

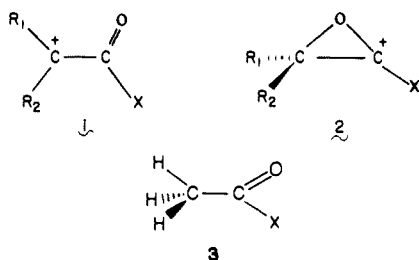
A Theoretical Study of α -Acylmethyl, Oxiranyl, and Acetyl Carbocations

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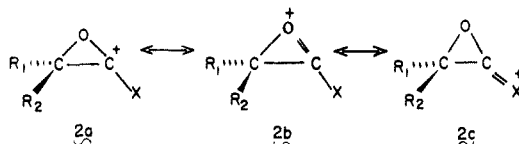
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Abstract: Structures for acylcarbenium ions **1**, XOCCH_2^+ ($\text{X} = \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$), and the oxiranyl cations, **2**, $\text{H}_2\text{C}^+-\text{O}-\text{CX}^+$, have been optimized at the HF 6-31G* level of theory, followed by single point calculations at the MP2/6-31G** level. All cyclic ions **2** are lower in energy than **1** and there is no barrier to conversion of **1** into **2**. β -Substituted acetyl cations (**7**, XCH_2CO^+) are lower in energy than **2**, and the barriers to rearrangement of **2** by 1,2-shifts of X are 14.9 kcal/mol for $\text{X} = \text{F}$ and 47.9 kcal/mol for $\text{X} = \text{NH}_2$ (the aminoacetyl cation $\text{H}_2\text{NCH}_2\text{CO}^+$ dissociates without barrier to give CH_2NH_2^+ and CO). Ions $^+\text{CH}_2\text{CHS}$ and $\text{H}_2\text{C}^+\text{CSNH}_2$ prefer the cyclic thiranyl structure, and these ions are strongly stabilized relative to the unsubstituted methyl cation. At the STO-3G//STO-3G level ions $(\text{CH}_3)_2\text{CCOX}^+$ ($\text{X} = \text{CH}_3, \text{NH}_2, \text{OH}$) have the oxiranyl structure but at higher level calculations (6-31G**//STO-3G) the open structure is preferred when $\text{X} = \text{CH}_3$ and OH. At the STO-3G//STO-3G level phenyl substitution results in the open structure being preferred for ion $\text{Ph}^+\text{CHCONH}_2$. The structures of eight isomers of $\text{C}_2\text{H}_2\text{FO}^+$ have been optimized and the fluoroacetyl cation (**7**) has the lowest energy followed by the cyclic ion **2**.

Several years ago it was discovered that carbenium ions containing an α -destabilizing group (e.g., CN,¹ COR,²⁻⁴ COOR,^{3,5} PO(OEt)₂⁶) are intermediates in solvolysis reactions and many diphenylmethyl cations containing α -destabilizing substituents are sufficiently stable to have been characterized by NMR at low temperatures.⁷⁻¹⁰ Most destabilizing substituents function as both σ - and π -acceptors in neutral molecules, but when they are ad-



acent to an electron-deficient cationic carbon they become π -donors and are less destabilizing than expected. One class of destabilizing groups, those with a lone pair on a heteroatom, are of particular interest since they can stabilize carbenium ions by donating electrons to the vacant orbital on the cationic carbon to form a 3-membered ring (structure **2**). The cyclic ion, **2**, is stabilized by delocalization of charge onto the oxygen (structure **2b**) and, if X has a lone pair of electrons (e.g., OH, NH₂), onto X (structure **2c**). Analysis of the stereochemistry of solvolysis products for ions with $\text{X} = \text{NMe}_2$, $\text{R}_1 = \text{R}_2 = \text{Me}$ and with X



$= \text{NMe}_2$, $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{H}$ indicates that cations have the open structure **1**, but decomposition of α -nitrodiarylmethyl cations to give benzophenone is postulated to occur through the intermediacy of the *N*-oxoaziridine.⁷ Also for ions where $\text{R}_1 = \text{R}_2 = \text{H}$ and $\text{X} = \text{H}$ ¹² and OH,¹³ ab initio molecular orbital calculations have shown the bridged structure, **2**, to be preferred.

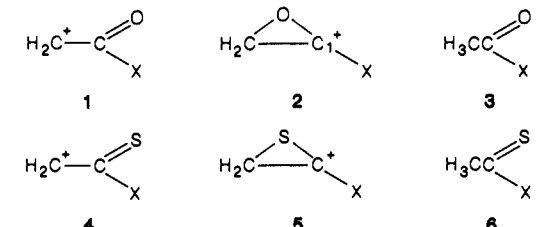
There have been several reports of α -acylcarbenium ions in the gas phase. Both theory¹² and mass spectrometric experiments^{14,15} show that the α -formylmethyl cation rearranges without activation to its most stable isomer, the acetyl cation. Attempts to generate the α -acetylmethyl cation were also unsuccessful due to rear-

rangement, possibly to the methyloxiranyl cation.¹⁶ The α -carbomethoxy- α -methylmethyl cation,¹⁷ $\text{H}_3\text{C}^+\text{CHCOOCH}_3$, and the α -acetyl- α , α -dimethylmethyl cation,¹⁶ $(\text{H}_3\text{C})_2\text{C}^+\text{COCH}_3$, both ions with α -methyl groups to assist in delocalizing the positive charge, are the only α -acylcarbenium ions lacking a stabilizing phenyl group which have been studied in detail. Protonation of lactamide and acetoin by CH_5^+ and C_2H_5^+ results in some loss of water presumably forming ions $\text{H}_3\text{CCH}^+\text{CONH}_2$ and $\text{H}_3\text{C}^+\text{CHCOCH}_3$,¹⁸ although these ions have not been further characterized. The metastable α -benzoylcarbenium ions undergo 1,2-phenyl migration followed by loss of carbon monoxide,¹⁹ while alkoxy migration occurs in α -carbalkoxycarbenium ions also with loss of carbon monoxide.^{18,20} Gas-phase protonation of derivatives of mandelic acid ($\text{PhCH}(\text{OH})\text{COOH}$) and benzoic acid ($\text{Ph}_2\text{C}(\text{OH})\text{COOH}$) leads to loss of water and the base peaks in the mass

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Table I. Structural Parameters from Optimization at the 6-31G* Level^a


Structures of Ions 1			
X	C-C ⁺	C-O	C-X
(a) H	1.502	1.189	1.082
(b) CH ₃	1.520	1.187	1.498
(c) NH ₂	1.517	1.189	1.330
(d) OH	1.517	1.175	1.298
(e) F	1.509	1.163	1.283

Structures of Ions 2				
X	C-C	C ⁺ -O	C-O	C ⁺ -X
(a) H	1.424	1.214	1.535	1.078
(b) CH ₃	1.428	1.227	1.509	1.464
(c) NH ₂	1.422	1.256	1.493	1.272
(d) OH	1.415	1.231	1.551	1.242
(e) F	1.414	1.203	1.610	1.231

Structures of Methanes 3			
X	C-C	C-O	C-X
H	1.504	1.188	1.095
CH ₃	1.514	1.192	1.514
NH ₂	1.514	1.197	1.359
OH	1.502	1.187	1.332
F	1.496	1.168	1.326

Structures of Ions 4			
X	C-C ⁺	C-S	C-X
H	1.405	1.627	1.076
NH ₂	1.429	1.651	1.331

Structures of Ions 5				
X	C-C ⁺	C ⁺ -S	C-S	C ⁺ -X
H	1.450	1.593	1.864	1.075
NH ₂	1.449	1.659	1.847	1.273

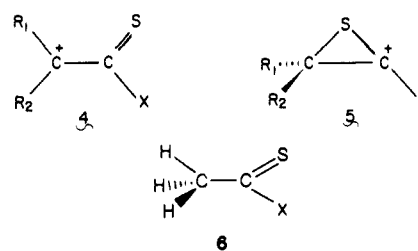
Structures of Methanes 6			
X	C-C	C-S	C-X
H	1.497	1.606	1.081, 1.088 (two)
NH ₂	1.509	1.655 ^b	1.328 ^b

^aBond lengths are in Å. ^bBond lengths from X-ray study on dithioamide are C-S 1.649 Å, C-N 1.323 Å (ref 34).

spectra of these molecules correspond to the α -acylcarbenium ions.¹⁸ For these ions there is no loss of carbon monoxide indicating that rearrangement to the potentially lower energy acylium ion does not occur. The relative ease of formation of α -acylcarbenium ions containing stabilizing phenyl groups suggests that these ions have the open structure **1**, and not the cyclic structure **2**.

In this study ab initio molecular orbital calculations are used to compare the energies of open cations **1** with the oxiranyl cations **2** when $R_1 = R_2 = H$ and when $R_1 = R_2 = CH_3$ with $X = H, CH_3, NH_2, OH,$ and F . Polarization functions are important in adequately describing small ring compounds and the 6-31G* basis set²¹ was therefore used in the structural optimization for ions **1** and **2** and for the methanes **3**, H_3CCOX .

Diphenylmethyl cations containing an α -thioamide group (**4**, $R_1 = R_2 = Ph$; $X = NMe_2$) have recently been reported,²² and since sulfur is more effective at bridging than oxygen in carbocations, we have extended our study to ions **4** and **5** where $R_1 = R_2 = H$ and $X = H$ and NH_2 .

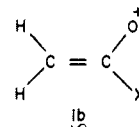


Method

Standard closed shell ab initio molecular orbital calculations were carried out with the Monstergauss program.²³ All structures were optimized at the 6-31G* level of theory²¹ with gradient optimization procedures^{24,25} (Table I). Single-point calculations at the MP2/6-31G** level²⁶ using the 6-31G* optimized geometry were performed using the Gaussian 82 program²⁷ (Table II). The transition structure for the rearrangement of **2** ($R_1 = R_2 = H, X = NH_2$) to **CO** and $CH_2NH_2^+$ was obtained by constructing the surface for rotation of NH_2 and CH_2 starting at structure **2**. The final transition structures, **8**, for $X = NH_2$ and F were obtained from the VA05AD method²⁸ in the Monstergauss program. Subsequent force calculations with Gaussian 82 showed both these structures to have one imaginary frequency.

Results and Discussion

Structural Details. (a) Open Ions, 1, and Methanes, 3. Ions **1** collapse into cyclic ions **2** with little or no barrier and C_s symmetry had to be imposed in order to carry out structure optimizations. The bond lengths in methyl cations, **1**, are remarkably similar to those of the methanes **3** (Table I), with the C-X and C-O being slightly shorter and the C-C bonds slightly longer in the cations. This last structural feature indicates that there is essentially no double bond character in the C-C bond of the cations i.e., valence tautomer **1b** is not a significant contributor.



Further evidence of lack of importance of **1b** is provided by the π -electron sites and the net charges. In structure **1b** the oxygen atom has a vacant p orbital, i.e., there is zero π -electron density on oxygen but for ions **1** the π -densities calculated from the gross orbital populations are large ($\sim 1.3e$). Also the net charges on the carbonyl oxygen atoms of cations **1** are all negative (between -0.32 and -0.44) and are on average only 0.18 less than those of the parent methanes. This lack of delocalization of the charge onto the oxygen atom of the carbonyl group is in marked contrast to the large delocalization of charge onto the cyano group. In the α -cyanocarbenium ions the C-CN bond is much shorter than in the alkyl cyanides and the nitrogen atom carries much of the positive charge of the ion.²⁹

Ions **1** have a plane of symmetry and the positive charge is formally located on the cationic carbon in the π -system. The interaction between COX and CH_2^+ may therefore be broken down into σ and π -contributions. From the Mulliken population analysis the π -populations of each heavy atom can be calculated and the amount of π -donation to the formally empty p orbital on C^+ is found to be small (Table III). However, the calculated

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Table II. Calculated Total Energies (hartrees) at HF 6-31G* Optimized Structures ($R_1 = R_2 = H$)

	HF 6-31G*	MP2/6-31G**
Oxygen-Containing Molecules		
(a) X = H		
1	-151.943 45	-152.366 59
2	-151.965 42	-152.403 81
3	-152.915 96	-153.376 35
(b) X = CH ₃		
1	-191.000 21	-191.560 35
2	-191.039 45	-191.623 35
3	-191.962 23	-192.569 41
(c) X = NH ₂		
1	-207.011 26	-207.603 81
2	-207.069 19	-207.680 85
3	-207.975 97	-208.609 69
(d) X = OH		
1	-226.832 12	-227.427 63
2	-226.860 62	-227.479 90
3	-227.810 64	-228.450 63
(e) X = F		
1	-250.797 27	-251.372 39
2	-250.811 35	-251.412 98
3	-251.798 46	-252.418 83
Sulfur-Containing Molecules		
(a) X = H		
4	-474.621 11	-474.993 26
5	-474.640 93	-475.037 91
6	-475.551 75	-475.962 54
(b) X = NH ₂		
4	-529.665 99	-530.230 28
5	-529.737 37	-530.305 51
6	-530.607 27	-531.191 51

Table III. Population Data^a for the CH₂ Group in Open Ions CH₂COX⁺

	substituent X	π -donation to CH ₂	net charge on CH ₂ group	σ -donation to CH ₂
(a) CH ₂ COX ⁺	H	0.093	0.716	0.191
	CH ₃	0.084	0.705	0.211
	NH ₂	0.075	0.712	0.213
	OH	0.060	0.762	0.178
	F	0.069	0.762	0.169
(b) CH ₃ ^b		0.000	0.643	0.357

^a At the 6-31G**//6-31G* level. ^b Reference 33.

net charges on CH₂⁺ are considerably less than unity indicating that the substituents COX also function as σ donors. Assuming that the CH₂⁺ formally carries all the positive charge then the amount of σ donation by COX may be calculated from the relationship

$$\sigma \text{ donation} = 1 - \text{net charge on CH}_2 \text{ group} - \pi \text{ population on CH}_2$$

The data obtained from this relationship (Table III) show that the electron-deficient CH₂⁺ group induces the COX groups to be more powerful σ -donors than π -donors (by a factor of 2 to 3 times). The relative order for σ donation is CONH₂ \approx COCH₃ > CHO > COOH > COF. Here it should be emphasized that the electronegative COX groups are usually strongly σ -withdrawing groups which under the influence of the adjacent electron-deficient cationic carbon have been induced to be σ -donating. This point is best illustrated by comparison with the parent CH₃⁺ ion where the hydrogen atom, despite its lack of polarisability, is a much stronger σ -donor than the best COX group, the amido group.

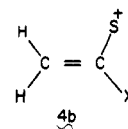
(b) Oxiranyl Cations, 2. Oxiranyl cations, **2**, have very short ⁺C-O bonds (1.203 to 1.256 Å), much closer in length to double than single bonds. The H₂C-C⁺ bonds (\sim 1.420 Å) also are shorter than in oxirane (1.471 Å),³⁰ while the H₂C-O bonds (1.49–1.61 Å) are longer but are comparable to the distal bonds

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in α -X-cyclopropyl cations.³¹ The C-X bonds in **2** are shorter than standard C-X single bonds³² and are comparable to those in primary cations CH₂X⁺³³ and α -X-cyclopropyl cations.³¹ All these structural data indicate considerable π -donation to C⁺ from both O and X, i.e., **2b** and **2c** are both important contributors to the structure of **2**. This conclusion is supported by the π -populations of the "vacant" p-orbital on C⁺ of **2** (0.452e for X = CH₃, 0.621e for X = NH₂, 0.564e for X = OH, 0.546e for X = F) which are higher than the π -populations of C⁺ in CH₂X⁺ (X = CH₃, 0.161e; X = NH₂, 0.533e; X = OH, 0.382e; X = F, 0.241e).³³

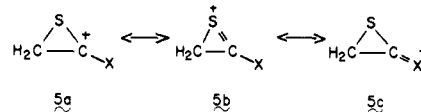
(c) Ions 4 and 5 and Methanes, 6. At the HF 6-31G* level thioacetamide (**6**, X = NH₂) is planar at nitrogen. In this respect it differs from acetamide but is in agreement with both X-ray diffraction data³⁴ and ab initio calculations³⁵ on dithioamide.

Removal of a hydride ion from the methyl group of **6** to form **4** results in a slight lengthening of C-S, but the C-C bond is shortened by about 0.09 Å. This large structural change, which does not occur in the analogous oxygen-containing methanes, indicates that valence tautomer **4b** is an important contributor to the structure. The net charge on S, +0.476 when X = H and



+0.303 when X = NH₂ (compared with charges of -0.110 and -0.265 in the methanes), and the high π -population of the terminal carbon (0.338e when X = H, 0.350e when X = NH₂) support this conclusion.

In cyclic ions, **5**, the H₂C-S bond lengths are slightly longer than the C-S bond of thiirane (1.815 Å³⁰). Also C-S is close to the bond length in thioformaldehyde (1.611 Å³⁰) and, as with the cyclic ions containing oxygen, contributions from three valence tautomers **5a**, **5b**, and **5c** are important. When X is NH₂ the π -populations are S 1.738e, C 0.674e, and N 1.573e, indicating that the relative importance of the resonance structures are **5c** > **5a** > **5b**.



Diphenylmethylcarbenium ions containing an α -thioamide group are stable at low temperatures, and the similarity of the NMR spectra of these ions to those of the parent diphenylmethyl cations establishes that these ions have an open structure. Nevertheless, there is some experimental evidence from solvolysis work for the bridged thiiranyl structure. In the acetolysis of optically active PhCH(OMs)CSOME there is net retention of the optical activity and in the acetolysis of (Me)₂C(OMs)CSOME one of the major products is (Me)₂C(SAc)COOME.³⁶ Furthermore, these solvolysis reactions occur at least 10³ times faster than those of the oxygen analogues. All these observations are most easily explained in terms of an intermediate thiiranyl cation.

Relative Energies of Open and Cyclic Ions. The formylmethyl (**1**, X = H)¹² and thioformylmethyl (**4**, X = H)³⁷ cations have previously been shown to collapse into cyclic ions **2** and **4** respectively with essentially no barrier. We now find that ions **1**

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Table IV. Energies (kcal/mol) of Cyclic Ions **2** and **5** below Open Ions **1** and **3**

X	6-31G*	MP2/6-31G**
Ions 2		
H	13.8	23.4
CH ₃	24.6	39.5
NH ₂	36.4	48.3
OH	17.9	32.8
F	8.8	25.5
Ions 5		
H	12.4	28.0
NH ₂	44.8	47.2

Table V. Isodesmic Energies (kcal/mol) for Reaction 1

X	6-31G*	MP2/6-31G**
Ions H ₂ C ⁺ COX		
H	-5.0	5.2
CH ₃	1.6	5.7
NH ₂	-0.1	7.7
OH	-8.8	-3.1
F	-23.0	-17.8
Ions H ₂ C ⁺ CSX		
H	21.3	30.6
NH ₂	14.6	35.7

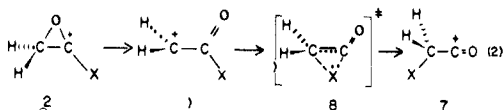
with X = NH₂ and F rearrange into **2** without barrier at the HF 6-31G* level. All cyclic ions are further improved relative to the open ions by including correlation energy (Table IV). The open cation structure **1**, then, is of no physical significance in primary methyl cations containing an α -carbonyl group. However, it seems probable that more highly substituted carbenium ions containing an α -carbonyl group are open ions^{4,18} and we have used the isodesmic reaction in eq 1 to assess the stabilizing effects of groups COX and CSX in open cations. The results in Table V show



CHO, CH₃CO, and CONH₂ to be weakly stabilizing while the more electron-withdrawing COOH and COF groups are destabilizing. Inclusion of correlation energy increases the stabilization by 5 to 7 kcal/mol. Previous theoretical work^{38,39} with small basis sets showed the α -formyl substituent to be stabilizing, but with larger basis sets it was destabilizing. Methyl cations containing the thiocarbonyl group (assessed by replacing O by S in eq 1) are stabilized by 25–30 kcal/mol more than their oxygen analogues, and sulfur is also more effective at stabilizing the cyclic ion.

Primary carbenium ions **1** and **4** are not at minima and using the cyclic ions **2** and **5** results in all ions being stabilized relative to CH₃⁺. However, detection of these cyclic ions may prove difficult as the barriers to rearrangement to the isomeric acylium ions are low.

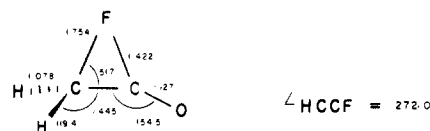
Rearrangement to the Acylium Ions. For all the ions, except when X is NH₂, the acylium ion, **7**, is the global minimum. Rearrangement of cyclic ions **2** to acylium ions **7** can be envisaged as an initial ring-opening to form cations **1** in the bisected conformation followed by a 1,2-shift of X via transition structure **8**. When X is H, the transition structure for this reaction at the



MP3/6-31G** level is 16 kcal/mol¹² above **2**. We now report transition structures **8** for X = NH₂ and F as optimized at the HF 6-31G* level (Figure 1). For the fluoro-substituted ion the barrier to formation of the acylium ion is 14.9 kcal/mol above

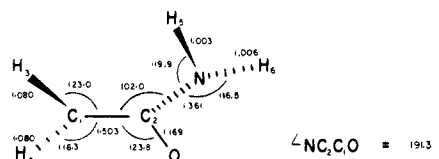
(38) Paddon-Row, M. N.; Santiago, C.; Houk, C. N. *J. Am. Chem. Soc.* **1980**, *102*, 6563. Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *Ibid.* **1984**, *106*, 3885.

(39) Hopkinson, A. C.; Lien, M. H. *J. Mol. Struct., THEOCHEM* **1983**, *104*, 303.

C_s symmetry

E_{6-31G*} = -250.78801

E_{MP2/6-31G**} = -251.38925

C₁ symmetry

E_{6-31G*} = -207.00897

E_{MP2/6-31G**} = -207.60455

∠NC₂C₂O = 191.3

∠H₃C₂C₂O = 238.0

∠H₃C₂C₂O = 62.4

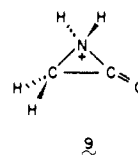
∠H₃N₂C₂C = 296.1

∠H₃N₂C₂C = 152.0

Figure 1. Transition structures for rearrangement of cyclic ions **2** to acylium ions **7**.

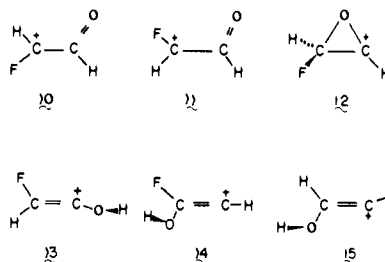
ion **2**, but for the amino-substituted ion the barrier is much higher (47.9 kcal/mol at MP2/6-31G**) and leads to the dissociation products CO and H₂CNH₂⁺. For the ions considered here, only when X = NH₂ are the dissociation products lower in energy than the acylium ion.⁴⁰

The α -imino group is more effective at bridging in carbenium ions than the α -keto group,¹³ but the amino-bridged ion, **9**, is not at a minimum and all attempts to optimize this structure led to the dissociation products.



Formation of the *tert*-butyl cation and carbon monoxide from the α -acetyl- α,α -dimethylmethyl cation (**1**, R₁ = R₂ = CH₃; X = CH₃) involves migration of the methyl group from the acetyl and is similar to the rearrangement of H₂NCOCH₂⁺. The rearrangement of the α -acetyl- α,α -dimethylmethyl cation has been observed in the gas phase, and MNDO calculations give the barrier to be 35.6 kcal/mol.¹⁶

Isomers of C₂H₂FO⁺. There are many plausible isomers for ions **2** and **5**, and while chemical intuition suggests the acylium ions are likely to be the global minima, we decided to examine one of the hypersurfaces in more detail. Ions **10–14** were subjected to structure optimization at HF 6-31G* and single point calculations performed at MP2/6-31G**.



Ions **10** and **11**, both doubly substituted methyl cations containing a stabilizing α -fluoro group, are lower in energy than the fluoroacetylium ion **1** but are higher than the cyclic ion **2** (Table VI). The cyclic ion **12**, formed by cyclization of **10** and **11**, is higher in energy than **10** and **11** at the Hartree-Fock level, but

(40) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.*, in press.

Table VI. Relative Energies (kcal/mol) of Isomers of $C_2H_2FO^+$

structure	6-31G*	MP2/6-31G**
7	0	0
CO + CH ₂ F ⁺	24.0	38.7
2	36.7	30.9
10	37.9	43.3
11	40.3	45.1
12	43.0	38.2
1	45.5	56.3
13	47.8	48.4
14	66.4	74.7
15	71.8	

Table VII. Relative Energies (kcal/mol) and Total Energy (hartrees) of Ions **1** and **2** with R₁ = R₂ = Me

X	energy of cyclic ions, 2 , below, tertiary ions 1		total energy of open ions at 6-31G**// STO-3G
	STO-3G// STO-3G	6-31G**// STO-3G	
CH ₃	8.4	-2.8	-269.133 63
NH ₂	33.2	7.2	-285.143 34
OH	9.4	-13.2	-304.967 43

Table VIII. Isodesmic Energies (kcal/mol) for Reaction 3

X	STO-3G//STO-3G	6-31G**//STO-3G
CH ₃	10.7 ^a	-7.4
NH ₂	4.9 ^a	-6.6 ^a
OH	3.2 ^a	-14.6

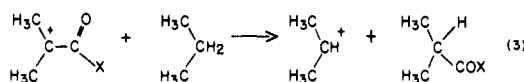
^aCyclic ion is lower in energy. Use of the cyclic structure in reaction 3 makes ΔE for these ions more positive.

inclusion of correlation energy favors the cyclic structure and at the MP2/6-31G** level **12** is lower in energy than all the methyl cations. Vinyl cations **13**, **14**, and **15** are all higher in energy than the methyl cations. Vinyl cations are stabilized by π -donors in the α -position,⁴¹ and ion **13** which has the stronger π -donor, OH, in the α -position has the lowest energy of the vinyl cations.

Tertiary Ions. Introduction of methyl groups at C₁ should stabilize the open cations, **1**, by hyperconjugation and have less effect on ion **2**. MNDO calculations show the α -acetyl- α,α -dimethylmethyl cation (**1**, X = R₁ = R₂ = CH₃) to be 11.7 kcal/mol lower in energy than the isomeric cyclic ion.¹⁶

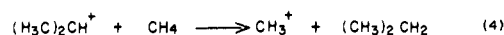
We have examined ions **1** and **2** with R₁ = R₂ = CH₃ and X = CH₃, OH, and NH₂, but the size of these ions has limited us to lower level calculations and, as polarization functions are particularly important to cyclic compounds, our results are less definitive. At the STO-3G//STO-3G level all ions are cyclic, but extension of the basis set has the effect of favoring the open structure and at the 6-31G**//STO-3G level only the amino-substituted ion is cyclic (Table VII) and even here ring-opening requires little energy (7.2 kcal/mol). We note with interest that Creary⁵ concludes that ion (CH₃)₂C⁺CONMe₂ and not its cyclic isomer is an intermediate in solvolysis reactions. Higher level calculations are required to determine whether these ions are cyclic, but inclusion of correlation energy will probably favor the cyclic structures as in the primary ions.

Stabilization of the isopropyl cation by introduction of an α -COX group can be assessed by using reaction 3. The positive

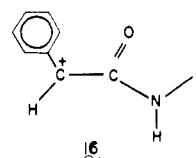


ΔE values at the STO-3G level (Table VIII) indicate all the substituents to be stabilizing, but at the higher 6-31G**//STO-3G level all are destabilizing, and the destabilization is larger than for the same substituents in the primary ions H₂C⁺COX.

Phenyl-Substituted Ions. The phenyl group is estimated to stabilize the methyl cation by 79 kcal/mol⁴² and this compares with a stabilization by two methyl groups of 50 kcal/mol,³¹ as estimated from reaction 4. This additional stability from the



phenyl group is sufficient to favor the open structure for the α -carboxamido- α -phenylmethyl cation, **16**. At the STO-3G level the open structure, **16**, is 4.1 kcal/mol lower than its cyclic isomer.



With use of reaction 5 the α -carboxamido group is weakly stabilizing in the benzyl cation. ΔE for this reaction is 5.6 kcal/mol at the STO-3G level, compared with 4.9 kcal/mol in the isopropyl cation. However, by analogy with the isopropyl cations, the α -carboxamido group will probably be destabilizing in benzyl cations at higher levels of theory.



Conclusions

In methyl cations electron-withdrawing substituents containing an α -carbonyl group, COX, range from weakly stabilizing (X = H, CH₃, NH₂) to destabilizing (X = OH, F). However, these α -substituted-methyl cations are of no physical significance as they cyclize without barrier to form the oxiranyl cations, **2**. Formation of the oxiranyl cations by hydride transfer to CH₃⁺ is exothermic, but ions generated by this method may not be observable in the gas phase as the exothermicity of the hydride transfer reaction provides approximately the energy required to overcome the barrier to form the lower energy β -substituted-acetyl cations.

Sulfur is more effective at bridging than oxygen in carbocations, and methyl cations containing an α -thiocarbonyl group are cyclic and are strongly stabilized. The only methyl cations containing an α -dimethylthioformamide group known experimentally also have two phenyl groups on the cationic carbon, and the NMR spectra of these ions show them to have the open structure.

Results on the more highly substituted ions, the α -substituted isopropyl cations and the α -carboxamidobenzyl cation, although necessarily at lower levels of theory, suggest that these ions prefer the open structure, **1**, and that α -COX substituents are destabilizing.

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(42) Mayr, H.; Schneider, R.; Wilhelm, D.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 5340.