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Matrix-Isolation and ab Initio Molecular Orbital Study of 2,2,2-Trifluoroethylidene

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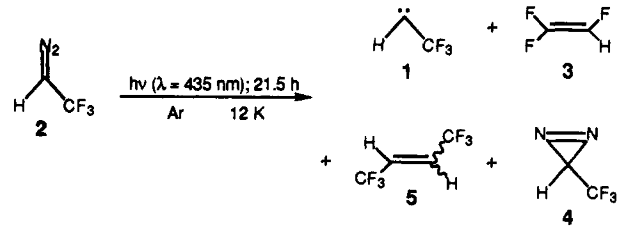
Abstract: Photolysis of 2,2,2-trifluorodiazoethane (**2**) in an argon matrix at 12 K generates triplet 2,2,2-trifluoroethylidene (**1**) in addition to a significant amount of trifluoroethylene (**3**) and small amounts of trifluoromethyldiazirine (**4**). These compounds were identified by IR and UV spectroscopy. Short-wavelength photolysis of the carbene **1** converts it to trifluoroethylene, while slowly warming the matrix to 35 K results in dimerization to the isomeric hexafluorobut-2-enes. High-level ab initio calculations (QCISD(T)6-311(2D,2P)//MP2-FC/6-31G**) are reported for the singlet and triplet states of 2,2,2-trifluoroethylidene as well as for methylene and ethylidene. The calculated IR spectrum for triplet 2,2,2-trifluoroethylidene is in good agreement with the experimental one, but the UV/vis spectrum calculated using the CIS method does not match very well. The transition structures for the 1,2-fluorine atom rearrangement of the single and triplet states of carbene **1** to trifluoroethene were calculated at the QCISD(T)-FC/6-311(2D,2P)//MP2-FC/6-31G** level of theory. The calculated barrier for 1,2-fluorine atom migration in the singlet carbene, 21.5 kcal/mol, is less than suggested by recent experimental results (29 ± 4 kcal/mol). The calculated barrier for the corresponding rearrangement in the triplet system was 51 kcal/mol. Previous reports concerning the energies and geometries of these calculated transition structures are shown to be in error.

The direct study of simple alkyl carbenes is complicated by the facile 1,2 atom migrations that take place during the preparation of many of these compounds.[1] We recently reported the chemistry of several halo(trifluoromethyl)carbenes, where the presence of fluorine as the migrating group permitted the direct observation of a series of singlet trifluoromethylcarbenes.[2] Here we report similar studies on the simplest trifluoromethylcarbene, 2,2,2-trifluoroethylidene (**1**). In contrast to the singlet ground-state nature of the previously reported halo(trifluoromethyl)carbenes, trifluoroethylidene is known to be a ground-state triplet carbene. It has been generated under low-temperature conditions by irradiation of trifluorodiazoethane (**2**) and observed by ESR spectroscopy.[3] Gas-phase and solution-trapping studies have also been reported for trifluoroethylidene generated in a similar manner.[4] There are no reports of IR or UV/vis spectroscopic studies of this reaction under matrix isolation conditions so that the relative proportions of 1,2-fluorine atom migration to carbene formation are not known. Recently an experimental measure of the activation energy for 1,2-fluorine atom migration of trifluoromethylcarbene to trifluoroethylene has appeared.[5] We report the infrared and ultraviolet spectra for 2,2,2-trifluoroethylidene generated under matrix isolation conditions and compare these results with those of the halo(trifluoromethyl)carbenes. High-level ab initio calculations are also reported and are compared with experimental and recent theoretical results. Significantly, the recent results of So[6] concerning the calculated transition structures for the 1,2-fluorine atom migration in singlet and triplet **1** are found to be in error.

Results and Discussion

2,2,2-Trifluorodiazoethane (**2**), prepared according to the literature procedure,[4b] was mixed with argon in a 1:2000 ratio and was deposited onto a cesium iodide salt plate cooled to 22 K. Irradiation of the matrix (λ = 435 ± 10 nm) at 12 K for 22 h resulted in the disappearance of the IR bands assigned to the diazo compound **2** and produced bands that are assigned to the carbene **1**, trifluoroethene (**3**), small amounts of diazirine **4**, and 1,1,1,4,4,4-hexafluoro-2-butenes **5a**,**b**. A spectrum of this mixture is shown in Figure 1. The IR bands assigned to 2,2,2-trifluoroethylidene were observed at 3153.6, 3146.4, 3135.6, 3131.9, 1294.4, 1292.4, 1286.4, 1151.6, 1120.0, 875.1, 758.7, 624.1, and 438.7 cm^{-1}. The rearrangement product, trifluoroethene, accounted for approximately 40% of the photolysis product. This is a much higher percentage of initially formed rearrangement product compared to carbene than was found in the corresponding matrix chemistry of the halo(trifluoromethyl)carbenes.[2] The ratio of carbene **1** to trifluoroethene remained approximately constant throughout the irradiation, suggesting that trifluoroethene is a primary photolysis product. Once formed at 12 K, 2,2,2-trifluoroethylidene is stable to further photolysis at this wavelength for at least several days.



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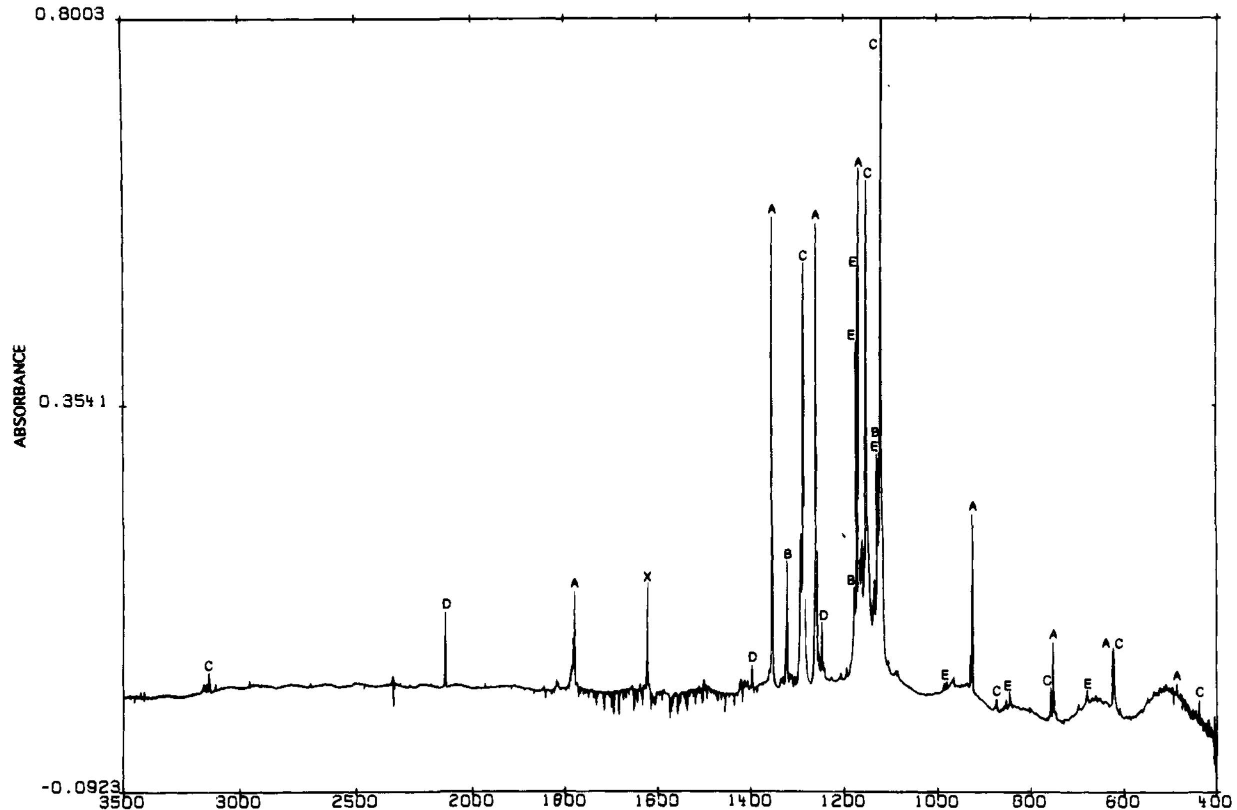
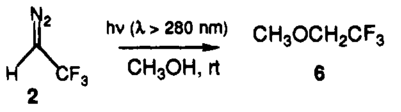


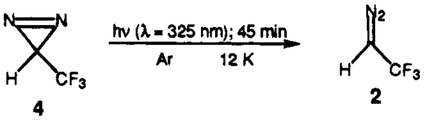
Figure 1. IR spectrum in an argon matrix at 12 K produced by irradiation at 435 nm of trifluorodiazoethane (**2**, D). Assigned bands are due to trifluoroethylidene (**1**, C), trifluoroethene (**3**, A), trifluoromethyldiazirine (**4**, E), and the hexafluoro-2-butenes (**5**, B). Bands marked X are impurities.

There have been several suggestions in the literature that diazirines and diazo compounmds can photochemically rearrange directly to alkenes by pathways not involving the singlet carbene.[7] This is based on the observation for some diazirines that a fraction of the photochemical reaction still yields rearrangement products even in the presence of large amounts of added trapping reagents. Excited-state diazo compounds and diazirines as well as excited-state carbenes have been invoked to explain these observations. When **2** was irradiated in a pure methanol solution, more than 90% of the carbene **1** could be trapped as the O−H insertion product **6**. Likewise, it has been reported that when **2** was irradiated in liquid *trans*-2-butene, no trifluoroethene was observed.[4b] However, irradiation of **2** in the gas phase with 2-butenes does produce substantial amounts of trifluoroethylene.[4c]



When nitrogen was used as the matrix material, the same chemistry was observed but with a few differences. First, a substantially longer time of irradiation was required to destroy the diazo compound **2** as compared to using argon as the matrix material. Second, a much higher ratio of rearrangement product to carbene was observed. These differences can be rationalized by proposing that the initially formed carbene can undergo readdition to dinitrogen to reform diazo compound **2**, undergo intersystem crossing to form triplet carbene **1**, or undergo 1,2-fluorine atom migration to form trifluoroethene. Only the first of these possibilities should be dependent on using nitrogen as the matrix material. Attempts to use other materials for the matrices, such as 3-methylpentane or sulfur hexafluoride, were unsuccessful owing to the overlap of the absorbed IR regions. Thus the rearrangement can be quenched in solution at room temperature while approximately 40% rearrangement takes place in the argon matrix at 12 K and a comparable amount in the gas phase at room temperature. "Hot molecule" effects are a consistent explanation of these results. Other examples of hot molecule chemistry have been reported where different matrices and solutions gave varying amounts of further reaction.[8] Matrix-isolation studies[9] of bis(trifluoromethyl)carbene generated from bis(trifluoromethyl)diazomethane or bis(trifluoromethyl)diazirine make no mention of the formation of the potential rearrangement product, hexafluoropropene. Perhaps "hot molecule" chemistry is taking place during the generation of **1**, but the additional trifluoromethyl group in bis(trifluoromethyl)carbene is able to effectively dissipate the excess energy.

The IR bands assigned to diazirine **4** were observed at 1173.6, 1170.2, 1123.2, 983.4, 981.0, 854.4, 681.5, and 679.8 cm^{-1}. These bands could be selectively destroyed using monochromatic irradiation (λ = 325 ± 10 nm) resulting in the generation



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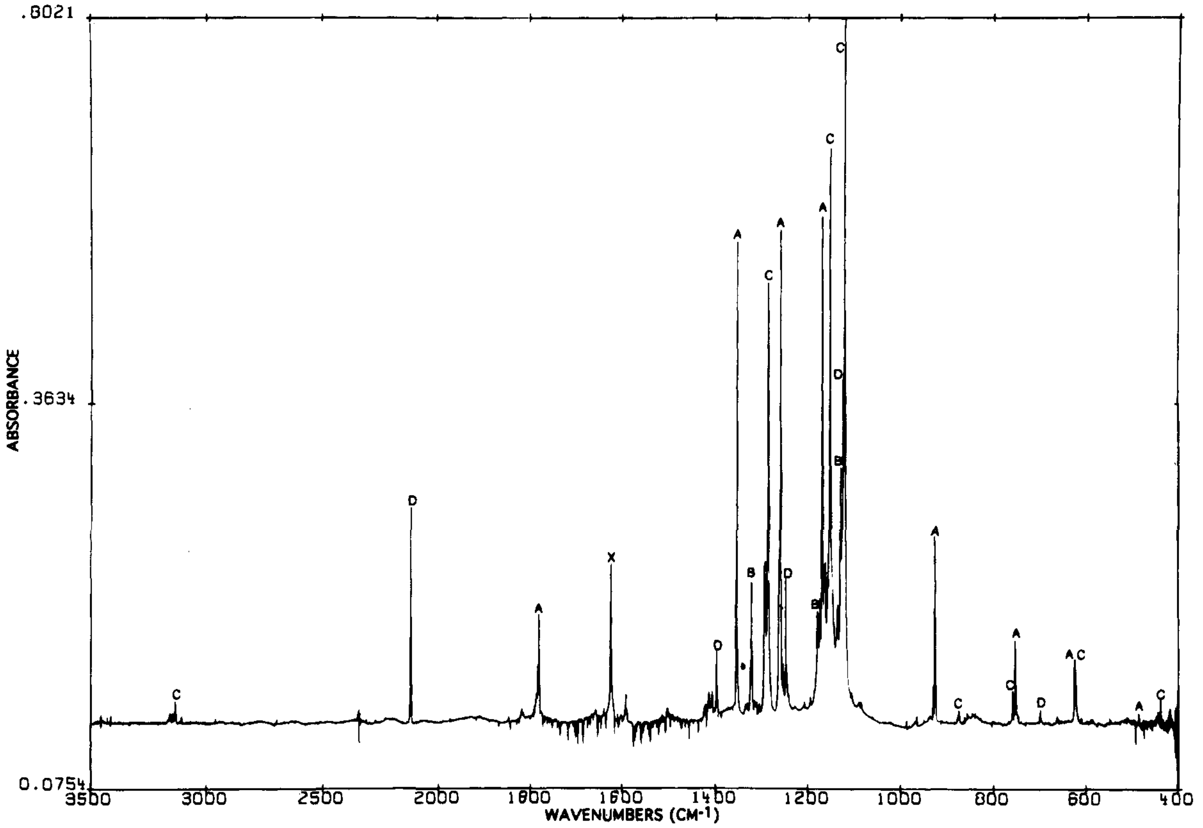


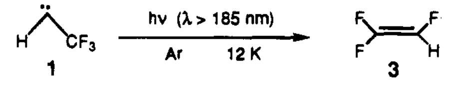
Figure 2. IR spectrum in an argon matrix at 12 K produced by irradiation at 325 nm of the matrix shown in Figure 1. The bands assigned to trifluoromethyldiazirine (**4**, E) have been eliminated while the bands assigned to trifluorodiazoethane (**2**, D), trifluoroethylidene (**1**, C), and trifluoroethylene (**3**, A) have increased slightly. Bands marked X are impurities.

of small amounts of carbene **1** and alkene **3**, but mostly in the regeneration of diazoethane **2**. The IR spectrum of carbene **1** and regenerated **2** from such an irradiation is shown in Figure 2.

The basis of assignment for **4** comes from its conversion to the diazo compound **2** using irradiation which is absorbed in the n$-\pi^*$ region of diazirines.[10] Diazirine fine structure was also observed in the 300-nm region of the corresponding UV/vis spectrum (see below). Continued photolysis of diazo compound **2** after diazirine destruction afforded no new diazirine growth, suggesting that **4** comes from an intramolecular side reaction of **2** and is not an intermolecular reaction. The photochemical interconversion of diazo compounds and diazirine is well precedented.[11] Maximum carbene formation after diazirine destruction and final diazo conversion is shown in Figure 3.

Examination of the UV/vis spectrum after irradiation of an argon matrix of diazoethane **2** revealed a reduction of the diazo UV/vis absorption at 205 nm and generation of three small peaks at 293, 301, and 307 nm. These three peaks are assigned to the fine structure absorptions of diazirine **4**, whereas the 205 nm absorption is assigned to a combination of diazoethane **2** and carbene **1**. Destruction of the diazirine absorption peaks was accomplished by monochromatic irradiation at 325 nm resulting in a slight increase at the 205 nm absorption. The increase at 205 nm is attributed to conversion of **4** to **1** and **2** as observed in IR investigations. Continued photolysis at 430 nm resulted in a slight decrease in the 205-nm absorption within the limits of detection. The UV spectrum prepared in this way is assigned to carbene **1**.

Further evidence for the assignment of the 205-nm absorption to carbene **1** comes from its photochemical destruction. Broadband irradiation of an argon matrix of **1** using a medium-pressure mercury arc filtered through quartz ($\lambda > 185$ nm) led to the complete bleaching of the 205-nm band leaving only the tail of an absorption originating in the vacuum UV. An examination by IR spectroscopy of a matrix treated in this way revealed that the matrix contained almost pure trifluoroethene, the 1,2-fluorine atom migration product. The spin state that is



responsible for this rearrangement is not known. The energy of a 200-nm photon (ca. 140 kcal/mol) makes the rearrangement process thermochemically reasonable from the vibrationally excited triplet state which has a calculated barrier of about 50 kcal/mol (see below). Intersystem crossing from the excited triplet to the lowest singlet state and then rearrangement is also a possibility.

When a matrix of **1** was warmed to and annealed at 37 K over 8 h, the intensity of IR bands assigned to carbene **1** decreased, and bands assigned to hexafluoro-2-butenes **5a,b** increased proportionally.[12] The relative amounts of **5a** and **5b** were not clear from the IR band intensities. The ratio was determined by collecting the products in a −196 °C cold trap during thawing of the cold finger. Material collected in this

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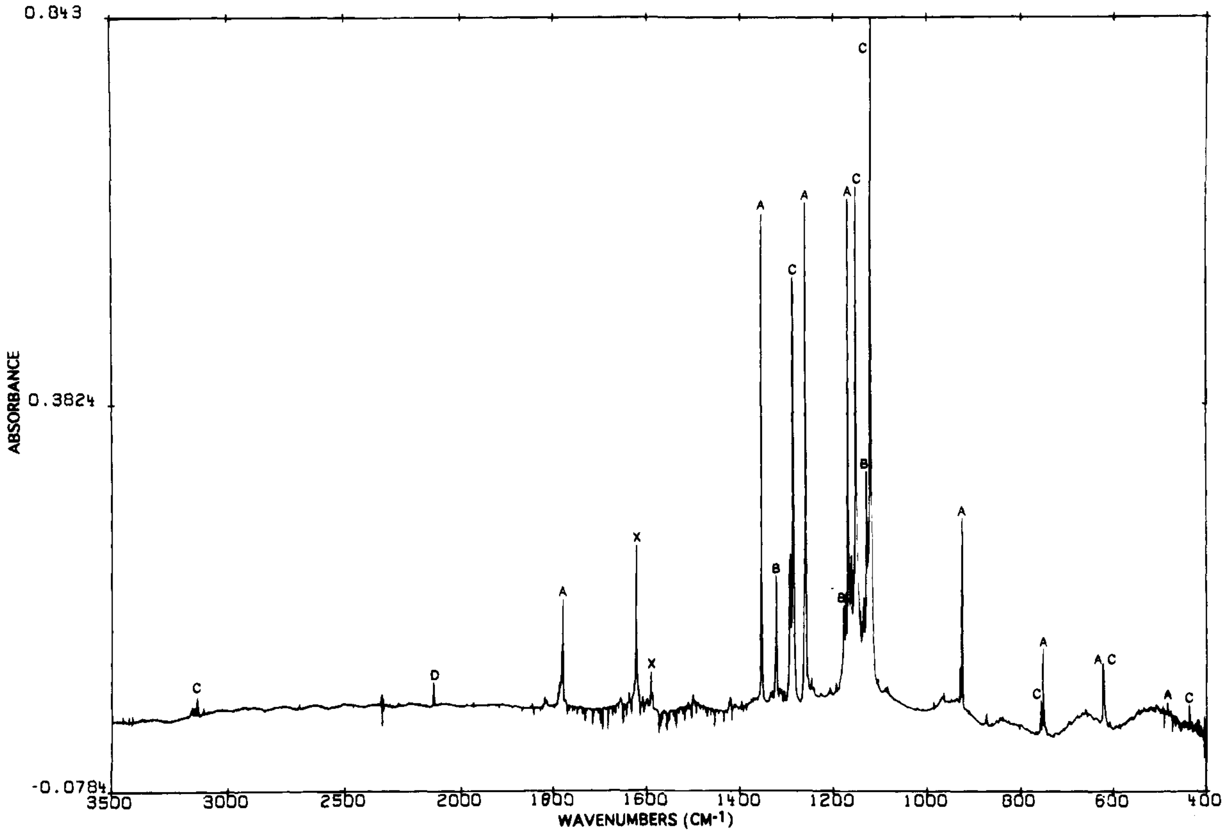
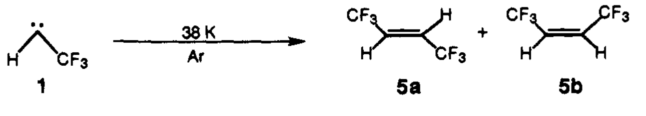


Figure 3. IR spectrum in an argon matrix at 12 K produced by irradiation at 435 nm of the matrix shown in Figure 2. The major bands are assigned to trifluoroethylidene (**1**, C), trifluoroethylene (**3**, A), and hexafluoro-2-butenes (**5**, B). Bands marked X are impurities.



way was analyzed by ^{19}F NMR spectroscopy. The formation of **5a** and **5b** in a 1.1:1 ratio was established by integration of resonances at −66.4 ppm and −60.7 ppm, respectively.[13] Unreacted diazoethane **2** (−55.4 ppm) was the only other observed resonance in the spectrum. Any trifluoroethene that was formed was lost due to its volatility.

Table 1. Geometries for 2,2,2-Trifluoroethylidene Determined Using ab Initio Calculations with 6-31G** Basis Set[a]

	singlet		triplet	
method	RHF	RMP2-FC	UHF	UMP2-FC
r(C1−H)	1.091	1.100	1.071	1.075
r(C1−C2)	1.507	1.499	1.479	1.475
r(C2−F1)	1.327	1.367	1.324	1.355
r(C2−F2)	1.313	1.339	1.319	1.348
r(C2−F3)	1.324	1.351	1.324	1.355
θ(HC1C2)	103.91	102.68	129.23	129.74
θ(C1C2F1)	105.42	98.87	111.72	111.70
θ(C1C2F2)	113.95	115.19	111.05	110.93
θ(C1C2F3)	113.28	117.56	111.72	111.70
θ(HC1C2F1)	73.74	81.55	59.86	59.81
θ(HC1C2F2)	192.09	197.24	180.00	180.00
θ(HC1C2F3)	314.73	324.81	−59.86	−59.81

[a] Distances in angstroms, angles in degrees.

Ab Initio Calculations

Ab initio molecular orbital calculations were carried out on the lowest singlet and triplet states for 2,2,2-trifluoroethylidene using complete geometry optimization at the SCF (HF and UHF) and correlated (MP2 and UMP2, fixed core) levels with the 6-31G** basis set using the Gaussian 92 code.[14] Dixon has previously reported computational results on trifluoromethylcarbene at the SCF and TCSCF level using a smaller basis set and imposing some symmetry constraints.[15] So has recently reported calculations on the singlet and triplet states of trifluoromethylcarbene in addition to the transition structures for the fluorine atom migration in the singlet and triplet states.[6] However, as we will show below, neither of the previously determined transition structures was the true transition structure which corresponds to the 1,2-fluorine atom migration in the singlet or triplet carbene to singlet or triplet alkene.

The optimized geometries are shown in Table 1. The structures of the singlet and triplet carbene at both the SCF and MP2 levels of theory are very similar. The calculated structures are similar to those reported by Dixon[15] with the exception that the singlet carbene has no symmetry rather than C_s symmetry as reported by Dixon. The largest difference for both the singlet and triplet states is the calculated carbon−fluorine bond lengths which are lengthened at the MP2 level. The structure of the singlet has a HCC bond angle of 103° while the angle in the triplet is much larger, 130°.

Analytical frequency calculations were carried out at the MP2 levels of theory and produced the harmonic frequencies and intensities given in Table 2. Using a scaling factor or 0.93 gives a reasonable agreement between the calculated and experimental frequencies for triplet trifluoroethylidene.

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(13) Eshtiagh-Hosseini, H.; Nixon, J. F.; Poland, J. S. *J. Organomet. Chem.* **1979**, *164*, 107−121.

(14) Gaussian 92, Revision A: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewert, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1992.

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Table 2. Calculated IR Spectrum of 2,2,2-Trifluoroethylidene at the RMP2-FC and UMP2-FC Levels with 6-31G** Basis Set[a]

singlet (RMP2-FC)			triplet (UMP2-FC)		
calcd	scaled	intens	calcd	scaled	intens
3124.7	2906	26	3378.0	3141	4
1382.8	1286	168	1369.2	1273	234
1309.7	1218	177	1259.8	1187	265
1160.0	1079	253	1204.4	1171	299
1088.8	1012	139	946.2	880	13
855.0	795	14	879.5	818	15
598.0	556	25	622.4	579	19
553.6	515	24	575.8	535	5
529.1	492	12	535.4	498	5
507.7	472	27	435.2	404	2
335.0	311	13	378.4	351	2
236.9	220	16	197.6	184	17

[a] Frequencies in inverse centimeters, intensities in kilometers per mole. The bands were scaled by a factor of 0.93.

Table 3. Geometries and Total Energies for CH_2 and CH_3CH Determined Using ab Initio Calculations at the Optimized MP2(fixed core) level with 6-31G** Basis Set and Single-Point Energies with the 6-311 (2D,2P) Basis Set[a]

	singlet	triplet
CH_2		
r(C1−H1)	1.106	1.074
θ(H1C1H2)	101.34	131.39
E(MP2)	−38.98720	−39.01930
E(MP4(sdtq)/6-311(2D,2P))	−39.04191	−39.06241
E(QCISD(t))/6-311(2D,2P))	−39.04601	−39.06405
ZPE	0.017321	0.018163
CH_3CH		
r(C1−H1)	1.100	1.075
r(C1−C2)	1.499	1.475
r(C2−H2)	1.367	1.355
r(C2−H3)	1.339	1.348
r(C2−H4)	1.351	1.355
θ(H1C1C2)	102.68	129.74
θ(C1C2H2)	98.87	111.70
θ(C1C2H3)	115.19	110.93
θ(C1C2H4)	117.56	111.70
θ(H1C1C2H2)	81.55	59.81
θ(H1C1C2H3)	197.24	180.00
θ(H1C1C2H4)	324.81	−59.81
E(MP2)	38.98720	39.01930
E(MP4(sdtq)/6-311(2D,2P))	−78.27985	−78.28967
E(QCISD(t)/6-311(2D,2P))	−78.28303	−78.29199
ZPE	0.048406	0.0494435

[a] Distances in angstroms, angles in degrees, total energies and ZPE in hartrees.

Table 4. Total and Relative Energies (in hartrees and kcal/mol, respectively) Calculated for Singlet and Triplet 2,2,2-Trifluoroethylidene and the Transition Structures for 1,2-Fluorine Shift at the MP2-(FC)/6-31G** Optimized Geometries Using the 6-311(2D,2P) Basis Set

	$HCCF_3$(s)	$HCCF_3$(t)	$HCCF_3$(s,ts)	$HCCF_3$(t,ts)
MP2	−375.53303	−375.55629	−375.50991	−375.46672
MP3	−375.53713	−375.55796	−375.50100	−375.46470
MP4sdtq	−375.58542	−375.60257	−375.56226	−375.51681
QCISD	−375.55468	−375.57249	−375.52076	−375.51681
QCISD(t)	−375.58368	−375.59943	−375.55440	−375.51541
ZPE(MP2-FC)	0.26612	0.26839	0.27108	0.26532
relative energy QCISD(t) + ZPE(kcal/mol)	8.5	0.0	30.0	50.8

The UV/vis spectra were calculated for single and triplet 2,2,2-trifluoroethylidene using the CIS method with the 6-31G** basis set at the SCF calculated geometries. For the singlet, the first electronic transition was calculated to occur at 762 nm, while for the triplet the first transition was calculated to occur at 147 nm. This latter value is much lower than the value which is observed experimentally (205 nm). Increasing the size of the basis set to 6-311++(D,P) had no effect on the value of the transition. It is not clear why there is such a large difference between the calculated and observed transition. For the halo(trifluoromethyl)carbenes which are all ground-state singlets, the calculated UV/vis spectra were in excellent agreement with the experimental spectra.

To obtain a measure of the single−triplet energy difference, single-point energy calculations were carried out at the MP2 optimized geometries. These calculations employed a large basis set, 6-311(2D,2P), and sophisticated correlated methods, QCISD(t) and MP4(sdtq), using the fixed core approximation. As a gauge on the performence of these methods, similar calculations were carried out on methylene and ethylidene, and these results are compared with previous high level computational results. The structures and total energies of the carbenes optimized at the MP2/6-31G** level are shown in Table 3.

The calculated singlet−triplet energy differences for methylene and ethylidene are 12.3 and 5.5 kcal/mol at the MP4(sdtq)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE level. At the more expensive QCISD(t)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE level of theory, the values are lowered to 10.8 and 5.0 kcal/mol, respectively, in very good agreement with the highest level calculations reported for these two systems.[16] The calculated single−triplet energy difference for trifluoromethylcarbene is 9.3 and 8.5 kcal/mol at the MP4(sdtq)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE level and QCISD(t)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE levels of theory, respectively. Compared to the effect of substitution of a hydrogen by a methyl group on the energy of the singlet and triplet states of a carbene (5.8 kcal/mol at the QCISD(t)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE level), a trifluoromethyl group causes approximately half the change in energy (2.3 kcal/mol at the QCISD(t)/6-311(2D,2P)//MP2-(FC)/6-31G** + ZPE level).

Recently, Holmes and Rakestra have provided an experimental estimate of the barrier for the 1,2-fluorine atom migration in 2,2,2-trifluoroethylidene.[5] Their method involves the preparation of chemically activated CF_3CH_2Cl by irradiation of a mixture of CF_3I and CH_2ClI and monitoring the percentage of trifluoroethylene produced as a function of pressure. Using several approximations, these authors arrived at a barrier of 29 ± 4 kcal/mol for the 1,2-fluorine atom migration in 2,2,2-trifluoroethylidene.

For comparison, the transition structure for 1,2-fluorine atom migration in singlet 2,2,2-trifluoroethylidene was calculated at the SCF and MP2 levels of theory with the 6-31G** basis set. So has recently reported the geometries and energies of several minima and transition structures on the singlet and triplet energy surfaces of C_2F_3H using geometry optimized ab initio calculations employing the 6-31G** basis set.[6] From these calculations, So concluded that the barrier calculated for rearrangement of singlet trifluoromethylcarbene was in good agreement with that experimentally obtained. Additionally, it was suggested that rearrangement of triplet 2,2,2-trifluoroethylidene to triplet ethylene was also a plausible process. We have examined the transition structures reported by So and have found that they do not correspond to the 1,2-fluorine atom shift in the singlet and triplet carbenes. Instead they correspond to rotation about the carbon−carbon bonds in singlet and triplet trifluoroethylene. This can be confirmed by examining the normal modes corresponding to the imaginary frequencies as well as intrinsic reaction coordinate (IRC) calculations.

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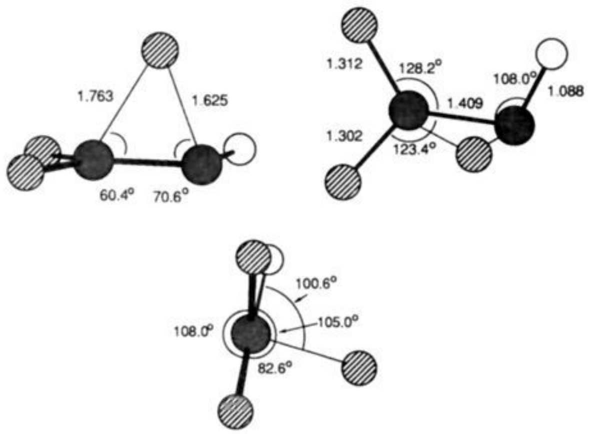

Figure 4. Three different views of the MP2-FC/6-31G** geometry optimized transition structure for fluorine atom migration in singlet trifluoroethylidene to produce trifluoroethylene. Bond distances are in angstroms.

The actual transition structure for the 1,2-fluorine atom migration in singlet trifluoroethylidene was calculated at both the HF and MP2(FC) levels of theory using the 6-31G** basis set. The MP2/6-31G** optimized geometry of the transition structure for 1,2-fluorine atom migration in singlet trifluoroethylidene is shown in Figure 4 and is qualitatively similar to that calculated for the 1,2-hydrogen migration in various singlet carbenes.[17] A frequency calculation confirmed that this structure has one imaginary frequency and that it corresponds to the 1,2-fluorine atom shift. A single-point energy calculation at the QCISD(t) and MP4(sdtq) levels using the 6-311(2D,2P) basis set was performed on this structure using the frozen core approximation. The total energies are shown in Table 2. At the QCISD(t)/6-311(2D,2P)//MP2/6-31G** level, the barrier to rearrangement is calculated to be 18.4 kcal/mol. Zero-point energy corrections bring this value to 21.5 kcal/mol. The barrier is significantly less than the experimental value reported by Holmes and Rakestraw (29 ± 4 kcal/mol).[5]

In contrast to the transition structure in singlet 2,2,2-trifluoroethylidene, no transition structure for the 1,2-fluorine atom shift could be located for the triplet at the UHF or ROHF level of theory using the 6-31G** basis set. Instead, attempts to locate this transition structure always led to the dissociation of a carbon–fluorine bond. However, use of the MP2(FC) level of theory and the 6-31G** basis set did allow the location of a transition structure for the 1,2-fluorine atom rearrangement. Interestingly, the transition structure for the 1,2-hydrogen shift in triplet ethylidene can be determined at the UHF/6-31G** level.[18] The geometry of the transition structure for the 1,2-fluorine atom migration in triplet **1** is shown in Figure 5. A single-point energy calculated at the QCISD(t) and MP4(sdtq) levels using the 6-311(2D,2P) basis set was performed on this structure using the frozen core approximation. The total energies are shown in Table 2. At the QCISD(t)/6-311(2D,2P)//MP2/6-31G** level, the barrier to rearrangement is calculated to be 52.7 kcal/mol. Zero-point energy corrections bring this value to 50.8 kcal/mol.

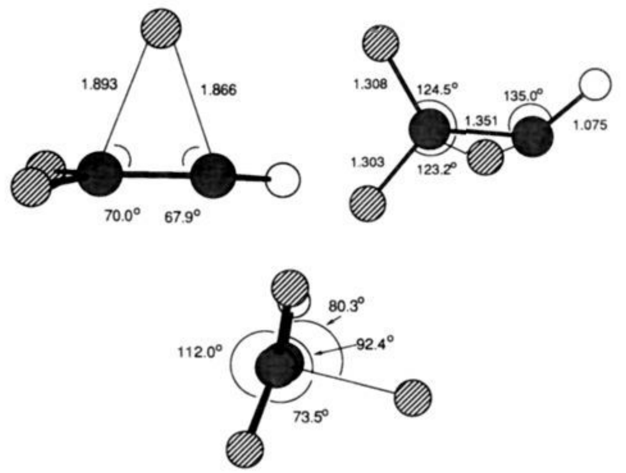

Figure 5. Three different views of the UMP2-FC/6-31G** geometry optimized transition structure for fluorine atom migration in triplet trifluoroethylidene to produce triplet trifluoroethylene. Bond distances are in angstroms.

Summary

Irradiation ($\lambda = 435 \pm 10$ nm) or 2,2,2-trifluorodiazoethane under matrix isolation conditions generates triplet 2,2,2-trifluoroethylidene together with substantial amounts (ca. 40%) of the 1,2-fluorine shift product, trifluoroethene, and small amounts of (trifluoromethyl)diazirine and the two isomers hexafluoro-2-butene **5a** and **5b**. These products were identified on the basis of their IR and UV spectra. Short wavelength photolysis of this matrix ($\lambda > 185$ nm) converts the carbene **1** and diazirine **4** to trifluoroethene. Ab initio calculations were performed on the singlet and triplet states of 2,2,2-trifluoroethylidene as well as the transition structures for 1,2-fluorine atom migration. At the QCISD(t)/6-311G(2D,2P)/MP2(FC)/6-31G** + ZPE level of theory, the singlet–triplet splitting is predicted to be 8.5 kcal/mol favoring the triplet as ground state. Transition structures calculated at the same level of theory predict a barrier of 21.5 kcal/mol for 1,2-fluorine atom migration in the singlet carbene and 50.8 kcal/mol in the triplet. The previously reported computational results of So concerning these transition structures were shown to be in error.

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Supplementary Material Available: Experimental procedures and spectroscopic data for **1**, **2**, **3**, **4**, **5a**, **5b** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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