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]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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

(14) Professor S. Winstein has independently studied the solvolytic reactivity of *endo*-tricyclo[3.2.0.0^{2,7}]hept-6-yl *p*-nitrobenzoate. We thank him for informing us of his results prior to publication.

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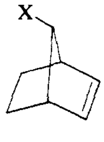
The "σ" Route to the 7-Norbornenyl Ion[1]

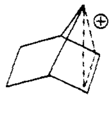
Sir:

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-OCH_3 has made possible the approach to II by the "σ" route.[2d,e] In FSO_3H as a solvent, both routes lead to ion II observed directly by nmr.[2e]

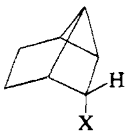
As regards solvolysis, the available tricyclic derivatives did not permit a solvolytic study under nonacidic conditions which would guarantee observation of the kinetic control product.[2d] Most recently, the tricyclic alcohol III-OH has become available,[5a] and we have now been able to study the hydrolysis 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 (CCl_4), 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 $(6.8 \pm 0.5) \times 10^{-2}$ 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.

$$\text{III-OPNB} \xrightarrow[90\%\ \text{acetone}]{k_1} \text{I-OH } (70\%) + \text{I-OPNB } (30\%) \qquad (1)$$

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.

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(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).

(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 CCl_4 to determine its nmr spectrum.

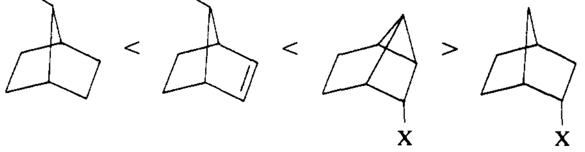
(8) (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, **78**, 2770 (1956).

Table I. Summary of Solvolysis Rates

Solvent	Temp, °C	k, sec^{-1}
	Bicyclic I-OPNB	
50% acetone	125.1	$(1.60 \pm 0.08) \times 10^{-5}$
	100.0[a]	$(1.36 \pm 0.07) \times 10^{-6}$
	23.0[b]	5.4×10^{-11}
70% acetone	125.1	$(2.82 \pm 0.15) \times 10^{-6}$
	100.0[c]	$(2.05 \pm 0.10) \times 10^{-7}$
	23.0[b]	4.3×10^{-12}
90% acetone	23.0[d]	8×10^{-14}
	Tricyclic III-OPNB	
90% acetone	23.0	$(6.8 \pm 0.5) \times 10^{-2}$

[a] $\Delta H^{\ddagger} = 28.2$ kcal/mol; $\Delta S^{\ddagger} = -10.2$ eu. [b] Extrapolated from data at higher temperatures. [c] $\Delta H^{\ddagger} = 30.0$ kcal/mol; $\Delta S^{\ddagger} = -9.0$ eu. [d] Extrapolated with the aid of the mY relation,[8] using Y values[8b] of 1.398, 0.130, and −1.856 for 50, 70, and 90% aqueous acetones, respectively.

This makes it *ca.* 10^{23} times as reactive as the saturated 7-norbornyl analog[2a] IV. Also, the tricyclic III system is seen to be some 10^{16} times as reactive as its *endo*-2-norbornyl analog[9] V without the cyclopropane group to provide anchimeric assistance to ionization.



	IV	I	III	V
k_{rel}	1	10^{11}	10^{23}	10^{7}

It is instructive to treat the rate comparison between tricyclic III-OPNB and bicyclic I-OPNB by means of eq 2 and 3, similar to those employed previously for the corresponding methyl ethers.[2d] In eq 3, K is the equilibrium constant between tricyclic and bicyclic isomers, (k_T/k_B) is a reactivity ratio R between tricyclic and bicyclic isomers, and (k_{-B}/k_{-T}) is a partition factor P representing kinetic control of products of reaction of R^+ with X^-.

$$\text{III-X} \underset{k_{-T}}{\overset{k_T}{\rightleftharpoons}} R^+ + X^- \underset{k_{-B}}{\overset{k_B}{\leftrightharpoons}} \text{I-X} \tag{2}$$

$$K = \frac{(\text{I-X})}{(\text{III-X})} = \left[\frac{k_T}{k_B}\right]\left[\frac{k_{-B}}{k_{-T}}\right] = RP \tag{3}$$

In acid-catalyzed methyl ether equilibration in MeOH, the tricyclic:bicyclic reactivity ratio R was observed[2d] to be 7×10^6. Since buffered neutral methanolysis of I-OTs yielded 99.7% bicyclic I-OCH_3 and 0.3% tricyclic III-OCH_3, the partition factor P for reaction of ion II with MeOH was 300. This led to an equilibrium constant K between the methyl ethers equal to 2×10^9. From the present work on the *p*-nitrobenzoates in 90% acetone, the tricyclic:bicyclic reactivity ratio is 8×10^{11}, some 10^5 times as great as the factor in the case of acid-catalyzed ether ionization. Approximating K for the *p*-nitrobenzoates to be the same as for the methyl ethers, we estimate P for reaction of ion II with *p*-nitrobenzoate ion to be $^1/_{400}$, 10^5 times more in favor of tricyclic product than in the case of reaction with neutral methanol.[10] Expressing the same thing in terms of transition-state free energies, the tricyclic transition state lies 3.4 kcal above the bicyclic in the reaction of II with CH_3OH, whereas it lies 3.5 kcal below the bicyclic transition state in the reaction with *p*-nitrobenzoate ion. The direction of the difference may be rationalized in terms of an expected[2d] lower degree of bond formation at the transition state when II reacts with *p*-nitrobenzoate ion rather than MeOH. The present results illustrate how much flexibility may exist in the ground- and transition-state free energy relationships in reactions of nonclassical carbonium ions, of which II is an example.

Regarding hydrolysis products from ion II, it was shown previously that neutral hydrolysis of bicyclic I-OTs in aqueous acetone leads quantitatively to bicyclic I-OH under conditions which tricyclic III-OH would survive.[2d,5a] Thus, bicyclic I-OH is the kinetic control product of hydrolysis of I-OTs, disproving the suggestion of Brown[11a] that the tricyclic alcohol is an intermediate in hydrolysis of I-OTs. The whole product of hydrolysis of tricyclic III-OPNB in 80% acetone containing excess $NaHCO_3$ was now examined by nmr in carbon tetrachloride solvent. The only product besides the 30% rearranged I-OPNB which was detected is the bicyclic I-OH. Using a computer of average transients in the region of the α-hydrogen quartet at τ 5.86 to detect tricyclic III-OH, the III-OH content was not as large as the threshold value for detection,[12] which we judged to be *ca.* 0.1%. A control experiment on III-OH under the conditions for hydrolysis of III-OPNB and extraction and analysis of the product showed III-OH to be stable to the whole procedure. Thus, we see that not even the tricyclic system III yields tricyclic alcohol as the kinetic control product of neutral hydrolysis.

Bicyclic I-OH is essentially quantitatively the kinetic control product of hydrolysis of either the bicyclic or tricyclic system. Thus, π-route ionization of I and "σ"-route ionization of III are shown to lead to the same intermediate even under solvolytic conditions where carbonium ion lifetime is so very short compared to those for nmr observation.[2e] All the criteria, rates,[2] products,[2] stereochemistry,[2,4,5a] and nmr[2e,13] point uniquely to structure II for this intermediate.[15]

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[9] S. Winstein, *et al., J. Am. Chem. Soc.*, **74**, 1127 (1952).

[10] Considerably enhanced proportions of tricyclic product are obtained in other reactions of II with anionic nucleophiles, such as $^-BH_4$,[2c,11a] ^-CN,[4b] ^-OMe,[2d] and $^-OCH_2C_6H_5$.[5a] The much lower P value for MeO^- than for MeOH was commented on previously,[2d] but the actual value of P for MeO^- in MeOH solvent was not available. This is because full control of product formation by MeO^- was not attained in the previous work.[2d]

[11] (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 159 (1964).

[12] It is interesting that the value of P for reaction of II with H_2O in aqueous acetone is even larger than it is for reaction of II with CH_3OH solvent.[2d]

[13] The nmr observations[2e,14] are especially compelling against the equilibrating tricyclic ion formulation formerly preferred by Brown[11a] and Deno[11b] for ion II, as well as the closely analogous 7-norbornadienyl cation. For the latter species, recent nmr evidence[14] on methyl-substituted 7-norbornadienyl cations makes the equilibrating tricyclic ion formulation completely untenable.

[14] M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6352 (1967).

[15] Tufariello and Lorence[5b] have independently studied the solvolysis of III-*p*-methoxybenzoate. We thank them for informing us of their results prior to publication.

[16] Fellow of the French Centre National de la Recherche Scientifique, on leave from the University of Strasbourg, 1967–1968.