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Masaji Matsunaga, Takashi Kawamura*
Department of Hydrocarbon Chemistry
Faculty of Engineering, Kyoto University
Kyoto 606 Japan

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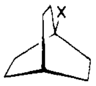
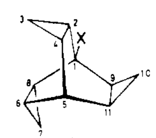
Structure Reactivity Relationship for Two Conformationally Restricted Tricyclopropyl Carbinyl Systems

Sir:

The "bisected" conformation of a cyclopropyl carbinyl cation is energetically favored over the "perpendicular" one by about 16 kcal/mol.[1] It is in the bisected orientation that the cyclopropyl group exhibits the largest stabilizing effect on an adjacent positively charged center whereas it destabilizes a carbenium ion when fixed in a perpendicular orientation.[2] Recently it has been shown[3,4] that a cyclopropyl carbinyl cation is stabilized also when the conformation of the system is locked at an intermediate position between "bisected" and "perpendicular". We here report our results of an electron diffraction structure analysis on trishomobarrelene (**2a**)[5] and trishomobullvalene (**4a**)[5] in the vapor phase and the correlation of relevant structural parameters with the stabilization energies of the corresponding bridgehead cations **2c** and **4c** respectively relative to those of bicyclo[2.2.2]octane (**1c**) and tricyclo[3.3.2.0^{2,8}]decane (**3c**).



1



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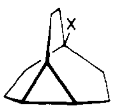

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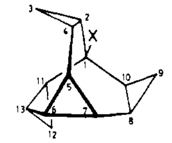

4

a X = H b X = Cl c X = ⊕

Diffraction photographs for both compounds were obtained on the "Oslo-Apparatus" and treated in the usual way.[6] The full sets of structural parameters resulting for the best models from least-squares refinements on the experimental intensity curves are listed in Table I.[7]

According to this analysis **2a** has C_{3h} and **4a** C_3 symmetry. All C-C bond lengths and CCC bond angles observed fall in the usual range,[8,9] except for the C^5-C^6 distance in **4a**, which appears to be significantly longer than normal cyclopropyl C-C-σ-bonds. However, this observed distance compares favorably with the corresponding distance in bullvalene (1.542 Å).[10] The structures of **2a** and **4a** differ in two important features, both of which are relevant to the relative solvolytic reactivity.

Table I. Structural Parameters of Trishomobarrelene (**2a**) and Trishomobullvalene (**4a**)[a]

Parameter	**2a**	**4a**
$r(C^1C^2)$, Å	1.536 ± 0.002	1.508 ± 0.010
$r(C^2C^3)$, Å $r(C^3C^4)$, Å	1.515 ± 0.001	1.516 ± 0.003
$r(C^2C^4)$, Å	1.516 ± 0.005	1.495 ± 0.009
$r(C^4C^5)$, Å	1.536 ± 0.002	1.516 ± 0.006
$r(C^5C^6)$, Å	–	1.542 ± 0.010
r (CH),[b] Å	1.102 ± 0.001	1.097 ± 0.002
$<(C^1C^2C^4)$, deg	110.1 ± 0.1	121.5 ± 0.5
$<(C^2C^4C^5)$, deg	110.1 ± 0.1	123.8 ± 0.7
$<(C^4C^5C^6)$, deg	–	123.9 ± 0.4
$<(C^2C^1C^9)$, deg	108.9 ± 0.1	–
$<(C^2C^1C^{10})$, deg	–	113.2 ± 0.5
$<\beta$,[c] deg	115.3 ± 0.3	112.1 ± 0.4
$<\varphi$,[d] deg	61.8 ± 0.5	66.1 ± 0.7
u_{CC},[e] Å	0.049 ± 0.001	0.049 ± 0.002
u_{CH},[e] Å	0.072 ± 0.001	0.076 ± 0.002

[a] For the numbering of the atoms see formulas **2** and **4**. All distances given are equilibrium distances r_g,[6] the errors listed are standard deviations; for realistic error limits these standard deviations should be multiplied by three. [b] Average C–H distance. [c] Angle between the planes $C^2C^3C^4$ and $C^1C^2C^4C^5$. [d] Angle between the axis of a bridgehead orbital (i.e., the molecular axis) and that of an adjacent cyclopropyl p orbital. [e] Root mean square deviations of the C–C and C–H distances, respectively.

Table II. Bridgehead Geometries and ^{13}C, ^{1}H Coupling Constants in the Hydrocarbons 1a–4a

Compound	Bridgehead CCC angle (deg)	Bridgehead $^1J(^{13}C, ^1H)/(Hz)$	Ref
1a	109.2[a]	134.3 ± 1.2	13
2a	108.9	137.0 ± 1.5	*b*
3a	?	122.0 ± 2.0	13
4a	113.2	127.0 ± 1.5	*b*

[a] Taken from ref 8c. [b] This work.

Whereas the bridgehead geometry in **2a** with a CCC angle of 108.9° ($C^2C^1C^9$ in Table I) is very similar to that in bicyclo[2.2.2]octane (**1a**),[8] the corresponding angle in **4a** is about 4° larger ($C^2C^1C^{10}$ in Table I). This means, that the bridgehead in **4a** is considerably flatter than that in **2a**, implying that the p character in the bridgehead C-X bond and the s character in the three bridgehead C-C bonds are larger than in normal sp^3 hybrid bonds. This is consistent with the ^{13}C,H coupling constants of 137 and 127 Hz observed for the bridgehead protons in **2a** and **4a**, respectively (see Table II), the smaller value indicating a lower s character[11] in the bridgehead C-H bond of **4a**. In addition, the bridgehead C-C bonds in **4a** are ≈0.03 Å shorter than those in **2a** (see Table I) as should be expected if the s character is increased in these bonds. The ^{13}C, ^{1}H coupling constant can also be used as a probe for the yet unknown bridgehead geometry in tricyclodecane (hexahydrobullvalene) **3a**;[12] the low value of 122 ± 2 Hz confirms the presumption that the bridgehead CCC angles in **3a** and **4a** should be very similar (see Table II). Therefore the bridgehead chloride **3b** may well serve as the reference compound to evaluate the carbenium ion stabilizing power of the three cyclopropyl groups in **4c**, in the same way as **1b** is an appropriate reference system for **2b**.

The solvolysis reactions of **2b**, **3b**, and **4b** were followed both acidimetrically and conductometrically. Special techniques had to be used for **2b** and **4b** because they react rather rapidly even in 80% aqueous dioxane.[14] In this solvent at 25°, **2b** gave $k = 6.87 \times 10^{-5}$ sec^{-1} with $\Delta H^\ddagger = 20.2$ kcal/mol and $\Delta S^\ddagger = -9.8$ eu and **4b** gave $k = 2.24 \times 10^{-1}$ sec^{-1} with $\Delta H^\ddagger = 15.5$ kcal/mol and $\Delta S^\ddagger = -9.5$ eu.

As Table III shows **2b** solvolyzes more than 10^8 times faster than **1b** and 1-trishomobullvalyl chloride **4b** reacts al-

Table **III**. Rates of Solvolysis of Bridgehead Chlorides 1b–4b in 80% Aqueous Dioxane

Compound	k_{25} (sec^{-1})	k_{rel}	k_{rel}	$\Delta\Delta G^{\ddagger}$, kcal/mol	$E_{(\varphi)}/E_{(\varphi=0)} = \cos^2\varphi$
1b	$\approx 2.6 \times 10^{-13}$[a]	1.0		11.5	0.223
2b	6.87×10^{-5}	2.7×10^{8}			
3b	5.81×10^{-8}[b]	2.2×10^{5}	1.0	9.0	0.164
4b	2.24×10^{-1}	8.6×10^{11}	3.9×10^{6}		

[a] Estimated from the experimental solvolysis rate of 1-bromobicyclo[2.2.2]octane[16] in 80% aqueous ethanol, the known rate ratio of *tert*-butyl chloride and *tert*-butyl bromide,[15] and the *Y* value from ref 15b. [b] Taken from ref 17.

most 10^{12} times faster than **1b**, by this **4b** is the most reactive bridgehead chloride known to date, being 1.6×10^5 times more reactive than *tert*-butyl chloride.[18] However, only part of this high reactivity of **4b** is due to cyclopropyl stabilization of the intermediate carbenium ion **4c**, the other part originates in a normal strain effect,[19] since the 1-hexahydrobullvalyl chloride **3b** also solvolyzes 2.2×10^5 faster than **1b**. In fact, the three cyclopropyl groups in **4b** cause a rate enhancement of only 3.9×10^6 over **3b**, whereas the same three cyclopropyl groups in **2b** enhance the rate by a factor of 2.7×10^8 over that of **1b**.

This remarkable difference in cation stabilizing power of the three cyclopropyl groups in **2c** and **4c** must be attributed to the second important structural difference between the skeletons **2a** and **4a**, i.e., the difference in the dihedral angles between the axis of a bridgehead orbital and that of an adjacent cyclopropyl p orbital (angle φ in Table I). Since the stabilization energy of a cation by a neighboring electron donating group should be proportional to the overlap between the two interacting orbitals and this overlap for two adjacent p orbitals is proportional to $\cos^2$ of the dihedral angle φ between the two orbital axes,[20] it can be assumed that the relative stabilization of the two tricyclopropyl carbinyl cations **2c** and **4c** can be expressed by

$$E_{(\varphi)}/E_{(\varphi=0)} = \cos^2 \varphi$$

With $\varphi(\mathbf{2a}) = 61.8°$ and $\varphi(\mathbf{4a}) = 66.1°$ this gives 0.223 and 0.164 (see Table III), meaning that the cyclopropyl groups should exhibit 22.3 and 16.4% of their maximum stabilizing ability in **2c** and **4c**, respectively. From the difference in orientation of the cyclopropyl groups in **2c** and **4c** alone one would conclude that **4c** experiences only 74% of the cyclopropyl stabilization effective in **2c**. Experimentally it is observed that the difference in the free energies of activation between **4b** and **3b** is only 78% of the one between **2b** and **1b** (see $\Delta\Delta G^{\ddagger}$ in Table III). This almost perfect agreement between the experimental ratio and the one predicted on the basis of structural differences excludes the possibility that a "leveling effect"[21] might be responsible for the decreased stabilizing ability of the three cyclopropyl groups in **4c**.

The results presented here strongly corroborate the conclusions drawn from CNDO calculations[22] by which the energy change of a cyclopropyl carbinyl cation upon rotation of the cationic center follows a function very similar to a $\cos^2\varphi$ relationship (with φ being the angle of rotation). It should be pointed out, however, that only the comparison of symmetrical systems such as **1–4** can yield a significant structure reactivity relationship for the cyclopropyl carbinyl system. In unsymmetrical systems such as 1-tricyclo[3.2.2.0^{2,4}]nonyl cation[4] distortion of the bridgehead geometry may play an important role.[23]

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Birgit Andersen
Department of Chemistry, University of Oslo
Oslo 3, Norway

Otto Schallner, Armin de Meijere*
Organisch-Chemisches Institut der Universität
D-3400 Goettingen, West Germany

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Concerning the Role of 4β-Methyl Sterols in Cholesterol Biosynthesis[1]

Sir:

The enzymatic conversion of lanosterol to cholesterol involves the removal of two methyl groups attached to C-4 of the sterol nucleus. Studies of the metabolism of 4,4-dimethyl sterols have indicated initial removal of the equatorial 4α-methyl substituent.[2] This process has been proposed to involve successive oxidations to yield the 4β-methyl-4α-car-