# α-Acylcarbenium Ions[1]

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Ten years ago, we were interested in the controversial question of the mechanism of the quasi-Favorskii rearrangement of α-halo ketones.[2,3] A stereochemical approach led us to conclude that in a general way the reaction proceeded by a mechanism similar to that of the benzilic acid rearrangement.

However, in Ag₂O-promoted dehalogenations, unexpected results obtained from some peculiar models caused us to suggest the hypothesis of a transient α-acylcarbenium ion. Such ions had already been postulated as intermediates for various reactions, but mostly without convincing arguments.[4] Nevertheless, in one favorable case, the formation of an α-acylcarbenium (1) had been observed during a ¹H NMR study.[5]
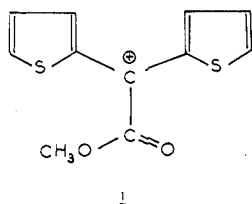
This carbocation is, of course, particularly stable inasmuch as it is tertiary, with two stabilizing aromatic rings. But, on the other hand, all workers who had reported studies of the solvolysis of α-halo ketones had come to the conclusion that α-acylcarbenium ions could never be implicated in those reactions.[6]

In another area, concerning the preparation of α-lactams, the dehalogenation reaction of α-halo amide 2, as shown in Scheme I, was described.[7] This result provided us with a strong argument in favor of cationic intermediates. Unsaturated amide 3 can only be formed as a result of Wagner–Meerwein rearrangement followed by elimination. One must emphasize that the conditions employed for this dehalogenation reaction, i.e., using a silver salt of superacid and a nonnucleophilic solvent, are very different from those of the usual solvolytic media.
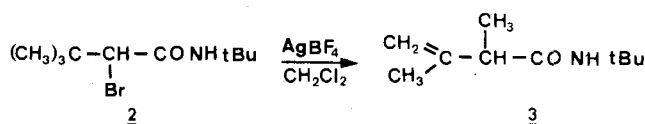
On the basis of these results, we became particularly interested in the possibility that the silver salts of superacids could in general ionize α-halocarbonyl com-

Scheme I

pounds to α-acylcarbenium ions. Early experiments of ours strikingly demonstrated that AgSbF₆/CH₂Cl₂ promotes ionization of an α-halogenocarbonyl compound,[8] as shown in Scheme II.[9]

Both isomers 4a and 4b lead in excellent yield to the same oxonium salt, 5, which by hydrolysis gives cis-δ-hydroxy compound 6. A cationic species must be involved in the reaction, and this cation might be the α-acylcarbenium ion 7 which by a process of hydride shifts leads to 6.

Questions arise concerning the structure and the stability of an α-acylcarbenium ion. A priori, electrostatic effects must reduce markedly the stability of such an ion. However, the electronic configuration of a carbonyl group is capable of stabilizing a positive charge on the adjacent carbon. This stabilization is achieved by the overlapping of the vacant orbital of the cationic α carbon with either the occupied lone pair orbital of oxygen or the π orbital of the carbonyl group (Figure 1).

These two modes of stabilization impose different geometries on the α-acylcarbenium ion, namely forms A and B which can be represented by a staggered or bridged structure and an eclipsed or planar structure, respectively. Recently, the stability of the carbocation C₂H₃O⁺ was evaluated by ab initio calculations using two different basis sets.[10,11] The results are conflicting:

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Jean-Pierre Bégué was born in Paris in 1938. He studied chemistry in Paris and received in 1968 his Ph.D. from the University of Orsay while working with Professor M. Fétizon. He worked first in the field of alkaloid synthesis. After mechanistic studies on α-acylcarbenium ions, his research is now focused on selective long-range functionalizations, especially in the steroid field.

Micheline Charpentier was born near Paris in 1925. She received her Ph.D. in 1958 from the University of Paris while working with Dr. B. Tchoubar in a laboratory of the Medical University of Paris. She transferred to Institut de Chimie des Substances Naturelles in Gif-sur-Yvette, where she worked for another 10 years. Her current research interests include reaction mechanisms, especially Favorskii and quasi-Favorskii rearrangements, stereochemistry of halogenation and protonation of enols and enolates, and, in general, studies of unstable intermediates.

(1) A reviewer of the original manuscript pointed out that the term "α-ketocarbenium" previously used by us and by other authors is incorrect. Positional labeling in carbenium ions has by long-standing consensus assigned α to the charge center carbon atom. The species with which this Account deals are therefore not "α-ketocarbenium" ions but "β-ketocarbenium" ions. However this last term might be confusing. For this reason, we have chosen the term "α-acylcarbenium".

(2) D. Baudry, J. P. Bégué, and M. Charpentier-Morize, *Bull. Soc. Chim. Fr.*, 1416 (1971).

(3) (a) E. E. Smissman and G. Hite, *J. Am. Chem. Soc.*, 82, 3375 (1960); (b) E. E. Smissman and J. L. Diebold, *J. Org. Chem.*, 30, 4005 (1965).

(4) Bibliography in M. Charpentier-Morize, *Bull. Soc. Chim. Fr.*, 343 (1974), and in W. Kirmse and G. Rauleder, *Justus Liebigs Ann. Chem.*, 1333 (1976).

(5) G. P. Nilles and R. D. Schuetz, *Tetrahedron Lett.*, 4313 (1969).

(6) This assertion was true up to the extremely recent work of X. Creary [*J. Org. Chem.*, 44, 3938 (1979)]. The results concerning the acetolysis of exo-3-methyl-2-oxobicyclo[2.2.1]heptan-endo-3-yl tresylate and exo-3-aryl-2-oxobicyclo[2.2.1]heptan-endo-3-yl mesylate and trifluoroacetate strongly support tertiary α-acylcarbenium ions as transient intermediates in the norbornyl system. This important paper came to our attention after our manuscript was submitted.

(7) J. C. Sheehan and J. H. Beeson, *J. Am. Chem. Soc.*, 89, 362 (1967).

(8) (a) J. P. Bégué and M. Charpentier-Morize, *Angew. Chem., Int. Ed. Engl.*, 10, 327 (1971); (b) J. P. Bégué, M. Charpentier-Morize, and C. Pardo, *Tetrahedron*, 31, 1919 (1975).

(9) Representation of cationic species in this Account with localized positive charge does not necessarily indicate the actual structure.
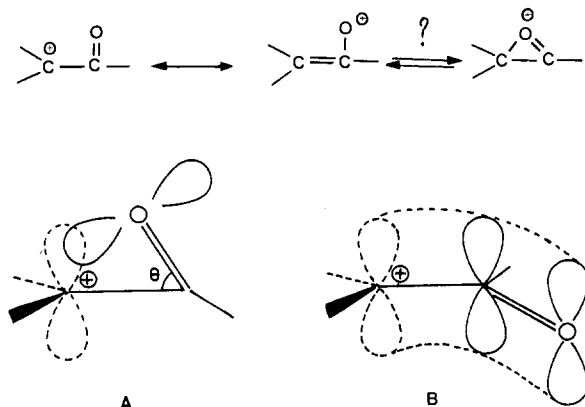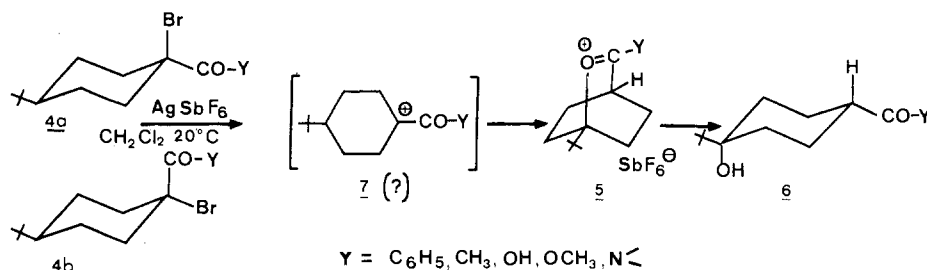
Scheme II

Y = C₆H₅, CH₃, OH, OCH₃, N<

Figure 1.

when the STO-3G basis set is used, form A ($\theta = 68°$)[12] is more stable than B ($\sim$16 kcal/mol); when a more extended basis set is used, form B is more stable than A (6–8 kcal/mol).

It is important to emphasize that ab initio calculations give static energy values and do not reflect dynamic reaction processes. The formation of an α-acylcarbenium ion in form A from an α-halo ketone is the result of an intramolecular S_N2 substitution. According to "perturbation theory"[13] (i.e., from a reactivity point of view), the S_N2 process will be favored: the n (oxygen) occupied and σ^*_{C-X} vacant orbitals in α-halo ketones are rather close in energy—overlapping is certainly much more important between these two relatively localized orbitals than with the $\pi_{C=O}$ MO (particularly when carbon bears a substituent such as phenyl).

Thus, even if electrostatic considerations do not favor the existence of a pure α-acylcarbenium ion, stabilization of the vacant orbital on cationic carbon by interaction with occupied ones (either the lone pair of oxygen or the $\pi_{C=O}$ of carbonyl) nevertheless warrants serious consideration of the possibility of such a cation in either its A or B form. These two structures could be in a conformational equilibrium with each other, with the equilibrium constant depending on the nature of the substituents.

(10) M. Charpentier-Morize, J. M. Lefour, and N. Trong Anh, *Tetrahedron Lett.*, 1729 (1974).

(11) (a) L. Radom, cited by L. Radom, D. Poppinger, and R. C. Haddon, *Carbonium Ions*, **5**, 2413 (1976); (b) D. R. Yarkony and H. F. Schaefer, *J. Chem. Phys.*, **63**, 4317 (1975).

(12) These two conformations, eclipsed B and bridged A with $\theta = 85°$, are said to have rather the same stabilities.[10] It is suggested[10] that this geometry does not constitute a "minimum minimorum". Thus, after optimization of this angle using the same STO-3G basis set, with $\theta = 68°$, it appears that the A-bridged species is more stable than the B-eclipsed one by 16.8 kcal/mol⁻¹.

(13) (a) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973), and references cited therein; (b) N. Trong Anh, *Actual. Chim.*, **1**, 9 (1974).

Scheme III
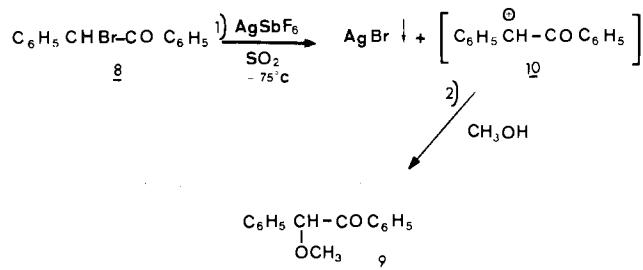
Scheme IV
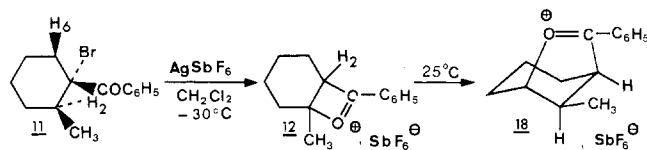
In this Account, *for practical purpose, we use both the term and the structure "α-acylcarbenium", but this formulation does not preclude the oxirenium form.*

Evidence for α-Acylcarbenium Ions

Formation. *From an α-Halobenzyl Ketone*[14] (Scheme III). Dehalogenation of **8** was performed by treatment with $AgSbF_6/SO_2$ at –75 °C. After AgBr precipitation, MeOH was added in order to trap the cationic intermediate. Methoxy ketone **9** was obtained in $\sim$40% yield.

When this dehalogenation was carried out in the NMR probe (¹H or ¹³C), the resulting signals were consistent with the carbocation structure **10**: ¹H NMR δ 10.5 (singlet, 1 H) (compare with $C_6H_5CHCH_3^+$, δ 10.5);[15] ¹³C NMR δ 192.4 and 199.5 (compare with $C_6H_5CHF^+$, δ 203.7).[16] The lifetime of the cationic species was too short to allow recording of off-resonance spectra.

From an α-Bromocyclohexyl Ketone[17] (Scheme IV). Dehalogenation of **11** (with $AgSbF_6$ in CH_2Cl_2 at –30 °C) leads to oxonium salt **12** as the kinetic product. Three processes may be involved in ionization of a C–X bond: nucleophilic assistance by the solvent and/or anion (k_s), intramolecular nucleophilic assistance (k_Δ), and electrophilic assistance by the solvent and/or cation (k_c).[18]
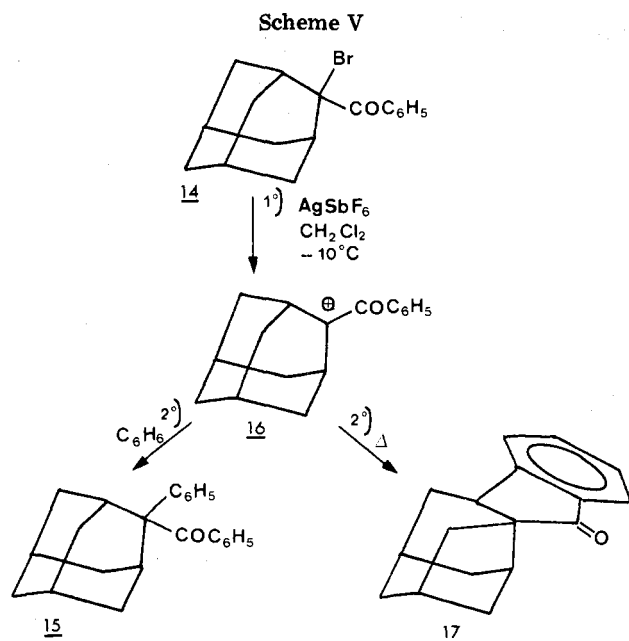
(14) D. Baudry and M. Charpentier-Morize, *Nouv. J. Chim.*, **2**, 255 (1978).

(15) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).

(16) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975).

(17) J. P. Bégué and M. Malissard, *Tetrahedron*, **34**, 2095 (1978).

(18) J. M. Harris, *Prog. Phys. Org. Chem.*, **11**, 89 (1974).

Scheme V

Figure 2.

In this case, involving AgSbF$_6$ in CH$_2$Cl$_2$, probably only the k_Δ and k_c contributions are significant. Although it is difficult to evaluate their relative importance, it seems likely that the term k_Δ plays an important role in the formation of an unstable cation such as an α-acylcarbenium ion.[18] For ionization of the C–Br bond in compound 11, *a priori* two k_Δ processes may be involved: k_Δ related to hydrogen migration ($k_{\Delta H}$) and k_Δ related to carbonyl oxygen participation ($k_{\Delta C=O}$). $k_{\Delta H}$ can certainly be neglected, as the migrating hydrogen H$_2$ is *cis* and not antiperiplanar to the leaving group. Therefore, it is reasonable to assume that 1–3 carbonyl participation ($k_{\Delta C=O}$) takes place in the formation of the corresponding α-acylcarbenium ion. One hydrogen-migration step must then occur to form 12, and another in the transformation of 12 into 18.

From an α-Bromoadamantyl Ketone.[19] Scheme V outlines significant results obtained with compound 14. Because 14 is a 2,2-disubstituted adamantane, any possibility of hydride shifts in the ionization process is excluded.[20] The formation of 15 when dehalogenation of 14 is followed by addition of benzene shows the presence of intermediate α-acylcarbenium 16. The latter rearranges into indanone 17 upon heating (rearrangement of 16 into a protoadamantyl cation followed, or accompanied by, intramolecular Friedel–Crafts reaction).

Significance. These three examples provide evidence of the formation of α-acylcarbenium ions. (It is noteworthy that under our experimental conditions these dehalogenations take place very easily at relatively low temperatures.)

The two last examples provide strong evidence in favor of carbonyl participation in ionization. Furthermore we note an earlier result of Pasto and Serve[21] in their studies of the solvolysis (in 80% EtOH with
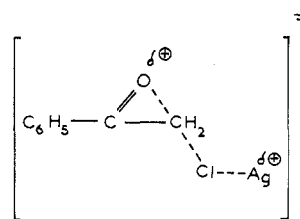
AgNO$_3$) of α, β-, γ-, and δ-chloroalkyl ketones. They observed approximately uniform negative values for the entropy of activation (about −20 eu) for β-, γ-, and δ-haloalkyl ketones but a larger value (−45.3 eu) for an α-halo ketone (phenacyl chloride). As one alternative interpretation, Pasto and Serve suggested participation by the carbonyl oxygen to form a three-membered ring including a carbon–oxygen bond in the transition state, as shown in Figure 2.

Reactivity of α-Acylcarbenium Ions

To what extent are α-acylcarbenium ions able to undergo the classic reactions of ordinary carbenium ions? In what ways are they similar and how do they differ?

Hydride Shift. Experiments involving the dehalogenation of α-bromocarbonyl compounds of many types have shown that, as for ordinary carbocations, the isomerization of α-acylcarbenium ions often takes place via hydride shifts. In the case of α-acylcarbenium ions the process is selective and leads to the formation of oxonium salts which are quite often observed (^{1}H and ^{13}C NMR) and in some instances isolated.

Hydride migrations have been observed in both cyclic and acyclic series.[8,22-25] The mechanism of these migrations has been thoroughly studied in the cyclohexane series.[16]

One conclusion that emerged is that migrations are 1–2 successive and not transannular (result obtained from deuterated compounds). Another is that the final product of these hydride migrations is the most stable oxonium salt. When dehalogenation of 11 (Scheme IV) is carried out at low temperature, the kinetically favored oxonium salt 12 is obtained, but upon raising the temperature it isomerizes to the less strained and more stable oxonium salt 18.

Wagner–Meerwein Type Rearrangement.[14,23] Neighboring group migrations occur in α-acylcarbenium ions as in ordinary carbocations. This process is selective and analogous to hydride shifts leading to oxonium salts. The results are similar for methyl and phenyl migrations. We report only some results concerning the latter.

The dehalogenation of ketone 19 (Scheme VI) by AgSbF$_6$ in C$_6$D$_6$ strikingly illustrates the specificity of the reaction process. In contrast to the dehalogenation of many secondary α-bromo ketones studied,[23] the dehalogenation of 19 is fast at room temperature, being essentially complete within 10 min. The reaction is

(19) J. P. Bégué, unpublished results.

(20) (a) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 9, 209 (1972); (b) P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 81, 539 (1969); (c) M. M. Sinnot and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1447 (1975); (d) J. R. Alford, B. D. Cuddy, D. Grant, and M. A. McKervey, *ibid.*, 2707 (1972); (e) M. L. Sinnott and M. C. Whiting, *ibid.*, 1446 (1975).

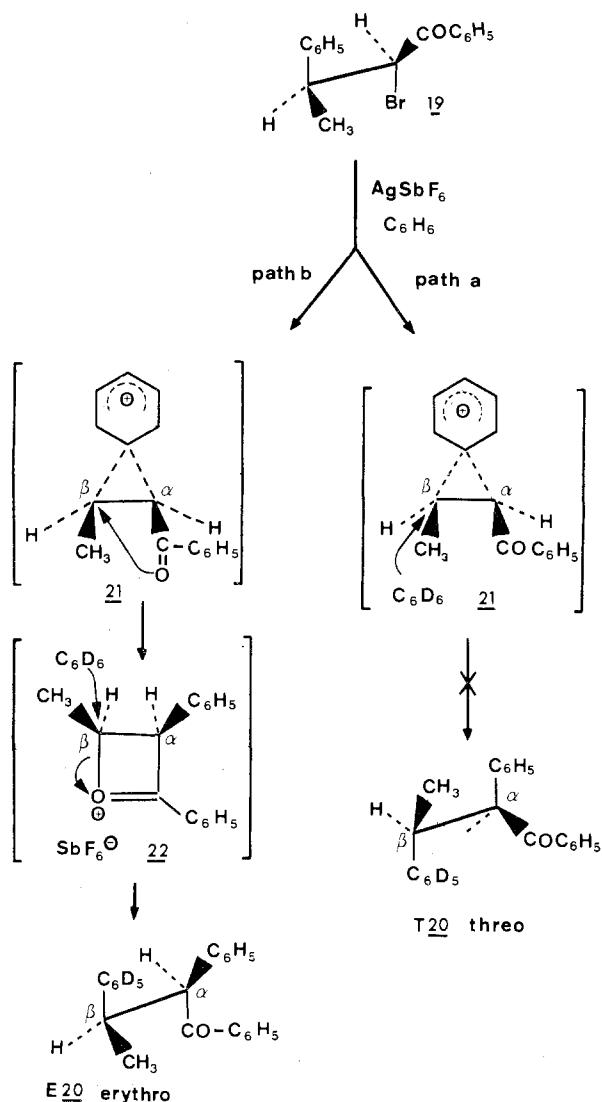(21) D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, 87, 1515 (1965).

(22) J. P. Bégué, D. Bonnet, M. Charpentier-Morize, and C. Pardo, *Tetrahedron*, 31, 2505 (1975).

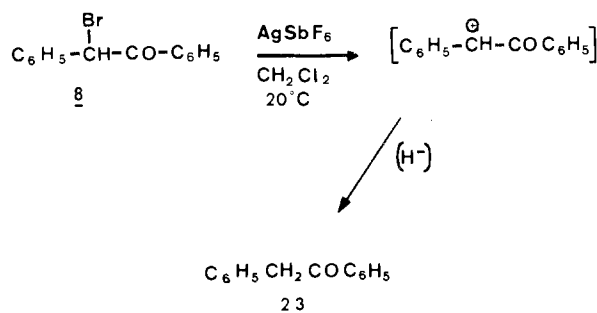(23) D. Baudry, Thèse d'Etat, University of Paris-Sud, 1975.

(24) J. P. Bégué and co-workers, unpublished work.

(25) (a) D. Baudry, M. Charpentier-Morize, D. Lefort, and J. Sorba, *Tetrahedron Lett.*, 2449 (1974); (b) C. Pardo, Thèse d'Etat, University of Paris-Sud, 1977.

Scheme VI

Scheme VII

stereospecific, leading exclusively to *erythro* ketone E20.[26]

In this case, the ease of ionization of the C–Br bond can only be explained by phenyl participation which leads to the phenonium ion 21. If this were the only intermediate, the attack of C_6D_6 on 21 (path a) would lead to the threo ketone T20 instead of the observed
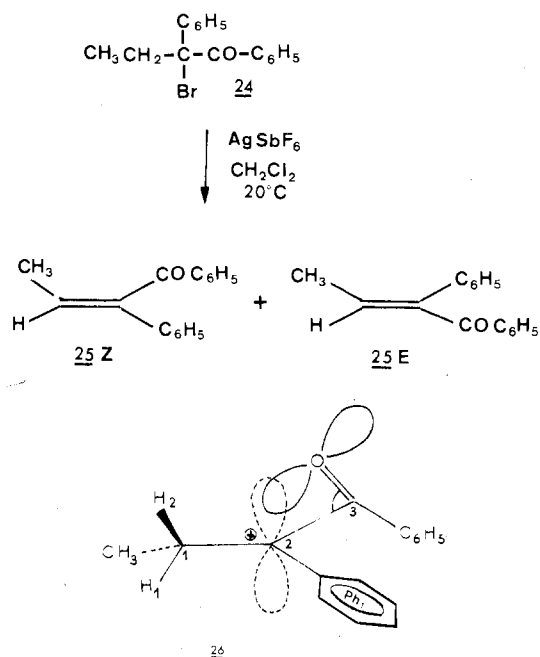
Scheme VIII

Figure 3.

erythro ketone E20. This discrepancy can easily be explained by isomerization of phenonium ion 21 to oxonium salt 22 followed by attack of C_6D_6 on the β carbon, leading to erythro ketone E20 (path b).

Intermolecular Hydride Transfer.[14] Dehalogenation of 8 by $AgSbF_6$ in CH_2Cl_2 in the presence of cyclopentane leads to deoxybenzoin 23 (Scheme VII). Evidently, α-acylcarbenium ion 10 can abstract a hydride ion from a saturated hydrocarbon in a manner similar to ordinary carbenium ions.[27]

Addition of Nucleophiles. α-Acylcarbenium ions, like ordinary carbenium ions, undergo nucleophilic addition reactions. Thus ions 10 and 16 add methanol and benzene, respectively (see Schemes III and V).
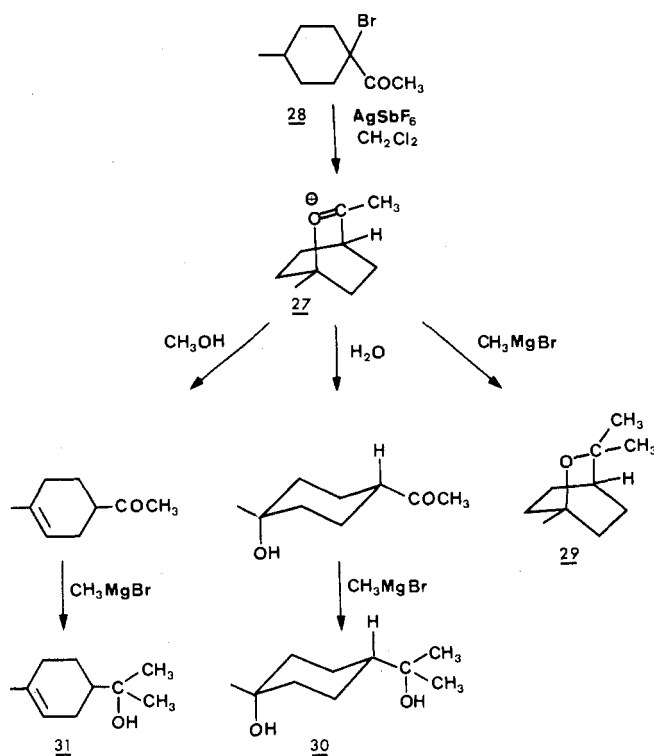
E1-Type Elimination.[14] Dehalogenation of ketone 24 by $AgSbF_6$ in CH_2Cl_2 at 20 °C (10 min) leads to ethylenic ketones 25Z and 25E (Scheme VIII). Low-temperature studies of dehalogenation reactions have shown that ketone 25Z is the exclusive kinetic product. Subsequently, at room temperature, 25Z isomerizes completely to ketone 25E (16 h at 25 °C). It is reasonable to assume that an E1-type reaction takes place under the conditions employed. However, unlike an ordinary acyclic carbenium ion, an α-acylcarbenium ion may undergo a stereospecific elimination. The bridge form A (vide supra) of ion 26 provides an explanation of the observed stereospecificity (Figure 3).

The carbonyl group is perpendicular to the plane of the carbocation defined by the three bonds C-2 to phenyl, C-1 to C-3, and C-1 to C-2; the methyl group occupies the furthest possible position relative to Ph_1 (steric repulsion). Elimination from this conformer will result in 25Z.[28]
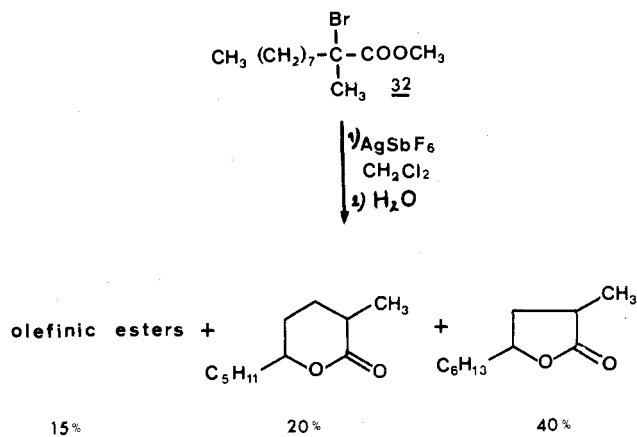
(26) (a) Thermodynamic equilibrium for the two isomers 20 was found to be 50:50 in EtONa/EtOH medium;[26b] it is unlikely that this equilibrium would be totally displaced toward E20 in the experimental conditions employed. Furthermore, dehalogenation ($AgSbF_6$, CH_2Cl_2) of the other diastereoisomer of 19 leads very slowly (24 h at room temperature) to the T20 isomer (see ref 14). (b) H. E. Zimmerman and W. H. Chang, *J. Am. Chem. Soc.*, 88, 5659 (1966).

(27) (a) P. Brewer and B. S. Greensfelder, *J. Am. Chem. Soc.*, 73, 2257 (1951); (b) Bibiliography in *Carbonium Ions*, 2, 475 (1970).

(28) A reviewer has suggested that the observed stereospecificity can be explained by a similar steric effect in the B planar form. This point of view cannot be definitively ruled out. However, careful examination of the models shows that, in form A, leading to the Z isomer, no conformations of the phenyl group adjacent to C=O are unhindered unlike in the corresponding form B.

Scheme IX

28 → AgSbF$_6$, CH$_2$Cl$_2$ → **27**

CH$_3$OH / H$_2$O / CH$_3$MgBr

31 ← CH$_3$MgBr

30 ← CH$_3$MgBr

29

Scheme X

$$CH_3 (CH_2)_7-\underset{CH_3}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-COOCH_3 \quad \textbf{32}$$

i) AgSbF$_6$, CH$_2$Cl$_2$
ii) H$_2$O

olefinic esters + [lactone, C$_5$H$_{11}$, CH$_3$] + [lactone, C$_6$H$_{13}$, CH$_3$]

15% 20% 40%

Scheme XI

33 → AgSbF$_6$, CH$_2$Cl$_2$ → [oxonium, C$_6$H$_5$, SbF$_6^{\ominus}$] → H$_2$O → **35**

34 → AgSbF$_6$, CH$_2$Cl$_2$ → [oxonium, OCH$_3$, SbF$_6^{\ominus}$] → H$_2$O → **36**

Scheme XII

$$R-X + Ag^{\oplus} \rightleftharpoons (R-X----Ag)^{\oplus}$$

$$Y^{\ominus} + (R-X----Ag)^{\oplus} \xrightarrow{\text{rate determining}} (Y^{\ominus} R^{\oplus} X^{\ominus} Ag^{\oplus}) \rightarrow \text{Products}$$
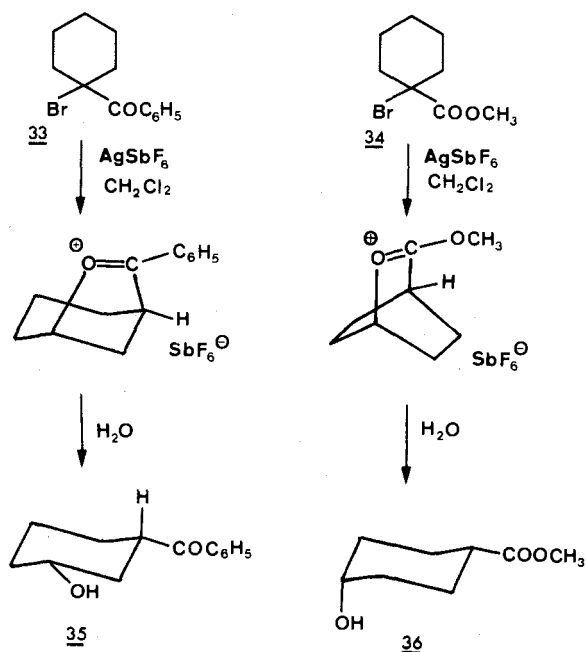
$$Y^{\ominus} = \text{anion or solvent}$$

Potential Synthetic Applications

When the structure of the precursor permits, α-acylcarbenium ions undergo hydride shifts preferentially. These reactions are often highly selective, leading to the most stable oxonium salts in good yield (vide supra). The ambident nature of these salts enables the straightforward synthesis of compounds which could otherwise be obtainable only with difficulty. In this way *long-range functionalization may take place.*
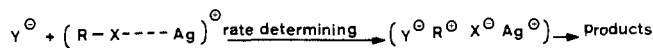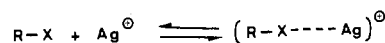
Scheme IX illustrates the synthetic versatility of AgSbF$_6$ dehalogenation of α-bromo ketones. The oxonium salt **27**, resulting selectively from dehalogenation of **28**, undergoes simple reactions leading to cineole **29**, to *cis*-terpin **30**, or to α-terpineol **31**.[24] In contrast, dehalogenation of **32**, with subsequent hydrolysis, leads to a mixture of γ- and δ-lactones[25a] (Scheme X).

In fact, thermodynamic factors govern the selectivity of the reaction, i.e., the relative stabilities of the resulting oxonium salts. In the literature, very few data are available concerning the stabilities of these com-

pounds.[29] Nevertheless, two features seem to be of importance: (i) methyl substitution at C$_\omega$ increases the stability markedly (about 3 kcal/mol);[29c] and (ii) the stabilities of five- and six-membered monocyclic oxonium salts are very similar,[29a,b,e] the five-membered ring being favored by only 0.6 kcal/mol.

However, other factors governing the stabilities of oxonium salts are still unknown. Scheme XI illustrates the problem. The difference in the selectivity observed in the dehalogenation of **33** and **34** is still unexplained. In any case, these reactions are valuable routes to compounds **35** and **36**; in each case a selective and stereospecific hydroxylation occurs on a nonactivated methylenic carbon, but not in the same position.[22]

The reported examples of synthetic applications are still limited. Taming of this chemistry must be accomplished before products can be predicted with confidence. To some extent, the reactivity of the resulting oxonium determines the structure of the products. This problem is under consideration in our laboratory.

Possible Initial Formation of a Complex

Several questions concerning the formation of α-acylcarbenium ions have received little or no attention. These include whether a complex (α-bromo compound, silver salt) forms before ionization of the C–Br bond.

(29) (a) D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, 91, 895 (1972); (b) D. M. Brouwer and A. A. Kiffen, *ibid.*, 92, 1335 (1973); (c) J. W. Larsen and S. Ewing, *J. Am. Chem. Soc.*, 93, 5107 (1971); (d) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *ibid.*, 94, 3354 (1972); (e) S. H. Pines and A. W. Douglas, *Tetrahedron Lett.*, 23, 1955 (1976).
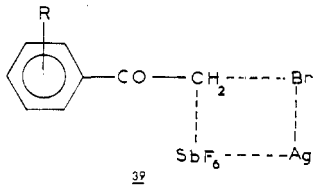
Scheme XIII
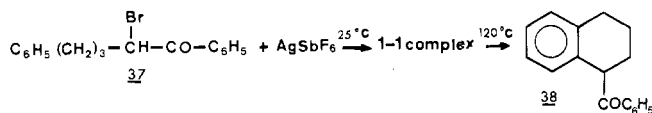
Recent studies of the solvolysis of alkyl halides in the presence of silver salts have concluded that these reactions occur by a mechanism (Scheme XII) involving the preliminary formation of an alkyl halide–Ag^+ complex.[30,31] This complex then undergoes rate-limiting heterolysis with anionic or solvent assistance. The mechanism may be termed, after Hughes and Ingold, Y^--S_N1-Ag^+.

Preliminary observations show that, in the presence of $AgSbF_6$, some secondary α-bromo or chloro ketones lead to crystalline complexes.[23,24] But, in the light of available data, it is impossible to specify the site of complexation as being carbonyl oxygen, or halogen, or both. Moreover, formation of complexes does not necessarily imply their involvement on the reaction path. Nevertheless, one experiment strongly suggests that this may be the case. Ketone **37** in the presence of $AgSbF_6$ forms a very stable complex (mp 120 °C) which, on thermal decomposition, leads to ketone **38**[23] (Scheme XIII).

Recently, complex **39** was invoked in an attempt to interpret the behavior of some phenacyl bromides in the presence of $AgSbF_6$ and N-nitrosodibenzylamine.[33]

Conclusions

Utilization of the silver salt of a superacid ($AgSbF_6$) in the ionization of a C–Br bond α to a carbonyl group has made it possible to obtain α-acylcarbenium ions

which, for a long time, had been considered too unstable to be formed.

Dehalogenation reactions take place with ease for tertiary bromo compounds, but are somewhat lethargic for secondary ones. This problem of ionization could be resolved by using better leaving groups than Br. This could be achieved, for example, by protonation of diazo ketones in superacid medium[34] or by $AgSbF_6$ dehalogenation of α-acyl chloroformates.[35]

α-Acylcarbenium ions undergo the classic reactions of carbenium ions, but the presence of a carbonyl group confers on them significant additional properties. They probably have a nonplanar structure, the bridged form A, owing to participation of carbonyl oxygen in C–X heterolysis. (The degree of participation of carbonyl oxygen depends on the structure of the incipient carbocation.) Moreover, they undergo specific reactions such as stereospecific E1 elimination and formation of four-membered-ring oxonium salts after neighboring group migration.

When the structure of an α-acylcarbenium ion allows hydride migrations, it undergoes them ultimately, giving the more stable oxonium salt. Owing to this property it is possible to obtain regio- and stereospecific long-range functionalization.

The α-acylcarbenium ions may be considered as a particular group of a general class of carbocations of type $>C^+$–A, where A is an electron-withdrawing group (e.g., A = $C\equiv N$, $S\rightarrow O$, NO_2,[36] etc. . .).

In the near future, experiments employing superacids or their derivatives may enable the extension of this new class of "a priori" unstable carbocations. Their low stability would, in a nonnucleophilic medium, allow their isomerization via intramolecular rearrangements to more stable carbocations. This process would be of great utility in achieving generally cumbersome long-range functionalizations.

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