Solvolyses of α-Keto Norbornyl Trifluoroacetates and Triflates. Discrete α-Keto Cations vs. σ-Assisted (k_Δ) Processes

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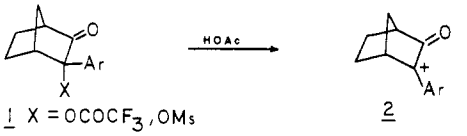
Abstract: Trifluoroacetate derivatives of *exo*-2-hydroxy-*endo*-2-aryl bicyclo[2.2.1]heptan-3-ones **13** and **14** have been prepared and solvolyzed in acetic acid. Small amounts of *endo*-trifluoroacetate products, via internal return, as well as major unrearranged products **15** attest to the involvement of classical aryl stabilized α-keto cations **16**. The exo/endo rate ratios are 126 and 141 and are considered normal in 2-norbornyl systems. In contrast, the exo/endo ratios for solvolyses in the secondary systems, *exo*- and *endo*-bicyclo[2.2.1]heptan-3-on-2-yl triflates **7** and **6**, are considerably larger (approaching 10^5). This has been interpreted in terms of increased σ-participation in the exo system **7** as a result of increased electron demand due to the inductive effect of the adjacent carbonyl group. Both **6** and **7** gave the same rearranged ester **25** on trifluoroethanolysis. Deuterium-labeling studies confirmed that different rearrangement pathways operate. A k_Δ process involving C_1C_6 participation is suggested for **7**, while C_1C_7 participation in **6** accounts for the results of the labeling study. No evidence for the discrete existence of secondary α-keto cations could be obtained.

Our previous studies have shown that α-keto cations can be generated solvolytically from trifluoroacetates and mesylates **1** and tresylate **3**.[1,2] Subsequent studies[3] have shown that many

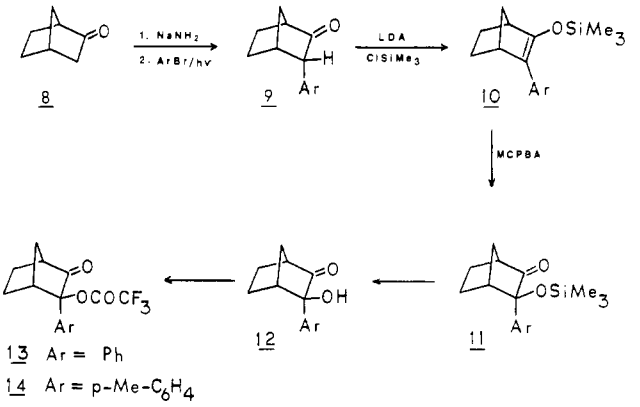


α-keto cations can be generated with surprising ease. This led to a suggestion that substantial stabilization can be derived from a resonance interaction represented by **5b**. This conjugative stabilization could largely offset the inductive destabilizing effect of the carbonyl group. To date, we have successfully generated tertiary benzylic, secondary benzylic α-keto cations, as well as dialkyl substituted tertiary α-keto cations. However, we have reported[1] that the secondary triflate **6** was unreactive even for extended periods in acetic acid. In view of the recently recognized potential for a stabilizing carbonyl conjugative interaction, and the availability of more highly ionizing nonnucleophilic solvents, we wanted to investigate the viability of secondary nonbenzylic α-keto cations. We have chosen to investigate the chemistry of triflates **6** and **7**. We also wanted to compare the solvolytic reactivity of **6** with that of the exo isomer **7**. This exo/endo ratio

should be of interest since it has still not been determined to what extent exo/endo ratios in norbornyl systems can be used as a diagnostic probe for neighboring σ-participation. We also wanted to compare the exo/endo ratio in the secondary systems **6** and **7** with the ratio in tertiary systems. Reported here are the results of these studies.

Results and Discussion

Exo/Endo Rate Ratios in Tertiary α-Keto Norbornyl Systems. The preparation and chemistry of mesylates and trifluoroacetates of structure **1** have been described previously.[1] The systems of current interest, the isomeric *exo*-trifluoroacetates, were prepared as shown below. Arylation of norcamphor enolate in a photoinitiated $S_{RN}1$ reaction[4] proved to be a convenient source of ketones **9**. Conversion of **9** to the silyl enol ether **10** was followed by peracid oxidation to the siloxy ketone **11**.[5] Desilylation of **11** and conversion to trifluoroacetates **13** and **14** are straightforward.



Both trifluoroacetates **13** and **14** were solvolyzed in acetic acid and gave unrearranged acetates **15** as the major products. Also produced were small amounts (4–7%) of the inverted trifluoroacetates, **1**, which are less reactive under the reaction conditions. These unrearranged products presumably arise from solvent

(1) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938–45.
(2) Creary, X. *J. Am. Chem. Soc.* **1981**, *103*, 2463–5.
(3) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151–62.
(4) (a) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407–10. (b) Rossi, R. A.; Bunnett, J. F. *Ibid.* **1973**, *38*, 3020–5. (c) Bunnett, J. F.; Sundberg, J. E. *Chem. Pharm. Bull.* **1975**, *23*, 2620. (d) Bunnett, J. F.; Sundberg, J. E. *J. Org. Chem.* **1976**, *41*, 1702–1706.
(5) For examples of this general transformation, see: (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319–22. (b) Brook, A. G.; Macrae, D. M. *J. Organomet. Chem.* **1974**, *77*, C19–21. (c) Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3427–9.

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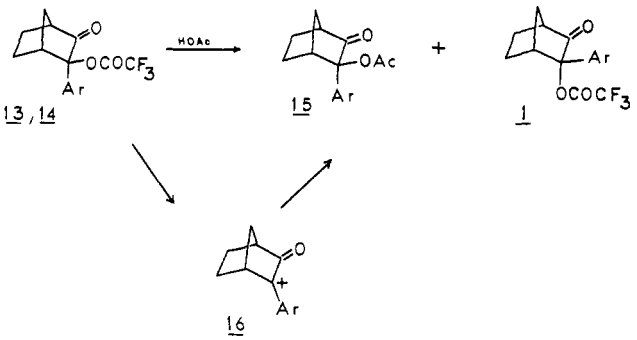
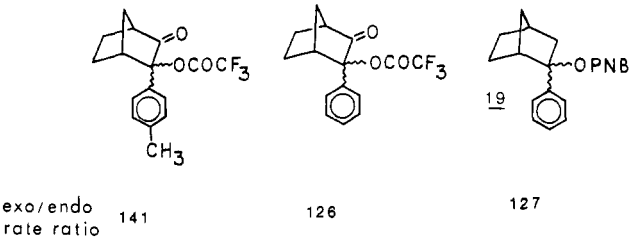
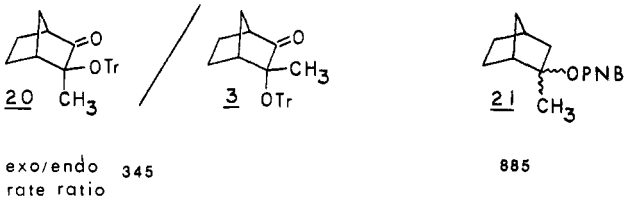


capture and internal return in the aryl-stabilized benzylic α-keto cation **16**. The formation of small amounts of **1** is significant in that this product rules out involvement of σ-delocalized nonclassical ions.[6] The same major product, **15**, is also seen in solvolyses of the *endo*-mesylates and trifluoroacetates **1** (Ar = Ph, *p*-$CH_3C_6H_4$), and the same cationic intermediate, **16**, was the suggested intermediate.[1,2]

Of immediate interest was the exo/endo ratio in these systems. Rate data, which permit computation of these values, are given in Table I. The exo/endo ratio **13**:**17** is 126 and is comparable



to the value of 141 for **14**:**18**. These are, in turn, quite comparable to the exo/endo ratios seen by Brown[7] in the deoxy systems **19**. These systems all solvolyze, giving classical tertiary benzylic norbornyl cations as intermediates. Our results therefore further substantiate Brown's contention[7] that exo/endo ratios of the magnitude seen are "normal" and do not implicate neighboring σ-participation. The values seen in the benzylic systems **13**/**17** and **14**/**18** are also similar to the value of 345 previously reported[1] for the tertiary tresylate **3** and its exo analogue **20**. A slightly larger value of 885 was seen in the deoxy system **21**.[8] We

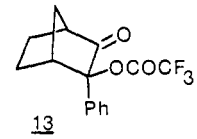
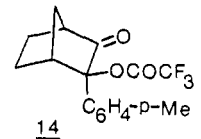
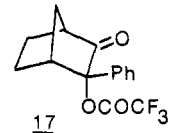
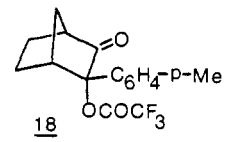
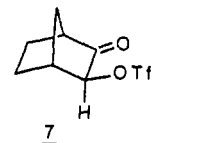
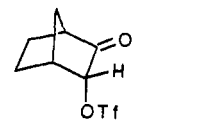
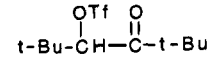


conclude that exo/endo ratios in the 10^2 to 10^3 range are also normal for the solvolytic generation of α-keto cations in the norbornyl system.

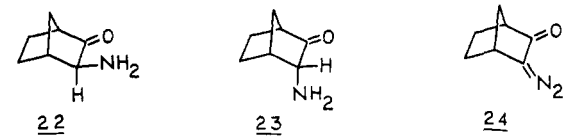
Solvolytic Studies on Secondary α-Keto Norbornyl Systems. The deamination of amines **22** and **23** has been reported[9] as has the chemistry of diazo ketone **24** under acid conditions.[10] These processes presumably lead to diazonium ions and resultant carbocationic intermediates. Solvolytic studies were therefore carried out on triflates **6** and **7** to permit determination of an exo/endo rate ratio and to compare their behavior with that of the diazonium ions derived from **22**, **23**, and **24**.

The *exo*-triflate **7** solvolyzes at a convenient rate at 25 °C in a variety of solvents (see Table I). In trifluoroethanol, **7** gave

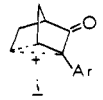
Table I. Solvolyses of α-Keto Norbornyl Trifluoroacetates and Triflates

compound	solvent[a]	temp (°C)	k (s^{-1})
 **13**	HOAc	90.0	7.56×10^{-4}
		70.0	8.59×10^{-5}
		25.0[b]	2.25×10^{-7}
 **14**	HOAc	25.0	2.66×10^{-5}
 **17**	HOAc	25.0[b,c]	1.78×10^{-9}
 **18**	HOAc	25.0[b,c]	1.89×10^{-7}
 **7**	TFE	50.0	3.52×10^{-4}
		25.0	2.17×10^{-5}
	HOAc	25.0[b,c]	2.58×10^{-6}
	HCO_2H	25.0	1.62×10^{-4}
	HFIP	25.0	3.33×10^{-5}
	TFA	25.0	4.6×10^{-5}
 **6**	TFE	140.1	5.45×10^{-5}
		100.0	2.30×10^{-6}
		25.0[b]	6.41×10^{-10}
	HCO_2H	120.0	2.09×10^{-4}
		110.0	8.07×10^{-5}
		100.0	2.90×10^{-5}
		25.0[b]	1.70×10^{-9}
	HFIP	130.0	2.44×10^{-5}
		100.0	2.27×10^{-6}
		25.0[b]	7.64×10^{-10}
 **42**	HOAc	25.0[b,c]	4.15×10^{-6}
	TFE	25.0	4.36×10^{-5}
	HCO_2H	25.0	2.22×10^{-4}
	HFIP	25.0	1.82×10^{-4}
	TFA	25.0	2.0×10^{-4}

[a] HOAc, 0.1 M in NaOAc with 1% acetic anhydride; TFE, trifluoroethanol, 0.025 M in 2,6-lutidine; HCO_2H, 0.05 M in sodium formate; HFIP, 97% hexafluoroisopropyl alcohol, 3% H_2O, 0.05 M in 2,6-lutidine; TFA, trifluoroacetic acid, 0.2 M in sodium trifluoroacetate with 1% trifluoroacetic anhydride. [b] Extrapolated from data at higher temperatures. [c] Reference 1.



(6) If nonclassical ions such as i were involved, then internal return would yield only the starting trifluoroacetate.



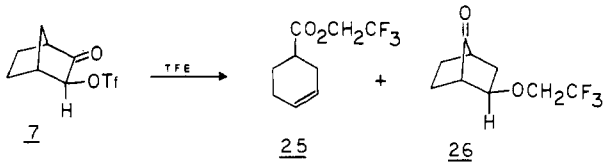
(7) (a) Takeuchi, K.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2693–4. For related pertinant studies, see also: (b) Brown, H. C.; Takeuchi, K. *Ibid.* **1968**, *90*, 2691–3.

(8) Brown, H. C.; Ikegami, S. *J. Am. Chem. Soc.* **1968**, *90*, 7122–4.

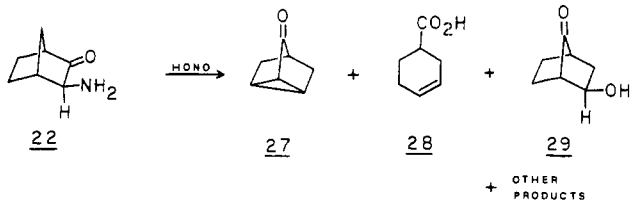
(9) Edwards, O. E.; Dixon, J.; Elder, J. W.; Kolt, R. J.; Lesage, M. *Can. J. Chem.* **1981**, *59*, 2096–2115.

(10) (a) Yates, P.; Crawford, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 1561–2. (b) Batattel, R. A.; Yates, P. *Tetrahedron Lett.* **1972**, 1069–72, 1073–6. (c) Siegfried, R. *Chem. Ber.* **1974**, *107*, 1472–82. For related studies, see: (d) Yates, P.; Kronis, J. D. *Tetrahedron Lett.* **1983**, 2419–2422.

the unraveled ester **25** as the major product (58%) along with smaller amounts of the rearranged product **26** (26%). In contrast,

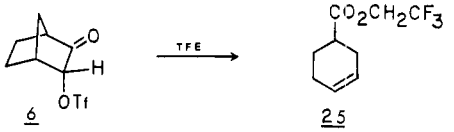


deamination of **22** in acetic acid gave a complex product mixture.[9] Aqueous deamination of **22** also gave a complex mixture containing only 6% of **28**. Also formed was 15% of **29** and 3% of **27**. We suggest that, because of longer cation lifetimes in the



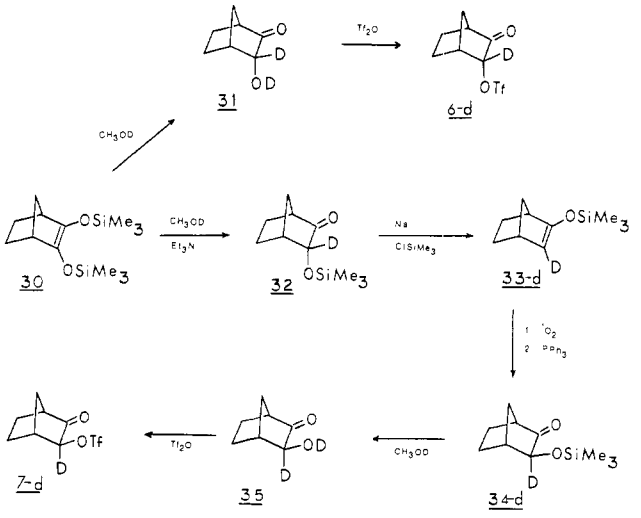
highly ionizing nonnucleophilic trifluoroethanol solvent,[11] rearrangement processes in cationic intermediates derived from **7** are more extensive. At the bottom of the rearrangement manifold is an acylium ion precurser to **25**.

Triflate **6**, which was unreactive in acetic acid,[1] could be induced to solvolyze at elevated temperatures in highly ionizing, nonnucleophilic solvents trifluoroethanol, hexafluoroisopropyl alcohol, and formic acid. Trifluoroethanolysis of **6** at 140 °C gave the same unraveled ester **25**, that was produced in trifluoroethanolysis of the exo isomer **7**. An analogous rearranged product is seen



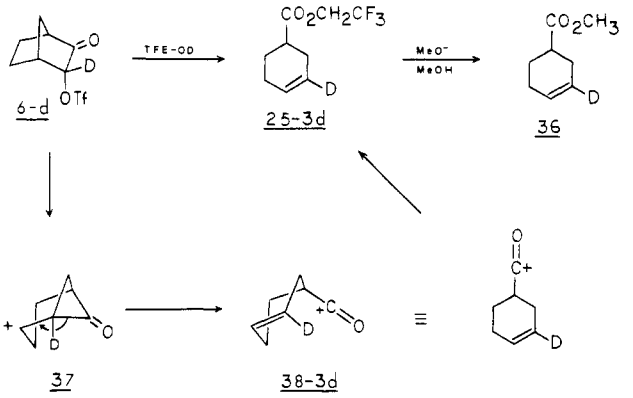
in solvolysis of the diazonium ion derived from **23**[9] and **24**.[10] However, the completely unraveled ester product is only a minor one from the diazonium ion in solvents of relatively high nucleophilicity. Interestingly, **25** becomes the major product derived from protonation of **24** in trifluoroethanol.[10c] This further supports the contention that longer cation lifetimes in trifluoroethanol can lead to more extensive cationic rearrangements.

To gain insights into the mechanistic origin of **25** from triflates **6** and **7**, the deuterated triflates **6-*d*** and **7-*d*** were prepared.



Methanolysis of **30** in CH_3OD gave **31** which was readily converted to **6-*d***. The key to the preparation of **7-*d*** involved the preparation of the deuterated silyl enol ether of norcamphor, **33-*d***. Difficulties were encountered in obtaining completely deuterated **33-*d*** from 3,3-dideuterionorcamphor[12] using standard silylation procedures. Therefore, an alternate route was developed. We have previously shown[13] that **30** can be selectively monodesilylated to give the corresponding α-siloxy ketone with triethylamine in methanol. Use of CH_3OD allowed preparation of **32** which contained the trimethylsiloxy leaving group adjacent to the carbonyl group. Reduction of **32** with sodium metal in ether in the presence of chlorotrimethylsilane results in loss of the α-trimethylsiloxy group and silylation of the resultant deuterated norcamphor enolate. Oxidation of **33-*d*** with singlet oxygen and deoxygenation of the resultant peroxide according to the Jefford procedure[14] gave **34-*d***. Methanolysis of **34-*d*** gave **35**. Conversion to **7-*d*** was accomplished by addition to a solution of triflic anhydride in pyridine immediately after removal of the methanol solvent (before extensive dimerization could occur). This procedure is more convenient than our previously described method[15] of preparation of **7** from the acyloin dimer.

Solvolytic studies were carried out on **6-*d*** and **7-*d***. The ester isolated from trifluoroethanolysis of **6-*d*** contained only about 0.5 D/molecule. The remainder of the deuterium was presumably lost via enolization under the strenuous conditions (140 °C) necessary to achieve solvolysis. To avoid this problem, tri-



fluoroethanolysis was therefore carried out in CF_3CH_2OD. In this solvent, only the monodeuterated ester **25-*3-d*** was produced. The position of the label was determined by ^{13}C NMR (see Experimental Section) and by transesterification to give the known[16] methyl ester **36**. The mechanism involving C_1C_7 participation followed by fragmentation of **37** to the acylium ion **38-*3-d*** accounts for the position of the deuterium in **25-*3-d***.

In contrast, trifluoroethanolysis of **7-*d*** gave only **25-*4-d*** as the ester product. A mechanism involving C_1C_6 participation would give **39-*d***. Fragmentation of **36-*d***[17] to the acylium ion **38-*4-d***

(11) For a discussion of the properties of trifluoroethanol, see: (a) Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838–43. For nucleophilicity and ionizing power values of trifluoroethanol, see also: (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667–74.

(12) (a) Schaefer, J. P.; Dagani, M. J.; Weinberg, D. S. *J. Am. Chem. Soc.* **1967**, *89*, 6938–44. (b) Tidwell, T. T. *Ibid.* **1970**, *92*, 1448–9.

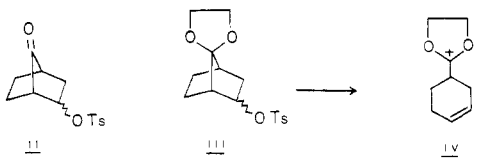
(13) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1979**, *44*, 1017–20.

(14) (a) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437–45. (b) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1977**, 2375–7.

(15) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4226–30.

(16) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4231–8.

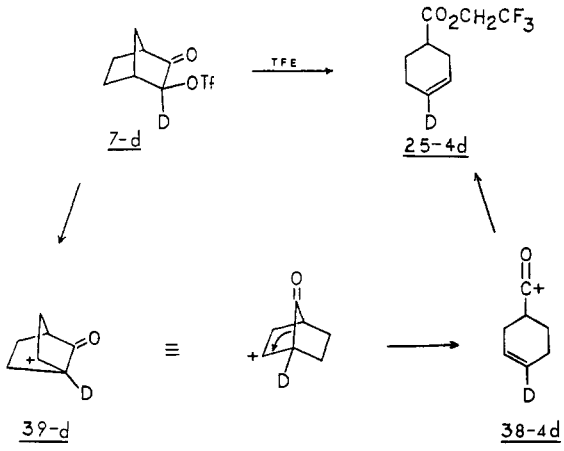
(17) For a discussion of the chemistry of cation **39**, derived from ii, see:



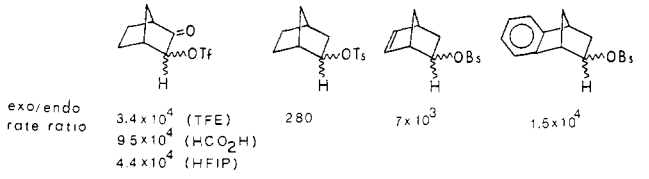
Gassman, P. G.; Marshall, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 2822–30. In contrast to the behavior of **7**, no fragmentation products analogous to **25** are formed in solvolysis of ii in acetic acid. However, an analogous fragmentation process giving iv has been observed in solvolysis of the ethylene glycol ketal iii. See: Gassman, P. G.; Macmillan, J. G. *Ibid.* **1969**, *91*, 5527–31.

would account for the observed product from **7-d**. These two labeling studies verify that the unraveled ester products found in solvolyses of **6** and **7** arise by completely different rearrangement pathways.

Exo/Endo Rate Ratios in Secondary α-Keto Norbornyl Triflates. Rate data in Table I allow calculation of the exo/endo ratio for solvolyses of **7** and **6** in trifluoroethanol, formic acid, and hexafluoroisopropyl alcohol. The exo isomer **7** is 3.4×10^4, 9.5×10^4, and 4.4×10^4 times more reactive than **6**, respectively, in these



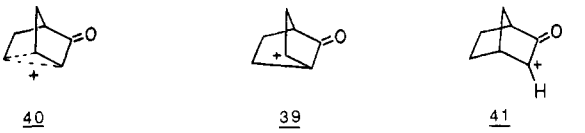
solvents.[34] These exo/endo ratios are considerably larger than the values seen for the tertiary systems which lead to discrete α-keto cations. The values seen for **7** and **6** also larger than the value of 280 seem in unsubstituted 2-norbornyl tosylates.[18] They are even slightly larger than exo/endo ratios in norborn-5-en-3-yl brosylates[19] and benzonorbornen-2-yl brosylates,[20] where neighboring π-participation has been firmly established. We suggest that the unusually large exo/endo ratios for **7** and **6** can be interpreted in terms of a k_Δ process in solvolysis of the exo isomer **7** involving the C_1C_6 σ bond. The presence of the electron-



withdrawing carbonyl group in **7** results in an increased demand for stabilization in the cationic intermediate and a resultant increase in the magnitude of anchimeric assistance due to neighboring σ-participation.

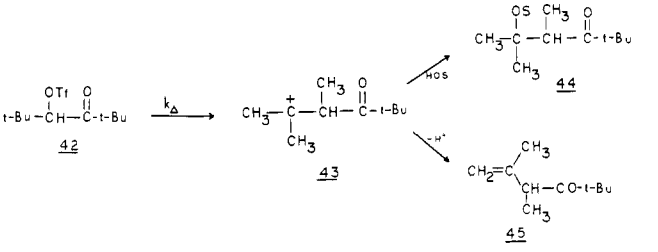
This phenomenon, an increase in the magnitude of anchimeric assistance due to increased demand for stabilization at a cationic center, is well documented. It was dramatically demonstrated by Gassman and Fentiman[21] who observed major decreases in π-participation in *anti*-7-norbornenyl systems as a result of aryl stabilization of the incipient cationic center. Brown[22] has used this technique on numerous occasions as a probe for neighboring-group participation. More recently,[23] Lambert has seen increased phenyl participation, leading to phenonium ions, as a result of increased electron demand. Increased π-participation has also been demonstrated by Gassman[24] by substitution of the cyano group for hydrogen at an incipient cationic center. The exo/endo ratio observed for **7** and **6** demonstrates that increasing electron demand can also result in increased σ-participation in the norbornyl system. This result contrasts with previous studies of Lambert[25] which failed to show increases in exo/endo rate ratios as a result of increasing electron demand in 2-norbornyl systems. When one considers the distinct possibility (based on the rearranged product) that solvolysis of *endo*-triflate **6** is also anchimerically assisted, then the ratio of the solvolysis rate of **7** to the unassisted rate of **6** is even larger than the exo/endo ratios given. We have not been able to rationalize such large exo/endo ratios by anything other than neighboring σ-participation in **7**.[26]

What is the nature of the first intermediate derived from solvolysis of **7**? Edwards[9] has suggested a nonclassical ion of type **40** (which is termed a corner-protonated cyclopropane) in deamination of **22**. While our results do not support or rule out such



an intermediate, we favor the view in which the classical ion **39** is the actual first intermediate. Neighboring σ-participation in **7** would lead to a delocalized transition state (**40**) as the system attempts to avoid the secondary σ-keto cation **41** and cascades downward to the β-keto cation **39**.

Solvent Effects in Solvolyses of Secondary α-Keto Triflates. It is of interest to examine the effect of solvents on the reactivity of **6** and **7**. For **7**, only minor rate increases are seen with increasing solvent ionizing power. The entire rate spread is only a factor of 63 in the five solvents studied. The correlation of rate with Y_{OTs} values[27] is poor ($m = 0.26$; $r = 0.81$). The behavior of **6** is analogous. To gain insight into this relatively small solvent effect on rate, the rate behavior of triflate **42** in various solvents was examined. Triflate **42**, which solvolyzes via a k_Δ process



(18) (a) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375–6. See also: (b) Winstein, S.; Trifan, D. *Ibid.* **1952**, *74*, 1147–54, 1154–60.

(19) (a) Winstein, S.; Walborsky, H.; Schreiber, K. C. *J. Am. Chem. Soc.* **1950**, *72*, 5795. See also: (b) Brown, H. C.; Peters, E. N. *Ibid.* **1975**, *97*, 7442–48.

(20) (a) Brown, H. C.; Tritle, G. L. *J. Am. Chem. Soc.* **1968**, *90*, 2689–91. See also: (b) Bartlett, P. D.; Giddings, W. P. *Ibid.* **1960**, *82*, 1240.

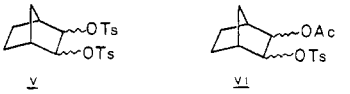
(21) Gassman, P. G.; Fentiman, A., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–51.

(22) For a summary and leading references, see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

(23) Lambert, J. B.; Mark, H. W.; Magyar, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 3059–67. For related examples, see: Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317–24.

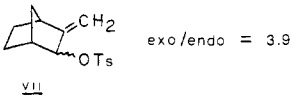
(24) (a) Gassman, P. G.; Doherty, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 3742–4. (b) Gassman, P. G.; Talley, J. J.; Saito, K.; Guggenheim, T. L.; Doherty, M. M.; Dixon, D. A. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1983**, 28 (2), 334–8.

(25) Previous studies by Lambert did not show evidence for increased σ-participation due to increasing electron demand in systems v and vi. See:



(a) Lambert, J. B.; Mark, H. W. *Tetrahadron Lett.* **1976**, 1765–8. (b) Lambert, J. B.; Mark, H. W. *J. Am. Chem. Soc.* **1978**, *100*, 2501–5. Apparently the carbonyl group attached directly to the incipient cationic center of **7** exerts a larger electronic demand for σ-participation than the β-tosyloxy of acetoxy groups of v and vi.

(26) While the exo/endo ratio for **7**/**6** increases (relative to unsubsituted 2-norbornyl tosylates), the exo/endo ratio decreases in the unsaturated analogs

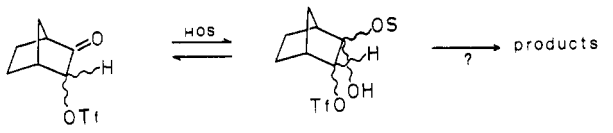


vii. While the comparison is interesting, we do not wish to speculate on the relevance of this trend. Problems associated with interpreting the exo/endo ratio in vii have been pointed out.[22]

(27) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–74.

involving methyl migration, also gives a small response to solvent ionizing power; the rate spread in the five solvents studied is only a factor of 53 and the correlation with Y_{OTs} is also poor. Previously we have observed decreased responses to increasing solvent ionizing power in solvolyses of cyclopropyl triflates.[28] Similar observations have been made by Schiavelli and Stang in solvolyses of certain vinyl triflates.[29] We attribute part part of this decreased response to the lowered solvation requirements of the stable trifluoromethanesulfonate ion. Delocalization of positive charge in the transition state for solvolyses of **6**, **7**, and **42** may further lower the solvent response.

These solvent effect data can be used to argue against a potential mechanism involving solvent addition to the carbonyl group of **6** or **7**, followed by solvolysis of the resultant tetrahedral adduct **46**. We feel that such a mechanism is unlikely owing to the low



46

nucleophilicity of HCO_2H, TFE, HFIP, and TFA. Additionally, solvent effects in reaction of **6** and **7** parallel those seen in solvolysis of **42**. The presence of the large *tert*-butyl groups should make solvent addition to the carbonyl group of **42** very unfavorable. If **6** and **7** reacted via **46**, then it would be quite fortuitous if solvent effect were the same as in solvolysis of **42**. One should bear in mind that, even if the tetrahedral adduct **46** were reversibly formed, solvolysis of such an adduct would be quite slow owing to the inductive effect of the adjacent electronegatively substituted tetrahedral center.[30] While the adduct **46** may well form reversibly under solvolytic conditions, we feel that it does not lie along the pathway leading to products.

Conclusions

Exo/endo ratios in norbornyl systems solvolyzing via discrete α-keto cation intermediates are in the "normal" range of 10^2 to 10^3. However, the exo/endo ratio in secondary 3-keto-2-norbornyl triflates **6** and **7** is much larger (10^4 to 10^5). Deuterium-labeling studies verify that these two systems, **6** and **7**, solvolyze in trifluoroethanol to give the trifluoroethyl ester of cyclohex-3-enecarboxylic acid (**25**) by completely different mechanisms. It is suggested that the large exo/endo ratio in these systems implicates neighboring σ-participation in the *exo*-norbornyl system. Increased σ-participation is a result of increased electron demand due to the inductive destabilizing effect of the carbonyl group. Carbonyl conjugation as a stabilizing feature is apparently not of sufficient magnitude to offset σ-participation and permit formation of discrete secondary α-keto cations.

Experimental Section

Preparation of *endo*-3-Phenylbicyclo[2.2.1]heptan-2-one (9, Ar = Ph). A solution of potassium amide in liquid ammonia was prepared by the addition of 4.1 g of potassium to 500 mL of ammonia followed by a trace of $FeCl_3$. After the blue color was discharged, 11.55 g of norcamphor (liquefied by addition of 4 mL of ether) was added dropwise to the mixture at about −50 °C. Bromobenzene (4.8 g) was then added to the solution at −33 °C. The mixture (under nitrogen) was then placed in a Griffin–Srinivasan photochemical reactor equipped with "350-nm" wavelength lamps. The mixture was irradiated for 3 h and 30 min. During this time, the frost which developed on the flask was periodically removed. Excess NH_4Cl was then added and the ammonia was allowed to evaporate. The residue was taken up into ether and water. The organic phase was dried over Na_2SO_4 and the solvent was removed by rotary evaporatory. The excess norcamphor and unreacted bromobenzene were removed by distillation at 15 mm. A 3.6-g fraction, bp 94–120 °C (0.04 mm), which contained ketone **9** (Ar = Ph), three higher boiling products, and a trace of 3,3-diphenylnorcamphor, was collected. This fraction was chromatographed on 60 g of silica gel and eluted with 3% ether in Skelly F. Initially, a mixture of **9** (Ar = Ph) and two of the higher boiling products eluted, followed by pure **9** (Ar = Ph). After solvent removal from these fractions, distillation gave 1.31 g (23%) of **9** (Ar = Ph),[31] bp 91 °C (0.04 mm): NMR (CCl_4) δ 7.2 (5 h, bs), 3.32 (1 H, br doublet, J = 4.5 Hz), 2.81 (1 H, m), 2.62 (1 H, m), 2.0–1. (6 H, m). No *exo*-3-phenylbicyclo[2.2.1]heptan-2-one was present.

Preparation of 2-Phenyl-3-trimethylsiloxybicyclo[2.2.1]hept-2-ene (10, Ar = Ph). A solution of lithium diisopropylamide was prepared by addition of 4.8 mL of 1.4 methyllithium to 0.74 g of diisopropylamine in 3 mL of ether at −78 °C. The mixture was allowed to warm to 0 °C and then recooled to −78 °C. A solution of 1.13 g of ketone **9** (Ar = Ph) in 5 mL of ether was then added dropwise. The mixture was slowly warmed to −40 °C, then recooled to −78 °C. One gram of chlorotrimethylsilane was added and the mixture was allowed to warm to room temperature. After 2 h and 15 min at room temperature, about 20 mL of pentane was added followed by water. The organic extract was washed with a solution of 5.2 g of $KHSO_4$ and dried over $MgSO_4$. After the solvent was removed by rotary evaporator, the residue was distilled to give 1.51 g (96%) of **10** (Ar = Ph), bp 89–94 °C (0.06 mm): NMR ($CDCl_3$) δ 7.7–7.0 (5 H, m), 3.25 (1 H, m), 2.80 (1 H, m), 2.0–1.0 (6 H, m), 0.30 (9 H, s); IR 1625 cm^{-1} (C=C). This moisture-sensitive silyl enol ether was immediately oxidized as described below.

Preparation of *exo*-2-Hydroxy-*endo*-2-phenylbicyclo[2.2.1]heptan-3-one (12, Ar = Ph). A solution of 1.51 g of silyl enol ether **10** (Ar = Ph) in 5 mL of methylene chloride was cooled to −20 °C, and 1.19 g of 85% *m*-chloroperbenzoic acid in 10 mL of CH_2Cl_2 was added dropwise. After 2 h and 15 min at −20 to −10 °C, the mixture was then taken up into ether and washed with a solution of 0.28 g of NaOH in water. The organic phase was dried over $MgSO_4$ and filtered; the solvent was removed by rotary evaporator. The crude siloxy ketone **11** (Ar = Ph) was dissolved in 25 mL of 0.5 M sodium methoxide in methanol, and after 10 min, 10 mL of water was added. The mixture was heated on a steam bath for 15 min and an aqueous workup followed with extraction into ether. The ether extract was washed with water and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator leaving 1.06 g (90%) of **12** (Ar = Ph)[32] as a clear oil: NMR ($CDCl_3$, 300 MHz) δ 7.33 (5 H, bs), 2.79 (1 H, m), 2.73 (1 H, m), 2.63 (1 H, br s), 2.47 (1 H, br doublet, J = 10 Hz), 1.95–1.79 (1 H, m), 1.71–1.50 (3 H, m), 1.19–1.05 (1 H, m); IR 3400 cm^{-1} (O—H), 1750 cm^{-1} (C=O).

Preparation of *exo*-2-Trifluoroacetoxy-*endo*-2-phenylbicyclo[2.2.1]-heptan-3-one (13). A solution of 137 mg of **12** (A = Ph) in 1.7 mL of dry pyridine was cooled to 0 °C and 285 mg of trifluoroacetic anhydride was added dropwise. After 15 min at 0 °C, the mixture was taken up into pentane and ether (50:50) and washed with cold water and 10% HCl solution. The organic extract was washed with saturated NaCl solution and dried over $MgSO_4$. Solvent removal by rotary evaporator gave 199 mg (98%) of **13**, mp 98–99 °C: NMR ($CDCl_3$) δ 7.8–7.2 (5 H, m), 3.40 (1 H, m), 2.89 (1 H, m), 2.30 (1 H, doublet of multiplets, J = 10.5 Hz), 2.0–1.1 (5 H, m). Trifluoroacetate **13** readily hydrolyzed one exposure to moisture. Studies were therefore carried out immediately on freshly prepared **13**. Anal. Calcd for $C_{15}H_{13}F_3O_3$: C, 60.41; H, 4.39. Found: C, 60.27; H, 4.28.

Preparation of *endo*-3-(*p*-Methylphenyl)bicyclo[2.2.1]heptan-2-one (9, Ar = *p*-Methylphenyl). The preparation of **9** (Ar = *p*-methylphenyl) was identical with the preparation of **9** (Ar = Ph) except for the use of 5.26 g of *p*-bromotoluene instead of bromobenzene. After removal of excess norcamphor and unreacted *p*-bromotoluene at 15 mm, a 2.01-g fraction, bp 93–100 °C (0.04 mm), was collected. This fraction was chromatographed on 55 g silica gel and eluted with 5% ether in Skelly F. Distillation gave 1.25 g (20%) of **9** (Ar = *p*-methylphenyl),[33] bp 93 °C (0.04 mm): NMR (CCl_4) δ 7.01 (4 H, br s), 3.30 (1 H, br doublet, J = 4.5 Hz), 2.95–2.55 (2 H, m), 2.30 (3 H, s), 2.0–1.2 (6 H, m).

Preparation of 2-(*p*-Methylphenyl)-3-trimethylsiloxybicyclo[2.2.1]-hept-2-ene (10, Ar = *p*-Methylphenyl). The preparation of **10** (Ar = *p*-methylphenyl) was identical with the preparation of **10** (Ar = Ph). LDA from 0.68 g of diisopropylamine and 4.4 mL of 1.4 M methyllithium with 1.12 g of ketone **9** (Ar = *p*-methylphenyl) and 0.91 g of chlorotrimethylsilane gave 1.33 g (87%) of silyl enol ether **10** (Ar =

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(30) For a discussion of the potent rate-retarding inductive effect of an adjacent dimethyl ketal function, see ref 16.

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(32) Collins, C. J.; Glover, I. T.; Eckart, M. D.; Raaen, V. F.; Benjamin, B. M.; Benjaminov, B. S. *J. Am. Soc.* **1972**, *94*, 899–908.

p-methylphenyl), bp 103–106 °C (0.06 mm): NMR ($CDCl_3$) δ 7.5–7.0 (AA′BB′ quartet), 3.25 (1 H, m), 2.75 (1 H, m), 2.31 (3 H, s), 1.9–1.0 (6 H, m), 0.30 (9 H, s); IR 1625 cm^{-1} (C=C). This moisture-sensitive product was immediately oxidized as described below.

Preparation of *exo*-2-Hydroxy-*endo*-2-(*p*-methylphenyl)bicyclo-[2.2.1]heptan-3-one (12, Ar = *p*-Methylphenyl). The preparation of hydroxy ketone **12** (Ar = *p*-methylphenyl) was identical with the preparation of **12** (Ar = Ph). The reaction of 1.33 g of **10** (Ar = *p*-methylphenyl) with 0.99 g of 85% *m*-chloroperbenzoic acid followed by reaction of crude **11** (Ar = *p*-methylphenyl) with 25 mL of 0.5 M $NaOCH_3$ in methanol and 10 mL of water gave 0.86 g (81%) of the hydroxy ketone **12** (Ar = *p*-methylphenyl), mp 69–72 °C): NMR ($CDCl_3$, 300 MHz) δ 7.3–7.1 (AA′BB′ quartet), 2.79 (1 H, m), 2.73 (1 H, m), 2.50 (1 H, s), 2.46 (1 H, br doublet, J = 10 Hz), 2.34 (3 H, s), 1.95–1.77 (1 H, m), 1.70–1.49 (3 H, m), 1.22–1.07 (1 H, m); IR (CCl_4) 3580, 3450 (OH), 1750 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.69; H, 7.36.

Preparation of *exo*-2-Trifluoroacetoxy-*endo*-2-(*p*-methylphenyl)bicyclo[2.2.1]heptan-3-one (14). The preparation of **14** was identical with the preparation of **13**. Ketol **12** (Ar = *p*-methylphenyl) (206 mg) in 3 mL of pyridine and 400 mg of trifluoroacetic anhydride gave 283 mg (95%) of **14** as a clear oil: NMR ($CDCl_3$) δ 7.6–7.1 (AA′BB′ quartet), 3.39 (1 H, m), 2.85 (1 H, m), 2.34 (3 H, s), 2.30 (1 H, doublet of multiplets, J = 10 Hz), 2.0–1.1 (5 H, m); IR 1790, 1770 cm^{-1} (C=O). Trifluoroacetate **14**, which readily hydrolyzes on exposure to moisture, was used immediately for solvolytic studies.

Preparation of Triflate 6. The preparation of this triflate was as previously described.[15] The yield is best when freshly prepared (free of dimer) *endo*-2-hydroxybicyclo[2.2.1]heptan-3-one is used: ^{13}C NMR ($CDCl_3$) δ 205.2, 118.5 (quartet, J = 320 Hz), 87.6, 48.1, 40.4, 31.3, 26.3, 19.4.

Preparation of Triflate 6-*d*. The preparation of triflate **6**-*d* was essentially the same as previously described[15] for the preparation of **6**. Methanolysis of 4.0 g of **30** in 21 mL of CH_3OD gave 1.5 g (79%) of **31** which was immediately converted to **6**-*d*. Reaction of 0.50 g of **31** with 1.38 g of triflic anhydride in 6 mL of pyridine at 0 °C for 30 min, followed by a standard workup using D_2O, gave 0.71 g (70%) of **6**-*d*: ^{13}C NMR of **6**-*d* ($CDCl_3$) δ 205.3, 118.5 (quartet, J = 320 Hz), 48.1, 40.3, 31.3, 26.3, 19.4. The signal at δ 87.6 (C-2) which appears in **6** was not visible under the spectral conditions.

Preparation of Triflate 7. A solution of 1.51 g of *exo*-2-trimethylsiloxybicyclo[2.2.1]heptan-3-one[14] in 16 mL of 2.6×10^{-4} M CF_3CO_2H in methanol was stirred at room temperature. Periodically, 15-μL aliquots were quenched in 100 μL of ether and analyzed by gas chromatography. After 15 min, no starting material remained. The methanol was immediately removed by rotary evaporator. The crude *exo*-2-hydroxybicyclo[2.2.1]heptan-3-one was immediately dissolved in 3 mL of $CDCl_3$ and the solvent was again removed by rotary (to remove the last traces of methanol). The crude ketol was immediately dissolved in 4 mL of CH_2Cl_2 and added to a solution of 3.15 g of triflic anhydride in 16 mL of pyridine at 0 °C. After 20 min at 0 °C, a cold rapid aqueous workup followed. The ether extract was washed with dilute hydrochloric acid and saturated sodium chloride solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator, leaving 1.55 g (80%) of **7** as a yellow oil. Triflate **7** discolors at room temperature and was stored at −80 °C. The procedure described above is superior to our previous method[15] of preparation of **7** from the dimer of *exo*-2-hydroxybicyclo-[2.2.1]heptan-3-one: ^{13}C NMR of **7** ($CDCl_3$) δ 205.7, 118.5 (quartet, J = 320.7 Hz), 85.0, 47.6, 41.1, 33.8, 23.5, 23.0.

Preparation of *exo*-2-Deuterio-*endo*-2-trimethylsiloxybicyclo[2.2.1]-heptan-3-one (32). A solution of 0.25 g of triethylamine in 50 mL of CH_3OD was added to 10.10 g of **30** at room temperature. The reaction was monitored by quenching 10-μL aliquots in 50 μL of ether and analyzing by gas chromatography. The reaction was substantially slower than in CH_3OH.[13] After 22 min, about 50% reaction had occurred. After 1 h, the mixture was stored at −20 °C for 11 h. The solvent was then removed by rotary evaporator. Gas chromatographic analysis showed the presence of **32** and a trace (about 3%) of **31**. The product was then taken up into 50 mL of Skelly F and washed with 15 mL of D_2O (to remove **31**). After drying over $MgSO_4$, the solvent was removed by rotary evaporator. The residue was distilled, giving 6.94 g (93%) of **32**, bp 84–85 °C (4 mm). The product contained no **31** by gas chromatography: NMR ($CDCl_3$) δ 2.60 (2 H, m), δ 2.2–1.3 (6 H, m), 0.16 (9 H, s). The doublet at δ 3.86, which appears in the undeuterated siloxy ketone,[13] was not present.

Preparation of 2-Deuterio-3-trimethylsiloxynorbornene (33-*d*). Sodium metal (4.0 g) was dispersed in 150 mL of dry refluxing toluene by rapidly stirring in a 1-L Morton flask. The toluene was cooled and withdrawn from the sodium sand. Dry ether (200 mL) was added followed by 14 g of chlorotrimethylsilane. The mixture was heated to reflux with rapid stirring as a solution of 6.90 g of **32** in 200 mL of ether was added dropwise over a 4-h period (Hirshberg addition funnel). After completion of the addition, reflux was continued for an additional 1.5 h. The mixture was cooled and filtered through Celite; the solvent was removed by rotary evaporator. The residue was distilled through a Vigreux column to give 4.55 g (72%) of **33**-*d*, bp 85–90 °C (2 mm). The NMR spectrum was identical with that previously reported[15] for the undeuterated product except for the absence of the doublet at δ 4.50. About 3% of the undeuterated material was present by NMR.

Preparation of *endo*-2-Deuterio-*exo*-2-trimethylsiloxybicyclo[2.2.1]-heptan-3-one (34-*d*). The general procedure of Jefford[14] was used. A solution of 4.53 g of **33**-*d* in 115 mL of methylene chloride containing 50 mg of tetraphenylporphyrin was cooled in an ethanol–ice bath and dry oxygen was bubbled through the system. The mixture was irradiated with Vicor-filtered light from a Hanovia 450-W lamp for 37 min. After about 35 min the solution became green. The solvent was then removed by rotary evaporator and the crude residue was dissolved in 20 mL of Skelly F. A solution of 6.3 g of triphenylphosphine in 20 mL of ether was added dropwise to the stirred mixture in a water bath over a 5-min period. After 45 min the precipitated triphenylphosphine oxide was removed by filtration and the solvent was removed from the filtrate by rotary evaporator. The residue was distilled through a short-path condenser. The fraction with bp 46–80 °C (0.8 mm) (3.95 g) was redistilled through a Vigreux column. After a small forerun, containing a small amount of norcamphor, 3.30 g (67%) of **34**-*d*, bp 59.5–61 °C (0.8 mm), was collected: NMR ($CDCl_3$) δ 2.50 (1 H, m), 2.39 (1 H, m), 2.20 (1 H, doublet of multiplets, J = 11 Hz), 1.95–1.20 (5 H, m), 0.13 (9 H, s). About 3% of the undeuterated material was present by ^1H NMR: ^{13}C NMR ($CDCl_3$) δ 215.3, 47.6, 42.9, 33.8, 24.1, 23.6, 0.1. The signal at δ 76.0 (C-2) which appears in the undeuterated siloxy ketone[14a] was not visible.

Preparation of Triflate 7-*d*. The preparation of triflate **7**-*d* from siloxy ketone **34**-*d* was identical with the preparation of triflate **7** from the undeuterated siloxy ketone. The reaction of 0.58 g of **34**-*d* in 6 mL of CH_3OD (approximately 10^{-3} M in CF_3CO_2H) was monitored by gas chromatography. On completion of the reaction (30 min) the solvent was removed by rotary evaporator. The crude **35** in 2 mL of ether was added to 1.15 g of triflic anhydride in 5 mL of pyridine at 0 °C. After 30 min at 0 °C, a standard workup gave 0.59 g (78%) of triflate **7**-*d*. The ^1H NMR spectrum of **7**-*d* showed about 4% of the undeuterated triflate **7**: ^{13}C NMR ($CDCl_3$) δ 205.8, 118.5 (quartet, J = 320.6 Hz), 47.6, 41.0, 33.8, 23.5, 23.0. The signal which appears in the undeuterated triflate **7**[15] at δ 85.0 (C-2) was not visible under the spectral conditions.

Preparation of CF_3CH_2OD. A mixture of 42 g of trifluoroethanol and 50 mL of D_2O was distilled through a 30-cm glass-helice-packed column. Separation from the D_2O was complete. An additional 50 mL of D_2O was added to the distilled trifluoroethanol and the mixture was redistilled. About 1 g of P_2O_5 was added to the distillate and the CF_3CH_2OD was decanted. Redistillation through a helice-packed column gave 37 g of CF_3CH_2OD, bp 73 °C. NMR analysis showed greater than 97% deuterium incorporation.

Solvolysis of Trifluoroacetate 13 in Acetic Acid. A solution of 219 mg of **13** in 10 mL of acetic acid (0.1 M in NaOAc) containing 1% acetic anhydride was heated (sealed tube) at 90 °C for 3 h. The contents of the tube as then taken up into about 30 mL of ether and washed with two portions of water and a solution of K_2CO_3 in water. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator leaving 169 mg (94%) of a mixture of **15** (Ar = Ph) and **1** (Ar = Ph, X = $OCOCF_3$) in a 96:4 ratio as determined by gas chromatography. Products **15** (Ar = Ph) and **1** (Ar = Ph, X = $OCOCF_3$) were identified by NMR spectral comparison with authentic samples.[1]

Solvolysis of Trifluoroacetate 14 in Acetic Acid. The procedure was analogous to the solvolysis of **13** in acetic acid. A solution of 106 mg of **14** in 9 mL of acetic acid for 30 min at 65 °C gave, after a standard workup, 89 mg (100%) of a mixture of **15** (Ar = *p*-methylphenyl) and **1** (Ar = *p*-methylphenyl, X = $OCOCF_3$) in a 93:7 ratio as determined by gas chromatography. These products were identified by NMR spectral comparison with authentic samples.[1]

Solvolysis of Triflate 7 in Trifluoroethanol. A solution of 141 mg of **7** in 10 mL of trifluoroethanol containing 71 mg of 2,6-lutidine was sealed in a tube and heated at 55 °C for 7 h. The contents of the tube was then taken up into ether, washed with dilute HCl, and dried over $MgSO_4$. Gas

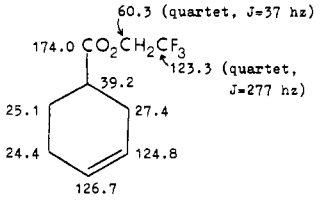
(33) DePuy, C. H.; Naylor, C. G.; Beckman, J. A. *J. Org. Chem.* **1970**, *35*, 2750–4.

(34) **Note Added in Proof**: An exo/endo ratio of 1.2×10^5 has now been measured in HOAc for **7** and **6**. Rate constants for **6** in HOAc are 5.11×10^{-5} s^{-1} at 145 °C and 2.71×10^{-4} s^{-1} at 165 °C.

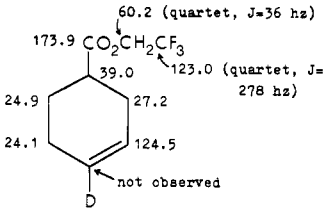
chromatographic analysis showed the presence of **25** and **26**. Samples of each product were isolated by preparative gas chromatography. In a separate run, the yield of these two products was determined by gas chromatography. The yield of **25** was 58% and the yield of **26** was 26%.

The structure of **26**[10c] was based on spectral data: IR 1783 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.95–3.68 (3 H, m), 2.13–1.78 (6 H, m), 1.54–1.37 (2 H, m). The structure of **26** was further confirmed by conversion to 7,7-dimethoxy-*exo*-2-trifluoroethoxybicyclo[2.2.1]heptane, which gave a more characteristic NMR spectrum. Treatment of 6 mg of **26** with 0.5 mL of methanol containing 17 mg of trimethyl orthoformate and 1.4 mg of *p*-toluenesulfonic acid dihydrate for 10 h at room temperature gave the dimethyl ketal: NMR (7,7-dimethoxy-*exo*-2-trifluoroethoxybicyclo[2.2.1]heptane ($CDCl_3$) δ 3.79 (2 H, quartet, J = 8.8 Hz), 3.58 (1 H, doublet of doublets, J = 8.0, 3.5 Hz), 3.27 (3 H, s), 3.25 (3 H, s), 2.23 (1 H, d, J = 4.2 Hz), 2.15 (1 H, t, J = 4.2 Hz), 1.96–1.65 (4 H, m), 1.09 (2 H, AB quartet).

The structure of **25**[10c] was based on spectral comparison with an authentic sample prepared by treatment of the acid chloride of 3-cyclohexene-1-carboxylic acid with trifluoroethanol: ^1H NMR ($CDCl_3$) δ 5.69 (2 H, b s), 4.49 (2 H, quartet, J = 8.5 Hz), 2.75–2.62 (1 H, m), 2.37–2.24 (2 H, m), 2.19–1.98 (3 H, m), 1.82–1.66 (1 H, m). ^{13}C NMR assignments are shown below.

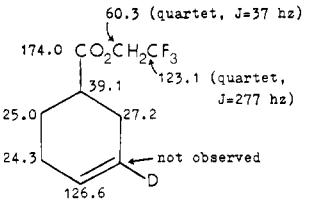


Solvolysis of 7-*d* in Trifluoroethanol. A solution of 401 mg of 7-*d* in 22 mL of trifluoroethanol containing 200 mg of 2,6-lutidine was heated in sealed tubes for 16 h at 56 °C. After a standard workup, gas chromatographic analysis showed **25**-*4*-*d* and **26**-*1*-*d* in a 2.2:1 ratio. Samples of **25**-*4*-*d* and **26**-*1*-*d* were isolated by preparative gas chromatography. The position of the deuterium **25**-*4*-*d* was determined by ^{13}C NMR. The assignments are shown below. C-4 was not visible under the spectral conditions.



Solvolysis of 6 in Trifluoroethanol. A solution of 347 mg of **6** in 30 mL of trifluoroethanol containing 189 mg of 2,6-lutidine was heated in heavy-walled sealed tubes for 41 h at 142.5 °C. After a standard aqueous workup and solvent removal by rotary evaporator, distillation gave 166 mg (59%) of **25**. Gas chromatographic analysis showed small amounts of two higher boiling, unidentified products in the distilled sample. The structure of **25** was established by spectral comparison with an authentic sample.

Solvolysis of 6-*d* in Trifluoroethanol-*O*-*d*. Solvolysis of **5**-*d* in trifluoroethanol gave partial loss of deuterium as determined by NMR integration of the olefinic region of the ^1H spectrum. The ^{13}C NMR spectrum also showed a mixture of **25** and **25**-*3*-*d*. A mixture of 354 mg of **5**-*d* and 194 mg of 2,6-lutidine in 25.5 mL of trifluoroethanol-*O*-*d* was heated in heavy-walled sealed tubes at 142.5 °C for 41 h. After a standard aqueous workup, distillation gave 138 mg of **25**-*3*-*d*. The position of the deuterium was determined by ^{13}C NMR. The assignments are shown below. C-3 was not visible under the spectral conditions.



The structure of **25**-*3*-*d* was confirmed by reaction with sodium methoxide in methanol. A solution of 120 mg of **25**-*3*-*d* in 2 mL of 0.5 M sodium methoxide was stirred at room temperature for 1 h. Gas chromatographic analysis showed complete transesterification of **25**-*3*-*d*. The mixture was taken up into ether and water was added. The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporator. The ^{13}C NMR spectrum of the product was identical with that of an authentic sample of **36**.[16] The signal due to C-3 of **36** was not visible under the spectral conditions.

Solvolyses of Trifluoroacetates 13 and 14. Kinetics Procedures. Rates of solvolyses of **13** and **14** were determined by gas chromatography. Approximately 100 mg of the trifluoroacetate and 20 mg of biphenyl (internal standard) in 10 mL of HOAc (0.10 M in NaOAc plus 1% acetic anhydride) was sealed in eight tubes and immersed in a bath at the given temperature. Periodically (over 2 half-lives) samples were quenched and 1-mL aliquots were added to 2 mL of ether. The mixture was extracted with two 2-mL portions of water and 1 mL of 1 M K_2CO_3 solution. The ether phase was then dried over Na_2SO_4 and analyzed by gas chromatography at 150 °C for unreacted trifluoroacetate. Rate constants were calculated by standard methods. Correlation coefficients were greater than 0.9995. Maximum standard deviations in multiple runs were ±2%.

Solvolyses of Triflates 6, 7, and 42. Kinetics Procedures. Solvolyses of **6**, **7**, and **42**,[1] in trifluoroethanol (0.025 M in 2,6-lutidine), formic acid (0.05 M in sodium formate), and 97% hexafluoroisopropyl alcohol (0.05 M in 2,6-lutidine) were monitored titrimetrically using the sealed-ampule method previously described.[3] Heavy-walled glass tubes were employed for runs using TFE, HFIP, and HCO_2H at elevated temperatures. Tubes containing formic acid developed pressure due to release of carbon monoxide at elevated temperatures. End points were determined potentiometrically. Rate constants were calculated by standard methods. Correlation coefficients were greater than 0.9999. Maximum standard deviations in duplicate runs were ±1.5%. Rates of solvolyses of **7** and **42** in CF_3CO_2H (0.2 M in sodium trifluoroacetate with 1% trifluoroacetic anhydride) were determined by NMR monitoring of the disappearance of doublet at δ 4.50 for **7** and the singlet at δ 5.37 for **42**. The standard deviation was 10%.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, for support of this research. We also acknowledge NIH for a grant used to purchase the 300-MHz NMR spectrometer.

Registry No. 6, 63715-74-2; **6**-*d*, 87518-27-2; **7**, 63715-76-4; **9** (Ar = Ph), 7485-53-2; **9** (Ar = 4-$CH_3C_6H_4$), 87518-19-2; **10** (Ar = Ph), 87518-20-5; **10** (Ar = 4-$CH_3C_6H_4$), 87518-21-6; **11** (Ar = Ph), 87518-22-7; **11** (Ar = 4-$CH_3C_6H_4$), 87518-23-8; **12** (Ar = Ph), 35234-67-4; **12** (Ar = 4-$CH_3C_6H_4$), 87518-24-9; **1**, 87518-17-0; **14**, 87518-18-1; **16** (Ar = Ph), 87518-25-0; **16** (Ar = 4-$CH_3C_6H_4$), 87518-26-1; **25**, 87518-34-1; **26**, 87518-32-9; **30**, 63715-72-0; **32**, 87518-28-3; **33**-*d*, 87518-29-4; **34**-*d*, 87518-30-7; **3k**, 87518-31-8; norcamphor, 497-38-1; phenyl bromide, 108-86-1; *p*-tolyl bromide, 106-38-7; 2,2,2-trifluoroethanol, 75-89-8; 3-cyclohexene-1-carbonyl chloride, 932-67-2; *exo*-2-trimethylsiloxybicyclo[2.2.1]heptan-3-one, 65318-49-2; *exo*-2-hydroxybicyclo[2.2.1]-heptan-3-one, 5164-67-0; *exo*-7,7-dimethoxy-2-(2,2,2-trifluoroethoxy)-bicyclo[2.2.1]heptane, 87518-33-0; CF_3CH_2OD, 77568-66-2.