# The Levelling Effect of the *p*-Anisyl Group on Solvolysis Reactions

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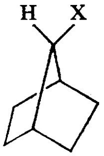
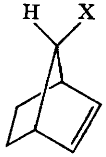
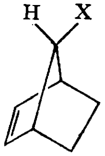
A dramatic case of $\pi$-electron participation in solvolysis reactions occurs in the acetolysis of 7-substituted norbornene derivatives, where there is a phenomenal rate difference of $10^{11}$ in the solvolytic loss of $X^-$ from (I) and (III).[1,2] Even in the case of the *syn*-isomer (II) an acceleration of $10^4$ is noted (although the role of the $\pi$-electrons differs mechanistically). We now report that replacement of the proton at C-7 in (II) and (III) by the *p*-anisyl group eliminates the participation of the $\pi$-electrons. This overwhelming levelling effect ($>10^{10}$) was found to be equally important in determining both the rates and the products of the solvolyses.



(I)
1



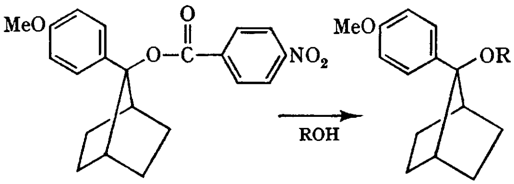
(II)
$10^4$



(III)
$10^{11}$

The *p*-nitrobenzoates of (IV), (V), and (VI) were prepared by treating pure samples of (IV), (V), and (VI)†‡ with sodium hydride and then with *p*-nitrobenzoyl chloride to yield (VII), (VIII), and (IX), respectively. The rates of solvolysis of (VII), (VIII), and (IX) in acetone–water are listed in Table 1. It should be noted that the relative rates of solvolysis of (VIII), (VII), and (IX) are 6, 2·5, and 1, respectively, at 85°. Thus the factor of $10^{11}$ between (I) and (III) was reduced to *ca.* 2 when the incipient carbonium ion was stabilized by the *p*-anisyl group. In order to ensure that alkyl–oxygen cleavage was occurring, rather than acyl–oxygen cleavage, the solvolyses were also run in 30:70 tetrahydrofuran–methanol. These rates are listed in Table 2. Here again the relative rates varied by less than an order of magnitude. In the methanolysis *no* alcoholic products were observed; only methyl ethers were present in the product mixture. Thus, solvolysis *via* alkyl–oxygen cleavage must have been the mechanistic pathway.

As anticipated, the saturated *p*-nitrobenzoate, (VII) gave only the corresponding alcohol.§ No trace of rearrangement product could be found, in contrast to the solvolysis of norborn-7-yl



(VII)

(IV) R=H
(X) R=Me

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† The tertiary alcohol (IV) was prepared *via* the reaction of *p*-anisyl Grignard with norbornan-7-one. The alcohols (V) and (VI) were obtained by the reaction of norbornen-7-one with either *p*-anisyl Grignard or *p*-anisyl-lithium.

‡ Correct elemental analyses were obtained for all new compounds.

§ When (VII) was solvolyzed in 30:70 tetrahydrofuran–methanol only the corresponding methyl ether was obtained. The rates of solvolysis of (VII) were not accurately determined in this solvent due to solubility problems. However, the approximate relative rate in tetrahydrofuran–methanol was similar to the relative rate in acetone–water.

TABLE 1

*Rates of solvolysis of* ***tertiary*** p-*nitrobenzoates in* 90:10 *acetone–water*

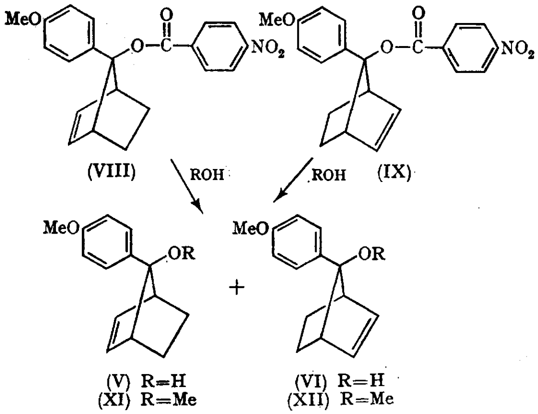
| Compound | Temperature (°c) | Rate (sec.$^{-1}$) | $\Delta H\ddagger$ (kcal./mole) | $\Delta S\ddagger$ (e.u.) |
|---|---|---|---|---|
| (VIII) | 65·00 ± 0·02 | (9·64 ± 0·03) × $10^{-6}$ | 26·1 | −4·4 |
| | 74·40 ± 0·02 | (2·87 ± 0·02) × $10^{-5}$ | | |
| | 85·00 ± 0·02 | (9·06 ± 0·05) × $10^{-5}$ | | |
| (VII) | 90·00 ± 0·02 | (5·75 ± 0·03) × $10^{-5}$ | 27·0 | −4·0 |
| | 99·30 ± 0·02 | (1·50 ± 0·01) × $10^{-4}$ | | |
| | 110·00 ± 0·02 | (4·33 ± 0·01) × $10^{-4}$ | | |
| (IX) | 85·00 ± 0·02 | (1·53 ± 0·02) × $10^{-5}$ | 26·0 | −8·2 |
| | 99·90 ± 0·02 | (6·68 ± 0·01) × $10^{-5}$ | | |
| | 109·85 ± 0·02 | (1·74 ± 0·00) × $10^{-4}$ | | |

TABLE 2

*Rates of solvolysis of* ***tertiary*** p-*nitrobenzoates in* 30:70 *tetrahydrofuran–methanol*

| Compound | Temperature (°c) | Rate (sec.$^{-1}$) | $\Delta H\ddagger$ (kcal./mole) | $\Delta S\ddagger$ (e.u.) |
|---|---|---|---|---|
| (VIII) | 75·00 ± 0·02 | (1·77 ± 0·00) × $10^{-4}$ | 24·5 | −5·8 |
| | 85·00 ± 0·02 | (4·76 ± 0·02) × $10^{-4}$ | | |
| | 95·00 ± 0·02 | (1·26 ± 0·03) × $10^{-3}$ | | |
| (IX) | 75·00 ± 0·02 | (2·56 ± 0·02) × $10^{-5}$ | 26·1 | −5·0 |
| | 85·00 ± 0·02 | (7·59 ± 0·06) × $10^{-5}$ | | |
| | 95·00 ± 0·02 | (2·07 ± 0·01) × $10^{-4}$ | | |

toluene-*p*-sulphonate which yields *ca.* 7% of skeletal rearrangement products.[3] More interesting is the fact that both (VIII) and (IX) yield *the same mixture of products.* In acetone–water (VIII) gave 94% of (V) and 6% of (VI). Under the same conditions (IX) gave 93% of (V) and 7% of (VI). Since ratios were determined to the nearest percent, these values are within experimental error of each other. In tetrahydrofuran–methanol (VIII) gave 94% of (XI) and 6% of (XII), whereas (IX) gave 95% of (XI) and 5% of (XII). Thus, for solvolysis in either acetone–water or tetrahydrofuran–methanol both (VIII) and (IX) gave 94 ± 1% of *anti*-substitution and 6 ± 1% of *syn*-substitution product. In contrast to the behaviour of *syn*-norborn-7-yl toluene-*p*-sulphonate[3] (XIII), no skeletal rearrangement product was obtained from (IX). Since the driving force for the rearrangement of (XIII) probably was formation of an allylic cation, this lack of rearrangement in the solvolysis of (IX) was expected because the *p*-anisyl group should provide greater stabilization than the vinyl group.



When either (XI) or (XII) was equilibrated in 30:70 tetrahydrofuran–methanol containing toluene-*p*-sulphonic acid at 130° for 24 hr. an equilibrium mixture was obtained which consisted of 95 ± 1% of (XI) and 5 ± 1% of (XII). Since the solvolysis product mixture had a composition similar to the thermodynamic mixture, it was necessary to determine whether the observed solvolysis products were actually the kinetically controlled products. When either (V) or (XI) was placed in the respective solvolysis solvent with one equivalent of *p*-nitrobenzoic acid and reacted at solvolysis temperatures for ten half-lives,¶ less than 1·5% of the *anti*-isomer was

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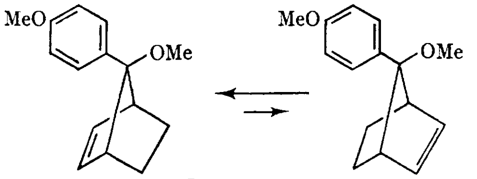
¶ This represents ten half-lives for (VIII) under these conditions. When starting with the *syn*-derivatives the reaction time corresponded to ten half-lives for (IX).

converted to the *syn*-isomer. Approaching the problem from the side of the epimer, when either (VI) or (XII) was placed with one equivalent of *p*-nitrobenzoic acid in the respective solvolysis solvent, approximately 45% of the *syn*-isomer was still present after ten half-lives.¶ Thus, the observed solvolysis product mixture was kinetically controlled.

In summary, it has been shown that the *p*-anisyl group is capable of changing the mechanism of a solvolysis reaction from one of overwhelming $\pi$-electron participation[4] to one involving insignificant $\pi$-electron participation. In accomplishing this feat the *p*-anisyl group was capable of overriding stabilization associated with a rate acceleration greater than $10^{10}$. This provides one of the first ***quantitative*** measures of the stabilizing capacity of the *p*-anisyl group. Experiments are in progress which are designed to determine the ***minimum*** amount of stabilization required to overcome $\pi$-electron participation.



(XI) (XII)

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[1] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183; S. Winstein and M. Shatavsky, 1956, **78**, 592.

[2] S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 505.

[3] S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 5895.

[4] It has been suggested (P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, 1960, **82**, 1240) that part of the acceleration noted in the norborn-7-yl toluene-*p*-sulphonates, relative to the saturated analogue, may be due to a spreading of the C(1)–C(7)–C(4) angle by the increased C(1)–C(2)–C(3)–C(4) bond angles of the olefin. A comparison of rates of solvolysis of (VII), (VIII), and (IX) indicates that if such a bond angle effect does exist, it must be relatively unimportant.