

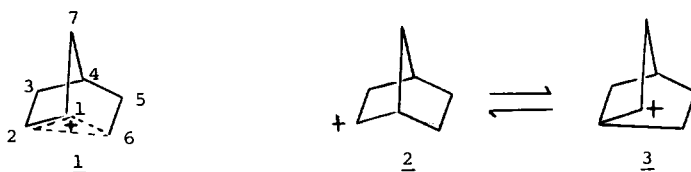
ACETOLYSIS OF 6-CARBOMETHOXY-2-NORBORNYL BROSYLATES

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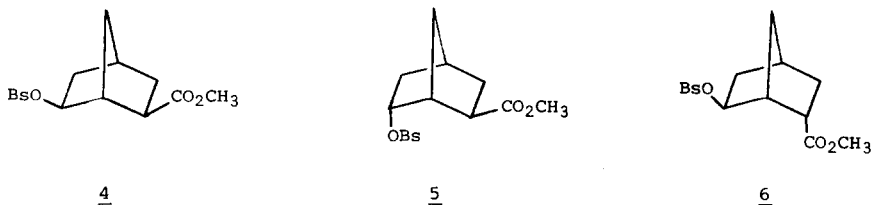
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The solvolysis of 2-norbornyl derivatives continues to command considerable interest, largely because of the controversy as to whether the 2-norbornyl cation is best formulated as a bridged, nonclassical ion 1, or as a pair of rapidly equilibrating classical ions 2 and 3.¹



An important property attributed to a bridged ion such as 1 is that nucleophilic attack should occur from the back side of the 3 centre bond to give exclusively exo-substituted product.¹ It has also been argued that the rapid oscillation of the C₁-C₆ bonding electron pair between C₁ and C₂ in the equilibrating ion formulation would prevent solvation of the endo-side of the norbornyl skeleton, and result again in exo-substitution^{2a} (the windshield wiper effect).^{2b} We felt that it might be possible to observe rapid equilibration and endo-substitution in a system in which an internal nucleophile is suitably positioned to capture the norbornyl cation intramolecularly from the endo-side. The 2-norbornyl cation generated from 6-exo-carbomethoxy-2-exo-norbornyl brosylate 4 and 6-exo-carbomethoxy-2-endo-norbornyl brosylate 5 constitutes such a system.

The rate data for the acetolysis of brosylates³ 4, 5 and 6 are shown in Table 1, and the product distribution is given in Table 2. The products were isolated by preparative vapour phase chromatography (vpc) and identified by spectral comparison with authentic samples. From the rate data it is immediately apparent that the electron-withdrawing carbomethoxy group causes a large rate retardation relative to the unsubstituted norbornyl brosylates (right



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Brosylate ^a	T, °C	k, sec ⁻¹	$\frac{k_{\text{exo}}}{k_{\text{endo}}}$ at 25°	$\frac{k_{\text{CO}_2\text{CH}_3}}{k_{\text{H}}}$ at 25°
<u>4</u>	100.0	1.88x10 ⁻⁴	4.4	8.4x10 ⁻⁵
	81.5	2.32x10 ⁻⁵		
	71.7	7.12x10 ⁻⁶		
	25.0 ^b	7.4 x10 ⁻⁹		
<u>5</u>	100.0	4.05x10 ⁻⁵	350	6.8x10 ⁻³
	81.5	5.07x10 ⁻⁶		
	25.0 ^b	1.7 x10 ⁻⁹		
<u>6</u>	58.6	5.25x10 ⁻⁴	350	5.5x10 ⁻²
	48.5	1.70x10 ⁻⁴		
	25.0 ^b	4.8 x10 ⁻⁶		
2-exo-norbornyl	24.98 ^c	8.79x10 ⁻⁵	350	
2-endo-norbornyl	25.0 ^c	2.52x10 ⁻⁷		

a [ROBs] = 0.02M, [NaOAc] = 0.022M

b Calculated from data at other temperatures

c S. Winstein and D. Trifan, *J.Amer.Chem.Soc.* **74**, 1147, 1154 (1952)
S. Winstein *et al*, *ibid*, **74**, 1127 (1952)

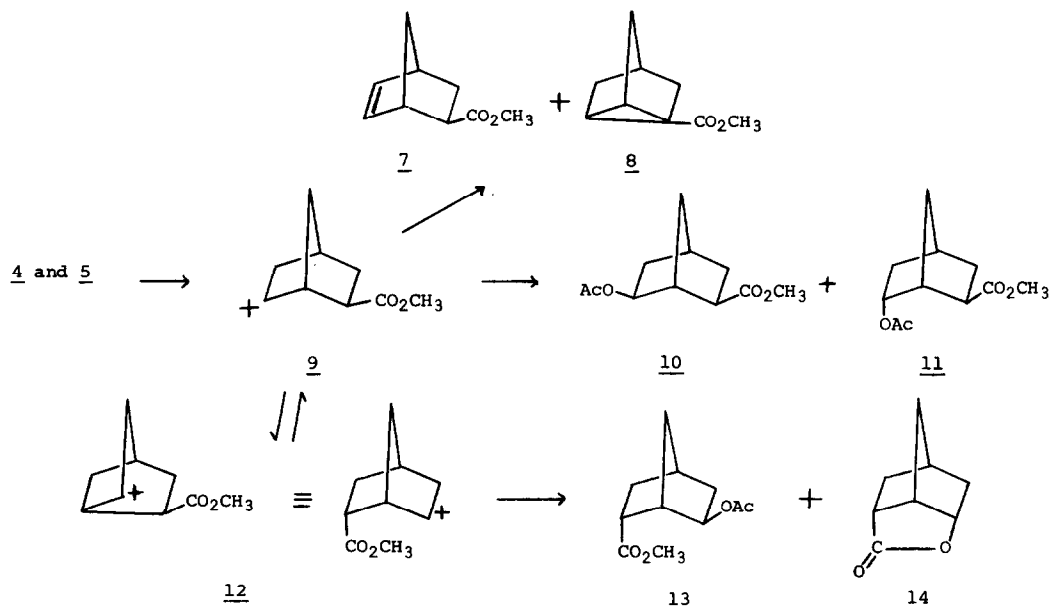
Table 1. First order titrimetric rate constants for acetolysis.

Brosylate	Product, % ^a						
	<u>7</u>	<u>8</u>	<u>10</u>	<u>11</u>	<u>13</u>	<u>14</u>	Unidentified
<u>4</u> ^b	22	4	32	3	5	33	1
<u>5</u> ^c	1	10	80	trace	2	6	1
<u>6</u> ^c						>99	<1

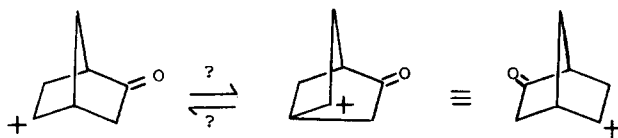
a Normalized percentages from vpc analysis;

b [ROBs] = 0.25M, [NaOAc] = 0.28M; c [ROBs] = 0.10M, [NaOAc] = 0.11M

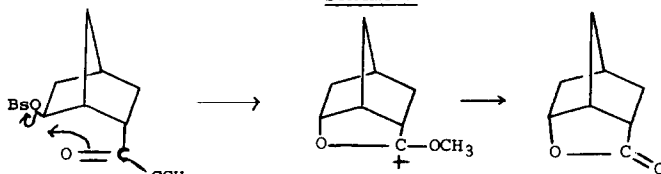
Table 2. Products of acetolysis of brosylates 4, 5 and 6.



Scheme 1



Scheme 2



Scheme 3

hand column of Table 1). Rate retardations of varying magnitudes have been observed in the acetolysis of 7-keto-2-norbornyl,⁴ 5-keto-2-norbornyl,⁵ syn- and anti-7-chloro-2-norbornyl,⁶ anti-7-methoxy-2-norbornyl,^{7,8} 5-exo- and 6-exo-methoxy-2-norbornyl⁸ and 1-cyanoapoisobornyl and 1-cyanobornyl⁹ sulphonates. A rather good Taft $\rho^*\sigma^*$ correlation has been found for the 7-substituted norbornyl tosylates,⁷ indicating that the substituent effects in these compounds are inductive in nature. Using the ρ^* value of -2.33 for the acetolysis of 2-exo-norbornyl sulphonates at 25°,⁷ and a value for σ^* of +0.71 for the $-\text{CH}-\text{CO}_2\text{CH}_3$ substituent (the value of +2.00 for σ^* for $-\text{CO}_2\text{CH}_3$ reduced by a factor of 2.8 for the additional carbon atom by which the ester function is disposed from the reaction centre)¹⁰

the calculated value $k_{\text{CO}_2\text{CH}_3} : k_{\text{H}}$ for 4 is 2.2×10^{-2} . The observed rate retardation $k_{\text{CO}_2\text{CH}_3} : k_{\text{H}}$ of 8.4×10^{-5} is thus greater by a factor of 260 than that calculated on the basis of the Taft equation. This additional rate retardation can be explained if it is assumed that 2-exo-norbornyl brosylate ionizes with participation of the 1, 6-bonding electrons, but that in 4, participation is largely repressed. For the endo-brosylate 5 the calculated rate retardation $k_{\text{CO}_2\text{CH}_3} : k_{\text{H}}$ of 4.2×10^{-2} is closer to the observed value of 6.8×10^{-3} ($\rho^* = -1.94^7$ and $\sigma^* = +0.71$). An alternative explanation is that because of the rigidity of the norbornyl skeleton, an additional rate retardation is observed for 4 due to unfavourable dipole-dipole interactions between the carbomethoxy group and the developing positive centre at C_2 in the transition state for ionization.

Because of these rate retardations, and the low exo-endo rate ratio observed for 4 and 5 and since the acetolysis of 4 and 5 results in the formation of a considerable amount of endo-substituted product, the ionization of 4 and 5 is most simply formulated as proceeding to the classical ion 9 (Scheme 1). Elimination to give 7 and 8, and capture by solvent to give acetates 10 and 11 then competes with Wagner-Meerwein rearrangement (equilibration) to ion 12. Capture of 12 by solvent gives exo-acetate 13, while intramolecular capture by the carbomethoxy group gives lactone 14. (Acetate 13 is stable under the acetolysis conditions).

Although the electron-withdrawing carbomethoxy group at C_6 perturbs the norbornyl system sufficiently so that ionization to a bridged norbornyl cation does not occur, the results observed are nevertheless of interest. For example, in the 5-keto-2-norbornyl cation 5, Wagner-Meerwein rearrangement causes no structural change (Scheme 2), and its detection would require the use of optically active or otherwise labelled substrate. The product distribution from 4 and 5 clearly shows that Wagner-Meerwein rearrangement can still occur in a norbornyl cation bearing a strongly electron-withdrawing substituent on the migrating carbon atom. This suggests that in the transition state for migration, little or no positive charge resides on the migrating carbon atom.

The rate of acetolysis of brosylate 6 at 25° is 650 times greater than that of brosylate 4. This observation, together with the fact that lactone 14 is the only product obtained, suggests that 6 undergoes ionization with anchimeric assistance from the carbomethoxy group (Scheme 3).

References and Footnotes

1. For a review of the literature through to 1966 see G.D.Sargent, Quart.Rev., 20, 301, (1966) and G.E. Gream, Rev.Pure and Appl. Chem., 16, 25 (1966). For leading reference to more recent work see references 4-9.
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