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NOVEL REGIOSPECIFICITY IN THE ACID-CATALYZED ADDITION OF ACETIC ACID TO <u>endo</u>-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE

M.A. Battiste,* J.M. Coxon[1] and R. Edelman

Department of Chemistry, University of Florida, Gainesville, Florida 32601, USA

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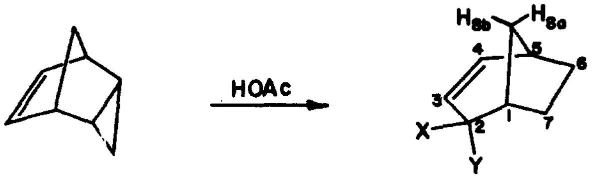
We report a striking example of unprecedented regiospecificity in the addition of acetic acid to endo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**). The addition proceeds with surprising ease in acetic acid at 80° (3 days) or at room temperature in the presence of catalytic amounts of toluenesulphonic acid to yield a mixture (22:78) of endo- and exo-bicyclo[3.2.1]oct-3-en-2-yl acetates (**2a** and **2b**). The endo- and exo-acetates (**2a** and **2b**),[2] after hydrolysis to alcohols (**3a** and **3b**), were



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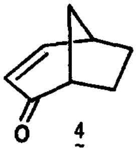
2a	X=H	Y=OAc
2b	X=OAc	Y=H
3a	X=H	Y=OH
3b	X=OH	Y=H
5	X=OPNB	Y=H



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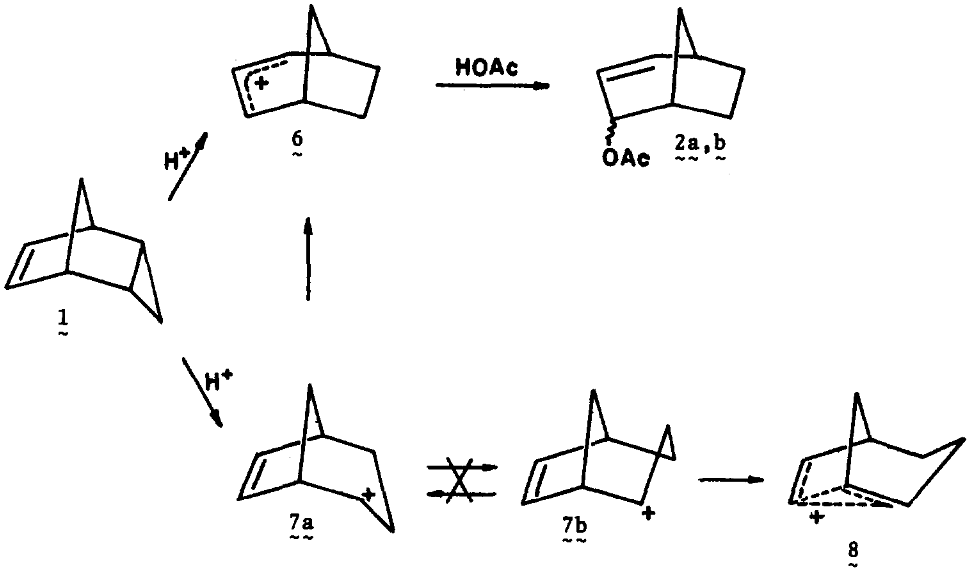
separable to glpc (carbowax 20M (2.5%) on chromosorb G. A.W. D.M.C.S.) with the *exo*-alochol **3b** eluted before the *endo*-alcohol **3a**. Previous attempts to separate these alcohols (**3a** and **3b**) by analytical glpc have only been successful using capillary columns.[3]

The identity of the alcohols (**3a** and **3b**) and hence the acetates (**2a** and **2b**) from which they were prepared follows from their nmr (60 MHz, $CDCl_3$) spectra (low field only) [**3a**, τ 5.44 ($W_{\frac{h}{2}}$=10 Hz; $>C^{2}\underline{H}OH$), 4.67 (ddd, $J_{3,4}$=9.5 Hz, $J_{2,3}$=2.5 Hz, $^{4}J_{3,5}$=1.5 Hz; $C^{3}H$), 4.03 (ddt, $J_{3,4}$=9.5 Hz, $J_{4,5}$=6.0 Hz, ^{4}J=1.5 Hz, ^{4}J=1.5 Hz; $C^{4}H$); **3b** (mp 88-89°), τ 6.23 (dd, $J_{2,3}$=4.0 Hz, $^{4}J_{2,8a}$=2.5 Hz, $>C^{2}\underline{H}OH$), 4.51 (ddd, $J_{3,4}$=9.5 Hz, $J_{2,3}$=4.0 Hz, $^{4}J_{3,5}$=1.5 Hz; $C^{3}H$), 3.90 (ddd, $J_{3,4}$=9.5 Hz, $J_{4,5}$=7.0 Hz, ^{4}J=*ca.* 1 Hz; $C^{4}H$)] and oxidation of the alcohol mixture with CrO_3-pyridine to the known α,β-unsaturated ketone **4**; λ_{max} 6.0 and 5.9μ.[4] An authentic sample of the *endo*-alcohol **3a**, mp 82-83°, was prepared by reduction of ketone **4** with lithium aluminum hydride. The minor component from the reaction of HOAc with hydrocarbon **1** was, after hydrolysis, identical with authentic *endo*-alcohol **3a**.

Formation of both *endo*- and *exo*-acetates (**2a** and **2b**) from reaction of olefin **1** with acetic acid, contrasts with the results from solvolysis of the *exo*-p-nitrobenzoate **5**. This latter reaction, known to proceed *via* the allylic ion **6**, afforded an almost quantitative yield (>98%) of the *exo*-alcohol **3b**. The intermediacy of the allylic ion 6 cannot, however, be excluded since a separate experiment demonstrated partial isomerization (*ca.* 60%) of *endo*-acetate **2a** to **2b** under the reaction conditions.

Proton attack on hydrocarbon **1** is regiospecific in cleavage of the C-2, C-4 bond with the reaction proceeding almost exclusively by migration of C-8 from C-5 to C-4 (Scheme I). This remarkable selectivity may result from quantitative trapping of a transient secondary carbonium ion, initially formed in the chair conformation **7a**, by the C-1, C-8 σ-bond. Conformational inversion of this ion (**7a**) to the boat conformation **7b** would permit capture of the carbonium ion by the C-6, C-7 double bond; however, the latter process does not occur as products of carbonium ion **8** are not observed.



Scheme I

The striking stereoselectivity and ease of reaction of hydrocarbon **1** with acetic acid can perhaps be better explained as a consequence of σ-orbital overlap between the strained edge (C-2, C-4) and bridge (C-1, C-8; C-5, C-8) bonds.[8] This overlap exerts stereoelectronic control over the direction of proton attack on the cyclopropyl ring (corner)[7b] and the subsequent sequence of product determining events.

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References

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2. Acetates 2a and 2b have proved inseparable to glc.[3] Two minor acetoxy compounds (<2%) have been isolated from the reaction, the structures of which are under investigation.

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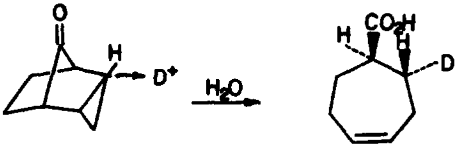
4. H.L. Goering, R.W. Greiner and M.F. Sloan; *ibid.*, 83, 1391 (1961).

5. H.L. Goering and J.C. Vlazny[6] report the acid catalyzed isomerization of *exo*-alcohol 3b is *ca.* three times slower than isomerization of *endo*-alcohol 3a.

6. J.C. Vlazny, Ph.D. Thesis, University of Wisconsin, 1968.

7. (a) While the question of edge versus corner attack of the proton on the cyclopropane moiety of olefin 1 remains to be established, by analogy with the related ring opening-fragmentation reaction (i)[7b] corner protonation is favored; (b) M.A. Battiste and J. Mackiernan, *Tetrahedron Lett.*, in press.;



(i)

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