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Spatial Orientation Effects on the σ-Assistance in the Solvolysis of Methyl Substituted 1-Norbornyl Triflates

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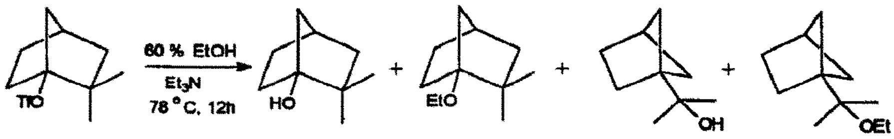
Abstract: The σ-participation of the C_2-C_3 and C_4-C_7 bonds in the solvolysis of methyl substituted 1-norbornyl triflates is evaluated by application of the additivity principle. It is concluded that the σ-participation of the C_2-C_3 bond is dependent on the spatial orientation of methyl substituents.

We have shown that the solvolysis of 2,2,3-, 2,3,3- and 4,7,7-trimethyl substituted 1-norbornyl triflate in 60% aqueous ethanol at 80 °C proceeds with σ-participation of C_2-C_3 and C_4-C_7 bonds, respectively.[1,2] In order to achieve an estimation of the magnitude of the σ-assistance in the solvolysis of 1-norbornyl triflate, we report here on the application of the additivity principle (AP)[3] to this subject. For this purpose we have prepared[4] *exo*- and *endo*-2-methyl-1-norbornyl triflate (**3** and **4**), 2,2-dimethyl-1-norbornyl triflate (**5**) and 3,3-dimethyl-1-norbornyl triflate (**6**). The rate constants *k* of the solvolysis in 60% aqueous ethanol are given in Table 1. The solvolysis of **3**, **4** and **6**, like the solvolysis of **1**, **2** and **7**, yield only the corresponding bridgehead alcohols (~60%) and ethers (~40%). However, the solvolysis of **5**, like **8**, **9** and **10**, affords a mixture of unrearranged **11** + **12** and ring-contracted products **13** + **14** (Scheme).[5] The product ratios were determinated by GC (OV-101, 25m, 150 °C). All compounds were characterized by MS, IR, ^{1}H- and ^{13}C-NMR spectral analyses.



5 **11** (10 %) **12** (4 %) **13** (65 %) **14** (21 %)

Scheme

Table 1. Rate Constants of Solvolysis of 1-Norbornyl Triflates in Buffered (Et_3N) 60% Aqueous Ethanol.

Triflate		Temp.(°C)	$k(s^{-1})^{a}$	$\Delta H^{\neq}$(Kcal/mol)	$\Delta S^{\neq}$(eu)	ΔE_{st}(Kcal/mol)	k_r(at 80.3°C)	Ref.[b]
1		80.3	1.08×10^{-5}	26.8[c]	-2.5[c]	1.3	1.0	2
2		80.3	4.04×10^{-5}	28.9	2.4	1.3	3.7	2
3		100.5 90.4 80.3	1.97×10^{-4} 6.21×10^{-5} 2.07×10^{-5}	28.4	2.3	1.5	1.9	tw
4		100.5 90.4 80.3	3.20×10^{-4} 1.08×10^{-5} 3.43×10^{-5}	28.2	2.7	0.5	3.2	tw
5		80.3 70.0 59.0 50.0	1.65×10^{-3d} 5.30×10^{-4} 1.45×10^{-4} 4.97×10^{-5}	26.1	2.2	0.1	153.1	tw
6		90.4 80.3 70.0	7.41×10^{-4} 3.10×10^{-4} 7.00×10^{-5}	28.7	5.5	1.7	28.7	tw
7		80.3	1.59×10^{-5}	28.9	-0.8	2.2	1.5	2
8		80.3	1.61×10^{-3d}	22.9	-6.3	1.4	149.0	1
9		80.3	9.63×10^{-4d}	23.3	-6.4	0.2	89	1
10		80.3	3.57×10^{-4}	26.3	1.4	2.1	33.0	2

[a] Determined by GC (experimental error ±5%). [b] tw= This work. [c] In 50% aqueous ethanol. [d] Extrapolated from other temperatures

The AP asserts that the molar values of a property are additive functions of independent contributions assignable to part-structures of the molecule. The AP is based on the tendency of such quantities as the standard free energy to be additive functions of molecular structure.[3]

The application of the AP to the solvolysis of **5**, **8-10** leads to equation [1]:

$$\ln(k_n/k_0)=\sum_{i=1}^{n-1}\ln k_{r_i}$$

where k_n represents the calculated solvolysis rate for a substrate with n methyl groups ($n = 2$ or 3), k_{ri} is the relative solvolysis rate (k_r in Table 1) of related substrates with i methyl groups ($i = 1$ or 2). The calculated k_n and the basis substrates are shown in Table 2.

Table 2. Calculated Solvolysis Rates (k_n) at 80.3 °C

Triflate	n	k_n(s^{-1})^a	Substrates for k_{ri}	k/k_n^{a}	$\Delta\Delta G^{\neq}$($\pm$0,15 Kcal/mol)^b
5	2	6.57x10^{-5}	**3** + **4**	25.10	-2.26
8	3	5.89x10^{-5}	**3** + **6**	2.73	-0.70
9	3	9.92x10^{-4}	**4** + **6**	0.97	+0.02
10	3	5.59x10^{-5}	**2** + **7**	6.39	-1.30

^{a}Experimental error ±10-15%. ^{b}$\Delta\Delta G^{\neq} = RT\ln k_n/k$

The AP is only fulfilled in the case of the solvolysis of **9**, because the calculated solvolysis rate k_n agrees with the observed k. The observed rate constants of all the other triflates are higher than the calculated pointing to the existence of an accelerating term[3] ($\Delta\Delta G^{\neq}$)(Table 2). The lack of relationship between ln$k$ and ΔE_{st}[6] (Table 1) excludes any significative contribution of steric effects (F- and B-strain) to the interaction term. Thus, the interaction terms observed in the cases of **5**, **8** and **10** are due to enhanced σ-assitance of the C_2-C_3 and C_4-C_7 bonds, respectively.[1,2] The solvolysis of these substrates takes place with formation of σ-bridged carbocations as intermediates,[1,2] which are stabilized in relation to the corresponding classical cations for at least the term $\Delta\Delta G^{\neq}$ (Table 2).[7] Indeed, the total σ-participation of a bond, σ, is given by $\sigma = \Delta\Delta G^{\neq} + \Sigma\sigma_i$, where σ_i is the σ-participation in the basis substrates. The $\Sigma\sigma_i$ can reach the necessary threshold to provoke a rearrangement. This seems to be the case for **9**.[1]

The different interaction terms observed in the cases of **8** and **9** show that the σ-assistance of the C_2-C_3 bond is dependent not only on the number and position of the methyl groups, but also on their configuration. The very different solvolysis rates of *endo*- and *exo*-2,2,3-trimethyl-1-norbornyl triflates[1] (k_r = 3805 and 589, respectively) can also be attributed to a spatial effect on the σ-assistance. Further work on the nature of this until now unknown[8] effect is under progress.

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References and Notes

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2. García Martínez, A.; Osío Barcina, J.; Rodríguez Herrero, M. E.; Iglesias de Dios, M.; Teso Vilar, E.; Subramanian, L. R. *Tetrahedron Lett.* **1994**, *35*, 1793. In this reference an extrapolated value for the rate of **7** (2.20x10^{-5} s^{-1}) instead of the correct experimental value (1.59x10^{-5} s^{-1})was given erroneously.
3. For a very good discussion of the AP, see: Leffer, J. E.; Grundwald, E. *Rates and Equilibria of Organic Reactions*; Wiley, New York,1963.
4. The triflates **3** and **4** were prepared by catalytic reduction of 2-methylidene-1-norbornyl triflate, and **5** and **6** from 2,2-dimethyl-3-oxo-1-norbornyl triflate and 2-oxo-3,3-dimethyl-4-norbornyl triflate, respectively. ^{13}C-NMR (75 MHz, CDCl$_3$, TMS): **3**: δ= 118.00 (q, CF$_3$); 103.62 (C$_1$); 39.02 (C$_7$); 38.05 (C$_2$); 37.15 (C$_3$); 33.06 (C$_4$); 31.43 (C$_6$); 29.17 (C$_5$); 18.05 (CH$_3$) ppm. **4**: δ= 118.00 (q, CF$_3$); 103.89 (C$_1$); 41.93 (C$_7$); 37.37 (C$_2$); 37.30 (C$_3$); 32.61 (C$_4$); 29.05 (C$_6$); 25.86 (C$_5$); 13.80 (CH$_3$) ppm. **5**: δ= 118.07 (q, CF$_3$); 105.81 (C$_1$); 45.87 (C$_3$); 39.13 (C$_2$); 39.07 (C$_7$); 31.84 (C$_5$); 28.44 (C$_6$); 28.19 (C$_4$); 27.13 (*exo*-CH$_3$); 23.66 (*endo*-CH$_3$) ppm. **6**: δ= 118.00 (CF$_3$); 100.50 (C$_1$); 49.00 (C$_2$); 42.93 (C$_4$); 41.53 (C$_7$); 37.98 (C$_3$); 31.71 (C$_6$); 30.90 (*exo*-CH$_3$); 26.96 (C$_5$); 25.08 (*endo*-CH$_3$) ppm.
5. Examples of ^{13}C-NMR: ^{13}C-NMR (75 MHz, CDCl$_3$, TMS): **11**: δ= 85.66 (C$_1$); 46.96 (C$_3$); 42.01 (C$_7$); 33.22 (C$_2$); 30.62 (C$_6$); 29.70 (C$_5$); 29.61 (C$_4$); 27.07 (*exo*-CH$_3$); 23.94 (*endo*-CH$_3$) ppm. **12**: δ= 90.01 (C$_1$); 60.82 (-O-CH$_2$-); 48.27 (C$_3$); 39.33 (C$_7$); 31.35 (C$_2$); 29.81 (C$_4$); 29.44 (C$_6$); 27.84 (C$_5$); 25.68 (*exo*-CH$_3$); 25.57 (-O-CH$_2$-$\underline{C}$H$_3$); 16.37 (*endo*-CH$_3$) ppm. **13**: δ= 71.16 (-C-OH); 60.00 (C$_1$); 37.81 (C$_5$, C$_6$); 34.92 (C$_4$); 28.79 (C$_3$); 27.22 (C$_2$); 25.75 (CH$_3$) ppm. **14**: δ= 74.54 (-$\underline{C}$-OEt); 59.49 (C$_1$); 57.56 (-O-$\underline{C}$H$_2$-); 39.50 (C$_5$, C$_6$); 35.38 (C$_4$); 28.43, 26.65 (C$_3$, C$_2$); 22.49 (CH$_3$); 16.46 (-O-CH$_2$-$\underline{C}$H$_3$) ppm.
6. ΔE_{st} is the difference between the steric energies of the carbocation and the corresponding triflate calculated with the MMX program. Eksterowicz, J. E.; Houk, K. N. *Chem. Rev.* **1993**, *93*, 2439.
7. For comparison, the σ participation in the 2-norbornyl cation amounts to ca. 5 Kcal/mol: Sieber, S.; Schleyer, P. v. R. *Angew. Chem.* **1993**, *105*, 1673.
8. For related effects, see: Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.

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