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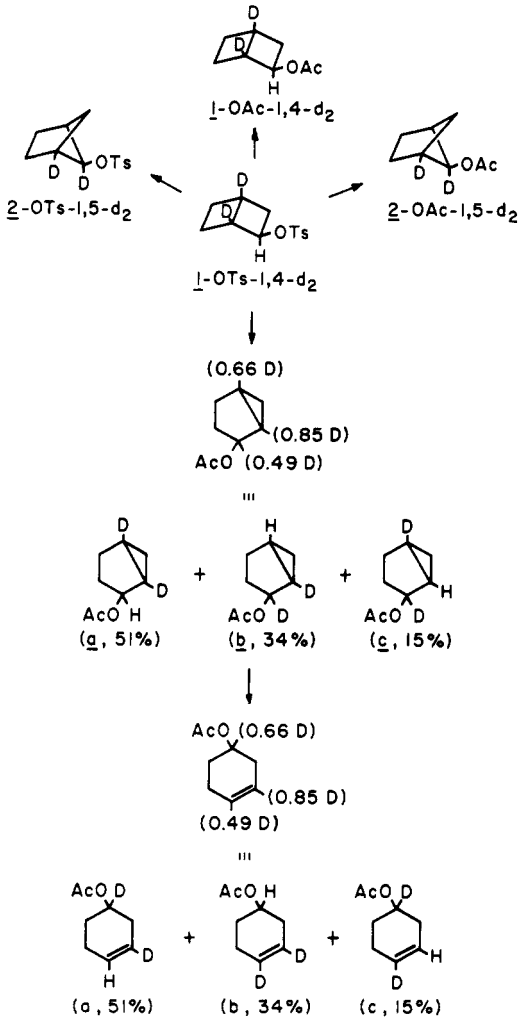
## Strained Ring Systems. 18.[1] Determination of the Rearrangement Pathways in the Buffered Acetolysis of Bicyclo[2.2.0]hex-*exo*-2-yl Tosylate with Specific Deuterium Labeling and Optical Purity Probes

*Sir:*

A prerequisite to defining the structures and number of carbonium ions produced in a solvolysis reaction is detailed knowledge of the various rearrangement channels leading from substrate to product(s). This is usually accomplished experimentally using structural probes (e.g., specific isotopic labeling and chirality) incorporated in the substrate and determining the overall changes following these probes in going to the product(s). We report herein the results of a study using three probes with the buffered acetolysis of bicyclo[2.2.0]hex-*exo*-2-yl tosylate (X-**1**-OTs) at 75 °C where the isolated products are bicyclo[2.1.1]hex-*exo*-5-yl OTs (X-**2**-OTs, 54%), X-**1**-OAc (2%), X-**2**-OAc (16%), bicyclo[3.1.0]hex-*exo*-2-yl OAc (X-**3**-OAc, 10%) and its endo epimer (N-**3**-OAc, 7%), cyclohex-3-enyl OAc (**4**-OAc, 10%), cyclohex-2-enyl OAc (**5**-OAc, 1%), and cyclopent-2-enylmethyl OAc (**6**-OAc, ~0.1%).

The first probe of the solvolytic rearrangements of X-**1**-OTs was carried out with X-**1**-OTs-*1,4-d*$_2$.[1,2] The products, dideuterated X-**2**-OTs, X-**1**-OAc, X-**2**-OAc, X- and N-**3**-OAc, and **4**-OAc, were separated and collected (GLC). The positions of deuterium substitution and the H and D content per position were then determined using $^{13}$C NMR spectroscopy for each of these products. While X-**1**-OAc-*d*$_2$ showed no scrambling of its bridgehead deuteriums, both X-**2**-OTs-*d*$_2$ and X-**2**-OAc-*d*$_2$ were the result of a single Wagner–Meerwein rearrangement with no further equilibration (Scheme I). The dideuterated acetates X- and N-**3**-OAc[3] and **4**-OAc showed deuterium at three carbons, as shown in Scheme I, which are analyzed in terms of three isomeric dideuterated species. These latter results uniquely demonstrate the direct rearrangement pathway of the cationic precursors ([3.1.0]-**2**$^+$ → 3-cyclohexenyl$^+$) of these acetates.

Scheme I




The second and third probes were combined using X-**1**-OTs-*exo-3-d* of 86% optical purity.[4] The deuterium analysis by $^{13}$C NMR spectroscopy readily identified the single sites of substitution in each of the above six products (Scheme II). The stereochemistry of the deuterium in X-**1**-OAc was clearly *exo*-3 by comparison of its $^1$H NMR spectrum with that of authentic X-**1**-OAc-*exo-3-d*.[4,6] In X-**2**-OTs-*d* and X-**2**-OAc-*d*, the $C_6$ syn-D stereochemistry was assigned based on the observed "W" coupling of the $C_6$ anti-H and $C_5$ endo-H and integration in the $^1$H NMR spectra.[7] In the $^1$H NMR spectra of X- and N-**3**-OAc, the exo and endo H's at $C_6$ are well separated and clearly the deuterium was exo in both epimers.

The optical purity of X-**1**-OAc-*exo-3-d* ($[\alpha]^{27}_D$ 40.0° ($CHCl_3$)) was found to be 86% with Eu-Opt$^R$ (Alfa-Ventron) shift reagent. Both hydrolysis and conversion of the alcohol to the tosylate ester (pyridine + TsCl) was assumed to occur without racemization. The optical purities of the GLC collected samples of the four chiral products are listed in Table I.

The results from all three probes establish that 6,2- and 3,2-hydride shifts do not occur in the carbonium-ion intermediates leading to X-**1**-OAc and X-**2**-OAc.[8,9] Further, an equilibrium involving classical chiral [2.2.0]-**2**$^+$ and achiral [2.1.1]-**5**$^+$ cations cannot be involved prior to solvent trapping and ion-pair return to yield these three solvolysis products. These same requirements must also be placed on the initially produced cations leading to X- and N-**3**-OAc and **4**-OAc.[9]

Equating the results from X-**1**-OTs-*1,4-d*$_2$ → X- and N-**3**-OAc (isomers a (51%), b (34%), and c (15%), Scheme III)

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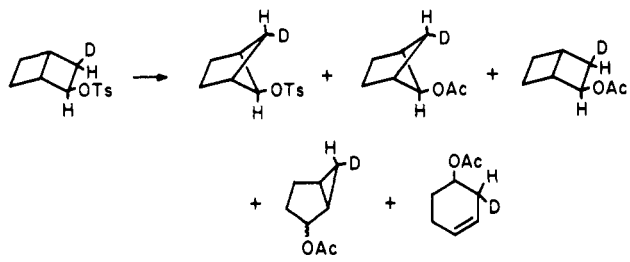
**Table I.** Optical Purities of Monodeuterated X-**1**-OAc, X- and N-**3**-OAc, and **4**-OAc Produced by Buffered Acetylysis of X-**1**-OTs-*exo*-3-$d_1$

| acetate | source | optical purity,[a] % |
|---|---|---|
| X-**1**-OAc-*exo*-3-*d* | starting material | 86 |
| X-**1**-OAc-*exo*-3-*d* | product | 86 |
| X-**3**-OAc-*exo*-6-*d* | product | 26 |
| N-**3**-OAc-*exo*-6-*d* | product | ~26[3] |
| **4**-OAc-2-*d* | product | ~17[b] |

[a] Determined by $^1$H NMR spectroscopy using the acetate $CH_3$'s in $CDCl_3$ with Eu-Opt$^R$ shift reagent. [b] This is the result of deconvoluting the XL-100 $^1$H NMR spectrum where two pairs of four partially overlapping $CH_3$ absorptions are observed.

Scheme II



and the loss in optical purity in the X-**1**-OTs-*exo*-3-*d* → X- and N-**3**-OAc-*exo*-6-*d* lead us to conclude that **3**-OAc isomer b is the enantiomer of isomers a and c. On this basis we would predict an enantiomeric excess of ~32% in X-**3**-OAc-*exo*-6-*d* giving an optical purity of ~27%; 26 ± 1% was observed.

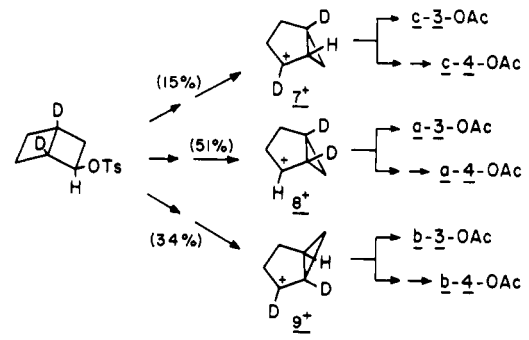
The structure of the **3**-OAc-$d_2$ isomer c with a 1,4 arrangement of the two deuterons is readily rationalized by a disrotatory opening of the $C_1$–$C_4$ bridge bond in the cation formed from X-**1**-OTs-*1,4*-$d_2$ ionization.[10] Formation of the major isomers a and b of **3**-OAc-$d_2$ requires overall two separate processes, each of which involves two single-bond rearrangements: (a) $C_6$–$C_1$ → $C_6$–$C_2$ and $C_2$–$C_3$ → $C_3$–$C_1$ gives isomer a and (b) $C_6$–$C_1$ → $C_6$–$C_2$ and $C_3$–$C_4$ → $C_3$–$C_1$ gives isomer b, with the first Wagner–Meerwein rearrangement common to both of these processes. Such rearrangements are totally compatible with the deuterium distributions and its stereochemistry observed in the products from solvolysis of X-**1**-OTs-*exo*-3-*d*.

We have carried out the buffered acetolysis of the tresylate (100 °C) and triflate (75 °C) esters of X-**2**-OH-*1,5*-$d_2$. As expected, only the isomers a and b of **4**-OAc were produced and in *equal amounts*. Significantly, X-**1**-OAc and X-**2**-OAc were not products from X-**2**-OTr or X-**2**-OTf, the latter acetate being a major product from X-**1**-OTs acetolysis.

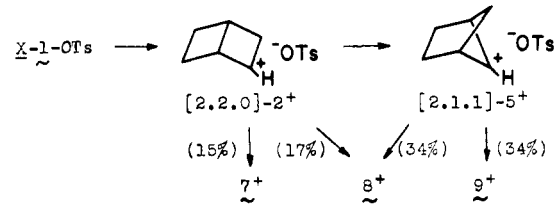
Use of classical cation structures, [2.2.0]-$\mathbf{2}^+$ and [2.1.1]-$\mathbf{5}^+$, can account for the formation of most of the products (*not* **6**-OAc) under several of the constraints required by the present results. However, an additional pathway from [2.2.0]-$\mathbf{2}^+$ → $\mathbf{8}^+$ → a-**3**-OAc (a-**4**-OAc) is required with this rearrangement being a concerted two $\sigma$-bond migration to preserve chirality (Scheme IV). This additional pathway ([2.2.0]-$\mathbf{2}^+$ → $\mathbf{8}^+$) must also be competitive with that of [2.2.0]-$\mathbf{2}^+$ → $\mathbf{7}^+$, the latter considered to account for the $k_{N\text{-}1\text{-}OX}/k_{X\text{-}1\text{-}OX}$ of ~$10^8$.[11] Furthermore, exclusive and high-yield formation of X-**2**-OAc from [2.1.1]-$\mathbf{5}^+$ contradicts the lithium aluminum hydride reduction of bicyclo[2.1.1]hexan-5-one which proceeds by predominate endo-hydride attack (82:18). *We, therefore, consider that classical ion representation of these precursor cations fails to account for the experimental results.*[12]

The nonclassical, $\sigma$-delocalized cation $\mathbf{10}^+$, however, readily accounts for production of X-**1**-OAc, X-**2**-OTs, and X-**2**-OAc. The structure of $\mathbf{10}^+$ can be expected to retard disrotatory

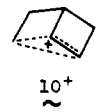
Scheme III



Scheme IV



1,4-bridge opening ($\mathbf{10}^+$ → $\mathbf{7}^+$) compared with [2.2.0]-$\mathbf{2}^+$ allowing the other two $\sigma$-bond rearrangements ($\mathbf{10}^+$ → $\mathbf{8}^+$ and $\mathbf{10}^+$ → $\mathbf{9}^+$) to become competitive.[11]



$\mathbf{10}^+$

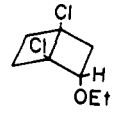
Observation of four $CH_3$ signals in the XL-100 NMR spectrum of optically active ($[\alpha]^{27}_D$ −6.3°) **4**-OAc with Eu-Opt$^R$ is believed to be due to the presence of 26% enantiomeric excesses in the optical antipodes of each of the two **4**-OAc-*2-d* diastereomers ($C_1$ OAc and $C_2$ D cis or trans). We conclude that the initially formed chiral 3-cyclohexenyl cation $\mathbf{11}^+$ (expected to yield enantiomers of *trans*-**4**-OAc-*2-d* from models) is labile to partially rearrange to the diastereomeric cation $\mathbf{12}^+$ (expected to yield enantiomers of *cis*-**4**-OAc-*2-d*). Based on the requirements that each diastereomer have 26% enantiomeric purity and that the chemical shift differences between two pairs of enantiomers are the same, the calculated and observed spectra are in good agreement with a 2:1 ratio of *trans*- and *cis*-**4**-OAc-*2-d*, respectively.

This supports the conclusion reported by Lambert and Featherman[13] concerning the chiral, delocalized structure of the 3-cyclohexenyl cation. The present results suggest that the 17% $k_\Delta$ process for 4-OTs buffered acetolysis at 100 °C[13] determined solely on the results of retention vs. inversion of configuration is a minimum value, and should more reasonably be considered to be ~25% $k_\Delta$ under those conditions.

**Acknowledgments.** The authors thank the National Science Foundation (GP-10691, CHE76-01410) for support of this research.

## References and Notes

(1) For paper 17 see McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7078.
(2) The synthetic sequence to 1-OTs-*1,4*-$d_2$ started with i-N-OET; the sequence of steps was (1) $RuO_4$, $CCl_4$, $H_2O$ → i-N-OAc; (2) $HO^-$, MeOH → i-N-OH; (3) $H^+$, dihydropyran → N-ether; (4) Li, THF, $(CH_3)_3COD$ → X-ether-*1,4*-$d_2$; (5) $H_3O^+$ → **1**-OH-*1,4*-$d_2$; (6) pyridine, TsCl → **1**-OTs-*1,4*-$d_2$.



(i-N-OEt)

(3) The deuterium substitution pattern and optical purity studies of **3**-OAc were most accurately determined using the GLC-collected sample of the exo epimer. The GLC collected N-**3**-OAc was less pure, containing small amounts of X-**3**-OAc and **5**-OAc. However, results from both samples were in very good agreement.
(4) This was prepared by asymmetric deuteroboration ($B_2D_6$ + *l*-α-pinene)[5] of bicyclo[2.2.0]hex-2-ene.[6]
(5) (a) Brown, H. C.; Ayyanger, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964,** *86,* 397. (b) McDonald, R. N.; Steppel, R. N. *Ibid.* **1970,** *92,* 5664.
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(8) That in the basic ethanolysis of N-**2**-OTs → **3**-OH + **3**-OEt hydride shifts do not occur was established: Wiberg, K. B.; Fenoglio, R. A.; Williams, V. Z.; Ubersax, R. W. *J. Am. Chem. Soc.* **1970,** *92,* 568.
(9) That X- and N-**3**-ODNB-*2-d* yield **3**-OH's and **4**-OH in 80% aqueous acetone at 100 °C with no deuterium scrambling was reported: Friedrich, E. C.; Saleh, M. A. *Tetrahedron Lett.* **1971,** 1373.
(10) The cation structures shown are those derived from (2*R*)-**1**-OTs. While we have not established the absolute configuration, we argue by analogy to the asymmetric hydroboration of norbornene.[5]
(11) McDonald, R. N.; Davis, G. E. *J. Am. Chem. Soc.* **1972,** *94,* 5078. The solvolysis of N-**1**-ODNB was considered to model that expected from a classical [2.2.0]-**2**$^+$ cation.
(12) Although we have not carried out labeling studies to verify C–O fission with X-**1**-OTs, the same products and yields are found (a) by varying the [KOAc] from 1.2 to 10 equiv and (b) from the tosylate and tresylate esters under the same buffered acetolysis conditions.
(13) Lambert, J. B.; Featherman, S. I. *J. Am. Chem. Soc.* **1977,** *99,* 1542.

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## Strained Ring Systems. 19.[1] The Nature of the Carbonium-Ion Intermediates Formed in the Buffered Acetolysis of Bicyclo[2.1.1]hex-*exo*-5-yl and Bicyclo[2.2.0]hex-*exo*-2-yl Derivatives: A Requirement for Delocalized, Nonclassical Carbonium Ions

*Sir:*

Previous studies of exo (X) and endo (N) derivatives of bicyclo[2.1.1]hexan-5-ol (**1**-OH)[2] and bicyclo[2.2.0]hexan-2-ol (**2**-OH),[3] while interesting in their own right, have given no more than suggestions of the nature of the intermediate carbonium ions involved and the processes by which they are produced and react. We report our preliminary results of buffered acetolysis of the 2,2,2-trifluoroethanesulfonate (X-**1**-OTr) and trifluoromethanesulfonate (X-**1**-OTf) esters of X-**1**-OH, X-**2**-OTs, X-**2**-OTr, and bicyclo[3.1.0]hex-*endo*-2-yl 3,5-dinitrobenzoate (N-**3**-ODNB) which supply considerable detail about the solvolytic processes involved. The *requirement* that several of these intermediate carbonium ions are delocalized, nonclassical structures is a direct result of this and previous investigations.[1,3]

The buffered acetolysis rate constants for these bicyclic esters are given in Table I, while their product studies are listed in Table II.

The products from X-**1**-OTr are major amounts of **3**-OAc's (X/N 1.54) and cyclohex-3-enyl OAc (**4**-OAc), along with smaller amounts of N-**1**-OAc, cyclohex-2-enyl OAc (**5**-OAc), and cyclopent-2-enylmethyl OAc (**6**-OAc). Inverted acetate N-**1**-OAc may be produced by solvent assisted ($k_s$) ionization of X-**1**-OX and/or solvent trapping of [2.1.1]$^{+-}$OX or **7**$^{+-}$OX (Scheme I). **6**-OAc is considered to be produced by solvent reacting at $C_1$ of delocalized **7**$^{+-}$OX ion pair. From X-**1**-OTf,[4] the same products are produced as those from X-**1**-OTr.[5]

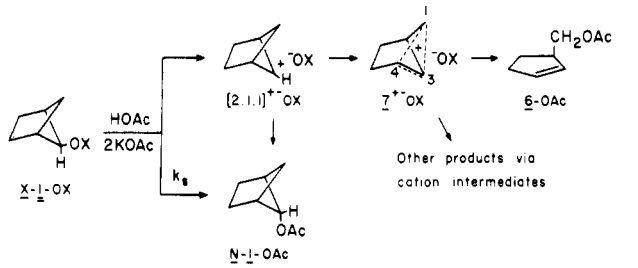
The large rate ratio, $k_{N\text{-}1\text{-}OX}/k_{X\text{-}1\text{-}OX}$ of $\leq 10^8$,[2b] appears to involve direct ionization of N-**1**-OX to the cation **7**$^+$. In that case, the counteranion $^-$OX should be located below (on the endo face of) the bridged cation **7**$^+$ (**7**$^+$-N-$^-$OX), and, thus,

**Table I.** Buffered Acetolysis Kinetic Data[b]

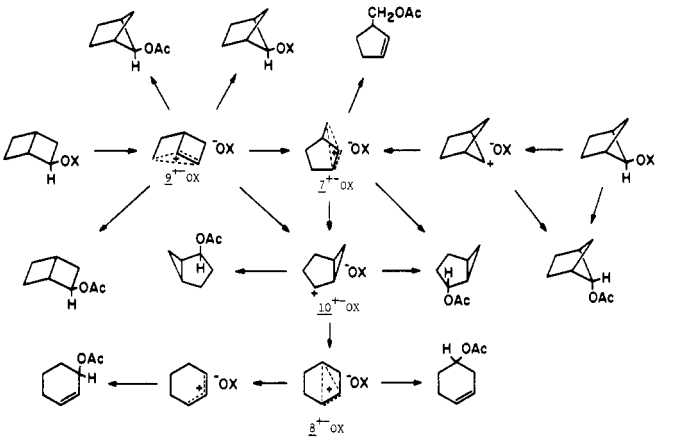
| sulfonate ester | temp, °C | $10^5 k_t$, $s^{-1}$ | $\Delta H^\ddagger$, kcal/mol | $\Delta S^\ddagger$, eu |
|---|---|---|---|---|
| X-**2**-OTs | 75.0 | 4.3 ± 0.1[a] | 24.8 | −7.5 |
| | 100.0 | 51 ± 1 | | |
| X-**1**-OTr-*1,5-d*$_2$ | 100.0 | 0.71 ± 0.01 | 29.6 | −3.2 |
| | 118.0 | 4.7 ± 0.1 | | |
| X-**1**-OTf-*1,5-d*$_2$ | 75.0 | 14 ± 1 | 25.7 | −2.7 |
| | 90.0 | 66 ± 1 | | |

[a] The $k_t$ of X-**2**-OTs in unbuffered HOAc was $3.6 \times 10^{-5}$ $s^{-1}$ at 74 °C.[3a] [b] Contains 2 equiv of KOAc.

Scheme I




Scheme II




may be structurally different from **7**$^{+-}$OX in Scheme I. It appears that ion pair **7**$^+$-N-$^-$OX does not react with HOAc–KOAc at 25 °C at $C_3$ to yield N-**1**-OAc.[2b] However, reaction of solvent at $C_4$ of **7**$^+$-N-$^-$OX (or **7**$^{+-}$OX) should produce exclusively X-**3**-OR which explains the large product ratio, X-**3**-OH/N-**3**-OH = 8, when *N*-**1**-OTs was solvolyzed in basic 80% ethanol.[2b]

Turning our attention to the products from buffered acetolysis of **2**-OTs and **2**-OTr, Table II, several important points are immediately obvious. (a) Even ignoring the large amount of ion-pair return product X-**1**-OTs formed from X-**2**-OTs, a major acetate product is X-**1**-OAc while a minor acetate product is X-**2**-OAc, neither of which is observed from X-**1**-OX. (b) N-**1**-OAc is not found to be produced from X-**2**-OX while 0.2% of this epimeric acetate is readily observed under our GLC conditions.[6] (c) The X-**3**-OAc/N-**3**-OAc ratio from X-**2**-OTs and X-**2**-OTr is the same as that derived from X-**1**-OTr and X-**1**-OTf,[7] and is independent of leaving group. (d) The relative amounts of X-**3**-OAc, N-**3**-OAc, and **4**-OAc produced under the same temperature conditions are the same from X-**1**-OX and X-**2**-OX when corrected for the established rearrangement of **3**-OAc → **4**-OAc and the X-**3**-OAc/N-**3**-OAc ratio.[7] (e) **6**-OAc is produced in amounts proportional to the total yields of **3**-, **4**-, and **5**-OAc formed from both isomeric substrates. Points c–e require that formation of the products X- and N-**3**-OAc, **4**-OAc, **5**-OAc, and **6**-OAc occur by solvent trapping of a common set of carbonium-ion inter-

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