# Synthesis and Solvolysis of 7-(Perfluoroalkyl)-7-bicyclo[2.2.1]heptyl Derivatives†

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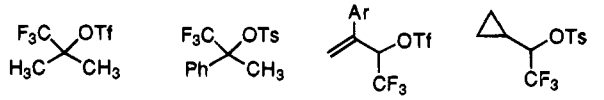
Several α-(trifluoromethyl)- and α-(pentafluoroethyl)carbinols were synthesized by the addition of perfluoroalkylating agents ($TMSCF_3$, $TMSC_2F_5$, and/or $C_2F_5Li$) to polycyclic ketones. An improved procedure for the preparation of α-(perfluoroalkyl)trimethylsilyl ethers from (perfluoroalkyl)-trimethylsilanes and ketones was developed to facilitate the synthesis of the compounds of interest. All of the alcohols featured the bicyclo[2.2.1]heptyl skeleton or some analog of this structure containing double bonds or cyclopropyl groups. Sulfonate esters of the carbinols were prepared, and these sulfonates were solvolyzed in different solvents to examine the competition between destabilization of the carbocationic intermediates by perfluoroalkyl groups and stabilization by neighboring-group participation. The extent of the destabilization of the cations was gauged by the difference in rates of solvolysis of the α-hydrogen and α-(perfluoroalkyl) derivatives. The $k_{\alpha\text{-H}}/k_{\alpha\text{-R}_F}$ ratios ranged from 8 to ~$10^4$, and the extent of anchimeric assistance that occurred in each system influenced the difference in rates. The pentafluoroethyl group exerted a slightly smaller rate-retarding effect when compared to the trifluoromethyl group ($k_{\alpha\text{-C}_2\text{F}_5}/k_{\alpha\text{-CF}_3}$ = 1.1–8.0). The products of the solvolysis reactions revealed a general trend of destabilization of both localized and delocalized cations by perfluoroalkyl groups.

## Introduction

The generation of destabilized carbocations possessing electron-withdrawing groups bound to the carbon bearing the positive charge has been studied extensively.[1] α-(Perfluoroalkyl) cations comprise a particularly interesting class of intermediates because perfluorinated alkyl groups are strong, inductively electron-withdrawing functionalities that have limited mesomeric interactions and are relatively inert toward chemical transformation. Numerous studies on the solvolysis of trifluoromethyl-substituted derivatives have appeared, and the influence of the $CF_3$ group on the rate of solvolysis and the distribution of products has been investigated. When compared to their α-hydrogen analogs, the α-$CF_3$ compounds generally solvolyze more slowly. However, the degree of rate retardation differs from system to system. The ratio $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3}$ ranges from 2 to $10^6$ and is influenced by sources of anchimeric assistance, steric interactions, and solvent effects.

The simple tertiary triflate **1** solvolyzed more slowly than 2-propyl triflate by a factor of $10^4$ in more nucleophilic solvents and by a factor of $10^6$ in strongly ionizing solvents.[2] Salt effects, isotope effects, and the formation of only the elimination product indicate an intermediate that resembles a tight-ion pair rather than a discreet carbocation. A ratio of $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3} = 10^5$ was determined for the α-$CF_3$ benzylic tosylate **2** in ethanol,[3] and several studies provide evidence for stabilization of this type of




**1** **2** **3** **4**

cation by aromatic π-electons.[4] The competition between allylic stabilization and perfluoroalkyl destabilization was investigated by solvolyzing allylic triflates such as **3**, but the observed values of $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3}$ (up to $10^6$) were considered to be inflated due a mechanism involving nucleophilic solvent participation.[5] For the cyclopropylcarbinyl tosylate **4**, the rate of solvolysis was retarded by a factor of $10^4$ in 80% ethanol, and a delocalized intermediate has been proposed.[6] These examples show the strong destabilizing influence of the trifluoromethyl group, even in systems where other functional groups can stabilize the cationic intermediates.

In certain substrates, however, the difference between the rates of solvolysis of the α-H and α-$CF_3$ compounds is relatively small. The pyrrole derivative **5** solvolyzed only 40 times more slowly than its hydrogen analog,[7] and the rate of solvolysis of tertiary adamantyl tosylate **6** is within 1 order of magnitude of the rate of 2-adamantyl tosylate.[8] The remarkable reactivity of **6** has been attributed to ground-state destabilization[9] which causes a rapid rearrangement via a tight-ion pair to a secondary, β-$CF_3$ protoadamantyl tosylate.[8]

The influence of the pentafluoroethyl group on carbocation stability has also been investigated, but to a lesser extent. The *exo* brosylate **7** and the *endo* brosylate

† In memory of the many contributions made by the late Professor Gassman to the field of carbocation chemistry.

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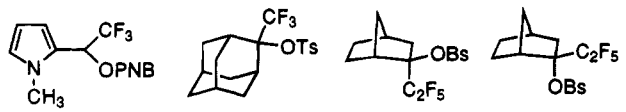


5 6 7 8

**8** solvolyzed $10^2-10^3$ times more slowly than the corresponding α-H norbornyl compounds.[10] This moderate rate retardation is consistent with that expected for the pentafluoroethyl group based on a simple analysis of the Hammett substituent parameters.[11] Interpretation of the data is complicated by the controversy surrounding the nature of the "nonclassical" intermediate.[12] As part of the work involving **7** and **8**, the α-$C_2F_5$ analog of benzylic tosylate **2** was solvolyzed in a variety of solvents, and an average ratio of $k_{\alpha\text{-}C_2F_5}/k_{\alpha\text{-}CF_3} = 3.4$ was determined.

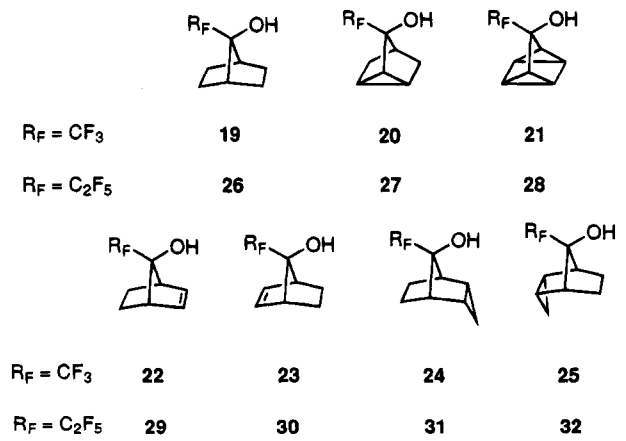
The study described here involves the synthesis and solvolysis of a series of 7-(perfluoromethyl)- and 7-(perfluoroethyl)-7-bicyclo[2.2.1]heptyl derivatives. The kinetic data from the solvolyses of these compounds provide insight into the capacity of closely related systems to respond to the destabilizing influences of perfluoroalkyl groups in different types of carbocationic intermediates. The solvolysis substrates include compounds which contain double bonds or cyclopropyl groups in different orientations with respect to the incipient cation and which solvolyze with different degrees of neighboring-group participation. In addition to the kinetic data, the products of selected solvolytic reactions are reported, and the nature of the intermediates in each of the systems is discussed.

## Results

**Synthesis of α-(Perfluoroalkyl) Alcohols.** The carbinols that served as precursors to the solvolysis substrates, compounds **19**–**32** shown below, were synthesized by the addition of perfluoroalkylating reagents to the appropriate polycyclic ketones. The trifluoromethyl compounds were prepared by the addition of (trifluoromethyl)trimethylsilane ($TMSCF_3$) to ketones to afford α-$CF_3$ silyl ethers.[13] The isolated yields of the protected alcohols were generally very high (Table 1). The initiation of the reaction proved difficult, however, and several anionic initiators were tested before a simple, efficient, and reproducible procedure was developed. Tetra-*n*-butylammonium fluoride (TBAF), the most commonly used initiator,[14] was found to be unsatisfactory because limited conversion of the starting material occurred. The addition of more TBAF resulted in deprotection of the silyl ethers and the formation of byproducts that were difficult to remove while failing to achieve complete conversion of the ketone. Other initiators, such as $K_2CO_3$, CsF, and KF, were investigated,[15] but the reactions often failed to initiate even in the presence of complexing agents such as crown ethers. The use of 20 mol % of anhydrous potassium fluoride and a few drops of a saturated solution of potassium *tert*-butoxide in THF initiated vigorous, exothermic reactions that produced *only* the silyl ethers and were complete in 5–10 min. The silyl ethers could be deprotected *in situ* by the addition of 1 N HCl, but the alcohols obtained from this one-pot procedure were difficult to purify. The silyl ethers were easily purified in high yield (>90%) by flash chromatography. Deprotection of the purified α-$CF_3$ silyl ethers in 1:1 1 N HCl/THF afforded the alcohols in good yield without the complication of contaminants (Table 1). In cases where only a single alcohol was formed, the product was isolated by flash chromatography. Regioisomeric carbinols (**22/23** and **24/25**) were separated easily by MPLC because of the complexation of the hydroxyl hydrogen with the double bond in **22** or the strained σ-bond in **24**.[16]

The majority of the (pentafluoroethy)carbinols were prepared by the addition of (pentafluoroethyl)lithium to the appropriate ketones (Table 2).[17] This method was very efficient for the preparation of many of the desired compounds, but the facial selectivity of the additions resulted in the formation of predominantly a single regioisomer in cases where epimeric products were possible. Another route to the remaining α-$C_2F_5$ carbinols (**30** and **32**) was required, so (pentafluoroethyl)trimethylsilane ($TMSC_2F_5$) was added to ketones **12** and **13** (Table 3).[18] The selectivity of these additions paralleled closely that observed in the additions of $TMSCF_3$ to the same ketones. As shown in Table 3, the $TMSC_2F_5$ additions provided a slightly better route to minor isomers **30** and **32**, but separation of the isomers was still required. The preparation and purification/separation of the pentafluoroethyl alcohols was accomplished by the same procedures used for the trifluoromethyl alcohols.

The final α-(perfluoroalkyl)carbinols required for this study were synthesized by valence isomerization of tetracyclic alcohols **21** and **28**. The isomerization, which can be accomplished by a wide variety of transition metal complexes,[19] was effected by the use of catalytic amounts of palladium(II) complexes (Scheme 1). Dienyl alcohols **35** and **36**, in addition to being precursors to interesting



| | | | | |
|---|---|---|---|---|
| $R_F = CF_3$ | **19** | **20** | **21** | |
| $R_F = C_2F_5$ | **26** | **27** | **28** | |
| $R_F = CF_3$ | **22** | **23** | **24** | **25** |
| $R_F = C_2F_5$ | **29** | **30** | **31** | **32** |

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(11) For example: $\sigma_p(CF_3) = 0.54$, $\sigma_p(C_2F_5) = 0.52$; $\sigma_I(CF_3) = 0.42$, $\sigma_I(C_2F_5) = 0.0.41$. This trend is not general, however, for all of the various σ parameters. Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; John Wiley & Sons: New York, 1979; pp 1–167.

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(19) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

**Table 1. α-$CF_3$ Silyl Ethers Prepared by the Addition of $TMSCF_3$ to Ketones and α-$CF_3$ Alcohols Prepared by Deprotection of the Corresponding Silyl Ethers**

| entry | ketone | silyl ether (isolated yield, %) | alcohol (isolated yield, %) |
|---|---|---|---|
| 1 | bicyclo[2.2.1]heptan-7-one (**9**) | **14** (93–98) | **19** (89–96) |
| 2 | tricyclo[2.2.1.$0^{2,6}$]heptan-7-one (**10**) | **15** (92–96) | **20** (91–96) |
| 3 | tetracyclo[3.2.0.$0^{2,6}$.$0^{4,7}$]heptan-3-one (**11**) | **16** (83–93) | **21** (93–98) |
| 4 | bicyclo[2.2.1]hept-2-en-7-one (**12**) | **17** (91–97)[a] | **22** + **23** (4:1, 90–95) |
| 5 | *endo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (**13**) | **18** (93–98)[a] | **24** + **25** (10:1, 94–97) |

[a] Isolated as inseparable mixtures of the silyl ethers in ratios comparable to the ratios of the deprotected alcohols.

**Table 2. α-$C_2F_5$ Alcohols Prepared by Addition of (Pentafluoroethyl)lithium to Ketones**

| entry | ketone | alcohol (isolated yield, %) |
|---|---|---|
| 1 | **9** | **26** (89–93) |
| 2 | **10** | **27** (89–96) |
| 3 | **11** | **28** (92–98) |
| 4 | **12** | **29** + **30** (50:1, 89–95)[a] |
| 5 | **13** | **31** + **32** (98:1, 96) |

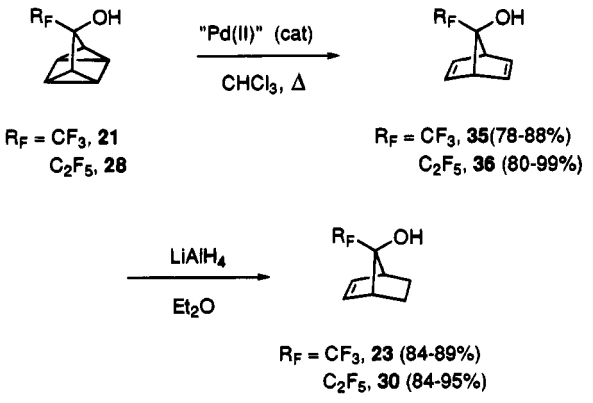
[a] In previous work, only the formation of **29** was reported. Careful GC analysis revealed the presence of the minor isomer. See ref 17.

**Table 3. α-$C_2F_5$ Silyl Ethers Prepared by Addition of $TMSC_2F_5$ to Ketones and α-$C_2F_5$ Alcohols Prepared by Deprotection of the Corresponding Silyl Ethers**

| entry | ketone | silyl ether (isolated yield, %) | alcohol (isolated yield, %) |
|---|---|---|---|
| 1 | **12** | **33** (91–97)[a] | **26** + **30** (4:1, 90–95) |
| 2 | **13** | **34** (93–98)[a] | **31** + **32** (10:1, 89–96) |

[a] Isolated as inseparable mixtures of the silyl ethers in ratios comparable to the ratios of the deprotected alcohols.

**Scheme 1**




solvolysis substrates, were reduced regiospecifically by lithium aluminum hydride to give **23** and **30** (Scheme 1).[20] These selective reductions provided an alternate route to alcohols that had previously been prepared as minor products requiring careful separation.

**Kinetic Data and Product Studies.** The solvolysis reactions were performed with sulfonate esters of the α-(perfluoroalkyl) alcohols. To accommodate the wide range of reactivies of these compounds, sulfonates with different capacities as leaving groups were employed. The trifluoromethanesulfonate esters (triflates) **37** and **38** were prepared by deprotonation of carbinols **19** and **26** with potassium hydride followed by treatment with trifluoromethanesulfonic (triflic) anhydride. The α-$CF_3$ triflate **37** was solvolyzed in five different solvent systems, and the kinetic data are summarized in Table 4. The extrapolated values of the rate constants at 25 °C were used in a modified Grunwald–Winstein analysis to determine if the rates of reaction correlated with the ionizing ability of the solvents. The Grunwald–Winstein equation usually employs two empirically derived constants, N and Y, which represent the influence of solvent nucleophilicity and ionizing power, respectively.[21] However, for the systems described here, the nucleophilicity term is omitted because steric restraints prevent any significant amount of displacement of the leaving groups by an $S_N2$ mechanism. In addition to neglecting the nucleophilicity parameter, the *Y* values used in the correlations presented here were selected to match as closely as possible the structure of the substrate and the particular leaving group. A plot of log $k_{25°C}$ vs the empirical solvent-ionizing parameter $Y_{OTf}$ showed a good linear correlation ($r = >0.99$) despite the limited number of solvents employed (Figure 1).[22] This correlation provides evidence for the dependence of the rate of reaction on the capacity of the solvent systems to solvate the carbocationic intermediate.

The α-$C_2F_5$ triflate **38** was solvolyzed only in anhydrous 2,2,2-trifluoroethanol (TFE), and the kinetic data are given in Table 4. Kinetic data for the solvolysis of


**37** **38**

7-norbornyl triflate in TFE have been reported previously,[23] and the ratios $k_{α\text{-H}}/k_{α\text{-}C_2F_5} = 8$ and $k_{α\text{-H}}/k_{α\text{-}CF_3} = 19$ at 25 °C can be calculated directly. These ratios represent some of the smallest known rate retardations caused by perfluoroalkyl groups in solvolysis reactions. As expected, the pentafluoroethyl triflate **38** was slightly more reactive than its trifluoromethyl analog, and the ratio $k_{α\text{-}C_2F_5}/k_{α\text{-}CF_3} = 2.5$ at 25 °C was calculated.

The preparative solvolyses of **37** and **38** in TFE yielded complex mixtures of products. As shown in Scheme 2, the major product formed from the solvolysis of **37** consisted of a mixture of the rearranged bicyclo[3.2.0]-heptenes **40a** and **40b**. These elimination products were formed in ~60% yield and are proposed to result from a pair of cationic intermediates (**39a** and **39b**). The position of the double bond in **40a** was confirmed by the coupling observed between the fluorine atoms and one of the vinylic resonances ($^3J_{CF} = 3$ Hz) of the major isomer in the $^{13}C$ NMR spectrum of the mixture of **40a** and **40b**. To provide additional evidence for the structures of **40a** and **40b**, the mixture was catalytically hydrogenated. The only product of the hydrogenation was the saturated compound **41**.

Several solvent-trapped products were also formed in the solvolysis of **37**. Due to difficulty in separating these

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**Table 4. Kinetic Data for the Solvolysis of Triflates 37 and 38**

| substrate | solvent | temp range (°C) | $k_{25°C}$ ($s^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|---|
| **37** | TFE[a] | 90.0–120.0[b] | $1.51 \times 10^{-8}$[c] | 24.2 ± 0.1 | −13.2 ± 0.4 |
| | 80% EtOH[d] | 110.0–140.0[b] | $2.22 \times 10^{-9}$[c] | 27.8 ± 0.8 | −4.9 ± 2.1 |
| | 80% $Me_2CO$[e] | 100.0–130.0[b] | $1.28 \times 10^{-9}$[c] | 28.9 ± 0.4 | −2.2 ± 1.0 |
| | EtOH[f] | 120.0–140.0[b] | $9.50 \times 10^{-11}$[c] | 30.1 ± 0.5 | −3.5 ± 0.5 |
| | AcOH[g] | 130.0–160.0[h] | $3.90 \times 10^{-11}$[c] | 32.3 ± 1.1 | +2.3 ± 2.6 |
| **38** | TFE[a] | 90.0–120.0[b] | $1.51 \times 10^{-8}$[c] | 24.2 ± 0.1 | −13.2 ± 0.4 |

[a] TFE = anhydrous 2,2,2-trifluoroethanol (buffered with 2,6-lutidine). [b] Duplicate measurements (±5%) at 10.0 °C intervals in this range were made. [c] The extrapolated rate constant obtained from an Arrhenius plot. [d] 80% EtOH = 80% ethanol/20% water, v:v (buffered with 2,6-lutidine). [e] 80% $Me_2CO$ = 80% acetone/20% water, v:v (buffered with 2,6-lutidine). [f] EtOH = anhydrous ethanol (buffered with 2,6-lutidine). [g] AcOH = anhydrous acetic acid (buffered with NaOAc). [h] Duplicate measurements (±5%) at 15.0 °C intervals were made in this range.

**Table 5. Kinetic Data for the Solvolysis of Triflates 42 and 43**

| substrate | solvent | temp range (°C) | $k_{25°C}$ ($s^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|---|
| **42** | TFE[a] | 70.0–100.0[b] | $1.97 \times 10^{-7}$[c] | 22.8 ± 0.3 | −12.9 ± 0.8 |
| | 80% $Me_2CO$[d] | 100.0–130.0[b] | $3.81 \times 10^{-8}$[c] | 25.4 ± 0.4 | −7.4 ± 1.2 |
| | 80% EtOH[e] | 100.0–130.0[b] | $3.18 \times 10^{-8}$[c] | 26.0 ± 0.8 | −5.7 ± 0.9 |
| | EtOH[f] | 110.0–140.0[b] | $1.75 \times 10^{-9}$[c] | 27.7 ± 0.6 | −5.7 ± 1.5 |
| | AcOH[g] | 115.0–145.0[h] | $1.31 \times 10^{-9}$[c] | 29.2 ± 0.7 | −1.2 ± 1.7 |
| **43** | TFE[a] | 90.0–120.0[b] | $2.09 \times 10^{-7}$[c] | 22.8 ± 0.1 | −12.5 ± 0.8 |

[a] TFE = anhydrous 2,2,2-trifluoroethanol (buffered with 2,6-lutidine). [b] Duplicate measurements (±5%) at 10.0 °C intervals in this range were made. [c] The extrapolated rate constant obtained from an Arrhenius plot. [d] 80% $Me_2CO$ = 80% acetone/20% water, v:v (buffered with 2,6-lutidine). [e] 80% EtOH = 80% ethanol/20% water, v:v (buffered with 2,6-lutidine). [f] EtOH = anhydrous ethanol (buffered with 2,6-lutidine). [g] AcOH = anhydrous acetic acid (buffered with NaOAc). [h] Duplicate measurements (±5%) at 15.0 °C intervals were made in this range.

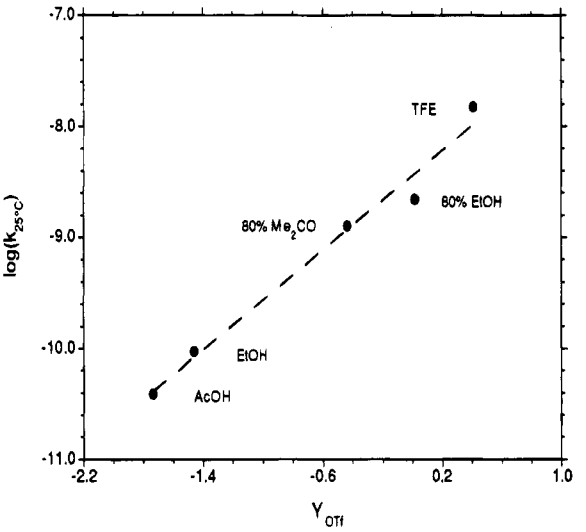
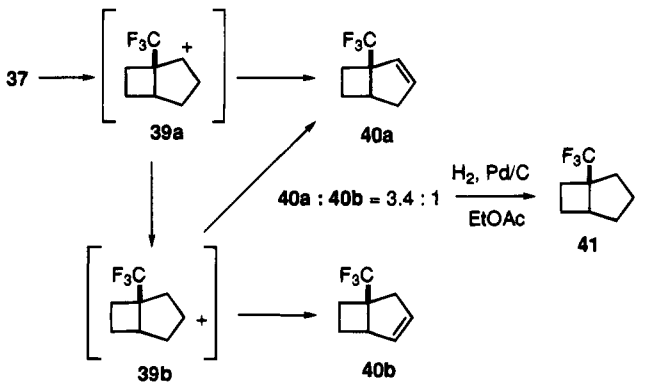



**Figure 1.** Plot of $\log(k_{25°C}$ vs $Y_{OTf})$ for the solvolysis of **37** in different solvents.

other products, they were not fully characterized. However, GC analysis and mass spectral data indicated that four different isomers were formed. The $^1H$ NMR spectra of these products revealed that each isomer lacks the symmetry that would be present if solvent-trapping occurred at C7 of the unrearranged norbornyl skeleton. The four products that comprise the remainder of the mass balance may arise from solvent-trapping of **39a** and **39b**, but this was not shown conclusively. Similar products, in approximately the same ratios, were observed in the preparative solvolysis of **38** in TFE.

For the carbinols **22** and **29**, in which the hydroxyl group is *syn* to the double bond, the triflate esters were found to be suitable derivatives for use as solvolysis substrates. Triflates **42** and **43** were prepared by the method previously described. The α-$CF_3$ triflate **42** was solvolyzed in the same five solvent systems used for the saturated triflate, and the kinetic data are summarized

**Scheme 2**




in Table 5. The extrapolated values for the rate constants at 25 °C were used in a modified Grunwald–Winstein analysis, and the plot of log $k_{25°C}$ vs $Y_{OTf}$ showed moderately good correlation ($r = >0.98$). The kinetic data for the solvolysis of α-$C_2F_5$ triflate **43** in TFE are listed in Table 5.


**42** **43**

The double bond *syn* to the leaving group in **42** increases the rate of solvolysis in the 7-(trifluoromethyl)-7-norbornyl systems by a factor of 13 compared to saturated triflate **37**. This rate enhancement is significantly smaller than the effect of the double bond in the α-H norbornyl compounds where the *syn* double bond causes an increase in rate of $10^3$.[24] Using the data from Table 5 for the solvolysis of **42** in different solvents and the application of an experimentally-determined correction factor that allows for the comparison of reaction rates of tosylates and triflates of the same systems,[23] the ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5} = 1200$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3} = 1300$ in TFE at 25 °C

(24) Winstein, S.; Stafford, E. T. *J. Am. Chem. Soc.* **1957**, *79*, 505.

**Table 6. Kinetic Data for the Solvolysis of Tosylates 46 and 47**

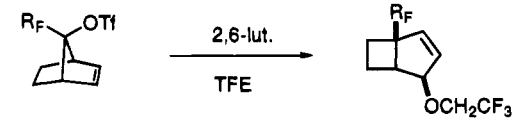
| substrate | solvent | temp range (°C) | $k_{25°C}$ ($s^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|---|
| **46** | TFE[a] | 20.0–50.0[b] | $2.24 \times 10^{-4}$[c] | 19.3 ± 0.1 | −10.5 ± 0.4 |
| | 80% EtOH[d] | 60.0–90.0[b] | $9.29 \times 10^{-6}$[c] | 21.9 ± 0.2 | −8.2 ± 0.7 |
| | 80% $Me_2CO$[e] | 70.0–100.0[b] | $3.03 \times 10^{-6}$[c] | 21.8 ± 0.6 | −10.6 ± 1.8 |
| | AcOH[f] | 65.0–95.0[g] | $1.50 \times 10^{-6}$[c] | 23.9 ± 0.4 | −5.0 ± 1.3 |
| | EtOH[h] | 80.0–110.0[b] | $8.81 \times 10^{-7}$[c] | 22.9 ± 0.2 | −9.3 ± 0.4 |
| **47** | TFE[a] | 90.0–120.0[b] | $2.09 \times 10^{-7}$[c] | 22.8 ± 0.1 | −12.5 ± 0.8 |

[a] TFE = anhydrous 2,2,2-trifluoroethanol (buffered with 2,6-lutidine). [b] Duplicate measurements (±5%) at 10.0 °C intervals in this range were made. [c] The extrapolated (interpolated) rate constant obtained from an Arrhenius plot. [d] 80% EtOH = 80% ethanol/20% water, v:v (buffered with 2,6-lutidine). [e] 80% $Me_2CO$ = 80% acetone/20% water, v:v (buffered with 2,6-lutidine). [f] AcOH = anhydrous acetic acid (buffered with NaOAc). [g] Duplicate measurements (±5%) at 15.0 °C intervals were made in this range. [h] EtOH = anhydrous ethanol (buffered with 2,6-lutidine).

were calculated. Interestingly, the pentafluoroethyl derivative was only slightly more reactive than the trifluoromethyl substrate in these systems.

A single product was observed in the solvolyses of **42** and **43** in TFE. The rearranged, allylic ethers **44** and **45** were formed in 93% as shown in eq 1. The yields of

(1)




$R_F = CF_3$, **42** $C_2F_5$, **43** $R_F = CF_3$, **44** (93%) $C_2F_5$, **45** (93%)

these reactions were determined by GC analysis vs an internal standard due to the difficulty of isolating the volatile products from dilute TFE solutions. The regiochemistry of the solvent-trapped products **44** and **45** was determined by their $^{13}C$ NMR spectra in which coupling was observed between the fluorine atoms of the perfluoroalkyl groups and one of the vinylic resonances ($^3J_{CF}$ = 2–3 Hz).

The 7-(perfluoroalkyl)-7-norbornenyl derivatives in which the double bond was *anti* to the leaving group were investigated next. Because of the greater reactivity of these compounds, the *p*-toluenesulfonate esters (tosylates) were prepared as solvolysis substrates. The tosylates were synthesized by deprotonation of carbinols **23** and **30** by potassium hydride followed by treatment with tosyl chloride. The α-$CF_3$ tosylate **46** was solvolyzed in the five solvent systems discussed previously, and the kinetic data are listed in Table 8. Again, the extrapolated


**46** **47**

(or interpolated) values for the rate constants at 25 °C were used in a Grunwald–Winstein analysis. However, a different set of empirical solvent ionizing parameters, the $Y_{OTs}$ values developed from the solvolysis of 2-adamantyl tosylate,[25] was plotted vs the log $k_{25°C}$ values. The linear fit of the data was moderately good ($r$ = 0.98) indicating a dependence of the reactions on solvent polarity. The kinetic data for the solvolysis of α-$C_2F_5$ tosylate **47** are listed in Table 9.

For the *anti* tosylates **46** and **47**, the rate retardation caused by the perfluoroalkyl groups was moderate. To

**Table 7. Kinetic Data for the Solvolysis of Mesylates 48 and 49 in TFE[a]**

| substrate | temp range (°C) | $k_{25°C}$ ($s^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|
| **48** | −15.0 to −5.0[b] | $8.50 \times 10^{-3}$[c] | 16.9 ± 0.3 | −11.4 ± 1.2 |
| **49** | 30.0–60.0[b] | $9.98 \times 10^{-5}$[c] | 19.6 ± 0.2 | −11.0 ± 0.8 |

[a] Buffered with 2,6-lutidine. [b] Duplicate measurements (±5%) at 10.0 °C intervals were made in this range. [c] The extrapolated rate constant was obtained from an Arrhenius plot.

provide the basis for a more accurate calculation of the $k_{\alpha\text{-H}}/k_{\alpha\text{-R}_F}$ ratios, the methanesulfonate ester (mesylate) **48** was prepared by treatment of *anti*-7-hydroxybicyclo-


**48** **49**

[2.2.1]hept-2-ene[26] with mesyl chloride in the presence of triethylamine. The mesylate was prepared because the tosylate, which had been prepared and solvolyzed previously,[27] was extremely difficult to obtain in pure form. Tosylates and mesylates exhibit similar behavior in solvolysis reactions, and the rates of mesylates are slower than the analogous tosylates by a factor of 2–3.[28] The exact correction factor necessary to correlate the rates of mesylate **48** and the α-perfluoroalkyl tosylates **46** and **47** was determined by solvolyzing mesylate **49** in TFE. The kinetic data for the solvolyses of **48** and **49** are listed in Table 7. The extrapolated rate constant for the solvolysis of **48** at 25 °C confirms the remarkable rate increase of $10^{11}$ caused by a double bond *anti* to the leaving group in the 7-H-7-norbornyl systems, even in different solvent systems.[27] The data in Table 7 allow the calulation of the ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5}$ = 150 and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3}$ 600 for the *anti* tosylates. The ratio $k_{\alpha\text{-}C_2F_5}/k_{\alpha\text{-}CF_3}$ 4.0 falls within the normal range.

The preparative solvolyses of **46** and **47** in TFE yielded only a single product in each case (eq 2). The tricyclic, solvent-trapped products accounted for only 67–72% of the mass balance in these reactions, and the remainder of the starting material was converted to a brown, intractable material that could be neither purified nor characterized.

The solvolysis of the appropriate derivatives of dienyl alcohols **35** and **36** completed the series of substrates in which anchimeric assistance was provided by double

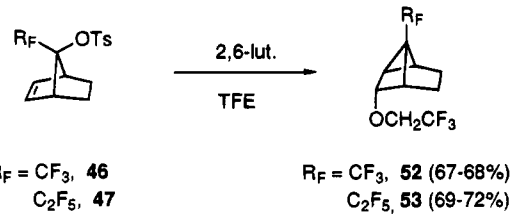
(25) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(26) Prepared by lithium aluminum hydride reduction of ketone **9** followed by chromatographic separation.

(27) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183.

(28) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643.

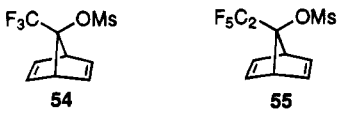
(2)




$R_F = CF_3$, **46**
$C_2F_5$, **47**

$R_F = CF_3$, **52** (67-68%)
$C_2F_5$, **53** (69-72%)

bonds. Mesylates **54** and **55** were prepared in the same

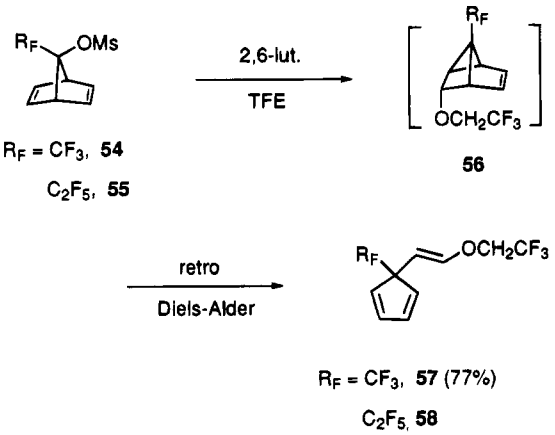



**54** **55**

manner as described for mesylate **49**. These compounds were formed readily but decomposed after 2–3 days when stored neat at −20 °C. The kinetic data for the solvolysis of **54** and **55** in TFE are summarized in Table 8. At 25 °C, mesylate **55** solvolyzed 1.6 times faster than its trifluoromethyl counterpart. Calculation of the exact $k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5}$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3}$ ratios is not possible because of difficulty in comparing the reactivities of substrates having leaving groups other than sulfonates. Kinetic data have been reported for the solvolysis of 7-chloronorbornadiene[29] and the *p*-nitrobenzoate ester of 7-hydroxynorbornadiene,[30] but the number of correction factors which need to be applied to these data to allow for a comparison with the data for **54** and **55** add substantial errors. Accounting for the relatively large margin of error, the perfluoroalkyl groups in **54** and **55** appear to retard the rate of formation of the carbocation by a factor of $\sim 10^4$.[31]

When solvolyzed in TFE, the α-perfluoroalkyl dienyl mesylates afforded geminally disubstituted cyclopentadienes as the only isolable products (eq 3). Due to the

(3)




$R_F = CF_3$, **54**
$C_2F_5$, **55**

**56**

$R_F = CF_3$, **57** (77%)
$C_2F_5$, **58**

extreme lability of the mesylates, the yield was determined only for the product of the more stable trifluoromethyl derivative. The proposed mechanism by which the cyclopentadienes are formed involves initial formation of a solvent-trapped, tricyclic structure (**56**) which then undergoes a retro Diels–Alder reaction to afford the cyclopentadienes. Several 7-substituted norbornadienes generate cyclopentadienes upon solvolysis, but the proposed tricyclic intermediate has not yet been isolated or observed.[30,32] No dimerization of either **57** or **58** was observed, and this is in direct contrast to the behavior of the α-cyano analog of these compounds, which spontaneously dimerizes even at low temperatures.[33]

The investigation into the competition between destabilization of carbocations by perfluoroalkyl groups and stabilization by the σ-bonds of cyclopropyl groups began with the solvolysis of nortricyclic tosylates **59** and **60**.


**59** **60**

These substrates were prepared from alcohols **20** and **27** in the manner previously described. The tosylates were solvolyzed only in TFE, and the kinetic data are summarized in Table 9. 7-Nortricyclic tosylate (**61**), the α-H analog of **59** and **60**, was prepared and solvolyzed in TFE to provide a more accurate basis for a comparison of the rates. The rate constant for the solvolysis of **61** in TFE at 25 °C was measured directly to be $9.42 \times 10^{-4}$ s$^{-1}$. This value is in close agreement with the rate predicted for TFE based on the rate determined in other solvents.[34] The ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5} = 22$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3} = 120$ are relatively small, but the difference between the rates of the pentafluoroethyl and trifluoromethyl compounds is in the expected range.

The preparative solvolyses of **59** and **60** in TFE resulted in the formation of substituted norbornenes

**Table 8. Kinetic Data for the Solvolysis of Mesylates 54 and 55 in TFE[a]**

| substrate | temp range (°C) | $k_{25°C}$ (s$^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|
| **54** | 0.0–30.0[b] | $8.50 \times 10^{-3c}$ | 16.9 ± 0.3 | −11.4 ± 1.2 |
| **55** | −10.0–20.0[b] | $1.41 \times 10^{-2c}$ | 17.6 ± 0.2 | −8.0 ± 0.8 |

[a] Buffered with 2,6-lutidine. [b] Duplicate measurements (±5%) at 10.0 °C intervals were made in this range. [c] The extrapolated rate constant was obtained from an Arrhenius plot.

**Table 9. Kinetic Data for the Solvolysis of Tosylates 59 and 60 in TFE[a]**

| substrate | temp range (°C) | $k_{25°C}$ (s$^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|
| **59** | 50.0–80.0[b] | $8.06 \times 10^{-6c}$ | 21.1 ± 0.1 | −11.1 ± 0.4 |
| **60** | 50.0–80.0[b] | $4.32 \times 10^{-5c}$ | 20.0 ± 0.2 | −11.4 ± 0.6 |

[a] Buffered with 2,6-lutidine. [b] Duplicate measurements (±5%) at 10.0 °C intervals were made in this range. [c] The extrapolated rate constant was obtained from an Arrhenius plot.

**Table 10. Kinetic Data for the Solvolysis of Tosylates 64 and 65 in TFE[a]**

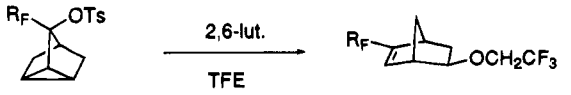
| substrate | temp range (°C) | $k_{25°C}$ (s$^{-1}$) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|
| **64** | 90.0–120.0[b] | $2.09 \times 10^{-7c}$ | 20.8 ± 0.1 | −19.4 ± 1.8 |
| **65** | 80.0–110.0[b] | $1.68 \times 10^{-6c}$ | 20.3 ± 0.3 | −16.8 ± 0.8 |

[a] Buffered with 2,6-lutidine. [b] Duplicate measurements (±5%) at 10.0 °C intervals were made in this range. [c] The extrapolated rate constant was obtained from an Arrhenius plot.

(29) Winstein, S.; Ordronneau, C. *J. Am. Chem. Soc.* **1960**, *82*, 2084.
(30) Lustgarten, R. K.; Lhomme, J.; Winstein, S. *J. Org. Chem.* **1972**, *37*, 1075.
(31) The approximate value for the rate retardation was obtained by multiplying the known rate of solvolysis of 7-norbornyl tosylate by $10^{14}$, correcting for the difference in rates of tosylates and mesylates, and using this value as a crude estimate for the rate of solvolysis of 7-norbornadienyl tosylate.
(32) Tanida, H.; Tsuji, T.; Irie, T. *J. Am. Chem. Soc.* **1966**, *88*, 864.
(33) Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1981**, 5253.
(34) (a) Winstein S.; Walborsky, H. M.; Schreiber, K. *J. Am. Chem. Soc.* **1950**, *72*, 5795. (b) Roberts, J. D.; Bennett, W.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3329.

having the structures shown (eq 4). As in the systems

(4)




$R_F = CF_3$, **59** $R_F = CF_3$, **62** (66-67%)

$C_2F_5$, **60** $C_2F_5$, **63** (61-65%)

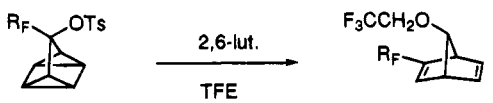
where double bonds provided stabilization of the cation, only 60–70% of the mass balance could be accounted for in the solvolyses of **59** and **60**. In each case, a dark, intractable material was filtered from the reaction mixture.

In addition to the nortricyclic tosylates, the tetracyclic (or quadricyclic) tosylates **64** and **65** were prepared and


**64** **65**

solvolyzed. The kinetic data for the solvolyses of **64** and **65** are given in Table 10. It is remarkable that these substrates are more stable than **59** and **60**, because this trend is opposite that observed in the α-H systems. Tosylate **64** was prepared, and the rate constant for its solvolysis at 25 °C in TFE was measured directly as $5.03 \times 10^{-3}$ s$^{-1}$. As in the case of the α-H nortricyclic tosylate, the rate of solvolysis of **64** agreed well with the predicted value based on data in other solvents.[35] The absolute rate constant for the solvolysis of **64** was used in the calculation of the ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5} = 3.0 \times 10^3$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3} = 2.4 \times 10^4$. These ratios are the largest determined in this study, and the ratio $k_{\alpha\text{-}C_2F_5}/k_{\alpha\text{-}CF_3} = 8.0$ is also the largest calculated. The solvolyses of **64** and **65** were complicated by decomposition of the reaction products under the solvolysis conditions. The reaction solutions became dark brown and considerable drift in the conductivity of the solutions was observed after the completion of the solvolysis reactions.[36] In spite of their instability, products **67** and **68** were isolated from the reaction mixtures (eq 5).

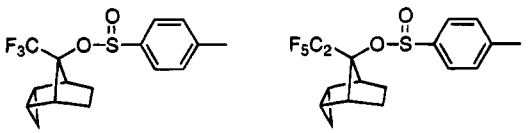
(5)




$R_F = CF_3$, **64** $R_F = CF_3$, **67** (47-48%)

$C_2F_5$, **65** $C_2F_5$, **68** (45%)

The derivatives of the *endo*-cyclopropyl compounds **25** and **32** were the final systems studied in this work. The extreme reactivity of these substrates prevented the isolation of either the mesylates or tosylates, so another leaving group was required. On the basis of the successful use of trihalosulfinate esters as leaving groups in solvolysis reactions[37] and a recent study involving the dissociation and recombination of 2-norbornyl *p*-toluenesulfinate esters,[38] sulfinates **69** and **70** were prepared and




**69** **70**

solvolyzed in TFE. Unfortunately, the kinetic data obtained from these reactions are of little value because product studies revealed that both carbocation formation and transesterification of the sulfinate occurred simultaneously. Attempts to partition the observed rate constants of the reactions into components attributable to the competing processes were unsuccessful. Derivatives other than sulfinates, possibly the 3,5-dinitrobenzoates, are necessary for these systems. The *apparent* reactivity of **69** and **70** indicates that the leaving group ability of the *p*-toluenesulfinate group is approximately equal to the dinitrobenzoate group.[39]

## Discussion

The wide range of $k_{\alpha\text{-H}}/k_{\alpha\text{-}R_F}$ values determined in this study confirms previous observations that the capacity of perfluoroalkyl groups to destabilize cationic intermediates is not constant. In order to assess the factors responsible for the variable destabilizing effects of the $CF_3$ and $C_2F_5$ groups, the features of the intermediates in each system studied must be considered. The transition states of the rate-determining steps in these reactions closely resemble the cationic intermediates (late transition states according to the Hammond postulate), and kinetic data, solvent effects, and product distributions provide important information about the mechanisms of the reactions. Each of the proposed intermediates is discussed below, and the differences between these systems and systems containing other substituents α to the leaving group are considered. The ability of each substrate to compensate for the influence of the destabilizing perfluoroalkyl groups apparently dictates the extent of rate retardation in the solvolysis reactions.

The exact description of the unsubstituted 7-norbornyl carbocation has been debated for some time. The main point of contention involves the degree of neighboring group participation of the C1–C2 σ-bond. Although the major product formed upon the solvolysis of 7-norbornyl triflate retains the bicyclo[2.2.1]heptyl skeleton, rearrangement products resulting from migration of the C1–C2 bond can also be formed.[40] In superacid media, the ionization of 7-norbornyl derivatives results in the exclusive formation of the 2-norbornyl cation.[41] Recent computational studies and low-temperature matrix IR experiments provide evidence for rearrangement of the

(35) Richey, H. G., Jr.; Buckley, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 3057.

(36) The steady drift in the conductivity of the reaction solutions made it necessary to approximate the infinity value of conductivity used in the rate calculations. See the Experimental Section for further details.

(37) (a) Braverman, S.; Ytzhak, D. *Tetrahedron* **1990**, *46*, 2975. Creary, X. *J. Org. Chem.* **1985**, *50*, 5080. (b) Creary, X. *J. Org. Chem.* **1985**, *50*, 5080.

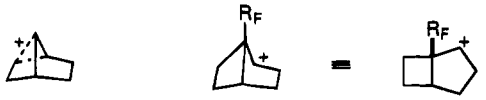
(38) Kirmse, W.; Herpers, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1018.

(39) 3,5-Dinitrobenzoates are less reactive than tosylates as leaving groups by a factor of ~$10^6$: Roberts, D. D. *J. Org. Chem.* **1969**, *34*, 285.

(40) Gassman, P. G.; Hornback, J. M.; Marshall, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 6238.

(41) Schleyer, P. v. R.; Watts, W. E.; Fort, R. C.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5679.

7-norbornyl cation to the 2-norbornyl cation via migration of the C1–C2 bond.[42] These studies indicate that the 7-norbornyl cation can best be described by the delocalized structure **71** shown below. In spite of the evidence

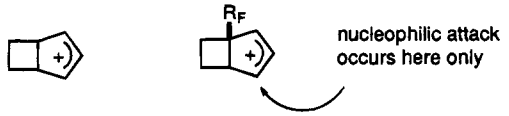



**71** **72**

supporting this delocalized intermediate, the cation is relatively unstable and is generated at very slow rates under solvolysis conditions. Previous work with 7-cyano-7-norbornyl triflate showed that a strong electron-withdrawing group could increase the degree of participation of the C1–C2 bond in the transition state by destabilizing the adjacent carbocation.[23] The rate retardation caused by an α-CN group in the 7-norbornyl system was substantial, but significantly less than that observed in many other systems. However, the cyano group can also provide mesomeric stabilization of α-carbocations, and these competing effects complicated the interpretation of the extent of delocalization in the intermediate.

The solvolysis of the 7-(perfluoroalkyl)-7-norbornyl triflates **37** and **38** provides another example of substantially increased participation of the C1–C2 bond in the transition state. This enhanced degree of anchimeric assistance in response to the destabilizing influence of the perfluoroalkyl groups explains the extremely small rate differences between the α-H and α-$R_F$ substrates ($k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5} = 8$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3} = 19$ in TFE at 25 °C). The formation of products having only rearranged structures implies that the cationic intermediate has a structure with an almost entirely localized positive charge. Structure **72** best describes the cationic intermediate formed initially in the solvolyses of **37** and **38**. The $m$ value of +1.1 calculated from a variation of the Grunwald–Winstein equation (a plot of $\log[k/k_o]$ vs $Y_{OTf}$) is consistent with a localized intermediate.[21] The formation of products which result from a 1,2-hydride shift in the cation is also consistent with an intermediate that is not stabilized by delocalization.

The migration of a bridgehead σ-bond is also a critical feature of the mechanism of the solvolysis of the 7-norbornenyl systems in which the double bond is *syn* to the leaving group. In the parent *syn*-7-norbornenyl system, the cationic intermediate resulting from participation of the C4–C5 σ-bond in the transition state can best be described by structure **73** in which the π-electrons of the




**73** **74**

double bond provide allylic stabilization of the positive charge.[43] This form of anchimeric assistance results in a relative rate of $10^3$ for the solvolysis of *syn*-7-norbornenyl tosylate when compared to 7-norbornyl tosylate.[44] The presence of the perfluoroalkyl groups in **42** and **43** results in rate retardations ($k_{\alpha\text{-H}}/k_{\alpha\text{-}C_2F_5} = 1.2 \times 10^3$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-}CF_3} = 1.3 \times 10^3$ in TFE at 25 °C) that are substantially greater than those observed in the saturated norbornyl system. These larger rate decreases may be explained by the fact that in the *syn*-norbornenyl series, bond migration occurs readily in the α-H system and the extent of the participation of this bond cannot increase significantly to compensate for destabilizing influences. Interestingly, the $k_{\alpha\text{-H}}/k_{\alpha\text{-}R_F}$ ratios are smaller than the values of $10^4$–$10^5$ encountered in most other systems. The $m$ value of +0.97 calculated from the Grunwald–Winstein plot ($\log[k/k_o]$ vs $Y_{OTf}$) for the solvolysis of **42** indicates that the transition state is stabilized by intramolecular influences to a greater extent than **35**. The $m$ value for the solvolysis of **42** is close to the $m$ value for the solvolysis of 7-norbornyl triflate.[22]

The regiochemistry of the solvent-trapped products **44** and **45** illustrates the capacity of the trifluoromethyl and pentafluoroethyl groups to affect remote cationic intermediates. Solvent-trapping by the relatively poor nucleophile trifluoroethanol occurs only at the terminus of the allylic cation farthest from the perfluoroalkyl groups. The steric bulk of the fluorinated substituents may also contribute to the regiochemistry of the trapped product.

The 7-norbornenyl compounds **50** and **51** represent a class of substrates, those with the double-bond *anti* to the incipient carbocation, that has been studied extensively. In the α-H compound, the double bond participates extensively in the transition state of the solvolysis reaction producing a rate increase of $10^{11}$ compared to the saturated substrate.[27] The cationic intermediate in this reaction is best described by the delocalized structure **75**. Evidence in support of the nonclassical structure of


**75** **76**

**75** has been provided by several studies on the effects of substituents at the double bond on the rate of solvolysis.[45] A recent computational study provided additional evidence for the existence of **75** as an intermediate,[46] and **75** has been prepared and characterized as a stable cation.[47] The influence of substituents at the 7-position has been extensively investigated, and the degree of participation of the double bond in the rate-determining step was found to be sensitive to electronic effects.[48] In particular, the participation of the double bond increased to counteract the destabilization caused by electron-withdrawing substituents at the 7-position. Conversely, electron-donating substituents could effectively eliminate anchimeric assistance by the double bond. The 7-cyano

(42) Sieber, S.; Schleyer, P. v. R.; Vancik, H.; Mesic, M.; Sunko, D. E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1604.
(43) Gassman, P. G.; Pascone, J. M. *J. Am. Chem. Soc.* **1972**, *95*, 7801.
(44) Several sources, including ref 43, state that the *syn* double bond causes a relative rate increase of $10^4$ compared to 7-norbornyl tosylate. Reexamination of the absolute rate constants for each substrate from ref 25 reveals a relative rate increase of only ~$10^3$.
(45) Gassman, P. G.; Hall, J. B. *J. Am. Chem. Soc.* **1984**, *106*, 4267.
(46) Bremer, M.; Schotz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W. Koch, W.; Pulay, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1604.
(47) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8698.
(48) Gassman, P. G.; Fentiman, A. F. *J. Am. Chem. Soc.* **1970**, *92*, 2549.

derivative has also been prepared and solvolyzed, and the rate retardation exerted by the cyano group was substantial, but less than usually observed value.[33]

The rate redardations resulting from the trifluoromethyl and pentafluoroethyl groups in **50** and **51** are of intermediate value ($k_{\alpha\text{-H}}/k_{\alpha\text{-C}_2\text{F}_5} = 150$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3} = 600$ in TFE at 25 °C). Neighboring group participation by the olefin increased to compensate for the destabilizing perfluoroalkyl groups. The only product observed in the solvolyses of **50** and **51** resulted from solvent trapping from the *endo* face of the delocalized intermediate **76**. Both steric hindrance caused by the relatively bulky perfluoroalkyl groups and destabilization of the partial positive charge at C7 contributed to the regiochemistry of product formation. An $m$ value of +0.72 from the Grunwald–Winstein equation (determined from a plot of $\log[k/k_o]$ vs $Y_{OTs}$) provides additional evidence for extensive delocalization of the positive charge in the transition state.

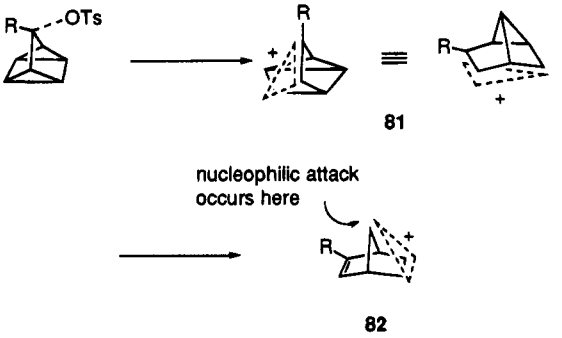
The final set of olefin-stabilized cations studied possessed the 2,5-norbornadienyl skeleton. The extreme reactivity of the α-H derivatives implies extensive neighboring group participation, and both low-temperature $^1$H NMR experiments[47,49] and computational studies[44] support the intermediacy of a delocalized cation having a structure similar to **77** shown below. The double bond

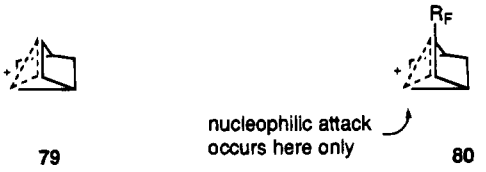

**77** **78**

*anti* to the leaving group provides the majority of the anchimeric assistance, and the *syn* double bond is involved in some manner that is not clearly defined. The rate enhancement caused by the olefins in the α-H 7-norbornadienyl derivatives, compared to 7-norbornyl tosylate, is the largest observed to date. Because of this extreme reactivity, exact quantification of the kinetic data obtained from the solvolyses of dienyl mesylates **54** and **55** is complicated by the lack of exact correction factors. The presence of a perfluoroalkyl group at C7 destabilized the intermediate by a considerable amount based on the approximate calculated rate retardations of $10^4$. This $k_{\alpha\text{-H}}/k_{\alpha\text{-R}_F}$ ratio is 1 order of magnitude, or more, larger than the ratios determined for the *anti* tosylates **50** and **51**. Apparently, the degree of participation in the dienyl compounds is near the maximum amount possible in the α-H derivatives, and increased anchimeric assistance to compensate for destabilizing influences is not possible. The 7-cyano analog of **54** and **55** has been solvolyzed, and the $k_{\alpha\text{-H}}/k_{\alpha\text{-CN}}$ ratio reported for this dienyl derivative is also among the largest measured for systems in which extensive neighboring group participation occurs.[33] The cyclopentadienyl products **57** and **58**, which result from initial solvent trapping from the face opposite the delocalized intermediate, provide evidence for delocalized cations of type **78**.

The saturated and olefinic substrates discussed to this point strongly support the idea that the structural and electronic characteristics of the functionalities which can provide anchimeric assistance are the most important factors in the generation of carbocations destabilized by perfluoroalkyl groups. The nortricyclic derivatives (**59** and **60**) and quadricyclic derivatives (**65** and **66**) represent interesting cases in which the influence of the $CF_3$ and $C_2F_5$ groups is manifested in very different ways. The carbocationic intermediate generated from 7-nortricyclic chloride was studied by low-temperature $^1$H NMR, and the delocalized structure **79** best describes this species.[50]

**Scheme 3**




**79** **80**

The extensive involvement of the strained σ-bond of the cyclopropyl group results in a rate enhancement of $>10^8$ for the solvolysis of 7-nortricyclic tosylate (compared to the rate for 7-norbornyl tosylate).[34] 7-Cyano-7-nortricyclyl tosylate has been solvolyzed, and the rate retardation caused by the nitrile is relatively small indicating increased participation of a σ-bond in response to a destabilized cation.[51]

The data presented in this study are compatible with a delocalized intermediate having the general structure depicted in **80**. The presence of perfluoroalkyl groups at C7 causes relatively small decreases in the rate of reaction as indicated by the ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-C}_2\text{F}_5} = 22$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3} = 120$ (in TFE at 25 °C). As in the cases of **35/36** and **46/47**, the extent of neighboring group participation apparently increased significantly to compensate for inductive destabilization. The stereochemistry of solvent-trapped products **62** and **63** is consistent with the pattern of destabilization of delocalized carbocations seen throughout this work.

The tetracyclic tosylates **64** and **65** exhibited behavior that was markedly different from their nortricyclic counterparts. The ratios $k_{\alpha\text{-H}}/k_{\alpha\text{-C}_2\text{F}_5} = 3000$ and $k_{\alpha\text{-H}}/k_{\alpha\text{-CF}_3} = 24\,000$ in TFE at 25 °C for **64** and **65**, respectively, are approximately 2 orders of magnitude greater than the corresponding ratios for **59** and **60**. The influence of the fluorinated substituents is so great in the tetracyclic systems that they are significantly less reactive than the perfluoroalkylated nortricyclic compounds. This order of reactivity is opposite that observed in the α-H systems in which the tetracyclic arenesulfonate solvolyzes approximately 10 times faster than the nortricyclic sulfonate.[35]

The cationic intermediate formed in the solvolysis of 3-quadricyclyl tosylate resembles the delocalized cation formed upon solvolysis of 7-norbornadienyl derivatives (Scheme 3). The cation generated from tetracyclic pre-

(49) Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352.

(50) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920.
(51) Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1981**, 5253.

**Table 11. Relative Rates of Solvolysis in Anhydrous TFE at 25.0 °C**

| |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| R = H | 1 | $9 \times 10^2$ | $2 \times 10^8$ | $1 \times 10^9$ | $6 \times 10^{10}$ | $10^{14}$ |
| R = $C_2F_5$ | $1 \times 10^{-1}$ | $7 \times 10^{-1}$ | $1 \times 10^7$ | $4 \times 10^5$ | $2 \times 10^8$ | $8 \times 10^9$ |
| R = $CF_3$ | $5 \times 10^{-2}$ | $7 \times 10^{-1}$ | $2 \times 10^6$ | $5 \times 10^4$ | $5 \times 10^7$ | $4 \times 10^9$ |

cursors differs in several important features, however. First, the α-H dienyl derivatives are more reactive by a factor of approximately $10^5$. Second, completely different products are formed from the two different starting materials. The substantial difference in rates of reaction implies that the extent of anchimeric assistance provided by the double bond(s) in the dienyl compounds is greater than the anchimeric assistance provided by the cyclopropyl group(s) in the tetracyclic valence isomers. The distinctly different products formed indicate that the intermdiates are not identical, even though they can be drawn in the same way. It is important to note that the large number of depictions of intermediate **81** do not represent resonance contributors to a delocalized species. Instead, it has been shown that movement of the atoms is necessary for interconversion of these species and energy barriers exist between nondegenerate intermediates of this type.[49]

The only isolable products formed from the solvolysis of **64** and **65** in TFE resulted from nucleophilic attack of the solvent at C7 on the face opposite the homoallylic cation in **82**. Although an energy barrier exists between **82** and the delocalized cation resulting from stabilization of the positive charge by the other double bond, the elevated temperatures at which the reactions were performed (>100 °C) provided enough energy to overcome the barriers easily. However, previous work has shown that the presence of a single trifluoromethyl group bound to one of the olefinic carbon atoms significantly decreases the ability of the double bond to provide anchimeric assistance.[45] Because of this, only the unsubstituted double bond stabilized the carbocation.

## Conclusion

The study described here comprises a thorough investigation into the influence of the trifluoromethyl and pentafluoroethyl groups on the generation of α-carbocations. These perfluoroalkyl groups destabilized the adjacent carbocations, and the extent of the destabilization was measured in two different ways. The difference between the rates of solvolysis of the α-(perfluoroalkyl) substrates and their α-hydrogen analogs was determined, and a remarkably wide range in rate retardation was found. In each system studied, the perfluoroalkylated derivatives solvolyzed more slowly than the analogous hydrocarbon compounds. The competiton between inductive destabilization and stabilization by anchimeric assistance dictated the extent of the impact on the rate of reaction. The ratio $k_{\alpha\text{-H}}/k_{\alpha\text{-R}_F}$ was relatively small in substrates in which the degree of anchimeric assistance could increase to compensate for destabilizing influences. This ratio was much larger for substrates in which anchimeric assistance was near its maximum in the α-H cases. Table 11 provides a concise summary of the kinetic data obtained in this study. Inspection of the products of the solvolysis reactions also revealed a general pattern of destabilization by the $CF_3$ and $C_2F_5$ groups. No evidence of a product resulting from nucleophilic attack at the carbon bearing the perfluoroalkyl group was found. Several of the systems are proposed to react via delocalized intermediates in which a partial positive charge exists α to the perfluoroalkylated substituents, but solvent-trapping always occurred at the more stable terminus of these intermediates. The presence of a trifluoromethyl or a pentafluoroethyl group can readily dictate the location of a positive charge in systems capable of rearrangement to afford more stable cations.

## Experimental Section

**General.** Melting points are uncorrected. NMR spectra ($^1H$, $^{13}C$, DEPT, COSY, and HETCOR) were recorded on an IBM (Bruker) NR/300 FT spectrometer. Chemical shifts are reported in ppm relative to resonances of the solvent ($CDCl_3$): 7.25 ppm (s) in the $^1H$ spectra and 77.08 (t) in the $^{13}C$ spectra. IR spectra were recorded on either a Mattson Polaris FT-IR or a Perkin-Elmer 1600 FT-IR. Preparative medium-pressure liquid chromatography (MPLC) was performed using a system which included a peristaltic pump, a pulse dampener, a 310 × 25 mm Michel column packed with 230–400 mesh silica gel, and a differential refractometer detector. Analytical samples of volatile compounds were obtained by preparative GLC using a column packed with either 10% Carbowax 20M or 10% OV-101 on 80–100 mesh Chromosorb W. All solvents were purified by standard methods and distilled prior to use.

**Preparation of (Perfluoroalkyl)trimethylsilanes.**[52] To a Schlenk flask containing a magnetic stir bar and fitted with a dry ice condenser with a balloon attached were added freshly distilled TMSCl and anhydrous benzonitrile (0.5 mL per mmol of TMSCl) under an atmosphere of dry nitrogen. The flask was cooled to −78 °C, and the condenser was filled with a dry ice/isopropyl alcohol slurry. Either bromotrifluoromethane or pentafluoroethyl iodide (1.25 equiv based on TMSCl) was condensed into the flask from a graduated tube into which it had previously been measured as a liquid. Tris(diethylamino)-phosphine (1.1 equiv based on TMSCl) was added dropwise via syringe over 30 min. The flask was allowed to warm to 0 °C, and the reaction was stirred for 2–4 h. The flask was then allowed to warm to 25 °C for 2–4 h while keeping the condenser at −78 °C. The silanes were isolated from the brown reaction mixtures by bulb-to-bulb transfer under a static vacuum to afford clear, colorless liquids in 80–90% yield. $TMSCF_3$ and $TMSC_2F_5$ were prepared in up to 50 g batches by this procedure, and the purity was usually >90%. Higher purity could be achieved by additional vacuum transfer, but material obtained after one transfer was suitable for addition to ketones.

**Preparation of α-(Perfluoroalkyl) Trimethylsilyl Ethers from Ketones.** To a two-necked, round-bottomed flask containing a magnetic stir bar and fitted with a reflux condenser attached to an inlet for maintaining an inert atmosphere was added finely ground, anhydrous KF (20 mol

(52) This procedure is similar to that described in ref 14.

% based on the ketone). Anhydrous THF (10 mL per mmol of ketone) was added via syringe. A solution of the ketone in the minimum amount of THF necessary to dissolve it was added via syringe followed by the addition of the (perfluoroalkyl)trimethylsilane (1.25 equiv based on the ketone). A saturated solution of *t*-BuOK in THF was added dropwise via syringe until the reaction started to reflux. The reaction was complete in 5–10 min (monitored by TLC or GC). After being cooled to room temperature, the golden mixture was poured into an equal volume of ice/water in a separatory funnel. The biphasic mixture was extracted with three portions of hexane, and the combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated to a brown oil with a rotary evaporator. The silyl ether was purified by flash chromatography (silica gel, hexane). Representative yields are given below.

**7-(Trifluoromethyl)-7-((trimethylsilyl)oxy)bicyclo[2.2.1]-heptane (14).** Prepared as a clear, colorless oil in 93–98% yield from **9**[53] and $TMSCF_3$: $^1H$ NMR ($CDCl_3$) $\delta$ 2.18–2.13 (m, 2H), 1.93–1.85 (m, 4H), 1.29 (br d, $J$ = 7.7 Hz, 4H), 0.15 (s 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.8 (q, $^1J_{CF}$ = 285 Hz), 88.1 (q, $^2J_{CF}$ = 28 Hz), 41.2 (d), 29.3 (t), 27.2 (tq, $^3J_{CF}$ = 3 Hz), 1.1 (q); IR (neat) 2978, 2896, 1321, 1255, 1176, 1127, 900, 844 $cm^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_{11}H_{20}F_3OSi$ (M + $H^+$) 253.1232, found 253.1227. Anal. Calcd for $C_{11}H_{19}F_3OSi$: C, 52.36; H, 7.59. Found: C, 52.42; H, 7.69.

**7-(Trifluoromethyl)-7-((trimethylsilyl)oxy)tricyclo-[2.2.1.0$^{2,6}$]heptane (15).** Prepared as a clear, colorless oil in 92–96% yield from **10**[54] and $TMSCF_3$: $^1H$ NMR ($CDCl_3$) $\delta$ 2.01 (d, $J$ = 10.4 Hz, 1H), 1.97 (br s, 1H), 1.89 (d, $J$ = 11.2 Hz, 1H), 1.44–1.36 (m, 2H), 1.33 (d, $J$ = 10.3 Hz, 1H), 1.29–1.26 (m, 1H), 1.23 (d, $J$ = 12.2 Hz, 1H), 0.17 (s, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.1 (q, $^1J_{CF}$ = 284 Hz), 86.8 (q, $^2J_{CF}$ = 29 Hz), 37.9 (d), 33.2 (t), 29.8 (tq, $^3J_{CF}$ = 4 Hz), 17.0 (d), 15.4 (d), 12.9 (d), 1.6 (q); IR (neat) 2962, 2896, 1307, 1255, 1170, 891, 844 $cm^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_{11}H_{18}F_3OSi$ (M + $H^+$) 251.1075, found 251.1073. Anal. Calcd for $C_{11}H_{17}F_3OSi$: C, 52.78; H, 6.84. Found: C, 52.92; H, 6.97.

**3-(Trifluoromethyl)-3-((trimethylsilyl)oxy)tetracyclo-[3.2.0.0$^{2,7}$.0$^{4,6}$]heptane (16).** Prepared as a clear, colorless oil in 83–93% yield from **11**[55] and $TMSCF_3$: $^1H$ NMR ($CDCl_3$) $\delta$ 1.87–1.83 (m, 2H), 1.80–1.76 (m, 2H), 1.45–1.40 (m, 2H), 0,17 (s, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.4 (q, $^1J_{CF}$ = 284 Hz), 90.2 (q, $^2J_{CF}$ = 28 Hz), 28.3 (d), 17.0 (d), 16.8 (d), 1.9 (q); IR (neat) 3081, 2962, 1315, 1255, 1169, 1077, 1013, 881, 844 $cm^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_{11}H_{16}F_3OSi$ (M + $H^+$) 249.0918, found 249.0915. Anal. Calcd for $C_{11}H_{15}F_3OSi$: C, 53.21; H, 6.09. Found: C, 53.26; H, 6.18.

**7-(Trifluoromethyl)-7-((trimethylsilyl)oxy)bicyclo[2.2.1]-hept-2-ene (17).** Prepared as a clear, colorless oil in 91–97% yield from **12**[56] and $TMSCF_3$. Isolated as an inseparable mixture of isomers[57] in a ratio of 5:1 where the major product contained the silyl ether *syn* to the double bond: $^1H$ NMR ($CDCl_3$) $\delta$ 6.07 (br s, 2H), 5.93 (dd, $J$ = 2.1, 2.1 Hz, 2H × 0.2), 2.88–2.85 (m, 2H), 2.78–2.74 (m, 2H × 0.2), 1.96–1.92 (m, 2H + [2H × 0.2]), 1.04–0.98 (m, 2H + [2H × 0.2]), 0.16 (s, 9H × 0.2), 0.08 (s, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 133.4 (d), *131.6 (d), 126.3 (q, $^1J_{CF}$ = 286 Hz)*, 125.9 (q, $^1J_{CF}$ = 284 Hz), *92.9 (q, $^2J_{CF}$ = 24 Hz)*, 92.8 (q, $^2J_{CF}$ = 28 Hz), 47.5 (d), *46.5 (d), 23.4 (t)*, 22.2 (t q, $^3J_{CF}$ = 3 Hz), 1.5 (q), *1.1 (q)*; IR (neat) 2962, 2899, 1268, 1177, 1117, 996, 894, 843 $cm^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_{11}H_{18}F_3OSi$ (M + $H^+$) 251.1075, found 251.1075. Anal. Calcd for $C_{11}H_{17}F_3OSi$: C, 52.78; H, 6.84. Found: C, 52.97; H, 6.97.

**8-(Trifluoromethyl)-8-((trimethylsilyl)oxy)-*endo*-tricyclo[3.2.1.0$^{2,4}$]octane (18).** Prepared as a clear, colorless oil in 93–98% from **13**[58] and $TMSCF_3$. Isolated as an inseparable mixture of isomers[57] in a ratio of 10:1 where the major product contained the silyl ether *syn* to the cyclopropyl group: $^1H$ NMR ($CDCl_3$) $\delta$ 2.30 (m, 2H × 0.1), 2.24 (m, 2H), 1.72–1.69 (m, 2H + [2H × 0.1]), 1.50–1.47 (m, 2H), 1.36–1.31 (m, 1H + [2H × 0.1]), 1.13 (d, $J$ = 7.4 Hz, 2H × 0.1), 1.08–0.97 (m, 3H + [1H × 0.1]), 0.72 (q, $J$ = 7.1 Hz, 1H × 0.1), 0.17 (s, 9H), 0.13 (s, 9H × 0.1); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.9 (q, $^1J_{CF}$ = 285 Hz), *125.1 (q, $^1J_{CF}$ = 286 Hz), 99.5 (q, $^2J_{CF}$ = 26 Hz)*, 98.0 (q, $^2J_{CF}$ = 24 Hz), *41.9 (d)*, 41.7 (d), 25.4 (t), *23.9 (tq, $^3J_{CF}$ = 3 Hz), 20.6 (d), 17.2 (t)*, 17.0 (dq, $^3J_{CF}$ = 3 Hz), 13.2 (t), *1.22 (q)*, 1.01 (q); IR (neat) 2979, 1314, 1255, 1169, 898, 846 $cm^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{12}H_{20}F_3OSi$ (M + $H^+$) 265.1232, found 265.1221. Anal. Calcd for $C_{12}H_{19}F_3OSi$: C, 54,52; H, 7.24. Found: C, 54.64; H, 7.31.

**7-(Pentafluoroethyl)-7-((trimethylsilyl)oxy)bicyclo-[2.2.1]hept-2-ene (33).** Prepared as a clear, colorless oil in 91–97% yield from **12**[56] and $TMSC_2F_5$. Isolated as an inseparable mixture of isomers[57] in a ratio of 5:1 where the major product contained the silyl ether *syn* to the double bond: $^1H$ NMR ($CDCl_3$) $\delta$ 6.08 (t, $J$ = 2.0 Hz, 2H), 5.89 (t, $J$ = 2.2 Hz, 2H × 0.2), 2.95 (br s, 2H), 2.61 (br s, 2H × 0.2), 2.00–1.90 (m, 2H + [2H × 0.2]), 1.07–0.98 (m, 2H + [2H × 0.2]), 0.16 (s, 9H × 0.2), 0.07 (s, 9H); $^{13}C$ NMR ($CDCl_3$) *$\delta$ 133.8 (d)*, 131.2 (d), *119.6 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz)*, 119.2 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 37 Hz), *115.4 (tq, $^1J_{CF}$ = 280 Hz, $^2J_{CF}$ = 35 Hz)*, 115.3 (tq, $^1J_{CF}$ = 280 Hz, $^2J_{CF}$ = 37 Hz), 93.2 (t, $^2J_{CF}$ = 17 Hz), *92.8 (t, $^2J_{CF}$ = 24 Hz), 47.9 (d)*, 46.6 (d), 23.4 (t), *22.3 (tt, $^3J_{CF}$ = 4 Hz), 1.8 (q)*, 1.3 (q); IR (neat) 2962, 2902, 1343, 1220, 1150, 1072, 891, 845 $cm^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{12}H_{18}F_5OSi$ (M + $H^+$) 301.1047, found 301.1030. Anal. Calcd for $C_{12}H_{17}F_5OSi$: C, 47.99; H, 5.70. Found: C, 48.09; H, 5.75.

**8-(Pentafluoroethyl)-8-((trimethylsilyl)oxy)-*endo*-tricyclo[3.2.1.0$^{2,4}$]octane (34).** Prepared as a clear, colorless oil in 90–99% yield from **13**[58] and $TMSC_2F_5$. Isolated as an inseparable mixture of isomers[57] in a ratio of 10:1 where the major product contained the silyl ether *syn* to the cyclopropyl group: $^1H$ NMR ($CDCl_3$) $\delta$ 2.41 (br s, 2H × 0.1), 2.36 (br s, 2H), 1.72 (d, J = 8.7 Hz, 2H), 1.71–1.70 (m, 2H × 0.1), 1.51–1.47 (m, 2H), 1.38 (m, 1H), 1.35–1.31 (m, 2H × 0.1), 1.15 (d, J = 8.1 Hz, 2H × 0.1), 1.07–1.00 (m, 3H + [1H × 0.1]), 0.69 (q, J = 7.3 Hz, 1H × 0.1), 0.16 (s, 9H), 0.12 (s, 9H × 0.1); $^{13}C$ NMR ($CDCl_3$) $\delta$ 119.7 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), *119.5 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz)*, 115.8 (tq, $^1J_{CF}$ = 261 HHz, $^2J_{CF}$ = 36 Hz), *114.5 (tq, $^1J_{CF}$ = 261 Hz, $^2J_{CF}$ = 36 Hz), 99.1 (t, $^2J_{CF}$ = 22 Hz)*, 97.8 (t, $^2J_{CF}$ = 18 Hz), *42.6 (d)*, 42.4 (d), 25.2 (t), *24.1 (tt, $^3J_{CF}$ = 5 Hz), 20.9 (d), 17.4 (t)*, 17.0 (dt, $^3J_{CF}$ = 5 Hz), 13.0 (tt, $^3J_{CF}$ = 4 Hz), *1.3 (q)*, 1.0 (q); IR (neat) 2979, 2909, 1339, 1219, 1159, 1056, 896, 845 $cm^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{13}H_{20}F_5OSi$ (M + $H^+$) 315.1204, found 315.1200. Anal. Calcd for $C_{13}H_{19}F_5OSi$: C, 49.67; H, 6.09. Found: C, 49.84; H, 6.15.

**Preparation of α-(Perfluoroalkyl)carbinols from Silyl Ethers.** To a round-bottomed flask containing a magnetic stir bar were added the silyl ether, THF (1 mL per mmol of the silyl ether), and 1 N HCl(aq) (1 mL per mL of THF). The flask was sealed, and the reaction mixture was stirred vigorously at 25 °C until a uniform emulsion formed. The progress of the reaction was monitored by GLC. When all of the starting material was converted, the reaction mixture was transferred to a separatory funnel and extracted with three portions of hexane. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporator. The alcohols were purified by flash chromatography (silica gel, 1:1 pentane/$CH_2Cl_2$) if only a single isomer was formed or by MPLC (silica gel, 2–5% ethyl acetate in hexane) if the separation of epimers was necessary.

**Preparation of α-(Pentafluoroethyl)carbinols by the Addition of (Pentafluoroethyl)lithium to Ketones.** The procedure of Gassman and O'Reilly was used without modification.[17]

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**7-Hydroxy-7-(trifluoromethyl)bicyclo[2.2.1]heptane (19).** Prepared as a white, crystalline solid in 89–96% yield from silyl ether **14**: mp 92 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.16–2.13 (m, 2H), 2.10 (br s, 1 H), 2.05–2.02 (m, 2H), 1.92 (br d, $J$ = 8.2 Hz, 2H), 1.37–1.33 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.8 (q, $^1J_{CF}$ = 283 Hz), 85.8 (q, $^2J_{CF}$ = 28 Hz), 40.8 (d), 28.9 (t), 28.0 (tq, $^3J_{CF}$ = 2 Hz); IR (KBr) 2981, 2898, 1379, 1321, 1203 cm$^{-1}$; HRMS (EI) calcd for $C_8H_{11}F_3O$ 180.0762, found 180.0761. Anal. Calcd for $C_8H_{11}F_3O$ ($M^+$): C, 53.33; H, 6.15. Found: C, 53.28; H, 6.24.

**7-Hydroxy-7-(trifluoromethyl)tricyclo[2.2.1.0$^{2,6}$]-heptane (20).** Prepared as a clear, colorless oil in 91–96% yield from silyl ether **15**: $^1$H NMR ($CDCl_3$) $\delta$ 2.58 (br s, 1H), 2.12 (d, $J$ = 10.7 Hz, 1H), 2.00 (br s, 1H), 1.96 (d $J$ = 11.5 Hz, 1H), 1.44 (br s, 1H), 1.42 (br s, 1H), 1.37 (d, $J$ = 10.5 Hz, 1H), 1.29 (d, $J$ = 12.3 Hz, 1H), 1.25 (td, $J$ = 5.2 Hz, 1.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.2 (q, $^1J_{CF}$ = 283 Hz), 84.3 (q, $^2J_{CF}$ = 29 Hz), 36.7 (d), 32.8 (t), 31.0 (tq, $^3J_{CF}$ = 3 Hz), 17.2 (d), 15.1 (d), 12.2 (d); IR (neat) 3392 (br), 3002, 2896, 1304, 1169, 1096, 1029, 985 cm$^{-1}$; HRMS (EI) calcd for $C_8H_9F_3O$ ($M^+$) 178.0606, found 178.0604. Anal. Calcd for $C_8H_9F_3O$: C, 53.94; H, 5.09. Found: C, 53.91; H, 5.22.

**3-Hydroxy-3-(trifluoromethyl)tetracyclo[3.2.0.0$^{2,6}$.0$^{4,7}$]-heptane (21).** Prepared as a white, crystalline solid in 93–98% yield from silyl ether **16**: mp 83 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.26 (br s, 1H), 1.90–1.85 (m, 4H), 1.50–1.47 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.4 (q, $^1J_{CF}$ = 283 Hz), 88.2 (q, $^2J_{CF}$ = 29 Hz), 28.9 (d), 17.6 (d), 15.6 (d); IR (KBr) 2965, 1312, 1189, 1130, 1009 cm$^{-1}$; HRMS (EI) calcd for $C_8H_7F_3O$ ($M^+$) 176.0449, found 176.0457. Anal. Calcd for $C_8H_7F_3O$: C, 54.55; H, 4.01. Found: C, 54.74; H, 4.12.

***syn*-7-Hydroxy-*anti*-7-(trifluoromethyl)bicyclo[2.2.1]-hept-2-ene (22).** Prepared as a low-melting, white solid in 73–81% yield from silyl ether **17**: mp 29 °C; $^1$H NMR ($CDCl_3$) $\delta$ 6.20 (br s, 2H), 2.95–2.93 (m, 2H), 2.64 (br s, 1H), 2.04–2.00 (m, 2H), 1.08–1.08 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 134.2 (d), 125.6 (q, $^1J_{CF}$ = 283 Hz), 90.1 (q, $^2J_{CF}$ = 29 Hz), 47.6 (d), 22.3 (tq, $^3J_{CF}$ = 2 Hz); IR (melt) 3459 (br), 2989, 1265, 1159, 1080 cm$^{-1}$; HRMS (EI) calcd for $C_8H_9F_3O$ ($M^+$) 178.0608, found 178.0608. Anal. Calcd for $C_8H_9F_3O$: C, 53.94; H, 5.09. Found: C, 54.00; H, 5.11.

***anti*-7-Hydroxy-*syn*-7-(trifluoromethyl)bicyclo[2.2.1]-hept-2-ene (23).** Prepared as a white, crystalline solid in 14–22% from silyl ether **17**: mp 50 °C; $^1$H NMR ($CDCl_3$) $\delta$ 5.97 (dd, J = 2.1, 2.1 Hz, 2H), 2.77–2.75 (m, 2H), 2.30 (br s, 1H), 2.06–1.98 (m, 2H), 1.07–1.04 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 132.4 (d), 126.4 (q, $^1J_{CF}$ = 285 Hz), 90.4 (q, $^2J_{CF}$ = 24 Hz), 45.9 (d), 23.1 (t); IR (melt) 3606, 3483 (br), 3073, 2986, 1299, 1165, 1007, 946, 860 cm$^{-1}$; HRMS (EI) calcd for $C_8H_9F_3O$ ($M^+$) 178.0608, found 178.0606. Anal. Calcd for $C_8H_9F_3O$: C, 53.94; H, 5.09. Found: C, 53.62; H, 5.18.

***syn*-8-Hydroxy-*anti*-8-(trifluoromethyl)-*endo*-tricyclo-[3.2.1.0$^{2,4}$]octane (24).** Prepared as a white, crystalline solid in 72–76% yield from silyl ether **18**: mp 101 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.85 (br s, 1H), 2.25 (br s, 2H), 1.77 (br d, $J$ = 9.2 Hz, 2H), 1.62–1.59 (m, 2H), 1.45–1.41 (m, 1H), 1.14–1.04 (m, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 125.0 (q, $^1J_{CF}$ = 284 Hz), 97.2 (q, $^2J_{CF}$ = 27 Hz), 41.4 (d), 24.4 (tq, $^3J_{CF}$ = 2 Hz), 19.8 (d), 17.3 (t); IR (KBr) 3415 (br), 3056, 2981, 2906, 1379, 1314, 1166, 1064, 1002 cm$^{-1}$; HRMS (EI) calcd for $C_9H_{11}F_3O$ ($M^+$) 192.0762, found 192.0750. Anal. Calcd for $C_9H_{11}F_3O$: C, 56.25; H, 5.77. Found: C, 56.44; H, 5.81.

***anti*-8-Hydroxy-*syn*-8-(trifluoromethyl)-*endo*-tricyclo-[3.2.1.0$^{2,4}$]octane (25).** Prepared as a white, crystalline solid in 7–12% yield from silyl ether **18**: mp 106 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.30 (br s, 2H), 2.14 (br s, 1H), 1.84 (br d, $J$ = 8.9 Hz, 2H), 1.38–1.37 (m, 2H), 1.18 (d, $J$ = 7.7 Hz, 2H), 1.09–1.07 (m, 1H), 0.76 (ddd, $J$ = 7.2, 7.2, 6.9 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 127.0 (q, $^1J_{CF}$ = 284 Hz), 95.9 (q, $^2J_{CF}$ = 25 Hz), 41.1 (d), 25.1 (t), 17.8 (dq, $^3J_{CF}$ = 3Hz), 13.2 (t); IR (KBr) 3363 (br), 2980, 2897, 1481, 1304, 1189, 1142, 1061, cm$^{-1}$; HRMS (EI) calcd for $C_9H_{11}F_3O$ ($M^+$) 192.0762, found 192.0775. Anal. Calcd for $C_9H_{11}F_3O$: C, 56.25; H, 5.77. Found: C, 56.22; H, 5.74.

**7-Hydroxy-7-(pentafluoroethyl)bicyclo[2.2.1]-heptane (26).** Prepared as a white, crystalline solid in 89–93% yield from ketone **9**[53] and $C_2F_5Li$: mp 35 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.27 (br s, 2H), 2.08 (br s, 1H), 2.03–1.92 (m, 4H), 1.38–1.33 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 119.6 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 116.2 (tq, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 35 Hz), 85.3 (t, $^2J_{CF}$ = 23 Hz), 41.2 (d), 28.7 (t), 28.1 (tt, $^3J_{CF}$ = 4 Hz); IR (KBr) 3481 (br), 2987, 2896, 1346, 1208, 1139, 1078, 917 cm$^{-1}$; HRMS (EI) calcd for $C_9H_{11}F_5O$ ($M^+$) 230.0730, found 230.0714. Anal. Calcd for $C_9H_{11}F_5O$: C, 46.96; H, 4.82. Found: C, 46.97; H, 4.93.

**7-Hydroxy-7-(pentafluoroethyl)tricyclo[2.2.1.0$^{2,6}$]-heptane (27).** Prepared as a white, crystalline solid in 89–96% yield from ketone **10**[54] and $C_2F_5Li$: mp 41 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.16–2.12 (m, 2H), 2.02 (br s, 1H), 1.98–1.93 (m, 1H), 1.50–1.30 (m, 5H); $^{13}$C NMR ($CDCl_3$) $\delta$ 119.5 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 115.1 (tq, $^1J_{CF}$ = 259 Hz, $^2J_{CF}$ = 35 Hz), 84.4 (t, $^2J_{CF}$ = 23 Hz), 37.3 (d), 33.0 (t), 31.1 (tt, $^3J_{CF}$ = 4 Hz), 17.9 (d), 15.4 (d), 11.9 (d); IR (KBr) 3609, 3378 (br), 3025, 2972, 1359, 1208, 1142, 1076, 911, 819 cm$^{-1}$; HRMS (EI) calcd for $C_9H_9F_5O$ ($M^+$) 228.0574, found 228.0569. Anal. Calcd for $C_9H_9F_5O$: C, 47.38; H, 3.98. Found: C, 47.67; H, 4.18.

**3-Hydroxy-3-(pentafluoroethyl)tetracyclo[3.2.0.0$^{2,6}$.0$^{4,7}$]-heptane (28).** Prepared as a white, crystalline solid in 92–98% yield from ketone **11**[55] and $C_2F_5Li$: mp 45 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.16 (br s, 1H), 1.88–1.86 (m, $J$ = 3.2 Hz, 4H), 1.57 (dd, $J$ = 3.9, 3.7 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 119.5 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 37 Hz), 115.2 (tq, $^1J_{CF}$ = 258 Hz, $^2J_{CF}$ = 36 Hz), 88.4 (t, $^2J_{CF}$ = 23 Hz), 29.4 (d), 18.0 (d), 15.1 (d); IR (KBr) 3259 (br), 2793, 1344, 1221, 1192, 1103, 1052, 957 cm$^{-1}$; HRMS (EI) calcd for $C_9H_8F_5O$ (M + H$^+$) 227.0495, found 227.0499. Anal. Calcd for $C_9H_7F_5O$: C, 47.80; H, 3.12. Found: C, 47.77; H, 3.19.

***syn*-7-Hydroxy-*anti*-7-(pentafluoroethyl)bicyclo[2.2.1]-hept-2-ene (29).** Prepared as a white, crystalline solid in 84–95% yield from ketone **12**[56] and $C_2F_5Li$ (silyl ether **33** afforded **29** in 59–64% yield). Spectral data agreed with the published values.[17]

***anti*-7-Hydroxy-*syn*-7-(pentafluoroethyl)bicyclo[2.2.1]-hept-2-ene (30).** Prepared as a white, crystalline solid in 17–21% yield from silyl ether **33**: mp 31 °C; $^1$H NMR ($CDCl_3$) $\delta$ 5.94 (dd, $J$ = 2.2, 2.1 Hz, 2H), 2.82 (br s, 2H), 2.18 (br s, 1H), 2.04–1.98 (m, 2H), 1.09–1.06 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 132.0 (dt, $^3J_{CF}$ = 2 Hz), 119.3 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 37 Hz), 115.4 (tq, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 36 Hz), 90.3 (t, $^2J_{CF}$ = 18 Hz), 46.2 (d), 23.0 (t); IR (melt) 3457 (br), 2988, 2965, 1340, 1204, 1125, 1047, 905 cm$^{-1}$; HRMS (EI) calcd for $C_9H_9F_5O$ ($M^+$) 228.0574, found 228.0569. Anal. Calcd for $C_9H_9F_5O$: C, 47.38; H, 3.98. Found: C, 47.57; H, 3.92.

***syn*-8-Hydroxy-*anti*-8-(pentafluoroethyl)-*endo*-tricyclo-[3.2.1.0$^{2,4}$]octane (31).** Prepared as a low-melting, white solid in 54–72% yield from silyl ether **34**: mp 28 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.99 (br s, 1H), 2.35 (br s, 2H), 1.79 (br d, J = 9.8 Hz, 2H), 1.61–1.58 (m, 2H), 1.50–1.46 (m, 1H), 1.16–1.07 (m, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 119.5 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 114.7 (tq, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 36 Hz), 96.7 (t, $^2J_{CF}$ = 23 Hz), 42.0 (d), 24.6 (tt, $^3J_{CF}$ = 4 Hz), 19.5 (d), 17.3 (t); IR (melt) 3607, 3502 (br), 2988, 2907, 1492, 1339, 1216, 1192, 1177, 1133 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_{11}F_5O$ ($M^+$) 242.0730, found 242.0719. Anal. Calcd for $C_{10}H_{11}F_5O$: C, 49.59; H, 4.58. Found: C, 49.47; H, 4.65.

***anti*-8-Hydroxy-*syn*-8-(pentafluoroethyl)-*endo*-tricyclo-[3.2.1.0$^{2,4}$]octane (32).** Prepared as a white, crystalline solid in 7–11% from silyl ether **34**: mp 49 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.42 (br s, 2H), 2.10 (br s, 1H), 1.82 (d, $J$ = 8.6 Hz, 2H), 1.41–1.39 (m, 2H), 1.21 (br d, $J$ = 8.2 Hz, 2H), 1.11–1.07 (m, 1H), 0.74 (ddd, $J$ = 7.2, 7.2, 6.4 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 119.7 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 116.2 (tq, $^1J_{CF}$ = 261 Hz, $^2J_{CF}$ = 35 Hz), 95.6 (t, $^2J_{CF}$ = 19 Hz), 41.9 (d), 25.0 (t), 17.9 (dt, $^3J_{CF}$ = 5 Hz), 13.1 (t); IR (melt) 3620, 3490 (br), 2973, 2889, 1481, 1338, 1212, 1142, 1123, 1092, 1039, 898 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_{11}F_5O$ ($M^+$) 242.0730, found 242.0723. Anal. Calcd for $C_{10}H_{11}F_5O$: C, 49.59; H, 4.58. Found: C, 49.71; H, 4.73.

**Valence Isomerization of Tetracyclic Carbinols 21 and 28.** To a two-necked, round-bottomed flask fitted with a reflux condenser and containing a magnetic stir bar were added the tetracyclic alcohol, chloroform (2 mL per mmol of the alcohol),

and the palladium catalyst (10 mg per 1 g of the alcohol). Either bicyclo[2.2.1]hepta-2,5-diene palladium dichloride[59] or bis(benzonitrile)palladium dichloride[60] worked effectively. The reaction mixture was heated to reflux under an inert atmosphere, and the progress of the reaction was monitored by TLC or GC. The isomerization usually required several hours. The mixture was cooled to 25 °C, and the majority of the solvent was removed by rotary evaporator. The product was isolated by flash chromatography (silica gel, 40% pentane in dichloromethane).

**7-Hydroxy-7-(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (35).** Prepared as a clear, colorless oil in 78–88% yield from **21**: $^1$H NMR ($CDCl_3$) $\delta$ 6.92 (br s, 2H), 6.60 (dd, $J$ = 2.2, 2.0 Hz, 2H), 3.71 (br s, 1H), 3.70–3.68 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 142.0 (d), 138.0 (d), 124.6 (q, $^1J_{CF}$ = 284 Hz), 106.9 (q, $^2J_{CF}$ = 24 Hz), 55.6 (d); IR (neat) 3454 (br), 3080, 3001, 1380, 1309, 1243, 1174, 1100, 962, 827 cm$^{-1}$; HRMS (EI) calcd for $C_8H_7F_3O$ ($M^+$) 176.0449, found 176.0437.

**7-Hydroxy-7-(pentafluoroethyl)bicyclo[2.2.1]hepta-2,5-diene (36).** Prepared as a clear, colorless oil in 80–99% yield from **28**: $^1$H NMR ($CDCl_3$) $\delta$ 6.93 (dd, $J$ = 2.3, 2.0 Hz, 2H), 6.58 (dd, $J$ = 2.2, 2.0 Hz, 2H), 3.85 (br s, 1H), 3.71–3.69 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 142.1(d), 137.5 (dt, $^3J_{CF}$ = 3Hz), 119.3 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 36 Hz), 114.3 (tq, $^1J_{CF}$ = 262 Hz, $^2J_{CF}$ =37 Hz), 107.4 (t, $^2J_{CF}$ = 18 Hz), 55.9 (d); IR (neat) 3557 (br), 3080, 3007, 1356, 1220, 1178, 1144, 1100, 1036 cm$^{-1}$; HRMS (EI) calcd for $C_9H_7F_5O$ ($M^+$) 226.0417, found 226.0405. Anal. Calcd for $C_9H_7F_5O$: C, 47.80; H, 3.12. Found: C, 47.75; H, 3.21.

**Preparation of Trifluoromethanesulfonate (Triflate) Esters.** To a round-bottomed flask containing a magnetic stir bar was added a mineral oil slurry of potassium hydride (~35% by weight). The flask was sealed with a septum, and an argon atmosphere was introduced. The mineral oil was rinsed with pentane, and the hydride was dried to constant weight. Anhydrous ether (10 mL per mmol of the alcohol) was added, and the flask was cooled to 0 °C. A solution of the alcohol in the minimum amount of ether necessary to dissolve it was added dropwise via syringe. The mixture was stirred for 15 min after gas evolution ceased. Neat trifluoromethanesulfonic (triflic) anhydride (1.05 equiv) was added dropwise with vigorous stirring. The reaction mixture was allowed to warm to 25 °C over 1 h. Intractable materials were removed by filtration of the reaction mixture through a plug of silica gel, and the product was isolated by flash chromatography (silica gel, pentane).

**7-(Trifluoromethyl)-7-bicyclo[2.2.1]heptyl Trifluoromethanesulfonate (37).** Prepared as a clear, colorless oil in 66–87% yield from **19**: $^1$H NMR ($CDCl_3$) $\delta$ 2.80–2.77 (m, 2H), 2.12–2.09 (m, 2H), 1.96 (br d, $J$ = 8.5 Hz, 2H), 1.58–1.48 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 123.6 (q, $^1J_{CF}$ = 282 Hz), 118.3 (q, $^1J_{CF}$ = 320 Hz), 104.5 (q, $^2J_{CF}$ = 31 Hz), 41.6 (d), 28.6 (t), 26.7 (tq, $^3J_{CF}$ = 2 Hz); IR (neat) 2989, 2906, 1412, 1249, 1211, 1154, 1141, 960, 885 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_9H_{14}NF_6O_3S$ ($M+NH_4^+$) 330.0587, found 330.0587. Anal. Calcd for $C_9H_{10}F_6O_3S$: C, 34.62; H, 3.23. Found: C, 35.05; H, 3.36.

**7-(Pentafluoroethyl)-7-bicyclo[2.2.1]heptyl Trifluoromethanesulfonate (38).** Prepared as a clear, colorless oil in 55–86% yield from **26**: $^1$H NMR ($CDCl_3$) $\delta$ 2.90 (br s, 2H), 2.13–2.10 (m, 2H), 1.99–1.96 (m, 2H), 1.58–1.48 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 118.8 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 36 Hz), 118.4 (q, $^1J_{CF}$ = 320 Hz), 113.1 (tq, $^1J_{CF}$ = 264 Hz, $^2J_{CF}$ = 38 Hz), 104.2 (t, $^2J_{CF}$ = 25 Hz), 42.3 (d), 28.6 (t), 26.9 (tt, $^3J_{CF}$ = 4 Hz); IR (neat) 2993, 2910, 1412, 1210, 1154, 1138, 969, 912, 870 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{10}H_{14}F_8NO_3S$ ($M+NH_4^+$) 380.0567, found 380.0543. Anal. Calcd for $C_{10}H_{10}F_8O_3S$: C, 33.16; H, 2.78. Found: C, 33.48; H, 2.85.

***anti*-7-(Trifluoromethyl)-*syn*-7-bicyclo[2.2.1]hept-2-enyl Trifluoromethanesulfonate (42).** Prepared as a clear, colorless oil in 49–81% from **22**: $^1$H NMR ($CDCl_3$) $\delta$ 6.23 (br s, 2H), 3.44 (br s, 2H), 2.05–2.01 (m, 2H), 1.28–1.24 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 133.1 (d), 122.7 (q, $^1J_{CF}$ = 283 Hz), 118.2 (q, $^1J_{CF}$ = 320 Hz), 107.2 (q, $^2J_{CF}$ = 32 Hz), 46.7 (d), 21.3 (tq, $^3J_{CF}$ = 2 Hz); IR (neat) 3001, 2977, 2905, 1406, 1322, 1218, 994, 964, 882 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_9H_{12}F_6NO_3S$ ($M+NH_4^+$) 328.0443, found 328.0460. Anal. Calcd for $C_9H_8F_6O_3S$: C, 34.85; H, 2.60. Found: C, 35.12; H, 2.72.

***anti*-7-(Pentafluoroethyl)-*syn*-7-bicyclo[2.2.1]hept-2-enyl Trifluoromethanesulfonate (43).** Prepared as a clear, colorless oil in 68–82% from **29**: $^1$H NMR ($CDCl_3$) $\delta$ 6.25 (br s, 2H), 3.52 (br s, 2H), 2.04 (br d, $J$ = 2.5 Hz, 2H), 1.26 (dddd, $J$ = 8.7, 8.6, 3.2, 3.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 133.3 (d), 118.7 (qt, $^1J_{CF}$ = 289 Hz, $^2J_{CF}$ = 36 Hz), 118.2 (q, $^1J_{CF}$ = 320 Hz), 112.4 (tq, $^1J_{CF}$ = 263 Hz, $^2J_{CF}$ = 38 Hz), 107.2 (t, $^2J_{CF}$ = 26 Hz), 47.3 (d), 21.5 (tt, $^3J_{CF}$ = 4 Hz); IR (neat) 3005, 2979, 2905, 1413, 1272, 1210, 1141, 1009, 954, 884 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{10}H_{12}F_8NO_3S$ ($M+NH_4^+$) 378.0411, found 378.0418.

**Preparation of *p*-Toluenesulfonate (Tosylate) Esters.** To a round-bottomed flask containing a magnetic stir bar was added a mineral oil slurry of potassium hydride (~35% by weight). The flask was sealed with a septum, and an argon atmosphere was introduced. The mineral oil was rinsed with pentane, and the hydride was dried to constant weight. Anhydrous ether (10 mL per mmol of the alcohol) was added, and the flask was cooled to 0 °C. A solution of the alcohol in the minimum amount of ether necessary to dissolve it was added dropwise via syringe. The mixture was stirred for 15 min after gas evolution ceased. A solution of *p*-toluenesulfonyl chloride (1.05 equiv) in the minimum amount of ether necessary was added dropwise with vigorous stirring. The reaction mixture was stirred at 0 °C for 1 h and then allowed to warm to 25 °C over 4 h. A fine white precipitate formed during the reaction. The mixture was poured into a separatory funnel containing an equal volume of ice/water, and the biphasic mixture was extracted with three portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated to a solid by rotary evaporator. Recrystallization from pentane at −78 °C afforded the pure tosylate.

***syn*-7-(Trifluoromethyl)-*anti*-7-bicyclo[2.2.1]hept-2-enyl *p*-Toluenesulfonate (46).** Prepared as a white, crystalline solid in 57–75% yield from **23**: mp 81 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 8.1 Hz, 2H), 5.98 (br s, 2H), 3.31 (br s, 2H), 2.43 (s, 3H), 2.11 (br d, $J$ = 8.5 Hz, 2H), 1.16 (br d, $J$ = 7.9 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.7 (s), 135.3 (s), 131.2 (d), 129.5 (d), 127.4 (d), 124.2 (q, $^1J_{CF}$ = 286 Hz), 100.7 (q, $^2J_{CF}$ = 25 Hz), 46.8 (d), 22.9 (t), 21.6 (q); IR (KBr) 3080, 3001, 2989, 2952, 1599, 1357, 1297, 1190, 995, 866 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{15}H_{19}F_3NO_3S$ ($M+NH_4^+$) 350.1039, found 350.1068. Anal. Calcd for $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.60; H, 4.85.

***syn*-7-(Pentafluoroethyl)-*anti*-7-bicyclo[2.2.1]hept-2-enyl *p*-Toluenesulfonate (47).** Prepared as a white, crystalline solid in 52–61% yield from **30**: mp 96 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.76 (d, $J$ = 8.2 Hz, 2H), 7.29 (d, $J$ = 8.2 Hz, 2H), 5.93–5.92 (m, 2H), 3.37 (br s, 2H), 2.42, (s, 3H), 2.17–2.14 (m, 2H), 1.20–1.17 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.4 (s), 135.5 (s), 130.5 (d), 129.4 (d), 127.2 (d), 118.6 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 37 Hz), 113.4 (tq, $^1J_{CF}$ = 264 Hz, $^2J_{CF}$ = 38 Hz), 100.8 (t, $^2J_{CF}$ = 18 Hz), 46.6 (d), 23.0 (t), 21.6 (q); IR (KBr) 3011, 2967, 1598, 1361, 1212, 1189, 1151, 1000, 851, 830 cm$^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_{16}H_{16}F_5O_3S$ ($M + H^+$) 383.0741, found 383.0762. Anal. Calcd for $C_{16}H_{15}F_5O_3S$: C, 50.26; H, 3.95. Found: C, 50.10; H, 3.99.

**7-(Trifluoromethyl)-7-tricyclo[2.2.1.0$^{2,6}$]heptyl *p*-Toluenesulfonate (59).** Prepared as a white, crystalline solid in 37–58% yield from **20**: mp 82 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.3 Hz, 2H), 7.32 (d, $J$ = 8.2 Hz, 2H), 2.44 (s, 3H), 2.24 (br s, 1H), 2.10 (dd, $J$ = 5.2, 5.2 Hz, 1H), 1.95–1.90 (m, 2H), 1.62–1.51 (m, 2H), 1.41–1.32 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.7 (s), 135.0 (s), 129.6 (d), 127.7 (d), 123.9 (q, $^1J_{CF}$ = 284 Hz), 97.4 (q, $^2J_{CF}$ = 32 Hz), 37.7 (d), 33.5 (t), 29.5 (tq, $^3J_{CF}$ = 3 Hz), 21.6 (q), 16.1 (d), 15.8 (d), 14.3 (d); IR (KBr) 2997, 2971, 1598, 1353, 1305, 1195, 1021, 972, 850, 818 cm$^{-1}$; HRMS (CI, $NH_3$

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as ionizing gas) calcd for $C_{15}H_{19}F_3NO_3S$ ($M+NH_4^+$) 350.1039, found 350.1041. Anal. Calcd for $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.28; H, 4.59.

**7-(Pentafluoroethyl)-7-tricyclo[2.2.1.0$^{2,6}$]heptyl *p*-Toluenesulfonate (60).** Prepared as a white, crystalline solid in 51–69% yield from **27**: mp 92 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.4 Hz, 2H), 7.31 (d, $J$ = 8.1 Hz, 2H), 2.44 (s, 3H), 2.27 (dd, $J$ = 5.1, 5.1 Hz, 1H), 2.20 (br s, 1H), 2.05–2.01 (m, 1H), 1.89–1.84 (m, 1H), 1.65–1.58 (m, 2H), 1.44–1.41 (m, 1H), 1.36–1.30 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.7 (s), 134.9 (s), 129.5 (d), 127.7 (d), 119.0 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 112.6 (tq, $^1J_{CF}$ = 262 Hz, $^2J_{CF}$ = 37 Hz), 96.9 (t, $^2J_{CF}$ = 24 Hz), 38.0 (d), 34.2 (t), 29.3 (t), 21.6 (q), 16.6 (d), 15.6 (d), 13.7 (d); IR (KBr) 3072, 2935, 1598, 1498, 1348, 1152, 994, 928, 846 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{16}H_{19}F_5NO_3S$ ($M+NH_4^+$) 400.1007, found 400.1009. Anal. Calcd for $C_{16}H_{15}F_5O_3S$: C, 50.26; H, 3.95. Found: C, 50.30; H, 4.06.

**3-(Trifluoromethyl)-3-tetracyclo[3.2.0.0$^{2,6}$.0$^{4,7}$]heptyl *p*-Toluenesulfonate (64).** Prepared as a white, crystalline solid in 48–59% yield from **21**: mp 115 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.82 (d, $J$ = 8.3 Hz, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H), 2.44 (s, 3H), 1.90–1.89 (m, 4H), 1.84–1.80 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.6 (s), 135.7 (s), 129.5 (d), 127.6 (d), 124.1 (q, $^1J_{CF}$ = 283 Hz), 100.0 (q, $^2J_{CF}$ = 30 Hz), 27.3 (d), 21.7 (q), 18.3 (d), 17.6 (d); IR (KBr) 3088, 3050, 2924, 1599, 1370, 1307, 1148, 1087, 1033, 994, 804 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{15}H_{17}F_3NO_3S$ ($M+NH_4^+$) 348.0882, found 348.0880. Anal. Calcd for $C_{15}H_{13}F_3O_3S$: C, 54.54; H, 3.97. Found: C, 54.17; H, 4.21.

**3-(Pentafluoroethyl)-3-tetracyclo[3.2.0.0$^{2,6}$.0$^{4,7}$]heptyl *p*-Toluenesulfonate (65).** Prepared as a white, crystalline solid from **28**: mp 68 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 8.1 Hz, 2H), 2.44 (s, 3H), 1.97–1.92 (m, 4H), 1.88–1.86 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.7 (s), 135.6 (s), 129.5 (d), 127.6 (d), 119.0 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 36 Hz), 113.4 (tq, $^1J_{CF}$ = 261 Hz, $^2J_{CF}$ = 37 Hz), 100.7 (t, $^2J_{CF}$ = 24 Hz), 27.6 (d), 21.6 (q), 18.4 (d), 18.0 (d); IR (KBr) 3083, 2935, 1598, 1365, 1336, 1222, 1129, 1095, 1025, 930, 827 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{16}H_{17}F_5NO_3S$ ($M+NH_4^+$) 398.0850, found 398.0849. Anal. Calcd for $C_{16}H_{13}F_5O_3S$: C, 50.53; H, 3.45. Found: C, 50.72; H, 3.63.

**Preparation of Methanesulfonate (Mesylate) Esters.** To a round-bottomed flask containing a magnetic stir bar were added the appropriate alcohol and anhydrous ethyl ether (10 mL per mmol of the alcohol). An inert atmosphere was introduced, and the flask was cooled to −10 °C. Triethylamine (3.5 equiv based on the alcohol) was added via syringe followed by the addition of neat methanesulfonyl chloride (1.25 equiv based on the alcohol) via syringe. The reaction mixture was stirred at −10 °C for 4 h and then allowed to warm to 0 °C for 1 h. A white precipitate formed in the flask. The mixture was transferred to a separatory funnel containing an equal volume of 1 N HCl/ice. The biphasic mixture was extracted with three portions of ether, and the combined extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent and volatile components were removed under vacuum. Due to the lability of these compounds, all manipulations were performed at temperatures of 0 °C or lower. The crude products contained small amounts of residual methanesulfonyl chloride, but this impurity did not affect the kinetic data.

***syn*-7-(Trifluoromethyl)-*anti*-7-bicyclo[2.2.1]hept-2-enyl Methanesulfonate (49).** Prepared as a clear, colorless oil in 76–87% yield from **23**: $^1$H NMR ($CDCl_3$) $\delta$ 5.99 (dd, $J$ = 2.1, 2.1 Hz, 2H), 3.30 (br s, 2H), 3.08 (s, 3H), 2.20–2.18 (m, 2H), 1.21 (br d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 131.1 (d), 124.5 (q, $^1J_{CF}$ = 285 Hz), 100.7 (q, $^2J_{CF}$ = 25 Hz), 46.8 (d), 39.9 (q), 22.9 (t); IR (neat) 2991, 2958, 2892, 1365, 1182, 1026, 947, 865, 836 cm$^{-1}$; HRMS (CI, isobutane as ionizing gas) calcd for $C_9H_{11}F_3O_3S$ ($M^+$) 256.0381, found 256.0363.

**7-(Trifluoromethyl)-7-bicyclo[2.2.1]hepta-2,5-dienyl Methanesulfonate (54).** Prepared as a pale yellow oil in 78–93% from **35**: $^1$H NMR ($CDCl_3$) $\delta$ 6.81 (br s, 2H), 6.67–6.64 (m, 2H), 4.02–4.00 (m, 2H), 3.00 (s, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 140.5 (d), 138.6 (d), 123.0 (q, $^1J_{CF}$ = 286 Hz), 111.9 (q, $^2J_{CF}$ = 25 Hz), 54.0 (d), 39.7 (q); IR (neat) 3022, 2944, 1365, 1186, 1018, 961, 854 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_9H_{13}F_3NO_3S$ ($M+NH_4^+$) 272.0569, found 272.0572.

**7-(Pentafluoroethyl)-7-bicyclo[2.2.1]hepta-2,5-dienyl Mesylate (55).** Prepared as a pale, yellow oil in 86–88% yield form **36**: $^1$H NMR ($CDCl_3$) $\delta$ 6.91 (br s, 2H), 6.62 (dd, $J$ = 2.5, 2.2 Hz, 2H), 4.10 (br s, 2H), 3.00 (3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 141.3 (d), 138.0 (d), 118.6 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 36 Hz), 112.4 (tq, $^1J_{CF}$ = 264 Hz, $^2J_{CF}$ = 37 Hz), 112.1 (t, $^2J_{CF}$ = 17 Hz), 54.0 (d), 40.0 (q); IR (neat) 3047, 2941, 1359, 1183, 1152, 1007, 962, 850 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) calcd for $C_{10}H_{13}F_5NO_3S$ ($M+NH_4^+$) 322.0537, found 322.0548.

**Procedure for Kinetic Analysis of Solvolysis Reactions Using the Conductimetric Method.**[61] A solution of the substrate ($5.0 \times 10^{-3}$–$8.0 \times 10^{-3}$ M) in a solvent system buffered with 2,6-lutidine (2.0 equiv based on the substrate) was prepared in a volumetric flask. The reaction solution was transferred by pipet to a glass conductance cell with platinum electrodes. The cell was sealed with a screw-cap Teflon plug and then immersed in a covered circulating bath. All solutions were prepared at temperatures at least 20 °C lower than the temperatures at which the kinetic data was obtained. Conductivity measurements were made at regular intervals after the reaction solution had reached thermal equilibrium (60–180 s). The reaction was monitored for a period of time corresponding to 3–5 half-lives, and an approximation of the infinity value of the conductivity was determined after 8–10 half-lives had expired. First-order rate constants were calculated from the slopes of plots of $\ln(C_\infty - C_t)$ vs time. Correlation constants of >0.999 were obtained for each fitted line from which a rate constant was calculated. The extrapolated values for rate constants at 25.0 °C were obtained from Arrhenius plots, and activation parameters were calculated from Eyring plots.

**Procedure for Kinetic Analysis of Reactions Using the Titrimetric Method.**[62] A solution of the substrate ($2.0 \times 10^{-2}$–$5.0 \times 10^{-2}$ M) in anhydrous acetic acid buffered with sodium acetate (2.0 equiv based on the substrate) was prepared in a 10 mL volumetric flask. Eight 1.1–1.2 mL aliquots of the reaction solution were transferred to resealable pressure tubes, and the tubes were immersed simultaneously in a covered circulating bath. Individual tubes were removed at regular intervals and quenched thermally by immediate immersion in an ice bath. The final aliquot was left in the bath until at least 8 half-lives had transpired to provide an approximation of the infinity titer. The aliquots were titrated with a standardized solution of perchloric acid ($2.0 \times 10^{-2}$ M) in anhydrous acetic acid to the bromphenol blue endpoint. The concentration of the substrate in each aliquot was calculated indirectly, and the first-order rate constants were obtained from the slopes of plots of ln[substrate] vs time. The extrapolated rate constants and activation parameters were calculated as described above.

**Procedure for Preparative Solvolyses in Anhydrous TFE.** A solution of the substrate ($1.0 \times 10^{-2}$ M) in anhydrous TFE buffered with 2,6-lutidine (2.0 equiv based on the substrate) was prepared in a 100-mL Carius tube. The tube was sealed with a screw-cap Teflon plug and immersed in a circulating bath maintained at a temperature near the middle of the range over kinetic data were obtained. The reaction was heated for a period of time corresponding to 8–10 half-lives and then allowed to cool to 25 °C. The solution was transferred to a separatory funnel, and water (half the volume of the reaction solution) was added. The aqueous solution was extracted with five portions of pentane. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated to a volume of 2–3 mL by careful distillation. The residue was passed through a small plug of silica gel to remove the amine and any intractable materials. Samples for characterization were obtained by preparative GLC. Yields were determined by GLC analysis using an internal standard.

**1-(Trifluoromethyl)bicyclo[3.2.0]heptane (41).** Prepared as a clear, colorless oil by the catalytic hydrogenation

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(62) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.

(Pd/C (10%) in ethyl acetate) of the mixture of **39** and **40**. The product was isolated by preparative GLC: $^1$H NMR ($CDCl_3$) $\delta$ 2.90−2.80 (m, 1H), 2.35 (ddd, $J$ = 12.5, 12.0, 6.2 Hz, 1H), 2.20−2.07 (m, 1H), 2.03−1.95 (m, 2H), 1.75−1.55 (m, 5H), 1.45−1.34 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 128.9 (q, $^1J_{CF}$ = 276 Hz), 51.0 (q, $^2J_{CF}$ = 27 Hz), 38.6 (dq, $^3J_{CF}$ = 2Hz), 33.0 (t), 32.9 (tq, $^3J_{CF}$ = 2 Hz), 25.1 (t), 23.6 (tq, $^3J_{CF}$ = 3Hz), 20.8 (t); IR (neat) 2956, 1446, 1373, 1311, 1299, 1218, 1144, 1046, 973 cm$^{-1}$; HRMS (EI) calcd for $C_8H_{11}F_3$ ($M^+$) 164.0813, found 164.0803.

***exo*-4-(2,2,2-Trifluoroethoxy)-1-(trifluoromethyl)bicyclo-[3.2.0]hept-2-ene (44).** Formed in 93% yield from the solvolysis of **33** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.17 (dd, $J$ = 5.2, 1.4 Hz, 1H), 6.09 (d, 5.6 Hz, 1H), 4.40 (br s, 1H), 3.78 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.77 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 2.92 (dd, $J$ = 9.9, 6.7 Hz, 1H), 2.55−2.45 (m, 1H), 2.31−2.19 (m, 1H), 1.81−1.72 (m, 1H), 1.52−1.39 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 135.2 (dq, $^3J_{CF}$ = 2 Hz), 134.1 (d), 126.1 (q, $^1J_{CF}$ = 277 Hz), 123.9 (q, $^1J_{CF}$ = 279 Hz), 90.4 (d), 65.5 (tq, $^2J_{CF}$ = 34 Hz), 57.1 (q, $^2J_{CF}$ = 30 Hz), 41.4 (dq, $^3J_{CF}$ = 2 Hz), 24.1 (tq, $^3J_{CF}$ = 2 Hz), 19.1 (t); IR (neat) 3007, 2956, 2871, 1333, 1280, 1162, 1115, 1067, 969, 937 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_{10}F_6O$ ($M^+$) 260.0636, found 260.0631.

**1-(Pentafluoroethyl)-*exo*-4-(2,2,2-trifluoroethoxy)-bicyclo[3.2.0]hept-2-ene (45).** Formed in 93% yield from the solvolysis of **34** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.17 (d, $J$ = 5.6 Hz, 1H), 6.08 (d, $J$ = 5.0 Hz, 1H), 4.34 (br s, 1H), 3.80 ($^3J_{HF}$ = 8.7 Hz, 1H), 3.79 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.05 (dd, $J$ = 10.0, 6.8 Hz, 1H), 2.63−2.53 (m, 1H), 2.31−2.19 (m, 1H), 1.79−1.71 (m, 1H), 1.51−1.39 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 135.1 (d), 133.7 (d), 123.9 (q, $^1J_{CF}$ = 279 Hz), 119.5 (qt, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 37 Hz), 114.3 (tq, $^1J_{CF}$ = 252 Hz, $^2J_{CF}$ = 36 Hz), 90.0 (d), 65.9 (tq, $^2J_{CF}$ = 34 Hz), 56.3 (t, $^2J_{CF}$ = 25 Hz), 41.5 (dt, $^3J_{CF}$ = 3 Hz), 24.1 (tt, $^3J_{CF}$ = 3 Hz), 19.4 (t); IR (neat) 3010, 2957, 2872, 1439, 1353, 1280, 1167, 1115, 1003 cm$^{-1}$; HRMS (EI) calcd for $C_{11}H_{10}F_8O$ ($M^+$) 310.0604, found 310.0600.

**2-(2,2,2-Trifluoroethoxy)-7-(trifluoromethyl)tricyclo-[2.2.1.0$^{3,7}$]heptane (52).** Formed in 67−68% yield from the solvolysis of **46** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 4.11 (dd, $J$ = 7.3, 4.1 Hz, 1H), 3.74 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.72 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.04−3.01 (m, 1H), 2.42−2.38 (m, 1H), 2.10−2.06 (m, 1H), 2.01−1.84 (m, 3H), 1.80−1.73 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.3 (q, $^1J_{CF}$ = 268 Hz), 123.7 (q, $^1J_{CF}$ = 279 Hz), 70.1 (d), 66.0 (tq, $^2J_{CF}$ = 34 Hz), 43.7 (d), 32.2 (q, $^2J_{CF}$ = 40 Hz), 28.6 (t), 28.5 (d), 28.3 (d), 24.2 (t); IR (neat) 2953, 1465, 1329, 1281, 1132, 1060, 976 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_{10}F_6O$ ($M^+$) 260.0636, found 260.0636.

**7-(Pentafluoroethyl)-2-(2,2,2-trifluoroethoxy)tricyclo-[2.2.1.0$^{3,7}$]heptane (53).** Formed in 69−72% yield from the solvolysis of **47** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 4.10 (dd, $J$ = 7.2, 4.1 Hz, 1H), 3.74 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.73 (q, $^3J_{HF}$ = 8.6 Hz, 1H), 3.02−3.00 (m, 1H), 2.46−2.42 (m, 1H), 2.09−2.06 (m, 1H), 2.01−1.73 (m, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 123.7 (q, $^1J_{CF}$ = 279 Hz), 119.3 (qt, $^1J_{CF}$ = 285 Hz, $^2J_{CF}$ = 39 Hz), 114.4 (tq, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 38 Hz), 70.0 (d), 66.0 (tq, $^2J_{CF}$ = 34 Hz), 44.3 (dd, $^3J_{CF}$ = 4 Hz), 30.6 (dd, $^2J_{CF}$ = 30, 27 Hz), 28.9 (dd, $^3J_{CF}$ = 5 Hz), 28.2 (t), 27.9 (d), 24.0 (t); IR (neat) 2954, 1442, 1350, 1281, 1170, 1091, 1021, 969 cm$^{-1}$; HRMS (EI) calcd for $C_{11}H_{10}F_8O$ ($M^+$) 310.0604, found 310.0620.

**1-[*trans*-5-(2,2,2-Trifluoroethyl)vinyl Ether]-1-(trifluoromethylcyclopenta-2,4-diene (57).** Formed in 77% yield from the solvolysis of **54** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.52 (d, $J$ = 5.1 Hz, 2H), 6.51 (d, $J$ = 11.9 Hz, 1H), 6.33−6.30 (m, 2H), 5.22 (d, $J$ = 12.7 Hz, 1H), 4.03 (q, $^3J_{HF}$ = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 146.3 (d), 134.5 (d), 134.2 (d), 125.7 (q, $^1J_{CF}$ = 282 Hz), 123.0 (q, $^1J_{CF}$ = 278 Hz), 99.6 (dq, $^3J_{CF}$ = 2 Hz), 66.7 (tq, $^2J_{CF}$ = 36 Hz), 62.7 (q, $^2J_{CF}$ = 28 Hz); IR (neat) 3088, 3067, 2951, 1674, 1656, 1268, 1169, 1087, 997, 979, 964 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_8F_6O$ ($M^+$) 258.0479, found 258.0476.

**1-(Pentafluoroethyl)-1-[*trans*-5-(2,2,2-trifluoroethyl)-vinyl ether]cyclopenta-2,4-diene (58).** Formed as the only isolable product from the solvolysis of **55** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.51 (d, $J$ = 4.5 Hz, 2H), 6.49 (d, $J$ = 12.8 Hz, 1H), 6.35−6.32 (m, 2H), 5.24 (d, $J$ = 12.6 Hz, 1H), 4.02 (q, $^3J_{HF}$ = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 145.7 (d), 134.1 (d), 133.9 (d), 123.0 (q, $^1J_{CF}$ = 278 Hz), 119.2 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 37 Hz), 115.6 (tq, $^1J_{CF}$ = 259 Hz, $^2J_{CF}$ = 36 Hz), 99.3 (dt, $^3J_{CF}$ = 4Hz), 66.7 (tq, $^2J_{CF}$ = 36 Hz), 61.5 (t, $^2J_{CF}$ = 22 Hz); IR (neat) 3090, 2951, 1672, 1651, 1342, 1316, 1286, 1203, 979, 924 cm$^{-1}$; HRMS (EI) calcd for $C_{11}H_8F_8O$ ($M^+$) 308.0447, found 308.0433.

***exo*-5-(2,2,2-Trifluoroethoxy)-2-(trifluoromethyl)bicyclo-[2.2.1]hept-2-ene (62).** Formed in 66−67% yield from the solvolysis of **59** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.38 (br s, 1H), 3.83 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.83 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.72−3.70 (m, 1H), 3.05 (br s, 2H), 1.85−1.75 (m, 3H), 1.56 (ddd, $J$ = 12.7, 2.9, 2.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 143.2 (q, $^2J_{CF}$ = 34 Hz), 135.8 (dq, $^3J_{CF}$ = 6 Hz), 123.8 (q, $^1J_{CF}$ = 279 Hz), 122.7 (q, $^1J_{CF}$ = 268 Hz), 81.4 (dq, $^3J_{CF}$ = 3 Hz), 67.1 (tq, $^2J_{CF}$ = 34 Hz), 47.5 (d), 46.6 (t), 40.2 (d), 34.2 (t); IR (neat) 2990, 2954, 1643, 1353, 1298, 1156, 1035, 992, 968 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_{10}F_6O$ ($M^+$) 260.0636, found 260.0640.

**2-(Pentafluoroethyl)-*exo*-5-(2,2,2-trifluoroethoxy)-bicyclo[2.2.1]hept-2-ene (63).** Formed in 61−65% yield from the solvolysis of **60** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.50−6.48 (m, 1H), 3.84 (q, $^3J_{HF}$ = 8.6 Hz, 1H), 3.83 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.72 (d, $J$ = 6.1 Hz, 1H), 3.09 (br s, 2H), 1.86−1.74 (m, 3H), 1.56 (ddd, $J$ = 14.0 3.0 2.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 142.3 (t, $^2J_{CF}$ = 24 Hz), 138.6 (dt, $^3J_{CF}$ = 8 Hz), 123.8 (q, $^1J_{CF}$ = 278 Hz), 118.9 (qt, $^1J_{CF}$ = 286 Hz, $^2J_{CF}$ = 38 Hz), 112.1 (tq, $^1J_{CF}$ = 249 Hz, $^2J_{CF}$ = 39 Hz), 81.2 (dt, $^3J_{CF}$ = 4 Hz), 66.9 (tq, $^2J_{CF}$ = 34 Hz), 47.9 (d), 47.1 (t), 40.8 (d), 34.2 (t); IR (neat) 2992, 2955, 1630, 1289, 1206, 1124, 1075, 970 cm$^{-1}$; HRMS (EI) calcd for $C_{11}H_{10}F_8O$ ($M^+$) 310.0604, found 310.0609.

***syn*-7-(2,2,2-Trifluoroethoxy)-2-(trifluoromethyl)bicyclo-[2.2.1]hepta-2,5-diene (67).** Formed in 47−48% yield from the solvolysis of **65** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 6.97 (br s, 1H), 6.77−6.74 (m, 1H), 6.67−6.64 (m, 1H), 3.85 (br s, 1H), 3.72 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.71 (q, $^3J_{HF}$ = 8.7 Hz, 1H), 3.70−3.66 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 140.7 (dq, $^3J_{CF}$ = 5 Hz), 140.6 (q, $^2J_{CF}$ = 35 Hz), 139.1 (d), 139.0 (d), 123.6 (q, $^1J_{CF}$ = 266 Hz), 123.6 (q, $^1J_{CF}$ = 280 Hz), 108.0 (d), 66.5 (tq, $^2J_{CF}$ = 35 Hz), 53.6 (d), 51.8 (d); IR (neat) 3006, 2942, 1643, 1560, 1345, 1302, 1128, 1033, 967, 834 cm$^{-1}$; HRMS (EI) calcd for $C_{10}H_8F_6O$ ($M^+$) 258.0479, found 258.0481.

**2-(Pentafluoroethyl)-*syn*-7-(2,2,2-trifluoroethoxy)-bicyclo[2.2.1]hepta-2,5-diene (68).** Formed in 45% yield from the solvolysis of **68** in TFE: $^1$H NMR ($CDCl_3$) $\delta$ 7.06 (br s, 1H), 6.74−6.72 (m, 1H), 6.68−6.64 (m, 1H), 3.85 (br s, 1H), 3.74−3.70 (m, 2H), 3.71 (q, $^3J_{HF}$ = 8.6 Hz, 1H), 3.70 (q, $^3J_{HF}$ = 8.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 143.4 (dt, $^3J_{CF}$ = 7 Hz), 139.6 (t, $^2J_{CF}$ = 26 Hz), 139.1 (d) 139.0 (dt, $^3J_{CF}$ = 2 Hz), 123.5 (q, $^1J_{CF}$ = 279 Hz), 118.6 (qt, $^1J_{CF}$ = 231 Hz, $^2J_{CF}$ = 39 Hz), 113.0 (tq, $^1J_{CF}$ = 249 Hz, $^2J_{CF}$ = 39 Hz), 107.9 (d), 66.4 (tq, $^2J_{CF}$ = 35 Hz), 54.0 (d), 52.5 (d); IR (neat) 3009, 2943, 1633, 1561, 1294, 1206, 1094, 1064, 967 cm$^{-1}$; HRMS (EI) calcd for $C_{11}H_8F_8O$ ($M^+$) 308.0447, found 308.0446.

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**Supplementary Material Available:** Tables of the absolute rate constants for the solvolyses of all substrates not fully listed in the text; Grunwald−Winstein plots for substrates **42** and **46** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.