acrylonitrile gave a 26% yield of difluorocyclopropane.



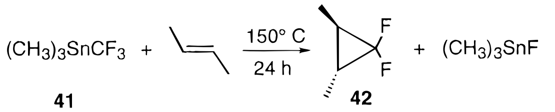
(32)

40 **39**
(83%)

In contrast to the organomercurial, trimethyl(trifluoromethyl)tin (**41**) when heated to 150 °C liberates difluorocarbene, which can be trapped with alkenes to form difluorocyclopropanes in good yields (eq 34).[155,156] Alkynes have also been used with success (eq 35), as well as trifluoropropynyl derivatives $(CH_3)_2AsC{\equiv}CCF_3$ (~50% yield), $(CH_3)_3SiC{\equiv}CCF_3$ (~90%), and $(C_2H_5)_3GeC{\equiv}CCF_3$ (~90%) (eq 36).[157] Lower temperatures can be used if sodium iodide is added.[158] The main drawback to **41** as a source of difluorocarbene is its difficult synthesis. However, Burton and Kesling have developed a more convenient preparation,[16] and experimental details have appeared (eq 33).[159]

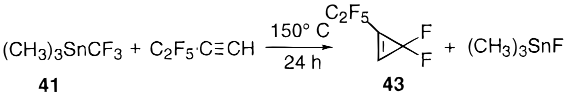
Even milder, purely thermal sources of difluorocarbene include CF_3SiF_3 (**45**),[160] and $(CF_3)_3PF_2$.[146,161-164] Of the two, **45** is the more convenient compound since an improved synthesis has been reported (eq 37).[165] Decomposition of **45** to difluorocarbene and tetrafluorosilane begins at 80 °C and has a half-life of 7 min at 100 °C. So far, there are few reports of difluorocyclopropanation of alkenes using **45** but it has found use in the preparation of difluoromethylsilanes that are otherwise difficult to prepare (eq 38).[165]

$$(CH_3)_3SnCl + KF + \underset{\mathbf{23}}{[Ph_3\overset{+}{P}CF_2Br]Br^-} \longrightarrow \underset{\substack{\mathbf{41}\\(36\%)}}{(CH_3)_3SnCF_3} \quad (33)$$



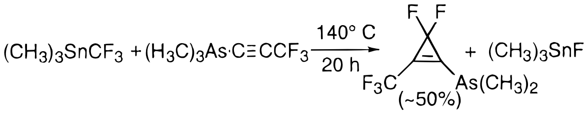
(34)

41 **42**
(91%)



(35)

41 **43**
(24%)



(36)

(~50%)
41 **44**

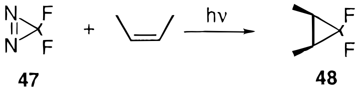
$$SiCl_4 \xrightarrow[(50\%)]{P(NEt_2)_3/CF_3Br} CF_3SiCl_3 \xrightarrow[(62\%)]{SbF_3} \underset{\mathbf{45}}{CF_3SiF_3} \quad (37)$$

$$\underset{\mathbf{45}}{CF_3SiF_3} + SiH_3Cl \xrightarrow[2\ h]{100°\ C} \underset{\substack{\mathbf{46}\\(60\%)}}{(CHF_2)SiH_2Cl} + SiF_4 \quad (38)$$

The thermal decomposition of the related compounds, CF_3SiH_3 and $(CF_3)_2SiH_2$, began at ~200 and ~100 °C, respectively.[166] The reaction was catalyzed by KF, and the carbene was quantitatively trapped by HBr. However, in the presence of a less reactive trapping agent such as cyclohexene, cyclopropanation was accompanied by secondary reactions.

The reaction of bis(trifluoromethyl)cadmium:glyme[167] with acid bromides in the presence of alkenes generates difluorocyclopropanes in good yields at temperatures as low as −78 °C. Also, treatment of compounds such as $FO_2SCF_2CO_2CH_3$ with nucleophiles generates products consistent with the intermediacy of difluorocarbene.[168-170]

Difluorodiazirine (**47**) is especially noteworthy since it is one of the few convenient photochemical sources of difluorocarbene.[171] When heated above 165 °C, it is also a thermal source of difluorocarbene. Reactions with alkenes give good yields of difluorocyclopropanes (eq 39).[172-174] However, drawbacks include its potentially explosive nature and the requirement of an elemental fluorination step during preparation. Photochemical decomposition of **47** in the gas phase with various alkenes allowed the determination of the relative reactivities of several alkenes toward free difluorocarbene.[173] Difluorodiazirine has been used to prepare and spectroscopically observe difluorocarbene under matrix isolation and gas phase conditions.[175,176]



(39)

47 **48**

Other photochemical methods for the preparation of difluorocarbene include the photolysis of tetrafluoroethene,[177-179] the multiphoton infrared laser irradiation of CF_2HCl,[180,181] CF_2Cl_2,[182] CF_2Br_2,[183,184] CF_2I_2,[185,186] CF_2ClBr,[187] and CDF_3,[188] and the electron-impact dissociation of CHF_3.[70]

Tang, Smail, and Rowland produced $CF^{18}F$ (**49**) by the reaction of CH_2F_2, CHF_3, or CF_4 with energetic ^{18}F atoms from nuclear recoil (Scheme 5).[36,37]

Scheme 5

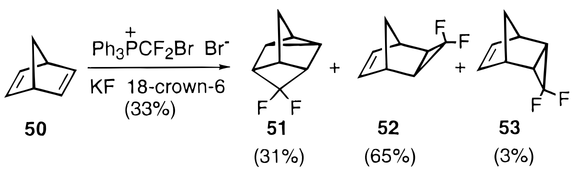
$$^{18}F + CH_2F_2 \longrightarrow CHF_2{}^{18}F^* + H$$

$$CHF_2{}^{18}F^* + H \longrightarrow \underset{\mathbf{49}}{CF^{18}F} + HF$$

The $CF^{18}F$ produced by Tang, Smail, and Rowland was shown to be unreactive toward ethene, although substituted olefins such as propene and the butenes were more reactive.[37] Other carbene scavengers such as the hydrogen halides readily reacted with $CF^{18}F$. The order of increasing reactivity, HCl > HBr > HI, was obtained by direct competition studies, with HI about 70 times as efficient as HBr, which was about 50 times more reactive than HCl. The scavenging of $CF^{18}F$ by HI was shown to be so much more efficient than by $CF_2{=}CF_2$ that no cyclopropane adduct was observed in the $HI-CF_2{=}CF_2$ system.

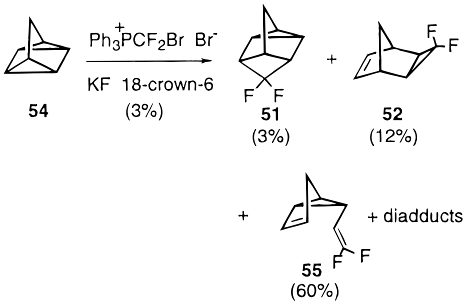
Relative rates of difluorocarbene addition to alkenes have been studied by competition methods.[173] At 36 °C, the relative rates of addition to a set of alkenes were 2,3-dimethyl-2-butene (13.1), 2-methyl-2-butene (3.5), 2-methylpropene (1.0), *cis*-2-butene (0.065), and *trans*-2-butene (0.74). According to Moss' carbene selectivity index, difluorocarbene is the most selective electrophilic carbene.[189-193] Limited competition studies have demonstrated that alkynes are more reactive than alkenes toward difluorocarbene. Difluorocarbene addition to octyne and 4-octyne occurs 2 and 10 times faster, respectively, than addition to *cis*-4-octene at 25 °C.[194] However it has been shown that there can be a large temperature dependence on selectivity. Giese and co-workers demonstrated that the selectivity of difluorocarbene addition decreased with increasing temperature while selectivities for less stabilized carbenes such as dibromocarbene increase with increasing temperature.[195-200] The reason for this is that the reaction of difluorocarbene with alkenes is more enthalpically controlled while that for less stable carbenes are more entropically controlled.[201] Ab initio calculations have been reported for the reaction of difluorocarbene with several alkenes.[201-204] The transition state structure calculations reveal that difluorocarbene addition has a much larger enthalpic barrier than that of less stable carbenes. In addition, the transition structures with difluorocarbene are more product-like than the transition structures of less stabilized carbenes.

In addition to the typical cyclopropanation reactions of a carbene, several other notable reactions have been reported. Reaction of difluorocarbene with norbornadiene (**50**) yields **51**, the product of homo-1,4-addition, in addition to the normal alkene cyclopropanation products **52** and **53** (eq 40).[205,206] The effect of norbornadiene substitution on the mode of carbene addition was also studied.[207,208]



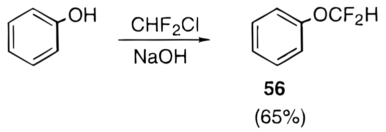
(40)

The major product **55** of difluorocarbene reaction with quadracyclane (**54**) corresponds to the cleavage of two of the strained sigma bonds (eq 41).[206,209] However, the overall yield was very low in this case.

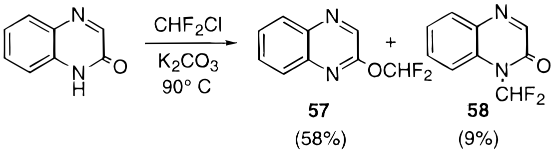


(41)

Difluorocarbene, generated from the action of base on chlorodifluoromethane, can be effectively trapped by alkoxides and related species to form difluoromethyl derivatives.[210-213] This reaction is very useful for the preparation of difluoromethyl ethers and related compounds (eqs 42 and 43). The reaction is believed to proceed via an anionic chain reaction involving the addition of difluorocarbene to the anion.



(42)



(43)

In related transformations, stabilized carbanions such as lithium acetylides (eq 44)[214,215] or malonates[214,216] undergo reaction with dibromodifluoromethane to form bromodifluoromethyl derivatives by an ionic chain mechanism involving difluorocarbene (Scheme 6). Phenoxides, thiophenoxides, and thiolates behave similarly.[212,217,218]

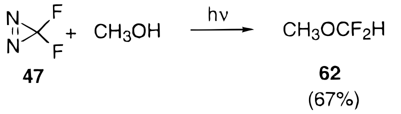
Scheme 6

$$RLi + CBr_2F_2 \longrightarrow RBr + \underset{\mathbf{24}}{\left[{}^{-}CF_2Br\right]} \longrightarrow \underset{\mathbf{14}}{\left[:CF_2\right]} + Br^-$$

$$\xrightarrow{RLi} \underset{\mathbf{61}}{RCF_2^-} \xrightarrow{CBr_2F_2} RCF_2Br + \underset{\mathbf{24}}{\left[{}^{-}CF_2Br\right]}$$

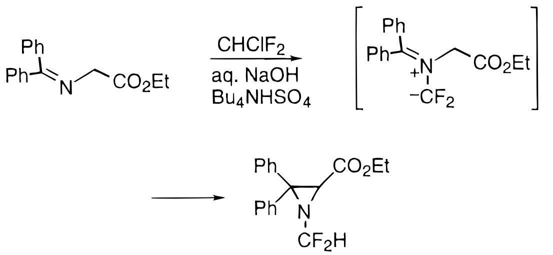
$$\underset{\mathbf{59}}{Ph\text{-}C{\equiv}C\text{-}Li} \xrightarrow[-78°\ C]{CBr_2F_2} \underset{\mathbf{60}}{Ph\text{-}C{\equiv}C\text{-}CF_2Br} \qquad (44)$$

The reaction of difluorocarbene, generated from difluorodiazirine, and alcohols or acids produces difluoromethyl esters and difluoromethyl ethers, respectively (eq 45).[219]



47 **62** (67%) (45)

An interesting reaction was reported between difluorocarbene and an imine. Generation of difluorocarbene from chlorodifluoromethane under phase transfer conditions in the presence of an imine produced *N*-(difluoromethyl)aziridine **63**.[220] The reaction can be rationalized by the following mechanism (eq 46).



63 (59%) (46)

Examples of difluorocarbene addition to representative alkenes are shown in Table 1.

Other reactions of singlet difluorocarbene that have been reported include its dimerization,[221] reaction with tetrafluoroethene,[222] butadiene,[223] O_3,[224] oxygen atoms,[225−227] N_2O,[228] Br_2,[229] Cl_2,[230] and hydrogen atom.[231] At room temperature, the rate of gas phase addition of singlet difluorocarbene to 2,3-dimethyl-2-butene is about five times faster than addition to 2-methylpropene.[232] It is noteworthy that singlet difluorocarbene appears unreactive toward H_2,[177] CO, and CO_2.[175] The reaction of difluorocarbene with silicon surfaces[233−245] has received considerable attention because of its industrial importance.

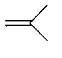
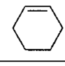
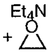
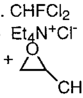
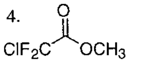
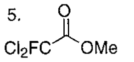
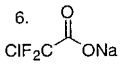
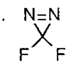
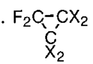
Triplet difluorocarbene has been produced as a reactive intermediate in several reactions including irradiation of tetrafluoroethene,[177] reaction of oxygen with tetrafluoroethene,[246,247] and reaction of carbon atoms with tetrafluoromethane.[248] The quenching of the triplet excited state by several small molecules has been studied.[232]

The equilibrium molecular geometry of difluorocarbene in its singlet ground state ($^1A_1$) has been determined by microwave spectroscopy and by analysis of rotational constants of gas phase absorption spectra.[253−257] The most accurate values obtained for the C−F bond length and F−C−F bond angle are 1.300 Å and 104.94°. The triplet excited state ($^1B_1$) geometry of difluorocarbene has also been determined by absorption spectroscopy.[257] The C-F bond length and F-C-F bond angle were 1.32 Å and 122.3°, respectively. The difference in energy between the ground state and the first excited triplet state has been experimentally determined to be 56.6 kcal/mol.[258,259]

Numerous calculations have been reported for difluorocarbene in its ground and excited states.[6,72,74,76−82,84−86,89−94,260] While the calculated structures for the singlet and lowest lying triplet states of difluorocarbene are well reproduced at most levels of theory, accurate calculations of the difference in energy between the two states requires large basis sets and inclusion of electron correlation. Various calculations of this kind can successfully reproduce the experimental singlet−triplet gap within 2 kcal/mol.[90,91,93,109,261−263]

Values reported for the heat of formation of difluorocarbene range from −39.4 to −56.0 kcal/mol.[113,264−266] Lias, Karpas, and Liebman[113] derived a value of −49.0 kcal/mol based on proton transfer bracketing experiments with CHF_2^+. More recently, Paulino and Squires[267] obtained a value of −39.4 kcal/mol based on measurements of the threshold energies for collision-induced halide ion dissociation from CF_3^-. However, to reconcile the almost 10 kcal/mol disparity with the value of Lias, Karpas, and Liebman, Paulino and Squires suggested that the experimental value reported for the gas phase acidity of fluoroform was too low and recommended a value of −44 kcal/mol for the heat of formation of difluorocarbene. Calculations at the MP4SDTQ/6-311++G-(2df) level predict a value of −51.1 kcal/mol.[92]

Table 1. Comparison of Difluorocarbene Generation Methods

Method/Alkene Trapping Reagent				Ref.
1. $CHClF_2$, NaOH		6%		121
2. CHF_2Cl + $Et_4N^+Br^-$ + 	13%	100%	29%	124,249
3. $CHFCl_2$ + $Et_4N^+Cl^-$ + 	85%	72-84%		250
4.  $ClF_2CC(O)OCH_3$ + LiCl:HMPA		90-100%	15-30%	126
5.  $Cl_2FCC(O)OMe$ KF:18-crown-6		85%	15%	135
6.  $ClF_2CC(O)ONa$ 30 h, reflux			11%	125
7. CF_2Br_2 or CF_2Cl_2 PPh_3 or $P(NMe_2)_2$ KF or CsF	66%	65-79%	21%	138
8. $BrCF_2\overset{+}{P}Ph_3Br^-$ PPh_3			35%	251
9. $BrCF_2\overset{+}{P}Ph_3Br^-$ KF, 18-crown-6			37%	127
10. CF_2Br_2, Zn I_2(cat.)		96%	7%	136
11. $HCBr_3$, CF_2Br_2 KOH, $(Bu)_4NHSO_4$		70%		141,142
12. $PhHgCF_3$, NaI			83%	153,154
13. CF_3HgI, NaI			89%	151
14. $Hg(CF_3)_2$, NaI			35%	152
15. Me_3SnCF_3, NaI		77%	89%	158
16. $(CF_3)_2Cd$:glyme		53%		252
17.  , hν or Δ	71%	85%		173,174
18.  X = F, Cl, H 160-220° C			67-100%	146,163

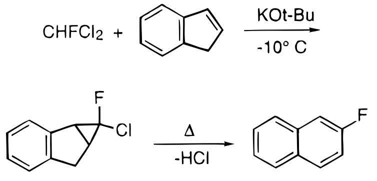
The spectroscopy of difluorocarbene has been well studied. The UV transitions for difluorocarbene have been observed using absorption[176,253,257] and emission spectroscopy,[268,269] and this has provided structural information about the ground state and excited singlet ($^1B_1$) and triplet states ($^3B_1$). The absorption spectrum of the singlet ground state begins around 265 nm. Many laser-induced fluorescence studies have been reported,[239,270−276] and the microwave spectrum[254−256] has provided very precise rotational and distortion constants for difluorocarbene. The infrared spectrum[277,278] has been measured several times and consists of three fundamental vibrations at 1222, 1102, and 668 cm^{-1}. High-resolution gas phase infrared studies[279−282] were reported, and the absolute infrared intensities have been determined.[283,284] In addition, the chemical shielding tensors of difluoromethylene have been calculated.[285]

3. Chlorofluorocarbene

The chemistry of chlorofluorocarbene (**64**) has received almost as much attention as that of difluorocarbene. Reasons for this increased interest include the following: the higher reactivity of chlorofluorocarbene than difluorocarbene toward electron-poor alkenes, the development of several useful methods for the generation of this carbene, and access to the formal monofluorocarbene adducts that might otherwise be difficult to obtain through the dechlorination of chlorofluorocyclopropanes.[16] The increased reactivity of chlorofluorocarbene compared with difluorocarbene is attributed to the fact that chlorine is less efficient than fluorine in stabilizing a carbene center. This enhanced reactivity has obviated the need to develop higher temperature synthetic methods for the formation of chlorofluorocarbene that are necessary for difluorocarbene. There are three generally useful methods for the generation of chlorofluorocarbene. One relies on the formation of the dichlorofluoromethyl anion (**70**) and its subsequent loss of chloride ion. A second is the organomercurial method of Seyferth employing $PhHgCFCl_2$ (**80**), and the third is based on a variation of the Simmons−Smith reaction using a metal and fluorotrichloromethane.

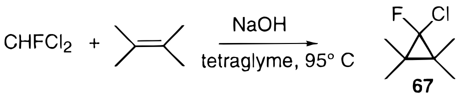
In a series of classic studies, Hine and co-workers investigated the formation of chlorofluorocarbene from the dehydrohalogenation of dichlorofluoromethane using potassium isopropoxide[286] and potassium *tert*-butoxide[287] or the decarboxylation of dichlorofluoroacetate.[288] Their mechanistic studies indicated that the dichlorofluoromethyl anion had a finite lifetime before eliminating chloride ion to form chlorofluorocarbene. This is in contrast to halodifluoromethyl anions that do not appear to have any lifetime in solution.

Using the dehydrohalogenation method, Parham and Twelves successfully trapped chlorofluoromethylene as the addition product of indene (**65**), which after HCl loss was isolated as pure 2-fluoronaphthalene (**66**) in 7−9% yield (eq 47).[289] The carbene was also trapped as the 1:1 adduct of cyclohexene, 7-fluoro-7-chloronorcarane, in 24% yield.



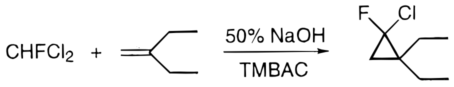
65 **66** (7-9%) (47)

Robinson reported that anhydrous sodium hydroxide can also be used to generate chlorofluorocarbene from dichlorofluoromethane, as shown by trapping studies with 2,3-dimethyl-2-butene (eq 48).[290]



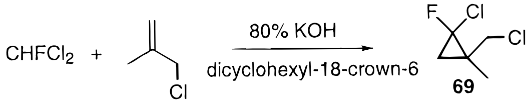
67 (43%) (48)

Phase transfer methodology improved the yields of chlorofluorocyclopropanes by minimizing reaction of chlorofluorocarbene with base. Weyerstahl et al. developed a two-phase reaction system for the preparation of chlorofluorocarbene from dichlorofluoromethane and sodium hydroxide with triethylbenzylammonium bromide (TEBAB) as the phase transfer catalyst.[291] Carbenes generated in this manner reacted with various alkenes to produce chlorofluorocyclopropanes in yields of 45−60%. Molines and co-workers used this procedure to cyclopropanate *n*-butyl vinyl ether in 79% yield.[292] Chau and Schlosser independently developed a similar two-phase system with potassium or sodium hydroxide and trimethylbenzylammonium chloride as the phase transfer catalyst (eq 49).[293,294] Yields of up to 71% were reported for the cyclopropanation of a wide range of olefins.[295]



68 (71%) (49)

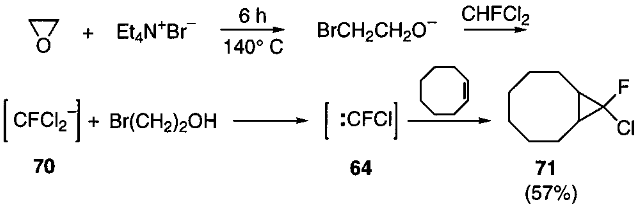
Other phase transfer catalysts such as dicyclohexyl-18-crown-6 (2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0]hexacosane) have also been used.[296] By use of this method, 2-methylallyl chloride was converted into **69** in 70% yield (eq 50).



69 (70%) (50)

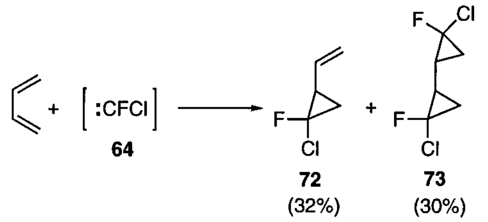
Weyerstahl et al. prepared chlorofluorocarbene from dichlorofluoromethane by the thermal reaction with ethylene oxide and a catalytic amount of tetraethylammonium bromide.[249] A low concentration of alkoxide base is generated in situ in this reaction by the nucleophilic attack of the bromide ion on ethylene oxide (Scheme 7). Chlorofluorocarbene was trapped by numerous alkenes including propene (15%), 2-methylpropene (39%), cyclohexene (45%), cyclooctene (57%), styrene (45%), and biphenylethene (20%). The addition to indene, resulting in the formation of fluoronaphthalene, was also reported.[297] However,

Scheme 7



the high-temperature conditions required for this method can lead to rearrangements.[124,298,299]

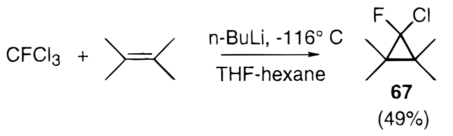
The addition of similarly generated chlorofluoromethylene to diolefins resulted in a mixture of mono- and dicyclopropane adducts in yields comparable to those for monoalkenes (eq 51).[300]



(51)

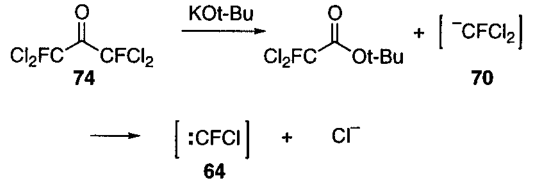
Methyllithium and *n*-butyllithium have been used as the basic component in the generation of chlorofluoromethylene from dichlorofluoromethane.[301,302] Cyclopropanation yields ranged from 45% for the reaction with 2,3-dimethyl-2-butene to 11% with heptene, producing a syn-Cl/anti-Cl ratio of 2.0. In a separate report, the reaction of methyllithium with dichlorofluoromethane, in the presence of 2-methyl-2-pentene, yielded 66% of the expected chlorofluorocyclopropane, while the reaction with fluorotrichloromethane resulted in a 50% yield.[303]

Burton and Hahnfeld have investigated the use of lithium dichlorofluoromethide, generated from the lithium halogen exchange reaction of fluorotrichloromethane and *n*-butyllithium, as a potential chlorofluoromethylene transfer agent (eq 52).[304] Moderate yields were obtained with electron-rich alkenes such as 2,3-dimethyl-2-butene (49%) and 2-methyl-2-butene (32%, 2.4 syn/anti ratio). However, poor or no yield was obtained with less nucleophilic alkenes such as *trans*-2-butene (8%) and cyclohexene (0%). In addition, the reaction with *trans*-2-butene was completely stereospecific.



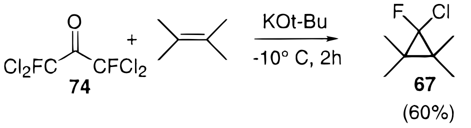
(52)

Farah and Horensky prepared chlorofluorocarbene by the reaction of **74** with potassium *tert*-butoxide in aprotic solvents.[305] The reaction involves the attack of the alkoxide at the carbonyl carbon displacing **70**, which subsequently loses chloride to generate the carbene (eq 53). In the presence of cyclohexene and α-methylstyrene, pure 7-chloro-7-fluorobicyclo[4.1.0]heptane and 1-chloro-1-fluoro-2-methyl-2-phenylcyclopropane were readily isolated in respective yields of 36% and 44%.



(53)

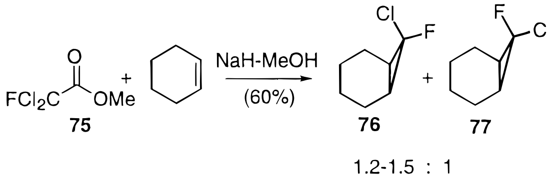
Moss et al. determined the relative rates of addition of chlorofluoromethylene, generated in the above manner, to a series of alkenes including 2,3-dimethyl-2-butene (31.0, 60% yield), 2-methyl-2-butene (6.5, 60%), 2-methylpropene (1.00), *cis*-butene (0.14, 35%), *trans*-butene (0.097, 30%), and butene (0.0087) (eq 54).[306,307] Compared to dichlorocarbene, chlorofluorocarbene was more selective, although with the less reactive olefins, dichlorocarbene was found to be more discriminating. This was explained by the differential steric requirements of chlorofluorocarbene and dichlorocarbene becoming more important with decreasing alkene reactivity. A kinetic selectivity favoring the formation of the more hindered product was also observed for chlorofluorocarbene. With *cis*-butene, a syn-Cl/anti-Cl ratio of 3.1 was detected, 1.5 for butene, and 2.4 for 2-methyl-2-butene.



(54)

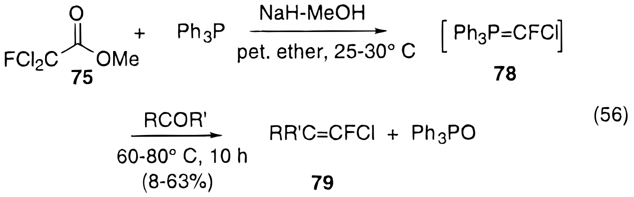
Kostikov et al. determined the relative reactivities of chlorofluorocarbene addition to a series of substituted styrenes.[308] Yields ranged from 15 to 40% with a predominance of the syn-Cl isomer in all cases except for α-methylstyrene, in which case the addition was nonstereospecific, and β-methylstyrene, in which a preference for the anti isomer was found. However, the stereoselectivity of addition was substantially lower than that observed for alkylethenes.

Other methods of generating chlorofluorocarbene from the dichlorofluoromethyl anion involve treatment of dichlorofluoroacetate esters with nucleophiles.[309,310] For instance, reaction of methyl dichlorofluoroacetate with sodium hydride and methanol as the base system, in the presence of cyclohexene, produced high yields (60%) of 7-chloro-7-fluoronorcarane (**76** and **77**) (eq 55).[311] Numerous additional bicyclic *gem*-chlorofluorocyclopropanes were prepared by this method in good yields.[312−314]



(55)

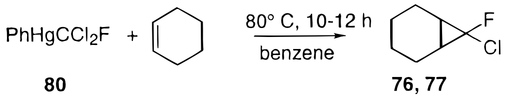
These methods of carbene generation were used to prepare 1-chloro-1-fluoroethenes.[315] An initial study reported that chlorofluorocarbene, generated from dichlorofluoromethane with potassium *tert*-butoxide, reacted with triphenylphosphine to form (chlorofluoromethylene)triphenylphosphorane (**78**), which subsequently reacted with benzophenone to yield 1-chloro-1-fluoro-2,2-diphenylethene (40%).[316] In the study by Yamanaka and co-workers, a wide variety of additional carbonyl compounds were used with the yields of the alkenes ranging from 63% for the reaction with p-ClC_6H_4CHO to 8% with PhCOMe (eq 56).[315]



(56)

Burton and Krutzsch prepared chlorofluoroethenes (**79**) from (chlorofluoromethylene)triphenylphosphorane (**78**) and various carbonyl compounds in a similar manner.[317,318] The carbenes in this study were produced by the reaction of dichlorofluoromethane and potassium *tert*-butoxide or the thermolysis of sodium dichlorofluoroacetate. However, an alternate mechanism for chlorofluoromethylene ylide formation was proposed for the thermal reaction, which involved the decomposition of an intermediate phosphobetaine salt, instead of the free carbene addition to triphenylphosphine. Alkene yields ranged from 70% with $C_6H_{11}COCF_3$ to 0% with $(C_6H_5)_2CO$. Higher yields were generally obtained from the pyrolytic method of carbene generation.

Seyferth et al. developed the use of phenyl(fluorodichloromethyl)mercury (**80**) as a chlorofluoromethylene transfer reagent.[319,320] The thermolysis (80 °C, benzene) of **80** in the presence of various alkenes afforded excellent yields of chlorofluorocyclopropanes ranging from 91% for allyltrimethylsilane to 65% with the poorly nucleophilic vinyltriethylsilane (eq 57). Other olefins successfully cyclopropanated include base-sensitive acrylonitrile and vinyl acetate. The cyclopropanes were produced as a mixture of isomers, with the syn-Cl isomer favored in all unsymmetrical alkenes. It was later found that reaction times of 10−12 h were sufficient for cyclopropanations, rather than the 48 h used in earlier reports.[321]



(57)

80

76, 77
(85%)

In addition, the reactions with *trans*- and *cis*-3-hexene confirmed the stereospecificity of the cyclopropanation with respect to the configuration of substituents at the C=C bond.

The reaction could be greatly accelerated by the addition of sodium iodide. A change in mechanism, in which the iodide ion displaces dichlorofluoromethide (**70**) from the mercury complex with subsequent loss of chloride ion to produce carbene **64**, was postulated for this activation (eq 58). The products obtained were the same as those produced under thermal reaction conditions with comparable yields and much shorter reaction times (3 h).

It was also reported that **64** undergoes insertion into reactive single bonds such as the Si−H bond of triethylsilane and the Sn−Sn bond of hexamethylditin (eq 59 and 60).

$$\underset{\mathbf{80}}{PhHgCCl_2F} + NaI \xrightarrow[80\text{-}85^\circ C]{DME} \qquad (58)$$

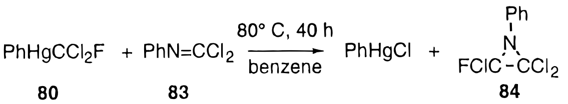
$$\underset{\mathbf{70}}{\left[Cl_2CF^-\right]} + PhHgI \longrightarrow \underset{\mathbf{64}}{\left[:CFCl\right]} + Cl^-$$

$$\underset{\mathbf{80}}{PhHgCCl_2F} + Et_3SiH \xrightarrow[benzene]{80^\circ C,\ 48\ h} PhHgCl + \underset{\substack{\mathbf{81}\\(83\%)}}{Et_3SiCFClH} \qquad (59)$$

$$\underset{\mathbf{80}}{PhHgCCl_2F} + Me_3Sn\text{-}SnMe_3 \xrightarrow[benzene]{80^\circ C,\ 48\ h} \qquad (60)$$

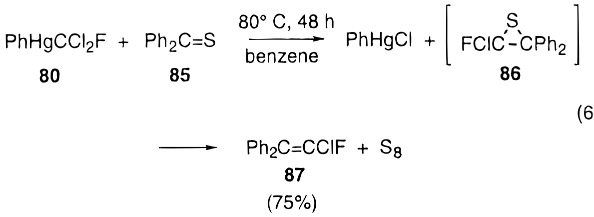
$$PhHgCl + \underset{\substack{\mathbf{82}\\(36\%)}}{Me_3Sn\text{-}CFCl\text{-}SnMe_3}$$

In addition, chlorofluorocarbene addition to the C=N bond in **83** produced **84** (eq 61). However, the addition product **86** derived from the reaction of **64** with the C=S bond of **85** was not stable at 80 °C and only decomposition product **87** was isolated (eq 62).



(61)

84
(74%)

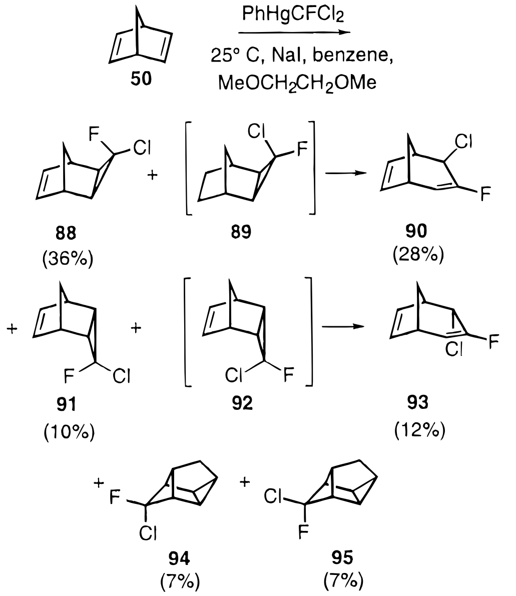


(62)

Other applications of organomercurial compounds as chlorofluoromethylene transfer reagents include the addition to various steroids,[322,323] the reaction with cholest-5-en-3-one 3-ethylene acetal,[190] the cyclopropanation of 1,3-dibenzyluracil, 3-methyl-2′,3′-isopropylidene-5′-acetyluridine, and 3-benzhydril-2′,3′-isopropylidene-5′-acetouridine,[324] the addition to 2,3-dialkylindoles,[325] and the reaction with pyrrolidine dienamines to generate ring-expanded ketones.[326]

The thermolysis of sodium dichlorofluoroacetate in the presence of norbornadiene (**50**) resulted in a 25% yield of a mixture of products corresponding to 1:1 addition of chlorofluorocarbene.[327] Further insight into the reaction was obtained using phenyl(fluorodichloromethyl)mercury (**80**) as the carbene source (eq 63).[205] The milder procedure led to the observance of **91**, which was not previously seen in the thermal preparation. Products **90** and **93** were postulated to arise from **89** and **92**, respectively. Compounds **94** and **95** are produced by homo-1,4 addition to **50**.

Burton and Van Hamme investigated the reaction of tris(dimethylamino)phosphine and fluorotrichloromethane in the presence of cesium fluoride to generate chlorofluorocarbene.[16] In this reaction, the phosphine abstracts a positive halogen from fluoro-



(63)

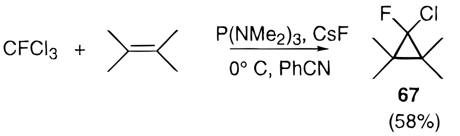
trichloromethane, resulting in dichlorofluoromethide (**70**), which loses a chloride ion forming chlorofluorocarbene (**64**) (Scheme 8). Cesium fluoride is necessary to prevent the formation of a phosphonium salt with the dichlorofluoromethide. However, the yields of alkene addition were moderate at best, ranging from 58% with 2,3-dimethyl-2-butene to 0% with cyclohexene (eq 64).

Scheme 8

$$(Me_2N)_3P + CFCl_3 \xrightarrow[PhCN]{0^\circ C} (Me_2N)_3P^+Cl + \underset{\mathbf{70}}{[^-CFCl_2]}$$

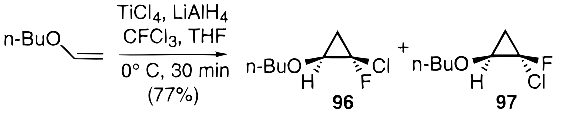
$$(Me_2N)_3P^+Cl \xrightarrow{CsF} (Me_2N)_3PFCl$$

$$\underset{\mathbf{70}}{[CFCl_2^-]} \longrightarrow \underset{\mathbf{64}}{[:CFCl]}$$



(64)

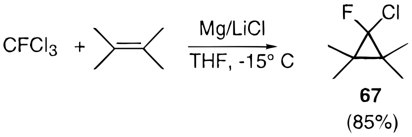
Recently, Dolbier and Burkholder reported the successful interception of chlorofluorocarbene from the reaction of $CFCl_3$ and reduced titanium, produced from the reduction of titanium tetrachloride with lithium aluminum hydride.[328,329] Initial reactions in the presence of α-methylstyrene gave yields of 40%. However, good yields were possible using a 3-fold excess of $CFCl_3$ and titanium compared to alkene, with the yield based on the alkene as the limiting reagent (eq 65). Yields of chlorofluorocyclopropanes ranged from 90% with 2,3-dimethyl-2-butene to 12% with hexene. In addition, it was concluded that the reaction involved a free carbene rather than a carbenoid species. The similar syn/anti product ratios obtained by this procedure and by other methods of carbene generation provide evidence to support this. Also, the use of $CFBr_2Cl$ in place of $CFCl_3$ had no effect on the syn/anti product ratio, which would be expected if carbenoids of the form $ClTiCFCl_2$ and BrTiCFClBr were involved, due to their differing steric requirements.



1.62 : 1.00

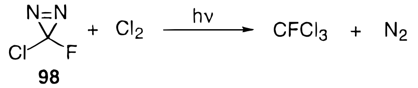
(65)

In a closely related reaction, Hu and Tu recently reported that chlorofluorocarbene could be generated from the reaction of trichlorofluoromethane and magnesium and lithium chloride, presumably from the decomposition of dichlorofluoromethylmagnesium chloride (eq 66).[330] No other alkenes were investigated in this study.



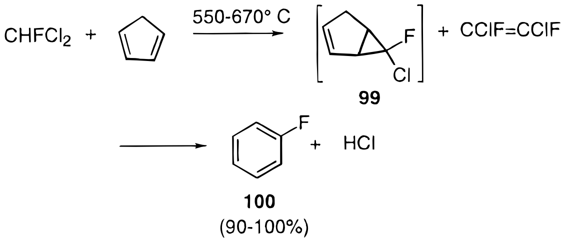
(66)

Chlorofluorodiazirine (**98**) has been prepared but only in low yield, and little has been reported on its use as a source of chlorofluorocarbene. One such example involves the photochemical generation of chlorofluorocarbene in the presence of chlorine to afford trichlorofluoromethane in high yield (eq 67).[219]



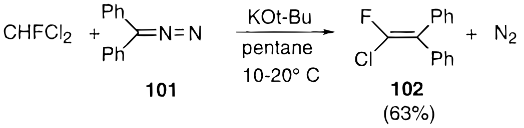
(67)

The high-temperature thermolysis of dichlorofluoromethane in a platinum or quartz flow-type reactor produced chlorofluoromethylene, which dimerized in the absence of a trapping agent.[331] In the presence of cyclopentadiene, fluorobenzene, hydrogen chloride, and 1,2-dichloro-1,2-difluoroethene were the major reaction products (eq 68).[332] Similarly, the pyrolysis of dichlorofluoromethane in the presence of indene produced 2-fluoronaphthalene in 55% yield.[333]



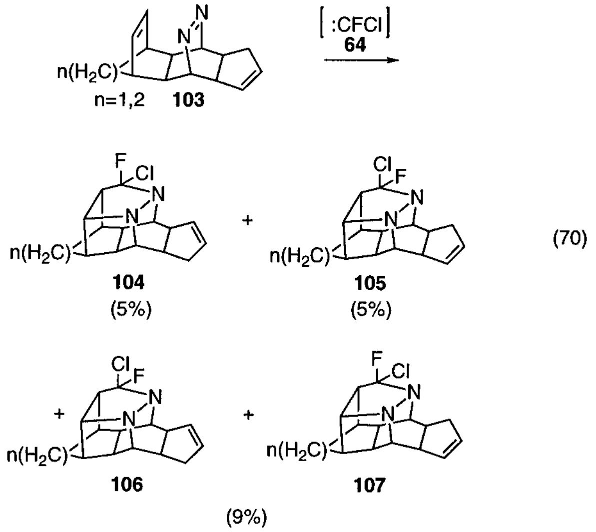
(68)

Remlinger reported that chlorofluorocarbene, produced by the dehydrohalogenation of dichlorofluoromethane, reacted with diazo compounds, such as diphenyldiazomethane (**101**) and diazofluorene, to generate olefins in respective yields of 63 and 67% (eq 69).[334,335]

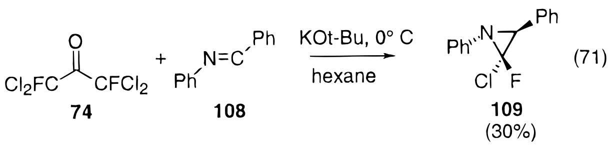


(69)

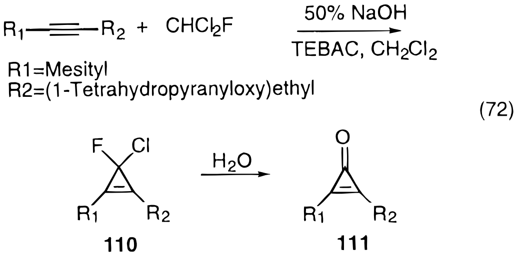
Hunig and Schmitt reported a formal [2 + 2 + 1] cycloaddition of chlorofluorocarbene, generated from $CHCl_2F$, 50% NaOH, and TEBAC, to compounds **103** with azo and olefin groups in close proximity (eq 70).[336] A mixture of products **104**−**107** was obtained. The authors favor a mechanism for this reaction involving the formation of an azomethinimine−1,3-dipole via attack of the carbene at the lone pair of nitrogen followed by a [3 + 2] dipolar cycloaddition closing the cage.



In the reaction of chlorofluorocarbene with benzylideneaniline (**108**), only one stereoisomeric aziridine **109** was produced in 30% yield (eq 71).[337] This stereoselectivity was explained by the greater interaction of a *syn*-fluorine than a *syn*-chlorine bond with the nitrogen lone pair. The σ^*C−X MO of the C−F bond interacts more favorably than that of the C−Cl bond because it is closer in energy to the nonbonding level of the nitrogen electrons. The difference in energy between these orbitals and the nitrogen nonbonding orbital was calculated as 2.0 and 4.2 eV, respectively.

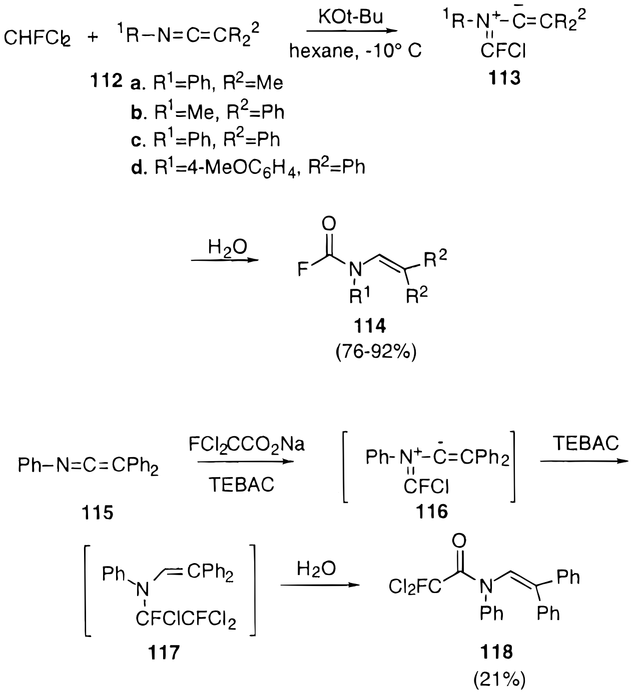


Dehmlow and Winterfeldt utilized phase transfer catalysis conditions to generate chlorofluoromethylene in the presence of alkynes, which resulted in the formation of chlorofluorocyclopropenes **110**, which were subsequently hydrolyzed in situ producing cyclopropenones **111** (eq 72).[338] Fair yields were obtained with alkynes containing aromatic or aliphatic groups of moderate steric bulk. However, a further increase in steric crowding resulted in extremely low yields. In addition, aromatic alkynes were found to be much better substrates than aliphatic ones. In the case of enynes, chlorofluorocarbene added first to the alkene in most cases, except for substrates containing highly sterically hindered olefins.



Recently, Khlebnikov et al. used carbenes produced from dichlorofluoromethane and potassium *tert*-butoxide to prepare carbamoyl fluorides **114** from ketenimines **112** (Scheme 9).[339] If the carbene was generated from the decomposition of sodium dichlorofluoroacetate in the presence of a phase transfer catalyst (TEBAC), dichlorofluoroacetamides **118** were formed. The yields of the carbamoyl fluorides **114** ranged from 76 to 92%, and the yield of **118** was 21%.

Scheme 9

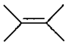
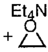
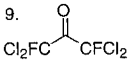
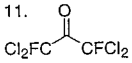
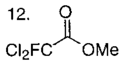
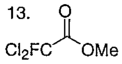


Examples of chlorofluorocarbene addition to representative alkenes are shown in Table 2.

Other methods of chlorofluorocarbene generation involved matrix reactions of alkali metal atomic beams with $CFCl_3$ in argon,[340] the flash photolysis of C_2F_3Cl,[341] the gas phase photolysis of $CHFCl_2$[116] and $CFCl_3$,[342−345] the α-Lyman photolysis of $HCCl_2F$,[346] the photolysis of $HCCl_2F$ or H_2CClF during matrix deposition,[347,348] the reaction of atomic oxygen with CF_2CFCl in a discharge flow system,[349,350] the argon resonance photoionization of $CHFCl_2$/argon matrix systems,[351] the laser-induced multiphoton dissociation of CF_2CFCl,[352] the metastable reaction with C_2F_3Cl,[353] the infrared multiphoton dissociation of $CFCl_3$,[187] $CHFCl_2$,[41,354,355] and C_2F_3Cl,[353,356] the vacuum ultraviolet photochemistry of CH_2ClF,[357] $CHFCl_2$,[117] and $CFCl_3$,[358] and the pyrolysis of CCl_2FH or $CFClBr_2$ using the pyrolysis jet technique.[359] In addition, rate constants for the reactions of chlorofluoromethylene and various scavengers in the gas phase have been determined.[41,343,349,355]

The structure of chlorofluorocarbene has been determined by rotational analysis of gas phase laser induced fluorescence spectra. The C−F bond length was found to be 1.307−1.32 Å, the C−Cl bond was

Table 2. Comparison of Chlorofluorocarbene Generation Methods

Method/Alkene Trapping Reagent				Ref.
1. $CHFCl_2$ + KOt-Bu			24%	289
2. $CHFCl_2$ + NaOH		43%		290
3. $CHFCl_2$ + NaOH, TEBAB		45-60%	45-60%	291
4. $CHFCl_2$ + NaOH, TMBAB	30%			293
5. $CHFCl_2$ + n-BuLi, TMBAB	53%			293
6. $CHFCl_2$ + $Et_4N^+Br^-$ + 	39%		45%	249
7. $CHFCl_2$ + n-BuLi or MeLi		45%	21%	301,302
8. $CFCl_3$ + n-BuLi		49%	0%	304
9.  $Cl_2FC(O)CFCl_2$ + KOt-Bu			36%	305
10.			60%	306,307
11.  $Cl_2FC(O)CFCl_2$ + NaOMe			38%	309
12.  $Cl_2FC(O)OMe$ + NaOMe			35-43%	
13.  $Cl_2FC(O)OMe$ + NaH-MeOH			60%	311
14. $PhHgCCl_2F$ 48 h, reflux			85-86%	319,320
15. $PhHgCCl_2F$ 20 h, reflux			84%	321
16. $PhHgCCl_2F$, NaI 3-5 h, 85° C or 48 h, rt			70-79% 85%	319,320
17. $CFCl_3$ $P(NMe_2)_3$, CsF	5%	58%	0%	16
18. $CFCl_3$ + $TiCl_4$, $LiAlH_4$		66%	53%	328,329
19. $CFCl_3$ + Mg, LiCl		85%		330

1.704–1.706 Å, and the carbenic bond angle was 107.6°.[359] Calculations based on density functional theory predict a singlet ground state for chlorofluoromethylene with a singlet–triplet energy difference of 43 kcal/mol and bond lengths of 1.325 and 1.763 Å for the C–F and C–Cl bonds of singlet chlorofluoromethylene and 1.332 and 1.671 Å for the triplet carbene.[360,361] The carbenic bond angle was calculated as 106.1° for the singlet state and 123.8° for the triplet. Additional theoretical studies on chlorofluorocarbene have been reported.[86,100,105,362]

In addition, the heat of formation of chlorofluorocarbene was found to be 11 ± 1.3 kcal/mol on the basis of measurements of appearance potentials,[363] −0.9 ± 2.5 kcal/mol on the basis of kinetic studies,[364] and −2 ± 7 kcal/mol on the basis of gas phase proton affinity measurements.[113]

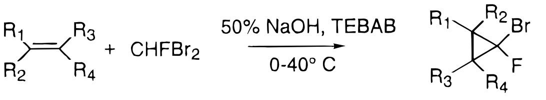
The IR spectrum of chlorofluoromethylene has been determined by numerous methods in the gas phase and in argon matrices. In argon matrices the fundamental frequencies were observed at 1146–1148, 738–742, and 379–442 cm^{-1},[340,347,348,351,357] whereas in the gas phase, absorptions at 1156–1158, 448–449, and 750–759 cm^{-1} have been reported.[352,353,356,359] IR frequencies at 1261, 391, and 720 cm^{-1} were also observed by Schlachta et al. using laser-induced fluorescence spectroscopy of supersonically cooled chlorofluoromethylene.[359]

The UV–vis spectra of chlorofluorocarbene in argon matrices exhibited absorptions in the 340–415 nm range.[340,346–348,351,356] Other methods have determined λ_{max} values ranging from 350 to 410 nm.[117,354,356,359,365]

4. Bromofluorocarbene

The reactivity of bromofluorocarbene (**119**) toward various substrates is similar to or slightly greater than that of chlorofluorocarbene. However, there are substantially fewer reports in the literature of bromofluorocarbene. The two methods that are generally useful for the generation of bromofluorocarbene include elimination of bromide ion from dibromofluoromethyl anion and Seyferth's organomercurial, $PhHgCFBr_2$.

The reaction of dibromofluoromethane with sodium hydroxide and triethylbenzylammonium bromide (TEBAB), as a phase transfer catalyst, in the presence of 2-methylpropene, 2,3-dimethyl-2-butene, or styrene afforded the corresponding bromofluorocyclopropanes in 40–50% yield (eq 73).[291]



(73)

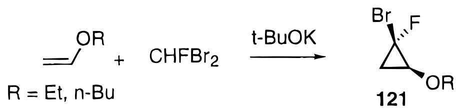
120

(40-50%)

a. $R_1=CH_3$, $R_2=H$, $R_3=CH_3$, $R_4=H$
b. $R_1=CH_3$, $R_2=CH_3$, $R_3=CH_3$, $R_4=CH_3$
c. $R_1=Ph$, $R_2=H$, $R_3=H$, $R_4=H$

Other alkenes cyclopropanated in a later study included 3,3-dimethylbutene, 2-ethylbutene, 2,3-dimethylbutadiene, phenoxyethene, and 2-phenylpropene in yields ranging from 51% for 1-bromo-2-*tert*-butyl-1-fluorocyclopropane to 88% for 1-bromo-1-fluoro-2-methyl-2-phenylcyclopropane.[366]

Under both homogenous (KO-*t*-Bu) and phase transfer catalysis conditions, Savinykh et al. reported that vinyl ethers were cyclopropanated, favoring the sterically more hindered products (eq 74).[367]



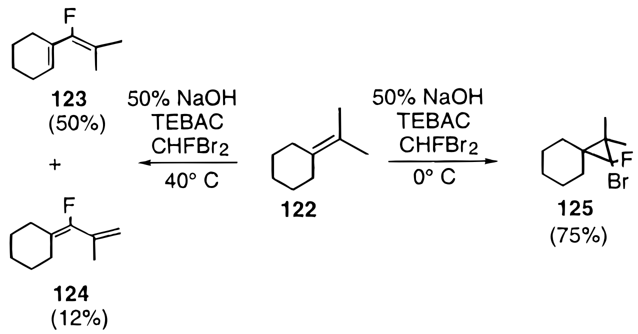
(74)

121

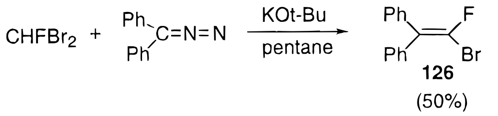
Under phase transfer conditions, the generation of bromofluorocarbene in the presence of phenylcyclohexylidene and bicyclo[4.4.0]dec-1,6-ene formed the expected bromofluorocyclopropanes.[368] However, only ring-opened products were obtained from the reaction of bromofluorocarbene with (*E*)-2,3-diphenyl-2-butene. Cyclopropanes **125** of other tetrasubstituted alkenes such as **122** were observed only at lower temperatures. At higher temperatures only ring-opened products **123** and **124** were observed (Scheme 10).

Bromofluorocarbene, generated by dehydrohalogenation of dibromofluoromethane, reacted with diazo compounds to form bromofluoromethylene olefins **126**

Scheme 10



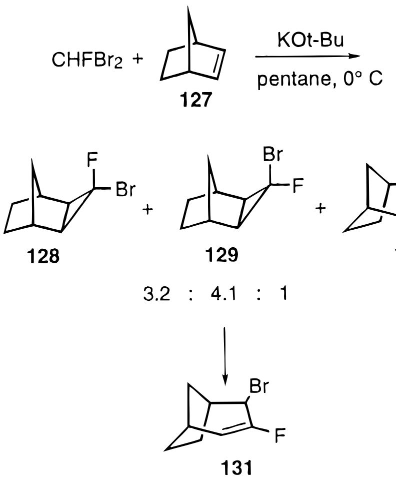
(eq 75).[334,335] A 50% yield was obtained for the reaction with diphenyldiazomethane.



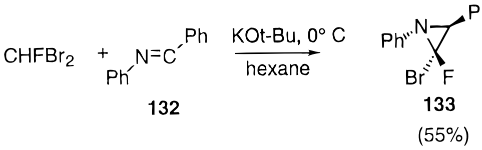
(75)

Bromofluorocarbene also reacted with norbornene (**127**) to form a mixture of products **128**–**131** (Scheme 11).[369]

Scheme 11

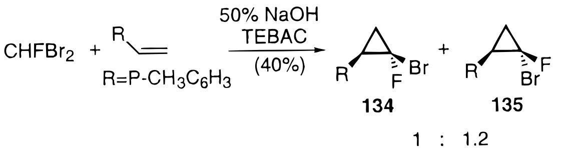


The reaction of bromofluorocarbene with imine **132** produced only one stereoisomeric aziridine **133** in 55% yield (eq 76).[337] This stereoselectivity was explained by the interaction of the *syn*-halogen with the nitrogen lone pair, i.e., the σ^*C–X MO of the C–X bond with the nonbonding level of the nitrogen lone pair. The σ^*C–X MO of the C–F bond interacts more favorably than that of the C–Br bond because it is closer in energy to the nonbonding level. The difference in energy between these orbitals and the nitrogen nonbonding orbital was calculated as 2.0 and 4.3 eV, respectively.



(76)

Relative rate constants for the addition of bromofluorocarbene to a series of arylethenes[370] and substituted styrenes[308] have been reported. The carbene was generated under standard two-phase conditions (50% NaOH, triethylbenzylammonium chloride (TEBAC), or dibenzo[18]crown-6) in the presence of alkene (eq 77). Electron-donating substituents in the para position accelerated the reaction, while electron-withdrawing substituents had the opposite effect. The selectivity of bromofluorocarbene (ρ = 0.58) was almost identical to the selectivity observed for dichloro- and difluorocarbene. The low reactivity of *o*-methylstyrene and mesitylethylene was attributed to steric hindrance. The addition of bromofluorocarbene resulted in a slight excess of anti isomer (*anti*-bromine, *syn*-fluorine), regardless of the nature of the substituent in most cases.[371] However, the reaction with (2,6-dimethoxyphenyl)-, (2,4,6-trimethylphenyl)-, and (pentafluorophenyl)ethenes resulted in a predominance of the syn isomer. The yields in these reactions ranged from 17% for (2,4,6-trimethylphenyl)ethene to 40% for (*p*-methylphenyl)ethene.

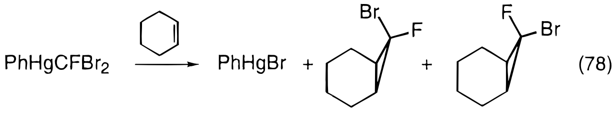


(77)

The preference of the anti addition in the first case was attributed to favorable dipole–dipole interaction between the carbene, the dipole of which lies along the C–F bond, and the opposing dipole, induced by the carbene, of the substituent–olefinic bond. In contrast, the predominance of syn addition for the latter case was explained by the interaction of the polarizable bromine lone-pair electrons with the partial positive charge on the olefin substituent. In the reactions with arylethenes with multisubstituted phenyl rings, the aromatic ring is displaced from the plane of the double bond, generating stronger interaction between the bromine substituent and the aryl group, overriding the dipole–dipole attraction. In addition, the reaction with *cis*- and *trans*-β-methylstyrene resulted in a *syn*-Br/*anti*-Br ratio of 2.5 for both isomers, where the methyl substituent was found to direct the course of addition.

Other interesting reactions of bromofluorocarbene, generated using the two-phase method, include the cyclopropanation of allenic phosphine oxides, in which addition occurred at the double bond allylic to the phosphine oxide substituent,[372] and the reaction with diphenylcyclopropene under ultrasonication, which generated the rearrangement products 1-bromo-1-fluoro-2,3-diphenylbutadiene (21%) and 2-bromo-3-fluoro-1,3-diphenylcyclobutene (14%).[373]

In general, Seyferth's organomercurial, phenyl(dibromofluoromethyl)mercury (**136**), is a more effective bromofluoromethylene transfer agent than the dehydrohalogenation of dibromofluoromethane.[374,375] Within 4 days at room temperature or 20 min at 80 °C, the mercury reagent was completely consumed upon treatment with an excess of alkene in benzene solution, and yields of the *gem*-bromofluorocyclopropanes were good to excellent (eq 78). Alkenes used in this study included cyclohexene (88–90%), heptene (72–78%), *cis*-2-butene (99%), *trans*-2-butene (98%), 3-(trimethylsilyl)propene (60–70%), (trimethylsilyl)ethene (55%), trichloroethene (58%), methylacrylate

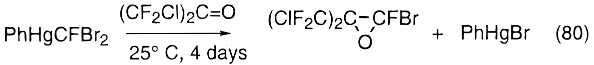


136 **137** (50%) **138** (32%)

(95%), acrylonitrile (33%), and 2,5-dihydrofuran (57%). The addition was stereospecific as shown by the results obtained with *cis*- and *trans*-2-butene.

In addition, bromofluorocarbene inserted into Si−H bonds and added to C=O bonds (eqs 79 and 80).

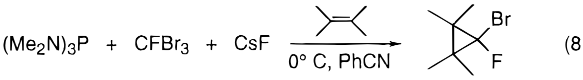
$$\underset{\mathbf{136}}{PhHgCFBr_2} \xrightarrow[25°\text{ C, 4 days}]{Et_3SiH} \underset{\substack{\mathbf{139}\\(87\%)}}{Et_3SiCHFBr} + PhHgBr \qquad (79)$$



$$\underset{\mathbf{136}}{PhHgCFBr_2} \xrightarrow[25°\text{ C, 4 days}]{(CF_2Cl)_2C{=}O} \underset{\substack{\mathbf{140}\\(74\%)}}{(ClF_2C)_2C\overset{}{-}CFBr\ (\text{epoxide, O})} + PhHgBr \qquad (80)$$

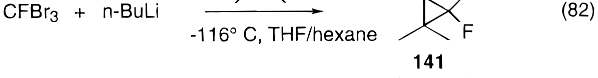
Drawbacks to using $PhHgCFBr_2$ for bromofluorocarbene transfer include the instability of **136**, which should be used soon after preparation, the modest yield of its preparation, and the difficulty of the preparation itself.[375] It is appropriate to use the mercurial route for reactions with base-sensitive or very valuable substrates, while for non-base-sensitive and more nucleophilic alkenes, the phase transfer reaction using dibromofluoromethane may be the better choice.

Another method to generate the dibromofluoromethyl anion is by reductive debromination of $CFBr_3$. In this manner, **141** was produced by the reaction of fluorotribromomethane with tris(dimethylamino)phosphine and cesium fluoride in the presence of 2,3-dimethyl-2-butene in 24% yield (eq 81).[16]



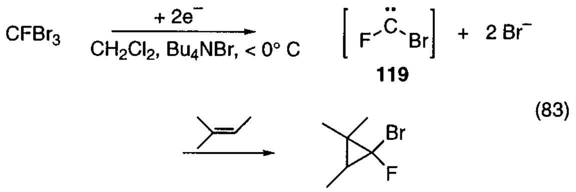
141 (24%)

The reaction of fluorotribromomethane and *n*-butyllithium (THF/hexane, −116 °C) in the presence of di-, tri-, and tetrasubstituted alkenes afforded good yields of the expected bromofluorocyclopropanes (eq 82).[16,376] The alkenes in this study included 2,3-dimethyl-2-butene (53−73%), 2-methyl-2-butene (44−71%, 1.8 ± 0.2 *Z*/*E* ratio), 2-methylpropene (55−60%), *trans*-2-butene (57%), *cis*-2-butene (61−69%, 2.4 ± 0.4 *Z*/*E* ratio), and cyclohexene (19−57%, 2.9 ± 0.8 *Z*/*E* ratio). Only a trace amount of product was obtained with hexene, and better yields were generally obtained with mechanical stirring as opposed to magnetic stirring. It was postulated that the reaction occurred through a (dibromofluoromethyl)lithium intermediate that was stabilized by THF and the low-temperature conditions.



141 (53-73%)

Electrochemical methods have also been used to generate bromofluoromethylene (**119**).[144,377] Using a lead cathode and Bu_4NBr as the supporting electrolyte, the two-electron reduction of $CFBr_3$ in the presence of 2-methyl-2-butene, styrene, or cyclohexene produced the respective cyclopropanes in ∼60% yield (eq 83).



142 (∼60%)

In mass spectral analysis using electron impact ionization, the location of double bonds in underivatized olefins often shifts, leading to ambiguous structural results. Scherch et al. investigated the use of halocarbenes in cyclopropane reactions to fix the location of the double bonds.[378] In their study employing CBr_2, CCl_2, CF_2, CClF, CHCl, CHF, and CBrF, they found that bromofluorocarbene was the most useful. This conclusion was based on the high reactivity of bromofluorocarbene coupled with the ease in identifying the adduct fragments due to its characteristic isotopic patterns.

Bromofluorocarbene, produced by the reaction of atomic oxygen with F_2CCFBr, was also studied by laser-induced fluorescence, and rate coefficients were determined for the reactions with O_2, NO, F_2CCFBr, Cl_2, and Br_2.[379,380]

By using assumed values for $r''_{C-F} = 1.30$ Å, $r''_{C-Br} = 1.93$ Å, $r'_{C-F} = 1.32$ Å, and $r'_{C-Br} = 1.85$ Å, bond angles of 127° and 110.9° were obtained for the upper and ground states of bromofluoromethylene from its partially resolved rotational structure.[351] Irikura et al. calculated that the singlet−triplet energy difference was 31.9 kcal/mol, favoring the singlet after the application of correction factors.[105] The energies of a series of carbenes were obtained by the use of simple basis sets with GVB(1/2) wave functions for singlet carbenes and ROHF wave functions for the triplet states. The calculated singlet−triplet gaps correlated linearly with experimental results by the following equation.

$$\Delta E_{st}^{\ exp} = A + B\Delta E_{st}^{\ calc}$$

$$A = 17.02 \pm 0.70 \text{ kcal/mol},\ B = 1.175 \pm 0.036$$

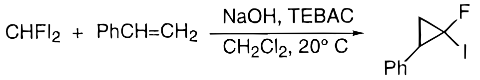
In addition, the singlet carbenic bond angle was found to be 106.3°, while the triplet bond angle was 122.8°.

Prochaska and Andrews determined fundamental CF and CBr stretching frequencies of 1157 and 656 cm^{-1} for bromofluoromethylene, which was generated as one of the products of the photoionization of CH_2CFBr by argon resonance radiation from a microwave discharge concurrently with the high dilution deposition (15 K).[348] In a related matrix study, Miller and

Andrews assigned a ground state bending mode of 327 cm^{-1} for bromofluorocarbene, produced by the vacuum ultraviolet photolysis of CH$_2$FBr and CHF$_2$Br, using laser-induced fluorescence.[381] An electronic origin near 23 300 cm^{-1} (429 nm) was also observed. Purdy and Thrush found a similar value of 325 cm^{-1} for the excited state bending vibration in their gas phase laser fluorescence studies, and the origin of the spectra was determined to be at or below 22 255 cm^{-1} (449 nm).[382] Bromofluoromethylene was generated by the reaction of atomic oxygen with CF$_2$CFBr. A later result found the origin to be at 20 906 cm^{-1} (478 nm) using CFBr$_3$ as the carbene precursor and a technique that combines dc discharge with pulsed supersonic expansion cooling of the products.[383]

5. Fluoroiodocarbene

Compared to the other fluorohalocarbenes, fluoroiodocarbene has received very little study. The reaction of fluorodiiodomethane and sodium hydroxide in the presence of alkenes, with triethylbenzylammonium chloride (TEBAC) as a phase transfer agent, afforded 1-fluoro-1-iodocyclopropanes (eq 84).[384,385] Cyclopropanation occurred in 60% yield with styrene, 18% with 1,1-diphenylethene, 17% with α-methyl styrene, and 20% with cyclohexene.



143
(60%)

(84)

Irikura et al. calculated that the singlet−triplet energy difference of fluoroiodocarbene was 25.5 kcal/mol in favor of the singlet ground state after applying an empirical correction. The singlet was predicted to have a bond angle of 107.2° and the triplet carbene a bond angle of 124.1°.[105]

The only spectroscopic study on fluoroiodocarbene was done by Prochaska and Andrews.[348] The carbene was generated as one of the products of the photoionization of CH$_2$CFI by argon resonance radiation from a microwave discharge during high dilution deposition (15 K). Infrared bands assigned to fluoroiodocarbene were observed at 1133 and 573 cm^{-1}.

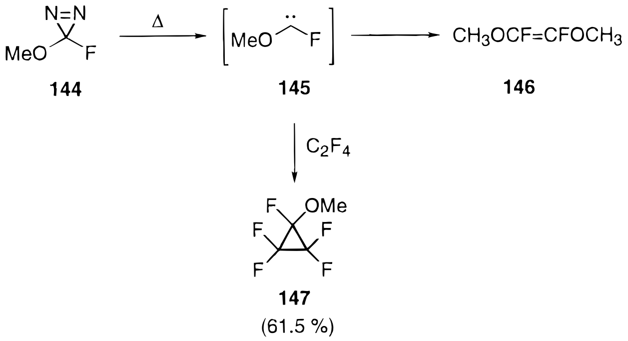
6. Alkoxyfluorocarbenes

Since an oxygen atom is more effective in stabilizing a carbene center, carbenes having both a fluorine and an oxygen atom directly attached to the carbene carbon will have a singlet ground state and will be more nucleophilic than carbenes lacking oxygen.

Fluoro(hydroxy)carbene has been prepared in the gas phase by dissociative ionization of methyl fluoroformate followed by neutralization of the fluoro(hydroxy)methylene radical cation with xenon.[386] While no experimental reports have appeared on the reactivity of fluoro(hydroxy)carbene, theoretical studies include calculations on the transition states and selectivities of the addition to alkenes[204,387] and the rearrangement of fluoro(hydroxy)methylene to formyl fluoride.[386,388,389] The calculated structures of the cis and trans conformers of fluoro(hydroxy)carbene have been reported.[388] At the CCSD/DZ+ P level, the trans conformer has a carbenic bond angle of 104.0°, a C−F bond length of 1.328 Å, and a C−OH bond length of 1.322 Å. The cis conformer was calculated to have a carbenic bond angle of 106°, a C−F bond length of 1.353 Å, and a C−OH bond length of 1.309 Å. Mueller et al. determined the singlet−triplet splitting as 23.7 kcal/mol favoring the singlet at the RHF/STO-3G and UHF/STO-3G level.[86] Additional computational results on the structure of fluoro(hydroxy)carbene are available.[204,386,389] The vibrational spectrum of fluoro(hydroxy)carbene has been calculated at the HF/6-31G* level.[388,390]

Mitsch found that 3-fluoro-3-methoxydiazirine (**144**) decomposed thermally (2 h, 50−95 °C) to fluoro(methoxy)carbene (**145**) and, in the absence of a coreactant, dimerized to 1,2-difluoro-1,2-dimethoxyethene (**146**).[219] In the presence of a 5-fold excess of tetrafluoroethene, methoxypentafluorocyclopropane (**147**) was formed in 61.5% yield. A smaller amount of the dimerization product was also formed (Scheme 12).

Scheme 12

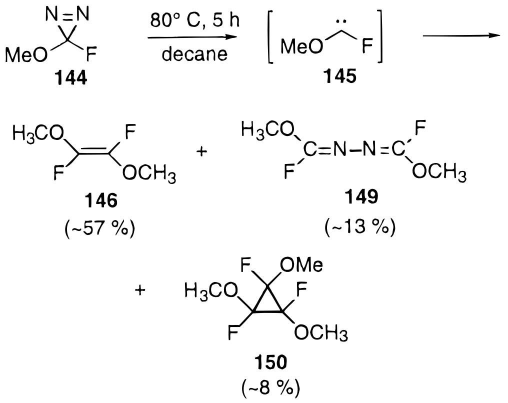


Moss and co-workers developed an alternative synthesis of **144** based on the “diazirine exchange reaction”.[391] When treated with fluoride ion, chloro- and bromodiazirines can be converted to the corresponding fluorodiazirines in good yields (eq 85). The reaction is quite general and can be carried out on halodiazirines containing electron-donating groups like alkoxy or electron-withdrawing groups like trifluoromethyl.[392] Originally, the transformation was suggested to occur via a dissociative-recombination mechanism involving tight ion pairs.[393] However, independent work by Dailey and Bainbridge[394] and Creary and Sky[395] suggested that the reaction occurred by an addition−elimination mechanism. Since chloro- and bromodiazirines are conveniently available from the Graham oxidation of amidines with hypohalite, this reaction is an important method for the synthesis of many fluorodiazirines. These compounds can be used as mild photochemical or thermal precursors to fluorocarbenes.

148 144

(85)

The thermal decomposition (decane, 80 °C, 5 h) of **144** mainly produced carbene dimer **146** (~57%) along with azine **149** (~13%) and a third product **150**, assigned as the cyclopropane adduct of fluoro(methoxy)carbene and the carbene dimer (eq 86).[396]

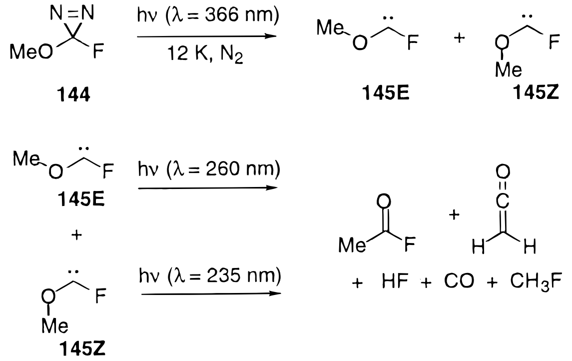


(86)

Thermolysis in the presence of acrylonitrile or methyl acrylate produced the syn and anti isomers of the corresponding cyclopropane adducts.[396] The yields were low (4−6%) due to the volatility of the cyclopropanes and the resulting inefficient GC collection. In addition, the photolysis ($\lambda > 300$ nm) of 3-fluoro-3-methoxydiazirine in methylacrylate also generated cyclopropane.

Fluoro(methoxy)carbene was generated in a nitrogen matrix at 12 K by the photolysis ($\lambda = 366$ nm) of **144** and was observed by IR and UV/vis spectroscopy ($\lambda_{max} = 245$ nm) (Scheme 13).[397] Subsequent photolysis ($\lambda < 280$ nm) led to the destruction of the IR bands assigned to the carbene and the growth of bands assigned to acetylfluoride, ketene, HF, CO, and CH_3F. Selective photolysis ($\lambda = 260$ nm) led to the disappearance of the *trans*-fluoro(methoxy)carbene (**145*E***) absorptions, and irradiation at 235 nm led to the destruction of the *cis*-fluoro(methoxy)carbene (**145*Z***) bands. In more concentrated matrices, warming to 29 K led to the disappearance of carbene IR bands and the appearance of bands assigned to carbene dimer **146**.

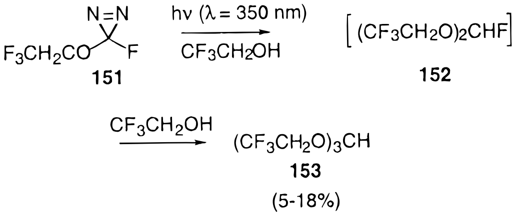
Scheme 13



Quenching experiments were reported in which **145** was generated in acetonitrile by LFP and reacted with various hydroxylic substrates.[397] Fluoro(methoxy)carbene was inert to most alcohols. Only hexafluoroisopropyl alcohol and acetic acid competed effectively with the decay of the carbene by dimerization and other pathways. A rate constant of $(9.1 \pm 1.2_2) \times 10^3$ was observed for the reaction with hexafluoroisopropyl alcohol. Rate constants of $(1.69 \pm 0.06_2) \times 10^7$ and $(8.66 \pm 0.94_2) \times 10^6$ M^{-1} s^{-1} were observed for the reactions of FCOMe with AcOH and AcOD, respectively. From these data, a k_H/k_D value of $1.95 \pm 0.21_2$ was obtained. This significant KIE suggested that there is a moderate degree of proton transfer in the transition state of the FCOMe/AcOH reaction.

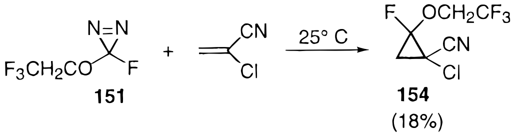
The singlet carbene bond angle calculated at the STO-3G level was 102.7°, with a C−F bond length of 1.331 Å and a C−OMe bond length of 1.372 Å.[204] The heat of formation of fluoro(methoxy)carbene was estimated at −53 kcal/mol.[397]

Fluoro(trifluoroethoxy)carbene was investigated since replacement of methoxy by trifluoroethoxy will temper the electron-donating ability of oxygen toward the carbene center. Photolytic decomposition ($\lambda = 350$ nm) of fluoro(trifluoroethoxy)diazirine (**151**) produced the *E*- and *Z*-dimers of fluoro(trifluoroethoxy)carbene in 10−15% isolated yield.[398] The yields were low because of the volatility and instability of the dimers. Irradiation of **151** in 2,2,2-trifluoroethanol afforded **153** (5−18%), formed by the self-catalyzed alcoholysis of **152** (eq 87).



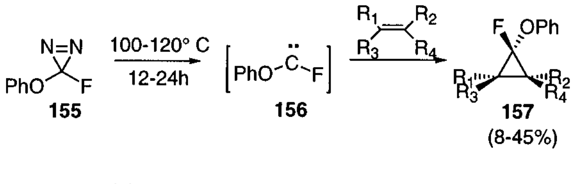
(87)

The photolysis of **151** in the presence of acrylonitrile, methylacrylate, 2-methylbutene, or 2-methyl-2-butene resulted in only carbene dimer. However, the more electrophilic α-chloroacrylonitrile reacted with fluoro(trifluoroethoxy)carbene to produce cyclopropane **154** in 18% isolated yield (eq 88). As a result, fluoro(trifluoroethoxy)carbene was provisionally deemed nucleophilic, possibly more nucleophilic than fluoro(methoxy)carbene. This was surprising because the trifluoroethoxy group is a less effective electron donor than the methoxy group due to the opposing inductive effect of the trifluoromethyl group.



(88)

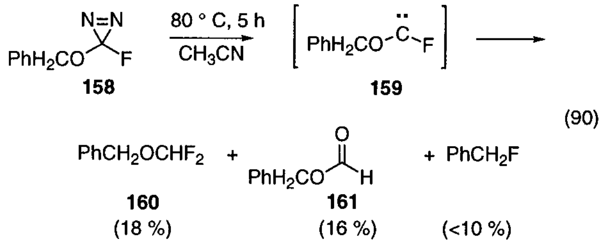
Further modification of the oxygen substituent by phenoxy was also investigated. Fluoro(phenoxy)carbene (**156**) was generated by the thermolysis (100−120 °C, 12−24 h) of 3-fluoro-3-phenoxydiazirine (**155**) and reacted with a series of alkenes including 2,3-dimethyl-2-butene, 2-methyl-2-butene, 2-methylpropene, hexene, methyl acrylate, and acrylonitrile to produce the corresponding cyclopropanes in 8−45% yield (eq 89).[399] Relative reactivities were 7.14 for the reaction of fluoro(phenoxy)carbene with 2,3-dimethyl-2-butene, 17.9 for 2-methyl-2-butene, 14.3 for 2-methylpropene, 1.00 for hexene, 18.7 for methyl acry-



(89)

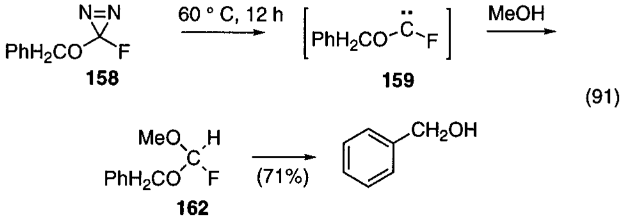
late, and 33.6 for acrylonitrile, respectively. From this data, it was concluded that fluoro(phenoxy)-carbene reacts as an ambiphile, a carbene that reacts rapidly with highly alkylated nucleophilic alkenes and with electrophilic alkenes containing electron-withdrawing groups but slowly with electronically intermediate alkenes such as hexene.[191,192]

Another oxygen-containing substituent investigated was benzyloxy. The thermolysis (80 °C, 5 h, acetonitrile) or photolysis (λ > 300 nm) of **158** produced (benzyloxy)difluoromethane (18%), benzyl formate (16%), and benzyl fluoride (<10%) (eq 90).[400]



Benzyl formate was formed by the addition of adventitious H_2O to benzyloxy(fluoro)carbene (**159**), followed by the loss of HF. (Benzyloxy)difluoromethane was produced by HF addition to the carbene, and the decomposition of the carbene generated CO and benzyl fluoride.

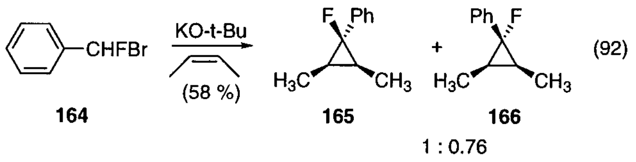
The decomposition of **158** in methanol (60 °C, 12 h) produced benzyl alcohol (71%). No benzylfluoride was detected. The benzyl alcohol arose from the HF-catalyzed methanolysis and methanol exchange of fluoro acetal **162**, the methanol carbene trapping product (eq 91).

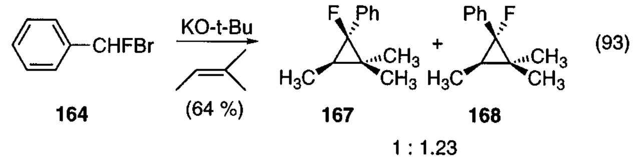


In addition, the thermolysis of the diazirine in acrylonitrile gave a mixture of diastereomeric cyclopropanes in 81% yield.

7. Arylfluorocarbenes

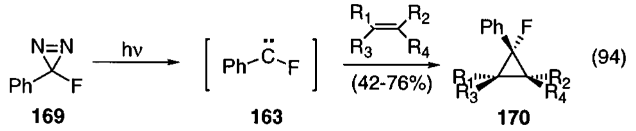
Fluorophenylcarbene (**163**), generated by the reaction of α-bromo-α-fluorotoluene (**164**) with potassium *tert*-butoxide, cyclopropanated 2,3-dimethyl-2-butene (81%), 2-methyl-2-butene (64%), 2-methylpropene (74%), *trans*-2-butene (56%), and *cis*-2-butene (58%), with relative reactivities of 2.7, 1.2, 1.00, 0.12, and 0.10, respectively.[401-403] The addition to *cis*- and *trans*-2-butene proceeded with greater than 98% stereospecificity (eqs 92 and 93). The reaction with *cis*-2-butene favored addition with the fluoro substituent syn to the two methyl groups (0.76 anti/syn ratio), whereas the reaction with 2-methyl-2-butene preferred the fluorine anti to the two methyl groups (1.23). In the case of *cis*-2-butene, the steric interaction between the methyl groups with the phenyl substituent was reasoned to be the cause of the preference. However, for 2-methyl-2-butene, the greater electrostatic attraction of the two methyl groups with the phenyl substituent as opposed to the single methyl group outweighed the increased steric interaction (of one additional methyl group) of this preferred mode of attack.





Similarly, Ando and co-workers[404] trapped **163** as the cyclopropane adducts of cyclohexene (23%), *cis*-2-butene (17%), 2-methyl-2-butene (54%), 2-methyl-2-pentene (62%), and 2,3-dimethyl-2-butene (76%). The *syn*-/*anti*-fluorine isomer ratios were 2.1, 2.0, 0.77, and 0.85, respectively.

However, when the cyclopropanations were repeated in the presence of 18-crown-6, the relative reactivities, determined by the olefin competition method, were altered, but remained in the same order.[405] The relative reactivity of 2,3-dimethyl-2-butene was 5.8 (2.7 without the crown ether), 2-methyl-2-butene, 3.0 (1.2), 2-methylpropene, 1.0 (ref), *cis*-2-butene, 0.28 (0.12), and *trans*-2-butene, 0.10 (0.20). From these data, it was concluded that the carbene species formed by the α-elimination of α-bromo-α-fluorotoluene was not a free carbene, but a carbene—base complex, or carbenoid. In the presence of 18-crown-6, the reactive species was presumed to be the free carbene, which displayed higher selectivity than the carbenoid. These conclusions were substantiated by the similar results obtained from the steady state or flash photolytic generation of fluorophenylcarbene from 3-fluoro-3-phenyldiazirine (**169**) in alkene or alkene/isooctane solutions, by comparison of absolute rate constants (eq 94).[406] The reaction with 2,3-dimethyl-2-butene took place with a relative reactivity of 5.52 (49% yield), using the alkene competition method, with 2-methyl-2-butene, 1.80 (52%), 2-methylpropene, 1.00 (70%), *cis*-2-butene, 0.21 (76%), and *trans*-2-butene, 0.15 (42%).[407] The only discrepancy was with 2-methyl-2-butene. However, when the base-induced elimination reaction with crown ether was repeated, the relative reactivity of 1.6 was very similar to the result using fluorophenyldiazirine as the precursor.

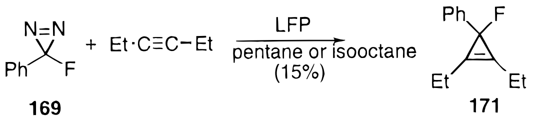


In order to confirm the original classification of **163** as an electrophile, the photochemically (λ > 300 nm) generated carbene was added to various *p*-X-substituted styrenes (X = MeO, Me, H, Cl, and CF_3) at 25 °C.[408] The resultant Hammet correlation reaffirmed the electrophilic nature of the carbene. There was no evidence of the curvature seen in the correlations of ambiphilic carbenes PhOCCl or MeOCCl. In the reaction of **163** with methyl acrylate and acrylonitrile, both alkenes were less reactive than *trans*-butene. This provided further evidence that fluorophenylcarbene is electrophilic. However, while the selectivity pattern of fluorophenylcarbene resembled those of electrophilic carbenes, MeCCl and CCl_2, **163** was much more reactive toward methylacrylate and acrylonitrile than chloromethylcarbene. The relative reactivity of fluorophenylcarbene toward methyl acrylate was 0.74 (normalized to *trans*-butene) and 0.80 with acrylonitrile, while the relative reactivity of MeCCl with methyl acrylate was 0.078 and 0.074 with acrylonitrile. This data suggested that nucleophilic interactions (carbene σ-alkene π^*) played a stronger role in the reaction of PhCF with electrophilic alkenes.

In addition, the "latent nucleophilicity" of fluorophenylcarbene was observed in the reaction with chloroacrylonitrile.[409] The carbene was shown to be 52 times more reactive toward chloroacrylonitrile than toward acrylonitrile. In this reaction, the HOMO (carbene)/LUMO (alkene) interaction appears to have dominated, resulting in nucleophilic selectivity, whereas in all of the other common alkenes previously considered the LUMO (carbene)/HOMO (alkene) interaction was favored, resulting in electrophilic selectivity.

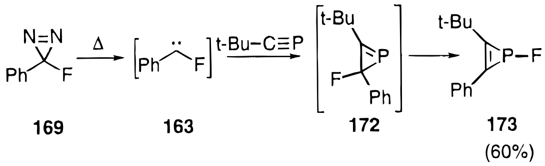
Additional work on the mechanism and activation parameters of the cycloaddition of **163** to alkenes has been reported.[410-412]

Fluorophenylcarbene reacted rapidly with various alkynes to produce the corresponding cyclopropenes (eq 95).[413] Carbene **163**, produced by the laser flash photolysis of **169** in pentane or isooctane solutions, reacted with 3-hexyne, phenylacetylene, ethoxyacetylene, heptyne, methyl propiolate, or dimethyl acetylenedicarboxylate. The absolute rate constants were 11×10^{-6} (l mol^{-1} s^{-1}) for phenylacetylene, 8.4×10^{-6} for 3-hexyne, 1.6×10^{-6} for heptyne, 1.1×10^{-6} for methylpropiolate, and 3.2×10^{-6} for dimethyl acetylenedicarboxylate. Similar to the alkenes, decreasing carbenic reactivity with increasing alkyne ionization potential was observed (electrophilic selectivity) until the ionization potential increased to 11 eV. With highly electron-deficient alkynes, the latent nucleophilicity of fluorophenylcarbene was again displayed. The rate increase for the addition to dimethyl acetylenedicarboxylate appeared to be predominantly nucleophilic, consistent with differential frontier molecular orbital considerations.



(95)

Fluorophenylcarbene, generated by the thermolysis of **169**, added to phosphoalkynes to form 1-fluoro-1*H*-phosphirenes **173**.[414] The initially formed 2*H*-phosphirenes **172** could not be detected because of the facile 1,3-halogen shift to the 1*H*-isomers (eq 96).



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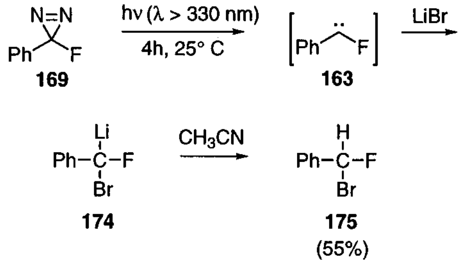
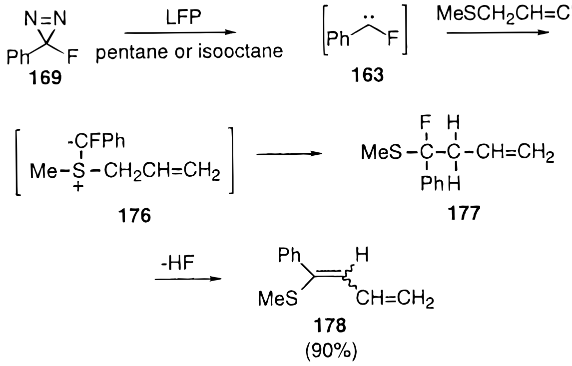


(97)

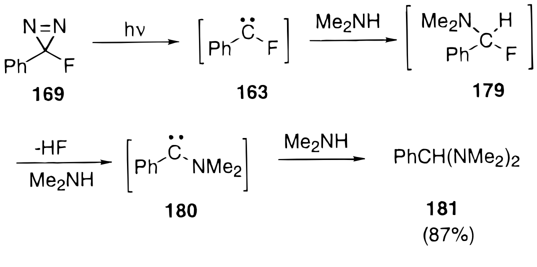
Fluorophenylcarbene (**163**) was trapped by LiBr to produce the corresponding carbenoid, which then abstracted a proton from the acetonitrile solvent (eq 97).[415] The quenching of the carbene involved kinetic contributions from both Li and Br. Other nonlithium salts such as $(Bu)_4N^+Br^-$ were not as effective (three times slower), and there was a modest rate dependence on the anion, $N_3^- \approx Cl^- > Br^- \approx I^-$, roughly in the order of anion nucleophilicity in polar aprotic solvents. The latent ambiphilic properties of **163**, where the electrophilic Li^+ interacts with the filled carbene sp^2 orbital while Br^- interacts with the vacant p-orbital, provided the rationale for these observations.

Laser flash photolysis of **169** produced **163**, which was readily captured by allylic sulfides to form transient ylides **176** that underwent [2,3] sigmatropic rearrangement (Scheme 14).[416] The sulfur atom was found to be an extremely effective carbene trap, much more reactive than the vinyl groups of these allylic sulfides.

Scheme 14

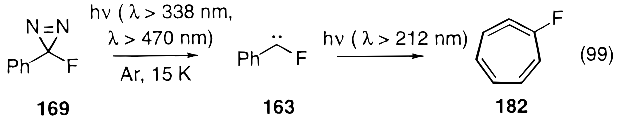


While fluorophenyldiazirine and dimethylamine failed to react thermally (25 °C, 24 h), the irradiation of **169** in the presence of the amine generated an aminophenylcarbene (**180**) presumably by the sequence shown in eq 98.[417] An 87% yield of the bis(dimethylamino) product (**181**) was obtained.



(98)

Photolysis ($\lambda > 338$ nm) of **169** in an argon matrix at 15 K produced **163** and the isomeric diazo compound, which upon further irradiation ($\lambda > 470$ nm) also generated carbene.[418,419] Subsequent irradiation (>212 nm) slowly produced fluorocycloheptatetraene (**182**) (eq 99).



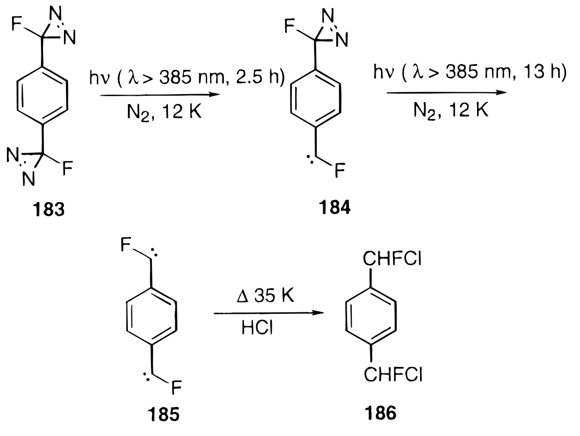
Flash vacuum thermolysis (325 °C) of **169** followed by cocondensation with argon generated **163**, **182**, and at least one unidentified product.

UV–vis spectra were taken of **163** photochemically generated in a 3-methylpentane matrix at 77 K and compared with point-by-point transient spectra of the carbene prepared by laser flash photolysis in aerated isooctane or benzene solution at 23 °C.[406,412] Good agreement was obtained between the two methods. Zuev and Sheridan observed a deep blue color associated with **163** in N_2 matrices at 13 K and UV/vis absorptions at 300 nm and in the 450–740 nm ($\lambda_{max} = 550$) range.[419]

Two related arylfluorocarbenes have been reported. The laser flash photolysis ($\lambda = 351$ nm) of 3-fluoro-3-(*p*-methoxyphenyl)diazirine in isooctane generated fluoro(*p*-methoxyphenyl)carbene, which reacted with 2,3-dimethyl-2-butene and hexene with absolute rate constants of $(1.1 \pm 0.04) \times 10^7$ and $(5.0 \pm 0.3) \times 10^4$ M^{-1} s^{-1} at 23–25 °C.[410] Compared to fluorophenylcarbene, there was a decrease in rate constant of ~14- and 19-fold, respectively. In addition, a transient absorption at 305 nm was assigned to the carbene.

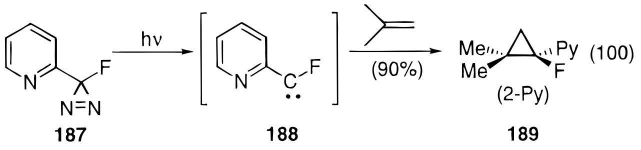
A second related carbene is *p*-phenylenebis(fluoromethylene) (**185**). Irradiation ($\lambda = 385$ nm) of an N_2 matrix at 15 K of diazirine **183** afforded monocarbenemonodiazirine **184**, upon which subsequent irradiation slowly generated biscarbene **185** (Scheme 15).[419] Warming an N_2 matrix of **185** doped with HCl (0.5%) to 35–40 K resulted in the identification of IR frequencies corresponding to **186**. Biscarbene **185** could also be generated in 3-methylpentane and methane matrices and survive annealing to 60 and 46 K, respectively. The biscarbene was stable in O_2-doped (2.5%) N_2 matrices up to 40 K.

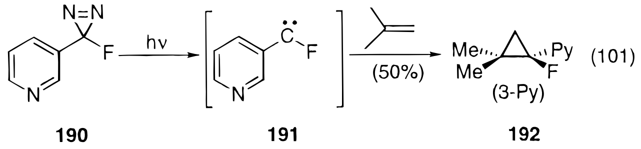
Scheme 15

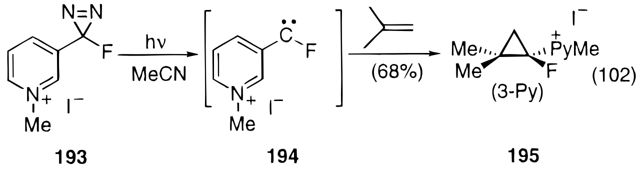


Spectroscopic data reported for **185** include IR and UV–vis absorptions. The observed IR spectra fit reasonably well with the predicted vibrational frequencies at the 6-31G* level. The CIS/6-31G* calculations predict a first excited singlet transition at 470 nm. The observed absorptions were at 300 and 480–800 nm with a λ_{max} at 600 nm.

In addition, fluoropyridylcarbenes **188** and **191** and fluoropyridinium carbene **194** were generated by the photolysis of the appropriate diazirines. In the presence of excess 2-methylpropene, good yields of cyclopropanes were obtained (eqs 100–102).



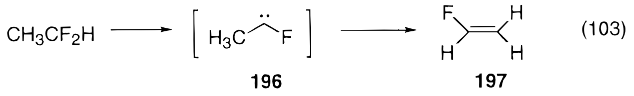




8. Alkylfluorocarbenes

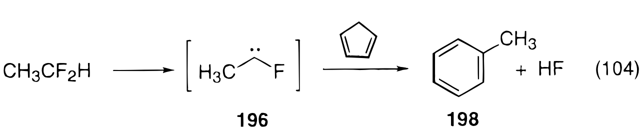
The isomerizations of simple alkyl carbenes by 1,2 hydride or alkyl shifts are usually too rapid for these carbenes to be trapped by unsaturated species[420] or studied by nanosecond laser flash photolytic methods.[421–423] However, the stabilization of the carbene afforded by a halogen substituent directly on the carbene center has permitted the investigation into the kinetics of the rearrangements of various alkylhalocarbenes.[424]

Fluoro(methyl)carbene (**196**) has been generated by the α,α elimination of DF from CH_3CDF_2 or HF from CH_3CHF_2 and detected as the 1,2-hydrogen migration product **197** (eq 103).[425,426] The deuterated analog has also been produced in the decomposition of chemically activated CD_3CHF_2 and detected as the rearrangement product alkene, CD_2CDF.[426,427] It was concluded by Kim et al. that the α,α-elimination pathway accounted for 10% of the total elimination in CH_3CHF_2,[426] whereas a value of 13% was found by Sekhar et al.[425] In addition, the activation energy toward 1,2-hydrogen migration in fluoro(methyl)carbene was calculated as 21 kcal/mol using the MP4/6-31G** basis set on MP2/6-31G*-optimized geometries.[420] Evanseck and Houk predicted an activation barrier of 19 kcal/mol, obtained by correcting the value of Dailey by 0.9 kcal/mol (difference between the MP2/6-311G** and MP2/6-31G** values for methylcarbene) and also correcting for the zero point



energy (0.9 kcal/mol).[420] Similar results were obtained by Palma and co-workers.[428]

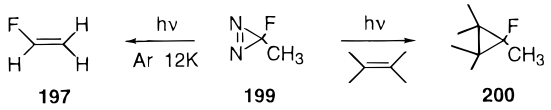
Fluoro(methyl)carbene, produced by the α,α-elimination of HF from CH_3CHF_2, was trapped by 1,3-cyclopentadiene (eq 104).[429]



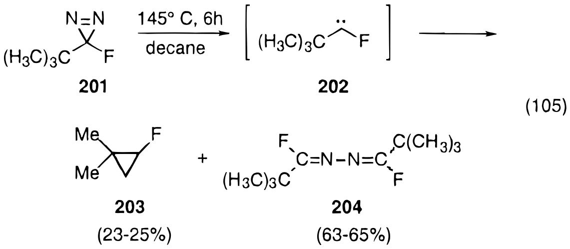
Schlosser et al. detected **196** in the reactions of methyllithium with trichlorofluoromethane (5.4%), dichlorofluoromethane (9.5%), dichlorodifluoromethane (47%), chlorodifluoromethane (33%), chlorotrifluoromethane (8.8%), and trifluoromethane (7.6%) as the cyclopropane adduct of 2-methyl-2-pentene.[303]

Fluoro(methyl)carbene can be trapped by alkenes in solution by the irradiation of fluoro(methyl)diazirine (**199**).[430] However attempts to generate **196** or the deuterated carbene under matrix isolation conditions led only to the rearrangement product, fluoroethene (Scheme 16).[431]

Scheme 16



Some alkyl(fluoro)carbenes do not undergo migrations to form alkenes but instead undergo C−H insertion. Photolysis (λ > 320 nm, 25 °C) of 3-fluoro-3-*tert*-butyldiazirine (**201**) in decane gave 75% azine **204** and <1% of the 1,3-insertion product **203**.[432] However, the thermolysis of **201** in decane (145 °C, 6 h, sealed tube) yielded 23−25% of **203** and 63−65% of **204** (eq 105).



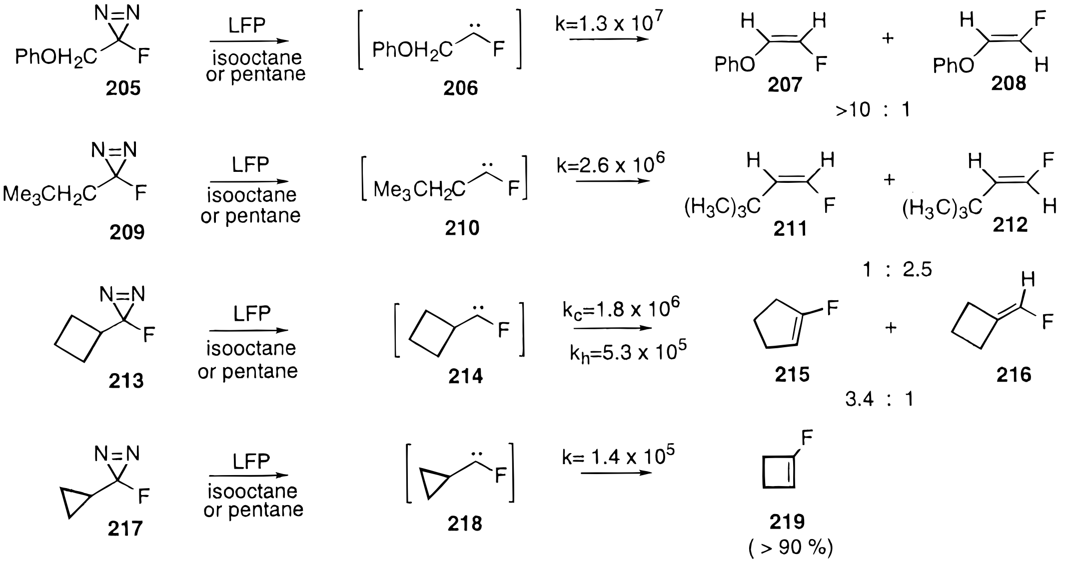
The kinetic parameters of the 1,2-migrations of a series of carbenes **206**, **210**, **214**, and **218** were determined by Moss et al. (Scheme 17).[433] The carbenes were generated by the laser flash photolysis of the corresponding diazirines **205**, **209**, **213**, and **217** in isooctane or pentane solutions and monitored by the pyridine ylide method. The activation energy for the rearrangement of **210** to **211** and **212** was determined to be 3.3 kcal/mol. For **214**, the alkyl migration barrier to produce **215** was 2.3 kcal/mol, and the barrier for the hydride shift to produce **216** was 3.8 kcal/mol. The activation energy for the rearrangement of **218** to **219** was 4.2 kcal/mol. The extremely rapid hydride shift in **206** was explained by the stabilization of the positive charge that accumulates at the migration origin in the transition state by the phenoxy substituent. Also, the faster rate of rearrangement for **214** than **218** was presumed to be a consequence of the greater stability of the latter.

In addition, a large kinetic isotope effect (1,2-H/1-2-D shift = ∼5−6) was observed for the rearrangement of fluoro(neopentyl)carbene.[434]

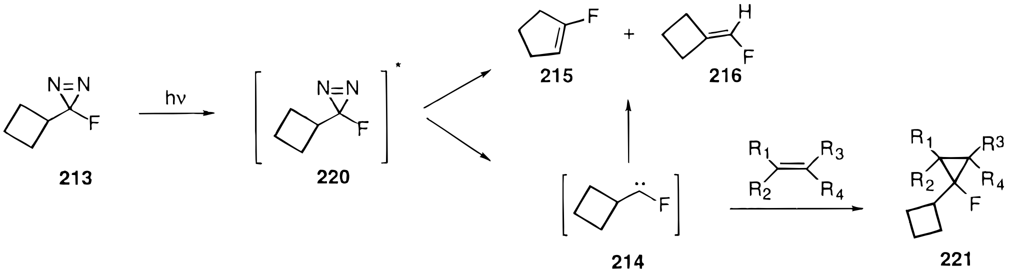
Recent work on the kinetics of carbene rearrangements has led to a modification of the above mechanism for alkene formation.[435−437] It was concluded that at least two pathways were involved in the rearrangements. An excited diazirine species, in which nitrogen extrusion occurs concurrently with hydride (or alkyl) migration, has been invoked as a second possible mode of rearrangement, in addition to the pathway of a hydride shift from the singlet carbene. Other possibilities include rearrangement occurring from an excited carbene state, as well as the involvement of a carbene−alkene complex.

Moss and Ho recently performed additional experiments on **214** where a nonlinear correlation between the ratio of rearrangement to addition vs alkene concentration was obtained, and a linear inverse relation was found.[438] This was inconsistent with the

Scheme 17

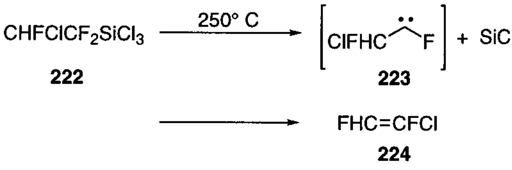


Scheme 18



simple mechanism involving a single reactive intermediate that adds to the alkene competitively with intramolecular rearrangement. A second pathway involving the excited state diazirine **220** would explain the results. It was estimated that the excited diazirine accounted for 12% of the rearrangement observed, with insignificant changes in the original rate constants k_c and k_h (Scheme 18).

A related series of fluorocarbenes containing halogenated alkyl groups was intensively studied by Haszeldine and co-workers. The first two carbenes studied, 2-chloro-1,2-difluoroethylidine (**223**) and 2,2-dichloro-1,2-difluoroethylidene (**226**), were prepared by the pyrolysis (250 °C) of trichloro(2-chloro-1,1,2-trifluoroethyl)silane (**222**) and trichloro(2,2-dichloro-1,1,2-trifluoroethyl)silane (**225**), respectively (eqs 106 and 107).[439] The major products were alkenes **224** and **227**, corresponding to 1,2-chlorine migration of the respective carbenes, **223** and **226**, formed by α-elimination of SiCl3F. Only a small amount (<10%) of the olefins resulting from β-fluorine elimination with respect to silicon was obtained. The thermal decomposition of trifluoro-(2,2-dichloro-1,1,2-trifluoroethyl)silane at 140 °C gave similar results.[440]



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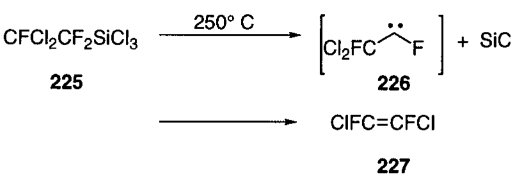

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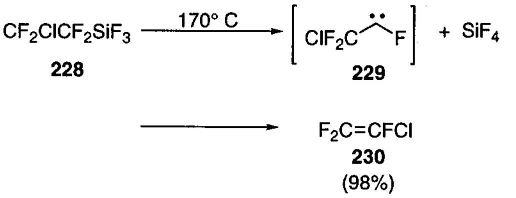
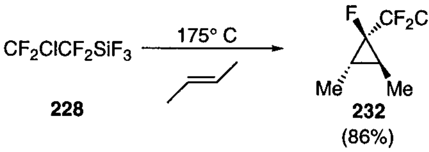


(108)

$$\underset{\mathbf{228}}{CF_2ClCF_2SiF_3} \xrightarrow[Me_3SiH]{175° C} \underset{\substack{\mathbf{231}\\(92\%)}}{CF_2CHFSiMe_3} + \underset{\substack{\mathbf{230}\\(6.5\%)}}{F_2C{=}CFCl} \quad (109)$$



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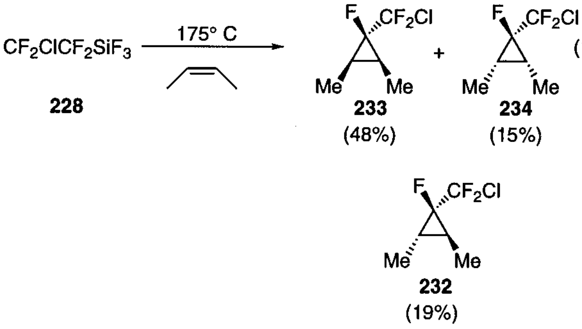
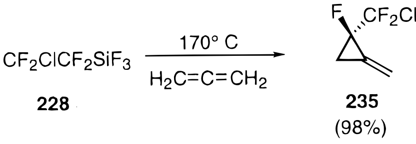


(111)

A related carbene, 2-chloro-1,2,2-trifluoroethylidene (**229**), was generated by the pyrolysis (170 °C) of (2-chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane (**228**)[441] or trichloro(2-chlorotetrafluoroethyl)silane at 220 °C.[440] In the absence of a trapping agent, a 98% yield of chlorotrifluoroethene (**230**), the carbene rearrangement product, was obtained by the first method and a 90% yield was obtained with the second method (eq 108). In the presence of excess trimethylsilane, Si−H insertion product **231** was obtained in 92% yield, as well as **230** (6.5%) (eq 109). The reaction with *trans*-2-butene gave a 86% yield of cyclopropane **232** resulting from stereospecific carbene addition, as well as chlorotrifluoroethene (11%) (eq 110). However, the reaction with *cis*-2-butene did not result in stereospecific addition (eq 111). The products were **230** (18%), cyclopropane **232** (19%), **233** (48%), and **234** (15%). This was explained by the presence of a small amount of *trans*-alkene in the product mixture, suggesting the occurrence of olefin isomerization prior to carbene addition, possibly due to the formation of radicals in the system.

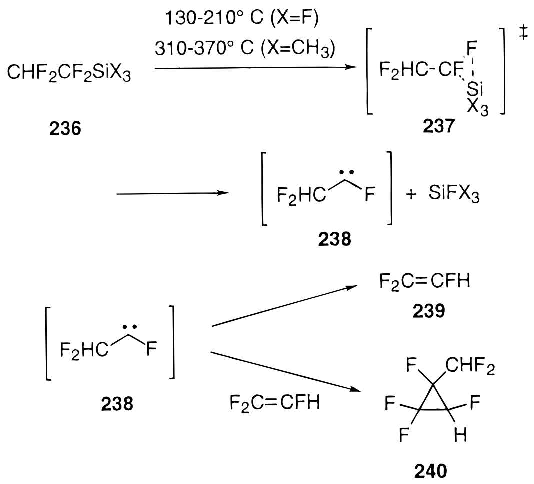
The reaction of **228** with allene at 170 °C generated 1-(chlorodifluoromethyl)-1-fluoro-2-methylenecyclopropane (**235**) in 98% yield (eq 112).[441] The 2:1 spiropentane adduct was not detected.



(112)

In a similar fashion, 1,2,2-trifluoroethylidene (**238**) was prepared by the thermal decomposition of trifluoro(1,1,2,2-tetrafluoroethyl)silane or trimethyl-(1,1,2,2-tetrafluoroethyl)silane (Scheme 19).[442] The rate of silane decomposition was markedly reduced when fluorine was replaced by methyl on silicon. In the absence of a carbene trap, trifluoroethene (**239**) is formed by a two-step mechanism in which the rate-

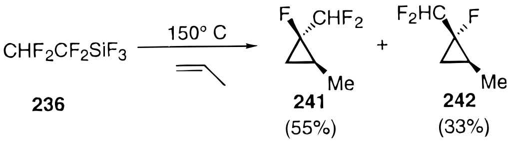
Scheme 19



determining step is the formation of **238** by the α-elimination of SiX_3F via an intramolecular 3-centered transition state (**237**). A carbene rearrangement involving a 1,2-hydride shift takes place in the second step. Kinetic studies confirm the first order and homogeneous nature of this reaction.[443−445] The activation energy for the carbene isomerization was found to be ca. 23 kcal/mol, and alkene addition and C−H insertion reactions had activation energies around 11−12 kcal/mol. In addition, the carbene isomerizations of 1-fluoro-, 1,2-difluoro-, and 1,2,2-trifluoroethylidenes have been extensively studied using MNDO calculations.[446]

Other products identified from the thermal decomposition reactions include *cis*- and *trans*-1-(difluoromethyl)-1,2,2,3-tetrafluorocyclopropane (**240**), resulting from the addition of **238** to trifluoroethene.[447]

In the presence of alkenes, such as ethene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, tetrafluoroethene, and cyclohexene, the yield of trifluoroethene (**239**) was greatly reduced and yields of the corresponding cyclopropanes ranged form 62 to 90%.[447,448] The reaction with *cis*- or *trans*-2-butene occurred with 100% stereospecificity and yields of 95%. In the reactions with propene, *cis*-2-butene, and 2-methyl-2-butene the carbene added predominantly in the direction of least steric interaction between the olefin methyl groups and the carbene CHF_2 group (eq 113).

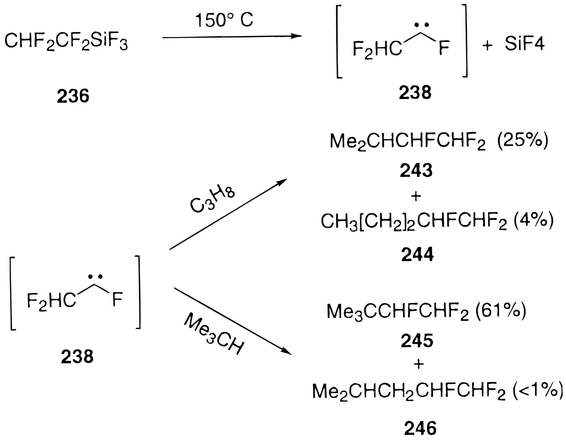


(113)

Lee and co-workers also reported the addition of fluoro(difluoromethyl)carbene to a series of methyl-substituted ethenes in the gas phase.[449]

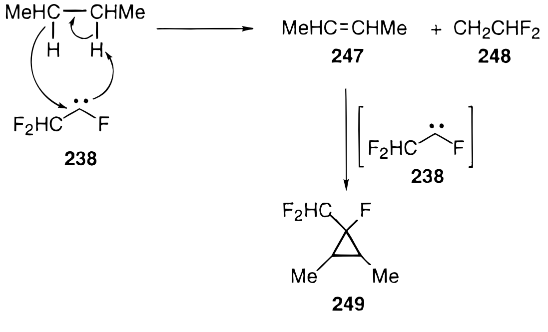
1,2,2-Trifluoroethylidene displayed a notable degree of selectivity during the insertion into the C−H bonds of alkanes.[441,447,450] The reactivity order was determined to be tertiary > secondary > primary. For example, in the reaction with propane, the secondary C−H insertion product, $Me_2CHCHFCHF_2$, was formed in 25% yield while the primary C−H insertion product, $CH_3(CH_2)_2CHFCHF_2$, was produced in 4% yield (Scheme 20). No reaction occurred with methane, and insertion into the primary C−H bonds of isobutane was not detected within the limits of GLC detection. The ease of tertiary C−H insertion was further confirmed by the decreased amount of trifluoroethene formed in the reaction with isobutane, as compared to other hydrocarbons. These relative reactivities were attributed to the number of *β* hydrogens adjacent to the C−H bond of interest and, therefore, to the bond order and bond dissociation energy. In addition, it was found that CH_2 groups nearest the end of a chain were more readily attacked than those near the center.

Scheme 20



Cyclopropanes were identified as minor side products in the insertion reactions with ethane, propane, butane, isobutane, pentane, and cyclopentane.[450] 1,1,2-Trifluoroethane was also detected in these reactions. It was suggested that these compounds were produced by a concerted hydrogen abstraction from the alkanes by the carbene, followed by a stereospecific addition of **238** to the resultant alkene (Scheme 21).

Scheme 21



1,2,2-Trifluoroethylidene (**238**) also inserted into the C−H bonds of diethyl ether (eq 114).[450] The secondary C−H bonds, which are adjacent to the oxygen atom, were found to be much more reactive (secondary to primary reactivity ratio 96:1) than those in a $MeCH_2CH_2$ grouping (*ca.* 15:1).

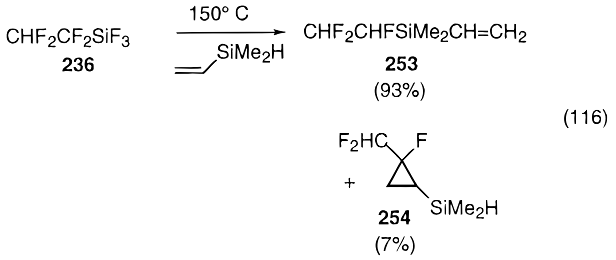
Evidence for the singlet nature of 1,2,2-trifluoroethylidene reactions include the retention of configuration upon tertiary C−H bond insertion of the optically active ether L-$CH_3[CH_2]_5CHMeOMe$, as well as the previously mentioned stereospecific addition to both *cis*- and *trans*-2-butene.[451]

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{(CH_3CH_2)O}]{150^\circ\ \mathrm{C}} \underset{\substack{\mathbf{250}\\(64\%)}}{\mathrm{EtOCHMeCHFCHF_2}} + \underset{\substack{\mathbf{251}\\(1\%)}}{\mathrm{EtOCH_2CH_2CHFCHF_2}} \qquad (114)$$

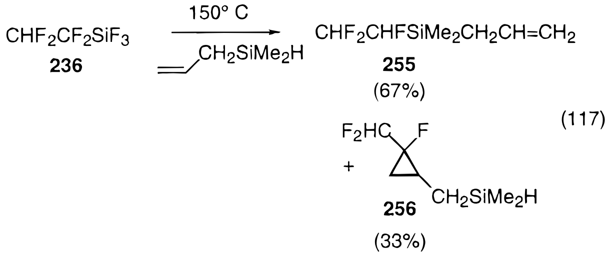
1,2,2-Trifluoroethylidene (**238**) also inserted into Si−H and Si−halogen bonds.[452] The insertion into the Si−H bonds of trialkylsilanes occurred readily (90−99%), indicating a higher reactivity than the tertiary C−H bond in isobutane (61%) under analogous conditions (eq 115). The insertion into a Si−D bond was found to be slightly less favorable (88%).[451]

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{R_3=Et_3,\ Et_2Me,\ Me_3}]{\substack{\mathrm{R_3SiH}\\150^\circ\ \mathrm{C}}} \underset{\substack{\mathbf{252}\\(98\text{-}99\%)}}{\mathrm{CHF_2CHFSiR_3}} \qquad (115)$$

In comparative reactivity studies of the Si−H and C=C bonds in the silanes $CH_2{:}CHSiMe_2H$ and $CH_2{:}CHCH_2SiMe_2H$, Si−H insertion predominated, although it was not the exclusive reaction (eqs 116 and 117).[451] While the Si−H bonds appeared to have the same reactivity toward insertion as those in the trialkylsilanes, no carbene rearrangement products were detected, and the olefinic double bonds showed much lower reactivity than those in hydrocarbon alkenes. This was explained by a decrease in nucleophilicity of the double bond caused by the overlap of the π-orbital with the vacant d orbitals on silicon, as well as by the destabilizing effect of the electropositive silicon atom on the transition state.

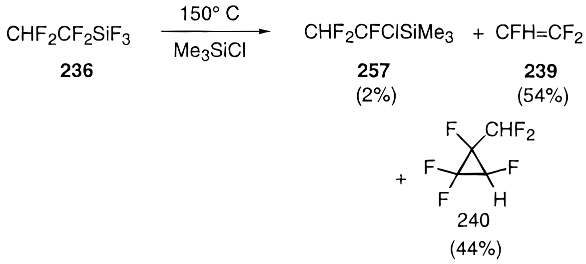


(116)

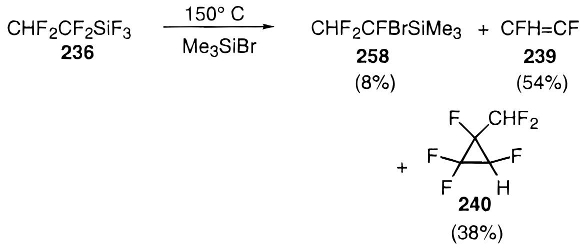


(117)

Insertion into the Si−Cl bonds of chlorosilanes or the Si−Br bond of bromotrimethylsilane was more difficult (2−15% yield) (eqs 118 and 119).[451,452] This was explained by the greater bond strength of the Si−Hal bond as compared to the Si−H bond. The reactivity toward Si−Cl insertion decreased in the series $Me_2SiCl_2 > MeSiCl_3 > Me_3SiCl, SiCl_4$.



(118)



(119)

The thermal decomposition of **236** in the presence of chlorodimethylsilane, dichloromethylsilane, or trichlorosilane resulted in both insertion products and carbene rearrangement products.[451,452] The insertion product yields and the ratio of Si−H to Si−Cl insertion dramatically decreased in the series Me_2ClSiH (98% yield, ∞ insertion ratio) > $MeCl_2SiH$ (58%, 2.0:1 ratio) > Cl_3SiH (53%, 0.7:1 ratio) (eqs 120−122). The deactivation observed upon increasing chlorine substitution was explained by the decreased electron density of the Si−H bond due to the strong inductive effect of chlorine, resulting in the Si−H bond being less susceptible to electrophilic attack by the carbene. Steric arguments were also invoked to explain the lower reactivity. However, as the reactivity of the Si−H bond decreased, the reactivity of the Si−Cl bond increased. The yields of the Si−Cl insertion products of $MeCl_2SiH$ (29%) and Cl_3SiH (43%) were much higher than those obtained from silanes containing only Si−Cl and Si−Me bonds (2−15%). This was explained by a decrease in steric hindrance in the transition states due to the replacement of a methyl group or chlorine atom by the smaller hydrogen atom.

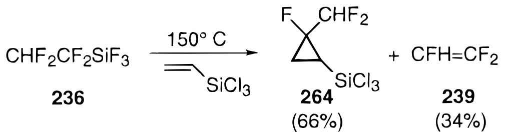
$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{Me_2ClSiH}]{150^\circ\ \mathrm{C}} \underset{\substack{\mathbf{259}\\(96\%)}}{\mathrm{CHF_2CHFSiClMe_2}} \qquad (120)$$

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{MeCl_2SiH}]{150^\circ\ \mathrm{C}} \underset{\substack{\mathbf{260}\\(29\%)}}{\mathrm{CHF_2CHFSiCl_2Me}} + \underset{\substack{\mathbf{261}\\(29\%)}}{\mathrm{CHF_2CFClSiHClMe}} \qquad (121)$$

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{Cl_3SiH}]{150^\circ\ \mathrm{C}} \underset{\substack{\mathbf{262}\\(10\%)}}{\mathrm{CHF_2CHFSiCl_3}} + \underset{\substack{\mathbf{263}\\(43\%)}}{\mathrm{CHF_2CFClSiHCl_2}} \qquad (122)$$

In order to determine whether Si−Cl insertion by 1,2,2-trifluoroethylidene could complete with addition to the olefinic double bond of trichloro(vinyl)silane, **236** was thermally decomposed in the presence of the carbene trapping agent.[451] A mixture of *cis*- and *trans*-1-fluoro-1-(difluoromethyl)-2-(trichlorosilyl)cyclopropane (**264**) was formed in a 1:2 ratio and in 66% yield (eq 123). Trifluoroethene was observed in 34% yield, and no Si−Cl insertion products were detected. Again, the yield of cyclopropanation was lower than those obtained from additions to hydrocarbon olefins.

An investigation into the reactivity of 1,2,2-trifluoroethylidene toward tetraalkylsilanes of the type Me_3SiR (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu,



236 **264** (66%) **239** (34%) (123)

isopentyl, cyclopentyl, $SiMe_3$, and $OSiMe_3$) was also reported (eqs 124–126).[453] This study was undertaken to determine the effect of the silicon atom on the various types of C–H bond insertions. In each case, carbene rearrangement products were detected in addition to the insertion adducts. Yields ranged from 0% in the case of tetramethylsilane to 28% for *sec*-butyltrimethylsilane. In some instances, fluorotrimethylsilane was detected and shown to be due to the decomposition of α-C–H insertion products. The β-C–H and γ-C–H insertion products were stable under the reaction conditions, and therefore, any fluorotrimethylsilane present was assumed to have arisen from α-C–H insertion adducts.

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{PrSiMe_3}]{150°\ \mathrm{C}} \underset{\substack{\mathbf{265}\\(1\%)}}{\mathrm{CHF_2CHFCHEtSiMe_3}} + \underset{\substack{\mathbf{266}\\(24\%)}}{\mathrm{CHF_2CHFCHMeCH_2SiMe_3}} \qquad (124)$$

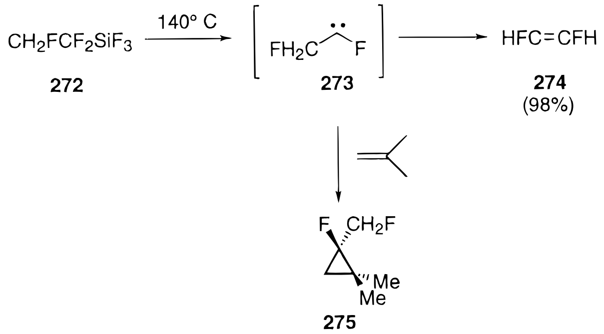
$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{i\text{-}PrSiMe_3}]{150°\ \mathrm{C}} \underset{\substack{\mathbf{267}\\(17\%)}}{\mathrm{CHF_2CHFCMe_2SiMe_3}} + \underset{\substack{\mathbf{268}\\(1\%)}}{\mathrm{CHF_2CHFCH_2CHMeSiMe_3}} \qquad (125)$$

$$\underset{\mathbf{236}}{\mathrm{CHF_2CF_2SiF_3}} \xrightarrow[\mathrm{BuSiMe_3}]{150°\ \mathrm{C}} \underset{\substack{\mathbf{269}\\(1\%)}}{\mathrm{CHF_2CHFCH(Pr)SiMe_3}} + \underset{\substack{\mathbf{270}\\(8\%)}}{\mathrm{CHF_2CHFCHEtCH_2SiMe_3}} + \underset{\substack{\mathbf{271}\\(12\%)}}{\mathrm{CHF_2CHFCHMeCH_2CH_2SiMe_3}} \qquad (126)$$

The results indicated that the reactivity of the C–H bonds followed the same trend, tertiary > secondary > primary, regardless of the positions of the C–H bonds relative to the silicon atom. In addition, α-C–H bonds were considerably deactivated. For example, insertion into secondary and primary C–H bonds β to silicon took place in the presence of tertiary C–H bonds in the α-position. However, if the tertiary C–H bond was in the β- or γ-position, insertion occurred virtually exclusively in this position. Primary C–H insertion adducts from bonds α to silicon were not observed, whereas insertion occurred in primary C–H bonds β or γ to silicon. In addition, the yields of products formed by carbene insertion into secondary C–H bonds in the α-position are much lower than the yields of products from insertion into secondary C–H bonds in the β- or γ-position. The reaction with *n*-$BuSiMe_3$ provided a direct comparison of the reactivities of secondary C–H bonds in the α-, β-, and γ-positions (eq 126). A ratio (α:β:γ) of 1:8:12 was observed. The lower reactivity of bonds α to silicon was explained by the steric hindrance of the bulky $SiMe_3$ group to the approach of the carbene to the adjacent α-C–H bond. A second explanation attributed it to the destabilization of the transition state due to the electropositive silicon atom. Also, the lower reactivity of the β-C–H bond in *n*-$BuSiMe_3$ was explained by the greater hyperconjugative stabilization of the transition state for a C–H bond adjacent to a methyl group than to a methylene group. This was previously noted in the reactions with alkane C–H bonds.

The related carbene, 1,2-difluoroethylidene (**273**), was prepared by the thermal decomposition of trifluoro(1,1,2-trifluoroethyl)silane (**272**) at 140 °C.[440] In the absence of an added trapping agent, 1,2-difluoroethene (**274**) was formed in 98% yield. In the presence of 2-methylpropene, 1-fluoro-1-(fluoromethyl)-2,2-dimethylcyclopropane (**275**) was produced in 79% yield, in addition to 1,2-difluoroethene (19%) (Scheme 22). Ab initio calculations on the structure and rotational barriers of **273** have also been reported.[454]

Scheme 22



272 **273** **274** (98%) **275** (79%)

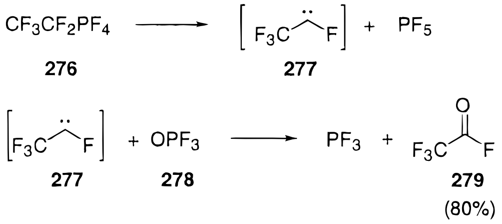
9. Fluoro(trifluoromethyl)carbene

Because there is a fluorine directly attached to the carbene carbon, tetrafluoroethylidene (fluoro(trifluoromethyl)carbene, **277**) is a ground state singlet. Additionally, it is kinetically stabilized toward rearrangement to tetrafluoroethene because of the resistance of fluorine to 1,2-migration. Thus, tetrafluoroethylidene can be generated using several different synthetic methods and undergoes intermolecular reactions in preference to intramolecular rearrangement.

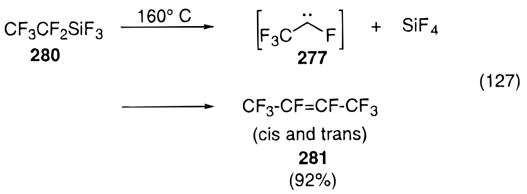
One of the first reports on the generation of tetrafluoroethylidene was by reaction of oxygen atoms, generated by the mercury-sensitized decomposition of N_2O at 24 °C, with hexafluoropropene.[455,456] In the absence of molecular oxygen, the rearrangement to produce tetrafluoroethene occurred as well as cyclopropanation of hexafluoropropene. In the presence of O_2, the carbene was effectively scavenged, resulting in trifluoroacetyl fluoride. However, CF_3-CF rearranged more readily as the temperature was raised and the 1,2-fluorine migration competed effectively with reaction with O_2, even with 50 mm of O_2 present.

Fluoro(trifluoromethyl)carbene (**277**) was identified as an intermediate in the decomposition of pentafluoroethyltetrafluorophosphorane (**276**) at 240 °C on platinum. In the presence of a 3-fold excess of OPF_3, trifluoroacetyl fluoride was obtained in 80% yield (Scheme 23).[457]

Scheme 23



Carbene **277** has been generated by the thermal decomposition of $C_2F_5SiF_3$ (**280**) at temperatures greater than or equal to 160 °C.[458,459] This reaction occurs by a unimolecular α shift of fluorine to silicon, liberating the carbene and SiF_4. In the absence of carbene trapping reagents, the thermal decomposition of $C_2F_5SiF_3$ afforded *cis*- and *trans*-perfluoro-2-butenes (**281**) by carbene dimerization (eq 127).[459]

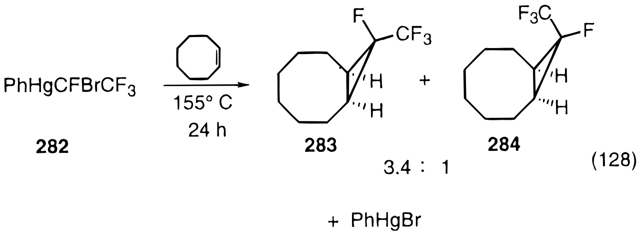


Tetrafluoroethene, the product of 1,2-fluorine migration, was absent from the reaction mixture.

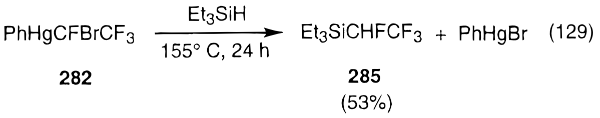
In the presence of HBr, high yields of the insertion product, CF_3CFHBr, were obtained. Similarly, the pyrolysis of $C_2F_5SiF_3$ in the presence of $(CH_3)_3SiH$ gave $(CH_3)_3SiCHFCF_3$ in nearly quantitative yield by insertion into the Si−H bond.

Carbene **277** has also been generated from $C_2F_5SiF_3$ by pulse adiabatic compression pyrolysis.[460] *cis*- and *trans*-2-butenes were formed in a 1:2.24 ratio. However, cis−trans isomerizations occurred at relatively low temperature. Fluoro(trifluoromethyl)carbene (**277**) resulting from the tautomerism of tetrafluoroethene by a 1,2-fluorine shift has also been detected and studied using kinetic spectroscopy during adiabatic compression.[461] In addition, the infrared multiphoton dissociation of 2-chloro-1,1,1,2-tetrafluoroethane produced tetrafluoroethylidene by three-centered elimination of HCl.[462] Carbene **277** produced in this manner was shown to undergo secondary IRMPD resulting in the formation of two CF_2 molecules.

The thermolysis (155 °C, 24 h) of phenyl(1-bromo-1,2,2,2-tetrafluoroethyl)mercury (**282**) in the presence of various olefins gave fluoro(trifluoromethyl)cyclopropanes (eq 128).[463,464] The alkenes used in this study included cyclooctene (98% yield), cyclohexene (87%), *trans*-4-octene (80%), *cis*-4-octene (77%), heptene (70%), (trimethylsilyl)ethene (16%), and 3-(trimethylsilyl)propene (93%). In all cases, where two stereoisomers were expected, the preferred isomer was the less hindered one, with the CF_3 group anti to the alkyl substituents. For example, the thermolysis in the presence of cyclooctene yielded the two products in a 3.4:1 ratio, favoring the product with CF_3 anti to the ring. The ratio of stereoisomers in the case of cyclohexene was 3.6:1, 5.8:1 for *cis*-4-octene, 1.9:1 for heptene, 3.1:1 for (trimethylsilyl)ethene, and 1.8:1 for 3-(trimethylsilyl)propene.

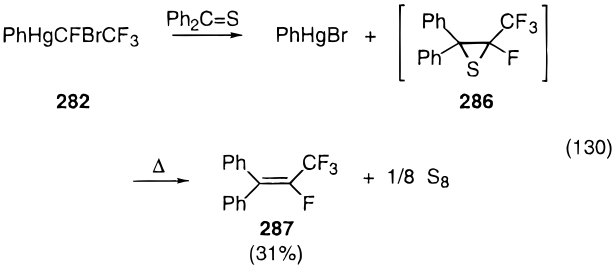


The thermolysis of **282** at 155 °C (24 h) in the presence of triethylsilane produced $Et_3SiCHFCF_3$ by Si−H insertion in 53% product yield (eq 129).

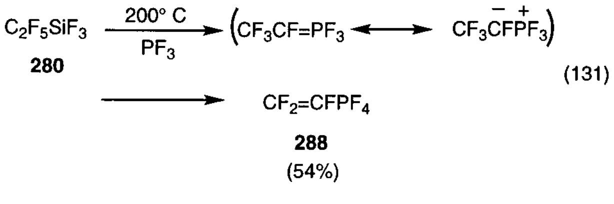


$$PhHgCFBrCF_3 \xrightarrow[155° C, 24 h]{Et_3SiH} Et_3SiCHFCF_3 + PhHgBr \quad (129)$$

In addition, the reaction of **282** with thiobenzophenone failed to form the expected thiirane **286**. Instead **287** was isolated in high yield. It was presumed that the thiirane formed but underwent sulfur extrusion (eq 130).



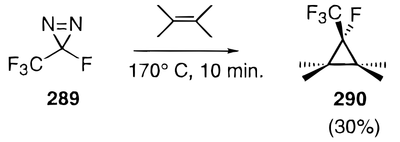
Tetrafluoroethylidene, generated by the pyrolysis of **280** at 200 °C, reacted with PF_3 in the gas phase to produce **288** as the major product (54%) and PF_5.[458] The reaction was thought to occur by ylide formation followed by β-fluorine transfer to phosphorus (eq 131).



Carbene **277** also reacted with $(CF_3)_3P$ to produce $(CF_3)_2PCF(CF_3)_2$ and perfluoro(2,3-dimethylbutane). The reaction is formally a P−C bond insertion. However, initial ylide formation followed by trifluoromethyl migration also accounts for the observed products. The reaction of (trifluoromethyl)fluorocarbene with $(CF_3)_2PCF(CF_3)_2$ generated perfluoro(2,3-dimethylbutane) and a smaller amount of $(CF_3)_3P$. This indicated that the source of perfluoro(2,3-dimethylbutane) in the reaction with $(CF_3)_3P$ was the reaction between the carbene and $(CF_3)_2PCF(CF_3)_2$.

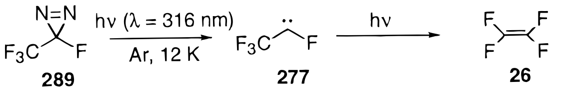
Tetrafluoroethyldine, generated by the thermolysis of 3-fluoro-3-(trifluoromethyl)diazirine (**289**) at 170

°C (10 min), has been trapped with 2,3-dimethyl-2-butene (2 equiv) producing **290** in 30% yield (eq 132).[392]



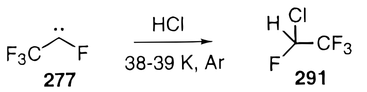
(132)

Irradiation (λ = 316 nm) of an argon matrix containing **289** produced **277**, which was observed by IR and UV spectroscopy.[119] Subsequent broad band irradiation (λ > 280 nm, 2.5 h; λ > 220 nm, 0.7 h; λ > 185 nm, 0.3 h) converted 60% of the carbene into tetrafluoroethene by a 1,2-fluorine migration (eq 133). Similar results were obtained when nitrogen was used as the matrix medium.



(133)

Chemical evidence for the formation of **277** was provided by trapping studies with HCl in an argon matrix. Irradiation (λ = 316 nm) of an argon/HCl/**289** (1570:4:1) matrix produced carbene **277** as well as a small amount of the HCl insertion product **291**. Also, warming the matrix to 38 K over several hours caused **277** to disappear and insertion product **291** to appear (eq 134). Dimerization of the carbene to *cis*- and *trans*-octafluoro-2-butenes was a minor side reaction.



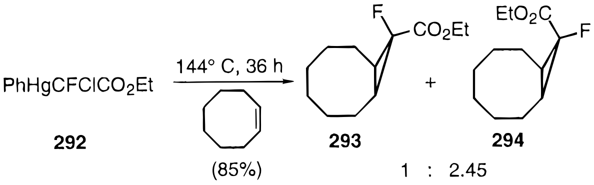
(134)

The value for the singlet−triplet energy difference for **277** calculated by O'Gara and Dailey using TCSCF/DZ+P(2P$_c$) and ROHF/DZ+P(2P$_c$) ab initio calculations was empirically corrected by 3.2 kcal/mol (favoring the singlet state) and resulted in a singlet−triplet energy difference estimate of 13.7 kcal/mol, with the singlet as the ground state.[119] This correction factor was obtained by calculating the energy difference of fluoromethylene at the same theory level and comparing the result to the best available calculations.[108] Dixon also calculated the singlet to be the ground state of the carbene but predicted a smaller energy difference (9.1 kcal/mol) than that found by O'Gara and Dailey.[5] The molecular structure calculations are all similar, with the singlet favoring a smaller carbenic bond angle ranging from 104 to 105.32° and a larger bond angle for the triplet state (~120°).

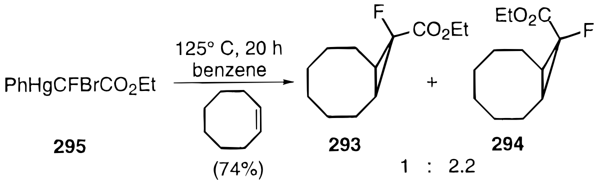
Experimental evidence for the singlet nature of the ground state of **277** was provided by the IR spectrum of the matrix-isolated species, which matched the scaled calculated values.[119] Further evidence included UV−vis spectral data, where the observed λ_{max} of 465 nm agreed very well with the theoretical value for the singlet state.

10. Other Fluorocarbenes

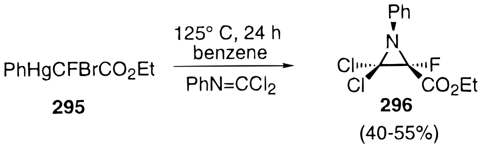
The organomercurial compounds $PhHgCFClCO_2R$ (R = CH_3 and CH_3CH_2) (**292**) and $PhHgCFBrCO_2Et$ (**295**) were found to be excellent carboalkoxy(fluoro)carbene transfer agents.[465] Numerous cyclopropanes were prepared using both reagents. In general, harsher conditions were required for $PhHgCFClCO_2R$ reactions. The yields for $CFCO_2Me$ transfer ranged from 24% (heptene) to 88% (cyclooctene). Using $PhHgCFClCO_2Et$ as the transfer reagent, $CFCO_2Et$ addition yields ranged from 18% (heptene) to 85% (cyclooctene), and for $PhHgCFBrCO_2Et$, the yields ranged from 15% (1,4-dihydrofuran) to 74% (cyclooctene) (eqs 135 and 136). Carbethoxy(fluoro)carbene addition (from **295**) to a C=N bond was also achieved (eq 137). Both reagents were successful in inserting the carboalkoxy(fluoro)carbene into the Si−H bonds of triethylsilane in good yield (71−74%). However, attempted C−H insertion reactions were unsuccessful.



(135)

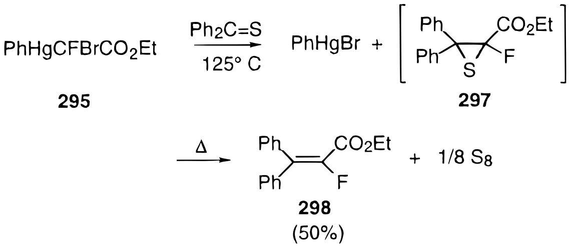


(136)



(137)

In addition, the reaction of **295** with thiobenzophenone at 125 °C produced **298** in 50% yield, presumably through the decomposition of thiirane intermediate **297** formed by the addition of carboethoxy(fluoro)carbene to the C=S bond (eq 138).[464]

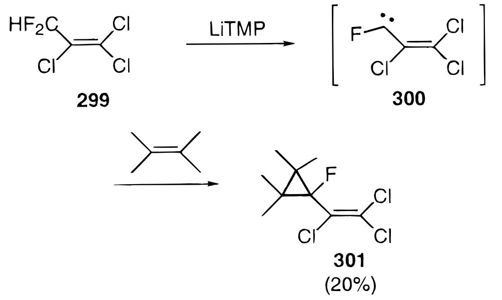


(138)

Fluoro(trichlorovinyl)carbene (**300**) has been generated by base-induced α-elimination of 1,1,2-trichloro-3,3-difluoro-1-propene (**299**) and trapped by various alkenes.[466,467] The cyclopropane yields were generally poor, ranging from 0 (ethene) to 20% (2,3-dimethyl-2-butene) (eq 139).

Dimethylamino(fluoro)carbene has been postulated as an intermediate in the reactions of (difluoromethyl)dimethylamine with hexafluoroacetone and (difluoromethyl)dimethylamine with perfluoro-2-methylpropene.[468]

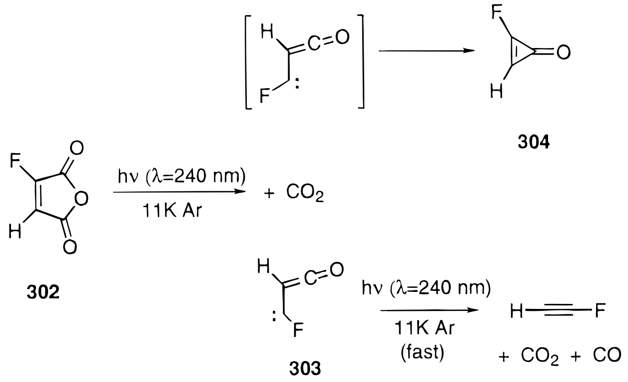
Dailey reported that irradiation of fluoromaleic anhydride (**302**) under matrix isolation conditions



(139)

generated fluorocyclopropenone (**304**) and fluoro(ketenyl)carbene (**303**) as primary photoproducts, both of which were identified by comparison with calculated vibrational spectra.[469] Further irradiation quickly converted carbene **303** to fluoroacetylene and carbon monoxide (Scheme 24).

Scheme 24

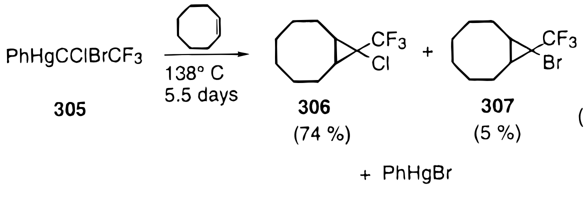


B. Other α-Heteroatom Carbenes (without Fluorine Bonded to the Carbene Center)

Heteroatoms, such as chlorine and bromine, stabilize the singlet state of a carbene by lone pair donation to the vacant p-orbital in a fashion similar to that of α-fluorine and α-oxygen substituents. However, differences in orbital sizes (2p vs 3p or 4p) make these heteroatoms less efficient carbene stabilizers.

1. Chloro(trifluoromethyl)carbene

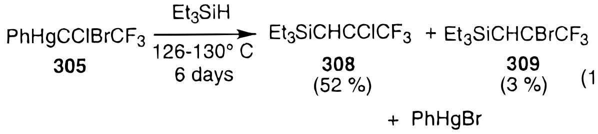
The generation and reactivity of chloro(trifluoromethyl)carbene (**319**) was first studied by Seyferth et al., who pyrolyzed **305** in the presence of cyclooctene to form **306**.[470,471] A minor side product **307** (5%) corresponding to bromo(trifluoromethyl)carbene addition was also observed (eq 140).



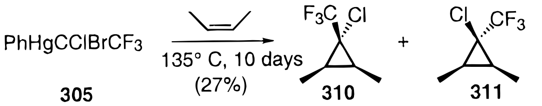
(140)

The thermolysis of **305** in the presence of triethylsilane produced the expected Si−H insertion product **308** as well as side product **309** from CF_3CBr insertion (eq 141).

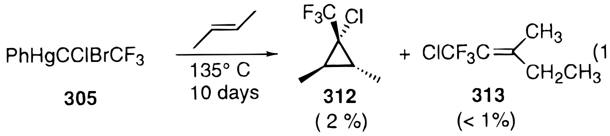
Compound **305** also reacted with cyclohexene in benzene solution (140 °C) yielding 7-chloro-7-(trifluoromethyl)norcarane (41%), the allylic CH insertion product (ca. 5% yield), and a minor amount (2%) of 7-bromo-7-(trifluoromethyl)norcarane. With allyltrimethylsilane, the yield of the expected 1-chloro-1-(trifluoromethyl)-2-(trimethylsilyl)cyclopropane was 9% (135 °C, 6 days). In the presence of 2,3-dimethyl-2-butene (130 °C, 54 h, benzene), the cyclopropane was produced in 58% yield, and 13% of the C−H insertion product was also observed. 2-Methyl-2-butene reacted with **305** (135 °C, 8 days) to give 1-chloro-1-(trifluoromethyl)-2,2,3-trimethylcyclopropane in 46% yield. In addition, the reaction with *cis*- and *trans*-butene proceeded in low yield with retention of the original double bond configuration (eqs 142 and 143).



(141)

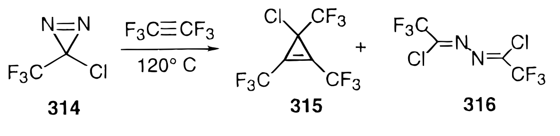


(142)



While **305** has proven to be a useful CF_3CCl transfer agent, it is not clear whether a free carbene or an organometallic transfer mechanism is involved in these reactions. In addition, many of the low yields observed are due to the instability of the products to the reaction conditions, namely high temperatures and long reaction times.

Grayston and Lemal relied on the addition of chloro(trifluoromethyl)carbene (**319**) to perfluoro-2-butyne in their synthesis of perfluorohexamethylbicyclopropenyl.[472] When 3-chloro-3-(trifluoromethyl)diazirine (**314**) was pyrolyzed (120 °C) in the gas phase in the presence of excess perfluoro-2-butyne, both cyclopropene **315** and azine **316**, corresponding to carbene attack on diazirine **314**, were present, with the azine as the major product (eq 144). Even with a 30-fold excess of perfluoro-2-butyne, the addition of the electron-deficient carbene to the similarly electron-poor acetylene was not a facile process. However, the ratio of **316**:**315** was minimized by charging a stirred gas-phase reactor (200 °C) with ∼0.5 atm of perfluoro-2-butyne followed by the slow addition of diazirine **314**. A 56% yield of **315** was obtained by this method.

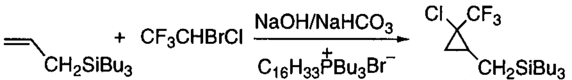


(144)

Chloro(trifluoromethyl)carbene (**319**), generated by the photolysis of diazirine **314** ($\lambda > 300$ nm), was shown to react stereospecifically with 2-butenes and other simple alkenes and did not insert into allylic

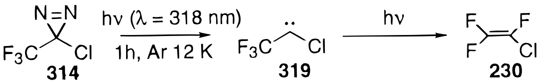
C−H bonds competitively with C=C addition. In the reaction with *cis*-2-butene, the cyclopropane isomer with chlorine syn to the methyl group formed in a 1.65:1 ratio.[473] In relative reactivity studies, chloro(trifluoromethyl)carbene (**319**) was less discriminating than chloro(methyl)carbene and dichlorocarbene. The relative reactivities were 2,3-dimethyl-2-butene (0.92), 2-methyl-2-butene (1.17), 2-methylpropene (1.00), *cis*-2-butene (0.88), *trans*-2-butene (0.62), butene (0.48), 3-methylbutene (0.25), and 3,3-dimethylbutene (0.11). The carbene was less reactive toward 2,3-dimethyl-2-butene than 2-methyl-2-butene, in contrast to typical electrophilic carbene behavior. As a result, chloro(trifluoromethyl)carbene was classified as a highly reactive, unselective carbene that adds to alkenes through an early, relatively open transition state, reflecting the destabilizing effect of the trifluoromethyl substituent.

Saxena et al. employed phase transfer catalysis conditions (18-crown-6, KOH) to generate chloro(trifluoromethyl)carbene from 2-bromo-2-chloro-1,1,1-trifluoroethane, which then inserted into the Sn−Sn, Si−Sn, and Si−Si bonds of various hexaorganobimetallic compounds.[474] The reaction with trisubstituted allyltin and allylsilicon compounds resulted in the formation of substituted cyclopropane derivatives. In the case of allyltri-*n*-butyltin and allyltriphenyltin, yields of 59% and 50% were achieved using a combination of sodium hydroxide, sodium bicarbonate, and hexadecyltri-*n*-butylphosphonium bromide as the phase transfer catalyst (eq 145).



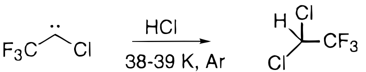
317 **318** (59%) (145)

Carbene **319** was prepared under matrix isolation conditions by irradiation ($\lambda = 318$ nm) of an argon matrix of **314**.[119] Subsequent broad band irradiation ($\lambda = 280-450$ nm, 2 h; $\lambda > 280$ nm, 0.5 h; $\lambda > 220$ nm, 0.5 h) led to a 70% reduction of the carbene IR absorptions and the growth of bands assigned to chlorotrifluoroethene (**230**), formed by a 1,2-fluorine migration (eq 146). Similar results were obtained using nitrogen as the matrix medium.



314 **319** **230** (146)

Additional evidence for the formation of **319** was provided by trapping studies with HCl in an argon matrix.[119] Irradiation ($\lambda = 318$ nm) of an argon/HCl/**314** (1650:4:1) matrix produced the carbene as well as a small amount of the HCl insertion product **320** and **230**. Warming the matrix to 38 K over several hours completely converted **319** to **320** (eq 147).

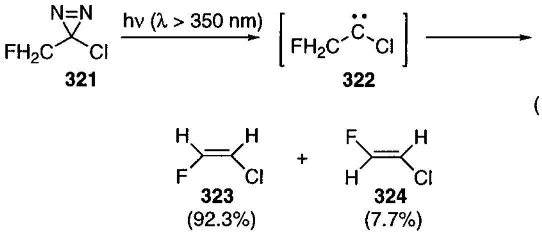


319 **320** (147)

The value for the singlet-triplet energy difference of **319** calculated by O'Gara and Dailey at the TCSCF/DZ+P(2P$_c$) and ROHF/DZ+P(2P$_c$) level was empirically corrected by 3.2 kcal/mol (favoring the singlet state) and resulted in an estimate of 3.2 kcal/mol, with the singlet as the ground state.[119]

Experimental evidence for the singlet nature of the ground state of **319** includes UV−vis spectral data of the matrix-isolated species.[119] The observed λ_{max} of 640 nm agrees very well with the theoretical value for the singlet carbene. In addition, Seburg and McMahon failed to observe an ESR spectrum for **319** at 16 K and concluded that the carbene was a ground state singlet.[475]

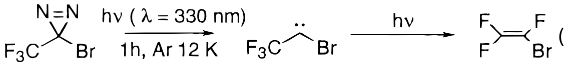
The related carbene **322** has been generated by the photolysis ($\lambda > 350$ nm) of chloro(fluoromethyl)diazirine (**321**).[476] Compounds **323** and **324**, the 1,2-hydride migration products, were formed in a 12:1 *Z*/*E* ratio (eq 148). This preference for the *Z*-alkene was explained by anionic hyperconjugation involving internal charge transfer between the occupied σ lone-pair orbital and the unoccupied C−F σ* orbital. This stabilization is greatest when the fluorine substituent is antiperiplanar to the carbenic lone pair, a conformation only accessible to the conformer leading to the *Z*-alkene.



321 **322** (148) **323** (92.3%) **324** (7.7%)

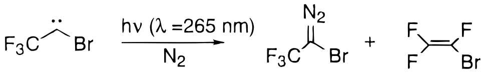
2. Bromo(trifluoromethyl)carbene

Bromo(trifluoromethyl)carbene (**326**) was prepared and spectroscopically characterized under matrix isolation conditions by the photolysis ($\lambda = 330$ nm) of an argon matrix of 3-bromo-3-(trifluoromethyl)diazirine (**325**).[119] Subsequent broad band irradiation ($\lambda = 280-450$ nm) converted over 95% of the carbene to bromotrifluoroethene (**327**) (eq 149).



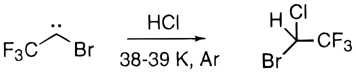
325 **326** **327** (149)

When nitrogen was used as the matrix material the same chemistry was observed except a small amount of a new compound, bromo(trifluoromethyl)diazomethane (**328**), was identified. It was demonstrated that selective photolysis of carbene **326** in a nitrogen matrix converted it to diazo compound **328** and alkene **327** (eq 150).



326 **328** **327** (150)

Additional evidence for the formation of **326** was provided by trapping studies with HCl[119] (eq 151).

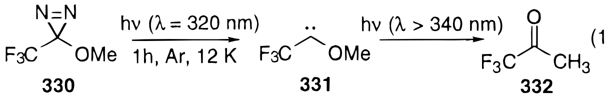


326 **329** (151)

On the basis of empirically corrected ab initio values at the TCSCF/DZ+P(2P$_c$) and ROHF/DZ+P-(2P$_c$) level, O'Gara and Dailey estimated the singlet–triplet gap in bromo(trifluoromethyl)carbene to be 0.5 kcal/mol, with the singlet as the ground state.[119] Evidence for the singlet nature of the ground state of **326** includes UV–vis spectral data of the matrix-isolated species.[119] The observed λ_{max} of 665 nm agrees very well with the theoretical value for the singlet state. Seburg and McMahon[475] suggested that their inability to observe an ESR spectrum for **326** in a xenon matrix at 73 K demonstrated that the triplet state was thermally inaccessible and that the singlet–triplet gap was larger than 0.5 kcal/mol. However, they offered no revised value for the lower limit of the difference.

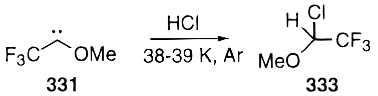
3. Methoxy(trifluoromethyl)carbene

Methoxy(trifluoromethyl)carbene is an interesting carbene since it contains both an electron-donating and an electron-withdrawing substituent on the carbene carbon. A matrix isolation study by O'Gara demonstrated that the photolysis of 3-methoxy-3-(trifluoromethyl)diazirine (**330**) in an argon matrix produced methoxy(trifluoromethyl)carbene (**331**) with small amounts of 1-methoxy-2,2,2-trifluorodiazoethane (<5%) and trifluoroacetone (**332**) (20%).[461] Subsequent broad band irradiation (30 min, λ > 340 nm) led to the destruction of carbene **331** and an increase in **332** (eq 152).



(152)

Additional evidence for the formation of **331** was provided by trapping studies with HCl (eq 153).[461]



(153)

O'Gara and Dailey also probed the reactivity of **331** by determining relative rate constants of carbene addition to a series of electron-rich and -poor alkenes (pentane, room temperature) using the classical competition method.[461] Carbene **331** was predicted to be a selective electrophilic carbene by its selectivity index ($M_{CF_3COMe} = 1.10$) calculated by Moss' method and using resonance and inductive constants. Alternately, FMO analysis suggested that the carbene would behave as an ambiphile similar to methoxy(chloro)carbene, and ab initio calculations predicted that the HOMO and LUMO energies were similar to those of ClCOMe. The alkenes cyclopropanated in this study included 2,3-dimethyl-2-butene (k_{rel} = 0.013), 2-methyl-2-butene (0.41), 2-methylpropene (0.50), *cis*-butene (0.20), *trans*-butene (1.00), methyl acrylate (2.10), acrylonitrile (0.42), and 2-chloroacrylonitrile (0.51). The low reactivity of the carbene toward 2,3-dimethyl-2-butene was attributed to the large steric interaction imposed by the four methyl groups. Steric interaction was also postulated to be the cause of the high diastereoselectivity in the additions to 2-methyl-2-butene (13:1), *cis*-2-butene (6:1), methyl acrylate (>200:1), acrylonitrile (30:1), and 2-chloroacrylonitrile (5:1). In each case, the preferred stereoisomer was the adduct with the trifluoromethyl group anti to the more sterically demanding side of the cyclopropane ring. From the relative rate constants observed, it was concluded that CF_3COMe is a highly unstable and unselective carbene in the cyclopropanation of both electron-poor and -rich alkenes.

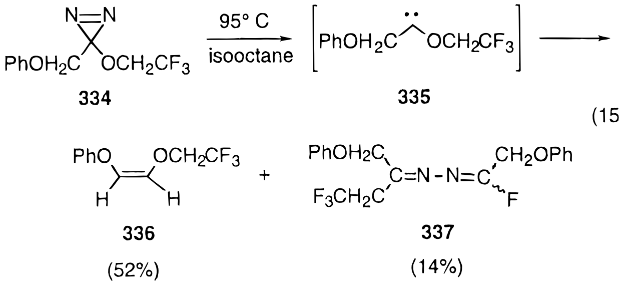
Similar to the work of O'Gara and Dailey, Moss et al. confirmed the indiscriminate nature of **331** using laser flash photolytic techniques and Platz's ylide competition method to monitor the carbene.[477] Alkenes such as 2-methyl-2-butene, 2-methylbutene, acrylonitrile, and methyl acrylate reacted with **331** with rate constants of $\sim$108 dm^3 mol^{-1} s^{-1}. As in the case for **319**, the high reactivity of **331** was attributed to the destabilizing influence of the trifluoromethyl group, which counteracts the stabilizing effect of the methoxy group.

Calculations predict the singlet state of **331** to be favored by 21 kcal/mol over the triplet state and the anti geometry to be lower in energy than the syn geometry by 9.8 kcal/mol.[461] Evidence for the singlet nature of the ground state of **331** includes UV–vis spectral data of the matrix-isolated species.[461] The observed λ_{max} of 380 nm agrees very well with the theoretical value calculated for the singlet state.

4. Trifluoroethoxy(phenoxymethyl)carbene and Related Carbenes

Moss and co-workers demonstrated that although 1,2-H migration is suppressed by an alkoxy substituent at the carbenic carbon, it can be restored by electronic tuning, at either the migration origin or terminus, and by thermal activation.[432] Electron-donating substituents attached to the origin of migration accelerate the reaction by counteracting the partial positive charge that develops in the transition state. Electron-releasing substituents at the carbenic carbon suppress hydride migration by decreasing the vacancy (electrophilicity) of the p orbital. The electronic tuning included in this study was the addition of an electron-withdrawing trifluoromethyl group to the otherwise electron-donating alkoxy substituent at the carbene center, as well as the addition of a π-donating phenoxy substituent at the migration origin.

While the photolysis (λ > 320 nm, 0 °C) or thermolysis (20 °C) of **334** in pentane gave only azine **337**, thermal activation by rapid injection of the isooctane–diazirine solution into isooctane at 95 °C yielded 52% of **336**, the 1,2-H migration product of trifluoroethoxy(phenoxymethyl)carbene, and 14% of **337** (eq 154).

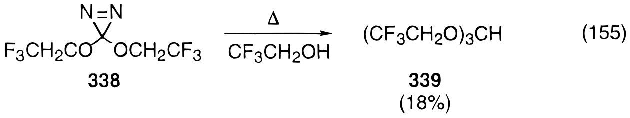


(154)

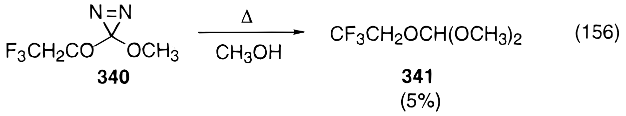
The pyrolysis of **334** on a hot glass surface (95 °C) gave 26% of rearrangement product **336** and 37% of azine **337**. In acetonitrile, which is known to enhance the rearrangement rate by stabilizing the polar transition state, the decomposition of **334** afforded 10% of **336** in addition to 66% of **337**. In pure acrylonitrile, the decomposition of **334** quantitatively formed the corresponding cyclopropane, while in acetonitrile with 0.013 M acrylonitrile the cyclopropanation was competitive with 1,2-H migration, and an addition/rearrangement product ratio of 2.3 was obtained on either photochemical or thermal carbene generation.

Other (trifluoroethoxy)carbenes that have been investigated include chloro(trifluoroethoxy)carbene, bis(trifluoroethoxy)carbene, and methoxy(trifluoroethoxy)carbene. They were all generated by the thermal, ambient temperature decompositions of the corresponding diazirines **338**, **340**, and **342**.[398] In the absence of an added substrate, dimers were formed in 10–15% isolated yield, and azines were generally absent. The low yields were due to the volatility and instability of the dimers.

The decomposition of **338** in trifluoroethanol afforded O–H insertion product **339**, which was isolated in 18% yield (eq 155). A comparable yield of O–H insertion was obtained with methanol. In addition, the reaction with acrylonitrile produced a 25% yield of cyclopropane and <4% carbene dimer.

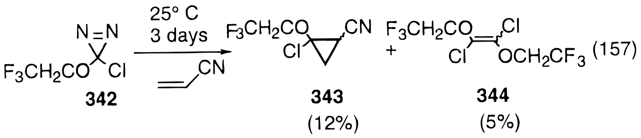


Similarly, the decomposition of **340** in trifluoroethanol produced $(CF_3CH_2O)_2CHOMe$, while in methanol, **341** was obtained in 5% yield (eq 156). The reaction with acrylonitrile afforded the isomeric cyclopropanes in 12% yield.



Both bis(trifluoroethoxy)carbene and methoxy(trifluoroethoxy)carbene were deemed nucleophilic and similar to bis(methoxy)carbene in reactivity, as they reacted with acrylonitrile and methyl acrylate but not with 2-methyl-2-butene.

Chloro(trifluoroethoxy)diazirine (**342**) in acrylonitrile thermally afforded the isomeric cyclopropanes **343** in 12% yield, as well as carbene dimer **344** (5%) (eq 157).



Upon photolysis in the presence of other alkenes, diazirine **342** produced the corresponding cyclopropanes from chloroacrylonitrile, methyl acrylate, *trans*-butene, 2-methylpropene, and 2,3-dimethyl-2-butene in 18–37% yield.[478] An absolute rate constant of 9.8 $\times 10^5$ M^{-1} s^{-1} was determined for the cyclopropanation of chloroacrylonitrile using laser flash photolytic methods. Competition methods allowed the determination of the other absolute rate constants. The derived absolute rate constants (with average errors of ±15%) were 9.0×10^4 M^{-1} s^{-1} for the reaction with 2,3-dimethyl-2-butene, 2.6×10^4 with 2-methylpropene, 1.0×10^4 with *trans*-2-butene, 4.4×10^4 with methyl acrylate, and 6.6×10^4 with acrylonitrile. By comparing the data to that similarly obtained for chloro(methoxy)carbene, it was concluded that chloro(trifluoroethoxy)carbene was also an ambiphile, but more reactive, as seen by the rate constants for chloro(trifluoroethoxy)carbene addition exceeding the corresponding values for chloro(methoxy)carbene for each alkene. With alkylethenes, chloro(trifluoroethoxy)carbene was 14–30 times more reactive than chloro(methoxy)carbene. However, with electron-poor alkenes it was only ~2–4 times more reactive. This enhanced reactivity was explained by the decreased stabilization of the carbene by the alkoxy group due to the opposing electron-withdrawing influence of the trifluoromethyl subunit. Similar rate enhancement was also seen for the 1,2-H shifts and alkene addition reactions of methyl(trifluoroethoxy)carbene as compared to methoxymethylcarbene.[479]

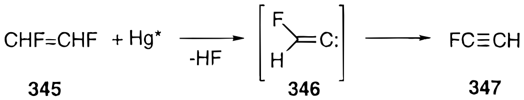
C. Vinylidenes

Another class of carbenes are the vinylidenes ($:C{=}CR_2$). This class of carbenes has received much attention lately, with the isomerization of the parent vinylidene to acetylene by a 1,2-hydrogen shift receiving the bulk of the attention. Ab initio calculations predict a barrier to rearrangement of 1.6 kcal/mol (ZPVE corrected),[480] and as a result the parent vinylidene has proven to be very elusive. Experimental data on monofluorovinylidene has also been scarce. While 1,2-fluorine migration possesses a high activation energy, predicted to be between 33 and 44 kcal/mol,[481–483] facile 1,2-hydrogen shift to fluoroacetylene can still occur. Earlier calculations predicted that the hydrogen rearrangement proceeds without a barrier,[481,483] although one result predicted barriers ranging from 15.3 to 27.0 kcal/mol.[482] Recent theoretical data predict activation energies of 0.8 kcal/mol[484] and 1.6–2.3 kcal/mol.[485] However, difluorovinylidene, as expected, has proven to be very resistant to alkyne formation in which a 1,2-fluorine migration is necessary. The barrier to rearrangement has been estimated by the majority of the calculations to range between 25 and 40 kcal/mol.[481–483,486] It has been postulated that the reason for the high activation energy is the antiaromatic character of the 4π e^- transition state involving a planar bridged fluorine structure.[481,483]

Vinylidenes have singlet ground states. In the singlet form, there is a favorable interaction between the occupied C–R orbital and the in-plane, empty p-orbital on the carbenic carbon through hyperconjugation.[485] This interaction lowers the energy of the C–R orbital while raising the energy of the empty p-orbital. Because the triplet state has an electron in the carbene p-orbital, less stabilization occurs from the orbital mixing, resulting in the favoring of the singlet as the ground state. Fluorine substitution leads to a lowering of the singlet−triplet energy difference, with the singlet still the ground state of the carbene. This is due to the C−F bond being lower in energy, resulting in a less effective interaction between the C−F bond and the empty p-orbital on the carbenic carbon. The effect of substitution on hyperconjugation, as seen by the electron population on the carbene carbon, was demonstrated by an ab initio (RHF/STO-3G and 4-31G) study of various substituted vinylidenes.[487]

1. Monofluorovinylidene

Strausz et al. postulated that monofluorovinylidene (**346**) was an intermediate in the formation of fluoroacetylene (**347**) during the photosensitization of 1,2-difluoroethene (**345**) with triplet mercury 6($^3P_1$).[488] On the basis of kinetic data, the possibility of an ethylidene-type intermediate for this process was eliminated. Instead, a mechanism involving the formation of **346** followed by facile 1,2-hydrogen migration to **347** was favored (eq 158).



345 **346** **347**

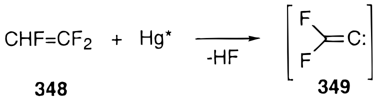
(158)

There are only a few accounts that deal with the geometric and energetic properties of monofluorovinylidine, with even fewer opportunities to compare theory with experiment. One area of discrepancy is the identity of the lowest triplet state. The two lowest lying triplet states were found to be very close in energy both experimentally and theoretically. Gilles et al. assigned the 3A″ state to be lower in energy by 0.038 eV based on negative ion photodetachment spectroscopic results,[485] whereas DeLeeuw et al. found the 3A′ state to be lower in energy by 0.12 eV.[484] Also, Gilles et al. found a singlet−triplet splitting energy of 1.32 kcal/mol favoring the singlet, using the 3A″ state as the lowest triplet state,[485] whereas DeLeeuw et al. calculated a value of approximately 1 kcal/mol also favoring the singlet, using the 3A′ state as the lowest triplet state.[484] Additional calculations have been reported.[481,482]

Only one report on the experimental vibrational frequencies for monofluorovinylidene has appeared, and this was done using photoelectron spectroscopy.[485] The vibrational frequencies were 1680, 960, and 205 cm^{-1} for the singlet carbene. Calculations generally agree well with the experimental frequencies,[484] with the exception of the FCC bending frequency. The predicted vibration of 296 cm^{-1} appears to be quite high compared to the 205 cm^{-1} frequency observed experimentally. It was suggested that the discrepancy was due to the fact that this vibrational mode is extremely anharmonic with a shallow potential energy well, causing the theoretical harmonic frequency for FCC bending to deviate more than usual from the experimental fundamental frequency.

2. Difluorovinylidene

Norstrom et al. prepared difluorovinylidene (**349**) by the photosensitization of trifluoroethene (**348**).[489] The proposed mechanism involves excited triplet ethene decomposition together with concerted intersystem crossing to produce ground state singlet difluorovinylidene and HF (eq 159). Evidence in favor of carbene formation in the singlet ground state included the insertion reaction of difluorovinylidene with alkanes and the fact that CF_4, C_2HF_3, and C_3D_8 suppressed the primary decomposition of C_2HF_3 but left the product yields (of the reaction of :C=CF_2 with starting material) unaltered.

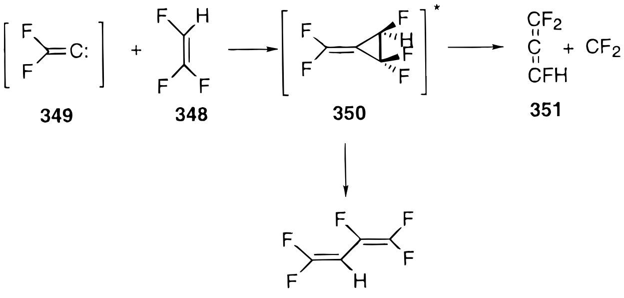


348 **349**

(159)

In the triplet mercury photosensitization of **348**, several products were formed.[489] These products included trifluoroallene, tetrafluoroethene, and 1,1,2,4,4-pentafluorobutadiene. The mechanism for the formation of these products was suggested to originate with cyclopropane adduct **350**, formed by the reaction of **349** with **348,** which then extruded difluoromethylene and trifluoroallene or rearranged to 1,1,2,4,4-pentafluorobutadiene (Scheme 25).

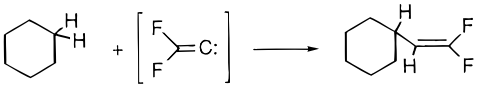
Scheme 25



349 **348** **350** **351**

352

To confirm the intermediacy of **349**, the triplet mercury photosensitization of **348** was performed in the presence of cyclohexane and cyclohexane-d_{12}. This resulted in the formation of **353** and the corresponding deuterated product in addition to the aforementioned products (eq 160). The absence of radical combination products such as bicyclohexyl and the inability of nitric oxide to influence the yield confirmed the concerted nature of the C−H insertion.

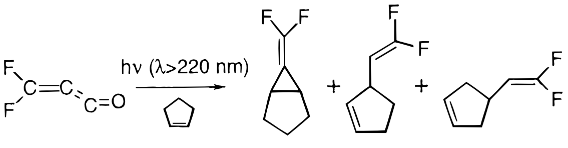

349 **353**

(160)

Trifluoroallene and tetrafluoroethene were also obtained by Stachnik and Pimental using multiphoton vibrational excitation of **348** to produce **349**.[490] In the presence of other alkenes, such as C_2H_4, C_2D_4, and C_2F_4, the corresponding allenes formed, respectively, allene, perdeuteroallene, and perfluoroallene.

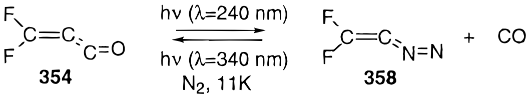
Reiser and Steinfeld observed tetrafluoroethene (67%) and trifluoroallene (33%) in addition to HCl in the production of difluorovinylidene from 2-chloro-1,1-difluoroethene by infrared multiphoton excitation.[491] In the presence of labile hydrogen sources such as H_2S or CH_3OH, $C_2F_2H_2$ (82%), C_2F_3H (12%), and C_2F_4 (6%) were formed, the dominant pathway being H abstraction to form olefins.

Brahms and Dailey trapped **349** by the broad-band irradiation ($\lambda > 220$ nm) of a gas-phase mixture of difluoropropadienone in the presence of a 10-fold excess of isopentane.[492] All four C−H insertion products were produced, and the selectivity of difluorovinylidene toward C−H bonds was 3.0:1.8:1.0 (3:2:1). When cyclopentene was the trapping agent a mixture of **355** and two C−H insertion products, **356** and **357**, were formed in a 4.5:2.1:1.0 ratio (eq 161).



354 **355** 4.5 **356** 2.1 **357** 1.0 (161)

Brahms and Dailey attempted to obtain spectroscopic evidence for **349** using argon matrix isolation techniques. However, the carbene produced by the CO extrusion of irradiated ($\lambda > 185$ nm) **354** efficiently recombined with CO to reform starting material. Evidence for this process was obtained by the irradiation of **354,** labelled with ^{13}C at the carbonyl position, in the presence of CO. Unlabeled **354** as well as a substantial amount of labeled ^{13}CO resulted. Further evidence includes the formation of difluorodiazoethene (**358**) in nitrogen matrix isolation experiments along with difluoroacetylene and CO. In addition, **358** quantitatively extruded nitrogen and recombined with carbon monoxide to regenerate **354** upon longer wavelength irradiation (eq 162).



(162)

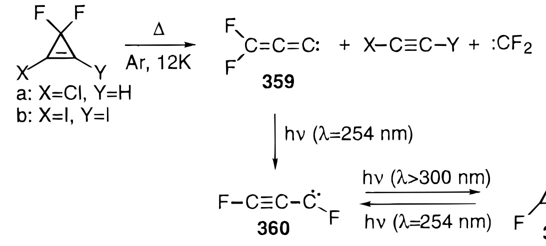
There are only two reports of experimentally observed vibrational frequencies for **349**. One is the tentative assignment by Burger et al. of 1247.5 cm^{-1} (neon matrix) and 1242 cm^{-1} (argon matrix) during the matrix isolation of difluoroethyne.[493] Gilles et al. reported vibrational frequencies of 1670, 950, and 510 cm^{-1} for **349** based on an analysis of photoelectron spectra.[485] The calculated vibrational frequencies compare well with the limited experimentally observed ones when correction factors are applied. The HF calculations require an approximate scaling factor of 0.9,[494] while the CCSD/DZP calculations are estimated to be roughly 5% above the true fundamentals.[495]

3. (Difluorovinylidene)Carbene and Related Carbenes

Maier et al. produced matrix-isolated (12 K) difluoropropadienylidene (**359**) by the pulsed flash pyrolysis of 1-chloro-3,3-difluorocyclopropene and 3,3-difluoro-1,2-diiodocyclopropene.[496] Subsequent photolysis of **359** generated difluoropropargylene (**360**) and difluorocyclopropenylidene (**361**) (Scheme 26).

Vibrational spectral calculations at the MP2/6-31G* level agreed well with the experimental results and were the basis of the carbene assignments.

Scheme 26



Geometries and vibrational frequencies for **359**, **360**, and **361** were calculated at the HF/3-21G, HF/6-31G(d), and MP2/6-31G* levels.[497] All three carbenes had singlet ground states, and in all cases, the singlet−triplet energy differences were larger than that of their hydrocarbon counterparts. At the highest level of theory employed, PMP4/6-31G(d)//MP2/6-31G(d) + ZPE, the singlet−triplet energy difference of **359** was calculated as 45.1 kcal/mol, 10 kcal/mol for **360**, and 50.1 kcal/mol for **361**. Also, **359** was 3.0 kcal/mol more stable than **361** and 25.4 kcal/mol lower in energy than **360**.

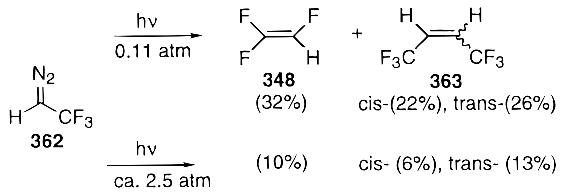
III. Triplet Carbenes

Fluorinated carbenes that do not have π-electron-donating substituents directly attached to the carbene center are typically ground state triplets. The direct study of their hydrocarbon counterparts has been limited by the facile 1,2-H or alkyl migrations that take place during the generation of alkylcarbenes.[420] However, (perfluoroalkyl)carbenes have proven more resistant to rearrangement[7,8] and have been trapped and observed experimentally. Fluorinated carbenes of this type were among the first triplet alkylcarbenes to be directly observed by ESR spectroscopy.[498]

A. (Trifluoromethyl)carbene

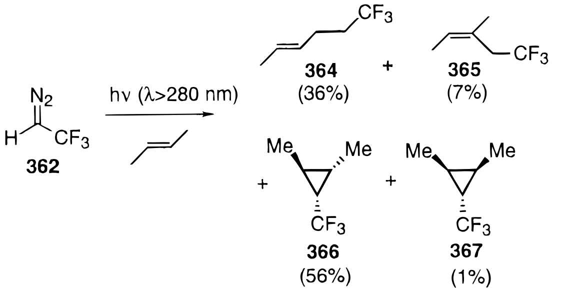
Probably the most convenient method of generating 2,2,2-trifluoroethylidene is by the photolysis of 2,2,2-trifluorodiazoethane (**362**).[7,8,499−501] Fields and Haszeldine found that the photolysis products were dependent on the initial pressure of the diazoalkane.[499] At low pressures (0.46 atm), the main products were trifluoroethene (22%), *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (20%), and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (41%). At even lower pressures, the yield of trifluoroethene increased to 32%, and the yields of the *cis*- and *trans*-butenes were 22% and 26%. At higher pressures, in which liquid 2,2,2-trifluorodiazoethane was present (ca. 2.5 atm), the carbene-derived products were trifluoroethene (10%), *cis*-(6%) and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (13%), and 1,1,2-trifluoro-3-(trifluoromethyl)cyclopropane (1%) (Scheme 27). The yield of the hexa-

Scheme 27



fluoro-2-butenes in the latter case appeared low because of secondary reactions with the excited diazo starting material, producing poly(trifluoromethyl)-carbene (7%) and 3,4,5-tris(trifluoromethyl)-2-pyrazoline (40%). In the absence of a reactive substrate, 1,2-fluorine migration occurs to form trifluoroethene.

The liquid phase photolysis (λ < 300 nm) of **362** in a 4-fold excess of *trans*-2-butene gave a mixture of C−H insertion and cyclopropanation products (eq 163).[7] No trifluoroethene was formed, indicating that fluorine migration is slower than reaction with the alkene or diazo compound.

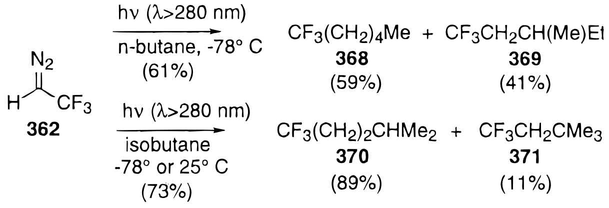


(163)

The photolysis of **362** in the presence of *cis*-2-butene afforded *trans*-hexafluorobut-2-ene (**363**) (23%), the two *cis*-2-butene C−H insertion products, and *cis*-dimethylcyclopropanation products (50%). From this data, Atherton and Fields concluded that the stereospecific reaction of 2,2,2-trifluoroethylidene with *cis*- and *trans*-butenes in the liquid phase occurs from the singlet state of the carbene. However, the irradiation of **362** with *cis*-2-butene in ether solutions caused increased nonstereospecific addition with increasing dilution, suggesting that in solution the singlet carbene relaxes to the triplet state by nonreactive collisions with the inert solvent before reacting with butene. In the vapor phase, irradiation in the presence of either butene isomer also led to nonstereospecific addition and an increase in trifluoroethene.

A further study on the reactivity of 2,2,2-trifluoroethylidene by Atherton and Fields showed that the carbene inserted virtually unselectively into the C−H bonds of saturated hydrocarbons.[501] The liquid phase photolysis of **362** at −78 °C in *n*-butane yielded 61% insertion reaction, with almost no reactivity difference between primary and secondary C−H bonds. The reaction with isobutane also yielded two different insertion products, with insertion into tertiary C−H bonds only slightly faster than primary bonds, $k(\text{tert})/k(\text{prim}) = 1.3 \pm 0.2$ (Scheme 28).

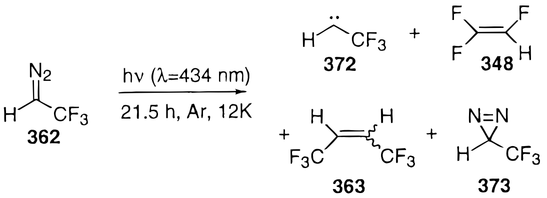
Scheme 28



However, in the vapor phase, with the same excess of *n*-butane and isobutane, the yields of insertion products were only 7% and 2%, and the isomer ratios were similar to the respective liquid phase experiments. Trifluoroethene (21 and 17%) and 1,1,1-trifluoroethane (2 and 13%) were also formed, the formation of trifluoroethene arising from 1,2-fluorine migration and the formation of 1,1,1-trifluoroethane presumably from two successive hydrogen abstractions.

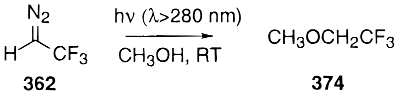
These results were explained by the involvement of an excited singlet carbene in the unselective insertion reactions, whereas 1,1,1-trifluoroethane formation arises from the triplet carbene. In the gas phase, a crossover to the triplet 2,2,2-trifluoroethylidene takes place, and the low yield of insertion products indicated that the triplet does not undergo significant amounts of insertion. Instead, the small amount of insertion product was due to residual singlet carbene, since the isomer ratio would be unlikely to remain the same if a different species were involved.

In a recent matrix isolation study, the irradiation (λ = 434 nm; 21.5 h) of **362** in an argon matrix afforded 2,2,2-trifluoroethylidene (**372**), trifluoroethene (**348**), *cis*- and *trans*-1,1,1,4,4,4-hexafluro-2-butenes (**363**), and a small amount of (trifluoromethyl)diazirine (**373**).[8] The 1,2-fluorine migration product, **348**, accounted for 40% of the observed product, and further broad band irradiation at wavelengths greater than 185 nm converted the remaining carbene **372** to **348** (eq 164).



(164)

Because the ratio of the carbene to trifluoroethene remained constant throughout the irradiation and **372** was stable to further photolysis at 434 nm for several days, **348** was considered a primary photoproduct. O'Gara and Dailey explained the formation of **348** as proceeding through an excited singlet state of the diazirine or "hot molecule" chemistry of the carbene **372** before relaxation to the ground state triplet could occur. Evidence for the latter explanation came from the following trapping experiment. When **362** was irradiated in methanol, more than 90% of the carbene was trapped as the O−H insertion product **374** (eq 165).



(165)

Holmes and Rakestraw found an experimental energy barrier of 29 ± 4 kcal/mol for the conversion of **372** to **348** by 1,2-fluorine migration.[502,503] Their method involved the use of a chemically activated carbene precursor, CF_3CH_2Cl, to produce the excited carbene by HCl elimination, which then rearranged to trifluoroethene, the percentage of which was pressure dependent. RRKM theory was then used to calculate the rate constants that were fitted to the experimental pressure dependence to determine the barrier to migration. At the QCISD(t)/6-311(2D,2P)/

/MP2/6-31G** level, the barrier to rearrangement of singlet 2,2,2-trifluoroethylidene was 21.5 kcal/mol.[8] The barrier for rearrangement of the triplet carbene was calculated as 50.8 kcal/mol.

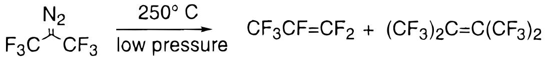
Carbene **372** has been shown by EPR studies to be a ground state triplet,[498] and theoretical studies have reproduced this assignment.[5,8,504] At the highest level of theory reported so far, the triplet is predicted to be 8.5 kcal/mol more stable than the singlet, almost exactly the value obtained for methylene.

The experimental IR frequencies observed by O'Gara and Dailey in an argon matrix (12 K) correlate well with the frequencies calculated for triplet **372** at the UMP2/6-31G** level after applying a scaling factor of 0.93.[8] The UV/vis spectrum consisted of a band at 205 nm.

B. Bis(trifluoromethyl)carbene

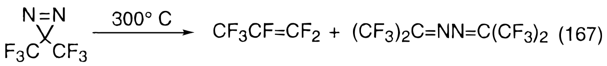
Bis(trifluoromethyl)carbene (**397**) is a highly electrophilic species due to the two electron-withdrawing trifluoromethyl groups. Two useful precursors for its photochemical or thermal generation are bis(trifluoromethyl)diazomethane (**375**) and bis(trifluoromethyl)diazirine (**378**).

The pyrolysis of **375** at 250 °C (in a helium flow system) produced hexafluoropropene (**376**), resulting from a 1,2-fluorine migration of bis(trifluoromethyl)carbene, and tetrakis(trifluoromethyl)ethene (**377**), from the reaction of the carbene with another molecule of **375**.[505] However, when the pyrolysis was done at low concentrations of **375** (flow system under high vacuum) **376** was produced in 92% yield (eq 166).



375 **376** (92%) **377** (166)

The pyrolysis of **378** at 300 °C gave **376** and hexafluoroacetone azine (**379**), resulting from the reaction of bis(trifluoromethyl)carbene and **378** (eq 167).



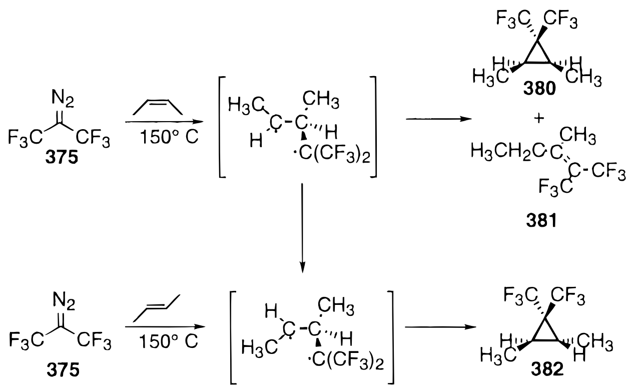
378 **376** **379** (167)

The decomposition of **375** at 150 °C in the presence of excess *cis,cis*-1,5-cyclooctadiene gave the corresponding cyclopropane in 36% yield. The reaction with *trans*-2-butene was stereospecific, forming **382** in 53% yield. Decomposition of **375** in the presence of *cis*-2-butene yielded 39% of the *cis*-cyclopropane **380**, 8% *trans*-cyclopropane **382**, and 49% of **381**, with a combined overall total yield of 57%. The product distribution was explained by the differing abilities of the biradicals to close to cyclopropanes due to steric repulsion (Scheme 29).

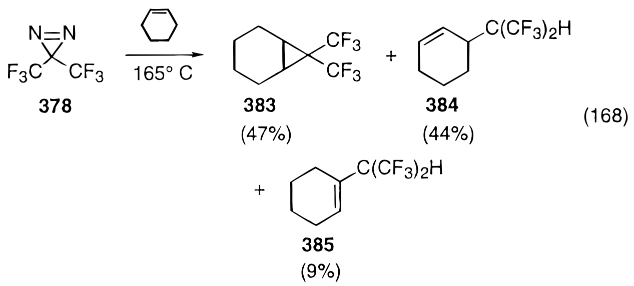
The reaction of **378** with cyclohexene produced cyclopropane adduct **383** as well as the allylic and vinylic C−H insertion products (**384** and **385**), which were presumed to arise from indiscriminate reaction of the singlet bis(trifluoromethyl)carbene (eq 168).

The reaction of **378** with *trans*- and *cis*-butenes resulted in the predominance of the cyclopropane adducts **380** and **382**, respectively, as well as both allylic and vinylic C−H insertion products. In the case of *cis*-2-butene small amounts of **380** and **381** were also formed (Scheme 30). Because the decomposition of **375** in the presence of cyclohexene or 2-butene did not produce C−H insertion products, it was concluded that a different intermediate, possibly involving pyrazolines, may be involved in the diazo precursor pyrolyses.

Scheme 29

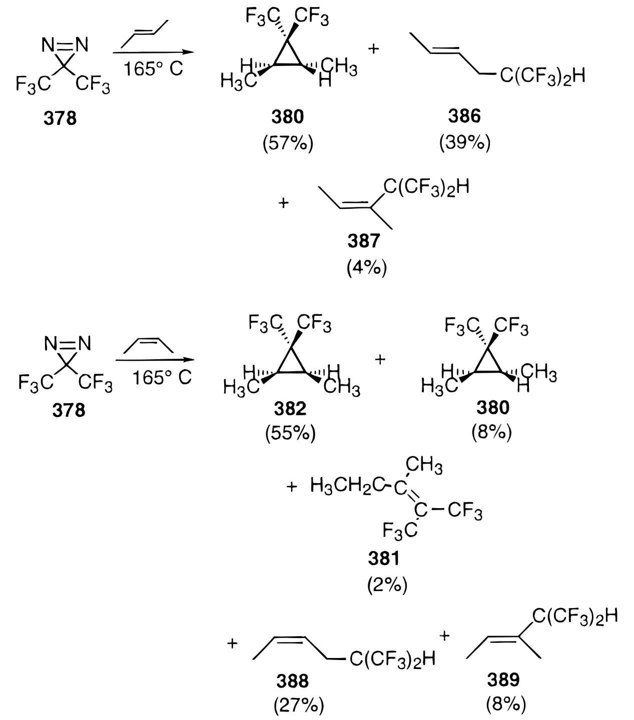


375 **380** **381** **375** **382**



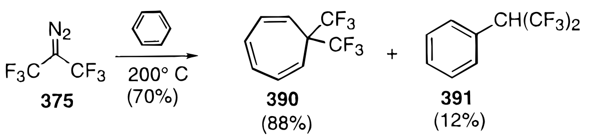
378 **383** (47%) **384** (44%) **385** (9%) (168)

Scheme 30



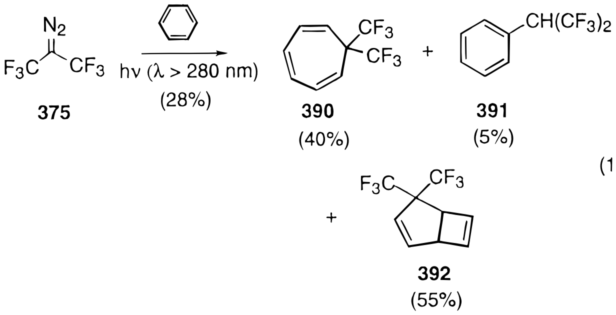
378 **380** (57%) **386** (39%) **387** (4%) **378** **382** (55%) **380** (8%) **381** (2%) **388** (27%) **389** (8%)

The pyrolysis of **375** at 200 °C in the presence of excess benzene gave **390** (88%) and **391** (12%) in 70% combined yield (eq 169).[506]



(169)

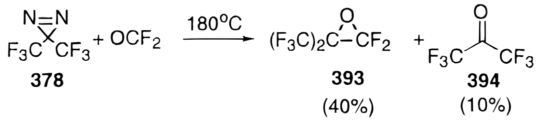
The photolysis of **375** in dry benzene yielded **390** (40%), **391** (5%), and **392** (55%) in 28% combined yield (eq 170).



(170)

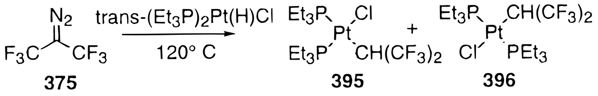
In hexafluorobenzene, the pyrolysis (150 °C) of bis(trifluoromethyl)diazomethane (**375**) gave perfluoro-7,7-dimethyl-1,3,5-cycloheptatriene in 20% yield.[507]

Mahler demonstrated the strong reducing capabilities of bis(trifluoromethyl)carbene.[457] The reaction of bis(trifluoromethyl)carbene, generated from **378**, with carbonyl fluoride at 180 °C gave a 40% yield of perfluoroisobutylene oxide (**393**) and a 10% yield of hexafluoroacetone (**394**) (eq 171). The carbene also reacted with OPF_3 at 160°C and in sunlight at room temperature to yield hexafluoroacetone.



(171)

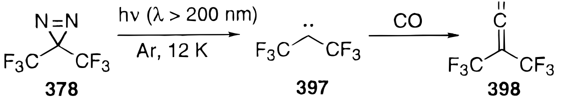
Bis(trifluoromethyl)carbene, from the pyrolysis (120 °C) of **375**, reacted with *trans*-$(Et_3P)_2Pt(H)Cl$ to form two isomeric complexes **395** and **396** of $(Et_3P)_2$-$Pt[CH(CF_3)_2]Cl$ (eq 172).[508,509]



(172)

While formal bis(trifluoromethyl)carbene insertion products are formed at room temperature from the reaction of **375** and many organometallic compounds such as octacarbonyldicobalt, pentacarbonylmanganese hydride, π-cyclopentadienyldicarbonyliron dimer, chlorocarbonylbis(diphenylmethylphosphine)iridium, bis(benzonitrile)palladium dichloride,[510] trimethyltin hydride,[511] and arylcopper compounds,[512] the reactions most likely do not involve the intermediacy of the free carbene.

Several matrix isolation studies of bis(trifluoromethyl)carbene (**397**) have been reported. During the photolysis of **378** in an argon matrix at 12 K, bis(trifluoromethyl)diazomethane (**375**) was observed along with bis(trifluromethyl)carbene.[513] The formation of **375** was attributed to either the photoisomerization of **378** or the recombination of **397** with a nitrogen molecule in the matrix cage. The irradiation of a 20% carbon monoxide doped matrix resulted in the formation of bis(trifluoromethyl)ketene (**398**) (eq 173).

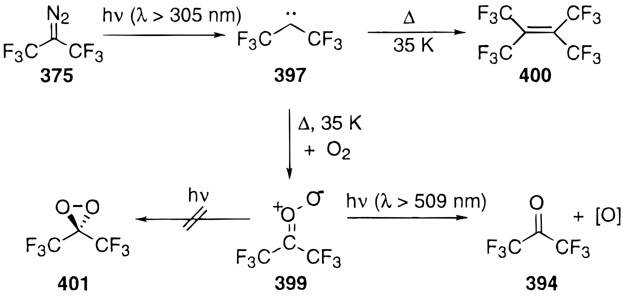


(173)

The flash vacuum pyrolysis (350–500 °C) of a mixture of argon and **378** with subsequent trapping of the mixture at 12 K did not lead to detectable amounts of **397**. Only bands for the 1,2-fluorine migration product, hexafluoropropene (**376**), were observed.

Wasserman et al. observed a white chemiluminescence during the irradiation of **378** at 77 K in the presence of oxygen.[498] The spectrum was identical to the phosphorescence of hexafluoroacetone and was presumed to occur by the reaction of **397** with oxygen to yield the lowest triplet state of hexafluoroacetone (**394**). Further work on the reaction of **397** with oxygen was reported by Sander.[514] Irradiation (λ > 305 nm) of **375** in an O_2 (0.5–4%) doped argon matrix produced **397**, CO_2, hexafluoroacetone, trifluoromethyl trifluoroacetate, and small amounts of carbonyl fluoride (especially at higher concentrations of O_2). The formation of CO_2 and carbonyl fluoride implies that the short-wavelength irradiation leads to secondary photooxidation and C–F bond cleavage. The warming (10–42 K) and recooling (10 K) of a matrix containing **397** and 1% O_2 formed the corresponding carbonyl *O*-oxide **399**, which proved to be photolabile. Long-wavelength irradiation (λ > 590 nm) produced hexafluoroacetone (**394**); however, short wavelength irradiation (λ > 295 nm) did not produce any further changes (Scheme 31).

Scheme 31



During the warming of the O_2 doped matrix containing **397** (10–60 K), a bright blue chemiluminescence was observed. The chemiluminescence spectrum was similar to the phosphorescence spectrum of **394**. From the temperature dependence of chemiluminescence, it was concluded that the reaction of **397** and O_2 was not the reaction responsible. Instead, it was postulated that the reaction of **397** with $O(^3P)$, produced by the photochemical decomposition of **399** resulted in the formation of the excited hexafluoroacetone. The maximum of the glow curve (temperature dependence of luminescence) was found at 46 K, a significantly lower temperature than that found for other carbenes.[515,516] This was explained by the rapid diffusion of **397** at T > 40 K, as evidenced by the presence of the carbene dimer **400**.

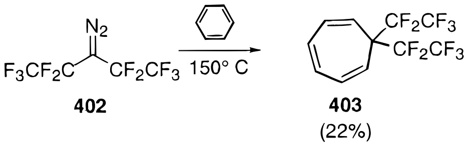
In addition, because fluorescence was not detected, it was concluded that **394** was formed in an excited triplet state.

Carbene **397** has been shown by EPR studies to be a ground state triplet, possessing a bent divalent carbon with a C−C−C bond angle of about 160°.[498] Similarly, calculations predict a triplet ground state but with a bond angle of 128°.[5,260] The singlet was predicted to be 18 kcal/mol less stable than the triplet and have a C−C−C bond angle of 113°.[5] The heat of formation of bis(trifluoromethyl)carbene is estimated as −212 ± 5 kcal/mol for the singlet state.[517]

The only published IR spectrum of **397** was observed by Mal'tsev in an argon matrix at 12K from the photolysis of bis(trifluoromethyl)diazirine.[513]

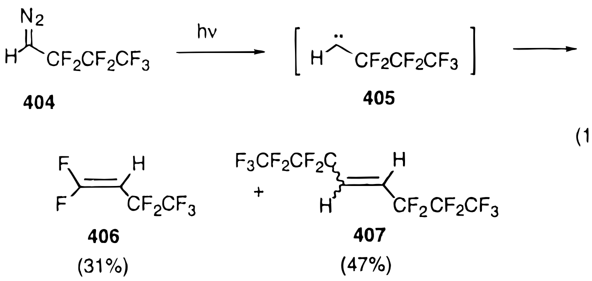
C. Other (Perfluoroalkyl)carbenes

Bis(pentafluoroethyl)carbene, produced by the pyrolysis of bis(pentafluoroethyl)diazomethane (**402**), added to benzene at 150 °C to give **403** in 22% yield (eq 174). No 1,2-fluorine or fluoroalkyl group migration product of the carbene intermediate was observed.[505]



(174)

Fields and Haszeldine generated carbene **405** by the photolysis (λ > 300 nm) of diazirine **404**[499,500] and demonstrated that **405** preferred 1,2-perfluoroethyl migration to 1,2-fluorine atom migration, yielding only **406** (31%) and dimer **407** (47%) (eq 175).[499]

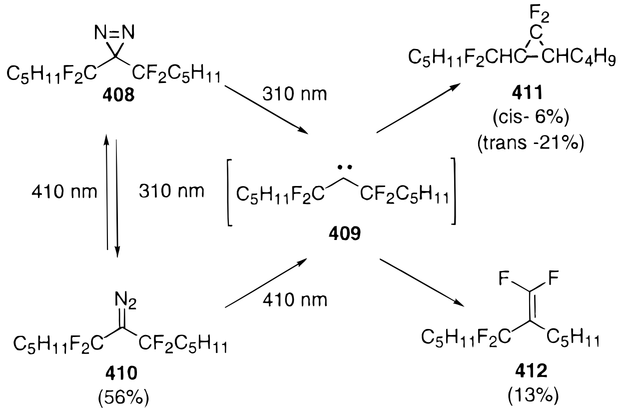


(175)

Carbene **405** was shown by EPR studies to be a ground state triplet.[498] Presumably, the rearrangement occurs from the initially formed singlet state before it relaxes to the triplet. A similar carbene, $HC(CF_2)_6CF_3$, was also shown by EPR studies to be a ground state triplet.[498]

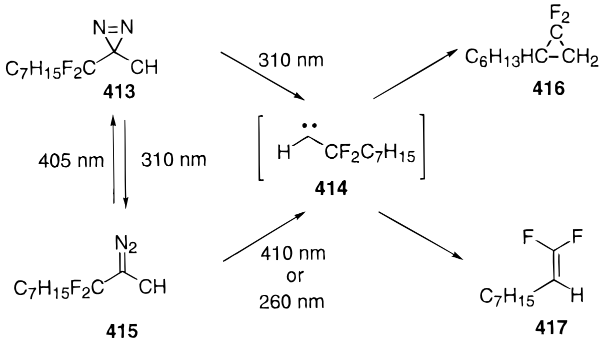
Two related carbenes were synthesized as potential labels in biological systems.[518] The photolysis (λ = 310 nm) of 3,3-bis(1,1-difluorohexyl)diazirine (**408**) generated the isomeric diazo compound **410** and carbene **409** as evidenced by the rearrangement products **411** and **412**. Compound **411** corresponds to an intramolecular C−H insertion, whereas **412** results from 1,2-alkyl migration. Diazo compound **410** was converted to diazirine **408** or carbene **409** upon subsequent irradiation at 410 nm (Scheme 32). In addition, the ratio of products was constant regardless of the solvent (cyclohexane, cyclohexene, or methanol).

Scheme 32



The irradiation (λ = 310 nm) of 3-(1,1-difluorooctyl)-3*H*-diazirine (**413**) in cyclohexane or methanol produced diazo compound **415** and rearrangement products **416** and **417** (Scheme 33). Again, no intermolecular C−H or O−H insertion products were identified.

Scheme 33



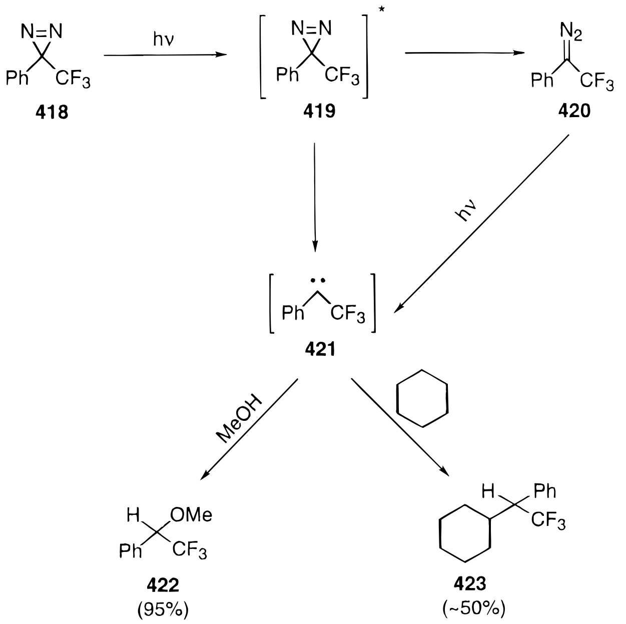
D. Phenyl(trifluoromethyl)carbene

1-Phenyl-2,2,2-trifluoroethylidene (**421**) was prepared in an argon matrix at 10 K by the photolysis (λ > 475 nm) of **420**.[514] Irradiation (λ > 340 nm) of phenyl(trifluoromethyl)diazirine similarly produced the carbene, with a small amount of the photoisomerization product, 1-phenyl-2,2,2-trifluorodiazoethane.[519]

Brunner and Semenza reported that the photolysis of phenyl(trifluoromethyl)diazirine (**418**) at wavelengths near 350 nm produced 65% carbene **421** and 35% of the isomeric diazo compound **420**.[520] Irradiation in methanol yielded **422**, the O−H insertion product, in near-quantitative yield (95%). In cyclohexane, a 50% yield of **423**, the C−H insertion product, was obtained (Scheme 34). In addition, no fluorine rearrangement was detected.

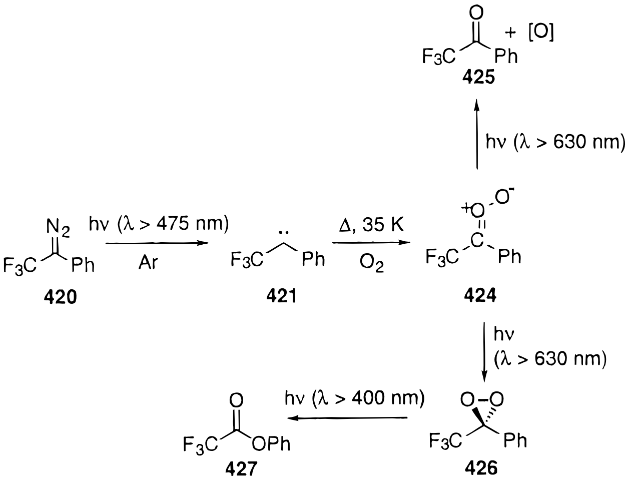
Irradiation (λ > 475 nm) of **420** in a 0.5−4% O_2 doped argon matrix produced **421** and the oxidation products trifluoroacetophenone (**425**) and phenyl trifluoroacetate (**427**).[514] The ratio of carbene to oxidation products was dependent on the O_2 matrix content. At concentrations of 0.5%, very little carbene was oxidized, whereas at 4% the carbene was nearly completely oxidized. Warming (10−42 K) and

Scheme 34



recooling the matrix converted **421** to **424**. Irradiation (λ > 630 nm) of **424** converted it to a mixture of **425** and **426** (Scheme 35).

Scheme 35

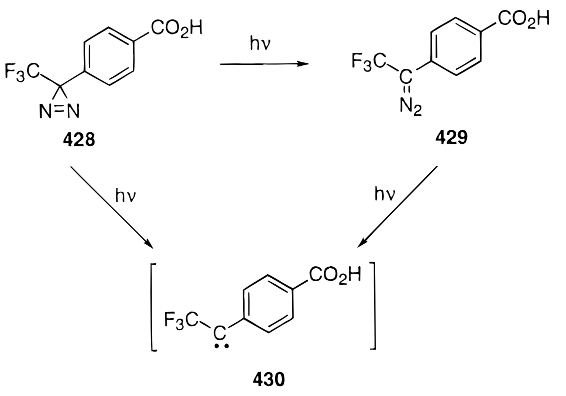


During the annealing of the O_2 doped matrix containing **421** (10–60 K), a bright blue chemiluminescence was observed and closely matched the phosphorescence spectra of **425**. The chemiluminescent reaction between oxygen and **421**, generated from the irradiation of phenyl(trifluoromethyl)diazirine in Freon 113 at or above 77 K, was also investigated by Turro et al.[521]

The argon matrix IR spectrum of **421** has been recorded.[514,519] In the UV spectra, **421** exhibited maxima at 415, 420, 429, 435, and 444 nm.[514]

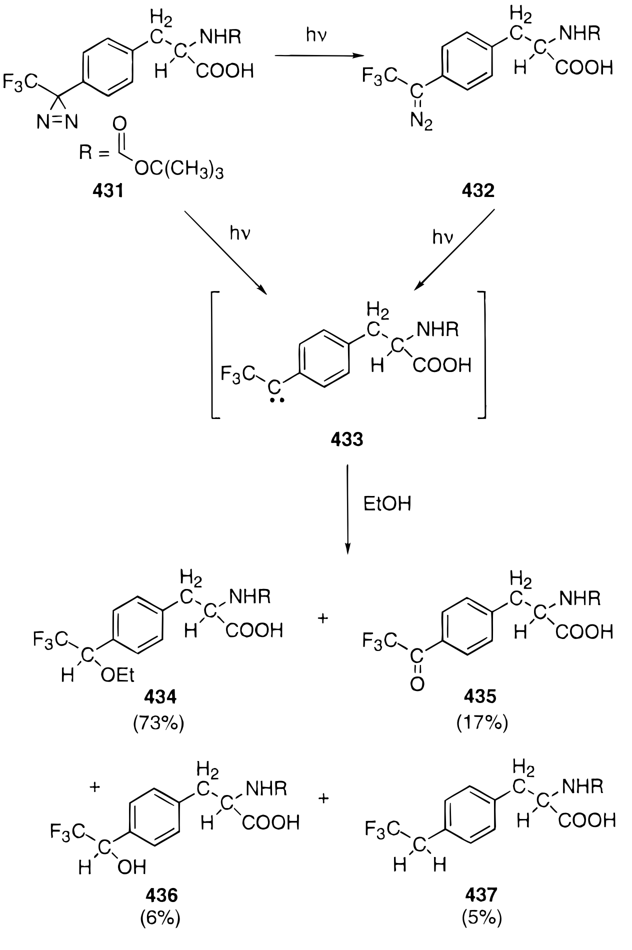
The photolysis (λ > 300 nm) of diazirine **428** in ethanol generated the related carbene **430** and the isomeric diazo compound **429**, which could also be converted into carbene (Scheme 36).[522] This carbene has been of interest because of its potential labeling applications for biological systems.

Scheme 36



In a later report, Nassal described the reactions of similar aryl(trifluoromethyl)carbenes, also of interest because of their labeling capabilities.[523] The irradiation (λ > 300 nm) of diazirine **431** in ethanol produced the O–H insertion product, ethyl ether **434** (73% relative yield), ketone **435** (17%), alcohol **436** (6%), and the reduced compound **437** (5%) (Scheme 37). In 2-methyl-2-propanol, the O–H insertion product was obtained (59%) in addition to **435** (9%) and **436** (10%). Photolysis in cyclohexane led to approximately 47% C–H insertion product, 34% **435**, and 18% **436**. Ketone **435** was explained by the reaction of the carbene, presumably in the triplet ground state, with triplet oxygen. Alcohol **436** was thought to be a photoreduction product of the ketone, and **437** was probably formed from the triplet carbene by double H-abstraction. The insertion reactions were assigned to the singlet excited state of carbene **433**. Isomer-

Scheme 37

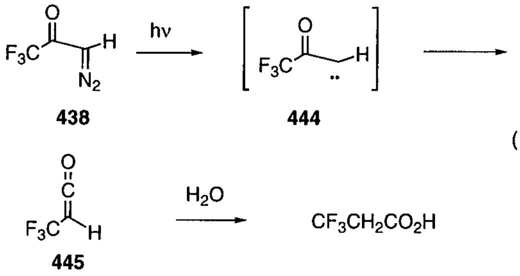


ization to the diazo compound was also observed in all photolyses.

Other related photogenerated carbenes, such as 3-(trifluoromethyl)-3-(*m*-[^{125}I]iodophenyl)carbene,[524,525] phospholipid bound (3-(trifluoromethyl)-phenyl)carbenes,[526] and oncadazole derived carbenes[527] were also used as labeling agents in biological systems.

E. Fluorinated Ketocarbenes

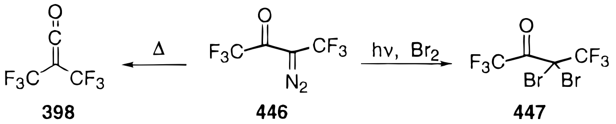
Weygand et al. demonstrated that the irradiation of **438** in aqueous dioxane formed 3,3,3-trifluoropropionic acid.[528] The reaction can be explained as a typical Wolff rearrangement to ketene **445** that may, or may not, proceed through the corresponding carbene **444** (eq 176).



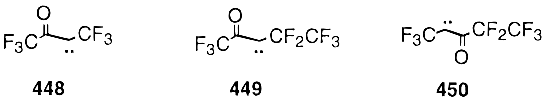
(176)

Early work on **446** includes the photolysis in the presence of bromine to produce **447** in 53% yield and the pyrolysis (300 °C) to generate **398** (Scheme 38).[529]

Scheme 38

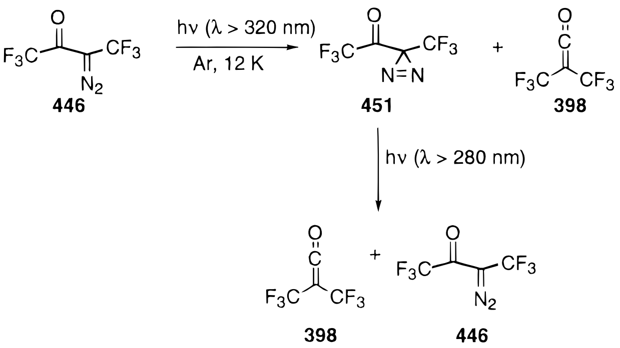


The photolysis of **446** at 30 K produced **448**, which was detected by ESR spectroscopy as a mixture of cis and trans conformers in a 9:1 ratio.[530] The cis conformer was found to be kinetically more stable than the trans and decays above 100 K with first-order kinetics, $E_a = 5.0$ kcal/mol. The analogous kinetic data on the trans conformer that decays between 50 and 70 K was not obtained because of the weak signal intensities. The derived activation energy was postulated to correspond to triplet–singlet intersystem crossing prior to, or in concert with, Wolff rearrangement to **398**. Similar chemistry was reported for carbenes **449** and **450**, which were also generated from the corresponding diazo compounds.

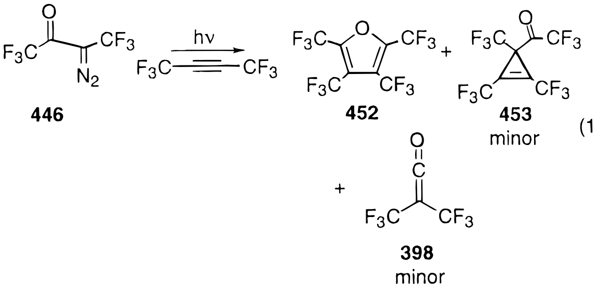


In an attempt to obtain IR spectroscopic data for carbenes **448**, **449**, and **450**, the corresponding diazo compounds were irradiated under matrix isolation conditions in argon at 10 K.[531] For instance, irradiation of **446** under these conditions produced **398**, and another compound originally identified as **448**, which upon further irradiation at $\lambda \geq 210$ nm augmented the ketene IR absorptions. The other diazo compounds behaved similarly. However, later work showed that the IR bands originally assigned to **448** were actually due to the corresponding diazirine **451** (Scheme 39).[532,533] Carbenes **448**–**450** are formed in such small quantities under the matrix isolation conditions that they cannot be observed by IR spectroscopy but can be observed by the much more sensitive ESR method. Maier et al. also found that similar acylcarbene intermediates could not be detected by IR in an argon matrix at 10 K.[534]

Scheme 39



Gas phase photolysis of the diazoketones **446**, **459**, and **460** in the presence of perfluoro-2-butyne led to furans as the major products with cyclopropenyl ketones and the ketenes as minor products (eq 177).[535]

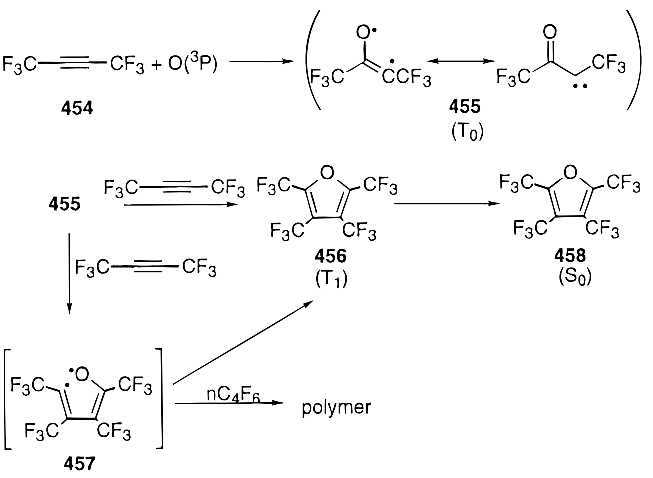


(177)

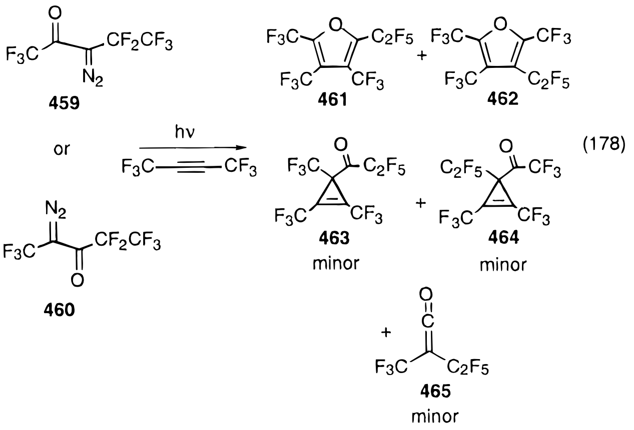
Tetrakis(trifluoromethyl)furan (**452**) was also the major product in the reaction between oxygen(^{3}P) atoms, generated from the mercury-sensitized photodecomposition of nitrous oxide, and hexafluoro-2-butyne.[536] This reaction presumably occurs by the formation of a triplet ketocarbene **455** that traps a second molecule of alkyne to give triplet furan directly or a 1,5-biradical **457** that subsequently undergoes ring closure to triplet furan. Because no ketene and cyclopropenyl ketone products were obtained in this reaction, it was concluded that the formation of furan adducts in the photochemical reaction between **446** and hexafluoro-2-butyne occurs from the triplet state of the carbene, while ketene and cyclopropenyl ketone adducts arise from an excited singlet state (Scheme 40).

Interestingly, the same product mixture consisting of isomeric furans **461** and **462** and isomeric cyclopropenyl ketones **463** and **464** was produced from either **459** or **460** (eq 178).[535]

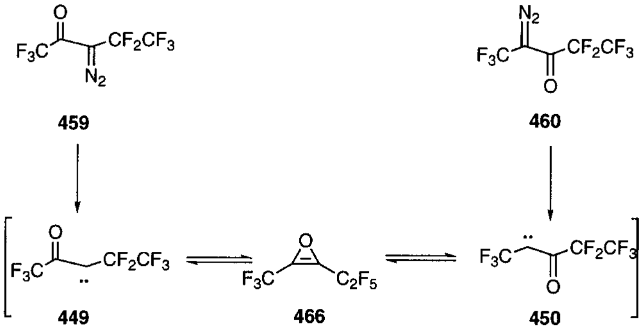
Scheme 40



The authors suggested that equilibration of the two isomeric ketocarbenes **449** and **450** through an oxirene intermediate **466** could account for the products (Scheme 41).



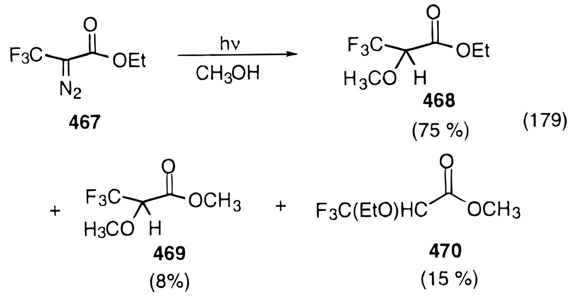
Scheme 41

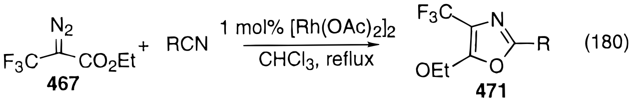


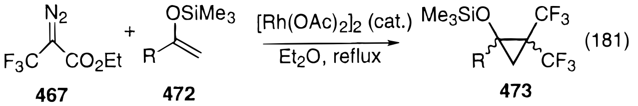
Modification of the keto group to an ester slows the Wolff rearrangement so that the carbene can be trapped by external reagents. For instance, photolysis of ethyl diazotrifluoropropionate in methanol gave ~85% O−H insertion and only 15% rearrangement (eq 179).[537]

The decomposition of **467** in the presence of rhodium acetate generated carbenoids that reacted with various nitriles to form CF_3-substituted oxazoles **471** in yields ranging from 92% (R = 4-ClC_6H_4) to 30% (R = EtO_2CCH_2) (eq 180).[538]

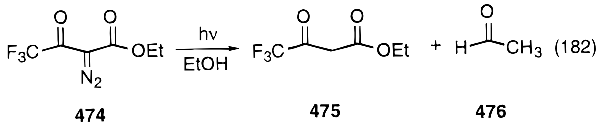
Similarly, the rhodium-catalyzed decomposition of **467** allowed the cyclopropanation of electron-rich and sterically undemanding silyl enol ethers in excellent yields (eq 181).[539] However, when sterically hindered silyl enol ethers such as those derived from cyclohexanone and 3-pentanone were used, very little cyclopropanation occurred. Instead, the competing dimerization reaction and C−H insertion into the solvent predominated.



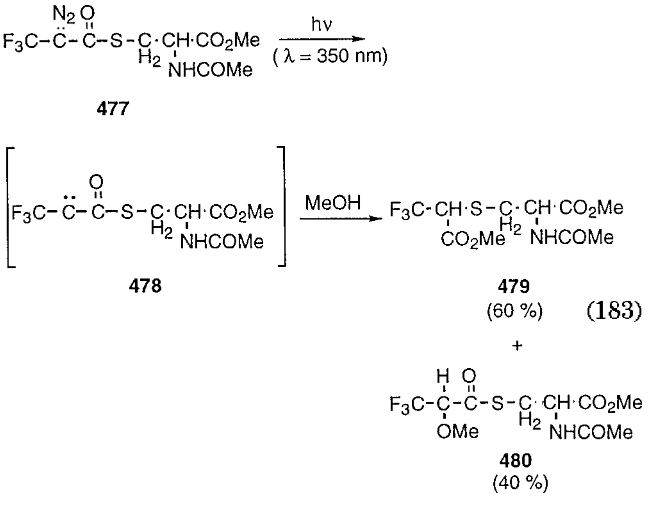




The irradiation of **474** failed to produce any ketene via Wolff rearrangement. Instead, it reacted with every solvent studied.[528,540] For example, ethanol was dehydrated to acetaldehyde, and the carbene was converted to **475** (eq 182).

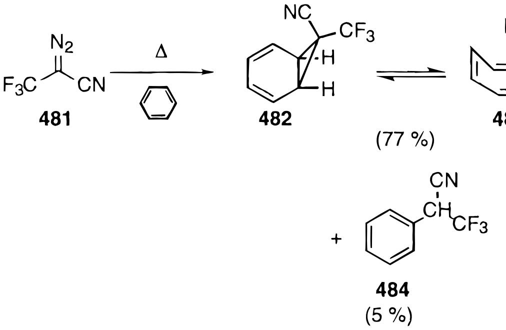


This lack of rearranged Wolff product has been used to advantage in developing photoaffinity reagents. For instance, irradiation of the diazotrifluoropropionyl ester of methyl *N*-acetylcysteine (**477**) did not exclusively lead to rearrangement products **479**, as compared to thiol derivatives of other photoaffinity reagents.[537] Instead, 40% of the products (**480**) arose from the O−H insertion by the carbene into the solvent (eq 183).



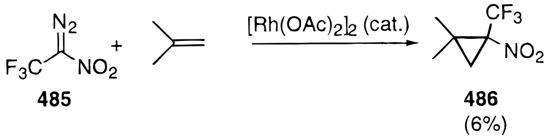
F. Other (Trifluoromethyl)carbenes

The thermolysis of (trifluoromethyl)diazoacetonitrile (**481**) in benzene produced a rapidly equilibrating mixture of **482** and **483** in 77% yield and **484**, the product corresponding to C−H insertion of cyano(trifluoromethyl)carbene into benzene, in 5% yield (eq 184).[541,542]



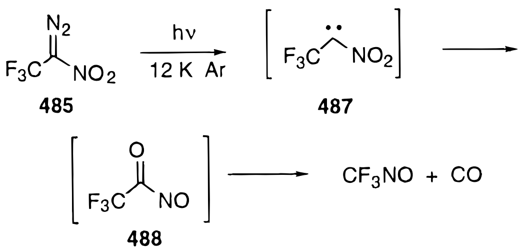
(184)

Schöllkopf and co-workers developed syntheses of nitrodiazo compounds from the treatment of diazo compounds containing electron-withdrawing groups with dinitrogen pentoxide.[543] In this manner, nitro(trifluoromethyl)diazomethane (**485**) was prepared. However, no chemistry of the resulting diazo compound was reported by this group. O'Bannon and Dailey demonstrated that nitro(trifluoromethyl)carbene could be transferred from the diazo compound using rhodium(II) as a catalyst.[544] Low yields of the corresponding cyclopropanes were reported (eq 185). A rhodium carbenoid was suggested as the intermediate since nitrocarbenes are predicted to have no barrier to 1,2-oxygen migration to form acyl nitroso compounds.[544]



(185)

A low-temperature matrix isolation study of **485** revealed that upon photolysis it is converted to carbon monoxide and CF_3NO. The following mechanism was proposed (eq 186).[544]



(186)

IV. Ackowledgments

We thank the National Science Foundation for supporting our efforts in this area. W.P.D. also thanks the Alfred P. Sloan Foundation for a research fellowship (1990−1994).

V. References

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