to give **5a**, mp 139–141 °C, in 80% yield.

Acknowledgment. Financial support for A.N. by a Grant Aid for Scientific Research is gratefully acknowledged. We thank Dr. J. A. Moore for many useful suggestions.

Registry No. **1b**, 71463-01-9; **1c**, 71463-02-0; **1d**, 71463-03-1; **1e**, 71463-04-2; **1g**, 71463-05-3; **1h**, 14491-89-5; **2a**, 41316-38-5; **2b**, 71463-06-4; **2c**, 71463-07-5; **2d**, 71463-08-6; **2e**, 71463-09-7; **3e**, 71463-10-0; **4e**, 71463-11-1; **5a**, 41316-45-4; **5c**, 71463-12-2; **5d**, 71463-13-3; **5e**, 71463-14-4; 1-*n*-butyl-3-methyl-3-phenyldiaziridine, 71463-15-5; 1-cyclohexyl-3-ethyl-3-phenyldiaziridine, 41316-28-3; α-methylbenzylidene-*n*-butylamine, 6907-75-1; α-ethylbenzylidenecyclohexylamine, 6125-76-4; HAOSA, 2950-43-8; *p*-methoxyphenyl isocyanate, 5416-93-3; 1-cyclohexyl-1,2-bis(phenylcarbamoyl)hydrazine, 41316-46-5; acetophenone, 98-86-2.

Supplementary Material Available: Table II, interatomic distances and angles; Table III, deviations from the best plane through various atom groups; Tables IV and V, final positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

Generation of α-Keto Cations. Quantitative Aspects

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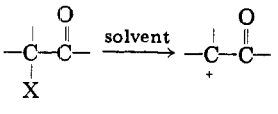
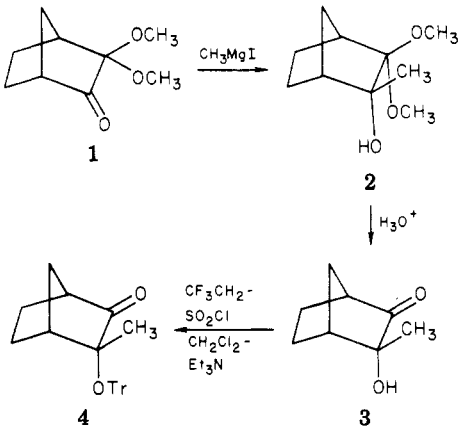
exo-3-Methylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl tresylate (**4**) undergoes acetolysis to give two unrearranged products, ketone **5** and keto acetate **6**, along with rearranged keto acetate **7** and ketone **8**. These products are suggested to arise via the intermediacy of a discrete α-keto cation **9**. The α-methyl-d_3 isotope effect is 1.47 and suggests an extremely large demand for hyperconjugative stabilization. The rate-retarding effect of the α-keto group is estimated at $10^{7.3}$ in this system. *exo*-3-Arylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl mesylates and trifluoroacetates **19–24** also give solvolysis products derived from α-keto cations. These benzylic α-keto cations are not prone to rearrange when the aryl group is phenyl, *p*-toluyl, *p*-thioanisyl, or *p*-anisyl, but rearrangement can occur with the *p*-trifluoromethyl substituent. The effect of aryl substituents on the rate of solvolysis suggests a ρ^+ value of about −7.1, again implying a large demand for aryl stabilization. Bicyclo[2.2.1]heptan-2-on-*exo*-3-yl triflate (**34**) also solvolyzes readily to give products consistent with neighboring σ participation and not via a discrete secondary α-keto cation. A similar k_Δ process also accounts for the rapid solvolysis of the triflate derivative of pivaloin, **39**. The triflate and mesylate derivatives of α-hydroxycyclohexanone are very labile and gave unrearranged acetolysis products. A deuterium-labeling study supports a mechanism involving enolization followed by solvolysis of an enol allylic triflate.

Recently we have been interested in the chemistry of α-keto triflates.[2] We have found that these substrates undergo a diversity of mechanistic processes when treated with bases and nucleophiles. During the course of these studies, it became obvious that certain of these triflates were surprisingly reactive even in the absence of strong nucleophiles. This suggested solvolytic processes despite the presence of the potent electron-withdrawing carbonyl group.



We therefore wanted to determine whether solvolytically generated α-keto cations were viable intermediates. While such intermediates have been suggested in the past,[3] not much is known about the effect of the carbonyl group on the rate of generation of a cationic species. Our additional objectives were therefore to determine, quantitatively, the destabilizing effect of the α-keto group on a carbocationic center and to evaluate rearrangement processes in such cations.

Scheme I



Results and Discussion

Tertiary α-Keto Systems. The norbornyl system, with its semipredictable rearrangement patterns, appeared to be ideal for an evaluation of α-keto cation systems. It was felt that, initially, tertiary α-keto cation systems would be the easiest to generate and evaluate quantitatively. Our initial synthetic target was, therefore, a derivative of keto alcohol **3**. This α-hydroxy ketone was prepared in a straightforward manner from the ketone **1** and methyl-

(1) Alfred P. Sloan Fellow, 1977–1979.
(2) (a) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4226–30. (b) Creary, X.; Rollin, A. J. *Ibid.* **1979**, *44*, 1017–20.
(3) (a) Karavan, V. S.; Temnikova, T. I. *J. Org. Chem. USSR. (Engl. Transl.)* **1966**, *2*, 1399–1404. (b) Temnikova, T. I.; Karavan, V. S. *J. Gen. Chem. USSR. (Engl. Transl.)* **1964**, *34*, 3204–10. (c) McDonald, R. N.; Tabor, T. E. *J. Am. Chem. Soc.* **1967**, *89*, 6573–8. (d) McDonald, R. N.; Tabor, T. E. *J. Org. Chem.* **1968**, *33*, 2934–41. (e) Begûe, J. P.; Malissard, M. *Tetrahedron* **1978**, *34*, 2095–103 and references therein.

0022-3263/79/1944-3938$01.00/0

Scheme II

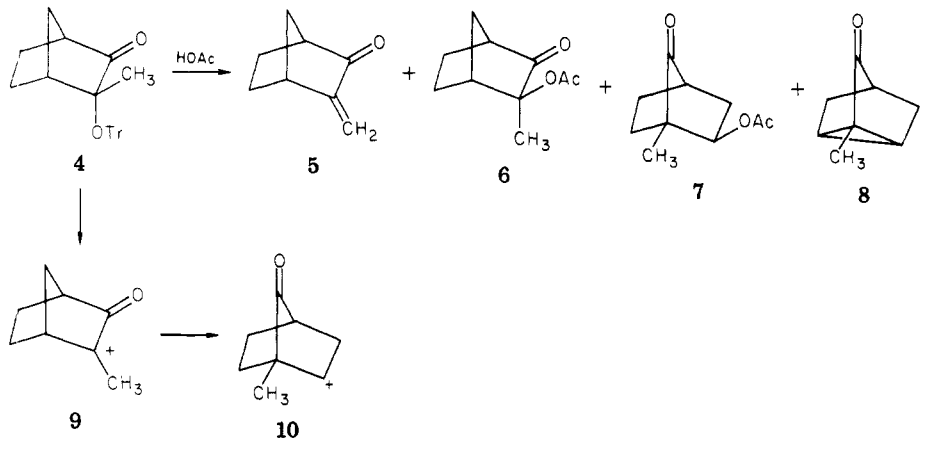


Table I. Solvolysis Rates in Acetic Acid-0.1 M NaOAc

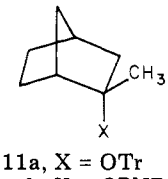
compd	temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
4	25.0[a]	4.29×10^{-8}		
	80.0	6.45×10^{-5}	27.2	−1
	100.0	5.44×10^{-4}		
4-d_3	80.0	4.39×10^{-5}		
15	25.0	1.48×10^{-5}	24.3	1
	50.0	3.86×10^{-4}		
19	16.0	1.21×10^{-4}		
	21.0	2.36×10^{-4}	22.1	0
	25.0[a]	3.97×10^{-4}		
20	25.0[a]	1.78×10^{-9}		
	100.0	4.66×10^{-5}	29.3	0
	120.0	3.67×10^{-4}		
21	25.0[a]	1.89×10^{-7}		
	70.0	7.34×10^{-5}	26.3	−1
	90.0	6.50×10^{-4}		
22	25.0	4.41×10^{-5}	22.3	−4
	50.0	8.80×10^{-4}		
23	25.0	3.45×10^{-4}		
24	25.0[a]	2.82×10^{-7}		
	70.0	9.52×10^{-5}	25.7	−2
	90.0	8.01×10^{-4}		
25	25.0	1.26×10^{-3}		
34	25.0[a]	2.58×10^{-6}		
	50.0	6.28×10^{-5}	23.8	−4
	70.0	5.80×10^{-4}		
39	25.0[a]	4.15×10^{-6}		
	45.0	5.79×10^{-5}	24.2	−2
	65.0	5.94×10^{-4}		
43	40.0	4.63×10^{-5}		
	60.0	2.62×10^{-4}	17.3	−23
	80.0[a]	1.22×10^{-3}		
45	60.0[a]	4.88×10^{-6}		
	80.0	3.05×10^{-5}	20.7	−21
	100.0	1.58×10^{-4}		

[a] Extrapolated value.

magnesium iodide followed by hydrolysis (Scheme I). The triflate derivative of **3** proved too reactive for convenient preparation, and hence the less reactive trifluoroethanesulfonate[4] (tresylate) derivative **4** was chosen so that solvolysis rates could be conveniently monitored. Acetolysis of **4** gave a mixture of four products as shown in Scheme II. Ketones **5** and **8** (40% of the products) were produced in a 1.2 to 1 ratio while keto acetates **6** and **7** (60% of the products) were found in a 0.6 to 1 ratio. Rate data are given in Table I.

The primary question concerning the solvolysis of **4** involves the formation of an α-keto cation as a discrete intermediate. It is felt that the acetolysis products strongly suggest that such an intermediate, cation **9**, is involved. The formation of **5** and **6** implies that the cation lives long enough to undergo elimination and solvent capture. Products **7** and **8** are suggested to arise via Wagner–Meerwein rearrangement of a classical ion **9**. It is important to note that the stereochemistry of the tresylate leaving group in **4** precludes concerted Wagner–Meerwein rearrangement. Therefore, the observation of rearranged products suggests a stepwise process involving **9**.

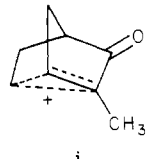
While supporting the discrete intermediacy of **9**, products **7** and **8** also attest to its inherent instability. The tertiary α-keto cation **9** rearranges to **10**,[5] a secondary cation. This suggests that the stabilizing effect of the methyl group[6] can be more than offset by the α-keto group. Quantitatively, what is the rate retarding effect of the α-keto group on the formation of **9**? The solvolysis rate of **11a** was chosen for comparison and is estimated[7] at 8



11a, X = OTr
b, X = OPNB

(4) Crossland, R. K.; Wells, W. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4217–22.

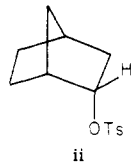
(5) We have no evidence supporting or ruling out the involvement of nonclassical ion i, and hence the discussion is in terms of the classical ion **10**.



i

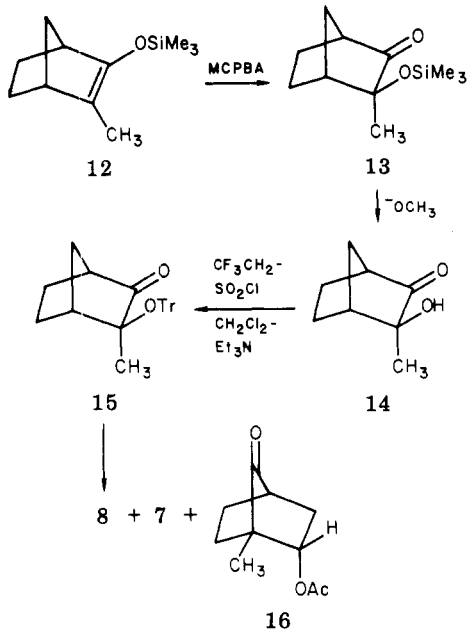
(6) Schleyer estimates that, in terms of rate, methyl stabilization can approach values of 10^8 for limiting solvolyses. See: Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540–2.

(7) This value was estimated by multiplying the acetolysis rate of ii (8.28×10^{-8} s^{-1})[8] by a factor of 10^2 (the tresylate/tosylate ratio)[4] and by a factor of $10^{4.98}$ (the α-CH_3/α-H ratio for the endo norbornyl system).[9]

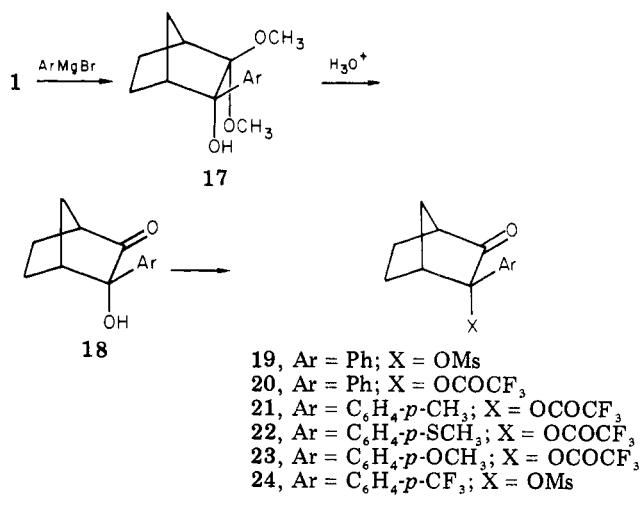


ii

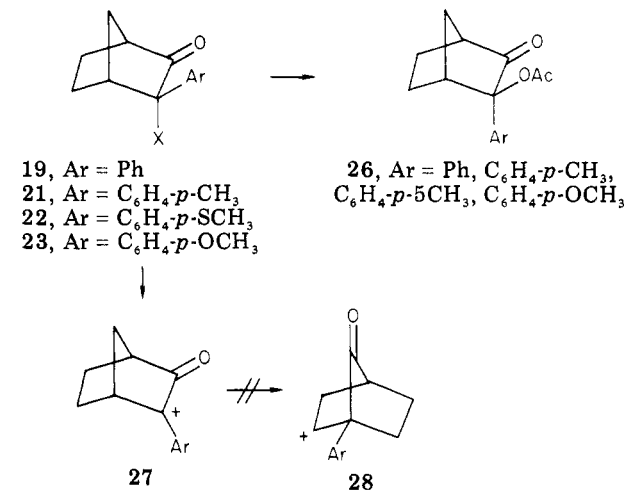
Scheme III



Scheme IV



Scheme V



$\times 10^{-1}$ s^{-1} at 25 °C in acetic acid. The **11a** to **4** ratio is therefore $10^{7.3}$ and hence implies a carbonyl group rate-retarding effect of this magnitude on the formation of α-keto cation **9**.

β-Deuterium isotope effects have been shown to be a good measure of the demands for hyperconjugative stabilization in a developing cationic center.[10,11] The methyl-d_3 isotope effect has been measured for **11b** and is 1.26,[11] a value considered quite normal for such tertiary systems. We therefore sought to determine the analogous isotope effect in **4**. The enormous inductive destabilizing effect of the carbonyl group should be manifested in an increased methyl-d_3 isotope effect. Hence the deuterated analogue **4**-d_3 was prepared. The synthetic scheme was identical with the preparation of **4** but employed methyl-d_3-magnesium iodide. The measured isotope effect was 1.47 ± 0.01, one of the largest methyl-d_3 isotope effects seen to date,[13] and attests to the huge demand for hyperconjugative stabilization in **9**. The β-deuterium isotope effect reinforces the notion based on product and rate data that **9** is quite destabilized.

Attention was next focused on the behavior of the epimeric tresylate **15**, prepared as shown in Scheme III. Treatment of silyl enol ether **12** with *m*-chloroperbenzoic acid (MCPBA) introduced oxygen from the exo face of **12** with resultant exo stereochemistry of the alcohol function in **14**. Preparation of the highly reactive tresylate **15** was accomplished in the standard manner.

Acetolysis of **15** occurred 300 times faster than that of **4** to give a mixture of ketone **8** (1 part) and acetates **7** and **16** (4 parts) in a 5:1 ratio. The formation of endo acetate **16** is reminiscent of the solvolysis of 7-keto-*exo*-norborn-2-yl tosylate which also produces significant amounts of an endo acetate product.[14] The products of acetolysis of **15** can all be derived from Wagner–Meerwein rearrangement of **15**. The exo/endo rate ratio (**15** to **4**) of only 300[15] does not allow one to classify the acetolysis of **15** as a σ-assisted (k_Δ) or a stepwise ionization (k_c)–rearrangement process. However, in view of the previously demonstrated demand for stabilization in classical ion **9**, and the stereochemistry of the leaving group in **15**, the k_Δ process appears quite attractive.

Benzylic α-Keto Systems. The effect of aryl stabilization on the α-keto cation was next investigated. The requisite substrates were prepared in a manner analogous to the preparation of **4** from ketone **1** and the corresponding Grignard reagents as shown in Scheme IV. Solvolytic studies were carried out on the mesylate or trifluoroacetates since these derivatives could be readily prepared despite high reactivity. Rate data are given in Table I. A comparison of the solvolysis rate of **20** with that of the deoxy derivative **25** implies a rate-retarding carbonyl effect of $10^{5.8}$. This is less than the estimated value of $10^{7.3}$ in the methyl analogues **4** and **11** and is in line with the

(8) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375–6.

(9) The α-CH_3/α-H ratio of $10^{4.98}$ for the endo norbornyl system was calculated from the data of Schleyer[8] and Brown. See: Brown, H. C.; Rei, M. H. *J. Am. Chem. Soc.* **1964**, *86*, 5004–5, 5009–10. This value corresponds well to the value of $10^{4.96}$ that can be calculated from the SBS relationship[10] using a value of 1.26 for the α-methyl-d_3 isotope effect.[11]

(10) Fisher, R. D.; Seib, R. C.; Shiner, V. J., Jr., Szele, I.; Tomič, M.; Sunko, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 2408–13.

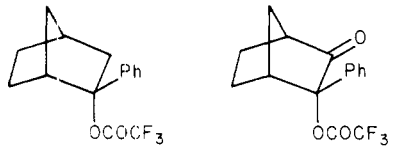
(11) Muller, R. J.; Winternitz, C.; Murr, B. L. *J. Org. Chem.* **1975**, *40*, 412–4.

(12) For leading references, see: Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418–26.

(13) We do not know to what extent rate-limiting elimination at an ion-pair stage increases the isotope effect. Shiner and Sunko have suggested that this occurrence can complicate the interpretation of β-deuterium isotope effects.[10]

(14) Gassman, P. G.; Marshall, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 2822–30.

(15) Brown has shown that systems giving classical substituted norbornyl cations can give exo/endo rate ratios of this magnitude. See: (a) Brown, H. C.; Takenchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691–4. (b) Brown, H. C.; Ravindranathan, M.; Takenchi, K.; Peters, E. N. *Ibid.* **1975**, *97*, 2899–900.



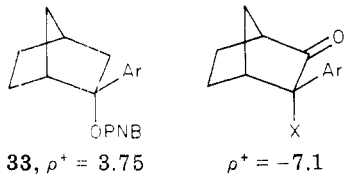
25 20

$k_{25}/k_{20} = 10^{5.8}$

greater stabilizing influence of the phenyl group relative to methyl.

Acetolysis of mesylate **19** and trifluoroacetates **21**, **22**, and **23** gave single products, exo acetates **26**, as shown in Scheme V. These products are suggested to arise via the aryl-stabilized α-keto cations **27**. No rearranged products are seen, implying that the phenyl, *p*-toluyl, *p*-thioanisyl, and *p*-anisyl groups are sufficiently stabilizing to offset rearrangement to **28**. This is in contrast to the behavior of **9** and also to the behavior of mesylate **24**. Acetolysis of **24** gave, in addition to 67% of unrearranged acetate **26** (Ar = C_6H_4-*p*-CF_3), significant amounts (18%) of **29** and tricyclic ketone **30** (15%) (Scheme VI). The products were all stable under the reaction conditions. The formation of **29** implies insufficient aryl stabilization in **31** to offset Wagner–Meerwein rearrangement. Ketone **30** could, in principle, arise from proton elimination in either **31** or **32**. However, if the elimination occurred from **32** and not **31**, this would account for the lack of analogous ketonic products in the solvolysis of **19**, **21**, **22**, and **23**.

The tool of increasing electron demand[16] has been used to explore the effect of structure on the stability of cations produced solvolytically. For example, Brown has found a good correlation between the ρ^+ value in solvolyses of 1-arylcycloalkyl *p*-nitrobenzoates and the cation stabilities as measured by absolute solvolysis rates of the corresponding 1-*p*-anisylcycloalkyl *p*-nitrobenzoates.[17] We have therefore used the rate data in Table I to calculate the ρ^+ value for the acetolyses of trifluoroacetates **20**, **21**, **22**, and **23**. The value is −7.1. While it is not entirely valid to compare ρ values obtained by using differing solvent systems and leaving groups, Brown has presented evidence that, for the cyclopropyl system, changes in ρ value on changing solvent and leaving group are small.[17b] The value of −7.1 seen in the present case is among the largest ρ values seen to date, being approached only by the "corrected" value of −7.1 recently reported by Brown for the cyclopropyl system.[18] This compares to a value of −3.75 for the deoxy system **33**.[15b] While the −7.1 value may

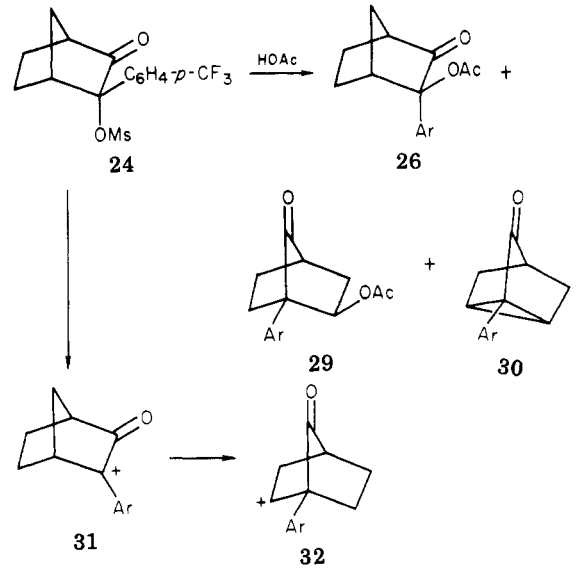


33, $\rho^+ = 3.75$ $\rho^+ = -7.1$

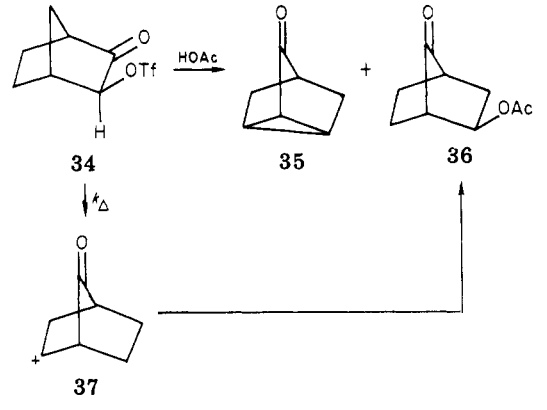
differ slightly with leaving group and solvent, this value again reinforces the idea of an enormous cation destabilizing effect due to α-keto substitution.

Secondary α-Keto Systems. With the above results in mind, efforts were turned to secondary systems. Surprisingly, triflate **34** was quite reactive in solvolysis despite being a secondary system (Scheme VII). Nor-

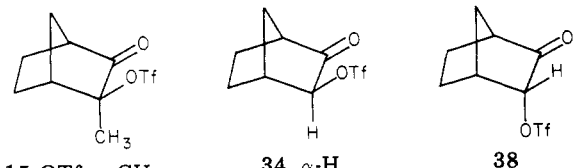
Scheme VI



Scheme VII



tricyclanone **35** and keto acetate **36** were the acetolysis products in a 1:4 ratio. From rate data on the formation of the tertiary α-keto cation **9**, it was felt that solvolysis of **34** was much too rapid to involve a secondary α-keto cation. The α-CH_3/α-H rate ratio (**15**-OTf:**34**) was only $10^{3.8}$, a value smaller than the value of 10^5 for the deoxy



15-OTf, α-CH_3 34, α-H 38

$k_{15\text{-OTf}}/k_{34} = 10^{3.8}$ $k_{34}/k_{38} > 10^4$

system and the suggested limiting value[6] of approximately 10^8. This reduced α-CH_3/α-H value is entirely consistent with a large rate enhancement in the solvolysis of **34**. This enhancement we attribute to σ participation in **34**.

The same conclusion is reached on the basis of the exo/endo rate ratio. We have been unable to achieve significant reaction of the endo triflate **38** even on heating at 150 °C in acetic acid or at 120 °C in the highly ionizing trifluoroacetic acid solvent[19] for 1 h. We can, therefore, only place a lower limit on the exo/endo rate ratio of **34**/**38**. This estimated exo/endo ratio is greater than 10^4, a value viable with significant rate enhancement in the solvolysis of **34**.

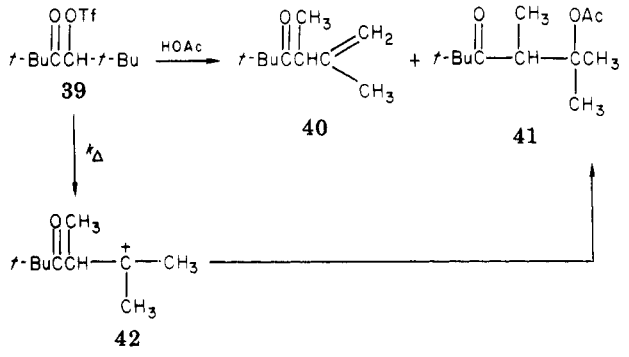
(16) (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–51. (b) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

(17) (a) Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Rao, C. G.; Rho, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 5373–8. (b) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *Ibid.* **1977**, *99*, 7663–7.

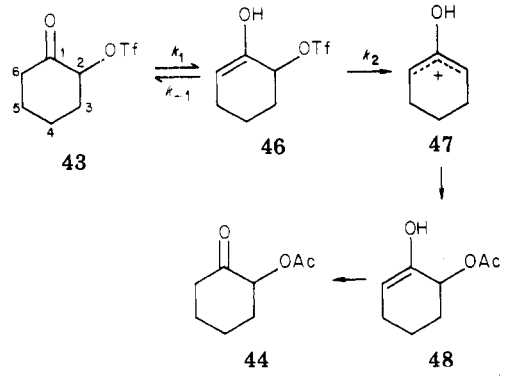
(18) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *Ibid.* **1978**, *100*, 7946–53.

(19) Peterson, P. E. *J. Am. Chem. Soc.* **1960**, *82*, 5834–7.

Scheme VIII

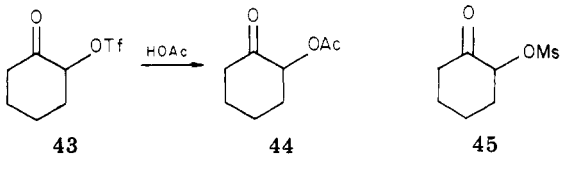


Scheme IX



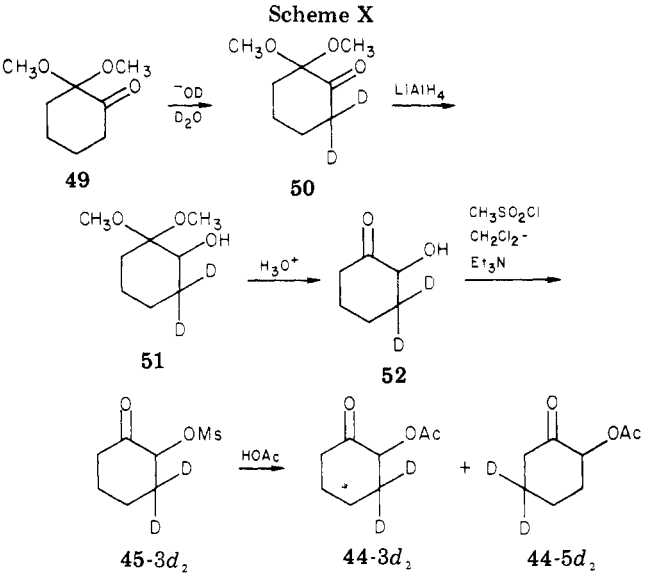
Rate data in Table I show that triflate **39** is also quite reactive. Examination of the acetolysis products (Scheme VIII) confirms the reasons for the high reactivity. Ketone **40** and keto acetate **41**, which are produced in comparable amounts, can be readily derived from neighboring methyl participation, bypassing the secondary α-keto cation.

α-Keto triflate **43** also undergoes acetolysis at a relatively low temperature. However, unlike triflates **34** and **39**, acetolysis of **43** gives an unrearranged acetate **44**. Rates



are much too fast to be explained by a k_c process. The unrearranged product argues against a k_Δ process. The corresponding mesylate **45** was prepared and solvolyzed. From the data in Table I it can be seen that triflate **43** solvolyzes only 40 times faster than mesylate **45**. This compares with normal triflate/mesylate rate ratios of the order of 10^4–10^5 for most solvolytic processes.[20] The entropy of activation for acetolysis of **43** was −23 eu, a value quite different from the other values in Table I and inconsistent with k_s, k_c, or k_Δ processes.

A possible mechanistic alternative is shown in Scheme IX. This mechanism involves solvolysis of an enol allylic triflate **46**. A similar mechanism has been suggested by Bordwell[21] in the reaction of certain halo ketones with alkoxide to account for simple substitution products. In the case of **43**, enol formation could be rate determining, and rate data would reflect the enolization process and not the ionization process. Such a mechanism would be consistent with the observed entropy of activation, trifScheme X



late/mesylate ratio, and unrearranged product. We therefore sought to verify this mechanism by means of a labeling study. If solvolysis of **43** (and **45**) indeed involves **47**, then solvent capture could occur at either position 2 or position 6. Placement of a label at position 3 should result in scrambling of the label to the 5 position of the product if the mechanism in Scheme IX is operative.

The requisite labeled substrate, mesylate **45**-3d_2, was prepared as shown in Scheme X. Exchange of ketone **49** followed by hydride reduction gave alcohol **51**. The ketal function could be hydrolyzed, without scrambling of the label, to **52**. The mesylate derivative was prepared by the Serivs procedure[22] since the standard Tipson procedure,[23] using pyridine as solvent, gave virtually no mesylate. Acetolysis of **45**-3d_2 gave equal amounts of **44**-3d_2 and **44**-5d_2 as determined by ^{13}C NMR. The ^{13}C spectral assignments (δ) in unlabeled acetate **44** are shown.

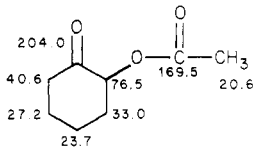


Figure 1 shows partial ^{13}C spectra of **44**, **44**-3d_2, and the acetolysis products of **45**-3d_2. The spectrum of an authentic sample of pure **44**-3d_2 (prepared by acetylation of **51** followed by hydrolysis) is identical with that of **44** except for the absence of the C_3 signal at δ 33.1. The unenhanced quintet due to C_3 is not visible under the spectral conditions. The acetolysis product from **45**-3d_2 shows signals at δ 33.0 (C_3) and 27.1 (C_5) of equal intensity but of about half of the intensity of the corresponding signals in the unlabeled acetate **44**. Therefore, scrambling of the label between the 3 and 5 positions has occurred. Additionally, the solvolysis product shows two closely separated C_6 signals at δ 40.6 and 40.4 as a result of a chemical-shift isotope effect[24] due to deuterium substitution at C_5 in **44**-5d_2. This further confirms that scrambling of the C_3 and C_5 positions has occurred. The remainder of the spectrum was identical with that of unlabeled **44**. The mechanism shown in Scheme IX is therefore entirely consistent with this labeling study.

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(21) Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3370–7, 3377–85.
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(23) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235–41.
(24) (a) Bell, R. A.; Chan, C. L.; Sayer, B. G. *J. Chem. Soc., Chem. Commun.* **1972**, 67–8. (b) Stothers, J. B.; Tan, C. T.; Nickon, A.; Huang, F.; Sridhar, R.; Weglein, R. *J. Am. Chem. Soc.* **1972**, *94*, 8581–2.

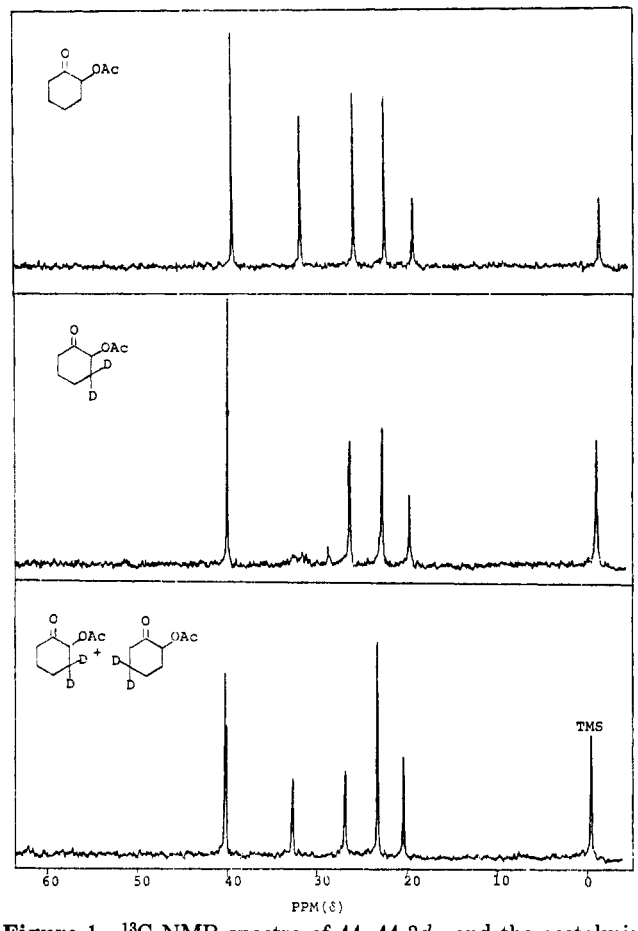

Figure 1. ^{13}C NMR spectra of **44**, **44**-$3d_2$, and the acetolysis products of **45**-$3d_2$.

Conclusions. The solvolytic generation of tertiary and tertiary-benzylic α-keto cations is entirely feasible. However, these cations are among the most unstable tertiary cations known as reflected by the rates of generation, the α-methyl-d_3 isotope effects, the large ρ^+ value in aryl systems, and their propensity for rearrangement. Secondary α-keto cations have so far eluded generation. Although certain secondary α-keto substrates give rapid solvolysis reactions, the mechanisms have been found to involve k_Δ processes or enolization–solvolysis processes and not the generation of discrete secondary α-keto cations.

Experimental Section

NMR spectra were recorded on a Varian A-60A or Varian XL-100 spectrometer and are reported in δ (parts per million) relative to tetramethylsilane. Mass spectra were recorded on an AEI Scientific Apparatus MS 902 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer.

Preparation of *exo*-3-Methyl-*endo*-3-hydroxybicyclo-[2.2.1]heptan-2-one, 3. Methyl Grignard reagent was prepared from 1.2 g of methyl iodide and 0.25 g of magnesium in 8 mL of ether. The solution was cooled to 0 °C, and 1.0 g of 3,3-dimethoxynorcamphor[25] (1) in 5 mL of ether was added dropwise. After 5 min, ammonium chloride solution was added, and a standard aqueous workup followed. Solvent was removed by a rotary evaporator, leaving crude alcohol **2**.[26] The crude alcohol was stirred with 8 mL of 2% sulfuric acid and 2.5 mL of tetrahydrofuran (THF) for 25 min. Solid $NaHCO_3$ was added, and the mixture was extracted with ether. After being dried over $MgSO_4$, the solvent was removed by rotary evaporator. The solid alcohol **3** was slurried with pentane and collected. The yield of **3** was 0.55 g (67% based on 1): mp 66–67 °C; NMR (CCl_4) δ 2.89 (1 H, brs, exchanges with D_2O), 2.69–2.30 (2 H, m), 2.3–1.3 (6 H, m), 1.22 (3 H, s); mass spectroscopic mol wt 140.0829 (calcd for $C_8H_{12}O_2$ 140.0837). An identical procedure was used for the preparation of the deuterated analogue of **3** by using methyl-d_3 iodide (Stohler Isotope Chemicals; 99.5% D).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.58; H, 8.53.

Preparation of 4 and 4-d_3. Alcohol **3** (400 mg) and 400 mg of triethylamine were dissolved in 14 mL of CH_2Cl_2 and cooled in an ice–salt bath. Tresyl chloride[4] (600 mg) was added dropwise. After being stirred for 10 min, the mixture was warmed to approximately 10 °C. The mixture was taken up into ether and extracted with water and dilute HCl. After being dried over $MgSO_4$, the solvent was removed by rotary evaporator. The yield of **4** was 750 mg (92%), and the crude product was used for further studies: NMR (CCl_4) δ 4.02 (2 H, q, J = 8.8 Hz), 2.98 (1 H, m), 2.70 (1 H, m), 2.3–1.4 (6 H, m), 1.64 (3 H, s). The deuterated analogue **4**-d_3 was prepared in an identical manner. The NMR spectrum was identical except for the absence of the singlet at δ 1.64.

Preparation of 12. Lithium tetramethylpiperidide was prepared from 2.73 g of tetramethylpiperidine and 13.2 mL of 1.4 M methyllithium. The mixture was cooled to −78 °C, and 2.0 g of *exo*-3-methylnorcamphor in 8 mL of ether was added over 30 min. The mixture was warmed to −40 °C and recooled to −78 °C, and 2.77 g of chlorotrimethylsilane was added. The mixture was stirred at room temperature for 2 h, and an aqueous workup followed. The amine was removed by washing the ether extract with a cold solution of 2.63 g of $KHSO_4$ in water. After being dried over Na_2SO_4, solvents were removed by distillation through a Vigreux column. The residue was distilled through a Vigreux column to give 2.76 g (87%) of **12**: bp 74 °C (14 mm); NMR (CCl_4) δ 2.50 (2 H, m), 1.9–0.7 (11 H, m with sharp singlet at 1.45), 0.13 (9 H, s).

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.03; H, 9.99.

Preparation of 14. The general procedure of Rubottom[27] was used. Silyl enol ether **12** (2.3 g) was dissolved in 10 mL of CH_2Cl_2 and cooled in an ice–salt bath. A solution of 2.16 g of 85% *m*-chloroperoxybenzoic acid dissolved in a minimum amount of CH_2Cl_2 was added dropwise. The mixture was stored for 2 h at −20 °C and then taken up into ether. The mixture was then washed with a solution of 0.5 g of NaOH in water. After being dried over Na_2SO_4, the solvents were removed by rotary evaporator. The crude residue was dissolved in 20 mL of 1 M sodium methoxide in methanol. Water (8 mL) was added, and half of the methanol was removed by distillation. After an aqueous workup, the entire product was chromatographed on 25 g of silica gel. The column was eluted with increasing amounts of ether in Skelly F. Three minor impurities eluted with 10% ether. The alcohol **14** (0.6 g, 37%) was eluted with 50% ether: NMR (CCl_4) δ 3.12 (1 H, brs, exchanges with D_2O), 2.7–2.1 (3 H, m), 2.0–1.0 (8 H, m with sharp singlet at 1.19); mass spectroscopic mol wt 140.0829 (calcd for $C_8H_{12}O_2$ 140.0837).

Preparation of 15. The preparation of **15** was analogous to the formation of **4**. A 0.42-g sample of **14** with 0.7 g of tresyl chloride gave 86% of **15** which was unstable on standing at room temperature: NMR of **15** (CCl_4) δ 3.90 (2 H, q, J = 8.7 Hz), 3.22 (1 H, m), 2.73 (1 H, m), 2.3–1.3 (6 H, m with sharp singlet at 1.63).

Preparation of *exo*-3-Aryl-*endo*-3-hydroxybicyclo-[2.2.1]heptan-2-ones 18. General Procedure. A solution of 3,3-dimethoxynorcamphor in ether was cooled to 0 °C, and a 20% excess of the appropriate aryl Grignard reagent (approximately 1 M) was added dropwise. After 10 min, ammonium chloride solution was added followed by a standard aqueous workup. Solvents were removed by rotary evaporator. The crude alcohol **17** was stirred with equal volumes of 2% H_2SO_4 and THF until gas chromatography showed no remaining **17**. After an aqueous workup, the entire product was chromatographed on silica gel and eluted with increasing amounts of ether in Skelly. The chro-

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(26) Alcohol **2** could also be prepared by addition of methyllithium to **1**. See: Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4231–8.
(27) (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.

Table II. Properties of *exo*-3-Aryl-*endo*-3-hydroxybicyclo[2.2.1]heptan-3-on-2-ols 18

alcohol	% yield from 1	mp, °C	NMR, δ	analysis C	analysis H
18-*p*-H	81	99-100	7.32 (5 H, brs), 3.03 (1 H, s), 2.9-2.5 (2 H, m), 2.4-1.3 (6 H, m)	77.20[a] 76.95[b]	6.98[a] 6.76[b]
18-*p*-CF_3	86	103-104	7.8-7.3 (4 H, AA'BB' quartet), 3.55 (1 H, s), 3.0-2.6 (2 H, m), 2.4-1.3 (6 H, m)	62.22[a] 62.37[b]	4.85[a] 4.92[b]
18-*p*-OCH_3	95	57-58	7.6-6.8 (4 H, AA'BB' quartet), 3.82 (3 H, s), 3.1-2.6 (2 H, m), 2.83 (1 H, s), 2.4-1.3 (6 H, m)	72.39[a] 72.25[b]	6.94[a] 6.72[b]
18-*p*-CH_3	88	oil	7.4-6.9 (4 H, AA'BB' quartet), 2.99 (1 H, s), 2.9-2.5 (2 H, m), 2.30 (3 H, s), 2.4-1.3 (6 H, m)	77.75[a] 77.69[b]	7.46[a] 7.19[b]
18-*p*-SCH_3	69	110-112	7.5-7.3 (4 H, AA'BB' quartet), 3.0-2.6 (2 H, m), 2.75 (1 H, s), 2.47 (3 H, s), 2.4-1.3 (6 H, m)	67.71[a] 67.66[b]	6.49[a] 6.44[b]

[a] Calculated. [b] Found.

matographed alcohols **18** were slurried in pentane and collected. Physical properties are listed in Table II.

Preparation of Mesylates. General Procedure. The general procedure of Servis[22] was used since reaction of alcohols **18** with methanesulfonyl chloride in pyridine was extremely slow. The alcohol and 2 equiv of triethylamine were dissolved in methylene chloride and cooled to 0 °C. Mesyl chloride (1.2 equiv) was added dropwise. After 15 min a standard aqueous workup followed. After being dried over $MgSO_4$, solvents were removed by rotary evaporator to give mesylates **19** and **22**. Mesylate **19**, mp 65–67 °C dec, had the following NMR (CCl_4): δ 8.1–7.8 (2 H, m), 7.7–7.3 (3 H, m), 3.87 (1 H, m), 2.68 (1 H, m), 2.33 (3 H, s), 2.3–1.6 (6 H, m). Mesylate **24**, mp 83–85 °C, had the following NMR ($CDCl_3$): δ 8.3–7.6 (4 H, AA'BB' quartet), 6.22 (1 H, m), 2.79 (1 h, m), 2.62 (3 H, s), 2.3–1.7 (6 H, m).

Anal. Calcd for $C_{15}H_{15}F_3O_4S$: C, 51.72; H, 4.34. Found: C, 52.01; H, 4.31.

Preparation of Trifluoroacetates. General Procedure. The alcohol was dissolved in pyridine and cooled to 0 °C. Trifluoroacetic anhydride (2 equiv) was added dropwise. After 10 min, the mixture was rapidly taken up into ether and washed with cold water and cold dilute HCl and dried over $MgSO_4$. Solvents were removed by rotary evaporator to give the crude trifluoroacetates **20**, **21**, **22**, **23**, and **25** which were used without further purification. Trifluoroacetate **25** decomposes within 5 min on solvent removal but is stable in solution. The spectra are as follows: NMR of **20** (CCl_4) δ 7.9–7.6 (2 H, m), 7.6–7.3 (3 H, m), 3.95 (1 H, m), 2.75 (1 H, m), 2.5–1.5 (6 H, m); NMR of **21** (CCl_4) δ 7.8–7.0 (4 H, AA'BB' quartet), 3.88 (1 H, m), 2.67 (1 H, m), 2.33 (3 H, s), 2.2–1.5 (6 H, m); NMR of **22** (CCl_4) δ 7.9–7.1 (4 H, AA'BB' quartet), 3.92 (1 H, m), 2.72 (1 H, m), 2.44 (3 H, s), 2.2–1.5 (6 H, m); NMR of **23** (CCl_4) δ 7.8–6.7 (4 H, AA'BB' quartet), 3.92 (1 H, m), 3.80 (3 H, s), 2.72 (1 H, s), 2.2–1.5 (6 H, m); NMR of **25** (CCl_4) δ 7.7–7.1 (5 H, m), 3.26 (1 H, m), 2.7–2.2 (2 H, m), 2.2–1.2 (7 H, m).

Preparation of 34 and 43. The preparation of triflates **34** and **43** has previously been described.[2a]

Preparation of 39. Triflic anhydride (7.0 g) was dissolved in 30 mL of pyridine at 0 °C. Pivaloin[28] (3.0 g) was added at room temperature since the reaction is relatively slow at 0 °C. After 3.8 h at 28 °C, an aqueous workup followed. Gas chromatographic analysis showed no unreacted pivaloin and a mixture of triflate **39** and ketone **40**. A control experiment showed that pure **39** in pyridine is converted to **40** under the reaction conditions. Pure triflate **39** could be isolated by distillation of the reaction products through a Vigreaux column which separates the lower boiling ketone **40**. Triflate **39** (1.45 g) was obtained: bp 52 °C (0.03 mm); mp 34–36 °C; NMR (CCl_4) δ 5.38 (1 H, s), 1.25 (9 H, s), 1.08 (9 H, s).

Anal. Calcd for $C_{11}H_{19}F_3O_4S$: C, 43.41; H, 6.29. Found: C, 43.22; H, 6.29.

Preparation of 45 and 45-3d_2. Freshly distilled adipoin (0.72 g) was dissolved in 8 mL of CH_2Cl_2 and cooled to −78 °C. Mesyl chloride (0.82 g) was added, and the mixture was placed in an ice–salt bath. Triethylamine (0.75 g) was added dropwise. The mixture was warmed to about 10 °C and then taken up into ether. A rapid cold aqueous workup followed. After being dried over $MgSO_4$, the solvent was removed by rotary evaporator to give 1.08 g (90%) of mesylate **45**: mp 55–57 °C; NMR (CCl_4) δ 5.00 (1 H, m), 3.13 (3 H, s), 2.7–1.5 (8 H, m).

Anal. Calcd for $C_7H_{12}O_4S$: C, 43.74; H, 6.29. Found: C, 43.54; H, 6.04.

Mesylate **45**-3d_2 was prepared by an identical procedure.

Exchange of 2,2-Dimethoxycyclohexanone (49) with D_2O. Sodium (300 mg) was dissolved in 60 mL of D_2O, and 2.9 g of **49**[29] was added. After 20 min the solution was saturated with Na_2SO_4 and extracted with ether. A standard workup gave 2.1 g of deuterated ketone **50**. The spectra are as follows: ^{13}C NMR of **49** ($CDCl_3$) δ 206.7, 100.6, 49.1, 40.0, 35.3, 27.4, 21.9; ^{13}C NMR of **50** ($CDCl_3$) δ 100.6, 49.1, 35.3, 27.3, 21.9 (the carbonyl and the labeled carbon are not visible under the spectral conditions).

Reduction of 50. A solution of 1.74 g of deuterated ketone **50** in 10 mL of ether was added dropwise to 0.28 g of lithium aluminum hydride. The mixture was decomposed with 20% sodium hydroxide, and a standard workup followed. Distillation gave 1.66 g (94%) of alcohol **51**: bp 59–60 °C (1.1 mm); ^{13}C NMR ($CDCl_3$) δ 100.6, 67.9, 48.1, 47.4, 27.8, 22.1, 19.5 (the labeled carbon of **51** is not visible under the spectral conditions.

Preparation of 3,3-Dideuterio-2-hydroxycyclohexanone (52). Ketal **51** (1.56 g) was dissolved in 30 mL of 10^{-3} M H_2SO_4. After 32 min (the hydrolysis half-life was approximately 4 min), the mixture was saturated with Na_2SO_4 and extracted with two portions of ether. The ether extracts were dried over Na_2SO_4. The solvent was removed by rotary evaporator. The hydroxy ketone **52** was isolated by distillation, giving 0.80 g (75%) of product, bp 47–50 °C (1.1 mm). Hydroxy ketone **52** did not dimerize rapidly when thoroughly cleaned and ammonia-washed glassware was used. ^{13}C NMR showed no scrambling of the label: ^{13}C NMR of 2-hydroxycyclohexanone ($CDCl_3$) δ 211.0, 75.3, 39.5, 36.8, 27.5, 23.5; ^{13}C NMR of **52** ($CDCl_3$) δ 211.0, 75.2, 39.5, 27.5, 23.2 (the labeled carbon of **52** is not visible under the spectral conditions).

Preparation of 3,3-Dideuterio-2-acetoxycyclohexanone (44-3d_2). Alcohol **51** (0.37 g) was dissolved in 3 mL of pyridine. Acetyl chloride (0.36 g) was slowly added. After 4 h, a standard workup followed. Distillation gave 0.34 g (73%) of 1,1-dimethoxy-2-acetoxy-3,3-dideuteriocyclohexane, bp 50 °C (0.08 mm). The acetate was dissolved in a solution of 0.5 g of H_2SO_4 in 7 mL of water and 7 mL of THF. After 105 min, the mixture was neutralized with $NaHCO_3$, and an aqueous workup followed. Distillation gave 0.25 **44**-3d_2: bp 78 °C (1.2 mm); ^{13}C NMR of **44** ($CDCl_3$) δ 204.0, 169.5, 76.5, 40.6, 33.0, 27.2, 23.7, 20.6; ^{13}C NMR of **44**-3d_2 ($CDCl_3$) 204.0, 169.5, 76.4, 40.6, 27.1, 23.5, 20.6. The labeled carbon of **44**-3d_2 is not visible under the spectral conditions.

Solvolysis Studies. General Kinetics Procedures. Acetolysis rates of mesylates and triflates were determined by the titrimetric method previously described.[30] Acetolyses of trifluoroacetates were monitored by gas chromatography or ultraviolet spectroscopy. By the gas chromatographic method, 1-mL aliquots of a solution of **20** or **21** in acetic acid (heated for given times) were diluted with 2 mL of a solution of biphenyl in ether

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(30) Creary, X. *J. Org. Chem.* **1975**, *40*, 3326–31.

or *n*-pentadecane in ether (internal standard). The mixtures were extracted with two 3-mL portions of water and 1 mL of 1 M Na_2CO_3 and dried over Na_2SO_4. The solutions were then analyzed by gas chromatography for unreacted **20** or **21**. Rate constants were calculated by standard methods. By the ultraviolet method, 1-mL aliquots of **20** in acetic acid were diluted with methanol to 10 mL. One milliliter of this solution was diluted with ether and 2 mL of 1 M Na_2CO_3 to a total volume of 25 mL. The mixtures were shaken vigorously, and absorbances were measured at 235 nm where the absorbance of **20** was considerably greater than that of the product **24**. Rate constants were calculated by standard methods.

Acetolysis of **23** was monitored by ultraviolet spectroscopy. A 12-mg sample of **23** was dissolved in acetic acid which was 0.1 M in sodium acetate. At given times, 1-mL aliquots were diluted with 20 mL of ether (to quench the reaction) and 2 mL of saturated sodium chloride solution (to prevent precipitation of sodium acetate in the ether solution), and the total volume was adjusted to 25 mL with ether. Absorbances were monitored at 255 nm where the absorbance of **23** was much greater than that of the product **26**. Acetolysis of **25**[31] was monitored by the same method at 260 nm. Acetolysis of **22** was monitored directly in acetic acid at 279 nm. The dilution and quenching methods described above were unnecessary since absorbance by acetic acid solvent at this wavelength did not interfere.

Solvolysis Studies. General Product Analysis Procedures. A sample of the substrate was dissolved in acetic acid, containing enough sodium acetate to neutralize the released acid, and heated for 10 half-lives. The mixture was then poured into ether and extracted with two portions of water and Na_2CO_3 until basic. The mixture was then analyzed by gas chromatography. In the case of reactions producing multiple products, pure samples were isolated by preparative gas chromatography. The structures of the products were determined by the usual spectroscopic methods or by comparison with independently prepared authentic samples. NMR data are given in the following sections.

Acetolysis of 4. Solvolysis of **4** for 4.5 h at 100 °C gave **5**, **6**, **7**, and **8** in a 22:23:37:18 ratio as determined by gas chromatography. Products **5** and **6**[32] were identified by spectral comparison with authentic samples: NMR of **6** ($CDCl_3$) δ 3.27 (1 H, m), 2.70 (1 H, m), 2.06 (3 H, s), 2.0–1.4 (6 H, m), 1.48 (3 H, s); NMR of **7** ($CDCl_3$) δ 4.92 (1 H, dd, J = 8, 1.2 Hz), 2.4–1.1 (7 H, m), 2.02 (3 H, s), 0.98 (3 H, s); NMR of **8** ($CDCl_3$) δ 2.06 (2 H, d, J = 10 Hz), 1.89 (3 H, brs), 1.68 (2 H, d, J = 10 Hz), 1.11 (3 H, s); IR of **8** $\nu_{C=O}$ 5.66 μ.

Acetolysis of 15. Solvolysis of **15** at 55 °C for 3 h gave **7** and **8**, whose NMR spectra are given above, and **16** in a 67:20:13 as determined by gas chromatography: NMR of **16** ($CDCl_3$) δ 4.94 (1 H, m), 2.12 (3 H, s), 2.3–1.2 (7 H, m), 1.03 (3 H, s); IR $\nu_{C=O}$ 5.60, 5.71 μ.

Acetolysis of 19. Solvolysis of **19** at 60 °C for 50 min gave 92% of **24**: NMR of **26** (Ar = Ph) (CCl_4) δ 7.9–7.5 (2 H, m), 7.5–7.1 (3 H, m), 3.71 (1 H, m), 2.70 (1 H, m), 2.5–1.3 (6 H, m), 1.90 (3 H, s). The stereochemistry of the acetate function **24** was established by saponification with potassium hydride in methanol–water. The alcohol product was different by gas chromatographic retention time and infrared and NMR spectrum from **18** (Ar = Ph) and hence was assigned the opposite stereochemistry.

Acetolysis of 21. Solvolysis of **21** for 3 h at 90 °C gave 91% of **26** (Ar = C_6H_4-*p*-CH_3): NMR (CCl_4) δ 7.8–7.0 (4 H, AA′BB′ quartet), 3.72 (1 H, m), 2.69 (1 H, m), 2.32 (3 H, s), 1.86 (3 H, s), 2.5–1.3 (6 H, m).

Acetolysis of 22. Solvolysis of **22** for 5 h at 50 °C gave 92% of **26** (Ar = C_6H_4-*p*-SCH_3): NMR (CCl_4) δ 7.8–7.1 (4 H, AA′BB′ quartet), 3.72 (1 H, m), 2.68 (1 H, m), 2.45 (3 H, s), 1.91 (3 H, s), 2.5–1.3 (6 H, m).

Acetolysis of 23. Solvolysis of **23** for 7 h at 23 °C gave 94% of **26** (Ar = C_6H_4-*p*-OCH_3): NMR (CCl_4) δ 7.8–6.7) (4 H, AA′BB′ quartet), 3.80 (3 H, s), 3.80 (1 H, m), 2.71 (1 H, m), 2.50–1.20 (6 H, m), 1.88 (3 H, s).

Acetolysis of 24. Solvolysis of **24** at 90 °C for 2.5 h gave 95% of **26** (Ar = C_6H_4-*p*-CF_3), **29**, and **30** in a 67:18:15 ratio as determined by gas chromatography and NMR: NMR of **26** ($CDCl_3$) δ 7.8–7.1 (4 H, m), 3.45 (1 H, m), 2.86 (1 H, m), 2.5–1.2 (6 H, m), 1.98 (3 H, s); NMR of **29** ($CDCl_3$) δ 7.8–7.1 (4 H, m), 5.27 (1 H, dd, J = 8, 2.2 Hz), 2.5–1.2 (7 H, m), 1.82 (3 H, s); NMR of **30** ($CDCl_3$) δ 7.7–7.4 (4 H, m), 2.56 (2 H, brs), 2.27 (2 H, d, J = 10 Hz), 2.22 (1 H, brs), 1.86 (2 H, d, J = 10 Hz); IR of **30** $\nu_{C=O}$ 5.66.

Acetolysis of 34. Solvolysis of **34** for 4 h at 70 °C gave **35** and **36** in a 20:80 ratio as determined by gas chromatography. These products were identified by spectral comparison with authentic samples.

Acetolysis of 39. Solvolysis of **39** for 2 h at 80 °C gave **40** and **41** in a 1:1 ratio as determined by gas chromatography: NMR of **40** (CCl_4) δ 4.80 (2 H, q, J = 2.7 Hz), 3.69 (1 H, q, J = 6.8 Hz), 1.73 (3 H, q, J = 2.7 Hz), 1.12 (3 H, d, J = 6.8 Hz), 1.13 (9 H, s); NMR of **41** ($CDCl_3$) δ 3.74 (1 H, q, J = 8 Hz), 1.96 (3 H, s), 1.57 (6 H, s), 1.18 (9 H, s), 1.08 (3 H, d, J = 8 Hz).

Acetolysis of 43. Solvolysis of **43** for 2.5 h at 80 °C gave 25% of **44**, which was identified by spectral comparison with an authentic sample prepared by acetylation (acetyl chloride in pyridine) of α-hydroxycyclohexanone. Acetolysis of **45** for 12 h at 100 °C gave the same product.

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Registry No. **1**, 35611-45-1; **2**, 63703-50-4; **3**, 69551-84-4; **4**, 71341-23-6; **4**-d_3, 71341-24-7; **5**, 5597-27-3; **6**, 71341-25-8; **7**, 71341-26-9; **8**, 28925-20-4; **12**, 71341-27-0; **14**, 71341-28-1; **15**, 71341-29-2; **16**, 71341-30-5; **18**-*p*-SCH_3, 71341-31-6; **18**-*p*-H, 71341-32-7; **18**-*p*-CF_3, 71341-33-8; **18**-*p*-OCH_3, 71341-34-9; **18**-*p*-CH_3, 71341-35-0; **19**, 71341-36-1; **20**, 71341-37-2; **21**, 71341-38-3; **22**, 71341-39-4; **22** (X = OMs), 71369-96-5; **23**, 71341-40-7; **24**, 71341-41-8; **25**, 71341-09-8; **26** (Ar = C_6H_4-*p*-CH_3), 71341-10-1; **26** (Ar = Ph), 71341-11-2; **26** (Ar = C_6H_4-*p*-SCH_3), 71341-12-3; **26** (Ar = C_6H_4-*p*-OCH_3), 71341-13-4; **26** (Ar = C_6H_4-*p*-CF_3), 71341-14-5; **29**, 71341-15-6; **30**, 71341-16-7; **34**, 63715-76-4; **35**, 695-05-6; **36**, 10265-36-8; **39**, 71341-17-8; **40**, 14705-55-6; **41**, 71341-18-9; **43**, 63715-81-1; **44**, 17472-04-7; **44**-3-d_2, 71341-19-0; **45**, 20187-64-8; **45**-3-d_2, 71369-97-6; **49**, 38461-13-1; **50**, 71341-20-3; **51**, 71341-21-4; **52**, 57573-82-7; *exo*-3-methylnorcamphor, 3915-75-1; chlorotrimethylsilane, 75-77-4; triflic anhydride, 358-23-6; pivaloin, 815-66-7; adipoin, 533-60-8; 1,1-dimethoxy-2-acetoxy-3,3-dideuteriocyclohexane, 71341-22-5.

(31) Acetolysis of **23** gave 2-phenylnorbornene and *endo*-2-phenylnorborn-*exo*-2-yl acetate. The olefinic product absorbs strongly at 260 nm.

(32) Acetate **6** could be prepared by acetolysis of the mesylate derivative of **2** at 120 °C. See ref 26 for an analogous process.