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SYNTHESIS AND REACTIVITY OF A $(CH)_{11}$-X SYSTEM
ANTI-PENTACYCLO$[5.4.0.0^{2,6}.0^{3,9}.0^{5,8}]$UNDEC-10-EN-4-YL TOSYLATE

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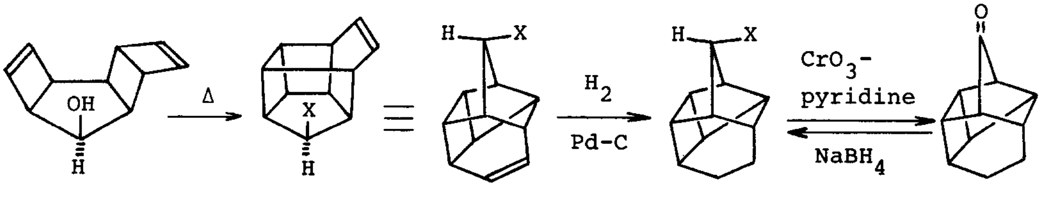
In the course of our study of chemical reactivities of polycyclic compounds, an intramolecular ring closure of *syn*,*exo*,*endo*-tetracyclo$[5.4.0.0^{2,5}.0^{8,11}]$undeca-3,9-dien-6-ol (1) into a cage molecule, *anti*-pentacyclo$[5.4.0.0^{2,6}.0^{3,9}.0^{5,8}]$undec-10-en-4-ol (2-OH), was observed on pyrolytic condition. In this communication, we wish to report acetolyses of its tosylate (2-OTs), which is a considerably interesting system since it is not only a highly strained cage compound[1] but also a precursor of $(CH)_{11}^{+}$ ion,[2] and of its saturated analogue, 3-OTs.

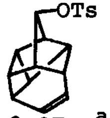
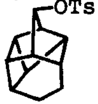
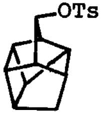
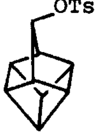
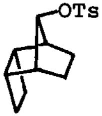
A solution of tetracyclic alcohol 1[3] (200 mg) in n-hexane (6 ml) was pyrolyzed at 320-330 °C under nitrogen atmosphere. The pyrolysate was crystallized from n-pentane to give white needles (50 mg, 25%); mp 100-101 °C; nmr ($CDCl_3$) δ 6.53-5.90 (m, 2H, vinyl), 3.98 (br.s, 1H, methine), 3.60-2.90 (m, 2H), 2.80 (m, 1H), 2.65-1.90 (m, 4H), 1.80 (m, 1H) and 1.70 (s, 1H, -OH). *Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.58; H, 7.59.

The alcohol (2-OH) was saturated by catalytic hydrogenation, followed



1 2-OH 2-OTs 3-OH 3-OTs 4

Table I Kinetic Data of The Tosylates

ROTs	Temp. (°C)	Rate Constant (sec^{-1})	Relative Rate (100 °C)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu.)	Strain Energy (kcal/mol).[g]
 2-OTs [a]	75[b]	$(2.27 \pm 0.10) \times 10^{-5}$ [c]				
	100[b]	$(2.20 \pm 0.04) \times 10^{-4}$ [c]	55	23.4	-12.9	93.4
 3-OTs [a]	75[b]	$(3.55 \pm 0.16) \times 10^{-5}$ [c]				
	100[b]	$(4.26 \pm 0.07) \times 10^{-4}$ [c]	106	25.6	-5.7	71.0
 5-OTs	100	4.05×10^{-5} [d]	10	28.4	-3.0	84.0
 6-OTs	100	$(3.38 \pm 0.09) \times 10^{-4}$ [e]	84	31.2	-0.4	123.8
 7-OTs	100	$(4.02 \pm 0.09) \times 10^{-6}$ [f]	1.0	30.8	-1.2	44.6

a. Ca. 0.026 M in acetic acid buffered with 0.044 M sodium acetate.

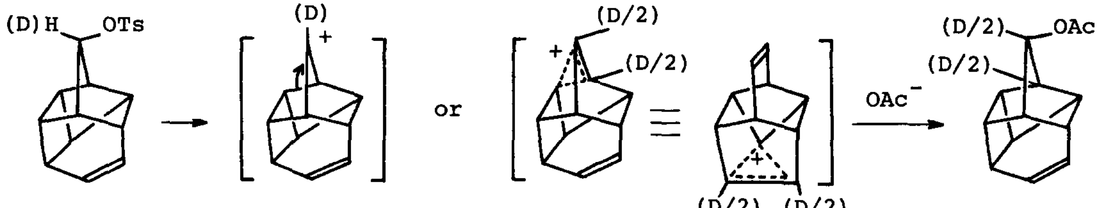
b. ± 0.3 °C   c. The errors are deviation from the average of two independent runs.

d. Extrapolated value from the data of reference 5.   e. Reference 10.   f. Reference 8.

g. Reference 11.

by chromium trioxide oxidation to give ketone **4** whose structure had previously been reported.[4] The anti orientation of the hydroxyl group in **3**-OH was proved by a stereospecific reduction (78%) of **4** to **3**-OH with sodium borohydride.[5] The alcohols (**2**-OH and **3**-OH) were converted to their corresponding tosylates (**2**-OTs, mp 83-85 °C and **3**-OTs, mp 48-49 °C) in the usual fashion.[6] The acetolysis rates were measured by UV absorbance method[7] displaying nice first-order behavior. The kinetic data are listed in Table I with literature values for related compounds.

Pentacyclic tosylates, **2**-OTs and **3**-OTs, undergo acetolysis at a rate 50-100 times faster than bicyclic tosylate **7**-OTs.[8] This would be explained by angle strains due to their cage structures.[9] Although homocubyl tosylate **6**-OTs[10] is assumed to be the most highly strained system (124 kcal/mol),[11] **3**-OTs is more reactive than **6**-OTs. Further, the rate ratio (ca. 10) of **3**-OTs/**5**-OTs[5] can not be explained by the decrease of strain energy (-13 kcal/mol)[11] from five-membered ring to six-membered ring. These findings suggest that the important factors effecting the solvolytic reactivity of these compounds are conformational requirements of their bond alignments adjacent to cationic centers[12] as well as their ground state strain energies.



2-OTs **8** **9** **2**-OAc

Buffered acetolysis of **2**-OTs (100 °C, 9 h) gave quantitatively an acetate **2**-OAc with the retained stereochemistry. This can be rationalized by a rapid equilibrating of 1,2-alkyl shift (**8**) or by a bridged carbonium ion (**9**) as a $(CH)_{11}^{+}$ intermediate followed by solvent capture with retention of configuration. The deuterium scrambling (1:1) by nmr spectral study may support the above mechanisms. These observations are in agreement with those in acetolyses of **5**-OTs[5,13] and **6**-OTs.[10] Preparative acetolysis of **3**-OTs (100 °C, 4.5 h) gave its corresponding acetate quantitatively through a similar ion structure to **9**.

References and Notes

1. For a review, see C. W. Jefford, *J. Chem. Educ.*, *53*, 477 (1976).

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   b) For a recent review, see R. E. Leone, J. C. Barborak and P. v. R. Schleyer in "Carbonium Ions", Vol. IV , G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., (1973) pp 1846-1889.

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4. Y. Yamashita and T. Mukai, The 26th. IUPAC Congress in Tokyo, September 1977. Abstract IV, p 883. The authors are indebted to Professor Mukai for sending the nmr and ir spectra of **4**.

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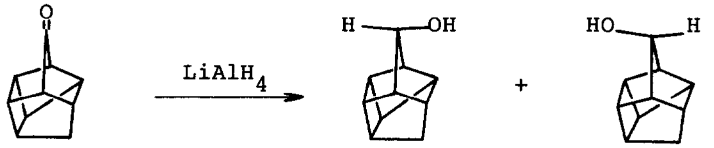
   A similar stereospecific reduction from the less hindered side of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (**11**) has been reported.



11 8 : 2

6. Elemental and spectral analyses of all new compounds reported here were consistent with their assigned structures.

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11. These values are roughly estimated by the sum of ring strains of the component. See J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, Inc., New York, N. Y., (1965) p 112.

12. A. Nickon and R. C. Weglein, *J. Am. Chem. Soc.*, *97*, 1271 (1975).

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