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SEMIEMPIRICAL CALCULATIONS ON THE RING OPENING OF α-LACTONES

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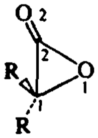
Abstract—We report the results of INDO calculations on the ring opening of acetolactone and its difluoro and dimethyl derivatives. Of the structures possibly important in the chemistry of α-lactones, the closed system is most stable. The open form, which we call methylenecarboxylate, is calculated by the INDO method to be more stable as a triplet. Finally a semi-open structure, favored in the older literature, is predicted to be chemically unimportant.

INTRODUCTION

The hydrolysis of optically active α-bromo-propionate, $CH_3CHBrCOO^-$, in dilute alkaline medium leads to lactic acid with retention of configuration at the optically active center.[1,2] Furthermore, the reaction kinetics are first order, and the rate limiting step is ionization of the halide.[3] These results are consistent with the formation of an α-lactone which then forms lactic acid, bond rupture occurring at the alkyl-oxygen linkage. More recently, α-lactones have actually been prepared, and their IR spectrum reported.[4] There is now no doubt that such systems can be obtained; however, their chemistry is sometimes difficult to explain in terms of the conventional structure 1, and it has been assumed that the system may form a ring-open structure which we call methylenecarboxylate.[4-8] The latter could have one of several possible structures. The CR_2 group can be perpendicular to the molecular plane 2; the entire system can be planar 3; or the molecule may exist in a semiopen form 4. This semiopen structure, which may have the advantage of decreased ring strain while maintaining some C-O sigma bonding, was favored in the earlier literature.[1-3] Molecular quantum mechanics can shed some light on the structure and chemistry of α-lactones, and using the INDO method of Pople,[9] we calculated the energy of acetolactone (R=H) and some of its derivatives in the closed, open, and semiopen geometries. For the open system, we calculated both singlet and triplet energies.



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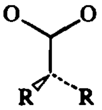

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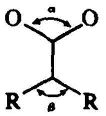

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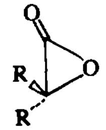

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Previous semiempirical results have been reported by Koenig and Barklow who performed both CNDO2 and Extended Hückel calculations.[8] These authors report on both cyclopropanone and acetolactone and show the CNDO method to be more reliable. They further find, as we did in subsequent studies,[10-13] that even this method overestimates the energy for ring opening. Thus, the calculated ring-opening energy for cyclopropanone is in the neighborhood of 200 kcal/mole,[8,10-12] while thermodynamic estimates place the value at a much more reasonable figure, approximately 50 kcal/mole.[13] Similarly, for acetolactone the CNDO2 result is much higher than the thermodynamic estimate.[8,13] The value of semiempirical methods such as CNINDO is that they provide the correct general shape to the early part of the reaction coordinate and further provide information on the ordering of electronic states. Such information is not at all easy to come by in any other way, and it is important since both singlet and triplet states may be involved in the reactions of α-lactones.[1-8,13,14] Huček, Barbas, and Leffler present evidence for radical intermediates while Crandall and Sojka show evidence of closed-shell dipolar intermediates.[7,14]

Acetolactone. The geometry of the closed lactone was obtained from model systems such as ethylene oxide[15] and cyclopropanone.[16] The CO distance was set at 1·200 Å, the C-H distance at 1·080 Å, and the CH_2 internal angle at 114°. The CO group and the local C_2-axis of the methylene group were assumed to bisect their respective angles.

The ground state of the α-lactone is best described as a closed-shell singlet of C_s symmetry, and we calculated the energy of $^1A'$ state of the lactone 1 for three slightly different geometries. The results are given in Table I; distances are in Angstroms, and the energy is in hartrees.

Methylenecarboxylate may exist as a closed-shell singlet, an open-shell singlet, or an open-shell triplet. Since not much is known about its structure, we first calculated the energy of the closed-shell singlet. We chose the planar form 3, assumed the system had C_{2v} symmetry, and calculated the energy of this $^1A_1$ state for a large number of different geometries. The results are given in Table II; the angles α and β are in degrees.

To determine the energy of the perpendicular form 2, we took the two best planar geometries, those having

Table I. The INDO energy of $^1A'$ acetolactone

	C-C	C_1-O_1	C_2O_1	E
1a	1.403	1.435	1.368	-50.1984
1b	1.403	1.453	1.368	-50.1974.
1c	1.415	1.465	1.380	-50.1972

Table II. The INDO energy of planar $^1A_1$ methylenecarboxylate **3**

C-C	C-O	α	β	E
1.466	1.26	125	117	-49.8618
1.466	1.31	125	117	-49.8744
1.466	1.36	125	117	-49.8570
1.466	1.31	120	117	-49.8710
1.466	1.31	130	117	-49.8755
1.466	1.31	135	117	-49.8744
1.430	1.31	130	117	-49.8810
1.400	1.31	130	117	-49.8825
1.370	1.31	130	117	-49.8808
1.430	1.31	125	117	-49.8805
1.400	1.31	125	117	-49.8825
1.370	1.31	125	117	-49.8813
1.400	1.31	130	110	-49.8831
1.400	1.31	130	100	-49.8785
1.400	1.31	125	110	-49.8830
1.400	1.31	125	100	-49.8782

energies −49·8831 h and −49·8830 h, and rotated the methylene group appropriately. The energies for perpendicular methylenecarboxylate are presented in Table III.

Since we did not reoptimize the structural parameters, the values in Table III represent upper limits to the INDO energy of the perpendicular system. Yet it is clear that, for the $^1A_1$ state, the INDO method favors this geometry, for **2** is calculated to be 10 kcal/mole more stable than the planar geometry **3**.

It remains to be seen if more rigorous calculations confirm these INDO predictions, but in any case **2** and **3** cannot both be intermediates on the same energy surface, for if one is the ground state, the other is the transition state for methylene rotation.

Table III. The INDO energy of perpendicular $^1A_1$ methylenecarboxylate **2**

C-C	C-O	α	β	E
1.40	1.31	130	110	-49.8995
1.40	1.31	125	110	-49.8981

We next turned our attention to the unsymmetrical structure **4**. As written in the older literature,[1-3] this structure maintains its methylene group perpendicular to the molecular plane, giving the system C_s symmetry. At least in the early stages of its formation from the lactone, this structure is best characterized as a closed-shell singlet, and in order for the system to exist in a geometry such as **4**, the $^1A'$ energy surface must have a relative minimum near the point. If no such minimum exists, then geometries such as **4**, are simply points on the energy surface from **1** to **2**, but they do not represent chemical intermediates. We varied the different structural parameters and calculated the energy of several unsymmetrical geometries; Table IV gives their energies. The numbers in parenthesis give the approximate fractional distance traveled along the reaction coordinate to **2**. Since no relative minimum is found, the unsymmetrical semiopen $^1A'$ structure is chemically unimportant. In fact, the $^1A'$ lactone geometries **1a** and **1b** in Table I differ only by a stretch of the alkyl-oxygen bond, and that slight stretch raises the energy of the system.

Since there exists evidence that open-shell methylenecarboxylates are important in the chemistry of α-lactones,[7,8] we calculated the energy of triplet **2** and **3** in C_{2v} symmetry, and of a triplet methylene-rotated geometry in C_2 symmetry. The ^3B methylene-rotated structure had that group 30° out of the molecular plane.

We did not do a geometry search for the best triplet geometry but chose the lowest energy geometry of $^1A_1$ **2** and **3** and opened up the shells. Thus, the results presented in Table V, represent upper limits to the INDO energies of triplet methylenecarboxylate.

The perpendicular $^3B_1$ geometry has both electrons in σ molecular orbitals. The planar $^3B_2$ geometry, on the other hand, has one electron in a σ and the other in a π-molecular orbital. Perpendicular σπ states appear not to be important.

It is obvious that although the INDO method overestimates the energy for ring opening,[8,10-13] open-shell systems will be important in the chemistry of

Table IV. The energy change of **4** upon passing along the $^1A'$ reaction coordinate

	E($^1A'$)
4(.10)	-50.1872
4(.25)	-50.1325
4(.50)	-50.0222
4(.75)	-49.9439

Table V. The energy of $^3B_1$, $^3B_2$, and ^3B methylenecarboxylate

	C-C	C-O	α	β	E
2($^3B_1$)	1.400	1.31	130	110	-49.9739
3($^3B_2$)	1.400	1.31	130	110	-49.9624
^3B	1.400	1.31	130	110	-50.0479

methylenecarboxylates, and it is possible for the $^1A'$ state of α-lactones to pass directly to an open-shell system.

We next took the geometries of the various systems **1–4** and repeated the calculations using the CNDO method. Geometries **1a** and **1b** were used for the lactone while the same points were employed for **4**. The optimal INDO geometry was chosen for planar methylenecarboxylate **3**, and the CH_2 group was rotated to give the perpendicular form **2**. The shells were then opened and the energies of the triplet states calculated. The data are presented in Table VI. Since the CNDO results do not differ substantially from those obtained by the INDO method, only the latter was employed with the substituted α-lactones.

Difluoroacetolactone. Geometries **1a** and **1b**, with H replaced by F, were employed for the difluorolactone, yielding INDO energies equal to −101·5517 h and −101·5494 h respectively for the $^1A'$ lactones. A rather complete optimization of the planar geometry **3** was performed, and some representative points are given in Table VII.

Perpendicular geometries were then obtained from the two best planar geometries by rotating the CF_2 group. These energies are presented in Table VIII. In the case of difluoromethylenecarboxylate, the planar and perpendicular $^1A_1$ forms have nearly the same INDO energy.

Unsymmetrical points on the $^1A'$ energy surface were also calculated, and these data are presented in Table IX. Once again, unsymmetrical structures of type **4** are not intermediates.

Using the best closed-shell geometries of difluoromethylenecarboxylate, we calculated the triplet energies and the ^3B system is preferred (see Table X).

Dimethylacetolactone. The geometries of the dimethyl systems **1–4** (R=Me) were obtained from the parent systems by replacing H with Me. Geometries **1a** and **1b**

Table VI. The CNDO energy of acetolactone in closed, open and semiopen geometries

	E
1a	-52.4162
1b	-52.4147
4(.10)	-52.3897
4(.25)	-52.3421
4(.50)	-52.2198
4(.75)	-52.1570
2($^1A_1$)	-52.0975
3($^1A_1$)	-52.0735
2($^3B_1$)	-52.1351
3($^3B_2$)	-52.1209
^3B	-52.2156

Table VII. The INDO energy of planar $^1A_1$ difluoromethylenecarboxylate 3

C–C	C–O	α	β	E
1.400	1.26	130	110	-101.3143
1.400	1.31	130	110	-101.3228
1.400	1.36	130	110	-101.3019
1.430	1.31	130	110	-101.3241
1.466	1.31	130	110	-101.3220
1.430	1.31	135	110	-101.3245
1.430	1.31	140	110	-101.3231
1.430	1.31	135	100	-101.3246
1.430	1.31	135	95	-101.3195
1.430	1.31	135	90	-101.3103

Table VIII. The INDO energy of the perpendicular $^1A_1$ form 2 of difluoromethylenecarboxylate

C–C	C–O	α	β	E
1.430	1.31	135	110	-101.3295
1.430	1.31	135	100	-101.3291

Table IX. The energy of the unsymmetrical difluoro system 4 at points along the $^1A'$ reaction coordinate

	E
4(.10)	-101.5351
4(.25)	-101.4770
4(.50)	-101.3868
4(.75)	-101.3362

Table X. The energies of triplet difluoromethylenecarboxylate in C_{2v} and C_2 geometries

	C–C	C–O	α	β	E
2($^3B_1$)	1.430	1.31	135	110	-101.3265
3($^3B_2$)	1.430	1.31	135	100	-101.3431
^3B	1.430	1.31	135	100	-101.4127

Table XI. The energy of dimethylacetolactone in closed, open and semiopen geometries

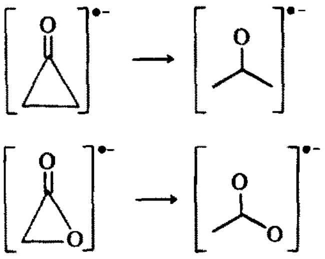
	E
1a	-67.0838
1b	-67.0840
3(β = 110°)	-66.8452
3(β = 120°)	-66.8471
3(β = 130°)	-66.8420
2(β = 120°)	-66.8677
3(β = 120°) ($^3B_2$)	-66.8893
2(β = 120°) ($^3B_1$)	-66.9054
(β = 120°) (^3B)	-66.9676
4(.10)	-67.0691
4(.25)	-67.0311
4(.50)	-66.9332
4(.75)	-66.8890

were employed for the lactone and afforded energies $-67\cdot0838$ h and $-67\cdot0840$ h. Since the energy of the planar $^1A_1$ methylenecarboxylates **3** proved in the previous two cases to be insenstive to small changes in geometry, we simply chose the best geometry for the parent system, that having energy equal to $-49\cdot8831$ h; however, with the introduction of the new substituent, the internal angle β was reoptimized. The results of all the calculations are summarized in Table XI.

The INDO method favors **2** over **3** for the closed-shell singlet while the triplet is more stable in the methylene-rotated ^3B geometry, and it appears that these open-shell systems will be important intermediates in the reactions of the α-lactones.

CONCLUSION

INDO calculations on acetolacetone, its difluoro, and dimethyl derivatives indicate that in all cases the closed lactone is more stable than the ring-open forms. While the method overestimates the energy requirements for the opening, it does provide information on its relative ease and on the importance of open-shell systems in the chemistry of α-lactones. Since solvation effects are not considered, our calculations correspond most closely to the gas phase, and here the ring-open forms of these systems seem to be more stable in the triplet state.



Finally, these semiempirical calculations on α-lactones and our *ab initio* results on cyclopropanone[10] show low-lying virtual orbitals for the ring-open form which are not present in the cyclic geometry, and this leads us to conclude that the radical anions of both systems should undergo thermodynamic opening. Symmetry restrictions, however, may slow down the rate of the process.

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