

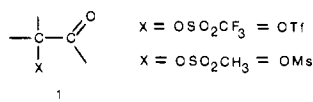
Carbocationic and Related Processes in Reactions of α -Keto Mesylates and Triflates

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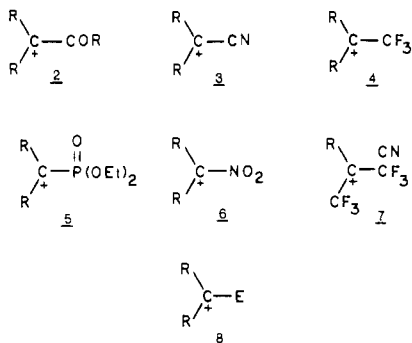
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Some years ago we began an investigation of the chemistry of α -keto triflates. Our initial objectives were the generation of α -keto carbenes by α -elimination processes. During the course of these studies, it became apparent that many systems 1,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



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 Bégue 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, 8} and 6⁹ under long-lived conditions have appeared, as well as studies on cation 7¹⁰ in which two formally electron-withdrawing groups are attached to the cationic center. One can now conclude that so-called "electron-deficient" cations^{4e} 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.

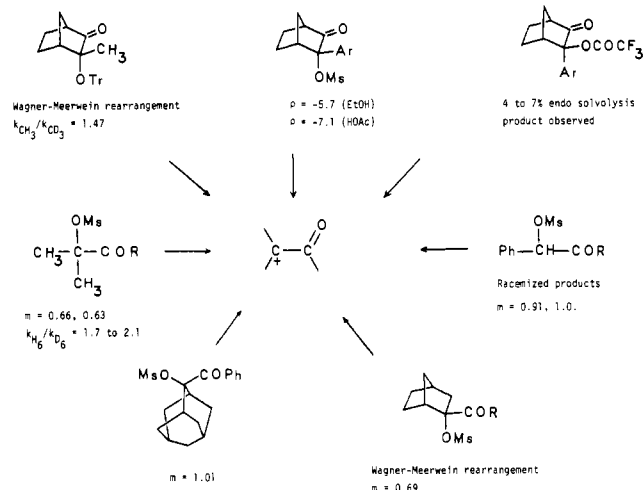


The k_c Process in Solvolyses of α -Keto Systems

At the outset of our studies we wanted to demonstrate the viability of solvolytically generating carbonyl-substituted cations as discrete intermediates. This

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has been done in a variety of studies, which are summarized below. When compared to the α -CH₂R ana-



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(4) (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* 1980, 102, 1214-6. (b) *Ibid.* 1980, 102, 2138-43. (c) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* 1980, 102, 7613-5. (d) Gassman, P. G.; Saito, K. *Tetrahedron Lett.* 1981, 1311-4. (e) Gassman, P. G.; Talley, J. J. *Ibid.* 1981, 5253-6. (f) Gassman, P. G.; Guggenheim, T. L. *J. Org. Chem.* 1982, 47, 3023-6. (g) For a review, see: Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* 1983, 16, 279-85.

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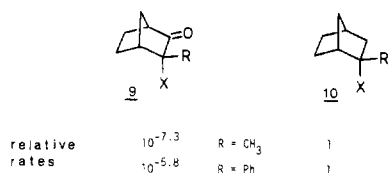
(7) (a) Takeuchi, K.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* 1983, 7. (b) Hopkinson, A. C.; Dao, L. H.; Duperrouzel, R.; Maleki, M.; Lee-Ruff, E. *Ibid.* 1983, 727-8. (c) Maleki, M.; Hopkinson, A. C.; Lee-Ruff, E. *Tetrahedron Lett.* 1983, 4911-2.

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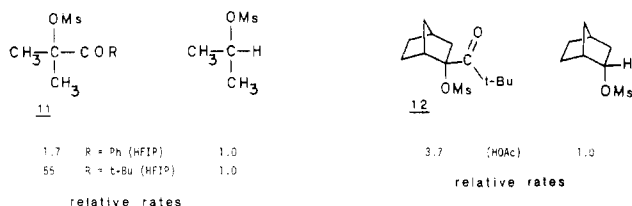
(9) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Krishnamurthy, V. V.; Narang, S. C. *J. Am. Chem. Soc.* 1984, 106, 2378-80.

(10) (a) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* 1977, 99, 4400-4404. (b) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *Ibid.* 1983, 105, 5961-2.

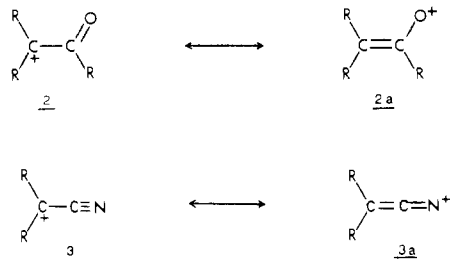
logues 10, the carbonyl-substituted systems 9 were substantially less reactive.^{1a} However comparison of



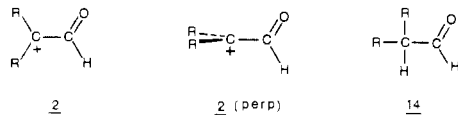
numerous substrates, exemplified by 11^{2e} and 12^{2c}, with those of secondary (α -H) analogues, revealed a lack of or a negligible rate-retarding effect of the carbonyl group relative to hydrogen. These studies pointed



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 McDonald¹¹ and demonstrated by Gassman⁴ 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 view-

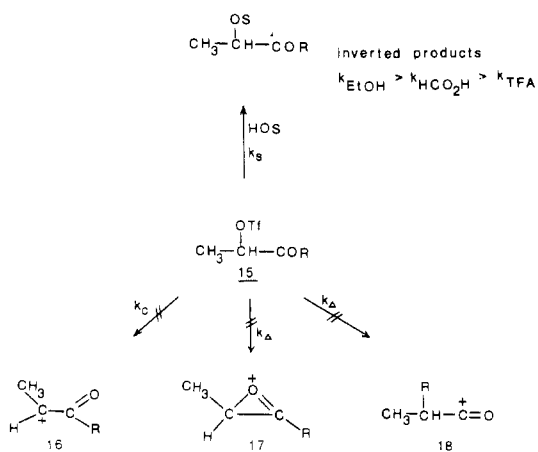
(11) McDonald, R. N.; Steppel, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5664-70.

(12) (a) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957-9. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *Ibid.* **1980**, *102*, 6561-3. (c) Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, 383-6. (d) Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885-91.

point,^{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 studies² 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 Process¹²

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_A 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.

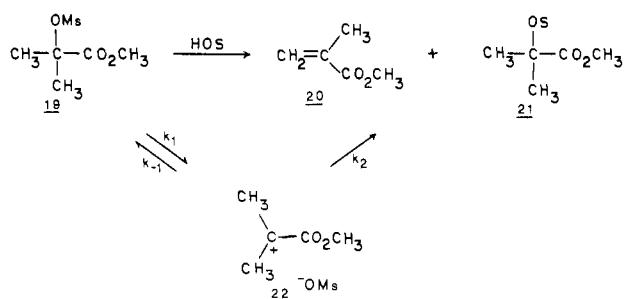
The "Borderline" Process¹⁵

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-

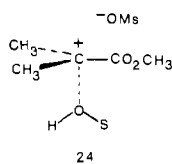
(13) The term k_s , as used by Schleyer,¹³ includes processes which are not completely limiting (k_c) but in which there can be substantial cationic development. It also includes direct solvent displacement with little cationic charge development. It is in this latter sense that we use the term k_s . (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) Winstain, S.; Allred, E.; Heck, R.; Glick, R. *Tetrahedron* **1958**, *3*, 1-13.

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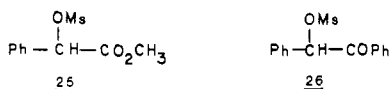
(15) This term is used to describe processes in which there is evidence for cation formation but also evidence for kinetically important solvent involvement.



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 isotope 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.



Further evidence for solvent involvement is seen in ethanolyse 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.

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

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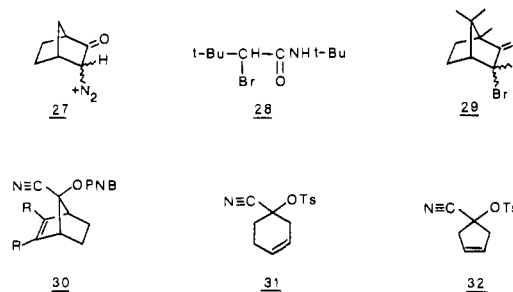
(17) Unpublished work in our laboratories.

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

(19) Sheehan, J. C.; Beeson, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 362–66.

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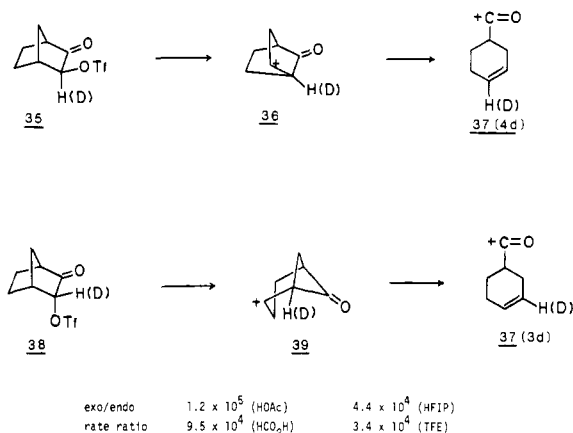
silver salts. Rate data showed increases in the mag-



nitude 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.

	(80% EtOH)	
1.0		1.79
1.0	(CF ₃ CH ₂ OH)	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, solvolyse by the different k_{Δ} processes shown below:



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

(21) Gassman, P. G.; Doherty, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 3742–4.

(22) Gassman, P. G.; Talley, I. J.; Saito, K.; Guggenheim, T. L.; Doherty, M. M.; Dixon, D. A. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1983**, 28(2), 334–8.

(23) Shiner, V. J., Jr.; Seib, R. C. *Tetrahedron Lett.* **1979**, 123–6.

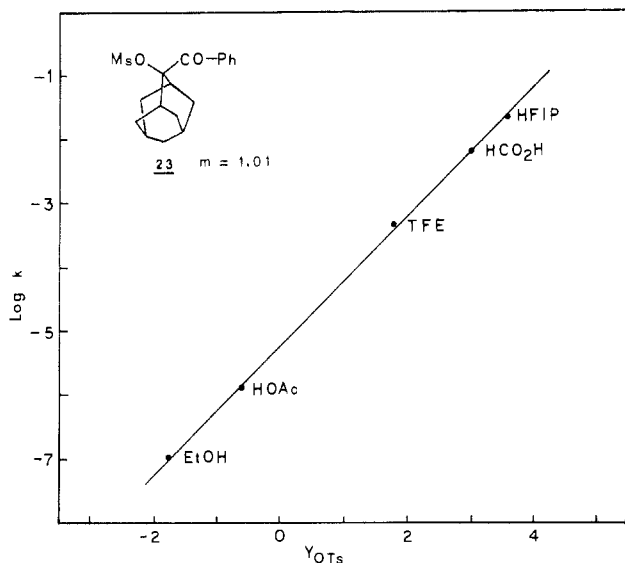


Figure 1. A plot of $\log k$ for solvolysis of **23** vs. Y_{OTs} .

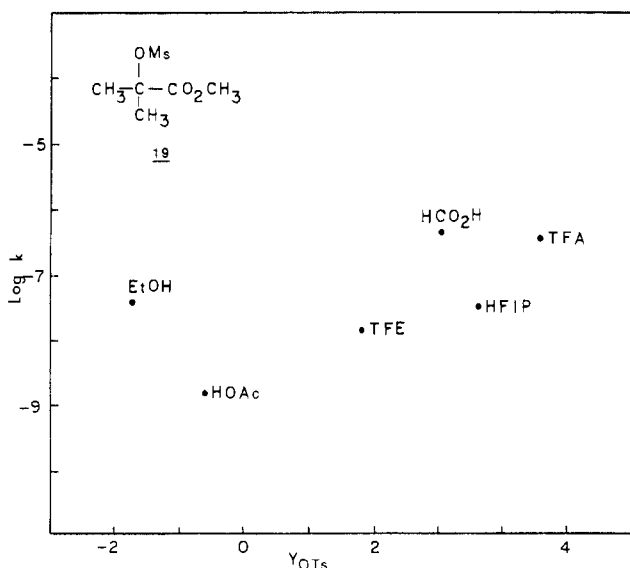
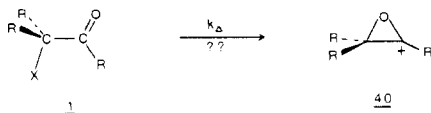


Figure 2. A plot of $\log k$ for solvolysis of **19** vs. Y_{OTs} .

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 assistance²⁴ due to σ -participation.

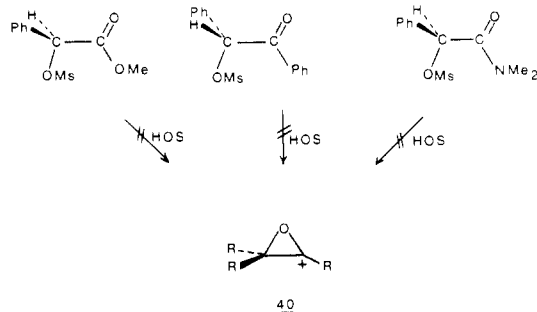
Another potential k_{Δ} process in solvolyses of α -keto substrates **1** is carbonyl participation giving oxiranyl type cations **40**. Theoretical studies²⁵ suggest that such a cation (where $R = H$) is lower in energy than the open



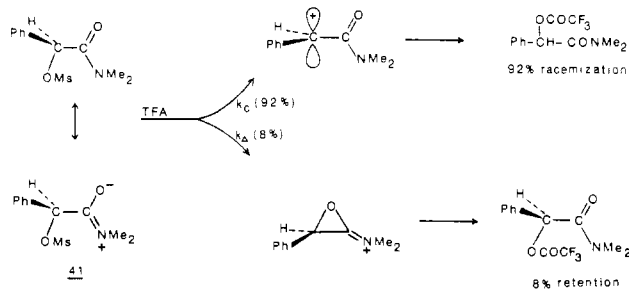
(24) For previous examples of increasing electron demand resulting in increases in π , phenyl, and cyclopropyl participation, see: (a) Gassman, P. G.; Fentiman, A., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–51, 2551–2. (b) Lambert, J. B.; Mark, H. W.; Magyar, E. S. *Ibid.* **1977**, *99*, 3059–67. (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.

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 sub-



stitution 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

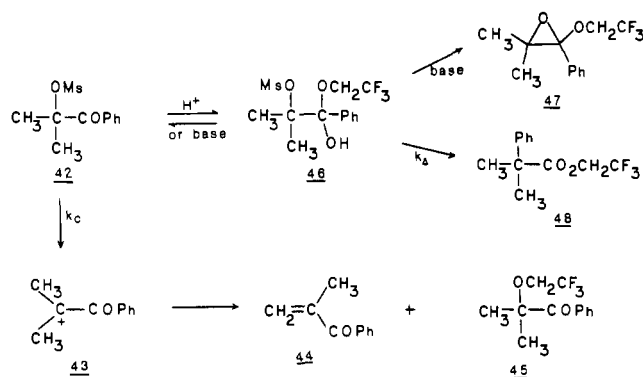


when the carbonyl oxygen is rendered quite nucleophilic (as in an amide) and the solvent is very good for a k_{Δ} process (as in TFA), then one may begin to see competing oxiranyl cation formation. However, the open carbonyl-substituted cation **2** appears to be the rule in solvolytic reactions of tertiary and benzylic substrates, the theoretical studies notwithstanding.

Carbonyl-Addition Processes

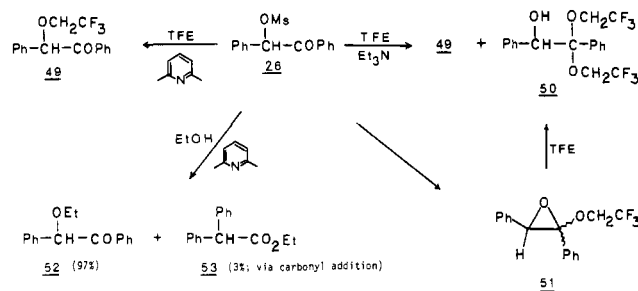
We have found²⁶ that mesylate **42** solvolyses in carboxylic acid solvents and hexafluoroisopropyl alcohol via a carbonyl-substituted cation **43** giving **44** and substitution products analogous to **45**. However, in trifluoroethanol, processes initiated by acid- or base-catalyzed addition to the 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-

(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.

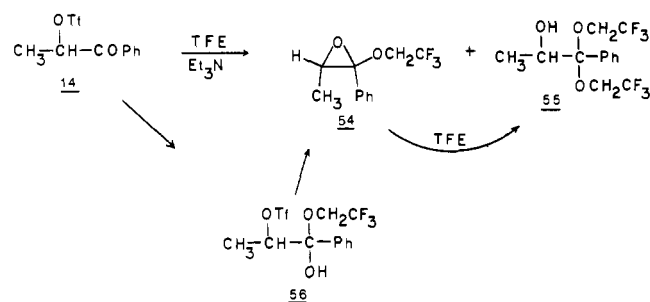


cesses can also explain the observed products.

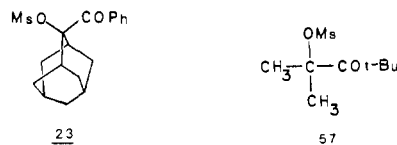
Since carbonyl-addition processes are not uncommon, we have carefully examined other systems for the intervention of such processes. In trifluoroethanol with 2,6-lutidine as an added buffer, mesylate **26** gave exclusively **49**, presumably via a k_c process. However, with added triethylamine, the 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** ($\text{R} = \text{Ph}$) gave simple substitution products in ethanol, methanol, HOAc, HCO_2H , and $\text{CF}_3\text{CO}_2\text{H}$. However, in trifluoroethanol containing triethylamine, the alkoxyoxirane **54** and the hydroxy ketal **55** (secondary product) were produced, presumably via the carbonyl adduct **56**.

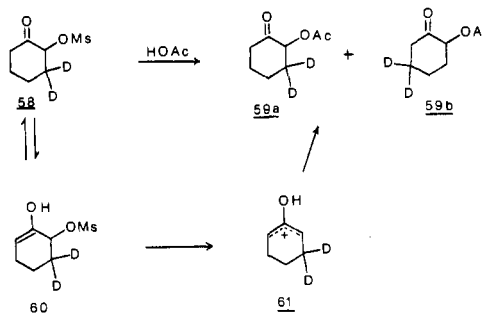


While base- or acid-catalyzed carbonyl addition processes may compete with k_c processes in trifluoroethanolyses of unhindered benzoyl systems, such processes have not been found in solvolyses of the more hindered carbonyl systems **23** and **57**. Mesylates **23** and **57** react exclusively by way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



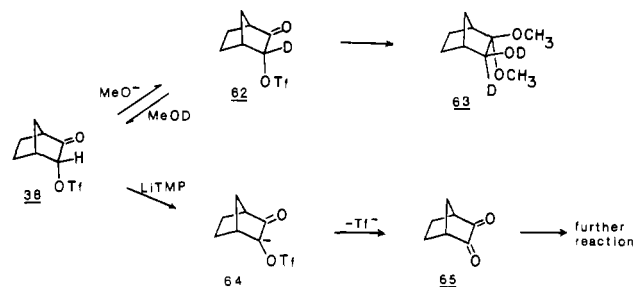
Enolization Processes

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 mechanism²⁸



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 solvolyses 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 observed³¹ in reaction of triflates **33** and **67** with potassium *tert*-

(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.

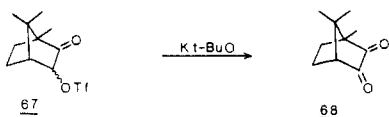
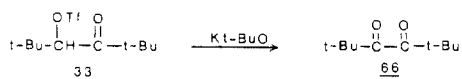
(28) For analogous processes involving α -halo ketones, see: Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* 1970, 92, 3377-85.

(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**.



Summary and Conclusions

α -Keto mesylates and triflates can solvolyze by a variety of mechanistic pathways including the inversion 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. Sec-

ondary 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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