

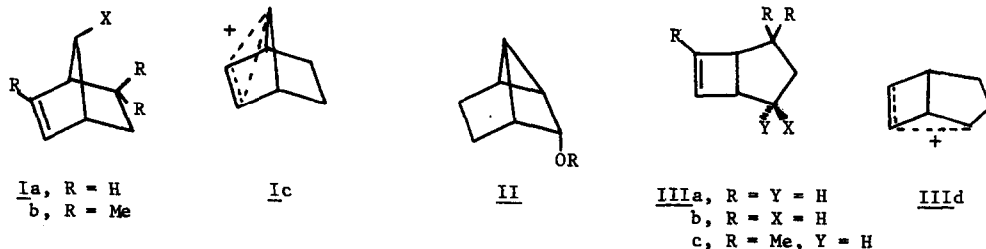
A NOVEL π -ROUTE TO THE 7-NORBORNENYL CATION

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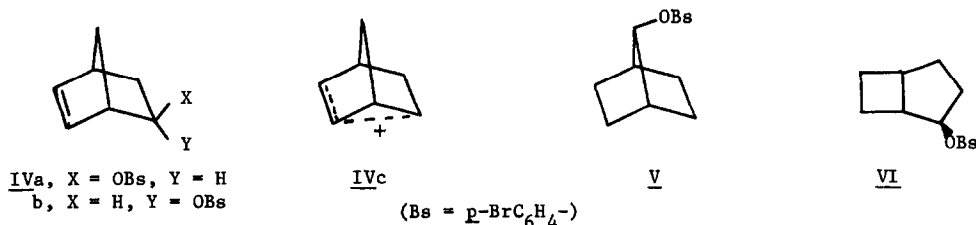
(Received in USA 27 February 1974; received in UK for publication 29 March 1974)

Among the most interesting of the cations described as nonclassical is the oft-studied 7-norbornenyl cation (Ic)¹. Some controversy² centered on the structure of this cation, but the most current views³ favor the nonclassical structure. There are two routes that result in direct formation of Ic as either a transient intermediate or a stable salt suitable for direct spectral studies. One, the π -route, involves solvolysis of anti-7-norbornenyl tosylate (Ia, X = OTs), or treatment of the corresponding alcohol with fluorosulfonic acid (FSO₃H) at low temperatures^{1c,d}. The other, termed the σ -route, involves treatment of endo-tricyclo[3.2.0.0^{2,7}] hept-3-yl methyl ether (II, R = Me) with dilute acid, or with FSO₃H at low temperatures, and solvolysis of the corresponding p-nitrobenzoate (II, R = PNB)⁴. We have studied the kinetics and products of solvolysis of exo- and endo-2-bicyclo[3.2.0.] hept-6-enyl tosylates (IIIa, X = OTs; IIIb, Y = OTs)⁵ and find that solvolysis of the exo-tosylate in media of widely differing nucleophilicity yields only products derivable from the 7-norbornenyl cation. Thus, the exo-tosylate appears to furnish an important alternate π -route to this cation. Comparison of the results from solvolysis of appropriate derivatives of Ia, II and IIIa is instructive in relating the several members of this family of cations.

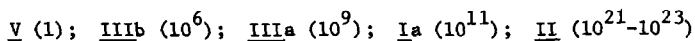


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Hydrolysis of exo-2-bicyclo[3.2.0.]hept-6-enyl tosylate (IIIa, X = OTs; 50% aq. acetone, 3 eq. NaHCO₃, 80% yield) gives anti-7-norbornenol (Ia, X = OH) as does similar treatment of anti-tosylate (Ia)^{1b}. Similarly, Tufariello^{4a} found that treatment of the tricyclic p-nitrobenzoate (II, R = PNB) with 50% aqueous acetone (10 eq. NaHCO₃) yields a product mixture consisting of 76% anti-alcohol (Ia, X = OH) and 23% of the corresponding p-nitrobenzoate. More surprising, however, was our finding that treatment of the exo-tosylate with 4M NaOCH₃ in methanol at 50° forms a 65:35 mixture (66% yield)⁷ of anti-7-methoxynorbornene (Ia, R = Me) and endo-tricyclo[3.2.0.0^{2,7}]hept-6-yl methyl ether (II, R = Me), identified by its characteristic n.m.r. spectrum^{1c}. Treatment of the anti-tosylate (Ia, X = OTs) under identical conditions forms a mixture (73% yield) of the same products in virtually identical (63:37) proportions. Thus, product studies of the S_N1 solvolysis of the aforementioned substrates yield identical findings, all three yielding only products derivable from the 7-norbornenyl cation. The norbornenyl and tricyclic substrates are thought to form this cation directly upon solvolysis^{1,4}. Our kinetic studies show that the new π -route (solvolysis of IIIa, X = OTs) is somewhat more circuitous.



Our exo- and endo-tosylates (IIIa, X = OTs; IIIb, Y = OTs) undergo S_N1 acetolysis (50.0°) at appreciably different rates, the exo-tosylate ($k = 1.9 \pm 0.1 \times 10^{-4} \text{ sec}^{-1}$) being ca. 2400 times more reactive than the endo-tosylate ($k = 8 \times 10^{-8} \text{ sec}^{-1}$). This indicates significant, but not dramatic participation of the homoallylic double bond during solvolysis of the exo-isomer, and is consistent with initial formation of an unrearranged bridged cation (IIIId), analogous in structure to the 2-norbornenyl cation (IVc; $k_{\text{IVa}}/k_{\text{IVb}} = 7000$)^{9,10}. We also note that Whitham¹¹ has shown that acetolysis of exo-4,4,6-trimethylbicyclo[3.2.0.]hept-6-en-2-yl tosylate (IIIc, X = OTs) yields a small but significant amount of the corresponding unrearranged acetate (IIIc, X = OAc) along with a high yield of the ring-enlarged acetate (Ib). A comparison of relative rates of solvolysis of the pertinent substrates corrected for differences in leaving group follows: (relative rates in parentheses)



A summary of approximate free energy relationships is provided as follows: In elegant kinetic and thermodynamic treatments of data from the solvolysis of 7-norbornenyl and tricyclic substrates (differing in energy by ca. 12.7 kcal)^{1c}, Winstein^{1c,4b} found that the transition state from solvolysis of anti-7-norbornenyl derivatives (Ia) ranged from 3.4 kcal lower to 3.5 kcal higher than that from tricyclic derivatives (II), depending on the nature of the leaving group, solvent, etc.. Assuming that our exo-tosylate (IIIa, X = OTs) is ca. 14.5 kcal higher in energy than is anti-7-norbornenyl tosylate (the free energy difference observed for the saturated analogs, V and VI)¹², then our data shows a significant energy difference in the solvolytic transition states for these substrates. Calculation directly from published^{1a} activation parameters yields a free energy of activation (ΔG^\ddagger) for acetolysis of anti-tosylate (Ia, X = OTs) at 50° of 21.5 kcal. The corresponding value for acetolysis of exo-tosylate (IIIa, X = OTs), calculated from our kinetic data, is 24.4 kcal. Thus, the solvolytic transition state for exo-tosylate is higher in energy than that for anti-tosylate by ca. 18-19 kcal. It is unlikely that solvolysis of substrates having transition states differing so dramatically in energy could proceed via pathways involving direct formation of a common intermediate. We conclude, therefore, that solvolysis of exo-tosylate (IIIa, X = OTs) proceeds by a pathway involving sequential formation of two discrete ions (IIIId and Ic). If this is, indeed, the case, then rearrangement of the first cation (IIIId) to the 7-norbornenyl cation (Ic) is exceedingly rapid, being virtually complete before reaction with solvent, or added strong nucleophile can occur to any measurable extent. Considering the extremely short lifetimes carbocations possess in conventional solvolysis media, plus the complete quenching of such rearrangements noted previously in the solvolysis of some closely related substrates¹³, this is, indeed, remarkable.

ACKNOWLEDGEMENT. We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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