

Fluorinated Carbanions

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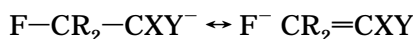
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I. Introduction

Perfluoroalkyl carbanions are well-recognized reactive intermediates in fluorocarbon chemistry.¹ Preparative methods include addition of nucleophiles, especially fluoride ion, to fluorinated olefins, deprotonation of hydrofluorocarbons, fragmentation of carboxylate-functionalized fluorocarbons, and electron-transfer reactions to give perfluoro aliphatic compounds of magnesium and lithium. The latter subject has been reviewed recently.² The lifetimes of these species are highly dependent upon structure, counterion, medium, temperature, and other conditions. Reagents capable of reversible adduct formation stabilize special aromatic and tertiary anions by additional electron delocalization,³ so one must carefully consider the ensemble of components under consideration, not just the "carbanionic fragment". Reactivity and synthetic utility are often defined by similar factors. Tertiary fluorinated carbanions have been isolated, but secondary and primary structures do not exhibit sufficient kinetic stability. This review will emphasize recently reported aspects of tertiary and selected secondary systems.

II. Structure

Fluorine has significant effects upon carbanion stability, and studies of hydrogen/deuterium exchange and pK_a estimates for highly fluorinated substrates have been reviewed.⁴ The electronic effect of fluorine located β to the carbanion center has been interpreted in diverse ways over the years. Initially suggested by J. D. Roberts⁵ in 1950, negative hyperconjugation was viewed in terms of linear combinations of resonance structures. This view was supported by some, but criticized by others⁶ who considered that polarization effects alone were sufficient to account for the calculated energy differences (for example in the fluoride ion + ethylene system):



The early studies in this area sought a unifying structural feature to explain an apparent kinetic



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trend, a difficult proposition steeped with assumptions. Even given irreproachable experimental results and analysis, quantitative assessment of the contribution of a singular structural effect would not be straightforward. A reinvestigation of relative rates of deuterium incorporation for tris(trifluoromethyl)methane, 1*H*-perfluorobicyclo[2.2.2]octane and -[2.2.1]heptane under neutral conditions showed much greater rates for the methane derivative, and reopened the question of involvement of negative hyperconjugation in anionic fluorinated species.⁷ More recently, the gas-phase acidities of the above hydrofluorocarbons were determined by pulsed FT-ICR techniques.⁸ Tris(trifluoromethyl)methane was found to be a much stronger acid (by 7.6 kcal/mol) than 1*H*-perfluorobicyclo-[2.2.1]heptane. This evidence qualitatively favors the concept of anionic hyperconjugation, although the quantitative contribution of this effect to the overall consequence of β fluorination is difficult to assess.

Structural significances of this phenomenon have been similarly a matter of conjecture. *Ab initio* calculations^{9–11} carried out on model systems in the early 1980s suggested that negative anionic hyperconjugation is an important factor in energy stabilization. In $CF_3CH_2^-$, for example, the C–C bond is shortened by 0.10 Å and the antiparallel C–F bond is lengthened by 0.13 Å compared to the neutral, CF_3CH_3 . In addition, an angular dependence of the hyperconjugative interaction was noted, whereby the antiparallel arrangement of carbanion lone pair and C–F bond (180° dihedral angle) is most favorable and leads to higher negative charge on fluorine (Mulliken

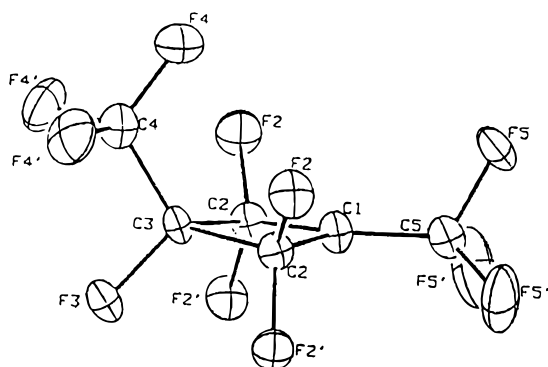


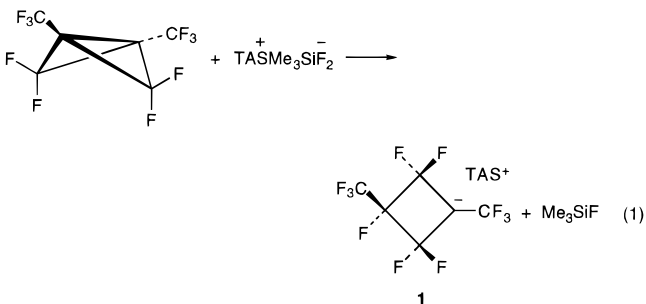
Figure 1. Plot of the structure of the carbanion **1** based on the X-ray coordinates. Note the disordered CF₃ group attached to the carbanion center C₁.

Table 1. Interatomic Distances (Å) for the TAS Salt of **1**

F ₂ –C ₂	1.388(3)
F _{2'} –C ₂	1.405(2)
F ₄ –C ₄	1.327(4)
C ₁ –C ₂	1.428(3)
C ₂ –C ₃	1.538(3)
C ₃ –C ₄	1.513(5)
C ₁ –C ₅	1.442(5)

population analysis). Calculated conformational preferences¹² have been offered to account for product distributions which can arise from carbanion intermediates, for example in reactions of various nucleophiles with tetrafluoroethylene.

More recent advances^{13–16} in *ab initio* molecular orbital theory dealing with fluorinated systems have provided a more convincing basis for judging the significance of negative anionic hyperconjugation in calculated structures. X-ray crystal structure analysis of tris(dimethylamino)sulfonium (TAS) perfluoro-1,3-dimethylcyclobutanide (**1**) (Figure 1, eq 1) gave the first experimental data for a fluorocarbanion, affirmed the importance of hyperconjugation and allowed a benchmark test for the *ab initio* methodology.¹⁷ A model cyclobutanide **2** which retained the



essential features of the experimental compound but reduced the number of fluorines to a manageable number (basis set of double- ζ quality on all atoms; carbon basis set augmented by a set of d functions) was selected by replacing the 3-CF₃ group with a fluorine atom. Excellent agreement was found for all of the calculated and experimental structural parameters which define the carbon framework, C–F distances, and dihedral angles. Comparisons are illustrated in Tables 1–3. The most important features include a *planar* carbanion center (bond angles at C₁ = 359.9°), shortened C₁–C₂ bond length, elongated C₂–F distances, small F–C–F angle at C₂, and a nearly planar cyclobutane ring. Minor differences in C–F distances at C₄ appear in the expected

Table 2. Selected Intramolecular Angles (Deg) for the TAS Salt of **1**

F ₂ –C ₂ –F _{2'}	100.9(2)
F ₂ –C ₂ –C ₁	120.3(2)
F ₂ –C ₂ –C ₃	116.2(2)
F ₃ –C ₃ –C ₂	114.7(2)
F ₃ –C ₃ –C ₄	105.7(3)
C ₂ –C ₁ –C ₂	94.9(3)
C ₂ –C ₁ –C ₅	132.3(1)
C ₁ –C ₂ –C ₃	88.9(2)
C ₂ –C ₃ –C ₄	117.6(2)

Table 3. Selected Geometry Parameters for **2a**

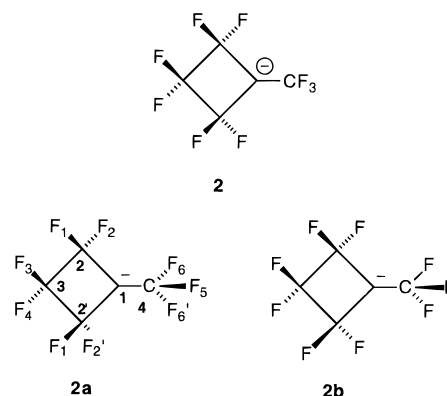
bond	value, Å	angle	value, deg
C ₁ –C ₂	1.444	C ₂ C ₁ C _{2'}	95.9
C ₁ –C ₄	1.456	C ₁ C ₂ C ₃	87.8
C ₂ –C ₃	1.536	C ₁ C ₂ F ₁	120.3
C ₂ –F ₂	1.370	C ₂ C ₁ C ₄	132.0
C ₃ –F ₃	1.341	C ₁ C ₂ F ₂	120.0
C ₄ –F ₆	1.343	F ₁ C ₂ F ₂	101.9
		C ₂ C ₃ F ₃	115.4
		F ₃ C ₃ F ₄	106.4
		F ₆ C ₄ F _{6'}	106.6 (103.1)

Table 4. Electronic Properties for **2a**

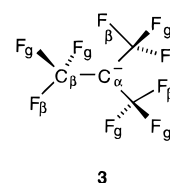
atom	<i>q</i> for 2a , e	atom	<i>q</i> for 2a , e
C ₁	–0.36	F ₂	–0.28
C ₂	0.38	F ₃	–0.24
C ₃	0.36	F ₅	–0.26
F ₁	–0.29	F ₆	–0.24

direction: aligned C₄–F₅ is 0.014 Å longer than C₄–F₆. Bond length differences indicate that these fluorines are less effective in hyperconjugation than are those at C₂.

Conformational energy difference between **2a** and **2b** is only 0.1 kcal/mol, and the rotational energy barrier is very low. Rotational disorder about the C–CF₃ bond in the X-ray structure prevents direct comparisons with the calculated results for this bond. (See also Section IV.)



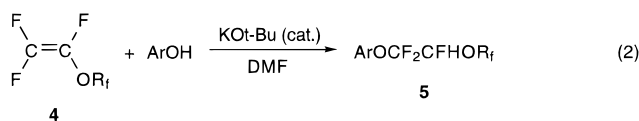
The orientation of the CF₃ group in **2b** is similar to those in perfluoro-*tert*-butyl carbanion (**3**). The Mulliken atomic charges (Table 4) indicate that much of the negative charge is delocalized to fluorines. The fluorine charges are greater in the carbanion than those in the corresponding neutral fluorocarbon.



III. New Reactions of Fluorinated Carbanions

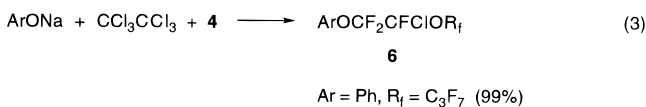
The susceptibility of fluorinated olefins to attack by anions and other nucleophiles has long been recognized.¹⁸ The generation of fluorocarbanions has been a mechanistic focus for understanding several reactions of fluoroolefins, including additions, substitutions, and rearrangements. This thematic material has seen extensive elaboration and has become a significant part of the library of reactions in fluorocarbon chemistry.^{4,19}

Fluorinated vinyl ethers exhibit some of the same susceptibilities to nucleophilic attack as do fluoroolefins without heteroatom substitution, but this class has not received as much attention. A recent report describes the base-catalyzed addition of phenols to perfluoroalkyl vinyl ethers (CF₂=CFOR_f, **4**) affording saturated ethers ArOCF₂CFHOR_f (**5**) in good to excellent yield (eq 2).²⁰ The carbanionic

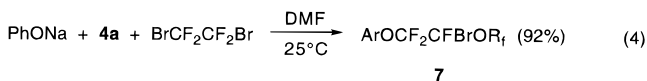


- 5a** Ar = Ph, R_f = C₃F₇ (86%)
5b Ar = Ph, R_f = CF₂CF(CF₃)OCF₂CF₂CO₂CH₂ (72%)
5c Ar = 3-NO₂Ph, R_f = C₃F₇ (96%)

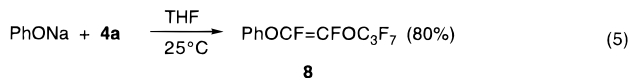
intermediates can be intercepted by reaction with hexachloroethane to provide the corresponding chloro derivatives, ArOCF₂CFClOR_f (**6**) (eq 3), or with 1,2-



dibromotetrafluoroethane to give the bromo derivative (eq 4). In the absence of suitable electrophile,

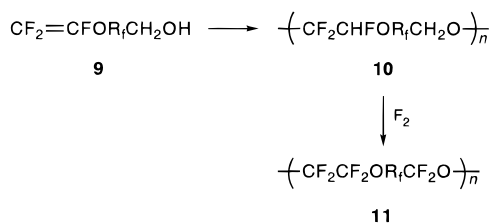


loss of fluoride ion to give unsaturated ether **8** is the preferred pathway (eq 5).



A similar base-catalyzed process is effective for the addition of partially fluorinated alcohols to perfluoroalkyl vinyl ethers.²¹ In the event that the functional groups constitute an AB monomer (**9**), polycondensation results and is the basis for a new route to polyfluorinated polyethers **10** and **11** (Scheme 1). Addition of controlled amounts of functionalized alcohols during the condensation reaction results in

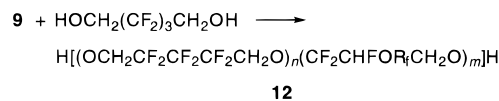
Scheme 1



R_f = perfluoroalkylene or perfluoroalkyleneoxy

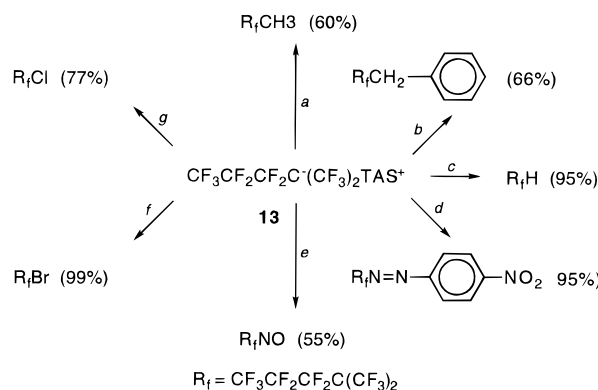
the formation of functionalized oligomeric alcohols; e.g., diols such as **12** which are useful for subsequent polymerization reactions (Scheme 2).²²

Scheme 2



Reactions of tertiary perfluorocarbanions with various electrophiles have been described using either preformed carbanion salts;^{23,24} e.g., **13**, or *in situ* generated (olefin and metal fluoride) reactive intermediates (Scheme 3).²⁵ These carbanions are

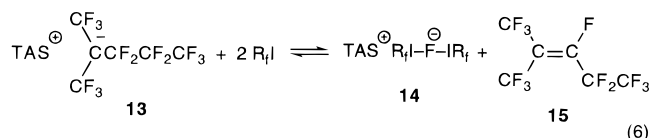
Scheme 3



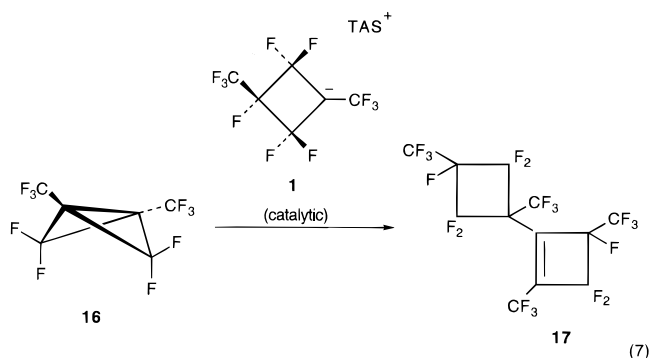
- ^a CH₃OSO₂F, C₆H₅CN, 0°C. ^b C₆H₅CH₂Br, CH₃CN, 25°C.
^c CF₃CO₂H, tetraglyme, -30°C. ^d 4-NO₂C₆H₄N₂+PF₅, 0-25°C.
^e NOF, C₆H₅CN, 0°C. ^f Br₂, C₆H₅CN, 0°C. ^g Cl₂, C₆H₅CN, 0°C.

rather weak nucleophiles, so alkylation is favored with more active alkylating agents. With the series of alkali metal fluorides and HFP dimer, cesium fluoride usually affords higher product yields. Although the cesium carbanion may have higher reactivity than the potassium salt, lower metal fluoride lattice energy and higher equilibrium constant for the formation of carbanion are contributing factors which tend to operate in the same direction. Alternate reaction pathways are available for the carbanions, and these are usually protonation at the tertiary carbon center and a fluoride-transfer process which gives, in the case of an alkylating agent, alkyl fluoride, olefin, and metal halide. Isolable carbanions have been reported only as cesium or tris(dialkylamino)sulfonium²⁶ salts which offer the best balance of properties of those investigated to date. Other cations could be utilized, provided they do not exhibit high fluoride affinities (or lattice energies) or untoward acidic sites.

Fluoride transfer from tertiary carbanions to other acceptors is a frequently encountered reaction, but this can lead to unexpected and unusual structures. Treatment of a perfluoroalkyl or perfluoroaryl iodide with TAS carbanion (**13**) leads to formation of fluoride-bridged adduct structures **14**²⁷ upon removal of the coproduct fluoroolefin **15** (eq 6).

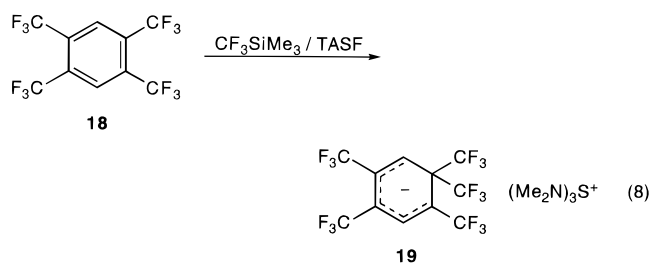


The role of fluoride ion and fluoride-transfer processes in connection with fluorocarbanions has been described in previous articles.^{4,24} Frequently, multiple reaction pathways can be accessed. For example, treatment of perfluoro-1,3-dimethylbicyclo-[1.1.0]butane (**16**) with an equimolar quantity of TAS trimethyldifluorosilicate leads to 1,3-bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide (**1**) quantitatively (eq 7). However, the cyclobutanide **1** also



serves as catalyst which converts the bicyclobutane to a neutral dimeric structure **17**. Addition of 2 molar equiv of TAS trimethyldifluorosilicate to the dimer **17** also gives only cyclobutanide. Although the rates of individual steps are unknown, all appear to be extremely rapid and are complete on the time scale needed for mixing at $-25\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$.

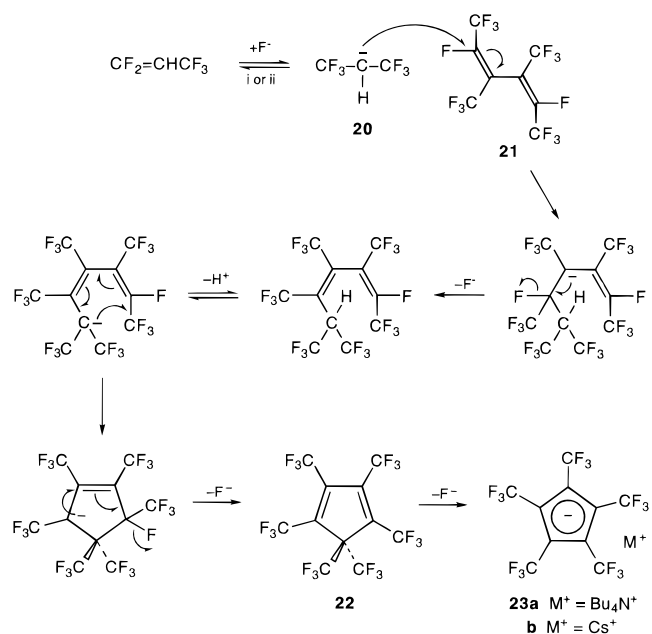
Anionic trifluoromethylation (see also Section V) of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**18**) with $\text{CF}_3\text{SiMe}_3/\text{TASMe}_3\text{SiF}_2$ gives the substituted TAS 2,5-cyclohexadienide (**19**, eq 8).²⁸ Unlike most other



systems discussed here, the carbon framework is not perfluorinated, but does contain CF_3 substituents for significant electron-withdrawing stabilization. Once again, the TAS cation appears to lend kinetic stability to the system.

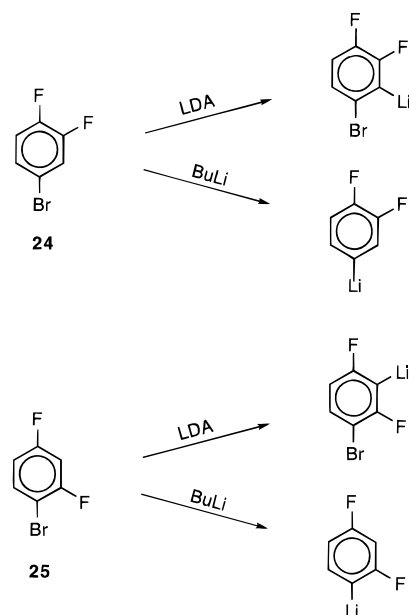
A recent and remarkable synthesis of pentakis(trifluoromethyl)cyclopentadienide anion **23** illustrates some recurring themes in fluorocarbanion chemistry. The overall scheme (Scheme 4) features reaction of *in situ* generated hexafluoropropanide **20** with the tetrasubstituted butadiene derivative **21**. In subsequent steps, fluoride apparently deprotonates the neutral adduct **22** to form another carbanion which cyclizes and suffers fluoride loss. Details of the dealkylation reaction to give cyclopentadienide **23** are unclear. Even more surprising is the single-pot reaction of hexachlorobutadiene with potassium fluoride to give pentakis(trifluoromethyl)cyclopentadienide anion **23**. This appears to result from dimerization of intermediate 2*H*-heptafluorobut-2-ene followed by a C_2F_5 loss.²⁹

Scheme 4^a



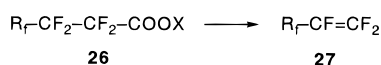
^a Reagents and conditions: i, CsF, MeCN, stirring, room temperature; ii, CsF, MeCN, autoclave, $100\text{ }^{\circ}\text{C}$.

Scheme 5

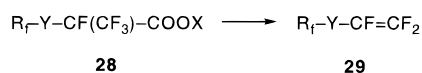
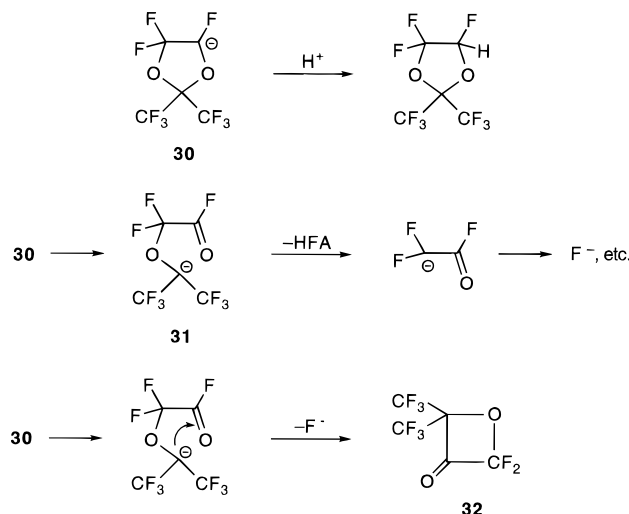


A variety of di-, tri-, and tetrafluorinated benzenes (e.g., **24** and **25**) were studied with respect to their deprotonation and bromine/lithium exchange reactions. Reaction pathways were found to depend upon the base (lithium diisopropylamide (LDA) or butyllithium) and solvent combination employed. In general, LDA use led to deprotonation at the most acidic site; butyllithium in ether-hexane afforded clean bromine-lithium exchange.³⁰ Two examples are illustrated in Scheme 5.

Decarboxylation of perfluoroalkylcarboxylic acid salts (**26**) to provide fluoroolefins (**27**) (Scheme 6) has long been known and is used commercially for production of fluorinated vinyl ethers (**28** \rightarrow **29**).³¹⁻³³ In the most useful cases, the carbanionic intermediate (produced by C-CO₂ cleavage) undergoes further bond cleavage of a leaving group in the β position (usually fluorine) to give the unsaturated product.

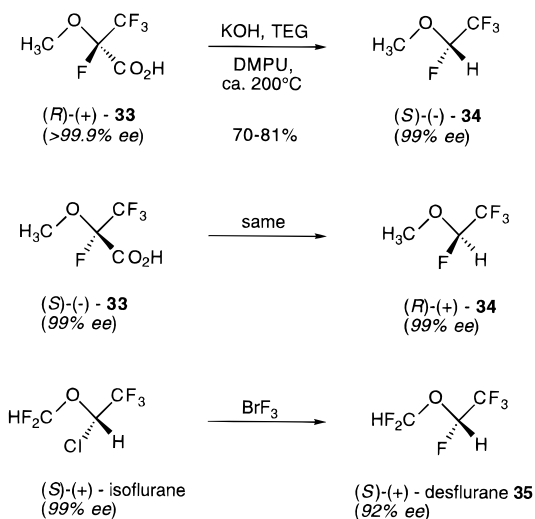
Scheme 6

(X = H, Alkali Metals)

(Y = O, N-R_f)**Scheme 7**

Structural modifications and medium effects can have a significant influence upon the course of this process.³⁴ Alternate bond cleavage pathways or protonation events undergone by the carbanion intermediate are the schemes most often invoked to account for the observed products. Substitution of a hydrocarbon group for the perfluorocarbon fragment of R_fOCF(CF₃) negatively impacts the synthetic utility of this approach. Other fragmentation/recombination processes; e.g., **30** → **31** → **32**, are understandable after the fact, but are often not anticipated (Scheme 7).³⁵

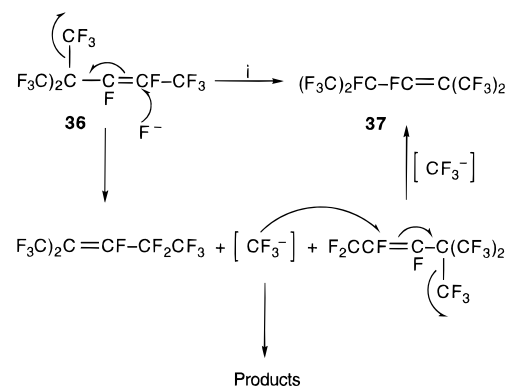
Just as medium effects can change the course of the reaction, certain species such as crown ethers, linear polyethers, sulfones, and pyrimidones can greatly facilitate the decarboxylation process.³⁶ Interionic interaction energy contributes to carboxylate

Scheme 8

stability, so it is reasonable to suggest that adjuvants which coordinate to the metal cation may lower the overall barrier to decarboxylation. The stereochemical integrity of the carbanion center has been examined in a few cases.³⁶ The enantiomeric excess of the hydrofluorocarbon **34**, obtained by decarboxylation of **33** under conditions accessible with the above adjuvants, can be very high (Scheme 8). The stereochemical course of the reaction, reported as inversion (based upon chemical correlation with an inhalation anesthetic desflurane (**35**) of previously assigned configuration), seems remarkable but unlikely and casts doubt on the vibrational circular dichroism configuration assignment for **35**.

IV. Rearrangements and Dynamic Properties

A variety of rearrangement processes have been noted in fluorocarbanions. Details of some of these examples, especially those involving a combination of fragmentation and recombination are somewhat uncertain. For example, the intermolecular transfer of trifluoromethyl anion recently reported for the branched 1-*tert*-butyl-2-methylperfluoroethylene (Scheme 9) may indeed involve this reactive inter-

Scheme 9^a

^a Reagents and conditions: i, CsF, sulfolane, 150–160 °C, 5 h.

mediate, or could proceed via combined difluorocarbene and fluoride ion mediated steps. Alternatively, formation of HFP and *tert*-butyl carbanion, followed by a high-temperature condensation to the trisubstituted olefin might be viable. Whether *tert*-butyl carbanion is a CF₃ source at 150–160 °C is unknown. Still another route would invoke a series of 1,2 shifts, some steps involving migration of F, others of CF₃. Of course, this would not account for the intermolecular trapping experiments reported. Although not commonly recognized, shifts of tertiary fluorine to an adjacent carbanion center take place very readily (see below). The possibility of intramolecular carbon shifts seems unlikely, but has not been tested.³⁷

[3,3]-Sigmatropic rearrangements in partially fluorinated systems have received study over an extended period.³⁸ This area has been reviewed and updated recently, with the main focus on rearrangements of carbanionic species of the form **38**.³⁹ These “anion-assisted” Claisen processes are frequently rapid and proceed in high chemoselectivity (Scheme 10).

Site equilibration by fluorine exchange has been noted previously,⁴ but these events are actually more

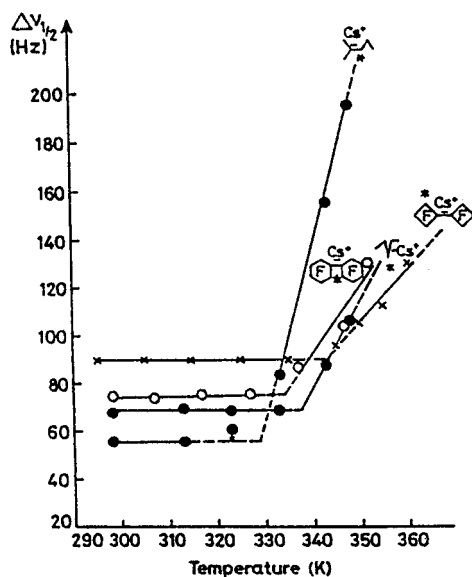
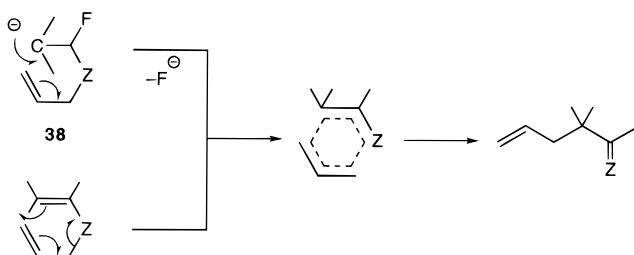


Figure 2. Variable-temperature line widths of Cs^+ carbanion solutions.

Scheme 10

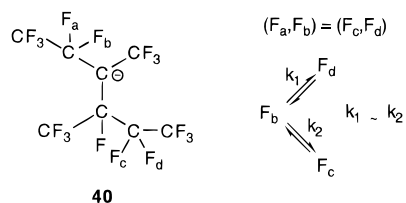


Z = O, NH, S

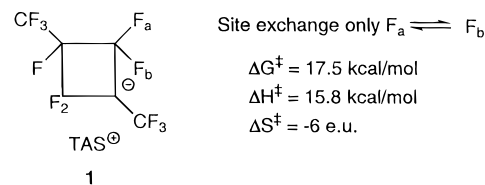
complicated than might have been anticipated, and full accounts have not been described yet. Preliminary spectroscopic results for a series of carbanions have been described. From variable-temperature experiments, the onset of line broadening was used to rank the relative propensity for fluoride exchange processes (Figure 2).²⁴ In a comparison of (Cs vs $(\text{Me}_2\text{N})_3\text{S} = \text{TAS}$) cation effects, it appeared that by comparison with Cs, TAS facilitated intermolecular exchange of β fluorines with excess olefin. On the other hand, line broadening of the β fluorine signals apparently takes place more readily in the case of Cs counterion. Tetrasubstituted olefins generally do not form carbanions with CsF , but do react with TAS Me_3SiF_2 whereupon trimethylfluorosilane is liberated. These apparently diverse results might lead to a confused picture of carbanion stability. However, one must take into account energies of all the species

involved in order to draw conclusions about the thermodynamic stability of one member.

We have studied several structures which feature a tertiary fluorine adjacent to the carbanion center.⁴⁰ These compounds (**39** and **40**) contain multiple NMR probes (for example, at least two different sets of diastereotopic CF_2 groups) which serve to define some details of the exchange process. In each case, the lowest energy dynamic process involved migration of the tertiary fluorine from the α carbon to the carbanionic center; i.e., a degenerate exchange event. Rates appeared to be concentration independent, so this exchange appeared to be unimolecular. Using a selective inversion/recovery technique, it was found for the cyclic case that exclusive, pairwise exchange of fluorines within diastereotopic CF_2 groups takes place. Thus in the 1,2-dimethylcyclobutanide **39**, F_a and F_c are exchange partners, as are F_b and F_d (Figure 3). Rates of CF_3 site exchange are identical with F_a , F_c and F_b , F_d exchange. The migrating fluorine remains on the same face of the cyclic carbon skeleton. Fluoride dissociation to give "free" olefin and $(\text{Me}_2\text{N})_3\text{SF}$, separated by sufficient numbers of solvent molecules, should result in a nonselective exchange pattern. We suggest that the counterion may play a role in this exchange process, assisting the migration by partial bonding to the tertiary fluorine. In the acyclic example **40**, such selectivity was not observed. Either multiple exchange path-



ways are operative, or several conformations are populated and result in different identities of exchange partners. Curiously, the energy barriers for these migrations are similar in magnitude to that for F_a - F_b exchange in perfluoro-1,3-dimethylcyclobutanide (**1**). In this case, the only observable



exchange is that for nuclei F_a and F_b . This exchange would seem to require somewhat more molecular

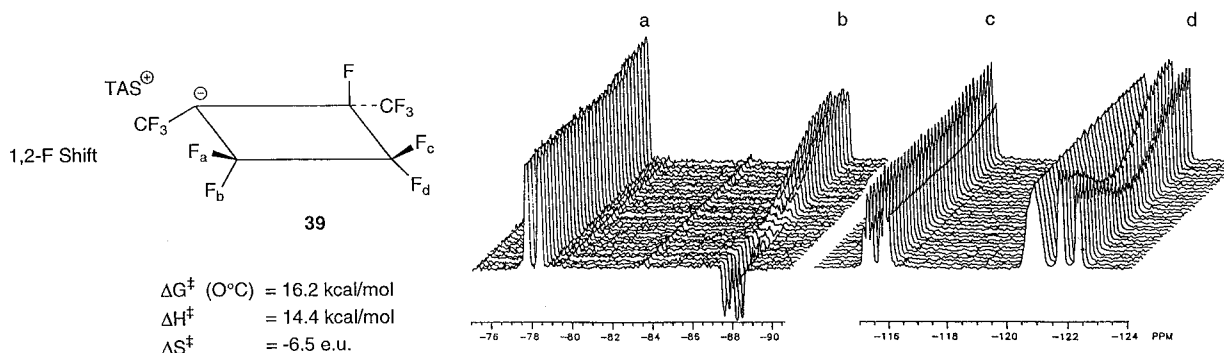


Figure 3. ^{19}F NMR selective inversion-recovery stack plot.

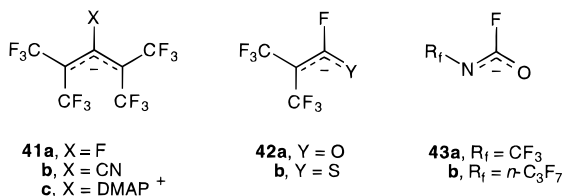
Table 5. Dynamic Properties of Fluorinated Allyl and Heteroallyl Anions

structure	G^* (T , °C)
41a	11.6 (−10)
41b	14.0 (48)
41c	17.5 (130)
42a	> 19 (75)

reorganization than that for a “suprafacial” migration. Since the CF_3 groups do not undergo exchange, sequential 1,2 shifts do not appear to operate in this case.

Calculation results indicate the rotational barriers involving the carbanion center are generally low.¹⁷ To test this prediction, we have examined temperature-dependent ^{19}F NMR spectra of TAS 1,3-bis(trifluoromethyl)-2,2,3,4,4-pentafluorocyclobutanide (**1**). The CF_3 signal at -50 ppm was found to be temperature invariant (to -100 °C), in agreement with expectation, although this is negative evidence. The other CF_3 signal, however, exhibited coalescence at ca. -80 °C, and displayed two signals in a 2/1 ratio at -100 °C. Clearly, the most favored conformation for this CF_3 group is staggered, with the $\text{F}_4\text{-C}_4\text{-C}_3\text{-F}_3$ (Figure 1) dihedral angle ca. 180° .⁴⁰

More highly substituted systems can exhibit substantially higher rotational barriers. 1,1,3,3-Tetrakis(trifluoromethyl)allyl anions **41**, obtained from the corresponding allene by nucleophilic addition at the central carbon, are twisted, propeller-shaped molecules with diastereotopic CF_3 groups. These groups undergo site exchange which signals an enantiomerization process. The measured barriers (Table 5) depend somewhat upon substitution at C_2 . X-ray crystal structure of the (dimethylamino)pyridine adduct **41c** demonstrates the general structure in this series (Figure 4). Since the four-bond F–F coupling (18.5 Hz) is maintained in the 2-F derivative **41a**, CF_3 group exchange ($1.2 \times 10^3 \text{ s}^{-1}$ at -10 °C) by C–F dissociation was ruled out. Barriers for related heteroatom systems could not be determined: exchange was too slow for the ketene adduct **42**, and C–F dissociation occurred too readily for the amidates **43**.⁴¹



V. Carbanion Equivalents

New methods for C–C bond formation using perfluorocarbanion functional equivalents have been reported. Ample literature describes nucleophilic perfluoroalkylation using organometallic reagents of lithium, magnesium, zinc, etc., but these reagents do not have attractive profiles of reactivity, selectivity, stability, and convenience, and do not generally apply to the special CF_3 case. Upon the basis of known chemistry of activated organosilanes, new processes have been developed for (trifluoromethyl)trimethylsilane (**45**) and other perfluoroalkylsilanes. These include catalyzed addition reactions with aldehyde

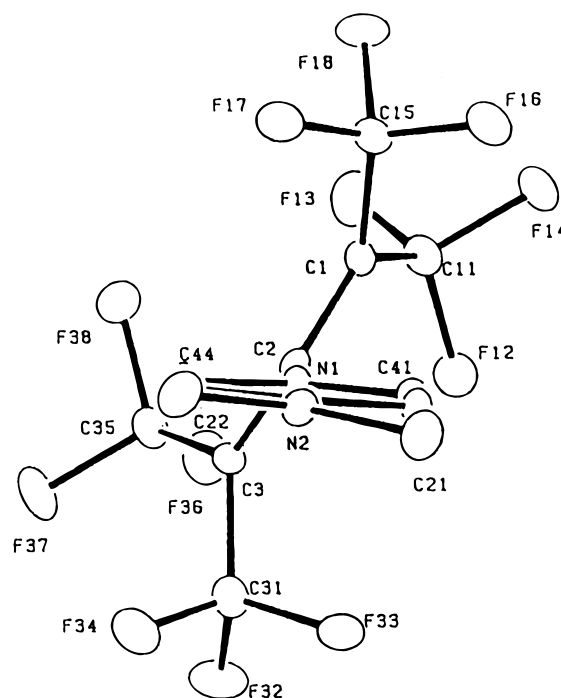
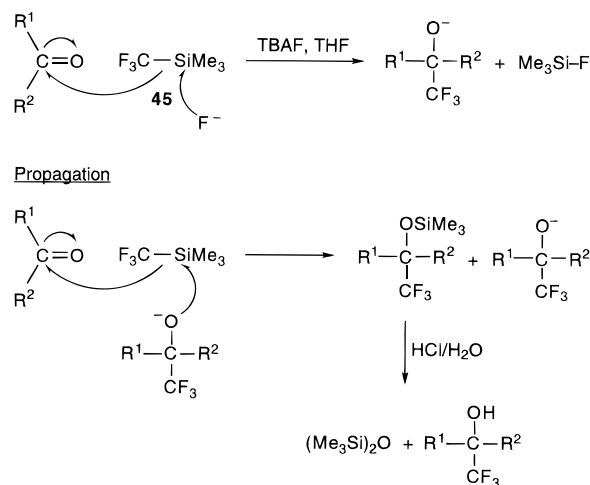


Figure 4. X-ray crystal structure of zwitterion **41c** viewed from the end of the pyridine ring along a pseudo C_2 axis (atoms are shown at the 25% probability level; hydrogen atoms removed for clarity). Featured dihedral angles (deg) between indicated planes, bond angles (deg): $\text{C}_{31}\text{-C}_3\text{-C}_{35}/\text{C}_1\text{-C}_2\text{-C}_3 = 36.5$; $\angle \text{C}_{11}\text{-C}_1\text{-C}_{15} = 114.6$ (3); $\angle \text{C}_{15}\text{-C}_1\text{-C}_2 = 123.2$ (4); $\angle \text{C}_{11}\text{-C}_1\text{-C}_2 = 122.4$ (4).

and ketone carbonyl substrates of considerable diversity (cyclic, linear, branched, aliphatic, aromatic, etc.).^{42–44} Exceptions to the generally good product yields were encountered with highly hindered substrates. General outlines of the reaction pathway have been offered, but many of the details remain uncertain (Scheme 11). “Free” carbanions are not

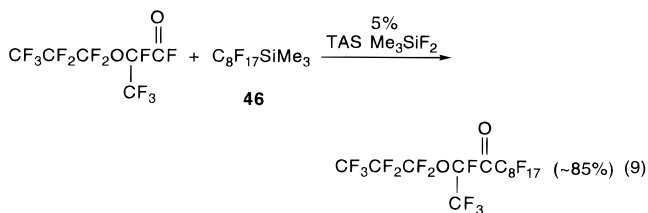
Scheme 11



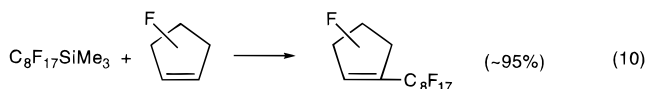
believed to intervene. Protodesilylation appears to be the most significant side reaction in the case of the (trifluoromethyl)trimethylsilane. Other reactive carbonyl substrates include α -keto esters, trifluoroacetates, lactones, and cyclic anhydrides. Other trifluoromethyl group acceptors reported include $\text{C}_6\text{F}_5\text{NO}_2$, arylsulfonyl fluoride,⁴⁵ and SO_2 .

Longer chain perfluoroalkylsilanes, e.g. **46**, conveniently prepared from the corresponding bromides,

are useful reagents for a general perfluoro ketone synthesis which employs an acid fluoride as electrophile (eq 9). Yields are generally good, and conversion of these ketones to tertiary (long chain) alcohol derivatives tends to be slow, in part due to rather low solubility of the long-chain ketones.⁴⁶



Fluorinated alkenes also undergo nucleophilic perfluoroalkylation, and cyclic examples are especially well behaved (eq 10). Terminal alkenes afford the



desired adducts, but chemo- and regioselectivities are lower in these cases due to isomerization and rearrangement pathways presumed to involve carbanion intermediates. The major identified side reaction is a catalyzed condensation of the perfluoroalkyl fragments of the silane to yield a mixture of isomeric perfluoroalkenes. This can be a serious side reaction especially with reactions of poor electrophiles.⁴⁶ Fluorinated aromatic substrates such as perfluorotoluene, perfluorobenzonitrile, and pentafluoropyridine can be fluoroalkylated, but selectivities are difficult to control and some multiple substitution takes place, resulting in modest yields of mono-adducts in the 30–50% range.

VI. Summary

Perfluoroalkyl carbanions are important intermediates in fluorocarbon chemistry and provide a useful framework for understanding nucleophilic additions to fluorinated alkenes, carboxylate fragmentation reactions, and deprotonation pathways. Recent theoretical and experimental advances have provided insight regarding structural features of isolable carbanions and additional confidence in computational results for fluorinated systems not amenable to experimental study. The structural impacts of anionic hyperconjugation are realized. New reactions which proceed by familiar carbanionic pathways continue to receive attention, and perfluorocarbanion equivalents, in the form of activated perfluoroalkyl-trimethylsilanes, offer new synthetic opportunities.

VII. References

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