interactions rather than the HO–LU interactions which govern thermal cycloadditions.[6,19]

Summary and Conclusions

A powerful method has been developed for the rationalization and prediction of substituent effects on rates, regioselectivity, and periselectivity of 1,3-dipolar cycloadditions. Although numerous refinements in the model proposed here are desirable and will undoubtedly develop, the rationalization of a massive body of experimental data on regioselectivity in 1,3-dipolar cycloadditions using a concerted transition state model provides a conceptual framework for the solution of "the biggest *unsolved* problem in the field"[36] of cycloadditions. The treatment presented here should lay to rest previous beliefs that "the nature of the orientation . . . is not adequately predicted by either concerted or biradical mechanisms,"[41] "the whole question of orientation or regiospecificity is still shrouded with uncertainty,"[56] and "orientation phenomena are still far from being understood."[50b]

Acknowledgments. Unpublished results kindly provided by Professor Albert Padwa, Dr. Reiner Sustmann, and Dr. Jean Bastide, and stimulating and illuminating discussions with Professors William C. Herndon and Rolf Huisgen were invaluable in the development of this treatment. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation, for financial support of this research.

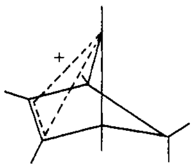
Electronic Structure of 1,2,3,4,5,6-Hexamethylbicyclo[2.1.1]hexenyl Cations and the Mechanism of Their Reaction with Nucleophiles

H. Hogeveen* and P. W. Kwant

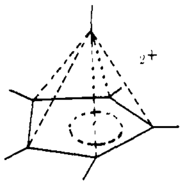
Contribution from the Department of Chemistry, The University, Zernikelaan, Groningen, The Netherlands. *Received April 23, 1973*

Abstract: Pmr and cmr data of various 5-substituted 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations are reported. From these data it is concluded that the positive charge resides mainly at carbon atoms 2 and 3. This is in agreement with the view that nucleophilic attacks at these positions, yielding tricyclic products, are kinetically controlled reactions, which occur at the site of the lowest electron density.

Numerous papers have dealt with the reaction of hexamethyldewarbenzene with acids. In strong acid[1,2] as well as in a hydrogen chloride–methylene chloride mixture[3a] a 1:3 equilibrium mixture of *exo*- and *endo*-methyl-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]-hexenyl cations (**1** and **2**) is obtained when the reaction is carried out at low temperature with excess acid. Recently reports have appeared concerning 5-substituted ions of this type, which are important as precursors of the stable dication **6**.[3b] The *endo*-5-chloro ion **3**[4,5] and the *endo*-5-bromo ion **4**[6] were prepared from hexamethyldewarbenzene by low temperature electrophilic addition of "Cl$^+$" and "Br$^+$," respectively. The *exo*-5-hydroxy ion **5** was prepared either from diol **7**[7] or from hexamethyldewarbenzene epoxide[7a] by reaction with a mixture of hydrogen chloride and methylene chloride at low temperature.[5] The ions **1–5** were shown to react with nucleophiles at C-2(C-3) or at C-6, the former mode of attack yielding tricyclic products and the latter one bicyclic products. Preliminary results showed the reactions that yield tricyclic products to be kinetically controlled. In this paper we report on the pmr and cmr spectra of the ions **1–5** and draw conclusions on the electronic structure, which forms the basis of the mechanism advanced for the reaction with nucleophiles.



1–5



6

— = CH$_3$

Results

The pmr[1-6] and cmr chemical shifts of the ions **1–5** at −70° are given in Table I and the pmr and cmr data of compounds **7**,[7] **8**,[8] and **9**[8] are listed in Table II for comparison purposes. The pmr[1,2] and cmr chemical shifts of the ions **1** and **2** do not differ essentially from those in strong acid. Ion **3** was reported[4] previously with AuCl$_4^-$ as gegenion, also with essentially the same pmr chemical shifts. This indicates that ions **1–5**

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(1) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968); **88**, 353 (1969).

(2) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968).

(3) (a) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3197 (1972); (b) *ibid.*, 1665 (1973); (c) H. T. Jonkman and W. C. Nieuwpoort, *ibid.*, 1671 (1973).

(4) R. Hüttel, P. Tauchner, and H. Forkl, *Chem. Ber.*, **105**, 1 (1972).

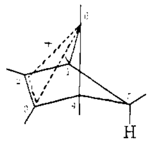
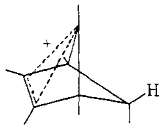
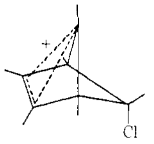
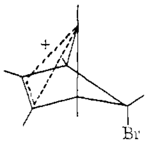
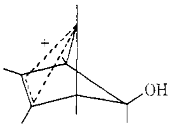
(5) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1351 (1973).

(6) H. Hogeveen and P. W. Kwant, *ibid.*, 423 (1973).

(7) (a) H. N. Junker, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967); (b) G. R. Krow and J. Reilly, *Tetrahedron Lett.*, 3129, 3133 (1972); (c) L. A. Paquette, S. A. Lang, Jr., S. K. Porter, and J. Clardy, *ibid.*, 3137, 3141 (1972).

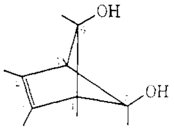
(8) H. Hogeveen and P. W. Kwant, *ibid.*, 5357 (1972).

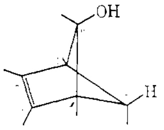
Table I. Pmr[a] and Cmr[b] Chemical Shifts of Ions **1–5** at −70°[c]

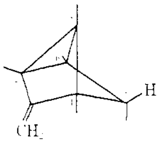
		C-1,4	C-2,3	C-5	C-6
 **1**	Pmr,[d] methyl hydrogens	1.47	2.07	1.42	1.39
	Cmr,[e] methyl carbons	8.6	9.0	12.5	1.8
	Cmr,[e] ring carbons	68.3	123.0	50.1	44.3
 **2**	Pmr,[f] methyl hydrogens	1.61	2.05	0.68	1.36
	Cmr,[e] methyl carbons	8.6	9.0	6.5	0.4
	Cmr,[e] ring carbons	69.1	120.3	52.7	39.7
 **3**	Pmr, methyl hydrogens	1.71	2.30	1.97	1.64
	Cmr, methyl carbons	7.1	11.8	24.1	3.9
	Cmr, ring carbons	75.4	123.7	76.4	44.3
 **4**	Pmr, methyl hydrogens	1.70	2.39	2.03	1.80
	Cmr, methyl carbons	7.8	12.5	26.0	5.9
	Cmr, ring carbons	76.4	124.8	70.9	48.5
 **5**	Pmr, methyl hydrogens	1.62	2.15	1.39	1.62
	Cmr, methyl carbons	7.0	11.5	20.5	2.1
	Cmr, ring carbons	74.5	121.5	83.8	43.3

[a] Relative to internal TMS. [b] Relative to external (capillary) TMS. [c] Cl^- as gegenion, except in the case of ion **4** (Br^- as gegenion); solvent for ions **3** and **4**, CH_2Cl_2 and for ions **1**, **2**, and **5**, CH_2Cl_2–HCl (2:1 (v/v)). [d] The chemical shift of the endo proton at C-5 is 2.35. [e] Chemical shifts differ by less than 0.1 ppm from those measured in $FHSO_3$. [f] The chemical shift of the exo proton at C-5 is 3.08.

Table II. Pmr[a] and Cmr[b] Chemical Shifts of Compounds **7–9** in Methylene Chloride

		C-1,4	C-2,3	C-5,6
 **7**	Pmr, methyl hydrogens	0.84	1.60	0.91
	Cmr, methyl carbons	4.6	11.9	18.4
	Cmr, ring carbons	62.1	139.6	102.8

		C-1,4	C-2,3	C-5	C-6
 **8**	Pmr, methyl hydrogens	0.78	1.56	0.63	0.93
	Cmr, methyl carbons	8.7	12.1	20.4	18.0
	Cmr, ring carbons	66.8	133.0	63.3	102.3

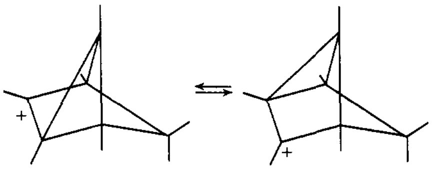
		C-1/C-6[c]	C-2/C-4[d]	C-3	C-5
 **9**	Pmr, methyl and methylene hydrogens	1.03/1.00	1.29/1.32	4.55	0.87
	Cmr, methyl and methylene carbons	4.7/4.3	8.7/9.5	97.4	18.5
	Cmr, ring carbons	27.2/24.8	45.0/47.7	166.2	45.0

[a] Relative to internal TMS. [b] Relative to external (capillary) TMS. [c] Assignments are not unambiguous and may have to be reversed. [d] See footnote *c*, Table II.

have to be considered as free ions in methylene chloride solution, rather than as ion pairs.

Electronic Structure of Ions 1–5. Discussion of the structure of ions **1–5** has been restricted thus far to a treatment in terms of rapidly equilibrating classical structures **10** and the nonclassical structures **1–5**.

Experimental results as the rate of carbonylation[9] of the ions **1** and **2** ($k_2 < 10^{-5}$ l. mol^{-1} sec^{-1} at $-23°$) and the ESCA spectrum of ion **3**, showing a broad signal,[4] are interpreted as support of a nonclassical structure. The cmr data presented in this paper offer additional evidence for nonclassical ions. It is possible to calculate the average chemical shift of C-2 and C-3 of structures **10** with use of suitable model compounds.[10] Using the chemical shift of C$^+$ in dimethylcyclopropylcarbinyl cation (281.4 ppm)[11] and the chemical shift of C-2 of **9** (45.0 ppm), the average chemical shift of C-2 and C-3 is calculated to be $(281.4 + 45.0)/2 = 163.2$ ppm. This value would increase still more on correction for adjacent positive charge.[10] Olah[12] reported that no deviations from the observed value larger than 10 ppm would occur on calculating the average cmr chemical shift in classical ions, so that the observed values in the range of 120–125 ppm cannot be explained with rapidly equilibrating ions. The alternative, classical structure **11**, already rejected on the basis of pmr data,[1] is equally inconsistent with the cmr chemical shift of C-6 in the ions **1–5**, indicating low positive charge.



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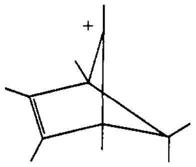

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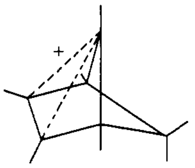
Once a nonclassical structure is accepted, the charge distribution and, by consequence, the proper representation in a structural formula have to be discussed. Quantitative data on charge distribution in the ions **1–5** are not available, but a semiquantitative correlation between charge densities and pmr and cmr chemical shifts can be used to discern between the possible nonclassical structures. Structures **1–5** are the structural formulas used thus far; the dotted line between C-2 and C-3, indicative of some double bond character, implies the presence of some positive charge at C-6. In structure **12**, the nonclassical equivalent of **10**, C-6 bears no appreciable positive charge, which is indicated in the structural formula by the absence of the dotted line between C-2 and C-3. Structure **13** assumes extended delocalization including also the 1-6 and 4-6 bonds, a delocalization of the type found to some extent from calculations on the norbornenyl cation.[13] It can be seen as the homo case of the $(CH)_5^+$ ion reported on recently.[14] In a formal sense **13** could arise by bringing $^+CCH_3$ toward pentamethylcyclopentadiene as in **14**.

The correlation of pmr methyl chemical shifts with charge densities is expected to be poor because the methyl protons are two bonds away from the positive centers considered, which makes the influence of other factors than charge relatively more important. Upon comparison of the pmr chemical shifts of the methyl groups of ions **1–5** with those of the same methyl groups of uncharged reference compounds **7** and **8**, a considerable downfield shift is noted for all methyl peaks. This indicates the positive charge to be delocalized, but a preference for one of the nonclassical structures presented above cannot be made. Roughly speaking, the pmr methyl chemical shifts present the same trends as the cmr chemical shifts treated below. A correlation between cmr chemical shifts and charge densities has been found in certain classes of compounds, including carbonium ions.[15] Recently, it has been observed that the charge distribution in dication **6** as deduced from cmr chemical shifts[3b] is in agreement with that based on *ab initio* molecular orbital calculation of its parent structure.[3c] Although several factors are influencing the cmr chemical shifts,[15a] we feel that cautious treatment of these data yields valuable information about charge distribution in carbonium ions. The cmr chemical shifts of C-1 and C-4 in ions **1–5** are found downfield from those of the bridgehead carbon atoms of **7** and **8** by an average of 7 ppm and by about 25 ppm from that of C-4 in **9**. There are no indications of effects inducing an upfield shift of the C-1 and C-4 peaks, so that it can be concluded that only low positive charge is present at these carbon atoms. The interpretation of the cmr chemical shifts of C-6 in ions **1–5** in terms of charge densities has to include the fact that one is dealing with a pentavalent carbon atom. The rehybridization in such a carbon atom causes an upfield shift, as found in the 2-norbornyl cation,[16] which is larger than can be accounted for by lowered positive charge. Another example is found in the $(CH_3)_2(CH)_5^+$ ion **15**, in which the pentavalent carbon atom resonates at -23 ppm.[14c] The chemical shifts of C-6 in the ions **1–5** can be compared with the chemical shifts of uncharged carbon atoms C-5 of **8** and C-1 of **9** and are found to lie between these shifts. Hence it is reasonable that the upfield shift caused by rehybridization of the pentavalent carbon atom and the downfield shift caused by positive charge nearly cancel. From this point of view some positive charge resides



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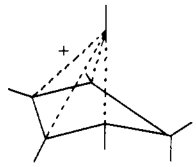

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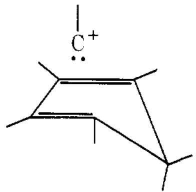

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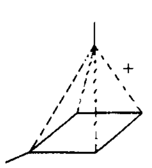

15

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[9] H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 395 (1970).

[10] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

[11] G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

[12] G. A. Olah, J. M. Bollinger, and A. M. White, *ibid.*, **91**, 3667 (1969).

[13] H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969).

[14] (a) W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 1661 (1972); (b) S. Masamune, M. Sakai, and H. Ona, *ibid.*, **94**, 8955 (1972); (c) S. Masamune, M. Sakai, H. Ona, and A. L. Jones, *ibid.*, **94**, 8956 (1972); (d) H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

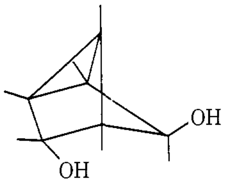
[15] (a) G. A. Olah and P. W. Westerman, *ibid.*, **95**, 3706 (1973), and references cited therein; (b) R. Ditchfield and D. P. Miller, *ibid.*, **93**, 5287 (1971). See, for another opinion, H. C. Brown and E. N. Peters, *ibid.*, **95**, 2400 (1973).

[16] G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

at C-6 in ions **1–5**. Atoms C-2 and C-3 of the ions are strongly rehybridized from sp^2 toward sp^3 and such rehybridization alone causes a large upfield shift. The cmr chemical shifts of these carbon atoms are, however, only about 10 ppm upfield from those of C-2 and C-3 of **7** and **8** and are still found in the range usual for neutral sp^2 hybridized carbon atoms. This can only be explained by locating high positive charge at C-2 and C-3.

Summarizing one can state that the cmr chemical shifts, interpreted in terms of charge density and hybridization indicate the positive charge to decrease in the following sequence C-2, C-3 > C-6 > C-1, C-4. Structure **13** therefore is only a minor resonance contributor to the actual structure. The preferred representation of the ions is shown by structures **1–5** rather than structure **12**, because the dotted line between C-2 and C-3 indicates the presence of at least some positive charge at C-6.

Mechanism of the Reaction of Ions 1–5 with Nucleophiles. The ions **1–5**, carrying positive charge at C-2 and C-3 and at C-6, react with nucleophiles at these sites, the former reactions yielding tricyclic and the latter one bicyclic products.[1–8] Examples of this behavior are formed by ion **5**, yielding tricyclic diol **16**,[6] and ion **2**, yielding bicyclic alcohol **8**[5] on reaction with OH$^-$ under different reaction conditions. The stereochemistry of the asymmetric diol **16** has been established by pmr spectroscopy, and the anti position of the hydroxy group in **8** has been further established by pmr shift enhancements upon addition of Eu(dpm)$_3$ and by the lack of hydrogen bonding of the hydroxy group with the double bond in the ir spectrum of a highly diluted solution. The conclusion from this stereochemistry agrees with the view that nucleophilic attack occurs from the backside of the two-electron, three-centered bond. From **17**, depicting the three atomic orbitals forming the bonding three-center MO, it can be seen that a nucleophile would prefer this direction of attack, because here is the lowest electron density.



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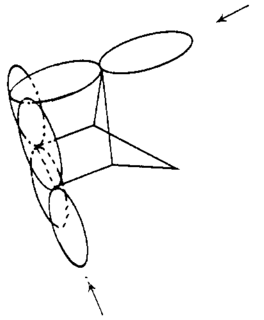
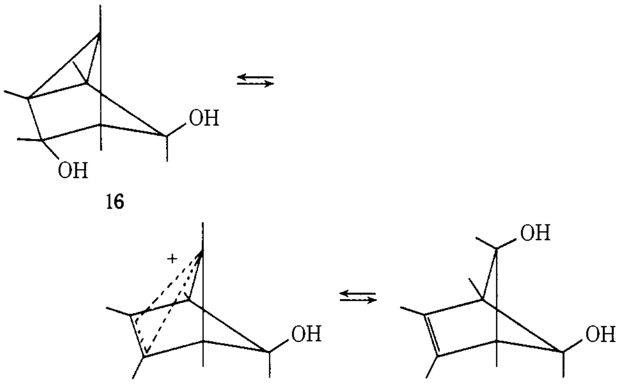


17

How can we account for the formation of bicyclic and tricyclic compounds in the various cases? It is obvious that the tricyclic compounds have a higher energy content than the bicyclic ones, because this involves comparison of the energy content of a cyclopropane and a cyclobutane ring with the energy of a double bond. Therefore the bicyclic products are thermodynamically favored over the tricyclic products. Kinetically the nucleophilic attack at C-2 and C-3 is favored over attack at C-6 by the statistical factor of 2 and by the greater positive charge. This agrees very well with the regioselectivity of H$^-$-abstraction by triethylamine[8] from one of the methyl groups attached to C-2 or C-3 of ion **2**, to yield **9**, rather than from the methyl group at C-6. Kinetic and thermodynamic control are illustrated with the reaction of **5** with excess OH$^-$ at low temperature yielding tricyclic diol **16**. When **16** is left in contact with acid at room temperature, the bicyclic diol **7** is formed.[6] This behavior is readily explained by considering the tricyclic compound to be the kinetically controlled product and the bicyclic compound as the thermodynamically controlled product, the latter being obtained through the equilibrium **16** ⇄ **5** ⇄ **7**.

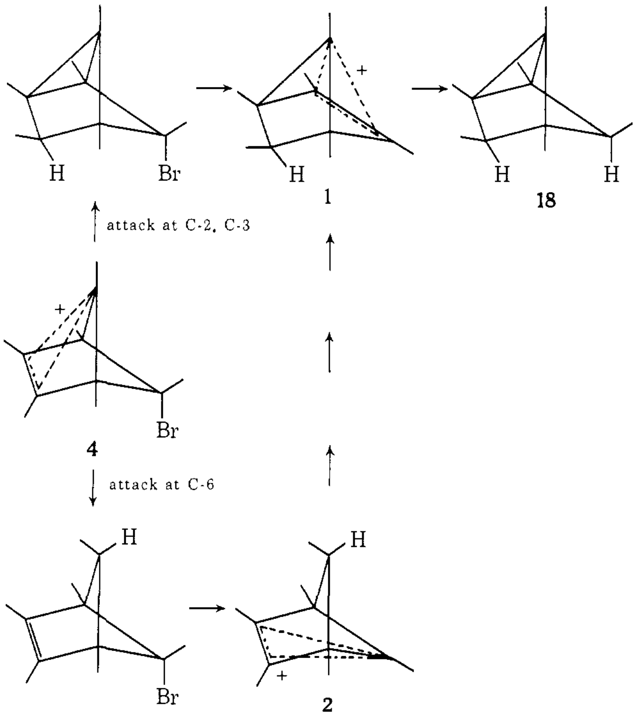


16

5

7

Now we can use this concept to construct mechanisms for some other reactions of the ions **1–5** with nucleophiles. The mechanism of the reaction of ion **3** and **4** with lithium aluminum hydride[5,17] can be drawn as follows.[18]



1

18

4

2

Lithium aluminum hydride attacks at C-2 and C-3 from the side of the lowest electron density, to give a tricyclic compound, which subsequently dissociates into **1** and a bromine anion followed by a new attack by lithium aluminum hydride to give **18**. This mechanism is more likely than the alternative involving initial at-

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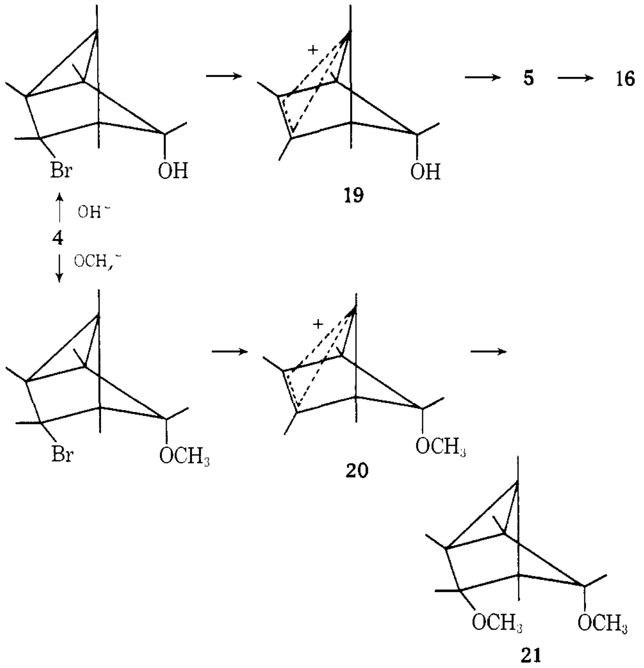
(17) P. Tauchner and R. Hüttel, *Tetrahedron Lett.*, 4733 (1972).

(18) This mechanism is equally valid for the analogous reaction in which the parent tricyclo[2.2.0.0^{2,6}]hexane is obtained: R. J. Roth and T. J. Katz, *J. Amer. Chem. Soc.*, **94**, 4770 (1972).

tack at C-6 followed by dissociation of the bicyclic bromide formed, because this would give ion **2** as the intermediate ion. In the latter mechanism ion **2** would have to rearrange[1] to the thermodynamically less stable ion **1**, because the product, **18**, cannot be explained by hydride attack at either C-2 or C-3 or at C-6 of ion **2**.

The reaction of ion **4** with OH^- and OCH_3^- [6] can be treated mechanistically in an analogous way: nucleophilic attack at C-2 or C-3 followed by dissociation to ions **19** and **20**.



From the structure of the product, **16**, it must be concluded that *endo*-OH ion **19** isomerizes rapidly[1] under the reaction conditions (−60°) to the *exo*-OH isomer **5**, before undergoing nucleophilic attack. This implies **5** to be considerably more stable than **19**, which is in agreement with the failure to observe **19** as a product of intramolecular rearrangement[1] in a solution of **5**,[5] even after a period of several hours at −70°. *endo*-OCH_3 ion **20** does not show such a rapid rearrangement to its *exo*-OCH_3 isomer, as can be concluded from product **21**. The question whether this is caused by a higher thermodynamic stability of *endo*-OCH_3 ion **20** compared with its *exo*-OCH_3 isomer or by kinetic factors making the rate of nucleophilic attack much higher than the rate of endo–exo interconversion cannot be answered until **20** or its *exo*-OCH_3 isomer is made independently.

In the reactions of ion **2** yielding **8** and related 6-substituted bicyclic compounds[2,3a] tricyclic products have not been observed, so that it remains an open question whether these bicyclic products are formed by kinetically controlled reactions at C-6 or as a result of equilibria lying on the side of the bicyclic products.

Experimental Section

Proton magnetic resonance spectra were recorded at 60 MHz using a Varian A-60D spectrometer equipped with a variable-temperature probe. All chemical shifts are given in ppm relative to internal TMS at $\delta = 0$.

Natural abundance carbon-13 nuclear magnetic resonance spectra were obtained with a Varian XL-100 spectrometer operating at 25.2 MHz. Spectra were recorded with use of Fourier transform and were proton-noise decoupled unless otherwise stated. The number of spectra accumulated varied between 500 and 5000, depending on sample concentration. Chemical shifts were calculated relative to external (capillary) TMS.

The assignment of the cmr chemical shifts was made by use of off-resonance decoupled spectra to determine the extent of proton substitution. Peak intensities were determined in spectra using different delays after the data aquisition following each pulse and it was established that the relaxation time T_1 of carbon atoms with the same number of attached protons was approximately the same, except when that carbon was bonded to a heteroatom. The nuclear Overhauser enhancements were assumed to be approximately the same for carbon atoms of the same class, so that it was possible now to correlate peak intensities with the number of carbon atoms causing the peak. The bromine substituted carbon atom in ion **4** was detected by means of its T_1 relaxation time, being much shorter than T_1 of the other skeleton carbon atoms.

Addition of successive portions of $Eu(dpm)_3$ to a solution of *anti*-5-hydroxy-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hex-2-ene (**8**) in methylene chloride gave rise to a pmr shift enhancement of the methyl groups attached to C-1,4, C-2,3, C-5, and C-6 and the proton attached to C-5 in a ratio of 2:1:1:3:4. The ir spectrum of **8** (1 mg/ml) in tetrachloromethane, using 1-cm cells, showed a single sharp absorption (3621 cm^{-1}) in the region 4000–3200 cm^{-1}; no peak was found that could indicate hydrogen bonding between OH and the double bond.[7b]

An 1:3 equilibrium mixture of the *exo*- and *endo*-methyl-1,2,3,-4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations (**1** and **2**) was obtained by dissolving hexamethyldewarbenzene in methylene chloride at −70° and introducing dry hydrogen chloride gas until the ratio of dissolved HCl:methylene chloride was 1:2 (v/v).

A solution of *exo*-5-hydroxy-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]-hexenyl cation (**5**) was prepared in a way identical with that used to prepare ions **1** and **2**. Starting material was here *anti*-5,6-dihydroxy-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hex-2-ene (**7**) or hexamethyldewarbenzene epoxide.

A solution of *endo*-5-chloro-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]-hexenyl cation (**3**) was obtained by dissolving hexamethyldewarbenzene in methylene chloride, followed by introduction of dry chlorine gas (1 equiv) at −70°.

A solution of *endo*-5-bromo-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]-hexenyl cation (**4**) was prepared by mixing methylene chloride solutions of equimolar quantities of hexamethyldewarbenzene and bromine at −70°.