Analysis of the Thermodynamic and Kinetic Factors which Control Entry into, and Wagner–Meerwein Rearrangement within, the $C_{12}H_{15}^+$ Systems

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Summary The relative kinetic and thermodynamic factors controlling the Wagner–Meerwein inter-relationship of the perhydromethenocyclopenta[*a*]pentalenyl brosylates (1a) and (2a) have been determined; the *endo*-brosylate (7a) was also examined and found to be unusually reactive for an *endo*-2-norbornyl derivative.

The availability of perhydro methenocyclopenta[*a*]pentalene derivatives from Diels–Alder reactions of 9,10-dihydrofulvalene[1,2] affords an opportunity to assess the solvolytic behaviour of the brosylate (1a), the missing member of the Wagner–Meerwein related pair (1) ⇌ (2). Conversion of

(1) into the σ-bridged cation (4) was expected to occur from the ideal C(3)–C(8) alignment,[3] but subsequent distribution between products (1) and (2) on solvent capture was uncertain. Although the cation (4) could also arise from ionization of (2), Winstein and Hansen[4] have reported that anchimeric assistance by the C(3a)–C(3b) bond operates exclusively to give (5), the identical ion formed upon solvolysis of (3a). This finding is intriguing since molecular models reveal the C(2)–C(8) bond in (2) to be nearly antiplanar to the leaving group, while the C(3a)–C(3b) bond deviates from antiplanarity. A recent study[3] of a closely related tricyclic system, where direct participation by either of two C–C bonds is similarly possible, showed that the pathway involving participation by the more favourably aligned bond predominated by a factor of 2·2 : 1 over that leading to the thermodynamically more stable product(s). To establish whether the formation of cation (5) was the result of contrasting enthalpic control, rapid conversion of (4) into (5), or some other factor, the acetolysis of (1a) was studied together with the acetolyses of (2a) and (3a).

(1)   (2)   (3)

(4)   (5)
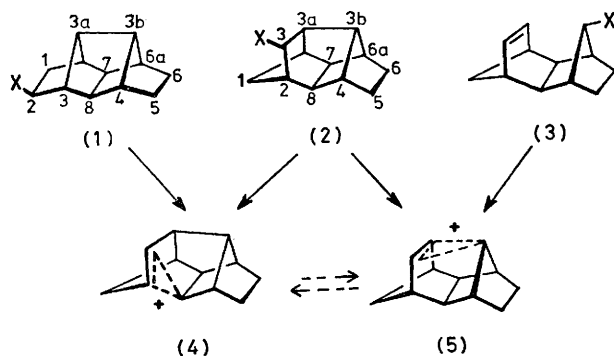
a; X = *p*-BrC₆H₄SO₃, b; X = OAc, c; X = OH
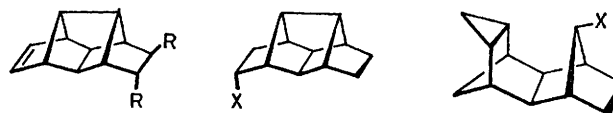
(6), R = CO₂Me   (7)   (8)

Preparation of the brosylate (1a) began with the catalytic hydrogenation (5% Rh–C) of the *trans* monoene diester (6) and decarboxylation of the derived diacid.[1b] Hydroboration–oxidation of the resulting olefin gave (1c), m.p. 78·2—79·2 °C. When oxidized (Collins) and reduced (LiAlH$_4$), (1c) was transformed into (7c), m.p. 47—51 °C. The brosylates (1a) and (7a) have m.p.s of 83·5—84·5 and 86·0—86·5 °C, respectively. In each instance, the inter-related brosylates (1a), (2a), and (3a) gave rise to mixtures of the acetates (1b) and (2b) on acetolysis (Table).

TABLE. Acetate product distribution from the acetolysis of (1a)—(3a).

Substrate	% (1b)	% (2b)
(1a)	90·1 ± 0·3	9·9 ± 0·3
(2a)	34·6 ± 0·3	65·4 ± 0·3
(3a)	8·5 ± 0·2	91·2 ± 0·3

The ratio of products obtained from (1) indicates that the ion (4) is captured by solvent with little or no ($<$ 9·9%) rearrangement to (5). Application of these limiting values (0—9·9%) for isomerization of (4) to (5) to the reaction of (3), which must ionize initially to (5), shows that (5) must undergo 8·5—9·4% rearrangement to (4) prior to covalent bonding with the solvent. Similar analysis indicates that the ionization of (2) is partitioned between (4) (34·6—38·4%) and (5) (61·5—65·4%) if counterion effects are unimportant. The current results for (2a) and (3a) are more consistent with expectations based on Nickon's findings[3] and the extensive rearrangement observed on acetolysis of (8).[5]

To assess the contribution of enthalpic (product stability) effects during the ionization of (2) to (4) and (5) various mixtures of (2b) and (1b) were subjected to acid-catalysed equilibration (HOAc, 75 °C). At equilibrium, the resulting product ratio [99·5% (2b); 0·5% (1b)] corresponds to a free energy difference of 3·7 kcal mol^{-1}. Thus, participation by

the proximate C(3a)–C(3b) bond in (2) is decidedly favoured by thermodynamic considerations, and the bifurcate reactivity of (2) is found to be opposite both in direction and magnitude to the behaviour of Nickon's twistbrendyl system.[3]

The reactivity of (1b) in acetolysis ($k = 5·30 \times 10^{-4}$ s^{-1} at 30·1 °C) is unusually high when compared to those of other ring fused *exo*-2-norbornyl brosylates[6] whereas the rate constant for ionization of (2a) ($k = 8·53 \times 10^{-8}$ s^{-1} at 25 °C)[4] is more closely aligned to those of these latter brosylates. If the free energy difference between (1) and (2) is closely comparable at 75 and 25 °C and the acetolysis products from (2) represent the relative levels of C(2)–C(8) and C(3a)–C(3b) participation, then most of the 5·3 kcal mol^{-1} difference in the free energy of activation for the respective ionizations to (4) results from the higher ground state energy of (1).

The *endo*-brosylate (7a) underwent ready acetolysis with formation of a mixture of (1b) (95·1 ± 0·15%) and (2b) (4·9%) at a rate ($k = 2·39 \times 10^{-4}$ s^{-1} at 30·1 °C) some 10^3 times faster than that exhibited by *endo*-2-norbornyl brosylate.[7] The low *exo/endo* rate ratio for (1)/(7) is thus a consequence of increased reactivity of the *endo* isomer rather than decreased reactivity of the *exo* isomer.[8] The high levels of (1b) produced may be accommodated by incursion of a k_s (anchimerically unassisted) process. Mutual bonding of the two bridge carbon atoms as in (7), while enhancing ground state strain, decreases steric congestion on the *exo* surface relative to 2-norbornyl. Models also show the trajectory followed by the departing brosylate ion to be less sterically encumbered than normal.

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