Extensive Delocalization in Potassium Bicyclo[3,2,1]octadienylide

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THE extreme ease of base-catalyzed isotope exchange at the 4-position of bicyclo[3,2,1]octadiene,[1] (Ia; $R^1 = R^2 = H$) has been explained in terms of charge delocalization from the allyl system to the proximate olefinic grouping in an anionic intermediate (II). This explanation is now substantiated by experiments which allow direct observation of this anion.

Bicyclo[3,1,0]hex-2-ene-*cis*-6-carboxyaldehyde,[2] reacts with methoxymethylenetriphenylphosphorane[3] in dimethyl sulphoxide to give, on work-up and alumina chromatography, first *cis*-6-(*cis*-2-methoxy)vinylbicyclo[3,1,0]hex-2-ene, (IIIb), *m/e* 136; ν_{max} 3050, 2830, 1660, 1595, 1255, 1100, 758, 731 cm.$^{-1}$, and then *endo*-4-methoxybicyclo[3,2,1]-octa-2,6-diene, (Ib) *m/e* 136; ν_{max} 3058, 3030, 2810, 1585, 1095, 735, 702 cm.$^{-1}$. The enol ether (IIIb) on heating to 180°, rearranges smoothly to an isomer, presumably *trans*-6-(*cis*-2-methoxy)-vinylbicyclo[3,1,0,]hex-2-ene, (I), *m/e* 136; ν_{max} 3045, 2830, 1660, 1595, 1270, 1100, 758, 715 cm.$^{-1}$. Both (III) and (IV) are converted at 220° into *exo*-4-methoxybicyclo[3,2,1]octadiene, (Ic), *m/e* 136; ν_{max} 3060, 3030, 2815, 1585, 1090, 730, 692 cm.$^{-1}$, in high yield, essentially free from (Ib). The structural assignments to (Ib) and (Ic) are supported by many aspects of their n.m.r. spectra (see Table). The isolation of one isomer of the intermediate *cis*-divinylcyclopropane (IIIb), and its reluctance to rearrange thermally[4] suggests a powerful steric retardation in the Cope rearrangement (IIIb) → (Ic), whereas the non-isolation of

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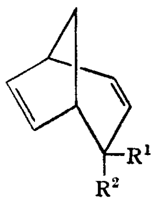
TABLE

N.m.r. spectra of bicyclo-octadienes. (Spectra taken as 5% solution in CCl_4 relative to Me_4Si internal standard at 100 mc./sec.)

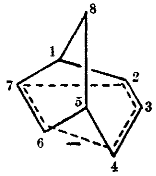
	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8‡	H-8 §
(Ia)	7·42	4·11	4·90	7·79 *exo* 8·24 *endo*	7·42	4·42	3·90	8·10	8·32
(Ib)	7·50	3·90	4·88	6·25	6·85	4·40	3·71	7·98	8·17
(Ic)	7·34	3·95	4·87	6·81	7·34	4·28	3·67	8·23	8.09

$J_{4,4'}$ (Ia) = 18 c./sec. $J_{8,8}$ = 9·5—10·5 c./sec.

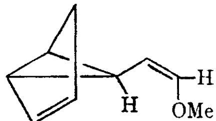
‡ *syn* to C-6,7; $J_{(1,5)8}$ = 4·5 c./sec.
§ *anti* to C-6,7; $J_{(1,5)8}\sim 0$



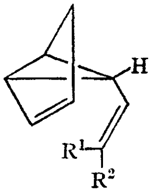
(Ia) $R^1=R^2=H$
(Ib) $R^1=H$, $R^2=OMe$
(Ic) $R^1=OMe$, $R^2=H$



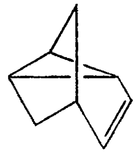
(II)



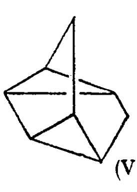
(IV)



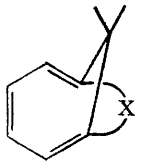
(IIIa) $R^1=H$, $R^2=OMe$
(IIIb) $R^2=OMe$, $R^2=H$



(V)



(VI)



(VIIa) $X=CH{:}CH{\cdot}CH^-$
(VIIb) $X=CH{:}CH{\cdot}CH{:}CH$
(VIIc) $X=CH{:}CH{\cdot}CH{:}CH{\cdot}CH^+$

(IIIa) is consistent with a lack of such hindrance to the (IIIa) → (Ib) rearrangement: a result to be expected on the basis of molecular models.

Compounds (Ib) and (Ic) react with sodium–potassium alloy in a variety of ether solvents. In tetrahydrofuran, (Ib), containing by g.l.c. analysis 2% of (Ic), reacts moderately slowly, and on quenching with methanol gives† (Ia), traces (< 0·5%) of other volatile compounds (V, VI?) and much recovered (Ib), now containing 6% of (Ic). Since (Ic) is very reactive towards the alloy, it appears that some of the carbanion (II) produced in the reaction abstracts *exo*-C-4 proton from further (Ib), producing the methoxy-analogue of (II). In contrast (Ic) reacts rapidly, and occasionally exothermically, under these conditions. After shaking for an hour at 0°, followed by centrifigation to remove excess of alloy and sodium methoxide, a clear orange solution is obtained, quite stable for many hours in the absence of air. Quenching the solution by syringing into water, methanol, acetic acid, or dimethyl sulphoxide gave in all cases, (Ia) with traces of recovered (Ic). The absence of isomeric hydrocarbons (V) and (VI) is in contrast to the observations of Winstein and Nicholson[5] on the products of various reductive reactions reasonably expected to have involved (II), where quite appreciable quantities of (V) and (VI) were observed, although (Ia) was always the major product.

The stability of (II) in tetrahydrofuran solution permits its spectroscopic evaluation: a flat-topped ultraviolet absorption band corresponding to two very broad overlapping bands centred at 320 and 380 mμ (ε plateau ~10^3) may be observed using microcell techniques and is completely destroyed on admission of air. Careful preparation of the anion solution in perdeuterotetrahydrofuran allows observation of an n.m.r. spectrum in which contamination by (Ia) and (Ic) is slight, although (Ia) is produced very slowly on prolonged standing of the solution at 33·5°.

Compared to the solution of (Ia) obtained after aqueous quenching, the most immediate and obvious feature of the spectrum is the 2·25 p.p.m.

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† G.l.c. analysis was carried out on a 4 m. GEO-column at 115°.

upfield shift sustained by C-6,7 protons, compared with an upfield shift of 0·1 p.p.m. for C-1,5 protons and 3·03 p.p.m. for C-2,4 protons [relative to C-2 in (Ia)] which are directly part of the allylic system.[6] Consequently the postulate of delocalization of charge in (II) is securely founded. An alternative explanation in which (II) is in rapid equilibrium with the conjugate base of (V) is inconsistent with both the acid quenching experiments and the n.m.r. spectrum.[7]

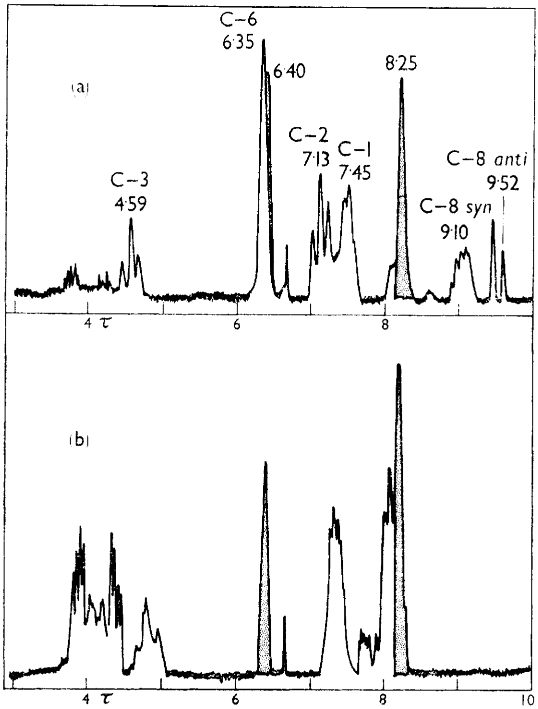

FIGURE. (a) (II) *in perdeuterotetrahydrofuran*; (b) H_2O *quench of* (a).

Delocalization over a 6π-electron system would be expected to produce a diamagnetic ring-current, although any effect on the line-positions of C-2 and C-6 protons is secondary to the shielding by negative charge-density which is difficult to assess quantitatively without more detailed knowledge of charge-distribution.[6] The C-3 line-position, at first-sight anomalously low-field, finds analogy in the n.m.r. spectrum of allyl-lithium in diethyl ether.[8] However, the 1·15 p.p.m. average upfield shift of C-8 protons appears to be too large to be accounted for on the basis of negative charge shielding alone particularly when the charge does not have an important systematic effect on the line position of the bridge protons of (VII) [(VIIa) $\tau = 10{\cdot}95$[9a]; (VIIb) $\tau = 10{\cdot}50$[9b]; (VIIc) $\tau = 11{\cdot}05$[9c]]. Reference to the Johnson–Bovey shielding tables[10] using a 6π-electron ring-current in a ring radius 1·4 Å in the plane of C-3,6,7 and centred equidistantly from these atoms gives much higher values for the magnetic shielding [H-8 *syn* 2·1; H-8 *anti* 3·4 p.p.m.] so that on this basis 30—40% of a fully developed 6π-electron ring-current is operative. Since (II) is more attenuated than any system yet reported to sustain a ring-current,[11] and since only that part of the total π-electron density on the *endo*-face of the molecule may delocalize, this is hardly surprising.

The synthesis of (II) afford a potential route to a number of interesting analogues of cyclopentadienylmetal derivatives.

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[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance", Pergamon Press, Oxford, 1965, p. 595. The absolute values obtained for C-8–H shielding are relatively insensitive to the actual parameters chosen and do not affect the qualitative argument.

[11] *cf.*, Homotropylium cation: S. Winstein, H. D. Kaesz, C. G. Kreiter and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1965, **87**, 3267; C. E. Keller and R. Pettit, *ibid.*, 1966, **88**, 604.