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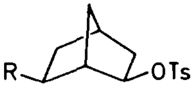
EPIMERIC 2-NORBORNYL CATIONS IN THE SOLVOLYSIS OF 6-exo- AND 6-endo-SUBSTITUTED 2-exo-NORBORNYL p-TOLUENESULFONATES

Cyril A. Grob*, Bettina Günther, Reinhard Hanreich & Adrian Waldner,
Institute of Organic Chemistry, University of Basel,
St. Johanns-Ring 19, CH-4056 Basel, Switzerland.

Summary. Solvolysis of 6-exo- and 6-endo-substituted 2-exo-norbornyl tosylates 1 and 3, respectively, yields identical or different product mixtures depending on the inductive effect of the substituent, indicating that induction involves graded σ-participation.

As recently reported, 6-exo-substituents control the solvolysis rates of 2-exo- and 2-endo-norbornyl tosylates, 1 and 2, respectively, by their inductive effects, unless the substituents are electrofugal groups (σ-electron donors) which give rise to elevated rates. In all cases, however, polar effects are transmitted more strongly in the 2-exo- series 1 than in the 2-endo- series 2 [1]. Also, hydrolysis of 1 and 2 leads to a wider range of products than is often assumed [2].



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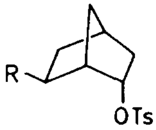

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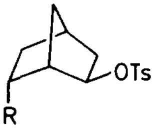

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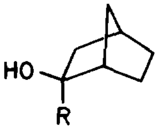
In continuation of these studies a series of 6-endo-substituted 2-exo-norbornyl tosylates 3, b - h, (TABLE) has been prepared in order to compare the effects of 6-endo substituents upon rates and products with those of the 6-exo substituents in 1, b - h. This comparison has provided a deeper insight into the nature of 2-norbornyl cations.

C(6)-epimeric pairs of 1 and 3, b, c and d [3], reacted at similar rates in 80% ethanol, as shown by the ratios k 1/k 3 in the TABLE. Also, when reacted in 70% aqueous dioxane, each pair of epimers led to identical ratios of products [4], which, TABLE. First order rate constants (s^{-1}) in 80 vol. % ethanol at 70.0° C.

	R =	1 (6-exo-R)	3 (6-endo-R)	k1/k3
a)	H	3.58×10^{-2}	3.58×10^{-2}	1
b)	CH_3	1.09×10^{-2}	5.58×10^{-3}	1.95
c)	$(CH_3)_2CH$	2.46×10^{-2}	4.32×10^{-3}	5.7
d)	$(CH_3)_3C$	6.09×10^{-2}	3.40×10^{-2}	1.8
e)	CH_2Br	1.06×10^{-4}	2.74×10^{-4}	0.39
f)	F	7.67×10^{-7}	4.68×10^{-7}	1.64
g)	Br	1.51×10^{-7}	1.95×10^{-7}	0.77
h)	CN	1.23×10^{-7}	4.33×10^{-8}	2.84

consequently, have a common origin. These products consisted mainly of tertiary exo-alcohols 4 and the olefins 5 and 6 (total > 50%) beside the secondary 6-exo-2-exo-alcohols 7 and small amounts (< 2%) of the 6-endo epimers 8 [5]. Therefore, extensive C(1)→C(2) carbon and C(6)→C(2) hydrogen shifts must occur in these reactions [6].



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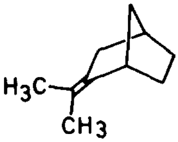

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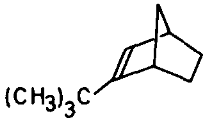

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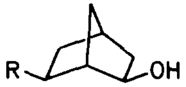

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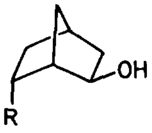

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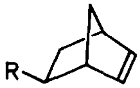

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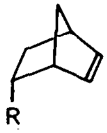

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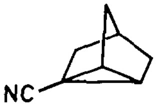

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The epimeric pairs 1 and 3, e - h, also reacted at similar rates (TABLE) and again showed no clear directional effect of R [7]. In contrast to the above series, however, widely different amounts of rearranged and unrearranged alcohols 7 and 8 and of the olefins 9 and 10 were obtained from each pair of epimers. But none of these products resulted from a C(6)→C(2) hydride shift. Furthermore, the cyano derivatives 1h and 3h yielded 44 % and 78 %, respectively, of the nortricyclene 11. Consequently, the products of the C(6)-epimers 1 and 3, e - h, do not have identical precursors, as do 1 and 3, a - d. It is also noteworthy that the logarithms of the

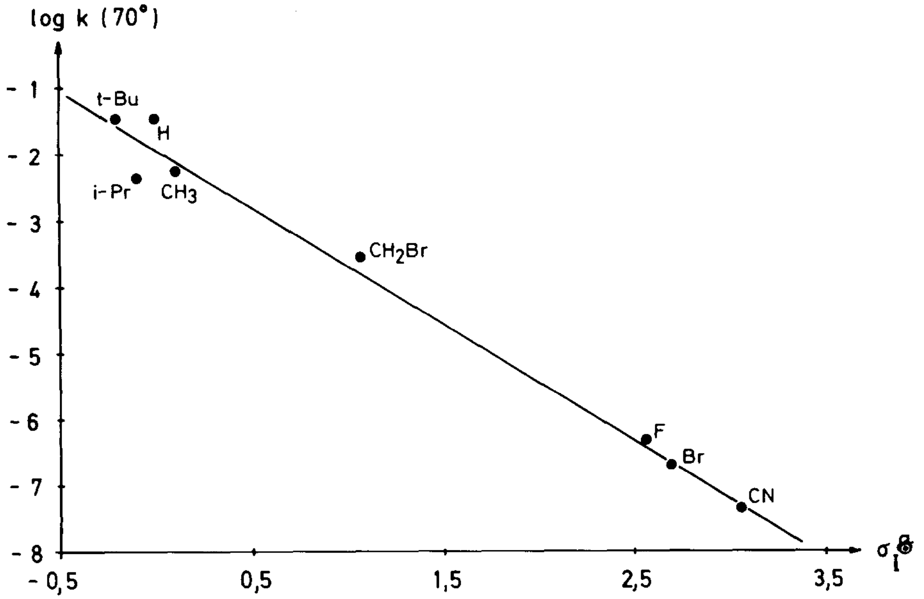
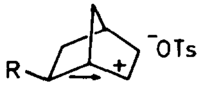


FIGURE. Plot of log k for 6-endo-substituted 2-exo-norbornyl tosylates 3 against inductive substituent constants σ_I^q.

rate constants for 3a - 3h correlate linearly with the inductive substituent constants σ_I^q of R [8] (FIGURE), as was the case with 1a - 1h [1], leading to reaction constants ρ of -1.76 and -2.0, respectively. Rate control by the inductive effect of R is therefore indicated in both series.



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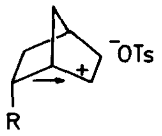

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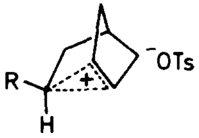

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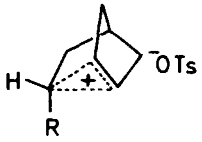

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If the relative rates of 1 and 3, a - h, reflect graded shifts of the R-C(6)-C(1) electrons towards C(2) in the transition state [9], they should also reflect varying degrees of bonding between C(6) and C(2) in the resulting epimeric ion pairs 12 and 13, as indicated by horizontal arrows. Such bonding is usually referred to as bridging or σ-participation [10] and symbolized by dotted lines, as in 14 and 15. The latter, however, are enantiomers and are unlikely to be symmetrically bridged if R is not hydrogen [11]. The fact that 1 and 3, e - h, yield different products proves that their intermediates are epimers 12 and 13 and not enantiomers. On the other hand, the formation of identical product mixtures from 1 and 3, a - d, shows that the energy barrier separating 12 and 13 [12] is so far lowered that their interconversion by a 1,2 carbon shift becomes faster than all subsequent reactions, i.e. C(6)→C(2) hydride shifts and reactions with solvent. The interconversion of the epimers 12 and 13 then likens a skeletal vibration, their chemical behaviour becoming indistinguishable from that of the enantiomers 14 and 15.

REFERENCES

1) W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner, Tetrahedron Letters 1979, 473, 1901, 1905.

2) W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner, Helv. Chim. Acta 63, 928 (1980).

3) 1 and 3 are racemates, only one enantiomer being shown; 1a and 3a are identical.

4) Determined by capillary gas chromatography on a carbowax 20 M-coated column; yields reproducible to ± 1.5% in at least two separate solvolyses.

5) The products from 1b listed in 2) are in error.

6) C(6)→C(2) hydride shifts were first detected by J.D. Roberts, C.C. Lee & W.H. Saunders, J. Am. Chem. Soc. 76, 4501 (1954).

7) Similar rates were also observed for 5-exo- and 5-endo-cyano-2-exo-norbornyl brosylates by Y. Apeloig, D. Arad, D. Lenoir & P. von R. Schleyer (private communication).

8) C.A. Grob, B. Schaub & M.G. Schlageter, Helv. chim. acta 63, 57 (1980).

9) C.A. Grob & A. Waldner, Tetrahedron Letters 1980, 4433.

10) see "The Nonclassical Ion Problem" by H.C. Brown with comments by P. von R. Schleyer; Plenum Press, New York 1977.

11) Symmetrical and unsymmetrical bridging has been discussed recently by P. von R. Schleyer, D. Lenoir, P. Mison, G. Liang, G.K. Surya Prakasch & G.A. Olah, J. Am. Chem. Soc. 102, 683 (1980).

12) Actually the enantiomer of formula 13.

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