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A THEORETICAL INVESTIGATION OF THE STRUCTURES AND ENERGIES OF $C_3H_5O^+$ ISOMERS

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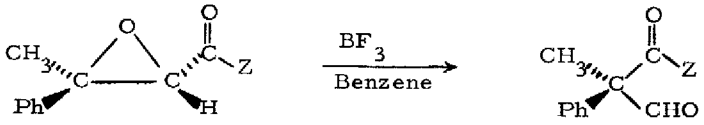
The 1,2-migration of an electron deficient carbonyl group to an adjacent developing positive center is a transformation that has been of long-standing interest to mechanistic chemists.[2] Our experimental studies have provided the first evidence that the acyl moiety in chiral glycidic esters[3] and ketones[4] migrates with inversion of configuration at the migration terminus, and with no detectable loss of optical activity (eq 1). In an effort to further delineate the mechanism of this highly concerted rearrangement, we have also initiated a complementary theoretical study on carbonyl migration.



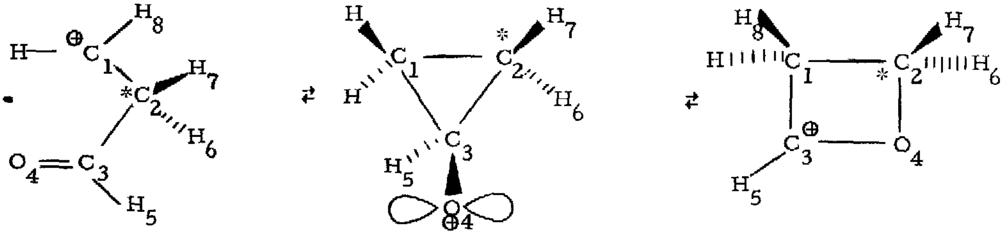
(eq 1)

$Z = OC_2H_5,\ C_6H_5$

We chose the 3-oxopropyl cation (**1**) and its structural isomers **2** and **3** as model substrates since this would enable us to compare our results on the $C_3H_5O^+$ cations to the previous theoretical investigation of the analogous interconversion of homoallyl (**4**), cyclopropylcarbinyl (**5**) and cyclobutyl (**6**) $C_4H_7^+$ cations. The well-established[5] involvement of the cyclopropylcarbinyl cation on the potential energy surface for homoallylic cation rearrangements suggested the intriguing possibility that a cyclopropyloxenium ion such as **2** may be on the reaction coordinate for acyl migration (fig 1).

The geometries[6] of **1**, **2** and **3** were completely optimized using theoretical *ab initio* molecular orbital calculations with a minimal STO-3G basis set[7] (fig 1). More accurate relative energies for these minimized structures were computed using a 4-31G extended basis set.[8] The relative energies for the $C_3H_5O^+$ cations and the related $C_4H_7^+$ cations[5] are summarized in Table 1. The cyclopropoxyl cation ion **2** is 22.46 kcal/mole higher in energy than the 3-oxopropyl cation while the 2-oxetanyl cation **3** is 12.19 kcal/mole lower in energy. This trend stands in marked contrast to that calculated by Hehre[5] for the $C_4H_7^+$ cations **4**, **5** and **6**. The magnitude of the calculated stabilization for the cyclopropylcarbinyl cation **5** is

Figure 1. Bond Angles and Distances for $C_3H_5O^+$ Cations



1

$r(C_1C_2) = 1.473$ Å
$r(C_2C_3) = 1.567$ Å
$r(C_3O_4) = 1.216$ Å
$r(C_3H_5) = 1.110$ Å
$r(C_2H_6) = 1.110$ Å
$r(C_1H_8) = 1.211$ Å
$\angle(C_1C_2C_3) = 111.73^\circ$
$\angle(C_2C_3O_4) = 123.9^\circ$
$\angle(H_5C_3C_2) = 117.50^\circ$
$\angle(H_7C_2C_1) = 105.90^\circ$
$\angle(H_7C_2C_3) = 113.59^\circ$
$\angle(H_6C_2C_3) = 113.59^\circ$

2

$r(C_1C_2) = 1.432$ Å
$r(C_2C_3) = 1.703$ Å
$r(C_3O_4) = 1.258$ Å
$r(C_3H_5) = 1.106$ Å
$r(C_2H_6) = 1.095$ Å
$r(C_2H_7) = 1.094$ Å
$\angle(C_1C_2C_3) = 65.14^\circ$
$\angle(H_6C_2C_3) = 107.30^\circ$
$\angle(H_6C_2C_1) = 120.65^\circ$
$\angle(H_7C_2C_3) = 109.30^\circ$
$\angle(H_7C_2C_1) = 120.75^\circ$
$\angle(H_5\text{-}C_3C_2C_1) = 119.71^\circ$
$\angle(O_4\text{-}C_3C_2C_1) = 116.63^\circ$

3

$r(C_1C_2) = 1.513$ Å
$r(C_1C_3) = 1.518$ Å
$r(C_3O_4) = 1.279$ Å
$r(C_3H_5) = 1.110$ Å
$r(C_2H_6) = 1.097$ Å
$r(C_2H_7) = 1.099$ Å
$r(C_1H_8) = 1.094$ Å
$\angle(C_2C_1C_3) = 83.25^\circ$
$\angle(O_4C_2C_1) = 87.88^\circ$
$\angle(H_5C_3C_1) = 140.73^\circ$
$\angle(H_6C_2C_1) = 116.12^\circ$
$\angle(H_7C_2C_1) = 120.70^\circ$
$\angle(H_8C_1C_3) = 118.48^\circ$

TABLE 1. RELATIVE ENERGY (kcal/mol)

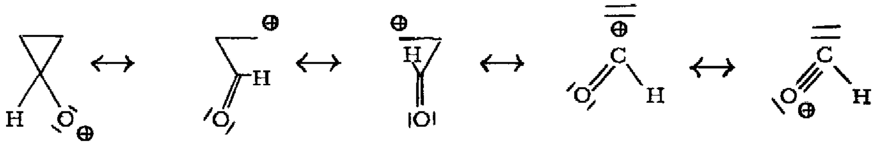
cation	4-31G[a]	STO-3G
3-oxopropyl (1)	0.0	0.0
cyclopropoxyl (2)	22.46	1.49
2-oxetanyl (3)	-12.19	-59.40
cis-staggered homoallyl (4)	0.0[b]	0.0
bisected cyclopropylcarbinyl (5)	-21.40	-35.00
puckered cyclobutyl (6)	- 9.4	

a) Geometry was minimized by STO-3G
b) Data taken from reference 5.

approximately equal and opposite to that calculated for the cyclopropoxyl ion 2 relative to their respective acyclic cations 4 and 1. This is a significant point since it is well established that the $C_4H_7^+$ cations undergo rapid interconversion in solution.[5] Thus, the relative energies of 1 and 2 do not appear to be sufficiently different as to preclude their interconversion provided a low energy pathway is available.

Insight into the nature of the bonding in 2 is provided by a comparison of bond orders and distances with those calculated (STO-3G) for the cyclopropylcarbinyl cation 5. The C_1-C_3 bond distances in 2 (1.703 Å) and in 5 (1.609 Å) are substantially longer than a normal C-C bond. In contrast, a relatively short C_1-C_2 bond distance (1.432 Å) is calculated for 2. Consistent with this observation, the calculated π-contribution to the total C_1-C_2 bond order (based upon the Mulliken overlap population) is 16.1 per cent in 2, 11.4 per cent in 5 and 32 per cent in ethylene. The C_3-O bond in 2 also exhibits substantial double bond character (35.1%) which compares in magnitude to that calculated (STO-3G) for $H_2C{=}O$.

In valence bond notation, cation 2 may be represented by canonical structures 7-11. The above calculations strongly suggest that 10 and 11 make a substantial contribution to the structure of 2 and that its bonding characteristics may be adequately described as a π-complex of ethylene and an acylium ion. The calculated charge distribution is also in accord with this bonding picture since the three carbon atoms in 2 all bear a small negative charge while the charge at oxygen (STO-3G) is +0.043 with most of the positive charge (0.16-0.18) being localized on the hydrogens.



7 8 9 10 11

In striking contrast to the cyclobutyl cation (6), which is puckered by 57.6°,[6] the 2-oxetanyl cation 3 is essentially planar (1.1° pucker) showing substantial delocalization of the positive charge by π-overlap (34.9%) with the adjacent oxygen. In principle, cation 3 may either be formed directly from the β-ketocarbenium ion 1, by C_1-O_4 bond formation, a process which does not involve acyl migration, or by carbonyl migration involving 2 as an intermediate or activated complex. A partial search of the potential energy surface for interconversion of these cations suggests that these two pathways have comparable activation energies. However, preliminary experimental results and theoretical studies in progress on an α,β-epoxyaldehyde suggest that in the rearrangement of glycidic esters (eq 1) the developing aldehyde functional group is a vital driving force and that a structure resembling 2 does lie on the reaction pathway.

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6. The acyclic cation **1** was minimized assuming a plane of symmetry containing all atoms except for the hydrogens at C_2. The transoid conformer of **1** was 4.25 kcal/mole higher in energy. Rotation about the C_1-C_2 or C_2-C_3 bonds in **1** failed to produce a conformer of lower energy. The geometry of cation **2** was optimized assuming a plane of symmetry bisecting C_1-C_2 and containing atoms $C_3H_5O_4$. Rotation of the $C_3H_5O_4$ moiety in **2** through 90° making the CHO group coplanar with C_1 and C_2 raises the energy by 35.67 kcal.
7. All computations were carried out with the Gaussian 70 program; W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana, program No. 236.
8. Molecular orbital calculations at the *ab initio* level are necessary to reliably compare the total energies of the acyclic and cyclic structures. CNDO/2 calculations exaggerate the stability of cyclic compounds. In this regard, the cyclopropyloxenium cation **2** was calculated (CNDO/2) to be 109 kcal *lower in energy* than the acyclic β-ketocarbenium ion **1**. In contrast, the 4-31G calculations appear to slightly favor the open form over cyclic structures.[9]
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