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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Paul G. Gassman,[5] Allison F. Fentiman, Jr.[6]
Department of Chemistry
The Ohio State University, Columbus, Ohio 43210
Received December 5, 1968

endo-Tricyclo[3.2.0.0²,⁷]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]

(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).

on the synthesis of *endo*-tricyclo[3.2.0.0^{2,7}]hept-6-yl systems (*i.e.*, I) provided the backdrop for our reported[4] successful synthesis of *endo*-tricyclo[3.2.0.0^{2,7}]heptan-6-ol (Ia).

Ia, X = OH
b, X = OPMB
c, X = OPNB
d, X = OCH$_3$

IIa, X = OH
b, X = OTs
c, X = OPNB
d, X = OCH$_3$
e, X = OPMB
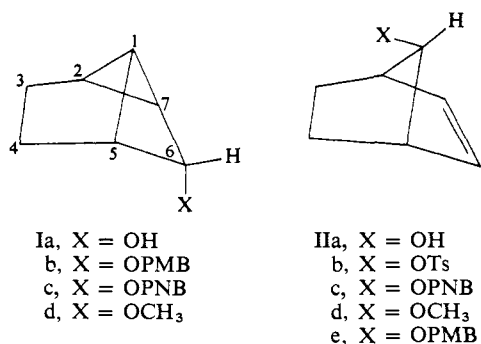
We demonstrated[4] that Ia is not an intermediate in the hydrolysis of *anti*-7-norbornenyl *p*-toluenesulfonate (IIb) under mildly alkaline conditions.[5]

We now report a remarkable solvolytic reactivity for *endo*-tricyclo[3.2.0.0^{2,7}]hept-6-yl *p*-methoxybenzoate (Ib). In an effort to study the reactivity of the tricyclic system under the usual neutral solvolytic conditions and in order to compare our results with the large body of accumulated data within the norbornyl series, we originally chose to employ the corresponding tricyclic *p*-nitrobenzoate Ic; however, the propensity of the *p*-nitrobenzoate Ic to undergo rearrangement to *anti*-7-norbornenyl *p*-nitrobenzoate (IIc) and its high solvolytic reactivity prompted us to investigate what we hoped would be the more manageable *p*-methoxybenzoate (Ib). Indeed, this derivative proved to be ideally suited for our purposes.

Attempted preparation of the *p*-methoxybenzoate by treatment of the tricyclic alcohol with *n*-butyllithium in hexane[6] led to the isolation of *anti*-7-norbornenyl *p*-methoxybenzoate in 82% yield. This may be attributed to electrophilic catalysis of rearrangement by the lithium salts produced in the reaction[7] since the use of amylsodium resulted in an 85% yield of a 90:10 mixture of tricyclic and *anti* *p*-methoxybenzoate, respectively. This material was used for the subsequent kinetic determinations. The tricyclic *p*-methoxybenzoate Ib was identified by the characteristic[2-4] four-line pattern centered at δ 5.03 ($J_{6,7}$ = 3.4, $J_{5,6}$ = 7.6 Hz) in its nmr spectrum (CCl$_4$, TMS).

The solvolysis of the tricyclic *p*-methoxybenzoate Ib, followed titrimetrically in 80 and 90% aqueous acetones, exhibited good first-order kinetics beyond 80% reaction; however, only 61 and 31% of the theoretical quantity of acid was produced in the 80 and 90% aqueous acetones, respectively, because of the substantial amount of rearrangement to the less reactive *anti*-7-norbornenyl *p*-methoxybenzoate in these solvents. The kinetics are consistent with the scheme proposed (*cf.* eq 1, R = *endo*-tricyclo[3.2.0.0^{2,7}]hept-6-yl, R' = *anti*-7-norbornenyl).

$$R'OPMB \xleftarrow{k_r} ROPMB \xrightarrow[H_2O]{k_s} R'OH + PMBOH \qquad (1)$$
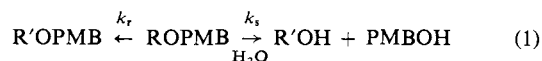
(4) J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967).

(5) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, 2324 (1963).

(6) H. C. Brown and F. Chloupek, *ibid.*, **86**, 1248 (1964).

(7) W. H. Puterbaugh and W. S. Gaugh, *J. Org. Chem.*, **26**, 3513 (1961).

The first-order rate constant was calculated on the basis of the experimental infinity value for acid production, and this rate constant (k_{obsd}) can be shown[8] to be equivalent to the sum of the rate constant for acid production (k_s) and the rate constant for rearrangement (k_r). The ratio of acid produced to rearranged ester (x/B) is equal to the ratio of the rate constants k_s/k_r, and since this ratio (x/B) can be evaluated from the value of acid produced at infinity, k_s and k_r are obtainable. In this way, it was found that when the tricyclic ester Ib was hydrolyzed in 90% aqueous acetone at 25°, rearrangement (k_r = 6.5 × 10^{-4} sec^{-1}) was faster than hydrolysis (k_s = 3.5 × 10^{-4} sec^{-1}) by a factor of *ca.* 2. For comparison, 7-norbornadienyl *p*-methoxybenzoate (III, X = OPMB) was hydrolyzed in 90% aqueous acetone at 195 and 220°. From the rate constants derived from these experiments (k = 3.20 × 10^{-5} sec^{-1} at 195° and k = 1.06 × 10^{-4} sec^{-1} at 220°), the tricyclic *p*-methoxybenzoate was calculated[9] to be *ca.* 10^7 times more reactive than the diene *p*-methoxybenzoate.

The hydrolysis of Ib (k_{obsd} = 3.8 × 10^{-3} sec^{-1} at 25°) and the diene *p*-methoxybenzoate (k = 6.20 × 10^{-5} sec^{-1} at 160° and k = 1.84 × 10^{-4} sec^{-1} at 180°) in 80% aqueous acetone followed titrimetrically also leads to the same rate factor (*i.e.*, *ca.* 10^7); moreover, the rate constant for the loss of tricyclic ester Ib in 90% aqueous acetone at 0° (k_{obsd} = 7.0 × 10^{-5} sec^{-1}) was also determined by an nmr investigation. Comparison of this value with the extrapolated, titrimetrically determined rate constant for the diene *p*-methoxybenzoate at 0° leads to a factor of 10^7–10^8 difference in rate. While the large temperature extrapolations involved in such comparisons and the extremely rapid rate of hydrolysis of the tricyclic ester limit the accuracy of this rate factor, these results clearly demonstrate the great solvolytic reactivity of the tricyclic system. Thus, these data show that the tricyclic system possesses a solvolytic reactivity approximately 10^{21}–10^{22} as great as the 7-norbornyl system.[1] The relative solvolytic reactivities of pertinent systems[1,10-12] within the norbornyl series are summarized in Chart I.

Chart I

IV[10]
1

II[10]
10[11]

III[11]
10[14]

V[12]
10[14]

I
10[21]–10[22]
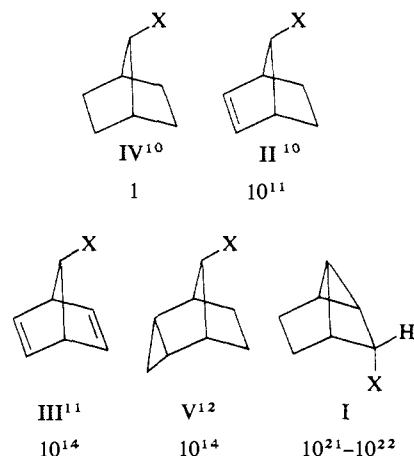
(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 160.

(9) These calculations are based on k_{obsd} for the tricyclic *p*-methoxybenzoate.

(10) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(11) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(12) (a) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); (b) M. Battiste, C. L. Deyrup, R. E. Pincock, J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

These results indicate a greater reactivity difference between the tricyclic and *anti*-7-norbornenyl systems in hydrolysis of the esters (10^{10}–10^{11}) than in the previously reported[3] acid-catalyzed cleavage of the corresponding methyl ethers (7×10^6), Id and IId, respectively. Since this reactivity difference is presumably associated to a large degree with a relief of ground-state strain in achieving the transition state, it is reasonable to expect (*cf.* Hammond postulate[13]) that in the ester hydrolysis the transition state more closely resembles the product carbonium ion than in the acid-catalyzed ether cleavage.[3] Hence, one would anticipate a greater relief of strain in attaining the transition state in the tricyclic ester hydrolysis and a greater rate difference when compared to *anti*-7-norbornenyl.

The only two products detected from the hydrolysis of Ib are *anti*-7-norbornenol and the *anti*-7-norbornenyl *p*-methoxybenzoate (IIe); however, we have shown that the tricyclic alcohol Ia rearranges readily under the hydrolytic conditions used for the kinetic determinations to afford *anti*-7-norbornenol.[4] Thus, we carried out the hydrolysis of Ib in 50% aqueous acetone containing 10 equiv of sodium bicarbonate and found a product mixture consisting of 76% *anti*-7-norbornenol and 23% *anti*-7-norbornenyl *p*-methoxybenzoate. The nmr spectrum of the product mixture reveals *less* than 2% of material which could even conceivably be tricyclic in nature. We believe that these data strongly suggest that both Ib and IIe proceed through the same intermediate in the hydrolysis experiments.[14]

(13) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(14) Professor S. Winstein has independently studied the solvolytic reactivity of *endo*-tricyclo[3.2.0.0²,⁷]hept-6-yl *p*-nitrobenzoate. We thank him for informing us of his results prior to publication.

J. J. Tufariello and R. J. Lorence

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

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The "σ" Route to the 7-Norbornenyl Ion[1]

Sir:

One of the most interesting and instructive nonclassical carbonium ions is the *anti*-7-norbornenyl cation[2] II, a bishomocyclopropenyl[3] ion. This species was originally encountered in solvolysis of bicyclic *anti*-7-norbornenyl derivatives I (π route).[2a,b] In recent times, the synthesis of the tricyclic methyl ether[2d,4a] III-OCH₃ has made possible the approach to II by the "σ" route.[2d,e] In

(1) Research was supported by the National Science Foundation.

(2) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) S. Winstein, A. Lewin, and K. Pande, *ibid.*, **85**, 2324 (1963); (d) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966); (e) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

(3) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

(4) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966); (b) H. Tanida and T. Hata, *J. Org. Chem.*, **30**, 977 (1965).

FSO₃H as a solvent, both routes lead to ion II observed directly by nmr.[2e]

As regards solvolysis, the available tricyclic derivatives did not permit a solvolytic study under nonacidic conditions which would guarantee observation of the kinetic control product.[2d] Most recently, the tricyclic alcohol III-OH has become available,[5a] and we have now been able to study the hydrolysis of the corresponding *p*-nitrobenzoate III-OPNB. The results, which provide increased perspective regarding products, reactivities, and ground- and transition-state free energy relationships in nonclassical solvolysis, are described and discussed in the present communication.

I   II   III
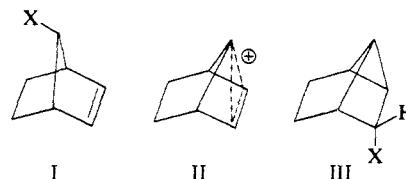
Tricyclic III-OH, prepared by a modification of the method of Tufariello,[5a] was converted to its *p*-nitrobenzoate III-OPNB by treatment with *p*-nitrobenzoyl chloride and pyridine in the cold. The III-OPNB,[6] mp 121.5–122.5°, with an excellent C and H analysis, and displaying the characteristic α-proton quartet signal[3d,4a,5a] at τ 4.78 in its nmr spectrum (CCl₄), could be isolated when great care was taken to avoid ionizing conditions.[7] In solvolysis, the tricyclic III-OPNB is probably the most reactive *p*-nitrobenzoate ever measured in these laboratories. In 90% acetone at 23°, the first-order rate constant for its disappearance (k_1 in eq 1) is (6.8 ± 0.5) $\times$ 10^{-2} sec.$^{-1}$ Considerable ion pair return accompanies solvolysis, the observed products being 30% of the relatively inert rearranged bicyclic I-OPNB along with 70% of rearranged bicyclic alcohol I-OH.

$$\text{III-OPNB} \xrightarrow[\text{90\% acetone}]{k_1} \text{I-OH (70\%)} + \text{I-OPNB (30\%)} \quad (1)$$
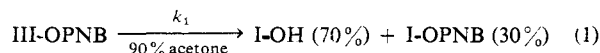
The solvolysis of the bicyclic I-OPNB[6] is so much slower than that of its tricyclic isomer that we measured its solvolysis rates at 100.0 and 125.1° in 50 and 70% acetone solvents and then estimated the rate constant at 23° in 90% acetone with the aid of two types of extrapolations. First, the rate constants at 23° in 50 and 70% acetone solvents were estimated by means of temperature extrapolations; then, the rate constant at 23° in 90% acetone was estimated by means of the Grunwald–Winstein *m*Y relation.[8] The results, summarized in Table I, show that tricyclic III-OPNB is more reactive in solvolysis than its bicyclic isomer by a factor of 8×10^{11}, nearly 12 powers of 10.

(5) (a) J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967); (b) J. J. Tufariello and R. J. Lorence, *J. Am. Chem. Soc.*, **91**, 1546 (1969).

(6) The melting point observed for III-OPNB by the ordinary capillary melting point technique, 121.5–122.5°, is that of the rearranged bicyclic I-OPNB. The latter, prepared separately from I-OH, had mp 121.5–122.0° and an excellent C and H analysis. Bicyclic I-OPNB, mp 121.8–122.8°, was first prepared in these laboratories by C. Ordronneau in 1959.

(7) When pure nonpolar solvents and carefully dried base-washed glassware were employed, and recrystallization was from cold petroleum ether, samples of III-OPNB were obtained which contained >90% tricyclic ester (the rest being bicyclic I-OPNB) even after the sample was dissolved in CCl₄ to determine its nmr spectrum.

(8) (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, **78**, 2770 (1956).