(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.

(6) McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1967**, *32*, 1878.

(7) Wiberg, K. B., Lowry, B. R.; Nist, B. J. *J. Am. Chem. Soc.* **1962**, *84*, 1594.

(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]-$\mathbf{2}^{+}$ 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 $\mathbf{7}^{+-}$OX (Scheme I). **6**-OAc is considered to be produced by solvent reacting at C_1 of delocalized $\mathbf{7}^{+-}$OX ion pair. From X-**1**-OTf,[4] the same products are produced as those from X-**1**-OTr.[5]

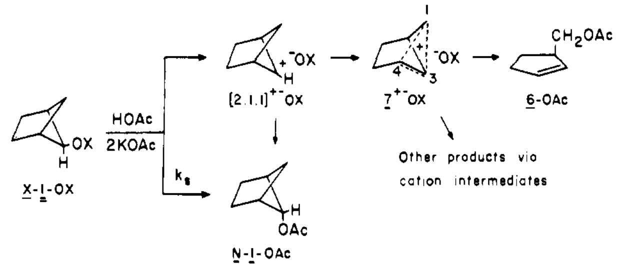
The large rate ratio, $k_{\mathrm{N\text{-}1\text{-}OX}}/k_{\mathrm{X\text{-}1\text{-}OX}}$ of $\leq 10^8$,[2b] appears to involve direct ionization of N-**1**-OX to the cation $\mathbf{7}^{+}$. In that case, the counteranion $^{-}$OX should be located below (on the endo face of) the bridged cation $\mathbf{7}^{+}$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

Table I. Buffered Acetolysis Kinetic Data[b]

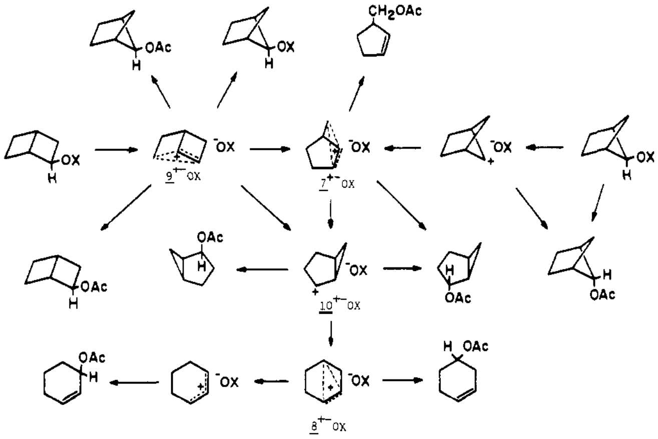
sulfonate ester	temp, °C	$10^5 k_t$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
X-**2**-OTs	75.0	4.3 ± 0.1[a]	24.8	−7.5
	100.0	51 ± 1		
X-**1**-OTr-*1,5-d*$_2$	100.0	0.71 ± 0.01	29.6	−3.2
	118.0	4.7 ± 0.1		
X-**1**-OTf-*1,5-d*$_2$	75.0	14 ± 1	25.7	−2.7
	90.0	66 ± 1		

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

Scheme I



Scheme II



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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Table II. Products from the Acetolysis of Bicyclo[2.1.1]hex-*exo*-5-yl and Bicyclo[2.2.0]hex-*exo*-2-yl Sulfonate Esters[a,b]

substrate	solvent	temp, °C	time, h	X-**1**-OX	X-**1**-OAc	N-**1**-OAc	X-**2**-OAc	N-**3**-OAc	X-**3**-OAc	**4**-OAc	**5**-OAc[c]	**6**-OAc	X-**3**-OAc/ N-**3**-OAc ratio	% of acetates recovered
X-**1**-OTr	HOAc, 2KOAc	100	106			3.0		13.8 [22]	21.3 [34]	53.6 [35]	7.5 [8]	0.9 [1]	1.54	94
X-**1**-OTr	HOAc, 2KOAc	100	70	30.0 (X = Tr)		2.2		11.4 [22]	17.6 [34]	33.4 [36]	4.6 [7]	0.8 [1]	1.54	64
X-**1**-OTf	HOAc, 2KOAc	75	25	0.2 (X = Tf)		3.2		24.8 [27]	38.4 [41]	31.7 [30]	2.1 [2]	0.2 [<1]	1.55	98
X-**2**-OTs	HOAc	75	50	56.6 (X = Ts)	19.1		2.4			20.6	1.2	*d*		42
X-**2**-OTs	HOAc, 2KOAc	75	50	54.0 (X = Ts)	16.3		2.2	6.9 [27]	9.5 [37]	9.7 [30]	1.3 [5]	0.1–0.2 [<1]	1.38	45
X-**2**-OTs	HOAC, 2KOAc	100	9	55.0 (X = Ts)	15.6		2.1	5.3 [20]	7.7 [30]	11.1 [38]	3.2 [12]	*d*	1.46	42
X-**2**-OTr	HOAc, 2KOAc	100	0.5	54.6 (X = Tr)	14.0		1.8	6.4 [22]	8.9 [30]	10.9 [36]	3.5 [12]	*d*	1.40	40

[a] Percent yields; recovered sulfonate esters are weighed samples after the acetates were removed by bulb-to-bulb distillation, and acetates were determined by GLC integration and comparison with authentic materials. [b] Values in [ ] are corrected for k_t of the sulfonate ester and known rearrangement of **3**-OAc → **4**-OAc at that temperature and adjusted to 100%. [c] Obtained by deconvolution method in good agreement with estimated values from ^{1}H NMR spectra. [d] Percent **6**-OAc was not determined in these runs since its GLC retention time is that of X-**2**-OAc.

mediates produced at some point in the reaction scheme for both X-**1**-OX and X-**2**-OX substrates.

We have already pointed out that a classical [2.2.0]$^+$ cation fails to account for the rearrangements occurring prior to forming the reaction products X- and N-**3**-OAc, and **4**-OAc from the buffered acetolysis of X-**2**-OTs.[1] *This same conclusion is reached when the present studies are considered.* Point a above requires that an additional intermediate cation be produced from X-**2**-OX to yield X-**1**-OAc, and probably X-**1**-OX. This cation must be the result of a single Wagner-Meerwein shift,[1] it cannot be in equilibrium with those cations generated from solvolysis of X-**1**-OX, and it must react with solvent exclusively from the exo face.[8]

Since the classical carbonium-ion modeling of these results fails both qualitatively and quantitatively, we are led to the nonclassical formalism shown in Scheme II, where cations $\mathbf{7}^+$, $\mathbf{8}^+$,[9] and $\mathbf{9}^+$ are delocalized, nonclassical structures. The unique feature of Scheme II defined by the present results is that $\mathbf{7}^{+-}$OX is the first common ion pair linking the buffered acetolyses of X-**1**-OX and X-**2**-OX derivatives. It also accounts for the known rearrangement channels from chiral X-**2**-OTs to its buffered acetolysis products.[1]

Entering the cascade of cations in Scheme II from various points produces some inconsistencies based on product analyses reported by several investigators. From the buffered acetolysis of cyclopent-2-enylmethyl β-naphthalenesulfonate (**6**-ONaph), the ratio X-**3**-OAc/N-**3**-OAc = 1.3 (70 °C) is lower than this ratio produced from X-**1**-OTf (75 °C), and **5**-OAc was not reported to be a product (2% **5**-OAc from X-**1**-OTf).[10]

The most serious inconsistency is found in the reported acetolysis of X- and N-**3**-OTs (in 83% HOAc-17% Et_2O and NaOAc at 24 °C).[11] The ratio X-**3**-OAc/N-**3**-OAc = 2.1 and no ion-pair return of **4**-OTs were observed from both epimeric tosylates. Buffered acetolysis (*no* Et_2O) of X- and N-**3**-ODNB at 100 °C gave a corrected ratio of X-**3**-OAc/N-**3**-OAc = 1.2[11] with ion-pair return to **4**-ODNB; in our hands, a small amount of **6**-OAc was observed suggesting some reversibility of $\mathbf{10}^+ \rightleftarrows \mathbf{7}^+$.

The recent report that buffered acetolysis of **4**-OTs involves 17% k_Δ (to $\mathbf{8}^+$) and 83% k_s,[12] and our optical activity studies[1] establish the chiral structure of $\mathbf{8}^+$ independent of how it is produced. While varying small yields (2–6%)[12,13] of X- and N-**3**-OAc are reported from buffered acetolysis of **4**-OTs, these yields become sizable (12–35%) based on the 17% k_Δ pathway for **4**-OTs.[12] This requires trapping of $\mathbf{8}^+$ and/or $\mathbf{8}^+ \rightarrow \mathbf{10}^+$ and trapping of $\mathbf{10}^+$ to produce the X- and N-**3**-OAc as a significant pathway.

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References and Notes

(1) For paper 18 see McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* preceding paper in this issue.

(2) (a) Wiberg, K. B.; Fenoglio, R. A. *Tetrahedron Lett.* **1963,** 1273. (b) Wiberg, K. B.; Fenoglio, R. A.; Williams, V. Z.; Ubersax, R. W. *J. Am. Chem. Soc.* **1970,** *92*, 568, revised product yields given.

(3) (a) McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1965,** *87*, 3020. (b) McDonald, R. N.; Davis, G. E. *J. Am. Chem. Soc.* **1972,** *94*, 5078.

(4) An impure sample of X-**1**-OTf containing 4% X-**1**-OH was used. The product yields are corrected for this impurity and X-**1**-OAc formed by its acetylation in the acetolysis medium.

(5) Su, T. M.; Sliwinski, W. F.; Schleyer, R. v. R. *J. Am. Chem. Soc.* **1969,** *91*, 5386.

(6) GLC analytical conditions: 0.95 × 265 cm column, 22% TCEP on C-22 firebrick (100–105 mesh); column temperature, 105 °C; He flow rate, 120 mL/min.

(7) The X-**3**-OAc/N-**3**-OAc product ratio from X-**2**-OTs is expected to be less than that from X-**1**-OX since 15% of these products are formed via intermediates derived from disrotatory C_1–C_4 bridge bond opening.[1] This product ratio was shown to be substantially less (0.7) from N-**2**-ODNB than from N-**3**-ODNB (1.2) in 60% aqueous acetone solvolysis.[3b] Using a value of 0.8–1.0 for this 15% of **3**-OAc produced gives a ratio of 1.55 formed via $\mathbf{7}^{+-}$OX in agreement with the ratio derived from X-**1**-OX.

(8) Wiberg, K. B.; Lowry, B. R.; Colby, T. H. *J. Am. Chem. Soc.* **1961,** *83*, 3998. The requirement for exclusive exo trapping of a [2.1.1]$^{+-}$OX ion pair is not reasonable since it was reported that $LiAlH_4$ reduction of bicyclo[2.1.1]hexan-5-one occurred preferentially (82:18) from the endo side.

(9) Buttrick, P. A.; Holden, C. M. Y.; Wittaker, D. *J. Chem. Soc., Chem. Commun.* **1975** 534. $\mathbf{8}^+$ is the only one of these cations reported under stable ion conditions.

(10) Hanack, M.; Schneider, H. J. *Tetrahedron*, **1964,** *20*, 1863.

(11) (a) Friedrich, E. C.; Saleh, M. A.; Winstein, S. *J. Org. Chem.* **1973,** *38*, 860. (b) Owing to the ease of rearrangement to **4**-OTs and high reactivities, X- and N-**3**-OTs were not analyzed or spectrally characterized. The effect on product ratios as a function of introducing 17 vol. % Et_2O to the buffered acetolysis medium is unknown.

(12) Lambert, J. B.; Featherman, S. I. *J. Am. Chem. Soc.* **1977,** *99*, 1542. **3**-OAc products were reported in <3% yield.

(13) (a) Reference 11a, footnote 13, gives 3% **3**-OAc with X-**3**-OAc/N-**3**-OAc = 2. (b) Reference 11a, footnote 14, gives 2% **3**-OAc with X-**3**-OAc/N-**3**-OAc = 1. (c) Hanak and Keberle (Hanak, M.; Keberle, W. *Chem. Ber.* **1963,** *96*, 2938) report 6.5% **3**-OAc with X-**3**-OAc/N-**3**-OAc = 1.8.

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