Tetrahedron Letters Vol. 22, pp 879 - 882
0040-4039/81/0222-0879$02.00/0

REMOTE INDUCTIVE EFFECTS ON SECONDARY AND TERTIARY 2-NORBORNYL SOLVOLYSIS RATES

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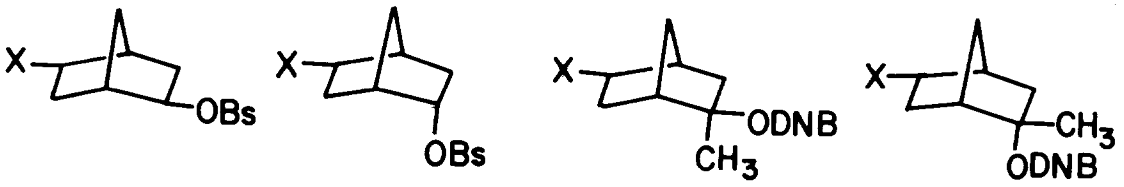
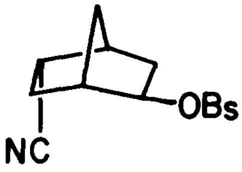
Abstract. - A 5-cyano substituent decelerates the solvolysis rate of exo-2-norbornyl brosylate (1-H) by a factor of 1790. A much smaller deceleration (24-90 fold) is observed for the secondary *endo* and for both *exo* and *endo* tertiary 2-norbornyl derivatives. These results support the occurrence of σ-participation in the solvolysis of 1-H.

Although the 2-norbornyl cation is probably the most thoroughly studied reactive intermediate in organic chemistry,[1] the controversy over the role of σ-participation in the solvolysis of 2-norbornyl systems has not been resolved.[1] The high *exo*/*endo* rate ratio in the solvolysis of the secondary 2-norbornyl brosylates 1-H and 2-H is attributed either to σ-participation or to steric effects.[1] The failure of aryl and methyl 2-substituents to reduce the high *exo*/*endo* rate ratios in norbornyl solvolysis is one of the central arguments against σ-participation.[1] As summarized below a 5-cyano substituent has a substantially larger effect on the solvolysis rate in *exo*-2-norbornyl brosylate (1) than in the corresponding secondary *endo* (2) or in either the *exo* (3) or the *endo* tertiary (4) derivatives. These results strongly support the hypothesis that a special electronic effect-σ-participation - contributes to the solvolysis of secondary *exo*-2-norbornyl derivatives. Such participation is selectively inhibited by the electron withdrawing 5-cyano substituent.

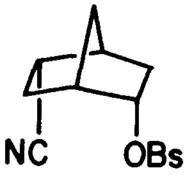
SCHEME I:



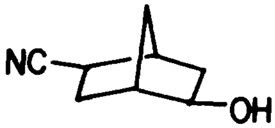
	1-H, X=H	2-H, X=H	3-H, X=H	4-H, X=H
	1-CN, X=CN	2-CN, X=CN	3-CN, X=CN	4-CN, X=CN
Rate ratio X=H/X=CN	1790	78.2	90.3	23.5



5-CN



6-CN



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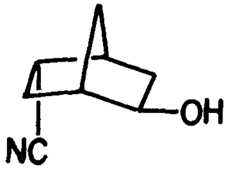

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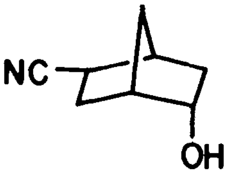

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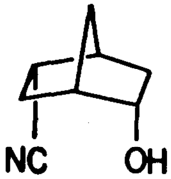

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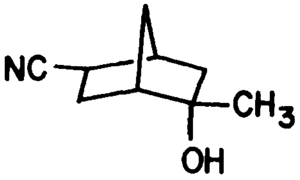

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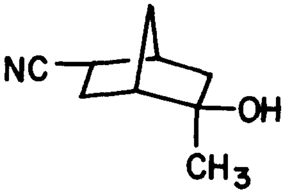

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The secondary exo-alcohols 7 and 8 were obtained by oxymercuration of exo or endo 5-cyano-2-norbernene respectively. Oxidation of 7 or 8 followed by reduction with sodium borohydride yields the endo alcohols, 9 and 10, respectively. 11 is obtained by the reaction of 5-cyano-2-norbornanone with methylmagnesium iodide. A Wittig reaction of 5-cyano-2-norbornanone and $Ph_3P^+CH_2^-$ followed by oxymercuration yields the exo alcohol 12. The 5-cyano-2-norbornyl derivatives 1-CN - 6-CN were obtained from the corresponding alcohols by standard procedures. Their solvolysis rate constants and those of the corresponding parent compounds (1-H - 4-H) are presented in Table 1.

Table 1. Solvolysis Rates of 5-Cyano-2-Norbornyl Derivatives.[a]

Compound	Solvent	temp.(C°)	$k\cdot sec^{-1}$	Compound	Solvent	temp.(C°)	$k\cdot sec^{-1}$
1-H[b]	60% ethanol	75.0	1.29[c]	6-CN[b,e]	60% ethanol	75.0	$1.55\cdot 10^{-5}$
2-H[b,d]	60% ethanol	75.0	$2.30\cdot 10^{-3}$	3-H[f,g]	60% acetone	100.0	$4.20\cdot 10^{-3}$
1-CN[b]	60% ethanol	75.0	$7.21\cdot 10^{-4}$	4-H[f,g]	60% acetone	100.0	$2.80\cdot 10^{-5}$
2-CN[b]	60% ethanol	75.0	$2.94\cdot 10^{-5}$	3-CN[g]	60% acetone	100.0	$4.65\cdot 10^{-5}$
5-CN[b]	60% ethanol	75.0	$8.38\cdot 10^{-4}$	4-CN[g]	60% acetone	100.0	$1.19\cdot 10^{-6}$

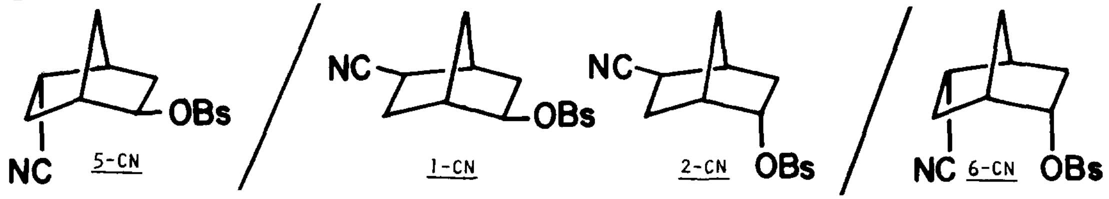
[a] Rate constants at other temp. will be reported in the full paper.[2] [b] Measured conductometrically. [c] Our data, assuming that k(OBs)/k(OTs) = 5.0 ; D.D. Roberts J.Org.Chem.,37,1510(1972). [d] A somewhat higher rate was reported by J.M. Harris ,D.L. Mount,D.J. Raber,J.Am.Chem.Soc.,100,3139(1978). [e] Extrapolated from higher temperatures. [f] From ref.5. [g] Measured titrimetrically.

The 5-position is farthest removed from the reaction site; the 5-cyano group should perturb the system inductively but not sterically. As expected the solvolysis rates of all systems (1-CN - 6-CN) are decreased by the strongly electron withdrawing 5-cyano substituent, but to the varying extents shown in Scheme I.[2] Comparison between the solvolysis rates of 3-H and of 4-H with those of 3-CN and of 4-CN respectively (Scheme I), measures the effect of the 5-cyano substituent on the rate of formation of a "classical" 2-norbornyl cation.[1] This deceleration is modest, 24-90 fold both in 3-CN and in 4-CN.[3] The secondary *endo* brosylates, 2-CN and 6-CN, are affected to a similar extent (Scheme I) pointing to the intermediancy of "classical" carbenium ions. The behaviour of only one compound, the *exo*-2-norbornyl brosylate, is exceptional; k(1-H)/k(1-CN)=1790, i.e. 20-76 times higher than in the secondary *endo* (2) or in the tertiary *exo* (3) or *endo* 2-norbornyl (4) derivatives.[4,5] A special electronic effect is involved in the solvolysis of 1-H, σ-participation of the C_1C_6 bond. The C_1C_6 bond is influenced in a 2-*exo* solvolysis transition state, either hyperconjugatively when the electron demand is small (e.g., 3 and 4), or participatively when the electron demand is greater (i.e., 1-H). The C_1C_6 bond is not involved in a 2-*endo* solvolysis transition state. The 5-cyano substituent withdraws electrons from the C_1C_6 bond reducing its nucleophilicity and its ability to stabilize the transition state. σ-participation is thus *partially* eliminated in 1-CN resulting in an unusually high rate decleration.[6] The rate decelerations due to the 5-cyano substituent are much smaller in 2-CN and 4-CN where σ-participation is not important, and in 3-CN, where only C_1C_6 hyperconjugation inhibition is involved.

The exceptional solvolytic behaviour of 1-H is also revealed in the *exo*/*endo* rate ratios. σ-participation, which is responsible for the high *exo*/*endo* rate ratios in the solvolysis of secondary 2-norbornyl derivatives is reduced in 1-CN and in 5-CN resulting in much lower *exo*/*endo* rate ratios.[4-6] The high tertiary 3-H/4-H=150 rate ratio, on the other hand, results mainly from steric effects and is therefore relatively insensitive to the strong inductive effect of the cyano substituent (3-CN/4-CN=39).

	1-H/2-H	1-CN/2-CN	5-CN/6-CN	3-H/4-H	3-CN/4-CN
Rate ratios[2]	561	24.5	54.1	150	39

Dipole-dipole interactions cannot explain these results. Solvolysis rate comparisons of 1-CN, 2-CN, 5-CN and 6-CN demonstrate that dipole orientation effects are small. Thus 1-CN and 5-CN (or 2-CN and 6-CN) solvolyse at similar rates although the C_5-CN bond dipole and the C_2-OBs bond dipole are nearly antiperiplanar in 1-CN, but nearly perpendicular in 5-CN.



Rate Ratios(75°C) 1.16 1.89

Analysis of the solvolysis products supports an S_N1 mechanism for *1-CN* - *6-CN*. The same product ratio, 7/8=1.21, results from solvolysis of *1-CN* and of *5-CN*. The initial orientation of the cyano group is unimportant.[7] The *endo* isomers *2-CN* and *6-CN*, on the other hand, yield *exo* products with preferred retention of stereochemistry at C_5. The *7/8* product ratios are 2.19 from *2-CN* but 0.48 from *6-CN*. Weakly nucleophilically solvated carbenium ion pairs, which undergo only partial equilibration (leakage) before capture by the solvent, are proposed as the solvolysis intermediates.

In conclusion, secondary *exo* 2-norbornyl derivatives are more sensitive to the inductive effect of a 5-cyano substitutent than either secondary *endo* or tertiary 2-norbornyl derivatives. We believe that this results from a *reduction* in the participation of the C_1-C_6 bonding electrons in the solvolysis of *1-H*.[6] Substituents which withdraw electrons from the C_1-C_6 bond more strongly are expected to reduce σ-participation and thus the *exo/endo* rate ratios in secondary 2-norbornyl derivatives even further.[8] A comprehensive analysis of the effect of various 5-substituents[5] on the solvolysis of secondary and tertiary 2-norbornyl derivatives will be presented in a forthcoming full paper.

References and Notes

1. H.C. Brown, "THe Nonclassical Ion Problem", with comments by P.v.R. Schleyer, Plenum Press, New York, 1977.
2. Rate comparisons are calculated at 75°C for the secondaries and at 100°C for the tertiaries, temperatures in which most measurements were taken. Rate extrapolations which may introduce significant errors are thus avoided.
3. The somewhat smaller effect of the 5-cyano substituent on the solvolysis rate of *4-CN* compared with *3-CN* (a factor of 3.8) probably results from a combination of more favorable dipole-dipole interactions, differences between the isomers in the degree of charge development in the transition state, and small changes in steric interactions.
4. Results similar to ours were reported recently for a series of 6-substituted secondary 2-norbornyl tosylates by W. Fischer, C.A. Grob, G. von Sprecher and A. Waldner, *Tetrahedron Lett.*, 1905, 1901, 473(1979). These authors interpret their data in terms of hyperconjugative/inductive effects which are transmitted more strongly in the *exo* series (see footnote 6,below).
5. For the solvolysis rates of the 5,5-dichloro and the 5-ethylene ketal 2-norbornyl derivatives see D. Lenoir, W. Rüll, E. Weiss and G. Wenke, *Tetrahedron Lett.*, 1911 (1976).
6. Results similar to ours were interpreted by Grob[4] without invoking the intermediancy of a bridged ion in the solvolysis of *1-H*. The high *1-H*/*2-H* rate ratio was attributed to stronger inductomeric or CC-hyperconjugative effects in the solvolysis of *1-H*.[4] However, the low *exo/endo* rate ratios observed in rigid 2-norbornyl analogs (where bridging is sterically inhibited) rules out, in our opinion, these effects as the major stabilizing mechanisms of the *1-H* solvolysis transition state. See: Y. Apeloig, D. Arad, J. Neff, J.E. Nordlander, S. Godleski, and P.v.R. Schleyer, Abstracts, Second Chemical Congress of the North American Continent, San Francisco, August 24-29, 1980; *Tetrahedron Lett.*, submitted.
7. This can be explained by invoking a common bridged cation or a rapidly equilibrating pair of classical cations.
8. Lower *exo/endo* rate ratios of 9.4 and 0.88 were reported for the 5,5-dichloro-2-norbornyl tresylates[5] and for the 6-cyano-2-norbornyl brosylates[4], respectively.

(Received in UK 1 December 1980)