Chemical Society, for support of this research.

Registry No. $Ph_2CHC(O)H$, 947-91-1; $Ph_2C{=}CHOH$, 113379-73-0; $Ph_2CHCH(OH)_2$, 113379-74-1.

Supplementary Material Available: Rate and equilibrium data for the dehydration of diphenylacetaldehyde hydrate in aqueous acetic acid buffer solutions at 25 °C (Table S1), rate data for enolization of diphenylacetaldehyde in aqueous acetic acid buffer solutions at 25 °C (Table S2), rate data for ketonization of diphenylacetaldehyde enol in aqueous acetic acid buffer solutions at 25 °C (Table S3), rate data for ketonization of diphenylacetaldehyde enol in aqueous perchloric acid solutions at 25 °C (Table S4), rate data for the ketonization of diphenylacetaldehyde enol in aqueous sodium hydroxide solutions at 25 °C in the presence of semicarbazide scavenger (Table S5), rate data for the ketonization of diphenylacetaldehyde enol in aqueous bicarbonate–carbonate buffer solutions at 25 °C (Table S6), rate data for the enolization of diphenylacetaldehyde in aqueous sodium hydroxide solutions at 25 °C (Table S7), and absorbance changes during the enolization of diphenylacetaldehyde in aqueous sodium hydroxide solutions at 25 °C (Table S8) (12 pages). Ordering information is given on any current masthead page.

Molecular and Electronic Structure of an Isolated Perfluorocarbanion. Crystal Structure of Tris(dimethylamino)sulfonium 1,3-Bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide

William B. Farnham,* David A. Dixon,* and Joseph C. Calabrese

Contribution No. 4486 from E. I. du Pont de Nemours & Company, Central Research & Development Department, Experimental Station, Wilmington, Delaware 19898.

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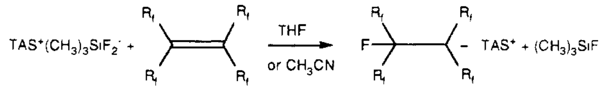
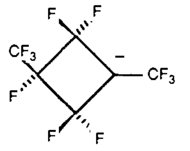
Abstract: The title compound has been synthesized, and its crystal structure has been determined by X-ray diffraction. This is the first experimental structure of a perfluorocarbanion and shows good evidence for fluorine negative anionic hyperconjugation. The C–C bond distances to the planar carbanion carbon are short, $r(C^{-}–CF_2) = 1.428$ Å and $r(C^{-}–CF_3) = 1.443$ Å. The C–F bonds on the CF_2 groups are long, $r(C–F) = 1.388$ and 1.405 Å, and $\theta(FCF)$ is small, 100.9°. Ab initio calculations with a DZ + D_C basis set were done on a model compound obtained by substitution of a F for the 3-CF_3 group. The agreement between the theoretical model and experimental structures is excellent. Two conformers of the CF_3 group bonded to the carbanion carbon were found to have almost the same energy. This is consistent with the observed disorder of this CF_3 group in the crystal structure.

Perfluoroalkyl carbanions are well-recognized reactive intermediates in fluorocarbon chemistry.[1] We recently employed the general reaction in eq 1 for the synthesis and characterization of

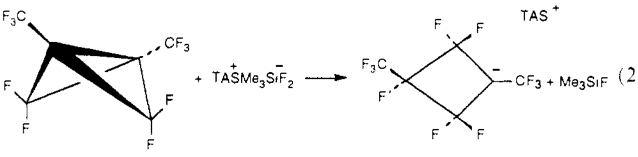


(1)

several TAS perfluoroalkyl carbanion salts where TAS is $[(CH_3)_2N]_3S^+$, tris(dimethylamino)sulfonium.[2] While the physical properties of the reported tertiary carbanions enable convenient isolation and solution studies, crystals of sufficient quality for X-ray diffraction analysis were not produced. We now report the crystal and molecular structure of tris(dimethylamino)sulfonium 1,3-bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide (**2**), prepared from the bicyclobutane **1**[3] by using a fluoride-promoted C–C cleavage reaction (eq 2).



2



(2)

We have also been interested in characterizing the molecular properties of fluorocarbons[4] by use of ab initio molecular orbital theory. We have previously reported theoretical evidence for negative anionic hyperconjugation in fluorocarbanions based on our calculated structures.[5,6] We have previously shown structural

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[1] (a) Smart, B. E. *The Chemistry of Functional Groups Supplement D: The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Part 1, Chapter 14. (b) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; Chapter 7. (c) Young, J. A. *Fluorine Chem. Rev.* **1967**, *1*, 359. (d) Dyatkin, B. L.; Delyagina, N. I.; Sterlin, S. R. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 607.

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[5] Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027.

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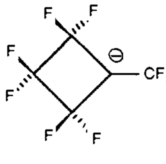
evidence for anionic hyperconjugation in a perfluorinated alkoxide, CF_3O^- (3),[6] but the structure of 2 provides the first experimental structural support for anionic hyperconjugation in a naked *fluorocarbanion*. We have performed high-level ab initio calculations on the simple fluorocarbanion 4, which differs from 2 only



4

in substitution of the 3-CF_3 group by a fluorine atom. The agreement between theory and experiment is remarkably good.

Experimental Section

Fluorine chemical shifts are reported in parts per million (ppm) from $CFCl_3$. Solvents with minimum water concentration are required for preparation and manipulation of the carbanion salt. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone and stored over activated molecular sieves. All reactions were carried out in an atmosphere of dry nitrogen, and manipulations of the carbanion salts were performed in a Vacuum Atmospheres drybox.

Tris(dimethylamino)sulfonium 1,3-Bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide. A mixture of tris(dimethylamino)sulfonium trimethyldifluorosiliconate (2.75 g, 10 mmol) and THF (10 mL) at ca. −10 °C was treated with perfluoro-1,3-dimethylbicyclo[1.1.0]butane[3] (2.62 g, 10 mmol), and the mixture was stirred for 15 min at ambient temperature. Volatiles were removed under vacuum to provide 4.2 g of the crude residue, which was triturated with ether and then recrystallized from THF/ether at low temperature to afford 3.2 g (72%) of white crystals, mp 160–162 °C. Crystals suitable for X-ray analysis were obtained from a THF solution at ca. −25 °C. ^{19}F NMR (THF-d_8): −50.15 (m, 3 F), −74.90 (apparent q, J = 9.0 Hz, 3 F), −78.28 and −83.45 (AB pattern with additional coupling, J_{AB} = 217 Hz, 4 F), −175.1 (m, 1 F). Anal. Calcd for $C_{12}H_{18}F_{11}N_3S$: C, 32.36; H, 4.07; N, 9.44; F, 46.93; S, 7.20. Found: C, 32.13; H, 4.34; N, 9.12; F, 47.01; S, 7.52.

Dimerization of Bicyclobutane 1. A mixture of bicyclobutane 1 (0.9 g) and THF (10 mL) at ca. −25 °C was treated with a solution of the salt 2 (25 mg) in 0.5 mL of THF. The mixture was warmed slowly to 25 °C. Separation of the resulting layers, facilitated by cooling at −25 °C, gave 0.9 g of fluorocarbon layer. ^{19}F NMR ($CDCl_3/F_{11}$) featured: −62.1 (m, 3 F), −64.0 (m, 3 F), −72.55 (m, 3 F), −75.1 (m, 3 F), −110.4 and −113.1 (J_{AB} = 218 Hz, 2 F), −106.6 and −116.1 (J_{AB} = 230 Hz, 2 F), −107.5 and −114.5 (J_{AB} = 245 Hz, 2 F), −163.0 (m, 1 F), −180.84 (m, 1 F), consistent with a structure containing four CF_3 groups, two CF groups, and three CF_2 moieties. GC/MS (60-m DB 210 capillary column) showed one major component with $M^+ = m/z$ 524 ($C_{12}F_{20}$).

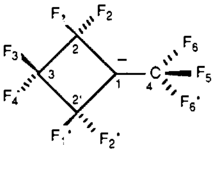
Reaction of $C_{12}F_{20}$ (Dimer of Bicyclobutane 1) with TASF. A sample of the $C_{12}F_{20}$ fluorocarbon (0.37 g, 0.69 mmol) was added to a mixture of TAS trimethyldifluorosiliconate (377 mg, 1.37 mmol) in THF (3 mL). ^{19}F NMR of the resulting homogeneous solution was identical with that described above for the carbanion salt 2. Evaporation provided 0.65 g of an off-white solid, i.e., a nearly quantitative yield of 2.

X-ray Analysis. A colorless, irregular crystal of the form 0.30 × 0.30 × 0.40 mm was used in the X-ray diffraction study. Unit cell data were obtained from 25 reflections. The unit cell is orthorhombic; space group P_{nma} (No. 62) with dimensions a = 19.146 (1), b = 11.502 (2), and c = 8.118 (4) Å. The unit cell volume is 1787.7 Å^3 and the value of Z is 4, giving a calculated density of 1.655 g/cm^3. All data was collected at T = −100 °C. The absorption coefficient, μ(Mo), is 2.81 cm^{-1}.

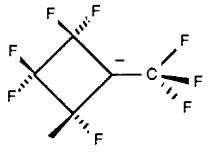
Data were collected on a Syntex R3 diffractometer equipped with a graphite monochromator with Mo Kα radiation. A total of 2390 data points were collected over the range $4.1 \leq 2\theta \leq 55$ by using the ω scan method (maximum h,k,l = 10,14,24). The typical half-height peak width was 0.23°. Three standards were collected 15 times each, and the data was corrected for a 3% decrease in intensity. A total of 1382 unique reflections were collected with $I \geq 3\sigma(I)$.

The structure was solved by direct methods,[7] and both ions were found to be on mirror planes. The hydrogens on the methyl groups were determined from difference Fourier maps and idealized. Refinement was done by full-matrix least squares on F. Scattering factors were taken from standard tables,[8] and anomalous terms were included for S. Nonhydrogen atoms were refined anisotropically, and the hydrogens were refined isotropically for a total of 151 parameters. The CF_3 on the carbanion carbon is twofold disordered on the mirror plane and was successfully refined as two half-weighted orientations. However, the resulting large thermal ellipsoids suggest complete rotational disorder about the C–CF_3 bond. The final fit values are R = 0.037 and R_w = 0.040, and the error of fit is 1.53.

Molecular Orbital Calculations. Ab initio molecular orbital calculations were done with the program GRADSCF[9] on a CRAY/1A computer. The basis set of double-ζ quality on all atoms, and the carbon basis set is augmented by a set of d functions. The basis set is from Dunning and Hay[10] and has the form (9s5p1d/9s5p)/[3s2p1d/3s2p] in the order C/F, resulting in a total of 156 contracted basis functions. The geometries were gradient optimized[11] in the following structures:



4A

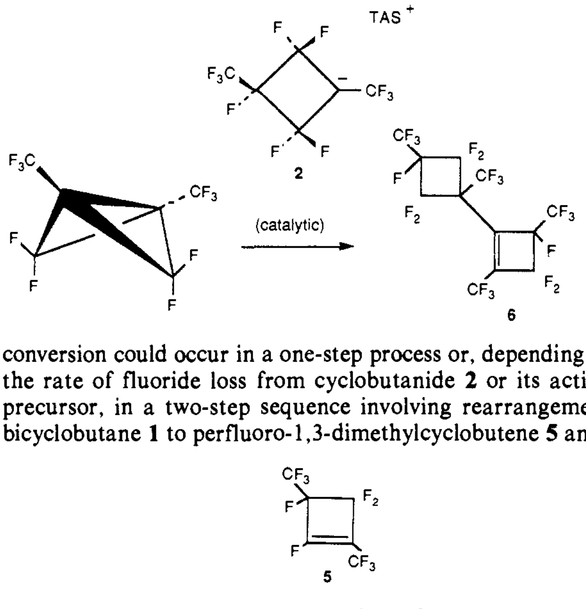


4B

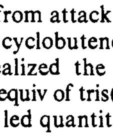
In 4A, the unique fluorine, F_5, is above the "plane" of the ring atoms, and F_5, C_4, C_1, C_3, F_3, and F_4 lie in the molecular symmetry plane. Structure 4B is obtained by rotating the CF_3 group by 90°, which places F_5 in the plane of the ring atoms, and F_5, C_4, C_1, C_2, C_2', and C_3 now define the molecular symmetry plane.

Results

Reactions. We have attempted to gain some insight regarding the details of the C–C bond cleavage reaction (eq 3). This conversion could occur in a one-step process or, depending upon the rate of fluoride loss from cyclobutanide 2 or its activated precursor, in a two-step sequence involving rearrangement of bicyclobutane 1 to perfluoro-1,3-dimethylcyclobutene 5 and addition of fluoride to give cyclobutanide 2. Our results suggest that the actual path followed is complex and may depend upon the conditions employed. For example, treatment of 1 in THF with 1.0 mol % of carbanion salt 2 at −25 °C followed by warming to 20 °C led rapidly to the dimer 6 in quantitative yield. The dimer 6 apparently results from attack of the carbanion 2 at the less-substituted carbon of cyclobutene 5 followed by fluoride elimination. We have realized the reverse of this process: treatment of dimer 6 with 2 equiv of tris(dimethylamino)sulfonium trimethyldifluorosiliconate led quantitatively to the salt 2. The overall process for fragmentation is similar to that proposed for



(3)



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[8] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

[9] GRADSCF is an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research.

[10] Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed. Plenum: New York, 1977, Chapter 1.

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Table I. Fractional Coordinates ($\times 10^4$) for the Salt of **2** and TAS and Isotropic Thermal Parameters

atom	x	y	z	B(iso),[a] Å^2
S_1	1723.3 (4)	2500.0	4233.0 (11)	1.6 (1)′
F_2	731 (1)	5707 (1)	8570 (2)	2.6 (1)′
$F_{2'}$	1812 (1)	5934 (1)	9223 (2)	2.4 (1)′
F_3	1479 (1)	7500	11471 (2)	2.4 (1)′
F_4	−180 (1)	7500	9635 (3)	3.3 (1)′
$F_{4'}$	195 (1)	6567 (1)	11752 (2)	3.5 (1)′
$F_{5'}$	1206 (4)	6608 (5)	5084 (6)	8.8 (2)′
F_5	904 (3)	7500	4894 (7)	5.3 (2)′
$F_{5'}$	1807 (3)	6581 (4)	5380 (5)	4.9 (1)′
$F_{5''}$	2110 (3)	7500	5518 (8)	8.0 (4)′
N_1	1567 (1)	2500	6273 (3)	2.0 (1)′
N_2	1319 (1)	3687 (2)	3757 (2)	2.4 (1)′
C_1	1281 (2)	7500	7619 (4)	1.9 (1)′
C_2	1218 (1)	6585 (2)	8798 (3)	1.8 (1)′
C_3	1040 (2)	7500	10114 (4)	1.7 (1)′
C_4	305 (2)	7500	10802 (5)	2.5 (1)′
C_5	1445 (2)	7500	5886 (4)	2.2 (1)′
C_6	1820 (1)	3556 (2)	7113 (3)	2.9 (1)′
C_7	607 (1)	3963 (3)	4285 (4)	3.1 (1)′
C_8	1559 (1)	4278 (2)	2267 (3)	2.9 (1)′
H_6	1646	3581	8203	3.0
$H_{6'}$	1669	4226	6526	3.0
$H_{6''}$	2320	3549	7144	3.0
H_7	519	3592	5314	3.0
$H_{7'}$	284	3697	3491	3.0
$H_{7''}$	564	4781	4419	3.0
H_8	2024	4037	2032	3.0
$H_{8'}$	1554	5094	2452	3.0
$H_{8''}$	1264	4088	1377	3.0

[a] Prime refers to the isotropic equivalent of the average anisotropic tensor values.

Table II. Interatomic Distances (Angstroms) for the Salt of **2** and TAS

S_1–N_1	1.683 (3)	F_5–C_5[a]	1.312 (6)
S_1–N_2	1.616 (2)	$F_{5'}$–C_5[a]	1.329 (4)
$F_{5'}$–F_5[a]	1.187 (8)	$F_{5''}$–C_5	1.307 (7)
$F_{5'}$–$F_{5'}$[a]	1.177 (7)	N_1–C_6	1.475 (3)
$F_{5'}$–$F_{5''}$[a]	1.210 (6)	N_2–C_7	1.463 (3)
F_2–C_2	1.388 (3)	N_2–C_8	1.462 (3)
$F_{2'}$–C_2	1.405 (2)	C_1–C_2	1.428 (3)
F_3–C_3	1.385 (4)	C_1–C_5	1.442 (5)
F_4–C_4	1.327 (4)	C_2–C_3	1.538 (3)
$F_{4'}$–C_4	1.338 (3)	C_3–C_4	1.513 (5)
$F_{5'}$–C_5[a]	1.299 (5)		

[a] Disordered CF_3 group.

Table III. Intramolecular Angles (Degrees) for the Salt of **2** and TAS

N_1–S_1–N_2	98.6 (1)	$F_{2'}$–C_2–C_1	119.3 (2)
N_2–S_1–N_2[a]	115.2 (2)	$F_{2'}$–C_2–C_3	112.0 (2)
S_1–N_1–C_6	113.4 (2)	F_3–C_3–C_2	114.7 (2)
S_1–N_2–C_7	124.0 (2)	F_3–C_3–C_4	105.7 (3)
S_1–N_2–C_8	116.1 (2)	F_4–C_4–C_3	112.8 (3)
C_6–N_1–C_6[a]	110.9 (3)	$F_{4'}$–C_4–C_3	111.1 (2)
C_7–N_2–C_8	115.7 (2)	C_2–C_1–C_2[b]	94.9 (3)
F_2–C_2–$F_{2'}$	100.9 (2)	C_2–C_1–C_5	132.3 (1)
F_4–C_4–$F_{4'}$	107.5 (2)	C_1–C_2–C_3	88.9 (2)
$F_{4'}$–C_4–$F_{4'}$[b]	106.6 (3)	C_2–C_3–C_2[b]	86.3 (2)
F_2–C_2–C_1	120.3 (2)	C_2–C_3–C_4	117.6 (2)
F_2–C_2–C_3	116.2 (2)		

[a] Generated by symmetry operation x, $^1/_2 - y$, z. [b] Generated by symmetry operation x, $^3/_2 - y$, z.

the cleavage of hexafluoropropylene-trimer anion.[2]

X-ray Structure. The fractional coordinates are given in Table I together with the isotropic thermal parameters. Interatomic distances are given in Table II while intramolecular angles are given in Table III. A drawing of the structure is given in Figure 1 with one of the orientations of the CF_3 group shown. The structure of the cation is as expected on the basis of previous studies[12] and will not be further discussed. The ionic packing shows well-separated ions with no atom in the cation closer than 3.4 Å to the carbanion atom C_1.

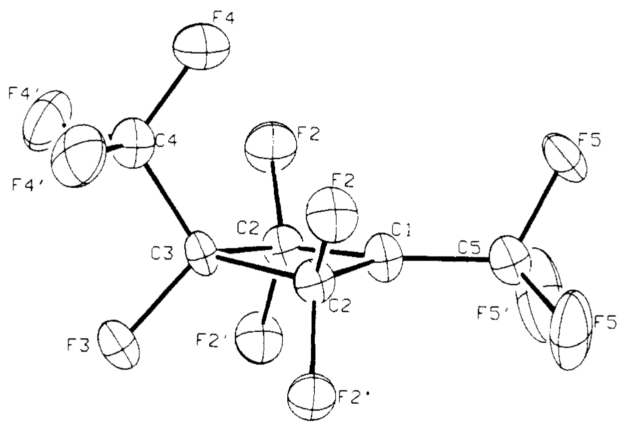

Figure 1. Plot of the structure of the carbanion **2** based on the X-ray coordinates. Note the disordered CF_3 group attached to the carbanion center C_1.

Table IV. Geometry Parameters for **4A**[a,b]

bond	value, Å	angle	value, deg
		$C_2C_1C_{2'}$	95.9
C_1–C_2	1.444	$C_1C_2C_3$	87.8
C_1–C_4	1.456	$C_2C_3C_{2'}$	88.5
C_2–C_3	1.536	$C_2C_1C_4$	132.0
C_2–F_1	1.372	$C_1C_2F_1$	120.3
C_2–F_2	1.370	$C_1C_2F_2$	120.0
C_3–F_3	1.341	$C_3C_2F_1$	113.4
C_3–F_4	1.341	$C_3C_2F_2$	113.6
C_4–F_5	1.357 (1.334)	$F_1C_2F_2$	101.9
C_4–F_6	1.343 (1.351)	$C_2C_3F_3$	115.4
		$C_2C_3F_4$	115.4
		$F_3C_3F_4$	106.4
		$C_1C_4F_5$	116.1 (111.5)
		$C_1C_4F_6$	112.7 (114.9)
		$F_5C_4F_6$	103.9 (105.7)
		$F_6C_4F_{6'}$	106.6 (103.1)

[a] Values in parentheses are for the CF_3 group in **4B**. [b] SCF:E(**4A**) = −1084.492009 au.

The carbanion center C_1 in cyclobutanide **2** is planar within experimental error. The sum of bond angles at C_1 is 359.5°, and C_1 is only 0.055 Å out of the plane of the bonded atoms. As expected from previous theoretical work, there is evidence for significant negative anionic hyperconjugation in **2** as revealed by the elongated C–F bond distances in the CF_2 groups and by the shortened value for the C_α–C_β bond distances (Table II). The C_1–C_2 bond length is 1.428 Å, and the C_1–C_5 bond length is 1.443 Å; both are almost 0.1 Å shorter than the C_2–C_3 bond length of 1.538 Å, which provides an internal comparison. We can also compare the ring bonds with the bond length for octafluorocyclobutane r(C–C) = 1.566 Å (expt)[13] and 1.564 Å (calcd).[14] and the calculated values for the C–C single bonds in hexafluoropropene (r(C–C) = 1.514 Å)[14] and octafluoroisobutene (r(C–C) = 1.520 Å).[14] The C–F bond distances on the CF_2 group β to the carbanion center in **2** are quite long, 1.388 and 1.405 Å. They are significantly longer than the C–F bond distances in octafluorocyclobutane, 1.333 Å (expt)[13] and 1.321 Å (calcd).[14] On the basis of previous results,[4] the calculated values should be 0.01–0.02 Å too short when compared to the experimental values. The disorder in the CF_3 attached to the carbanion center makes comparison of the C–F bond lengths in this group to those in other structures impossible.

The ring bond angles sum to 359.0°, showing the planar nature of the ring. The largest internal ring angle is $\theta(C_2C_1C_{2'})$ = 94.9°.

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(13) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Mol. Struct.* **1971**, *7*, 89.

(14) Dixon, D. A., unpublished results.

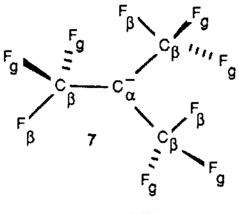
The most interesting external angles are at C_2 where the angle $\theta(F_2C_2F_{2'})$ is very small, 100.9°. The values for $\theta(C_1C_2F_2)$ and $\theta(C_1C_2F_{2'})$ are large, near 120°. The values of $\theta(C_3C_2F_2)$ and $\theta(C_3C_2F_{2'})$ are smaller at 116.2° and 112.0°, respectively. The value for $\theta(C_4C_3F_3)$, the external angle at C_3, is also small, 105.7°.

Theoretical Structures. The calculated structural parameters for **4A** are given in Table IV. We first discuss the lower energy structure, which is not required by symmetry to have a plane containing the four carbons. The cyclobutane ring is almost planar with a flap angle about the C_2–$C_{2'}$ axis with a maximum value of 1.7°. This is consistent with the experimental structure, although the flap angle is somewhat larger, ~10°. The calculated C_1–C_2 bond length of 1.444 Å is 0.016 Å longer than the experimental value but is much shorter than the calculated C–C bond length in perfluorocyclobutane.[14] The C_1–C_4 bond is calculated to be 0.012 Å longer than $r(C_1$–$C_2)$ as compared to the experimental difference of 0.014 Å. The C_2–C_3 bond length is calculated to be much longer, 1.538 Å, in excellent agreement with the experimental value.

The bond angles at C_1 sum to 359.9°, showing that the carbanion is planar, just as found experimentally. The internal ring angle at C_1, $\theta(C_2C_1C_{2'})$, is 1° larger than the experimental value. The calculated angle $\theta(C_1C_2C_3)$ is 1° smaller than the experimental value while the calculated internal ring angle at C_3, $\theta(C_2C_3C_{2'})$, is 2° smaller than the experimental value. Overall, the agreement between the calculated and experimental parameters for the carbon framework is excellent, especially considering the perturbation of the CF_3 group at C_3 in the experimental structure.

The calculated values for r(C–F) at C_2 are shorter than the average experimental value of 1.396 Å by 0.025 Å. This difference is about 0.01 Å larger than that typically observed for C–F bond length at this level of calculation.[4] The calculated C–F bond lengths at C_2 are 0.03 Å longer than the C_3–F bond lengths. The C_3–F bond lengths can be compared to the calculated value for r(C–F) in c-C_4F_8 of 1.321 Å[14] and are 0.02 Å longer. Thus the calculated C_2–F bond lengths are 0.05 Å longer than the value for r(C–F) in c-C_4F_8. These results are all consistent with a significant amount of anionic fluorine hyperconjugation at C_2. There may also be a small effect from the carbon in the γ-position at C_3 since the C–F bonds are longer here. We cannot compare the calculated r(C–F) at C_3 in **4A** with the experimental value for **2** since there is only one fluorine bonded to C_3 in **2**, and it is well-established that the C–F bond length decreases with increasing number of fluorines bonded to carbon.[15]

The bond angles involving the ring carbons and fluorine show some interesting features. As found experimentally, the most striking value is the angle $\theta(F_1C_2F_2)$, which is very small, 101.9°. This angle is much less than $\theta(F_3C_3F_4)$, which is 106.4° and θ(FCF) in c-C_4F_8, which is 109.3°.[14] The small value for $\theta(F_2C_2F_{2'})$ is very similar to the value for $\theta(F_gC_\beta F_g)$ in **7** of 102.6°,



7

which is the smallest known θ(FCF) at a carbon β to a carbanion. This is again consistent with significant anionic fluorine hyperconjugation in **2** and **4A**. The calculated value for $\theta(F_3C_3F_4)$ is very similar to $\theta(C_4C_3F_3)$ in **2** with the calculated value being 0.7° larger.

The calculated parameters for the CF_3 attached to C_1 cannot be compared with experimental parameters due to the disorder. The C_4–F_5 bond length is 1.357 Å, 0.014 Å longer than the C_4–F_6 bond length. This is not surprising, since in this orientation, F_5 can better hyperconjugate with the lone pair at C_1 than can F_6. The C_4–F_5 bond length is shorter than the C_2–F bond lengths by more than 0.01 Å. This is somewhat surprising because one would expect the orientation of F_5 to give better hyperconjugation. The value for $\theta(F_5C_4F_6)$ is quite small, 103.9°.

Table V. Electronic Properties for **4A**

atom	q for **4A**, e	atom	q for **4A**, e
C_1	−0.36	F_2	−0.28
C_2	0.38	F_3	−0.24
C_3	0.36	F_4	−0.24
C_4	0.62	F_5	−0.26 (−0.24)[a]
F_1	−0.29	F_6	−0.24 (−0.25)[a]

[a] Values in parentheses are for the fluorines on the CF_3 group in **4B**.

The structure **4B**, with the CF_3 group rotated by 90°, is less than 0.1 kcal/mol higher in energy than **4A**. Thus there is a very low rotation barrier for the CF_3 group, and the observed disorder in the X-ray structure is not surprising. The only parameters that change in **4B** as compared to **4A** are those of the CF_3 group, and only these values are given in Table IV. As expected, the C_4–F_5 bond becomes shorter because it cannot hyperconjugate while the C_4–F_6 bonds are longer. The orientation of the CF_3 group is now just like that in **7** and the geometry parameters are similar. The shorter C–F bond lengths in **4B** as compared to **7** suggest that the CF_3 group is not hyperconjugating as much in **4B** as in **7**, consistent with the large hyperconjugation effects found for the CF_2 groups at C_2 and $C_{2'}$.

Electronic Properties. The Mulliken atomic charges are given in Table V for **4A**.[16] The charges show that much of the negative charge is delocalized to the fluorines since the carbanion carbon C_1 has a negative charge of only −0.36 e. By comparison, the charge on C_α in **7** is −0.57 e, showing the large amount of delocalization in **4A** and **4B**. All of the fluorines have considerably more negative charge than found in neutral fluorocarbons. For example, the Mulliken population on fluorine is −0.18 e in C_4F_8. The most negative fluorines are those on C_2 ($C_{2'}$). This is consistent with these fluorines having the longest C–F bonds, indicative of the largest negative anionic hyperconjugation. The fluorines on C_2 ($C_{2'}$) have the largest negative charge that we have observed in a perfluorocarbon for fluorines on a β carbon. For example, the largest negative charge on a β fluorine in $CF_3CF_2^-$ is −0.27 e whereas fluorine F_g has a negative charge of −0.26 e and F_β has a charge of −0.25 e in **7**. The charges on the CF_3 group β to C_1 in **4A** and **4B** are more like those in **7**. Fluorine F_5 has a charge of −0.26 e whereas F_6 ($F_{6'}$) has a charge of −0.24 e. This is consistent with $r(C_4$–$F_5)$ being longer than $r(C_4$–$F_6)$. The charge on C_4 of 0.62 e in the CF_3 group is very similar to the charges of 0.62 e on C_β in **7**. Rotation of the CF_3 group to form **4B** changes the charges on the fluorines. Since F_6 and $F_{6'}$ are now in a better orientation for hyperconjugation, they have more negative charge than does F_5. The negative charges on the fluorines at the γ carbon C_3 are still quite negative, −0.24 e, and are quite similar to the charges on F_6 and $F_{6'}$ in **4A** or F_5 in **4B**.

The HOMO of **4A** is strongly bound (5.56 eV), showing the stability of the anion. The HOMO eigenvalue in **4A** and **4B** is 0.32 eV more stable than that in **7**.

Discussion

The most striking result is the geometry at C_2 ($C_{2'}$). There is clearly more hyperconjugation here than at the CF_3 as evidenced by the larger negative charge on the fluorines, the longer C_2–F bond lengths, and the shorter C_1–C_2 bond length. This occurs despite the fact that the CF_3 group has a fluorine in a better orientation for hyperconjugation as compared to the fluorines bonded to C_2. In the valence-bond picture, this can be explained by the relative stability of the cyclobutene isomers **8A** and **8B**. Because **8A** is expected to be significantly more stable than **8B**,

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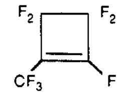
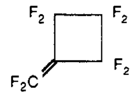
(15) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, p 141.

(16) It is well-established that Mulliken populations should be compared to different conformations of the same molecule or to similar molecules. Furthermore, the same basis set should be used in all comparisons as is done here.

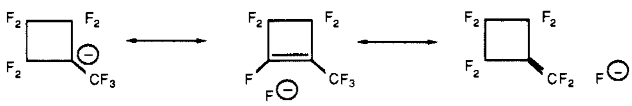


8A



8B

the hyperconjugating structures involving **8A** will be more energetically accessible than those involving **8B**. Thus $r(C_1-C_2)$ should be shorter than $r(C_1-C_4)$ as is observed. Furthermore, the hyperconjugating structures involving **8A** should have more s character in the C_1-C_2 bond, making the C_2-F bonds have more p character. This is consistent with the longer C–F bonds and the small value found for $\theta(F_1C_2F_2)$.



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Supplementary Material Available: Table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

Kinetics and Mechanisms of α- and β-Eliminations of Alkoxysilanes from Saturated and Unsaturated Carbon Frameworks

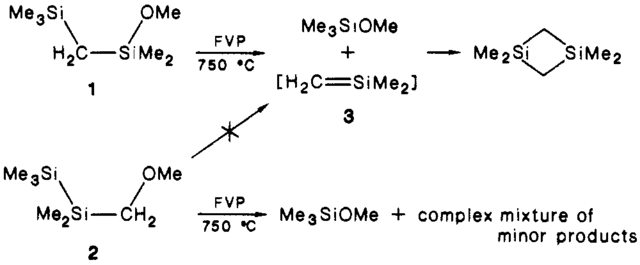
Sukhamaya Bain, Sina Ijadi-Maghsoodi, and Thomas J. Barton*

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011, and the Ames Laboratory—Department of Energy, Ames, Iowa 50011. *Received September 21, 1987*

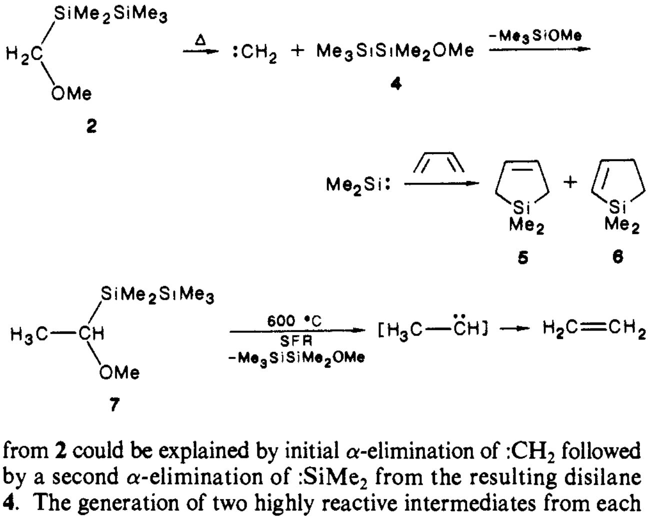
Abstract: Although $Me_3SiCH_2SiMe_2OMe$ undergoes thermally induced β-elimination of Me_3SiOMe to afford dimethylsilene, the thermodynamically favorable elimination of Me_3SiOMe from $Me_3SiSiMe_2CH_2OMe$ does not occur. From kinetic studies and trapping experiments, this is found to be due to a more favorable *A*-factor for three-centered elimination of $:CH_2$. Three-centered elimination of Me_3SiOMe from an sp^2-hybridized carbon to afford a vinylidene is found to be more facile than the analogous elimination from an sp^3-hybridized carbon due both to more favorable energy of activation and *A*-factor. Thus, silaallene formation from $H_2C{=}C(OMe)SiMe_2SiMe_3$ does not occur due to the greater facility of α-elimination to $H_2C{=}C$:.

Thermally induced β-elimination of Me_3SiOMe from silyl ethers of type **1**, first reported by Gusel'nikov,[1] has proved to be a convenient route to a variety of interesting silenes.[2] One would assume that the analogous elimination from disilanes of type **2** would be much more facile since it would involve breaking the considerably weaker Si–Si and C–O bonds rather than the robust Si–C and Si–O bonds. Indeed, consideration of available bond strengths[3] leads to the conclusion that β-elimination from **2** should be at least 45 kcal/mol more favorable than from **1**. Thus, it was somewhat perplexing to find that flash vacuum pyrolysis (FVP) of **2**, although producing the expected Me_3SiOMe as the major product, afforded a complex mixture of products, none of which seems (from GCMS analysis) to originate from silene **3**.

Scheme I



Scheme II



One possible explanation for the surprising dichotomy between the thermolyses of **1** and **2** would be that **2** eschews β-elimination in favor of α-elimination[4] to produce $:CH_2$, a process that is not available to **1**. Carbene formation by reductive elimination of Me_3SiOR is a well-established process[7] although to our knowledge the internal competition between α- and β-elimination presented in **2** has never been probed. Thus, the complexity of the pyrolysate from **2** could be explained by initial α-elimination of $:CH_2$ followed by a second α-elimination of $:SiMe_2$ from the resulting disilane **4**. The generation of two highly reactive intermediates from each molecule of **2** would virtually guarantee a complex product

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[3] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[4] This is also known to be the case for the decomposition of $CHF_2CF_2SiCl_3$[5] and $CHF_2CF_2SiMe_3$.[6]

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