Application of Semiempirical Molecular Orbital Theory to Cationic Intermediates Involved in the Solvolysis of 1-Halobicyclo[*n*.1.1]alkanes

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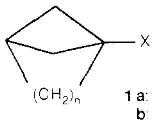
Received November 2, 1987

The structures of the bicyclo[*n*.1.1]alkylium cations (2), *n* = 1–3, have been determined by using various molecular orbital methods. We find that the AM1 and MNDO semiempirical molecular orbital methods give geometries contrary to chemical expectation. Surprisingly, MINDO/3 geometries correlate most closely with the RHF/6-31G* (ab initio) results for **2a** and **2b**, predicting extremely short transannular separations (**2a**: 1.583 Å using MINDO/3, 1.537 Å at RHF/6-31G*; **2b**: 1.693 Å using MINDO/3, 1.690 Å at RHF/6-31G*). Partitioning of the total molecular energy into mono- and bicentric terms, within the MINDO/3 framework, leads to a qualitative understanding of the unusual rates and trends in the solvolyses of bicyclo[*n*.1.1]alkyl halides (1). A delicate balance of unfavorable strain and favorable through-space orbital effects is found to be operating in the cations (2).

Introduction

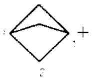
Twenty years ago Wiberg and co-workers showed that 1-chlorobicyclo[1.1.1]pentane (**1a**, X = Cl) solvolyses about 3 times faster than *tert*-butyl chloride in 80% aqueous ethanol. Not only was the solvolysis considerably faster than expected on the basis of strain but only rearranged products were observed.[4] A few years earlier, they had also shown that 1-bromobicyclo[2.1.1]hexane (**1b**, X = Br) solvolyses considerably more slowly (~10^{-6}) than *tert*-butyl bromide, again giving only rearranged products.[5] More recently, work in our laboratories[6] has revealed the higher homologue, 1-bromobicyclo[3.1.1]heptane (**1c**, X = Br) to display greater solvolytic reactivity, reacting about 8 times more rapidly than *tert*-butyl bromide; giving both rearranged and unrearranged products.



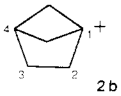
1 a: n=1
b: n=2
c: n=3

In a recent communication,[7] we demonstrated that semiempirical molecular orbital theory could be used to give a satisfactory account of the observed rates of rearrangement. But what of the unusual trends in solvolytic reactivity?

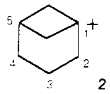
Wiberg and Williams suggested that the unusually fast solvolysis rate observed for **1a** could be "attributed to the driving force for ring fragmentation, relieving considerable strain".[4] They went on to suggest an alternative explanation which essentially involves the concept of through-space stabilization of the bicyclo[1.1.1]pentylium cation (**2a**). In light of our calculations[7] and the observation that **1b** both rearranges and solvolyses at a considerably reduced relative rate when compared to **1a**, the latter of the two explanations appears the more appealing.



2a



2b



2c

Through-space stabilization in the solvolysis of strained systems is not a new concept. As early as 1967, Wiberg used CNDO[8-10] through-space bond indices to account for the difference in the rates of solvolysis of axially and equatorially substituted cyclobutyl-like systems.[11]

Davis and Black[12] have postulated a favorable through-space effect, which they term *percaudal homoconjugation*, to explain rate accelerations in the solvolysis of trimethylmetal-substituted methanesulfonates. Grob[13] has discussed bridging and inductivity effects in relation to the solvolysis of bi- and tricyclic tosylates, while Davidson and Shiner[14] have calculated the effect of the through-space stabilizing tendency of silicon in the 3-silylpropylium cation. More recently McKee[15] reported high level ab initio calculations on the cyclobutylium ion. These calculations suggest pronounced stabilization, reflected in the short (1.650 Å at MP2/6-31G*) transannular separation and significant deviation from planarity.

In their ongoing studies, Schleyer and co-workers[16,17] and Mueller et al.[18-20] have had considerable success in correlating the strain engendered in the formation of the intermediate cation with the rates of solvolysis of a number of bridgehead substituted bi- and tricycloalkanes. Their studies did not, however, include the bicyclo[*n*.1.1]alkyl series.

In this paper, we demonstrate that semiempirical molecular orbital theory, especially MINDO/3,[21] together with molecular mechanics[22] (MM2) can be used in a qualitative sense to explain the rates and trends observed in the solvolyses of the bicyclo[*n*.1.1]alkyl systems (1). MIN-

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Table I. MM2 Calculated Values of $\Delta E_S(R^+ - RH)$,[a] Relative Rates,[b] and Free Energies[a,b] of Solvolysis, at 25 °C, for the Bicyclo[*n*.1.1]alkyl Systems

structure	ΔE_S-($R^+ - RH$)	k(25 °C)	ΔG^* (25 °C)
bicyclo[2.1.1]hex-1-yl	+35.4	1.8×10^{-3}[c]	+3.7
bicyclo[1.1.1]pent-1-yl	+49.6	4.0×10^{3}[c]	−4.9
bicyclo[3.1.1]hept-1-yl	+27.1	5.3×10^{3}[d]	−5.1

[a] Energies in kcal·mol^{-1}. [b] Relative to adamantyl. [c] Fort, R. C., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1980; Vol. 4, Chapter 32. [d] Della, E. W.; Elsey, G. M. *Tetrahedron Lett.* **1988**, *29*, 1299.

DO/3, through the use of energy partitioning, gives a good qualitative picture of the degree of through-space stabilization in the intermediate cations while MM2 gives an indication of the degree of strain engendered in their formation.

Methods

All molecular mechanics calculations were performed by using Allinger's MM2 program[22] incorporating suitable parameters[23] for four-membered carbocations.[18] All semiempirical molecular orbital calculations were performed through the AMPAC[24] system of programs, incorporating the MINDO/3,[21] MNDO,[25] and AM1[26] methods. The ab initio calculations were performed by using the Gaussian 82[27] or Gaussian 86[28] packages. All calculations were carried out on a PRIME-9955 computer, except ab initio which were carried out on a FACOM M360R or VP-100 computer.

Results and Discussion

Previous workers[16-20] were concerned with the strain–reactivity relationship of suitably substituted bi- and tricycloalkanes. To that end, Mueller and co-workers[20] correlated the free energies of solvolysis (ΔG^*) of 14 suitable substrates with the MM2 calculated strain energy differences between the cation (R^+) and the parent hydrocarbon (RH) [$\Delta E_S(R^+ - RH)$]. The authors claim excellent correlation (r = 0.997), using their MM2 cation parameters, indicating that the rates of solvolysis are mainly affected by the strain engendered in the formation of the carbocation (R^+).

As we were interested in the solvolysis of bicyclo[*n*.1.1]alkyl systems, it was instructive to compare their strain–reactivity relationships with the other systems previously examined.

Table I lists the relevant data for the bicyclo[*n*.1.1]alkyl systems of interest. The strain–reactivity correlation is shown in Figure 1, together with the data of Mueller.[20] Inspection of Figure 1 reveals that the bicyclo[*n*.1.1]alkyl systems **1a–c** do not fit the correlation observed for the other systems. It is clear that **1a–c** solvolyze many orders of magnitude faster than expected on the basis of strain. It is also clear that on the basis of strain alone, **1c** is expected to solvolyze faster than **1b** which in turn is expected to solvolyze faster than **1a**.

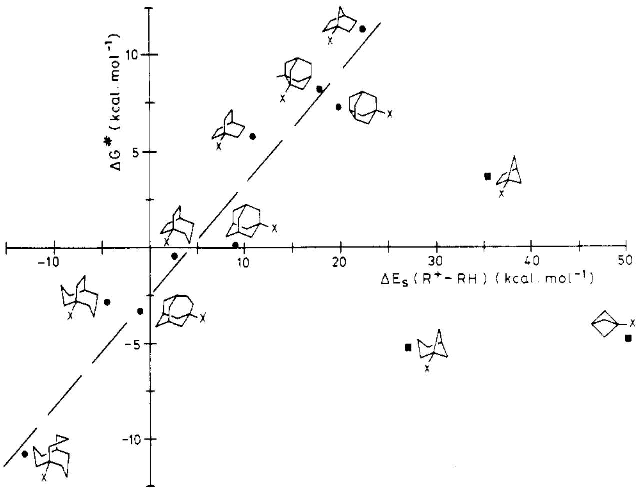

Figure 1. Plots of the free energies of solvolysis (ΔG^*) vs strain energy differences between cation and parent hydrocarbon ($\Delta E_S(R^+ - RH)$ for the systems of interest.

Assuming that the enthalpy differences between cation and parent hydrocarbon do correlate with the free energy of solvolysis, then, it would appear that the bicyclo[1.1.1]pentylium cation (**2a**) is stabilized by about 50 kcal·mol^{-1} beyond the unfavorable strain engendered in the system. Similarly, **2b** is stabilized by about 25 kcal·mol^{-1} while **2c** is stabilized by approximately 30 kcal·mol^{-1}. It should be noted that these values are approximate, as scatter in Figure 1 should be taken into consideration (~±5 kcal·mol^{-1}).

In order to gain an understanding of the factors operating in these systems, we chose to examine the bonding in the bicyclo[*n*.1.1]alkylium ions (**2**) using molecular orbital theory. We were aware of the importance of polarization functions[29] (d orbitals) in the bonding of highly strained systems; however, RHF/6-31G*[30] descriptions of all the cations (**2**), especially **2c**, was a task beyond our current resources. We chose, therefore, to use semiempirical molecular orbital theory, through which, we felt, a qualitative idea of the features of these highly strained cations could be achieved.

To assess the reliability of the semiempirical methods, the structures of **2a** and **2b**, determined by using RHF/6-31G* (assuming C_{3v} and C_s symmetry, respectively) were compared with the available semiempirical data.[7,32] Table II lists the RHF/6-31G* geometries of **2a** and **2b** while Table III displays the bridgehead–bridgehead separations in the cations **2** at various levels of theory, together with the MM2 calculated value.

It is immediately clear that the inclusion of polarization functions (6-31G*) has a marked effect on the geometry of **2a**. The C_1C_3 separation (bridgehead–bridgehead) is predicted to be extremely short (1.537 Å) at the RHF/6-31G* level (cf. 1.87 Å at the RHF/6-31G* for the parent hydrocarbon (**1a**, X = H)[31]), indicating extensive through-space interaction. In fact, the RHF/6-31G* geometry suggests that the C_1C_3 separation is shorter than the corresponding bond in the [1.1.1]propellane (**3**), as calculated by Jackson and Allen[31] and is consistent with

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Table II. RHF/6-31G* Data[a] for the Bicyclo[1.1.1]pentylium (2a) and Bicyclo[2.1.1]hexylium (2b) Ions

2a		2b					
$R(C_1C_2)$	1.455	$R(C_1C_2)$	1.515	$R(C_5H_e)$	1.076	$\theta(C_4C_5H_e)$	109.3
$R(C_1C_3)$	1.537	$R(C_1C_4)$	1.690	$R(C_5H_n)$	1.075	$\theta(C_4C_5H_n)$	117.9
$R(C_2C_3)$	1.593	$R(C_1C_5)$	1.432	$\theta(C_1C_2C_3)$	89.9	$\omega(C_2C_1C_4C_5)$	116.5
$R(C_2H)$	1.075	$R(C_2C_3)$	1.567	$\theta(C_1C_2C_5)$	113.7	$\omega(C_1C_4C_3H)$	117.8
$R(C_3H)$	1.075	$R(C_3C_4)$	1.540	$\theta(C_2C_3C_4)$	94.7	$\omega(C_3C_4C_5H_e)$	177.9
$\theta(C_1C_2H)$	118.5	$R(C_4C_5)$	1.636	$\theta(C_3C_4C_5)$	106.7	$\omega(C_3C_4C_5H_n)$	43.2
$\theta(HC_2H)$	116.5	$R(C_2H)$	1.079	$\theta(C_1C_2H)$	113.2	$\omega(C_4C_1C_2H)$	116.8
		$R(C_3H)$	1.080	$\theta(C_3C_4H)$	126.8		
E^b	−193.04241	$R(C_4H)$	1.076	$\theta(C_4C_3H)$	112.7	E^b	−232.11751

[a] Distances in Å. [b] Energies in hartrees (1 H = 627.5 kcal·mol^{-1}).

Table III. Comparison of the Calculated Bridgehead–Bridgehead Separations[a] for the Cations (2) at Various Levels[b] of Theory

structure	MM2	MINDO/3	MNDO	AM1	STO-3G	4-31G	6-31G*
2a	1.743	1.583[c]	1.649	1.608	1.640[c]	1.591[d]	1.537
2b	1.780	1.693	1.790	1.822	1.800	1.754	1.690
2c	1.829	1.750	1.885	1.929			

[a] Distances in Å. [b] Calculations using RHF approximation. [c] Reference 32. [d] Reference 31.

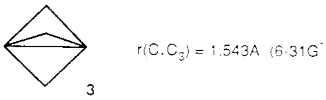
Table IV. MINDO/3 Partitioned Energies[a,b] and Bond Indices (W_{ab})[c] for the Bridgehead-Bridgehead Interactions in the Bicyclo[*n*.1.1]alkylium Cations (2)

structure	E_{ab}^{res}	E_{ab}^{V}	E_{ab}^{core}	E_{ab}^{el}	E_{ab}	W_{ab}
2a	−6.93	−215.23	115.15	102.82	−4.19 (−96.6 kcal·mol^{-1})	0.331
2b	−5.46	−205.27	109.87	97.33	−3.52 (−81.3 kcal·mol^{-1})	0.304
2c	−5.07	−201.23	107.29	95.5	−3.50 (−80.5 kcal·mol^{-1})	0.293

[a] Energies in eV. [b] For the definition of E_{ab}, and components thereof, see text. [c] Reference 11.

the short transannular separation found in the case of the cyclobutylium ion.[15] In many respects, **2a** can be likened to a "protonated propellane". Schleyer and co-workers[32] have described **2a** as a "CH$^{+\bullet}$ trimethylmethylene complex" due to the unusual shape of the carbon skeleton predicted by using MINDO/3 and RHF/STO-3G.

Similar results are obtained for **2b**. The bridgehead–bridgehead separation of 1.690 Å at RHF/6-31G* is also extremely short, suggesting substantial "protonated propellane" character.



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Intuitively, the MM2 calculated bridgehead separations should be too large, as no favorable through-space orbital effects are taken into account in the molecular mechanics treatment. Thus, one would expect the molecular orbital calculations, which take this effect into account, to predict *shorter* separations than MM2. This is clearly evident in the case of the bicyclo[1.1.1]pentylium system (**2a**) at all levels of theory. The higher homologues (**2b, 2c**) are clearly not handled well within the MNDO and AM1 frameworks, as both theoretical methods predict separations *larger* than calculated by MM2. This is clearly inconsistent with chemical intuition. Only MINDO/3 gives consistently shorter separations than MM2. In fact, MINDO/3 is in surprisingly good agreement with RHF/6-31G* in the description of the geometries of **2a** and **2b**.

It is well established that MNDO overestimates core–core repulsion terms when atoms are separated by about their van der Waals radii.[26] A solution to this problem has been attempted in the development of AM1, with the introduction of Gaussian correction terms,[26] but the effectiveness of these terms, when applied to four-membered ring systems, has not yet been established. Dewar and Thiel[33] have indicated that MINDO/3 performs considerably better than MNDO for four-membered ring compounds.

It is for the above-mentioned reasons that we felt MINDO/3 to be the semiempirical method of choice in the study of the highly strained cations (**2**).

A method of investigating the favorable through-space interaction in these cations (**2**) is through the partitioning of the total molecular energy into mono- and bicentric terms. This partitioning is unique to the semiempirical methods; the theory is well established[34-36] and will not be discussed here.

Essentially, the total energy can be expressed as

$$E_t = \sum_a E_a + \sum_{a>b}\sum E_{ab}$$

The bicentric energy, E_{ab}, is composed of core–core repulsion (E_{ab}^{core}) and electron–electron repulsion (E_{ab}^{el}) terms, which, of course, are destabilizing, and two-center core-electron attraction (E_{ab}^{V}) and resonance (E_{ab}^{res}) terms, which are stabilizing. As Dewar and Lo remarked,[35] "the dissection of the total energy into one- and two-center terms conforms, of course, to the usual picture of molecules as composed of atoms linked by chemical bonds. E_{ab} provides a good quantitative measure of bond strength, both from its sign and its magnitude. A large negative

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value for E_{ab} implies strong bonding between atoms a and b, while a positive value implies an anti-bonding interaction."

Energy partitioning has been applied to the study of the Cope rearrangement,[35] the basicity of heterocyclic amines,[36] and the investigation into nonclassical bonding in cations.[34]

When the total molecular energies of the cations (**2**) are partitioned within the MINDO/3 framework, as discussed, a net *bonding* interaction is observed between the bridgeheads in all cases. The MINDO/3 calculated energy components are displayed in Table IV, along with the calculated bond indices (W_{ab}).[11]

To our surprise, the MINDO/3 partitioned energies and bond indices suggested that both **2b** and **2c** are stabilized transannularly by approximately the same amount. The calculations indicate that E_{ab} for **2b** is −81.3 kcal·mol^{-1}, while the similar quantity for **2c** is −80.5 kcal·mol^{-1}. Inspection of Table IV reveals why this is so. The bicyclo[2.1.1]hexylium cation, **2b**, having the *shorter* bridgehead–bridgehead separation and the more favorable transannular angle (C_1C_4H = 154.1° in **2b**, C_1C_5H = 141.5° in **2c**) is advantaged with greater orbital overlap, reflected in the larger negative values for E_{ab}^{res} and E_{ab}^{V}, over **2c**. Conversely, **2b** is disadvantaged over **2c** with less favorable values for E_{ab}^{core} and E_{ab}^{el}, reflecting the closer proximity of both bridgehead nuclei and electrons in the case of **2b**. When all effects are taken into consideration, **2b** and **2c** are predicted to possess similar stabilization energies. The respective bond indices are 0.30 and 0.29.

Fischer and Kollmar[34] suggest that the bicentric terms (E_{ab}) should be used in a qualitative fashion, as the numerical values do not correspond to bond energy in the conventional sense, being often much larger than the observed bond dissociation energies. Thus, the observation that both **2b** and **2c** are stabilized by similar amounts is consistent with the conclusions drawn from the strain–reactivity relationship that **2b** is stabilized by about 25 kcal·mol^{-1} while **2c** is stabilized by approximately 30 kcal·mol^{-1}.

The calculations for **2a** suggest a greater degree of through-space stabilization. Thus, MINDO/3 suggests a bond index of 0.33[32] and a value of E_{ab} of −96.6 kcal·mol^{-1}. Clearly, in this case, the shorter bridgehead–bridgehead separation and ideal orbital angle (C_1C_3H = 180°) results in extremely favorable values for resonance (E_{ab}^{res}) and core–electron attraction (E_{ab}^{V}) terms; so favorable, in fact, as to more than compensate for the unfavorable repulsion terms (E_{ab}^{core} and E_{ab}^{el}). The calculated increase in the stabilization energy of **2a** over **2b** and **2c** of about 15 kcal·mol^{-1} is consistent with the ~20 kcal·mol^{-1} increase expected on the basis of the strain–reactivity relationship as previously discussed.

Thus, it would appear that the through-space stabilization energies, predicted on the basis of the strain–reactivity relationship, in the cations (**2**) are not unreasonable when compared with the MINDO/3 results in a qualitative sense. The observed trend in solvolysis rates (viz, **2c** > **2a** > **2b**) can be understood in terms of a delicate balance of opposing unfavorable strain energies and favorable transannular stabilization energies engendered in the cations (**2**). In **2a** the orbital effects dominate over strain considerations, thereby rationalizing the rapid solvolysis observed in the case of **1a**. As the strain decreases in progressing to the higher homologues, so does the favorable transannular stabilization. Considering that the stabilization effects are similar in **2b** and **2c**, and that the strain is markedly reduced in **2c**, it is not surprising that the higher homologue (**1c**) solvolyses the more rapidly. Clearly, strain considerations in **2b** dominate over the transannular orbital considerations, as **1b** is observed to solvolyse many orders of magnitude slower that either **1a** or **1c**.

Conclusions

As the data have shown, MINDO/3 appears to outperform both MNDO and AM1 in the description of the bicyclo[*n*.1.1]alkylium cations (**2**). When the MINDO/3 calculated energies are partitioned into mono- and bicentric components, the cations (**2**) are seen to be stabilized beyond the unfavorable strain engendered in their formation by favorable through-space effects. These effects can be invoked in rationalizing the unusual trends and rates of solvolysis observed for the 1-halobicyclo[*n*.1.1]-alkanes.

Acknowledgment. We are indebted to the Australian Research Grants Scheme for financial support.

Registry No. **2a**, 22907-79-5; **2b**, 22907-78-4; **2c**, 113851-50-6.

Thermal Aromatization of Alkylidenecyclopentenes and Related Hydrocarbons

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Received June 24, 1987

3- and 4-alkylidenecyclopentenes (dihydrofulvenes) undergo thermal aromatization upon flash vacuum pyrolysis (FVP) at 700 °C. For example, toluene and *m*-xylene are the principal products formed from 3- and 4-isopropylidenecyclopentene. Similar behavior is observed for other dihydrofulvenes that have alkyl groups on the exocyclic methylene carbon. Cyclohexadienes are believed to be the intermediates immediately preceding the aromatics, and the aromatization step is believed to occur by a free radical process involving successive loss of an alkyl group and a hydrogen atom. Small amounts of secondary aromatics are formed from the primary products by free radical aromatic substitution, dealkylation, etc. Upon FVP, 6,6-dialkylbicyclo[3.1.0]hexenes give mixtures of aromatics which are very similar to those obtained from the isomeric dihydrofulvenes, and it is proposed that these bicyclic derivatives may be intermediates in the formation of cyclohexadienes from dihydrofulvenes. Other possible pathways from dihydrofulvenes to cyclohexadienes are presented.

Aromatization, the conversion of nonaromatic into aromatic substances, is an important process in petroleum refining and coal liquefaction. Aromatization may occur under the influence of heat alone, but it is usually accompanied by extensive side reactions. In the industrial processes catalysts are generally employed that increase

0022-3263/88/1953-4357$01.50/0 © 1988 American Chemical Society