The Stability of the 2-Bicyclo[2,1,0]pentyl Cation and Anion

By P. R. BROOK* and B. V. BROPHY

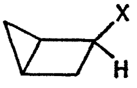
(*Department of Organic Chemistry, The University, Leeds* LS2 9JT)

Summary In contrast to the 2-bicyclo[2,1,0]pentyl cation, the corresponding 2-carbanion, stabilized by a carbomethoxyl group, shows no tendency to ring-open.

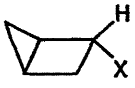
SOLVOLYSIS of suitable derivatives of the epimeric bicyclo-[2,1,0]pentan-2-ols (IIa and IIb) should give information on the nature of the transition states leading to the 2-cation. A similar method had been employed for the 2-bicyclo-[3,1,0]hexyl series.[1]

Use of *exo*-2-acetylbicyclo[2,1,0]pentane (Ib) in the Baeyer–Villiger reaction (monopermaleic acid), followed by basic hydrolysis of the acetate, gave the *exo*-alcohol (IIb), (*p*-nitrobenzoate, m.p. 94°). The *endo*-series proved more labile and the best *endo*-acetate [from reaction of ketone (Ia) with *m*-chloroperbenzoic acid] contained 3-cyclopentenyl acetate (5% : n.m.r. analysis). After basic hydrolysis, the crude alcohol mixture, from its n.m.r. spectrum, contained 67% of cyclopenten-3-ol and only 33% of the required *endo*-alcohol (IIa). The large proportion of unsaturated alcohol formed is explained if solvolysis of the acetate group (with resultant ring-opening) competes with hydrolysis of the ester.

This marked difference in behaviour of *endo*- and *exo*-derivatives is in line with the solvolytic behaviour of the corresponding 3,5-dinitrobenzoates[2] ($k_{\text{endo}}/k_{\text{exo}}$ *ca.* 10^7) and in contrast with solvolysis of the 2-bicyclohexyl derivatives ($k_{\text{endo}}/k_{\text{exo}}$ 1·52). The special reactivity of the *endo*-2-bicyclopentyl derivatives suggests an early transition state, with relief of strain in the 1,4-cyclopropyl bond as the rearward participation increases. Thus the transition state is probably stabilised more by monohomoallylic or bicyclobutonium ion character† than by the bishomoallylic resonance found for the 2-bicyclo[3,1,0]-hexyl cation, where a late transition state is envisaged.[1]



(a)

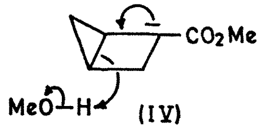


(b)

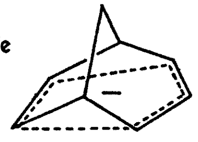
(I) X = Ac

(II) X = OH

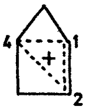
(III) X = CO_2Me



(IV)



(V)



(VI)

The *endo*- and *exo*-2-carbomethoxybicyclopentanes [respectively (IIIa) and (IIIb)] are suitable substrates for generation of the 2-carbanion. In addition to resonance-stabilization of the anion by the carbomethoxy-group, the acidity of the C-2–H bond may be increased by the ring strain in the bicyclic system.[3] The latter assumption was not confirmed by the ^{13}C satellites in the n.m.r. spectrum

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†If 1,3-interactions (in this case between C-2 and C-4) are considered, the transition state must have some of the character of the bishomocyclopropenium ion (VI) and therefore be of lower energy than that from the *exo*-derivative.

of the *endo*-ester (IIIa), however, which gave ^1J (^{13}C-2,H) = 138 ± 1 Hz. corresponding to 28% *s*-character in the bond.[4] This is close to the value for the allylic methylene group in cyclobutene.[5] The cyclopropyl methylene value was normal ^1J (^{13}C-5, H) = 162 ± 1 Hz. (cyclopropane value 161 Hz.).[4,6]

With 1·4 M-NaOMe in boiling MeOH the esters reached equilibrium (57% *endo*-ester) within 4 hr. Surprisingly, this epimerisation involving the C-2 carbanion gave no ring-opened products even though a process such as (IV) would relieve some 28 kcal/mole of ring-strain.[7] Such a ring-opening has been observed for simple cyclopropylcarbinylmagnesium halides which react to give allylcarbinyl derivatives.[8] An equilibrium involving classical ions has been postulated here.[9]‡ In contrast, an example of a non-classical cyclopropyl carbinyl anion is found in the bishomoaromatic ion (V): quenching yields 0·5% of cyclopropyl compounds.[10]

We suggest two reasons for the difficulty of ring-opening of the 2-bicyclo[2,1,0]pentyl anion. Firstly, the 2-methoxycarbonyl group stabilises the charge at C-2 mesomerically, and secondly the transition state involving interaction of the strained 1,4-bond with the carbanion resembles the high-energy, antiaromatic bishomocyclopropenyl anion (*cf.* footnote†).

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‡ The role of magnesium compounds as Lewis acids may be important in facilitating this equilibrium.

[1] P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Comm.*, 1968, 425.

[2] K. B. Wiberg, V. Z. Williams, jun., and L. E. Frederick, *J. Amer. Chem. Soc.*, 1968, **90**, 5338.

[3] C. A. Coulson and W. Moffitt, *Phil. Mag.*, 1949, **40**, 1.

[4] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 768.

[5] I. Fleming and D. H. Williams, *Tetrahedron*, 1967, **23**, 2747.

[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1966, vol. II, p. 1010.

[7] Footnote 8 in ref. 2.

[8] J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, 1951, **73**, 2509.

[9] M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1960, **82**, 2647.

[10] S. Winstein , M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, 1967, **89**, 3657; J. M. Brown, *Chem. Comm.*, 1967, 639.