found that the free energy required for conversion of $\text{I-R}^+$ to $\text{II-R}^+$ is 22.3 kcal/mol, a barrier high enough to strongly implicate $\text{I-R}^+$ as the electroactive species.[8] The radical formed first by electron transfer to $\text{I-R}^+$ must be $\text{I-R}\cdot$, in accord with the Franck–Condon principle. However, if the radical $\text{I-R}\cdot$ were further reduced directly to $\text{I-R}^-$ (or the hydrocarbon RH), by analogy with tropylium and dibenzotropylium, the potential for this reduction should be more negative than the reduction of $\text{I-R}^+$ to $\text{I-R}\cdot$.[9] Alternatively, $\text{I-R}\cdot$ could convert to $\text{II-R}\cdot$ before electron transfer, and, from the HMO descriptions of an electron-accepting nonbonding MO in $\text{II-R}\cdot$ and an antibonding MO in $\text{I-R}\cdot$, the reduction of $\text{II-R}\cdot$ is expected to occur at a more positive potential than $\text{I-R}\cdot$. The overall scheme is summarized in eq 4. The scheme as presented implies that $\text{I-R}\cdot$ is antihomoaromatic, *i.e.*, that it is less stable than the isomeric radical $\text{II-R}\cdot$ in which the conjugated system is not cyclic. Extension of the available orbital argument to the anions suggests that $\text{II-R}^-$ is preferred to $\text{I-R}^-$, but experimental confirmation is lacking.

$$\text{I-R}^+ \xrightarrow{e} \text{I-R}\cdot \longrightarrow \text{II-R}\cdot \xrightarrow{e} \text{II-R}^- \xrightarrow{H^+} \text{RH} \qquad (4)$$

Breslow[10] has demonstrated the utility of electrochemical methods in obtaining otherwise unavailable information on very unstable antiaromatic species, such as triphenylcyclopropenyl anion. We suggest that this method is even more valuable in the study of antihomoaromatic species because these may be generated by electron-transfer reactions of the corresponding homoaromatic species, before they revert to the more stable linearly conjugated isomer. Attempts to prepare antihomoaromatic species by chemical reactions such as protonation[11] should yield preferentially the linearly conjugated species and not the desired intermediate.

**Acknowledgment.** We record our debt to the late Professor S. Winstein who encouraged us in this work.

---

[8] If the isomerization of $\text{I-R}^+$ to $\text{II-R}^+$ precedes electron transfer to $\text{II-R}^+$, then the reduction potential reflects the free-energy changes for the isomerization and the electron transfer, as in the reduction of cyclooctatetraene to its planar radical anion: T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Amer. Chem. Soc.*, **84**, 802 (1962). If the free energy for isomerization is accounted for, the potential for $\text{II-R}^+ + e \rightleftarrows \text{II-R}\cdot$ is approximately 0 V, which appears to be more positive than is reasonable. The antiaromatic 9-phenylfluorenyl cation[1] is reduced at −0.19 V in 14 *M* $H_2SO_4$.

[9] An apparent two-electron reduction is also observed for other ions in very concentrated acid because the first peak shifts to more negative potentials as acid concentration is increased and is eventually superimposed on the second.[1] It may be inferred that the solvent-insensitive potential for reaction 2 of homotropylium ion cannot be more negative than −0.92 V, the observed potential in 14 *M* $H_2SO_4$, and thus the potential for reaction 2 is more positive than reaction 1 in 17 *M* $H_2SO_4$. This behavior is unique among the ions studied to date.

[10] R. Breslow and K. Balasubramanian, *J. Amer. Chem. Soc.*, **91**, 5182 (1969).

[11] P. Warner and S. Winstein, *ibid.*, **91**, 7785 (1969).

[12] NASA Predoctoral Trainee, 1965–1968; American Chemical Society Division of Analytical Chemistry Summer Fellow, 1968.

**Martin Feldman, William C. Flythe**[12]
*Department of Chemistry, Howard University*
*Washington, D. C. 20001*

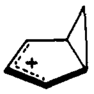
*Received January 20, 1971*

---

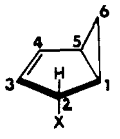
## Solvolytic Behavior of Bicyclo[3.1.0]hex-3-en-2-yl Derivatives. Some Observations on the Mechanism of Photolysis of Benzene in Hydroxylic Media[1]

*Sir:*

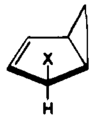
As an extension of earlier studies[2] of degenerate sigmatropic rearrangements in which a cyclopropane ring circumambulates the periphery of a cyclic conjugated system, we have investigated the behavior of bicyclo[3.1.0]hex-3-en-2-yl cation (**1**). A companion paper[3] reports the rearrangement, which occurs only in strongly acidic medium. The present work describes the solvolytic chemistry of the bicyclo[3.1.0]hex-3-en-2-yl system and its relevance to a study of the mechanism of the photochemical hydration of benzene.



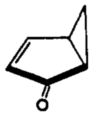
**1**



**2**



**3**



**4**

Reaction of exo alcohol **2**–OH[4] with thionyl chloride or better with hydrogen chloride in $CH_2Cl_2$ gives chloride **2**–Cl containing minor amounts of epimeric chloride **3**–Cl. Hydrolysis or methanolysis of the chloride mixture in the presence of buffer gives exo alcohol **2**–OH or exo methyl ether **2**–OMe. The absence of endo alcohol **3**–OH is established by comparison of the nmr spectrum of the crude hydrolysis product with that of authentic **3**–OH, obtained as the major alcohol (~70%) from $LiAlH_4$ reduction of the corresponding ketone **4**. A mixture of **2**–OH-*2-d* and **3**–OH-*2-d* results from **4** and $LiAlD_4$.

Methanolysis (in 50 vol % $MeOH-CH_3CN$) of the deuterated trifluoroacetates **2**–$O_2CCF_3$-*2-d* and **3**–$O_2CCF_3$-*2-d* gives exo methyl ether **2**–OMe with 0.5 deuterium at positions 2 and 4 but none at position 1, 3, or 5 (analysis by nmr). Similarly, treatment of an acetonitrile solution of **2**–OH-*2-d* and **3**–OH-*2-d* with 3 mol % of *p*-toluenesulfonic acid results in complete mixing of the deuterium label between positions 2 and 4 within 1 min but no detectable deuteration elsewhere even after 26 hr.[5] The latter experiment involves repeated formation of the cationic intermediates and shows that the solvent capture rate ($k_s$) is at least $1.6 \times 10^3$ times the rate of sigmatropic rearrangement ($k_r$).

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to the National Institute of General Medical Sciences (Grant No. GM-16962) and the National Science Foundation (Grant No. GP-11017X) for research grants and to the latter agency for an institutional grant (GU-3282).

[2] (a) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, 87, 2751, 2752 (1965); **88**, 2494 (1966); *Rec. Chem. Progr.*, 27, 139 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); (c) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

[3] P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

[4] (a) E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966); (b) the stereochemical assignment[4a] is confirmed by the nmr spectra of **2** and **3**: N. M. Hasty, Jr., Ph.D. Thesis, University of Wisconsin, 1970, p 22 ff.

[5] More vigorous conditions, *e.g.*, treatment of the chloride with $AlCl_3$ or pyrolysis of the trifluoroacetate, give polymeric materials and small yields of benzene.

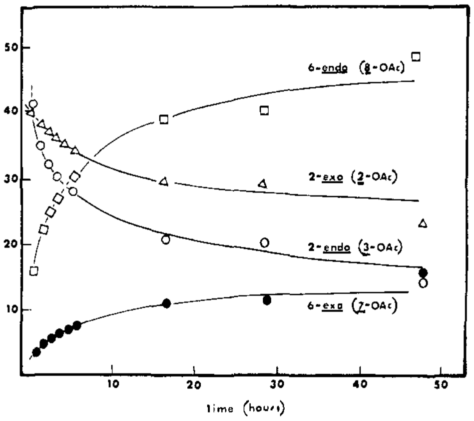
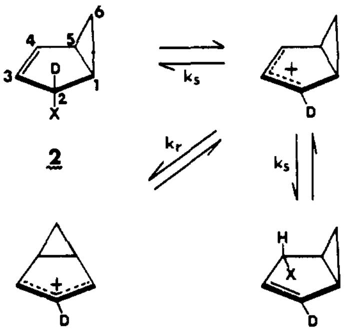


Figure 1. Product composition as a function of time in the photolysis of benzene in acetic acid solution.



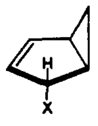
Photolyses of benzene or substituted benzenes in hydroxylic media give substantial quantities of bicyclo[3.1.0]hex-3-en-2-yl and -6-yl derivatives.[4,6] Benzvalene (**5**) or substituted benzvalenes have been invoked as intermediates in these reactions,[6] but an alternative hypothesis[7] proposes that benzenonium ion **6** may be the precursor of bicyclo[3.1.0]hex-3-en-2-yl cation **1**.

**5**

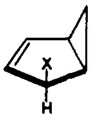
**6**

The subsequently observed[8] photoisomerization of heptamethylbenzenonium ion to heptamethylbicyclo[3.1.0]hex-3-en-2-yl ion appears to lend plausibility to a mechanism involving **6**. However, permissive evidence for the benzvalene mechanism comes from the isolation of this hydrocarbon and the demonstration that it reacts with acidic methanol to give bicyclo[3.1.0]hex-3-en-2-yl and -6-yl methyl ethers.[9]

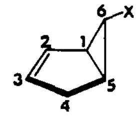
The present study examines the photolysis of benzene in acetic acid further. This reaction gives acetates **2**-OAc, **3**-OAc, **7**-OAc, and **8**-OAc, but the composition changes with time (Figure 1), presumably because of instability of the products. Extrapolation to zero time suggests that the endo acetate is formed in amounts as great as or greater than the exo isomer in both the 2 and the 6 series (**3** > **2**; **8** > **7**).



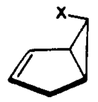
**2**



**3**



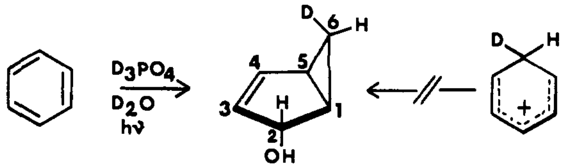
**7**



**8**

This behavior is not expected of bicyclo[3.1.0]hex-2-en-6-yl cation, at least in the ground state, since nucleophilic capture predominantly from the exo side (to give **7**-OAc) instead of from the endo side (to give **8**-OAc) would be reasonable. Moreover, the observed formation of predominantly endo 2-acetate **3**-OAc cannot involve the ground state of cation **1**, since the solvolytic chemistry of this species, as described above, gives at least 90% exo product **2**.

Photolysis of benzene in 0.1 *N* deuteriophosphoric acid (quartz vessel, 2537-Å mercury lamps) provides some insight into the stereochemistry of the protonation step in the formation of exo alcohol **2**-OH. The absorptions of the 6 protons in the nmr spectrum of **2**-OH are readily assigned from the chemical shift (6-endo, $\delta$ −0.15; 6-exo, $\delta$ 0.92) and from the multiplicity resulting from coupling with the 1 and 5 protons (6-endo, pseudoquartet, with spacings of ~4 cps; 6-exo, multiplet, with spacings ~4, 7, and 8 cps). The exo alcohol **2**-OH[10] isolated from photolysis of benzene in $D_2O$-$D_3PO_4$[11] shows 0.86 deuterium/molecule (mass spectral analysis of the derived methyl ether **2**-OMe: 14% $d_0$, 86% $d_1$, 0% $d_2$). Careful integration of the nmr spectrum of **2**-OH shows 0.13 proton at the 6-endo position (0.15 proton in **2**-OMe) and 1.0 proton at the 6-exo (both relative to the proton at $C_2$ taken as 1.00). These data show that *all of the deuterium is incorporated in the 6-endo position.* Benzenonium ion **6**, the proposed intermediate in the formation of the bicyclo[3.1.0]hex-3-en-2-yl products,[7] has chemically equivalent hydrogens in its methylene group. This requires that essentially equal amounts of 6-exo and 6-endo deuterium appear in product **2**-OH. The data therefore exclude this mechanism.



**2**-OH-6-*endo*-*d* **6**

The predominance of endo attack by both the proton and the nucleophile[12] is strongly reminiscent of the observation by Wiberg and Szeimies[13] that the bridged bicyclobutane **9** reacts with DOAc to give mainly

---

[6] L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **88**, 2881 (1966).

[7] D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

[8] R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968).

[9] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).

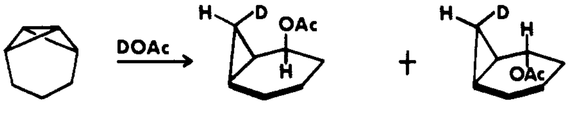
(10) The endo alcohol **3**-OH is unstable in acidic media and rapidly epimerizes to the exo isomer **2**-OH.

(11) Prepared by dissolution of phosphorus pentoxide in deuterium oxide.

(12) A similar predominance is observed in the photolysis of 1,3,5-tri-*tert*-butylbenzene,[6] but the interpretation in terms of a benzvalene intermediate[6] is less straightforward because the large steric demand of the *tert*-butyl groups for an exo configuration in the bicyclo[3.1.0]-hexenyl products might well force endo attack by outside reagents, regardless of mechanism.

(13) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

product **10** and some product **11** (in the ratio 62:12) but, significantly, no products of exo deuteration. If this behavior is taken as a model for the stereochemistry of additions of hydroxylic reagents to bicyclobutanes, the present observations are readily rationalized with benzvalene (**5**) as the key intermediate in the photolytic hydration of benzene.



**9** **10 (62%)** **11 (12%)**

**Acknowledgment.** We thank Professor S. Masamune for spectra of authentic samples of 7-OAc and **8**-OAc.[14a]

(14) (a) S. Masamune, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969). (b) Supported by NIH Fellowship No. 5-FO1-GM-38,024-02.

**Jerome A. Berson,* Noel M. Hasty, Jr.**[14b]
*Department of Chemistry, Yale University*
*New Haven, Connecticut 06520*
*Department of Chemistry, University of Wisconsin*
*Madison, Wisconsin 53706*

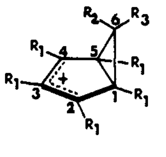
*Received December 31, 1970*

---

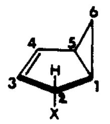
## Bicyclo[3.1.0]hex-3-en-2-yl Cation[1]

*Sir:*

Recently developed synthetic procedures[2] for specific introduction of deuterium at the 2- and 6-endo positions of the parent bicyclo[3.1.0]hex-3-en-2-yl cation **1** make possible the study of the properties of this species by nuclear magnetic resonance (nmr) spectroscopy of its solutions in strongly acidic media. These spectra reveal a slow sigmatropic rearrangement not observable in the unlabeled compound. They also serve as probes for the special electronic effects anticipated for **1**, a potentially "homoantiaromatic" relative of cyclopentadienylium cation.[3] The results provide instructive comparisons with those obtained for the heptamethyl (**2**),[4] hexamethyl (**3** and **4**),[4,5] pentamethyl (**5**),[6a] tetramethyl,[6b] and hydroxy substituted[7] derivatives.



**1**: $R_1,R_2,R_3$ = H
**2**: $R_1,R_2,R_3 = CH_3$
**3**: $R_1,R_3 = CH_3$; $R_2$ = H
**4**: $R_1,R_2 = CH_3$; $R_3$ = H
**5**: $R_1 = CH_3$; $R_2$, $R_3$ = H



**6**: X = Cl
**7**: X = OH

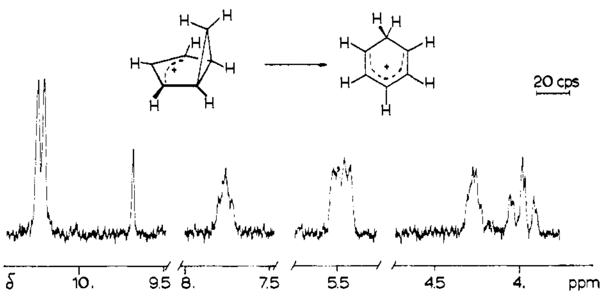


Figure 1. Nmr spectrum (100 MHz) of the bicyclo[3.1.0]hex-2-enyl cation **1** at −63° in $SbF_5$–$SO_2ClF$ with external tetramethylsilane reference. The sharp singlet at $\delta$ 9.68 is the spectrum of the benzenonium ion, the protons of which suffer rapid exchange under these conditions and thereby have averaged chemical shifts [*cf.* G. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970)]. The rest of the spectrum is interpreted in Table I. The chemical shifts are converted to those of Table I (internal $CH_2Cl_2$ reference) by subtraction of 0.25 unit from each $\delta$ value.

Distillation under vacuum of 2-chlorobicyclo[3.1.0]-hex-3-ene (**6**) in $SO_2ClF$ into a mixture of $SbF_5$–$SO_2ClF$ kept at −100° gives dilute solutions of cation **1**, which has the proton nmr spectrum shown in Figure 1 and interpreted in Table I. An alternative preparation is achieved by extraction of a solution of 2-hydroxybicyclo[3.1.0]hex-3-ene (**7**) in $CD_2Cl_2$ with $FSO_3H$–$SO_2ClF$ at −120°. The cation solutions obtained in this way are more concentrated but less stable than those generated by the first procedure.

**Table I.** Nmr Spectral Assignments of Protons of Bicyclo[3.1.0]hex-3-en-2-yl Cation (**1**)

| Position | Rel intensity | Chemical shift, $\delta^a$ | Coupling constant, Hz | |
|---|---|---|---|---|
| $H_2$, $H_4$ | 2 | 9.97 | $J_{1,2}$ | <1 |
| $H_3$ | 1 | 7.49 | $J_{2,3}$ | 3.5 |
| $H_5$, $H_1$ | 2 | 5.27 | $J_{1,6}$ (endo) | 3.5 |
| $H_6$ (endo) | 1 | 4.03 | $J_{1,6}$ (exo) | 7 |
| $H_6$ (exo) | 1 | 3.73 | $J_{3,6}$ | >0 |
| | | | $J_6$ (endo), $J_6$ (exo) | ~2 |

[a] In parts per million relative to internal $CH_2Cl_2$. Chemical shifts relative to external tetramethylsilane (Figure 1) lie 0.25 ppm downfield from those given here.

The assignments of the absorptions at $\delta$ 4.03 and 3.73 respectively to the 6-endo and 6-exo protons follow from the disappearance of the lower field ($\delta$ 4.03) band from the spectrum of the 6-endo-deuterio cation, prepared from 6-*endo*-deuterio-2-chlorobicyclo-[3.1.0]hex-3-ene.[2] The small difference in chemical shift ($\delta_{endo} - \delta_{exo} = +0.30$ ppm) of the 6 protons of **1** is in striking contrast to that ($\delta_{endo} - \delta_{exo} = -5.8$ ppm) of the 8 protons of the bicyclo[5.1.0]octa-2,4-dienyl ("homotropylium") cation, one resonance structure of which is **8**.[8,9] This presumably results

---

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to the National Institute of General Medical Sciences (Grant No. GM-16962) and the National Science Foundation (Grant No. GP-11017X) for research grants and to the latter agency for an inistitutional grant (No. GU-3282).

(2) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971).

(3) For the properties of some cyclopentadienylium derivatives, see R. Breslow, R. Hill, and E. Wasserman, *ibid.*, 86, 5349 (1964); R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967).

(4) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).

(5) V. H. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Manatyuk, *Chem. Commun.*, 389 (1969).

(6) (a) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968); (b) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970).

(7) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).