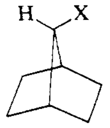
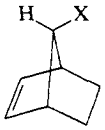
Aryl Delocalization *vs.* Neighboring Group Participation in the Stabilization of Carbonium Ions

Sir:

Recently we demonstrated that the 10^{11} rate difference between **1** and **2** could be leveled to a factor of 3 by replacing the C-7 hydrogen by a *p*-anisyl group.[1] This phenomenal stabilization of the carbonium ion center by the *p*-anisyl group was sufficient to virtually eliminate participation by the double bond, which, in **2**, not only accounted for the dramatic rate difference of 10^{11} but also controlled the stereochemistry of the reaction product. Since *p*-anisyl stabilization essentially canceled double bond participation, the solvolysis of **3** was not stereospecific, but instead gave a mixture of **4** and **5**. This study[1] firmly established, on a quantitative basis, the ability of the *p*-anisyl group to eliminate neighboring group participation of a magnitude which could account for a rate acceleration of $10.^{11}$ Since various aryl groups have been used to "overcome" neighboring group participation, we have investigated the efficiency of certain aryl groups, other than *p*-anisyl, in removing neighboring group participation. We report here on the carbonium ion stabilizing power of the phenyl and *p*-trifluoromethylphenyl groups.

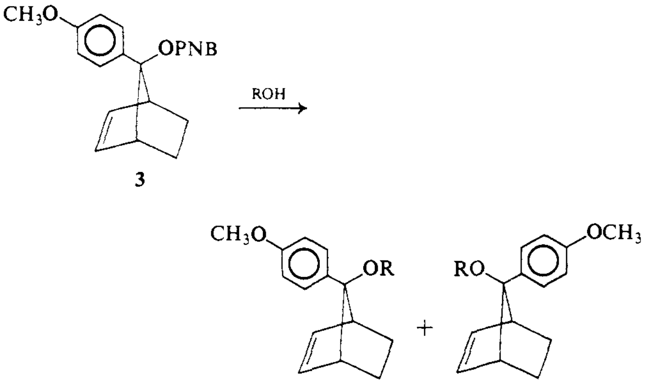


1



2

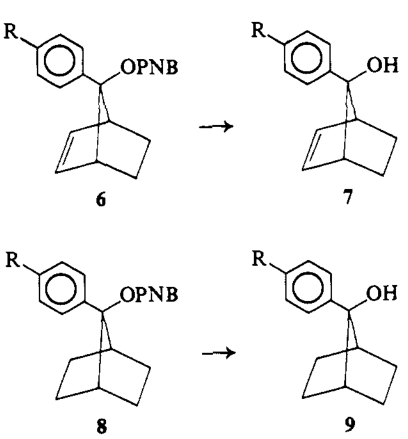
k_{rel} 1 10^{11}



3 **4** **5**

Our approach to establishing the degree to which phenyl and *p*-trifluoromethylphenyl can overcome or "level" neighboring group participation was to pit the appropriate aryl stabilization against the double bond participation in the suitably substituted *anti*-7-norbornenyl derivatives.[2] Comparison of the rates and products of the solvolyses of **6a** and **6b** with **8a** and **8b**, respectively, should then allow a quantitative evaluation of carbonium ion stabilization by phenyl and *p*-trifluoromethylphenyl groups.

Table I lists the rates of *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates in 70:30 dioxane–water [compound **10** is *syn*-7-(3,5-ditrifluoromethylphenyl)-*anti*-7-norbornenyl *p*-nitrobenzoate]. A $\rho\sigma^+$ plot of these data gave a ρ that was exceptionally low compared to the ρ for carbonium ion generation from other *t*-cumyl systems. Normally ρ varies between -4 and -6 for the generation of various types of *t*-cumyl cations. For our system ρ was -2.03 at 170° (correlation coefficient 0.999) and -2.30 at 25° (correlation coefficient 0.997).



6 **7**

8 **9**

a, R = H
b, R = CF_3

Table II lists the corresponding rates of solvolysis of the 7-aryl-7-norbornyl *p*-nitrobenzoates (compound **11** is 7-*p*-methoxyphenyl-7-norbornyl *p*-nitrobenzoate). For the solvolyses of these saturated compounds ρ was -3.60 at 200° (correlation coefficient 1.000) and -5.17 at 25° (correlation coefficient 0.990).

The unusually low ρ observed in the solvolysis of the unsaturated series indicated the presence of less stabilization of the incipient carbonium ion by the aryl group for this series than for the analogous saturated series which had a normal ρ. This decrease in aryl stabilization in the unsaturated series was most consistent with partial stabilization of the developing carbonium ion through neighboring group participation by the π electrons of the norbornenyl double bond. This theory was strongly supported by our product studies. Whereas **3** gave a mixture of **4** and **5**, compounds **6a**, **6b**, and **10**, which had less powerful carbonium ion stabilizing groups in the 7 position, each gave only a single product *with complete retention of stereochemistry.* We attribute this stereospecificity to double bond participation.[3]

On the basis of the product studies and the $\rho\sigma^+$ relationship discussed above it appears that aryl groups which are more electron donating than phenyl are required to overcome the double bond participation in *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoate solvolyses. Since phenyl and *p*-trifluoromethylphenyl substitutions do not completely remove double bond participation in our system, we can use the comparison of rates of individual members of the unsaturated series with the corresponding rates of members of the saturated series to determine how much neighboring group participation can be eliminated by the phenyl and *p*-trifluoromethylphenyl groups. The *p*-anisyl group wipes out essentially all rate effects (and all participation) of the double bond. The residual rate

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(1) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

(2) Satisfactory elemental analyses have been obtained on all new compounds.

(3) In order to ensure that alkyl oxygen cleavage was occurring and not acyl oxygen cleavage we studied the methanolysis of the very unreactive *anti*-7-norbornenyl *p*-nitrobenzoate. We found only *anti*-7-methoxynorbornene, even though this molecule was less reactive than **10**.

Table I. Rates of Solvolysis of Tertiary Norbornenyl *p*-Nitrobenzoates in 70:30 Dioxane–Water

Compd	Temp, °C	Rate, sec^{-1}	k_{rel} at 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3	90.0 ± 0.01	$(1.20 \pm 0.03) \times 10^{-3}$			
	80.0 ± 0.01	$(4.10 \pm 0.03) \times 10^{-4}$		24.9	−3.9
	70.0 ± 0.01	$(1.52 \pm 0.00) \times 10^{-4}$			
	(25)[a]	5.18×10^{-7}	17,000		
6a	130.0 ± 0.01	$(7.01 \pm 0.20) \times 10^{-4}$			
	120.0 ± 0.01	$(2.98 \pm 0.08) \times 10^{-4}$		26.6	−7.7
	110.0 ± 0.01	$(1.18 \pm 0.02) \times 10^{-4}$			
	(25)	4.23×10^{-9}	140		
6b	170.0 ± 0.03	$(1.23 \pm 0.01) \times 10^{-3}$			
	160.0 ± 0.03	$(5.37 \pm 0.18) \times 10^{-4}$		26.7	−12.5
	150.0 ± 0.03	$(2.80 \pm 0.05) \times 10^{-4}$			
	(25)	2.94×10^{-10}	9.6		
10	190.0 ± 0.05	$(5.14 \pm 0.07) \times 10^{-4}$			
	170.0 ± 0.03	$(1.19 \pm 0.03) \times 10^{-4}$		26.7	−16.8
	160.0 ± 0.03	$(6.59 \pm 0.13) \times 10^{-5}$			
	(25)	3.06×10^{-11}	1		

[a] Rates at 25° are extrapolated from higher temperatures.

Table II. Rates of Solvolysis of Tertiary Norbornyl *p*-Nitrobenzoates in 70:30 Dioxane–Water

Compd	Temp, °C	Rate, sec^{-1}	k_{rel} at 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
11	90.0 ± 0.01	$(4.60 \pm 0.01) \times 10^{-4}$			
	80.0 ± 0.01	$(1.64 \pm 0.01) \times 10^{-4}$		25.8	−3.1
	70.0 ± 0.01	$(5.41 \pm 0.20) \times 10^{-5}$			
	(25)[a]	1.54×10^{-7}	18,000,000		
8a	170.0 ± 0.03	$(4.66 \pm 0.12) \times 10^{-4}$			
	160.0 ± 0.03	$(2.23 \pm 0.07) \times 10^{-4}$		26.9	−13.9
	150.0 ± 0.03	$(1.05 \pm 0.02) \times 10^{-4}$			
	(25)	1.02×10^{-10}	12,000		
8b	220.0 ± 0.1	$(1.06 \pm 0.01) \times 10^{-4}$			
	210.0 ± 0.1	$(5.03 \pm 0.13) \times 10^{-5}$			
	200.0 ± 0.1	$(2.36 \pm 0.03) \times 10^{-5}$		33.9	−9.1
	(25)	8.52×10^{-15}	1		

[a] Rates at 25° are extrapolated from higher temperatures.

acceleration k(unsaturated)/k(saturated), a factor of 41 in the case of the phenyl-substituted norbornene and 35,000 for the *p*-trifluoromethylphenyl case, serves as a measure of the participation of the double bond in the rate-determining step, when these groups are situated *syn* in the 7 position. Consequently, we can assign a "leveling" effect of approximately 10^{10}, 10^{9}, and 10^{6} to the *p*-anisyl, phenyl, and *p*-trifluoromethylphenyl groups, respectively.

As the carbonium ion stabilizing ability of the aryl group decreased, the carbonium ion stabilizing role of the double bond increased. Thus, relative to the σ^{+} value of the aryl substituents, the neighboring group participation of the double bond had a positive ρ in our unsaturated system.[4] This shows that *neighboring group participation, at least in the case of the anti-7-norbornenyl cation, is a linear function of the electron demand of the incipient carbonium ion.*

If the dependence of neighboring group participation on electron demand is a general phenomenon, it could have far-reaching implications on the interpretation of a broad range of solvolytic data. We are currently studying these implications.

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[4] For the particular cases which we are studying this ρ should be equal to ρ(saturated) − ρ(unsaturated) or ρ(double bond) = −2.30 − (−5.17) = +2.87.

[5] Alfred P. Sloan Research Fellow, 1967–1969.

[6] Battelle Memorial Institute Staff Fellow, 1967–1969.

endo-Tricyclo[3.2.0.0^{2,7}]hept-6-yl *p*-Methoxybenzoate. Pronounced Solvolytic Reactivity within the Norbornyl Series

Sir:

The solvolytic reactivity of norbornyl systems has been the subject of extensive investigation, and these systems have provided a much used vehicle for the study of carbonium ion structure and reactivity.[1] Recent work[2,3]

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[1] For general treatments of this subject, see (a) P. D. Bartlett, Ed., "Nonclassical Ions: Reprints and Commentary," W. A. Benjamin, Inc., New York, N. Y., 1965; and (b) J. Berson in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 111.

[2] H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965); H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864, 1953 (1966).

[3] A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).