Pergamon

Tetrahedron Letters, Vol. 35, No. 11, pp. 1793-1796, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0144-M

σ-Assistance of the C_4-C_7 Bond in the Solvolysis of 1-Norbornyl Triflates

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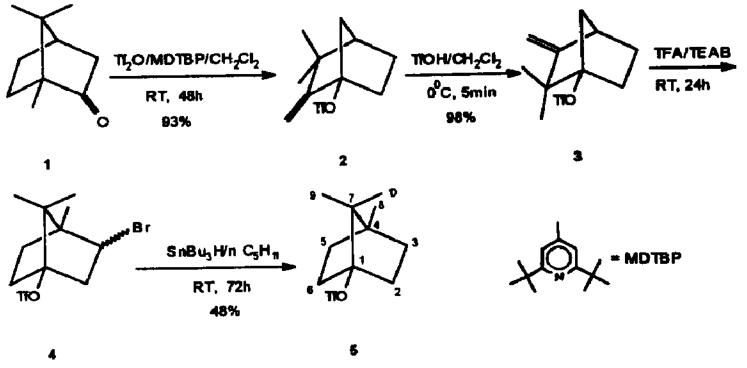
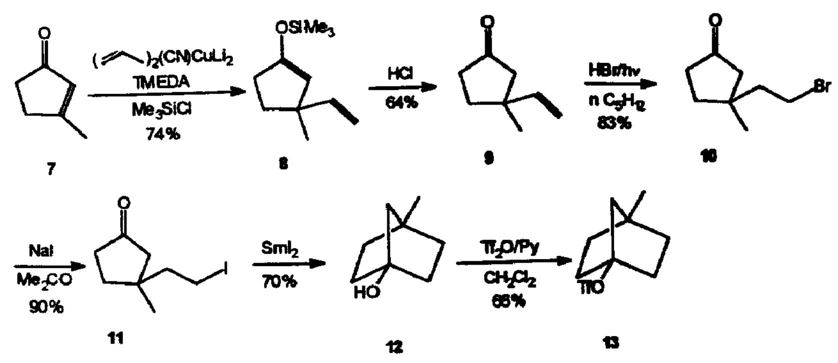
Abstract: The solvolysis of 4,7,7-trimethyl-1-norbornyl triflate (**5**) proceeds under σ-participation of the C_4-C_7 bond, with formation of the σ bridged cation **22** as intermediate.

The interpretation of the rate constants of the solvolysis of bridgehead derivatives is a topic of standing interest in physical organic chemistry.[1] In a previous publication,[2] we have reported that the solvolysis of *exo*- and *endo*-2,2,3- and 2,3,3-trimethyl-1-norbornyl triflates in 60% aqueous ethanol at 80°C proceeds with σ-participation of the C_2-C_3 bond. In order to investigate the hitherto unknown σ-assistance of the C_4-C_7 bond, we have synthesized 4,7,7-trimethyl-1-norbornyl triflate (**5**)[3] (Scheme 1) and 4-methyl-1-norbornyl triflate (**13**)[4] (Scheme 2).

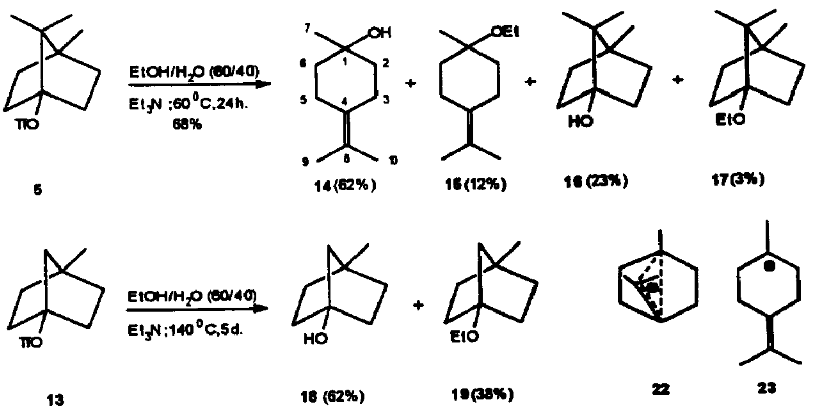
Solvolysis of a 2.5×10^{-2}M solution of **5** in 60% aqueous ethanol with triethylamine as buffer (5.0×10^{-2}M) affords a mixture of terpinyl (**14** + **15**)[5] and bornyl (**16** + **17**)[5] compounds in 2.8:1 ratio, determined by GC (OV-101, 25m, 150°C) (Scheme 3). Thus, the reaction proceeds mainly with fragmentation of the C_4-C_7 bond. Such fragmentation has not been observed until now. The solvolysis of a 2.5×10^{-2}M solution of **13** in the same solvent as in the case of **5**, yields only products with structural retention[5] (Scheme 3).



Scheme 1



Scheme 2



Scheme 3

The solvolysis rates of **5** and **13** (2.5 x 10^{-4}M) in 60% aqueous ethanol buffered with triethylamine (5.0 x 10^{-4}M) were determinated by GC using *trans*-2-decalone as internal standard (Table 1). The rates of 7,7-dimethyl-1-norbornyl triflate (**20**)[6] and 1-norbornyl triflate (**21**)[6,7] were measured under the same conditions in order to obtain reference values for the acceleration of **5** and **13**. The k values for **20** and **21**, extrapolated from literature data[6,7] are shown in Table 1 for comparison; the m value for **21** ($m = 0.72$) was calculated from the rates in acetic acid and 50% aqueous ethanol at 100°C. In agreement with the results reported in the literature,[6,7] the solvolysis of **20** and **21** takes place without rearrangement.

The lacking relationship between k (log k) and ΔE_{st}[8] or E_r[9] (Table 1) exclude any significant contribution of steric effects to the relative solvolysis rates (k_r, Table 1) of our substrates because every steric assistance to ionization should induce a decrease of ΔE_{st} and/or an increase of E_r.

The magnitude of the acceleration (k_r) in the case of **13** and **20** is in agreement with the acceleration effected by the introduction of methyl groups in some rigid bi- and polycyclic compounds,[1a,10] although methyl groups usually exert a slight decelerating effect on the solvolysis of these substrates.[10a,11] The actual value of the methyl effect can be explained by their σ- and π-interactions with the HOMO of the carbocation,[10a] changes of charge density and hybridization of the parent compound[12] and through-space interactions.[13] However, the rate increase in the case of **5** is clearly too high[14] to be accounted satisfactorily for these factors only. Thus, the acceleration of **5** points to an enhanced σ-participation of the trimethyl substituted C_4-C_7 bond.[15] The σ-participation should lead to a bridged cation **22**, depicted conventionaly in Scheme 3. Such delocalized structure corresponds not only to the transition state of the solvolysis, but also to the reactive cationic intermediate, since 1-norbornylic products (**16** and **17**) are found among the reaction products. Fragmentation products are formed by nucleophilic attack of the solvent at C_4 of **22**. However, formation of these products *via* a terpinyl cation **23**, generated from **22**, can not be excluded.

Further work including the spectroscopic characterization of cation **22** is in progress.

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

Triflate	Temp.(°C)	$k(s^{-1})^a$	$\Delta H^{\neq}$ (Kcal/mol)	$\Delta S^{\neq}$ (eu)	ΔE_{π}^{8} (Kcal/mol)	E_r^{9} (Kcal/mol)	k_r (at 80.3°C)	Ref.
	70.3	1.74×10^{-4}	26.3	1.4				tw
5	80.3	3.57×10^{-4}			2.1	8.3	33.0	tw
	88.5	1.38×10^{-3}						tw
	80.3	1.38×10^{-5}	28.9	2.4	1.3	3.6	3.7	tw
13	90.2	1.17×10^{-4}						tw
	98.5	3.26×10^{-4}						tw
	80.3	2.20×10^{-5b}	28.9	-0.8				6
20	80.3	2.20×10^{-5}			2.2	7.2	2.0	tw
	75.2	3.05×10^{-5c}	26.8^c	-2.5^c				7
21	80.3	2.22×10^{-5d}						7
	80.3	1.08×10^{-5}			1.3	3.8	1.0	tw

tw = this work. [a] Experimental error ±5%. [b] Extrapolated from other temperature. [c] In 50% aqueous ethanol. [d] Extrapolated to 80.3°C and 60% aqueous ethanol from literature data.[7]

Acknowledgment

We thank the DGICYT (Spain) for finantial support of this work (Grants PB91-0354 and PB90-0070).

References and Notes

1. (a) Takeuchi, K.; Yoshida, M. *J. Org. Chem.* **1993**, *58*, 2566. (b) Müller, P.; Milin, D.; Feng, W. Q.; Houriet, R.; Della, E. W. *J. Am. Chem. Soc.* **1992**, *114*, 6169. (c) Wiberg, K. B.; McMurdie, N. *J. Org. Chem.* **1993**, *58*, 5603. (d) Mareda, J. *J. Chem. Soc. Chem. Commun.* **1993**, 1280. (e) Olah, G. A.; Lee, C. S.; Prakash, G. K.; Moriarty, R. M.; Rao, M. S. C. *J. Am. Chem. Soc.* **1993**, *115*, 10728.
2. García Martínez, A.; Teso Vilar, E.; Osío Barcina, J.; Hanack, M.; Subramanian, L. R. *Tetrahedron Lett.* **1989**, *30*, 1503.
3. ^{13}C-NMR (75 MHz, $CDCl_3$, TMS): δ= 102.8 (C_1); 49.0, 40.7 ($C_{4,7}$); 34.5, 31.2 ($C_{2,3(6,5)}$); 16.2 (C_8); 15.8 ($C_{9(10)}$) ppm.
4. The samarium iodide catalized cyclisation of **11** to **12** takes place at -40°C, 3h (cf. Molander, G. A.; McKie, J. A. *J. Org. Chem.* **1991**, *56*, 4112). ^{13}C-NMR (75 MHz, $CDCl_3$, TMS): δ= 100.4 (C_1); 47.6 (C_7); 39.5 (C_4); 34.3, 38.9 ($C_{2,3(6,5)}$); 21.3 (C_8) ppm.
5. All compounds were characterized by MS, IR, ^{1}H- and ^{13}C-NMR spectral analysis. ^{13}C-NMR (75 MHz, $CDCl_3$, TMS): **14**: 130.1 (C_4); 121.1 (C_8); 69.7 (C_1); 40.1, 29.3 ($C_{2,3(6,5)}$); 25.6 (C_7); 19.9 ($C_{9(10)}$) ppm. **15**: 130.6 (C_4); 120.4 (C_8); 72.9 (C_1); 55.7 (-OCH_2-); 37.1, 24.3 ($C_{2,3(6,5)}$); 25.2 (C_7); 19.8 ($C_{9(10)}$); 16.1 (-OCH_2-$\underline{C}H_3$) ppm. **16**: δ= 83.2 (C_1); 46.6, 43.4 ($C_{4,7}$); 34.4, 34.0 ($C_{2,3(6,5)}$); 17.0, 15.9 (C_{8-10}) ppm. **17**: δ= 87.0 (C_1); 59.9 (-OCH_2-); 47.48, 43.1 ($C_{4,7}$); 34.9, 30.8 ($C_{2,3(6,5)}$); 16.8, 16.7 (C_{8-10}); 16.3 (-OCH_2-$\underline{C}H_3$) ppm. **18**: δ= 82.1 (C_1); 49.9, 41.3 ($C_{4,7}$); 36.8, 36.7 ($C_{2,3(6,5)}$); 21.8 (C_8) ppm. **19**: δ= 86.7 (C_1); 60.2 (-OCH_2); 47.0, 40.5 ($C_{4,7}$); 36.7, 33.3 ($C_{2,3(6,5)}$); 23.1 (C_8); 16.1 (-OCH_2-$\underline{C}H_3$) ppm.
6. Sherrod, S. A.; Bergman, R. G.; Gleicher, G. J.; Morris, D. G. *J. Am. Chem. Soc.* **1972**, *94*, 4615.
7. Bingham, R. C.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 3471.
8. ΔE_{st} is the difference between the steric energies of the carbocation and the corresponding triflate calculated with the MMX program.[9] There is a good relationship between log k and MM2 (MMX) strain energies in the case of bridgehead derivatives: Eksterowicz, J. E.; Houk, K. N. *Chem. Rev.* **1993**, *93*, 2439.
9. E_r is the rotational barrier about the C_1-OTf bond calculated with: PCMODEL, Serena Software, Bloomington, IN 47402-3076, U.S.A.
10. (a) Eaton, P. E.; Yang, C. X.; Xiang, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225. (b) Gassman, P. G.; Marshall, J. L.; MacMillan, J. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 4282. (c) Lenoir, D. *Chem. Ber.* **1985**, *118*, 2055.
11. (a) Fuso, F.; Grob, C. A.; Sawlewicz, P.; Yao, G. W. *Helv. Chim. Acta* **1986**, *69*, 1079. (b) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375. (c) Grob, C. A.; Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502. (d) Bielmann, R.; Grob, C. A.; Küng, D.; Yao, G. W. *Hel. Chim. Acta* **1985**, *68*, 2158. (e) Grob, C. A.; Yang, C. X.; Della, E. W.; Taylor, D. K. *Tetrahedron Lett.* **1991**, *42*, 5945.
12. (a) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001. (b) Wiberg, K. B.; Shobe, D.; Nelson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 10645.
13. (a) Wiberg, K. B.; McMurdie, N. *J. Am. Chem. Soc.* **1991**, *113*, 8995. (b) Grob, C. A.; Yang, C. X. *Tetrahedron Lett.* **1991**, *42*, 5945.
14. The triflate **5** shows the highest accelerating methyl effect ever found in the solvolysis of bridgehead derivatives.[1,10,11] The only exceptions are the related 2,3,3- and 2,2,3-trimethyl-1-norbornyl triflates,[2] with k_r ranging from 91 to 3846.
15. (a) le Noble, W. J. *Croat. Chim. Acta* **1992**, *65*, 489. (b) Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1992**, *57*, 2519.

(*Received in UK* 31 *December* 1993; *accepted* 14 *January* 1994)