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ACETOLYSIS OF THE DITOSYLATE OF exo-cis-BENZONORBORNENE-2,3-DIOL AND RELATED COMPOUNDS. EVIDENCE AGAINST THE FORMATION OF A DICATIONIC INTERMEDIATE

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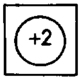
According to simple HMO calculations, the cyclobutadiene dication (1) as well as the benzocyclobutadiene dication (2) are expected to be relatively stable.[1,2] An interesting observation was recently reported by Lambert and Holcomb,[3] which is that the unsaturated ditosylate 3 acetolyzes at a constant first-order rate 500 times faster than the saturated ditosylate 4, produces two isomeric bicyclo-[2.2.1]heptenyl diacetates and two tricyclo[2.2.1.$0^{2,6}$]heptyl diacetates, and at about the first half-life the reaction mixture contained only product diacetates and starting-material ditosylate, but no acetoxy tosylates.



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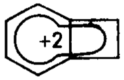

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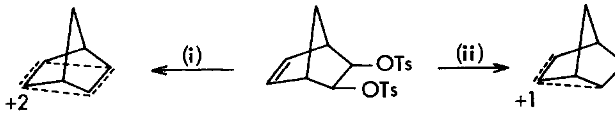
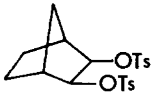


5 3 6



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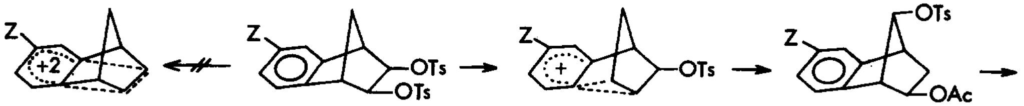
The two alternative mechanisms (i and ii) were proposed and (i) was favored: (i) concerted loss of both tosylate groups to form a cyclobutenium-stabilized dication (5); (ii) 3 passes stepwise through a monocation 6, an acetoxy tosylate, and another monocation to lead to the ultimate products, diacetates. We have independently examined acetolyses of the ditosylates of exo-cis-benzonorbornene-2,3-diol (7-OH) and its 6-methoxyl derivative (8-OH) and have found evidence making the dicationic 9 improbable.

Oxidations of benzonorbornadiene and 6-methoxybenzonorbornadiene[4] with alkaline $KMnO_4$ solution, as performed for norbornene,[5] yielded 7-OH, mp 177-178.5°, and 8-OH, m.p. 106-107.5°,[6] which were esterified with tosyl chloride to obtain 7-OTs, mp 138-138.5°, and 8-OTs, mp 143-145°. The acetolyses were carried out in glacial acetic acid containing equivalent sodium acetate and the rate data are summarized in TABLE I.[7] The kinetic data indicate that an argument similar to that proposed for the result of 3 is possible here and involvement of 9 is not unreasonable. The retarding effect of the second tosylate group in the saturated system (18/4 in TABLE I) is 2.9 x 10^{-6}. The acetolyses of 7-OTs and 8-OTs proceed, respectively, 19.6 and 1320 times faster than 4 and 3.3 x 10^{-4} and 2.2 x 10^{-2} times more slowly than exo-2-benzonorbornenyl tosylate (16). Therefore, the benzene rings in 7-OTs and 8-OTs are rate-accelerating and the second tosylates are less rate-retarding than in 4.

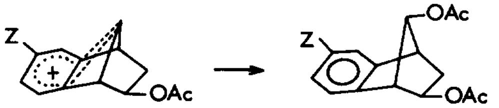


9

Z = H: 7-OTs
Z = CH_3O: 8-OTs

10

Z = H: 11
Z = CH_3O: 12



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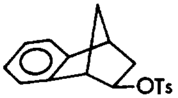
Z = H: 14
Z = CH_3O: 15



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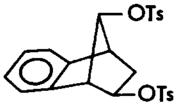

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TABLE I
Rates of Acetolysis at 75°

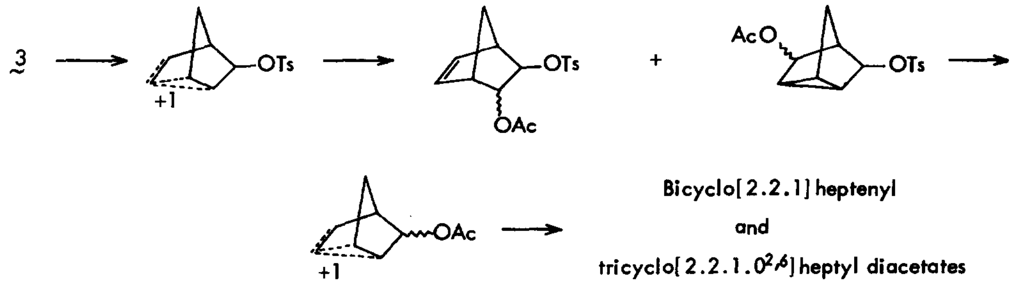
Compound	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate
7-OTs	3.33 x 10^{-7}	29.3	-0.92	1.96 x 10^{1}
8-OTs	2.24 x 10^{-5}	25.4	-1.56	1.32 x 10^{3}
3	8.6 x 10^{-6} [a]	27.6	-3	5.06 x 10^{2}
4	1.7 x 10^{-8} [a]	31.4	-4	1
16	1.0 x 10^{-3} [b]			5.88 x 10^{4} (0.169)
exo-2-Norbornenyl-OTs (17)	1.7 x 10^{-3} [a]	21.2	-11	1.0 x 10^{5} (0.288)
exo-2-Norbornyl-OTs (18)	5.9 x 10^{-3} [a]	22.2	-5	3.42 x 10^{5} (1)

[a] Ref. 3. [b] Calcurated from the rate of the brosylate[c] with the factor of OBs/OTs = 3.

[c] H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, J. Amer. Chem. Soc. 91, 0000 (1969).

The product was, however, quantitatively the diacetate of exo-2-anti-9-benzonorbornendiol (14, mp 79-80°, or 15, oil) formed with the Wagner-Meerwein rearrangement. When analyzed at about the first half-life, the reaction mixture of 7-OTs consisted of the rearranged acetoxy tosylate (11),[8] mp 106-107°, the recovered 7-OTs, and 14 in a ratio of 62, 23, 15%, respectively, but the retained 7-OAc was absent. It was observed that 8-OTs reacts similarly. Accordingly, rationalization of the products is difficult on the basis of the dication 9, but not on the basis of a step mechanism through the monocations 10 and 13. It has not been solved whether the rearranged ditosylate 19 is formed or not by internal return before the first tosyloxy is displaced by solvent. The kinetics are also compatible with the step mechanism. Since 11 was captured, the rate of 11 must be comparable with or slower than the rate of 7-OTs. Although anti-9-benzonorbornenyl tosylate acetolyzes eleven times faster than 7-OTs,[9] the factor of eleven will be overcome by the inductive effect of OAc in 11 or OTs in 19, judging from the fact that the introduction of exo-2-bromo group into anti-7-norbornenyl tosylate makes the rate 20 times slower (at 25°).[10]

Finally, we suggest the following monocation mechanism for the reaction of 3.



Bicyclo[2.2.1]heptenyl
and
tricyclo[2.2.1.$0^{2,6}$]heptyl diacetates

REFERENCES

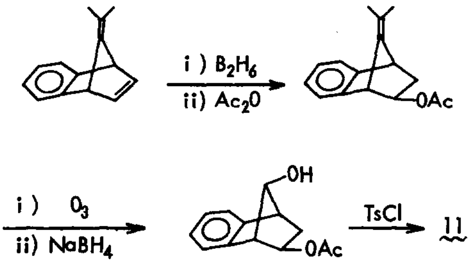
1. The stabilization energies (ΔE) of 1 and 2 are 2.00 and 1.85β, respectively, when necessary values for calculation are taken from J. D. Roberts, Notes on Molecular Orbital Calculations, pp 73-76, W. A. Benjamin, Inc., New York (1961) and A. Streitwieser, Jr. and J. I. Brauman, Supplemental Table of Molecular Orbital Calculation, Vol. 1, pp 38-39, Pergamon Press, Oxford (1965).
2. We calculated ΔE, varying the values of resonance integral (kβ) between the reaction center and the benzene juncture, Coulomb integral (α + hβ) at the center, and the resonance integral (lβ) between the centers. ΔE increase with increasing k, h, l. When k, h, and l are 0.3, 0.2, and 0.8, respectively, ΔE for 1 and 2 are obtained as 0.6 and 0.5β. See FIG. 1.
3. J. B. Lambert and A. G. Holcomb, J. Amer. Chem. Soc. **91**, 1572 (1969).
4. H. Tanida, R. Muneyuki, and T. Tsuji, Bull. Chem. Soc. Japan **37**, 40 (1964).

5. K. B. Wiberg and K. A. Saegebarth, J. Amer. Chem. Soc. 79, 2822 (1957).

6. The structures are supported by spectral data. exo-cis configuration of the diol groups is clear by infrared hydroxyl bands and NMR. For 7-OH, IR (CCl_4) 3634 (free OH) and 3525 (OH internally-associated with H); NMR ($CDCl_3$) δ 3.80 (d, 2, J = 1.7 Hz, C_2, C_3-H), 3.22 (t, 2, J = 2.0 Hz, C_1, C_4-H), 2.33-1.83 (m, 2, C_9-H).

7. The first-order plots were linear to 50% completion of the reactions, then showed slightly upward curvature (the rates became slower). A similar observation was reported in the acetolysis of 3.[3]

8. An authentic sample for identification was prepared through the following route:



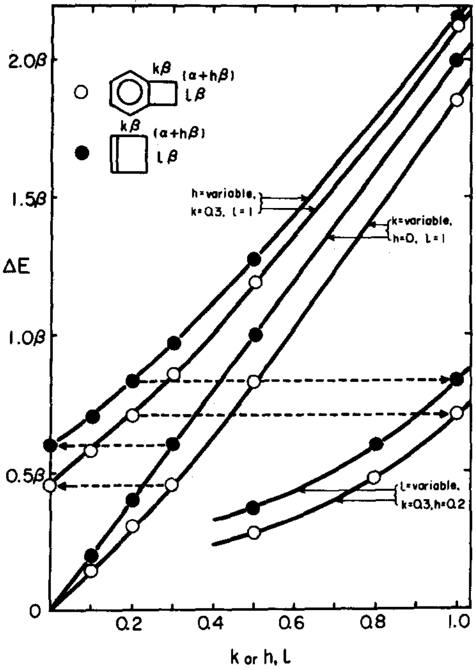


FIG. 1

NMR ($CDCl_3$) for 11, δ 4.66 (split q, 1, C_{endo-2}-H), 4.42 (m, 1, C_{syn-9}-H), 3.62 (m, 1, C_1-H), 3.39 (split d, 1, C_4-H), 2.45 (s, 3, CH_3-C_6H_5-), 2.07 (s, 3, CH_3COO); and 2.50-1.63 (m, 2, C_3-H). Long range coupling is observed between C_{endo-2} and C_{syn-9} protons at 100 Mc, when C_1, C_4-H are decoupled. NMR ($CDCl_3$) for 15, δ 4.82-4.58 (m, 2, C_{endo-2}, C_{syn-9}-H), 3.76 (s, 3, CH_3O-C_6H_5-), 3.65 (m, 1, C_1-H), 3.35 (m, 1, C_4-H), 2.07 and 2.02 (two s, 6, CH_3COO), ~2.0 (m overlapped with CH_3COO, 2, C_3-H). NMR for the aliphatic part of 14 is substantially identical.

9. P. D. Bartlett and W. P. Giddings, J. Amer. Chem. Soc. 82, 1240 (1960); H. Tanida, T. Tsuji, and H. Ishitobi, ibid. 86, 4904 (1964).

10. S. Winstein and M. Shatafsky, J. Amer. Chem. Soc. 78, 592 (1956).