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UNUSUAL REACTIVITY OF NORBORNANE BRIDGEHEAD DERIVATIVES

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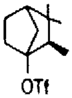
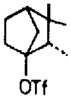
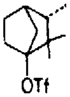
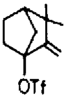
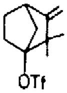
Summary - The solvolysis of 2,2,3- and 2,3,3-trimethyl substituted 1-norbornyl triflates **1** and **6** in 60% aqueous ethanol at 60°C proceeds via novel σ-bridged carbocations affording products mainly from hitherto unknown Wagner-Meerwein rearrangement and fragmentation reactions, respectively.

The low solvolysis rate of norbornane bridgehead derivatives has been shown to be due to the nonplanar structure of the corresponding intermediate carbocations.[1] Only by using the very reactive trifluoromethanesulfonate (triflate) group,[2] it was possible to achieve a k_c solvolysis of these substrates, which only gave unrearranged products.[3]

We report here the unusual solvolyses of bridgehead triflates **1** and **6**, which in contrast to other solvolysis reactions of bridgehead triflates afforded mainly extensive fragmentation and rearranged products. The triflates **1** and **6** were prepared by Pd-catalyzed hydrogenation of the triflates **11** and **14**,[4] respectively.

The triflates **1** and **6** (as a mixture of exo- and endo-isomers) were solvolyzed in 60% aqueous ethanol. Their rates of solvolysis are given in Table 1 in comparison with those of unsaturated bridgehead triflates. As shown in Table 2 exo-/endo-1 form the fragmented products **2** and **3** (65%), while 24% solvolyzed in the presence of triethylamine as base with retention of the original structure (**4** and **5**). The exo-/endo-6 solvolyzed up to 84% to form rearranged products **7** and **8** (with ring contraction) and 10% with retention of structure. Under the same conditions, the unsaturated bridgehead triflates **11** and **14**, reacted relatively slowly (Table 1) with formation of the corresponding unrearranged alcohols (**12**, **15**) and ethers (**13**, **16**).[4]

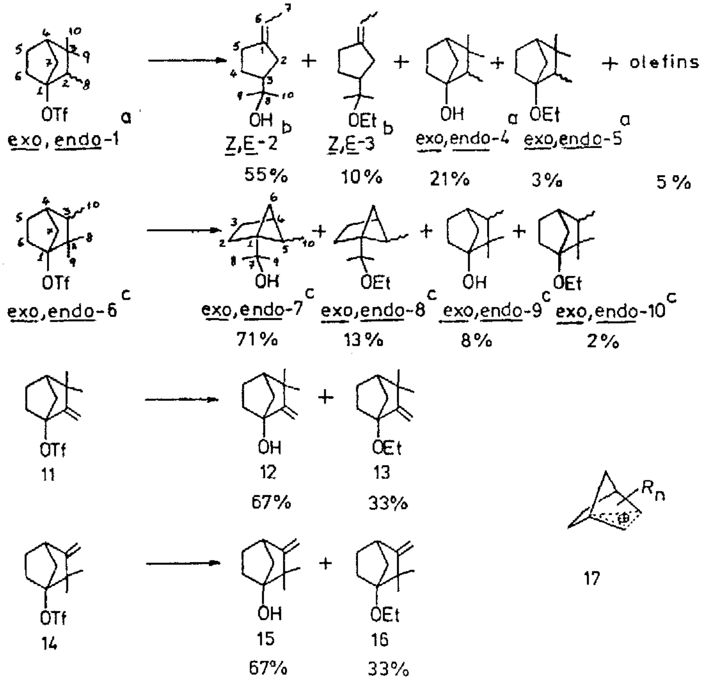
Table 1 Rate of Solvolysis of Bridgehead Derivatives in Buffered (Et_3N) Aqueous 60% Ethanol.

Triflate		Temp. (°C)	$k(s^{-1})$	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$(eu)	Ref.
exo-1		38.1	1.85×10^{-5}	22.9	-6.3	this work
		48.0	6.24×10^{-5}			
		58.0	1.73×10^{-4}			
		80.3	1.61×10^{-3}(a)			
endo-1		38.1	1.17×10^{-5}	23.3	-6.4	this work
		48.0	2.75×10^{-5}			
		58.0	1.14×10^{-4}			
		80.3	9.63×10^{-4}(a)			
endo-6		20.1	1.06×10^{-4}	20.4	-7.0	this work
		30.0	3.10×10^{-4}			
		40.1	1.00×10^{-3}			
		80.3	4.11×10^{-2}(a)			
exo-6		20.1	1.33×10^{-5}	21.3	-8.0	this work
		30.0	3.30×10^{-5}			
		40.1	1.40×10^{-4}			
		80.3	6.36×10^{-3}(a)			
11		80.3	2.50×10^{-5}	-	-	4
14		80.3	7.00×10^{-5}	-	-	4
18		80.3	2.20×10^{-5}(a)	28.9	-0.8	3
19		80.3	ca. 2.2×10^{-5}(a)		-	3

(a) extrapolated

As seen from Table 1, the bridgehead triflates 1 and 6 reacted about 13 - 550 times faster than the bridgehead triflates 11, 14, 18[3] and 19[3], which solvolyzed without formation of any rearranged products. The high solvolysis rate of 1 and 6, together with the fragmentation and rearrangement reactions observed, points to σ-participation of the C_2-C_3 bond during cleavage of the C-OTf bond.

Table 2 Solvolysis Products of Bridgehead Derivatives 1 and 6 in Buffered (Et_3N) Aqueous 60% Ethanol at 60°C for 24 h[5]



a) exo/endo = 68/32

b) Z/E = 69/31

c) endo/exo = 83/17

The driving force for σ-participation during the ionization process seems due mainly to the stabilization of the positive charge at the quarternary carbon atom, C-3 for 1 and C-2 for 6. In accordance with this, the solvolysis of 1 proceeds via fragmentation, while triflate 6 undergoes a new type of Wagner-Meerwein rearrangement with ring contraction. The generation of a positive charge at C-2 or C-3 during the solvolysis of triflates 11 and 14 is more difficult, because the fragmentation of **11** should lead to an allene and the rearrangement of **14** should take place with migration of a vinylic C-C bond.

Neither the fragmentation nor the rearrangement reaction of **1** and **6**, respectively, can proceed synchronously with the ionization step, since the bridgehead alcohols **4**, **9** and the bridgehead ethers **5**, **10** are found among the reaction products. Hence the bridgehead cation **17** stabilized by σ-participation is proposed as an intermediate to explain the rates and products of the solvolysis reaction of **1** and **6**. The position and number (n) of substituents R in the bicyclic compounds determine the charge density at C-1, C-2 and C-3 and hence the product distribution.

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2. T.M. Su, W.F. Sliwinski, P.v.R. Schleyer, J. Am. Chem. Soc. **91**, 5786 (1969).
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4. A. García Martínez, M. Gómez Marín, L.R. Subramanian, An. Quím. **74**, 972 (1978).
5. All the products were separated by preparative GC and were characterized by their spectral data. ^{13}C-NMR ($CDCl_3$/TMS,δ) of some separated new products are given below: Z/E-**2**: 142.7 (C-1); 114.2 (C-6); 71.3 (C-8); 50.9 (C-3); 34.5 (E-C-2); 33.1 (Z-C-2); 29.7, 27.0 (Z-C-4,5); 28.1, 26.6 (E-C-4,5); 27.7 (C-9,10); 14.3 (Z-C-7); 14.1 (E-C-7). exo-**4**: 83.2 (C-1); 50.1 (C-2); 45.3 (C-4); 41.8 (C-3); 40.0, 36.0, 25.0 (CH_2); 28.0 (exo-C-10); 24.6 (endo-C-9); 11.4 (exo-C-8). endo-**8**: 74.7 (C-7); 60.4 (C-1); 56.9 (OCH_2); 41.0 (C-4); 38.1 (C-5); 38.0, 24.8, 23.1 (CH_2); 23.0, 22.2 (C-8, 9); 16.4 (OCH_2CH_3), 11.5 (endo-C-10). exo-**10**: 90.6 (C-1); 60.3 (OCH_2); 49.1 (C-4); 40.4 (C-3); 36.1, 29.6, 24.6 (CH_2); 33.0 (C-2); 25.9 (exo-C-8); 20.0 (endo-C-9); 16.1 (exo-C-10); 15.9 ($OCH_2\underline{C}H_3$).

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