Tetrahedron Letters, Vol.22, No.34, pp 3231 - 3234, 1981
Printed in Great Britain

0040-4039/81/343231-04$02.00/0

BRIDGED AND UNBRIDGED NORBORNYL CATIONS

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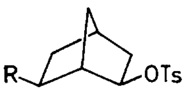
Summary. The solvolysis rates and products of 6-substituted 2-norbornyl-p-toluenesulfonates 1 and 5 are controlled by 1,3-bridging, i.e. by the degree of bonding between C(6) and C(2) in the intermediate norbornyl cations.

The unusual sensitivity of the solvolysis rates of 2-exo-norbornyl tosylates 1 to substituents at C(6) indicates a strong interaction of the latter carbon atom with the incipient cationic center at C(2). Thus, in 80 vol. % ethanol the sodium salt of 1, R = COONa, reacted ca. 500'000 times as fast as the bromide, R = Br [1]. This rate difference was attributed to graded electron shifts leading to partial bonding or 1,3-bridging of C(6) and C(2), as in 2 and 3, when R was a σ-electron donor and little or no bonding as in 6 when R was a σ-electron acceptor [2]. In contrast to 1 the rates of the 2-endo-tosylates 5, R = COONa and Br, differed by only 286 [1], a sign that 1,3-bridging is far less advanced in the transition state for the sickle-like tosylates 5 than in the case of the W-like tosylates 1.



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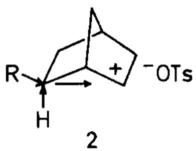

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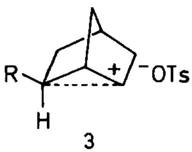

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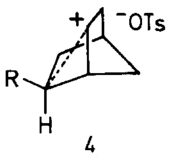

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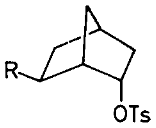

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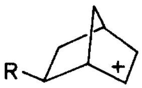

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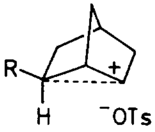

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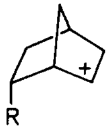

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TABLE 1

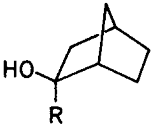
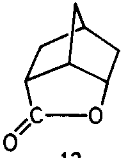
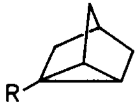
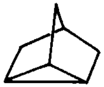
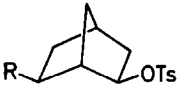
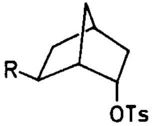
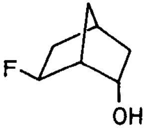
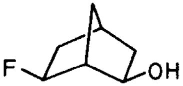
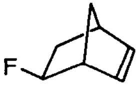
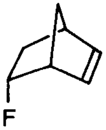
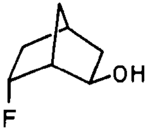
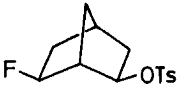
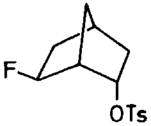
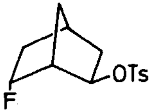
% yield from : R = COONa	 11	 12	 13	 14	 15
 9	40	20	8	13	12
 10	50	21	3	20	3

TABLE 2

% yield from :	 19	 20	 21	 22	 23
 16	57	9	24	3	
 17	7	87	4	2	
 18	4	5		81	5

According to this view 1,3-bridging should accelerate the reversible rearrangement of 3 to the epimeric cation 4, as already observed for R = alkyl [3], since rearrangement involves only a tightening of the C(6)-C(2) bond and a loosening of the C(6)-C(1) bond. In addition, 1,3-bridging should favor the formation of 2-exo-substitution products from 3 and 4. Conversely, unbridged 2-norbornyl cations 6 should show less tendency to rearrange and should tend to form 2-endo-substitution products also. These conclusions are supported by the following comparison of the rates and products of the sodium salts 9 and 10 (TABLE 1) and the fluorides 16, 17 and 18 (TABLE 2).

The exo-tosylate 9 reacted 607 times as fast as the endo-epimer 10 [1]. When hydrolyzed in 70 % dioxane both compounds led to different yields of the same products (TABLE 1), as is commonly observed in reactions via stereoisomeric ion pairs such as 3 and 7, respectively [5]. The main products formed were the exo-alcohols 11 and 12, the latter by way of a 1,3-hydride shift. The lactone 13, undoubtedly formed by endo-cyclization of the rearranged cation 4, R = COO^-, accounted for 8 % of the products. The fact that 13 is formed at all indicates that the bonding between C(6) and C(2) is not strong enough to prevent endo attack at C(2).

Formation of nortricyclane carboxylic acid 14 and nortricyclane 15 from 9 and 10 involves loss of a proton (1,3-elimination) and loss of CO_2 (homofragmentation), respectively, from 3 and 4, R = COONa. These reactions are of special interest because they imply prior 1,3-bridging and concomitant loosening of the bonds to the substituents at C(6) in these cationic intermediates.

The rate ratios for the exo- and endo-tosylates 1 and 5 with the electron withdrawing substituents Br and F are 0.37 and 0.48, respectively [1,6]. These low ratios indicate that 1,3-bridging is not important in the transition state for the solvolysis of these tosylates. Unfortunately, it was not possible to determine accurately the products derived from the bromides because the first-formed bromo-alcohols and bromoolefins underwent secondary reactions, viz. fragmentation and homoallylic rearrangement [4]. These complications did not arise in the solvolysis of the fluorides 16, 17 and 18 in 70 % dioxane (TABLE 2), the decisive result being the high yield (57 %) of the endo-alcohol 19 from 16. In the case of 17 and 18 the yields of 19 were much lower, viz. 7 and 4 %, respectively. These results constitute strong evidence that 1,3-bridging is at least as important a factor in controlling the direction of attack on 2-norbornyl cations as a steric effect [7,8].

TABLE 2 also confirms the low tendency of the cations 6 and 8, R = F, to rearrange, since 16 and 17 yield 90 % and 98 %, respectively, of the exo-fluorides 19, 20 and 21, whereas 18 led to 86 % of the endo-fluorides 22 and 23.

REFERENCES

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

2) C.A. Grob & A. Waldner, ibid. 1980, 4433.

3) C.A. Grob, B. Günther, R. Hanreich & A. Waldner, ibid. 1981, 835.

4) W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner, Helv. chim. acta 63, 928 (1980). The yields listed in TABLE 1 differ considerably from those previously reported in ref. 4) because a much improved gas chromatographic technique was employed.

5) K.B. Becker & C.A. Grob, Helv. chim. acta 56, 2723, 2733, 2747.

6) The rate constants for 16 and 17 in 80 vol. % ethanol at 70.0° are 7.21×10^{-7} and 1.50×10^{-6} $\sec^{-1}$, respectively.

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

8) For reasons given elsewhere unsymmetrical bridging, as in 3, is preferred to symmetrical bridging as originally proposed by S. Winstein (see ref. 7).

(Received in Germany 21 May 1981)