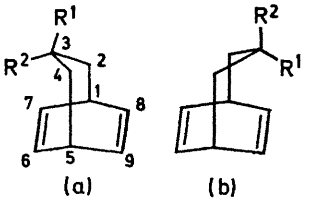
Synthesis and Conformational Mobility of Bicyclo[3,2,2]nona-6,8-dienes

By A. J. BAKER,* A. M. CHALMERS, W. W. FLOOD, D. D. MACNICOL, A. B. PENROSE, and R. A. RAPHAEL

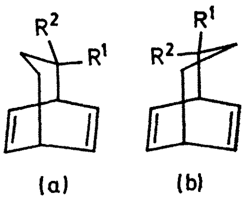
(*Chemistry Department, University of Glasgow, Glasgow, W.2*)

Summary An efficient synthesis of bridge-oxygenated bicyclo[3,2,2]nona-6,8-dienes is described and evidence for high conformational mobility in this system is presented.

IN contrast to the voluminous literature on 3,6-bridged cyclohexa-1,4-dienes with one- and two-carbon bridges investigation of the bicyclo[3,2,2]nona-6,8-diene system has been meagre,[1,2] mainly due to lack of a general synthetic method. We now report a flexible route to bridge-oxygenated members of this system and the finding of high conformational mobility in the series. Electrolytic bisdecarboxylation[3] of the cycloheptadiene–maleic anhydride adduct[4] gave the parent hydrocarbon (I),[†] m.p. (sealed tube) 83—84°. Similar treatment of the cyclohepta-3,5-[‡] and -2,4-dienyl benzoate[§]–maleic anhydride adducts followed by hydrolysis, gave the alcohols (II) and (V). Electrolysis yields were in the 40—60% range. Jones oxidation of (II) and (V) gave the corresponding ketones (IV), m.p. 52—55°, and (VII), m.p. *ca.* 15°. Ketone (VII) was more readily prepared by electrolysis of the cyclohepta-2,4-dienone–maleic anhydride adduct and was also obtained as a 70 : 30 mixture with bicyclo[3,2,2]nona-3,6,8-triene-2-one[2] on electrolysis of the tropone–maleic anhydride adduct.[5]



(I) R¹ = R² = H
(II) R¹ = OH, R² = H
(III) R¹ = CH₃, R² = OH
(IV) R¹ = R² = O



(V) R¹ = H, R² = OH
(VI) R¹ = CH₃, R² = OH
(VII) R¹ = R² = O

High-dilution i.r. measurements (in CCl_4) on alcohols (II), (V), and (VI) showed the presence of free hydroxyl (II, 3620;

[†] All new compounds gave satisfactory analytical and spectral data.

[‡] Obtained as two epimers, m.p. 222—225° and 196—199° in which the benzoyloxy-group is equatorial (*exo*) and the three-carbon bridge adopts a preferred *syn-* and *anti*-configuration with respect to the C-6, C-7 double bond. The anhydride group is *endo* in all the adducts described.

[§] Obtained as a single epimer with an equatorial benzoyloxy-group.

V, 3622; VI 3610 cm^{-1}) and bonded HO $\cdots\cdots\pi$-hydroxyl (II, 3588; V, 3585; VI 3585 cm^{-1}) with the former predominating. This shows that these alcohols exist in solution as an equilibrium mixture of conformers (a) and (b). In contrast, the tertiary alcohol (III), obtained from ketone (IV), adopts, in solution, the fixed conformation (IIIa) as evidenced by the presence *only* of strong HO $\cdots\pi$-bonded absorption at 3580 cm^{-1}. This preferential conformation must be induced by the unfavourable steric requirements of the methyl group in the alternative conformation (IIIb).

The n.m.r. spectra of the hydrocarbon (I), the alcohols (II), (V), and (VI), and the ketones (IV) and (VII) are indicative of rapid interconversion between conformers by bridge flipping, *e.g.* (Ia) $\rightleftharpoons$ (Ib). For example, the C-2 and C-4 methylene protons in the ketone (IV) are isochronous and appear as a doublet at τ 7·63 (J_{12} 3·7 Hz) which collapse on irradiation of 1-H (5-H) the C-6—C-9 vinylic protons give rise to a sextet centred at τ 3·69 (J_{67} 8·3, J_{16} 1·3, J_{17} 6·2 Hz) also have chemical-shift equivalence.

Attempts to "freeze out" conformations at low temperatures were unavailing. Thus, the 100 MHz spectra (in CF_2Cl_2) of (I), (IV), and (VII) remained essentially invariant down to −140°. From this it may be inferred¶ that the free energy of activation ($\Delta G^{\ddagger}$) at −140° is less than 8 kcal/mole.[6]

We thank the S.R.C. (A.M.C. and A.B.P.) and the Carnegie Trust (W. W. F.) for financial support.

(*Received, November 24th,* 1969; *Com.* 1780.)

¶ That is, if one makes the assumption that at least one shift which would be expected to emerge for slow (n.m.r. sense) exchange is $\geqslant$ *ca* 0·05 p.p.m. In (VII), for example, there are four such distinct shifts which might be observed in the "frozen" spectrum, reducing, though not eliminating, the possibility of accidental isochrony (or near isochrony).

[1] J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 6536.
[2] M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, 1967, **89**, 6356.
[3] P. Radlick, R. Klems, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Letters*, 1968, **5117**; H. H. Westberg and H. J. Dauben, jun., *ibid.*, 5123.
[4] K. Alder and H. H. Molls, *Chem. Ber.*, 1956, **89**, 1960.
[5] T. Nozoe, T. Mukai, T. Nagase, and T. Toyooka, *Bull. Chem. Soc. Japan*, 1960, **33**, 1247.
[6] F. A. L. Anet and M. A. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 2389 have reported analogous rate processes relating to [3,3]paracyclophane.