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Carbocationic and Related Processes in Reactions of α-Keto Mesylates and Triflates

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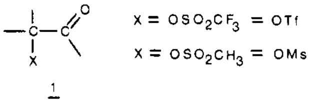
Some years ago we began an investigation of the chemistry of α-keto triflates. Our initial objectives were the generation of α-keto carbenes by α-elimination processes. During the course of these studies, it became apparent that many systems 1, with nucleofugic groups



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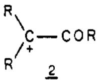
substituted on the carbon α to the carbonyl group, could react under solvolytic conditions, generating cationic intermediates. Carbonyl-substituted cations 2 have now become well-established intermediates.[1] We have generated a wide variety of such intermediates under solvolytic conditions.[2] Bégué and Charpentier-Morize have carried out detailed studies describing the generation and reactivity of such intermediates from silver salts and α-halocarbonyl compounds.[3] In related studies, the Gassman group has generated cyano-substituted cations 3 via the solvolytic route,[4] and extensive studies on α-trifluoromethyl cations 4 have been carried out by the Tidwell group.[5] We have generated phosphoryl-substituted cations 5.[6] Indeed, studies on cations of type 2,[7] 3,[8] and 6[9] under long-lived conditions have appeared, as well as studies on cation 7[10] in which two formally electron-withdrawing groups are attached to the cationic center. One can now conclude that so-called "electron-deficient" cations[4g] of general type 8 are well-established intermediates. This Account will deal with our studies on the carbonyl-substituted cation 2 and with reactions of potential precursors of 2 by a diversity of other mechanistic processes.



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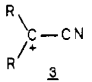

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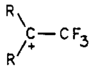

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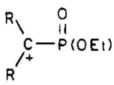

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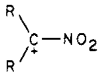

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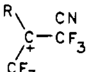

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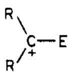

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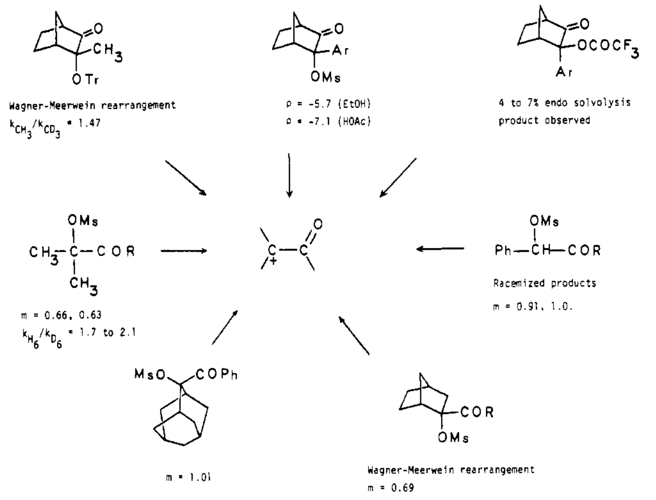
The k_c Process in Solvolyses of α-Keto Systems

At the outset of our studies we wanted to demonstrate the viability of solvolytically generating carbonyl-substituted cations as discrete intermediates. This has been done in a variety of studies, which are summarized below. When compared to the α-CH_2R ana-



Xavier Creary, a native of Montclair, NJ, received his B.S. from Seton Hall University in 1968. His Ph.D. was obtained from The Ohio State University in 1973. After a year as a postdoctoral at the University of California, Santa Cruz, he joined the Department of Chemistry at the University of Notre Dame in 1974, where he is now Associate Professor. His major research interests are in the area of novel organic reactions, mechanisms, and reactive intermediates.

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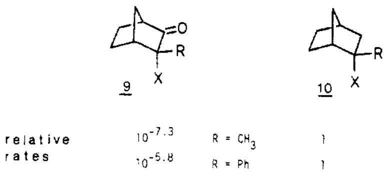
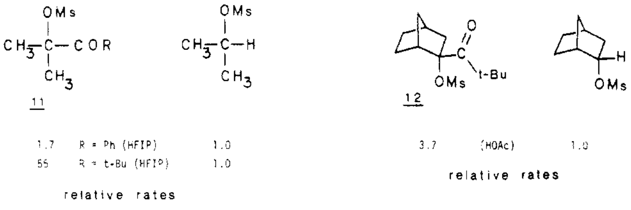
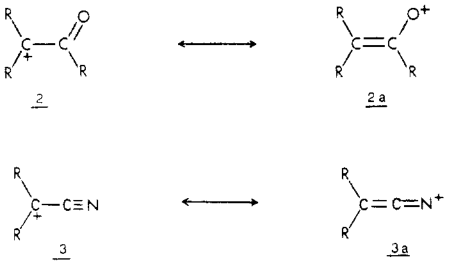
logues **10**, the carbonyl-substituted systems **9** were substantially less reactive.[1a] However comparison of



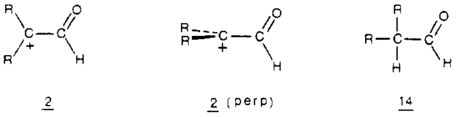
numerous substrates, exemplified by **11**[2e] and **12**[2c], with those of secondary (α-H) analogues, revealed a lack of or a negligible rate-retarding effect of the carbonyl group relative to hydrogen. These studies pointed



strongly to existence of a cation-stabilizing feature which offset the inductive destabilizing effect of the carbonyl group. π-Conjugation is the proposed cation-stabilizing feature. The studies provide experimental evidence for a stabilizing conjugative interaction, as hypothesized earlier by McDonald[11] and demonstrated by Gassman[4] to operate in certain cyano-substituted cations. This conjugation, as represented in **2a**, and **3a**, results in the formation of carbonyl- and cyano-substituted cations much more readily than naively expected on the basis of σ (or σ^+) values of these substituents.



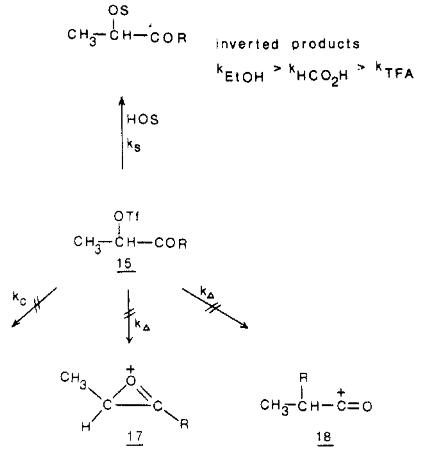
The type of carbonyl conjugation represented by **2a** and cyano conjugation as in **3a** has been supported by theoretical studies.[12] Ab initio molecular-orbital calculations[12d] show decreased C–C bond lengths and increased C–O bond lengths in **2** relative to the uncharged analogues **14**. The cation **2** (perp) (C=O rotated 90° with respect to the "vacant" orbital) in the nonconjugating conformation was less stable than the planar **2**.



What are the relative stabilities of carbonyl cations **2** and cyano cations **3**? From a theoretical viewpoint,[12a,d] the type of cyano conjugation in **3a** was judged to be more effective than carbonyl conjugation (as expected on the basis of relative electronegativities of nitrogen and oxygen). Yet both theoretical and experimental studies[2] suggest that the carbonyl cation **2** is more stable than the cyano cation **3**. Stability of **2** vs. **3** therefore appears to be a delicate function of inductive vs. conjugative ability of the substituent. The cyano group is a better cation-conjugating group but more electron withdrawing, whereas the poorer conjugating carbonyl group is less electron withdrawing. These offsetting factors result in the carbonyl-substituted cations **2** forming at faster rates than **3**.

The k_s Process[12]

Buoyed by the relative ease of solvolytic generation of tertiary and benzylic cations of type **2**, attention was focused on simple secondary systems **15**.[2e] These systems readily gave substitution products. However



solvent-effect studies and studies on an optically active triflate indicated that these substrates reacted by a k_s process involving negligible carbocationic character. Secondary cations **16** were not involved. Neither were potential k_Δ processes leading to acylium ions **18** or carbonyl-bridged ions **17**. The most facile process, even in highly ionizing, relatively nonnucleophilic solvents, was nucleophilic solvent displacement. Reactivity of secondary triflates **15** therefore parallels that of primary α-halo ketones in silver-assisted solvolyses.[14] Carbonyl conjugation in the secondary systems examined is apparently of insufficient magnitude to permit formation of cations **16**.

The "Borderline" Process[15]

Solvolyses of mesylate **19**[2c] gave varying amounts of elimination and substitution products **20** and **21**. This could be interpreted in terms of a carbonyl-substituted cationic intermediate. However the usual large rate increases with solvent ionizing power were not observed. In sharp contrast to the behavior of 2-benzoyl-2-

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(11) McDonald, R. N.; Steppel, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5664–70.

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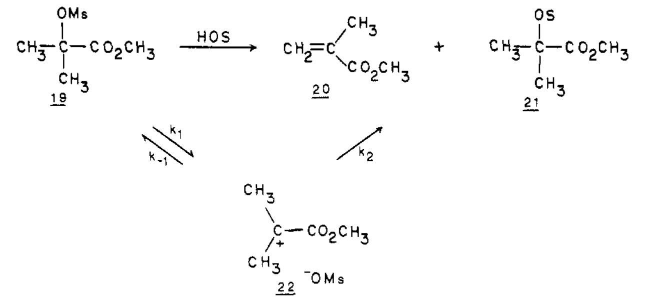
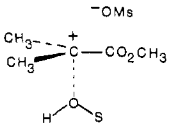
(13) The term k_s, as used by Schleyer,[13] includes processes which are not completely limiting (k_c) but in which there can be substantial cationic development. It also includes direct solvent displacement with little cationic charge development. It is in this latter sense that we use the term k_s. (a) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 2542–4. For the original definition of this term, see: (b) Winstein, S.; Allred, E.; Heck, R.; Glick, R. *Tetrahedron* **1958**, *3*, 1–13.

(14) Pasto, D. J.; Garves, K.; Serve, M. P. *J. Org. Chem.* **1967**, *32*, 778–81.

(15) This term is used to describe processes in which there is evidence for cation formation but also evidence for kinetically important solvent involvement.



adamantyl mesylate, 23 (Figure 1), mesylate 19 gave a scattered Winstein–Grunwald plot (Figure 2). The rate behavior of 19 was analogous to that of isopropyl tosylate, a so-called "borderline" substrate whose solvolysis rate responds to a blend of solvent ionizing power and nucleophilicity.[16] Considerable controversy has arisen as to the mechanism of such borderline substrates. On the basis of the observation that β-deuterium isotopes effects for solvolyses of 19 increased as the amount of elimination product 20 increased, we have suggested the involvement of a reversible ion-pair mechanism where k_2 may become rate limiting. Nucleophilic solvent assistance in the formation of a cationic intermediate 24 (the S_N2 (intermediate) mechanism)[16] also remains a possibility.



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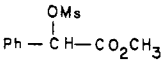
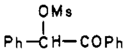
Further evidence for solvent involvement is seen in ethanolyses of 25[2c] and 26.[17] The optically active substrates gave racemized products in the highly ionizing nonnucleophilic solvents hexafluoroisopropyl alcohol and trifluoroacetic acid. In ethanol, substantial amounts of inverted substitution products were seen. Rate data in ethanol showed deviations from the Winstein–Grunwald plot. This also suggests that, in the more nucleophilic ethanol solvent, one is beginning to see a change from virtually limiting to "borderline" behavior; i.e., cationic intermediates are involved, but solvent nucleophilicity is also of importance.


$\mathrm{Ph-\overset{OMs}{\overset{|}{C}}H-CO_2CH_3}$

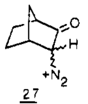
25


$\mathrm{Ph-\overset{OMs}{\overset{|}{C}}H-COPh}$

26

The k_Δ Process

Processes involving neighboring-group participation have previously been observed in α-keto and α-cyano systems. Rearranged products were isolated in solvolyses of 27[18] and in dehalogenation of 28[19] and 29[20] with silver salts. Rate data showed increases in the magnitude of π-participation in solvolyses of 30,[21] 31,[22] and 32. We have observed k_Δ processes in solvolyses of the secondary triflates 33,[2a] 35,[2d] and 38. This has been verified in terms of both anchimeric assistance and rearranged products. The facile solvolysis of 33, a secondary substrate giving only rearranged products, implies a substantial rate enhancement due to methyl migration. The solvolysis rate of 33 is comparable to that of neopentyl triflate,[23] 34, a substance which also reacts via a k_Δ route.



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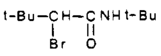
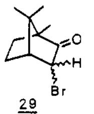

$\mathrm{t\text{-}Bu-\underset{Br}{\underset{|}{C}}H-\underset{O}{\underset{\|}{C}}NH\,t\text{-}Bu}$

28



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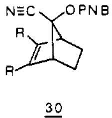

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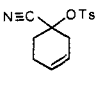

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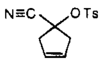

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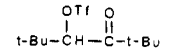
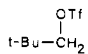

$\mathrm{t\text{-}Bu-\overset{OTf}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-t\text{-}Bu}$

33

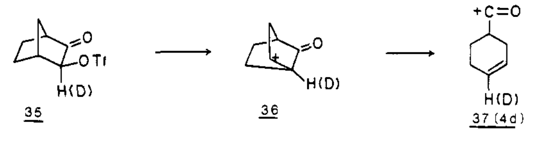

$\mathrm{t\text{-}Bu-\overset{OTf}{\overset{|}{C}}H_2}$

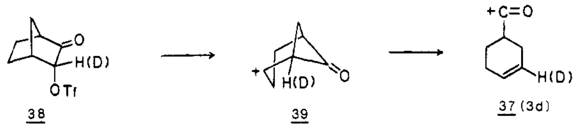
34

33		34
1.0	(80% EtOH)	1.79
1.0	(CF_3CH_2OH)	2.97

relative rates

Solvolyses of the triflates 35 and 38 permit a better evaluation of the magnitude of anchimeric assistance due to σ-participation. These systems, based on deuterium-labeling studies, solvolyze by the different k_Δ processes shown below:





exo/endo rate ratio		
	1.2×10^5 (HOAc)	4.4×10^4 (HFIP)
	9.5×10^4 (HCO_2H)	3.4×10^4 (TFE)

The exo/endo rate ratio approached 10^5, a value substantially larger than in unsubstituted 2-norbornyl systems (10^2 to 10^3). The presence of the inductively electron-withdrawing carbonyl group results in an increased demand for stabilization in the transition state. This results in an increase in the magnitude of anchimeric assistance in 35 due to neighboring C_1C_6 σ-participation leading to the cation 36 as the first intermediate. The carbonyl group in the endo-isomer 38 apparently leads to C_1C_7 participation leading to 39 and

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[16] (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658–66. (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667–74. (c) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, 5463–75.

[17] Unpublished work in our laboratories.

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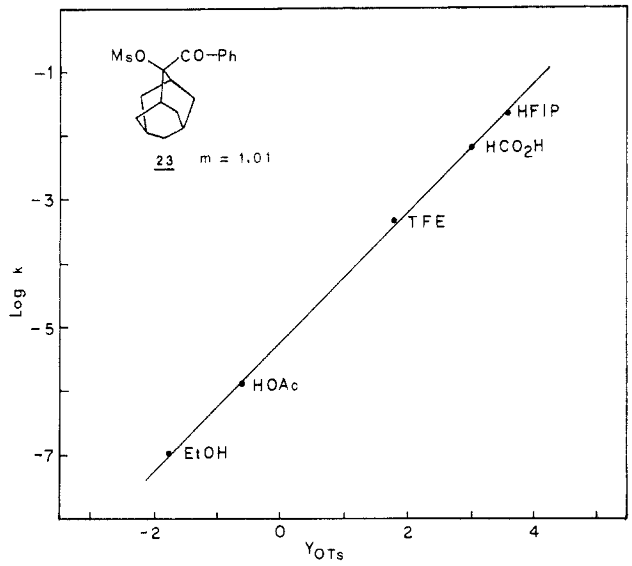


Figure 1. A plot of log k for solvolysis of **23** vs. Y_{OTs}.

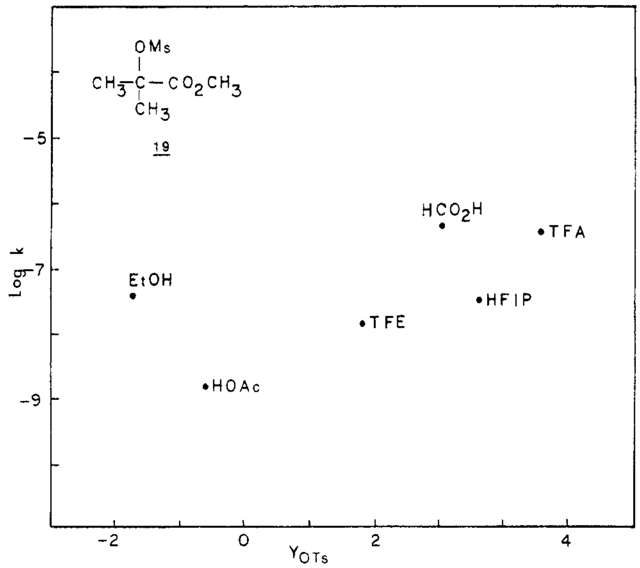
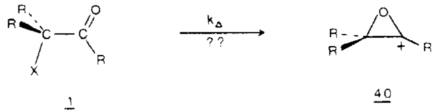


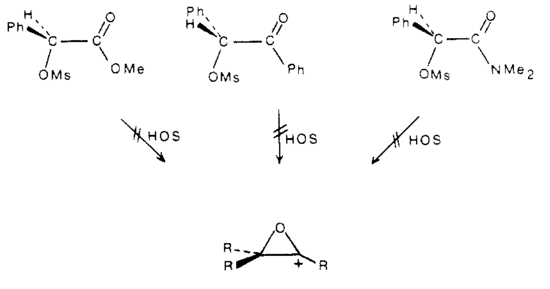
Figure 2. A plot of log k for solvolysis of **19** vs. Y_{OTs}.

37–3d as evidenced by the labeling study. The carbonyl group in secondary α-keto triflates therefore has demonstrated the importance of electron demand as a major factor in determining the magnitude of anchimeric assistance[24] due to σ-participation.

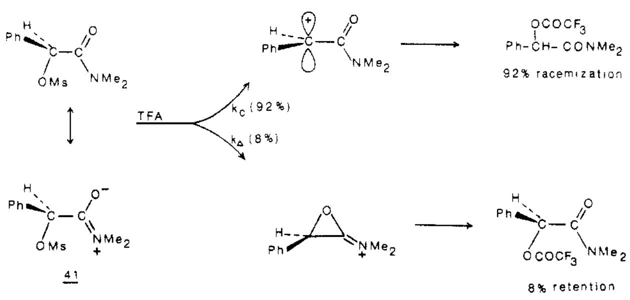
Another potential k_Δ process in solvolyses of α-keto substrates **1** is carbonyl participation giving oxiranyl type cations **40**. Theoretical studies[25] suggest that such a cation (where R = H) is lower in energy than the open carbonyl-substituted cation. We have searched for this k_Δ process using the optically active substrates shown. If k_Δ processes involving oxiranyl type cations **40** were involved, then solvolysis products would have retained configuration. These substrates gave racemized substitution products in highly ionizing nonnucleophilic solvents and partially inverted products in more nucleophilic solvents such as ethanol or acetic acid. This argues *against oxiranyl cations* and in favor of open carbonyl-substituted cations. The lone exception is the behavior of the mesylate derived from (*S*)-(+)-*N*,*N*-dimethylmandelamide, **41**, in trifluoroacetic acid. One observes 8% retention (along with 92% racemization) in the trifluoroacetate product.[17] It appears that only when the carbonyl oxygen is rendered quite nucleophilic (as in an amide) and the solvent is very good for a k_Δ process (as in TFA), then one may begin to see competing oxiranyl cation formation. However, the open carbonyl-substituted cation **2** appears to be the rule in solvolytic reactions of tertiary and benzylic substrates, the theoretical studies notwithstanding.



1 40



40



Carbonyl-Addition Processes

We have found[2e] that mesylate **42** solvolyses in carboxylic acid solvents and hexafluoroisopropyl alcohol via a carbonyl-substituted cation **43** giving **44** and substitution products analogous to **45**. However, in trifluoroethanol, processes initiated by acid- or base-catalyzed addition to the carbonyl group can compete. Under "neutral" conditions, the k_c process dominates. With added triethylamine, base-catalyzed formation of the hemiketal **46** followed by base-catalyzed mesylate displacement led to the alkoxyoxirane **47** as the product observed. Under acidic conditions, the major process is solvolysis of the adduct **46** via phenyl participation, resulting in the rearranged ester **48**. Under certain conditions the chemistry of mesylate **42** can therefore resemble that of α-bromoisobutyrophenone when treated with silver ion,[26] where carbonyl addition pro-

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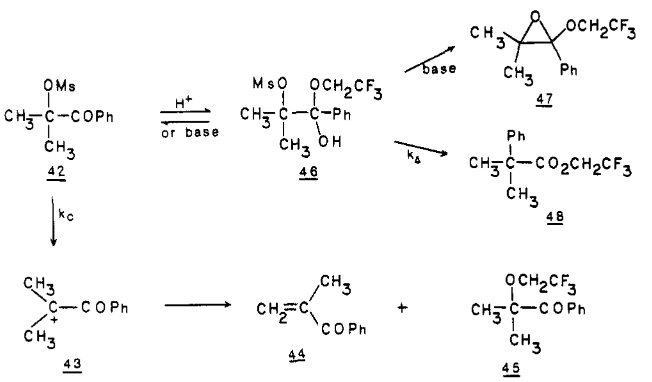
(24) For previous examples of increasing electron demand resulting in increases in π, phenyl, and cyclopropyl participation, see: (a) Gassman, P. G.; Fentiman, A., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–51, 2551–2. (b) Lambert, J. B.; Mark, H. W.; Magyar, E. S. *Ibid.* **1977**, *99*, 3059–67. (c) Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317–24. For a summary and leading references, see: (d) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 163–186.

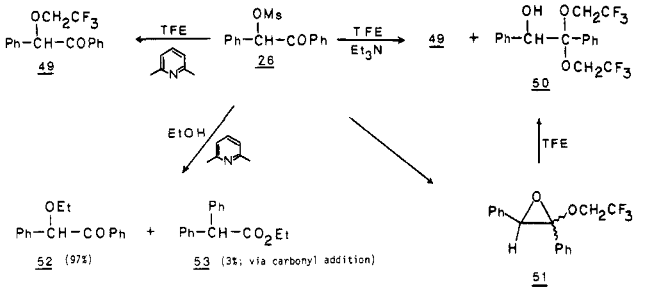
(25) (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309–14. For earlier studies, see: (b) Charpentier-Morize, M.; Leflour, J. M.; Trong Anh, N. *Tetrahedron Lett.* **1974**, 1729–32. (c) Yarkony, D. R.; Schaefer, H. F., III *J. Chem. Phys.* **1975**, *63*, 4317–28.

(26) (a) Cope, A. C.; Graham, E. S. *J. Am. Chem. Soc.* **1951**, *73*, 4702–6. (b) Pasto, D. J.; Sevenair, J. P. *Ibid.* **1971**, *93*, 711–6. (c) DeKimpe, N.; DeBuyck, L.; Verke, R.; Schamp, N. *Chem. Ber.* **1983**, *116*, 3631–6.

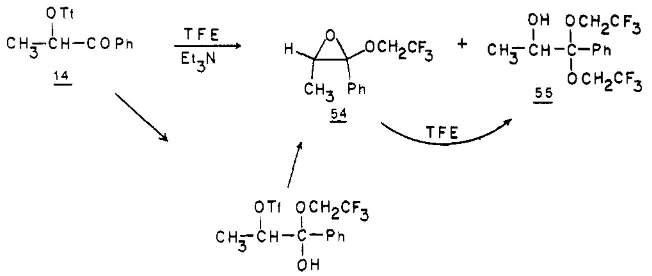


cesses can also explain the observed products.

Since carbonyl-addition processes are not uncommon, we have carefully examined other systems for the intervention of such processes. In trifluoroethanol with 2,6-lutidine as an added buffer, mesylate **26** gave exclusively **49**, presumably via a k_c process. However, with added triethylamine, the hydroxy ketal **50** was also produced, presumably via a carbonyl adduct–alkoxy epoxide, **51**, mechanism. Additionally, careful examination of the products formed on ethanolysis of **26** with added 0.025 M 2,6-lutidine showed 3% of the rearranged ester **53** as well as the major product **52**. This minor product **53** is suggested to arise from a carbonyl adduct which solvolyses with phenyl participation (as in formation of **48**).



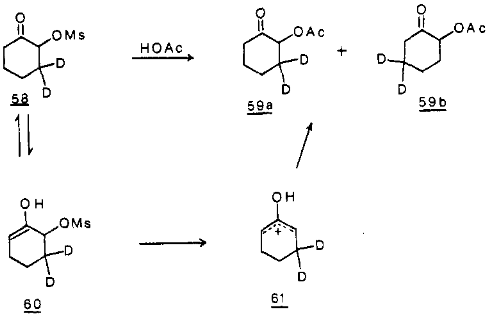
Solvent addition to the carbonyl group can also compete with the direct solvent displacement. The secondary triflate **14** (R = Ph) gave simple substitution products in ethanol, methanol, HOAc, HCO_2H, and CF_3CO_2H. However, in trifluoroethanol containing triethylamine, the alkoxyoxirane **54** and the hydroxy ketal **55** (secondary product) were produced, presumably via the carbonyl adduct **56**.



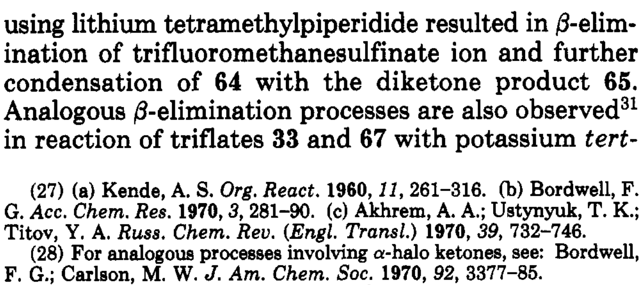
While base- or acid-catalyzed carbonyl addition processes may compete with k_c processes in trifluoroethanolyses of unhindered benzoyl systems, such processes have not been found in solvolyses of the more hindered carbonyl systems **23** and **57**. Mesylates **23** and **57** react exclusively by way of α-keto cations even in the presence of triethylamine.

Enolization Processes

Enolization processes in α-halo ketones (leading to the Favorskii rearrangement) are well documented.[27] The possibility of an enolization process competing with other processes was revealed in our early study[2a] on mesylate **58**-OMs and triflate **58**-OTf. Acetolysis gave a structurally unrearranged product **59** via an enolization mechanism. Evidence for the proposed mechanism[28] included a triflate/mesylate rate ratio of only 40, an entropy of activation of −23 eu, and scrambling of a deuterium label between the 3- and 5-positions. Since solvolysis of enol allylic mesylates (or triflates) analogous to **60** is expected to be a facile process, we have avoided this complication in studies designed to generate carbonyl-substituted cations. Incorporation of the carbonyl group into a benzoyl, pivaloyl, ester, or bicyclic framework prevents formation and solvolysis of enol derivatives.



Deprotonation of secondary α-keto triflates at carbon bearing the triflate group has also been observed under nonsolvolytic conditions. Triflate **39**, which solvolyzes with neighboring C_1C_7 participation, reacted with methoxide in CH_3OD to give the deuterated hydroxy ketal **63**.[29] This product arises via the reversibly formed enolate ion **64**. Irreversible formation of **64**[30] using lithium tetramethylpiperidide resulted in β-elimination of trifluoromethanesulfinate ion and further condensation of **64** with the diketone product **65**. Analogous β-elimination processes are also observed[31] in reaction of triflates **33** and **67** with potassium *tert*-



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(27) (a) Kende, A. S. *Org. React.* **1960**, *11*, 261–316. (b) Bordwell, F. G. *Acc. Chem. Res.* **1970**, *3*, 281–90. (c) Akhrem, A. A.; Ustynyuk, T. K.; Titov, Y. A. *Russ. Chem. Rev. (Engl. Transl.)* **1970**, *39*, 732–746.

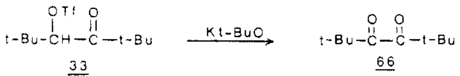
(28) For analogous processes involving α-halo ketones, see: Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3377–85.

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

(30) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1979**, *44*, 1798–1806.

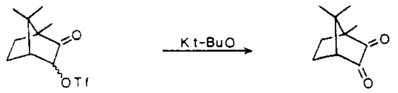
(31) Creary, X. *J. Org. Chem.* **1980**, *45*, 2419–25.

butoxide, which gave the isolable diketones **66** and **68**.



$$\text{t-Bu-}\overset{\text{OTf}}{\text{CH}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-t-Bu} \xrightarrow{\text{K t-BuO}} \text{t-Bu-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-t-Bu}$$

33 66



67 68

Summary and Conclusions

α-Keto mesylates and triflates can solvolyze by a variety of mechanistic pathways including the intervention of carbonyl-substituted cations. k_c processes can dominate when tertiary or benzylic carbonyl-substituted cations can be formed. These cations are formed at rates comparable to that of the α-H analogues; i.e., the rate-retarding effect of the carbonyl group relative to hydrogen is small or negligible. Secondary aliphatic systems lead to k_s or k_Δ processes, bypassing discrete α-keto cations. "Borderline" behavior (i.e., evidence for cationic intermediates but also evidence for solvent involvement) can be observed in certain tertiary and benzylic systems, especially in the more nucleophilic ethanol solvent.

Carbonyl-addition and enolization processes may be superimposed on the k_c, k_s, k_Δ reactivity spectrum. The carbonyl-addition process leads to alkoxyoxiranes or benzylic acid type rearrangements. Enolization can lead to competing solvolysis of enol alkylic mesylates (or triflates) via allylic cations. α-Keto mesylates and triflates can therefore undergo a remarkably diverse set of transformations, not the least of which is the facile generation of cationic intermediates.

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