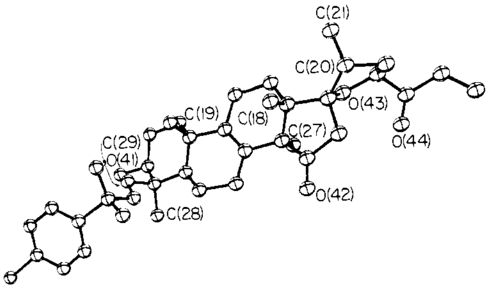

Figure 1. A perspective drawing of the *p*-bromobenzenesulfonate derivative of eucosterol (**1**). Hydrogens are not shown, and a standard triterpene numbering system is employed.

sulfonate **6**, colorless plates from benzene–*n*-hexane of mp 158–159°, $M^+ - C_6H_4BrO_3S$ at *m/e* 454.

These crystals proved to be suitable for a structural analysis by X-ray diffraction belonging to the common monoclinic space group $P2_1$ with a = 18.61 (2) Å, b = 7.84 (1) Å, c = 12.09 (2) Å, and β = 106.31 (3)°. The calculated density for two molecules of $C_{35}H_{53}O_7SBr$ per unit cell was 1.31 g/cm^3. All unique diffraction maxima with $\theta \leq 55°$ were collected on a fully automated four-circle diffractometer using θ–2θ scans. A total of 2317 reflections were collected in this manner of which 1823 were judged observed after correction for Lorentz, polarization, and background effects ($F_o \geq 3\sigma(F_o)$).

A three-dimensional Patterson synthesis[10] was readily deconvoluted to yield both the bromine and sulfur atomic positions. Subsequent electron density syntheses revealed all 44 nonhydrogen atoms. Full-matrix least-squares refinement, followed by a difference electron density synthesis showed all nonmethyl hydrogens. Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms, and anomalous scattering corrections for bromine and sulfur lowered the conventional discrepancy index to 0.061 and 0.062 for the structure and its mirror image, respectively.[11] A careful remeasurement of the ten most enantiomorph sensitive reflections also showed that the absolute configuration depicted correctly predicted the difference ten out of ten times. The final X-ray model is shown in Figure 1. All bond distances and angles generally agree well with accepted values. See paragraph at end of paper regarding supplementary material.

The absolute configuration is that anticipated for triterpenes. The A/B and C/D ring junctions are trans and there is a C(8)–C(9) double bond. The most novel feature is the spiro-fused furanoid system at C(17).

Nortriterpenes which lack the carbon atom at the terminus of the side chain are rare. The biogenetic implications of the eucosterol structure will be considered in a later publication.

Acknowledgments. The investigations in Basel were supported by the "Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung" (Projects No. 2.48.68, 2.460.71, and 2.675.72), which is gratefully acknowledged.

Supplementary Material Available. The fractional coordinates (Table I), bond distances (Table II), and important bond angles (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-3518.

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(12) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee 1972–1977 and Fellow of the Alfred P. Sloan Foundation 1973–1975.

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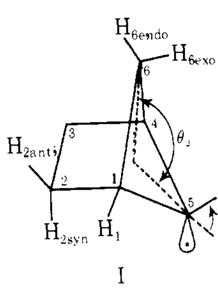
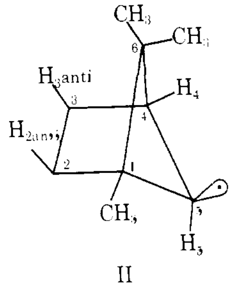
Electron Spin Resonance Study of Bicyclo[2.1.1]hex-5-yl Radicals

Sir:

The bicyclo[2.1.1]hex-5-yl radical is of interest with respect to the geometry around the radical-center carbon atom and the stereoselective delocalization of the odd electron. In this communication we report electron spin resonance (ESR) spectra and stable configurations of the bicyclo[2.1.1]hex-5-yl (I) and the 1,6,6-trimethylbicyclo[2.1.1]hex-5-yl (II) radicals.



I



II

An ESR spectrum shown in Figure 1A was observed during photolysis of bis(bicyclo[2.1.1]hexane-5-carbonyl) peroxide[1] in cyclopropane[2] at −90°. Figure 1B shows the spectrum of the lowest field group of absorptions which was obtained by seven accumulations.[3] The spectra were analyzed as two sets of doublets (26.8 and 9.42 G) split into 1:4:6:4:1 quintets (0.76 G) further into 1:3:3:1 quartets of 0.50 G. Wiberg and his coworkers[1c] reported that the thermolysis of *tert*-butyl bicyclo[2.1.1]hexane-5-peroxycarboxylate in cymene gives bicyclo[2.1.1]hexane (via I) with a fairly high yield without skeletal rearrangement. When a cyclopropane solution of a mixture of the diacyl peroxide and nitrosodu-

Table I. INDO Hyperfine Splitting Constants (G) for the Bicyclo[2.1.1]hex-5-yl Radical

θ_1 (deg)[a]	θ_2 (deg)[b]	H_{2anti}	H_{2syn}	H_4	H_5	H_{6endo}	H_{6exo}
57	139	−1.06	−0.53	−0.20	4.31	16.3	−1.15
29	139	−0.03	−1.08	1.89	−13.4	9.88	−1.28
0	139	2,53	−1.36	4.03	−25.9	2.07	−1.29
−29	139	5.16	−1.10	4.63	−8.46	−2.27	−0.85
−58	139	6.88	−0.58	4.31	6.92	−1.12	−0.37
35	119	−1.33	0,14	−0.47	−12.9	43.3	0.71
I obsd			(±0.76 or ±0.50)		±9.42	±26.8	±0.50
II obsd		±4	*c*	±4	±12	—	—

[a] The angle between the $C_1C_5C_4$ plane and the C_5-H_5 bond; the positive value corresponds to the tilting of the C_5-H_5 bond toward the exo direction. [b] The angle between the $C_1C_5C_4$ and $C_1C_6C_4$ planes; the geometry of the radical at $\theta_2 = 139°$ is the same as that of bicyclo[2.1.1]-hexane suggested by Wilcox; C. F. Wilcox, Jr. *J. Am. Chem. Soc.*, 82, 414 (1960). [c] Not resolved.

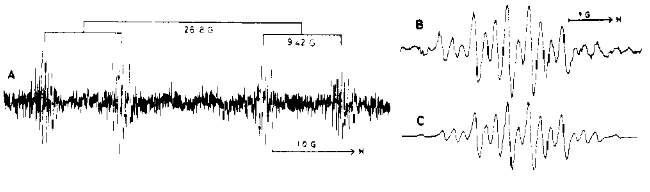


Figure 1. (A) ESR spectrum of I at −90°; (B) the lowest field wing of A obtained by seven accumulations; (C) the lowest field wing of the simulated spectrum.

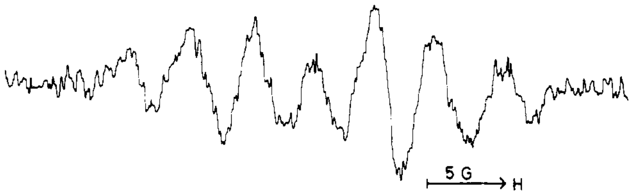


Figure 2. ESR spectrum of II at −100°. The third line from the highest field absorption is distorted due to the signal of the color center of the quartz sample tube.

rene was irradiated at −90°, only a double triplet spectrum (12.6 G one proton, 12.6 G one nitrogen nucleus) was observed. This shows that a secondary alkyl radical was trapped by the nitroso compound.[4] On the basis of these results the spectrum of Figure 1A is attributed to I.

One of the three protons with the hyperfine splitting constant (hfsc) of 0.50 G, the proton of 26.8 G, and the proton of 9.42 G should be identified with H_5, H_{6exo}, and H_{6endo}. A comparison of these values with α proton hfsc's of bicyclic alkyl radicals[5] reveals that it is reasonable to assign the hfsc of 9.42 G to H_5. This assignment assumes that the deviation from planarity around the radical-center carbon atom of I would be similar to those of 7-norbornenyl,[5a] 9-benzonorbornenyl,[5d] and 9-benzonorbornadienyl[5d] radicals. The remaining six protons with the hfsc's of 0.76 and 0.50 G should be assigned to H_1, H_{2anti}, H_{2syn}, and their equivalents. The smallness of the hfsc of the bridgehead proton (0.76 or 0.50 G) shows that the dihedral angle between the axis of the odd electron orbital on C_5 and the C_1-H_1 bond is nearly 90°, which shows that this radical exists dominantly at the configuration with the C_5-H_5 bond bent toward the exo direction ($\theta_1 > 0$) with the odd electron orbital on the radical site expanding in the endo direction.

In this configuration the odd electron orbital and the C_6-H_{6endo} bond forms a double W-plan arrangement, which suggests $a(H_{6endo})$ would be fairly large.[6] Thus the largest doublet of 26.8 G is attributed to H_{6endo}. To our knowledge this is the largest γ proton hfsc ever reported. One proton with the hfsc of 0.50 G is identified with H_{6exo}.

Table I summarizes the proton hfsc's of I calculated with the INDO-UHF method.[7,8] The good agreement between the observed hfsc's and those calculated with the geometries of $\theta_1 = 29°$ and $\theta_2 = 139°$, and $\theta_1 = 35°$ and $\theta_2 = 119°$, supports the present assignment of the hfsc's and the deduced stable configuration of I. The calculated $a(H_{6endo})$ drastically increased when the distance between C_5 and C_6 was decreased from 2.130 to 1.963 Å (the decrease of θ_2 from 139 to 119°, Table I). This suggests the odd electron on C_5 is delocalized directly onto the C_6-H_{6endo} bond (homohyperconjugation, "through-space" interaction).

It should be pointed out that the C_5-H_5 bond is nearly eclipsed with the C_1-H_1 and C_4-H_4 bonds in the stable configuration of I. We propose that the stabilization of the doubly eclipsed configuration is probably due to the homohyperconjugation as is suggested by the large long range hfsc of H_{6endo}.

A double triplet spectrum (12.3 G one ^{14}N nucleus, 15.3 G one proton) was observed when a cyclopropane solution of a mixture of nitrosodurene and bis(1,6,6-trimethylbicyclo[2.1.1]hexane-5-carbonyl) peroxide[9] was irradiated at −110°. This is consistent with the formation of II upon the photolysis of the peroxide. Figure 2 shows the ESR spectrum of II generated by the photolysis of a cyclopropane solution of bis(1,6,6-trimethylbicyclo[2.1.1]hexane-5-carbonyl) peroxide at −100°. The spectrum was analyzed as a double quartet (12 G one proton, 4 G three protons). It is reasonable to assign hfsc's of 12 and 4 G to H_5 and H_4, respectively. The fairly large value of $a(H_4)$ shows that the axis of the odd electron orbital on C_5 is more eclipsed with the C_4-H_4 bond than in the case of I. This reveals that the C_5-H_5 bond bends toward the endo direction. At this stable configuration H_{2anti} and H_{3anti} are arranged in a W-plan with respect to the odd electron orbital on C_5 and are expected to have fairly large hfsc's. Thus two protons of 4 G are identified with H_{2anti} and H_{3anti}. The calculated hfsc's of I at the geometry of $\theta_1 = -29°$ and $\theta_2 = 139°$ (Table I) agree well with the observed hfsc's of II. This supports the present assignment of the hfsc's as well as the deduced stable configuration of II.

We propose that the direction of the tilting of the C_5-H_5 bond of II is probably the result of the release of the destabilization otherwise expected due to eclipsing of the C_5-H_5 bond with the bulky methyl substituent on C_1.

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References and Notes

(1) (a) Prepared by reaction of sodium peroxide and the corresponding acid chloride,[1b] which was prepared according to the method of Wiberg, Lowry, and Colby;[1c] (b) cf. H. Hart and R. A. Cipiani, *J. Am. Chem. Soc.*,

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(9) (a) Prepared from 1,6,6-trimethylbicyclo[2.1.1]hexane-5-carboxylic acid;[9b] (b) J. Meinwald, A. Lewis, and P. G. Gassman, *J. Am. Chem. Soc.,* **84,** 977 (1962).

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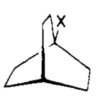
Structure Reactivity Relationship for Two Conformationally Restricted Tricyclopropyl Carbinyl Systems

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**).



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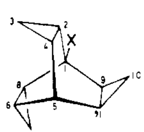

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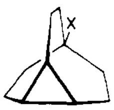

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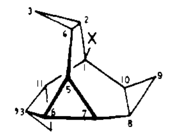

4

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, ^1H 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, ^1H 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-