2-Methylenebicyclo[3,2,1]octa-3,6-diene, a Bishomofulvene-type Structure

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Summary From a study of its n.m.r. and u.v. spectra and its dipole moment, it has been shown that the resonance contribution of a bishomofulvene-type structure is important in 2-methylenebicyclo[3,2,1]octa-3,6-diene (**2**).

WE report the syntheses and properties of 2-methylenebicyclo[3,2,1]octa-3,6-diene (**2**) and 2-methylenebicyclo[3,2,1]oct-3-ene (**4**). The olefin (**2**) was obtained in good yield either from the reaction of (**1**)[1] with triphenylphosphine methylide in THF or from the addition of methylmagnesium iodide to (**1**) followed by dehydration of the resulting methylcarbinol. The structure of (**2**) followed from its ^{1}H n.m.r.‡ [τ 3·60—4·20 (4H), 4·95 (1H, m), 5·19 (1H, m), 6·71 (1H, m), 7·18 (1H, m), and 7·85 (2H, m)] and mass

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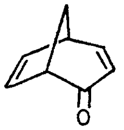
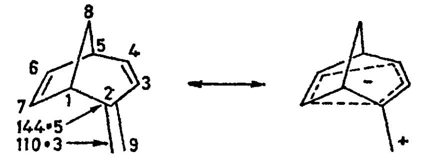
‡ Detailed analysis of ^{1}H and ^{13}C n.m.r. spectra will be reported in a forthcoming full paper.

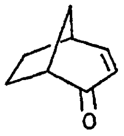
spectra. The latter spectrum confirmed the molecular weight (118) and the base peak was attributed to $(M - 1)^+$, corresponding to $C_9H_9^+$. Compound (**4**) was similarly prepared from (**3**)[2] τ 4·20 (2H, m), 5·20 (2H, m), and 7·5—8·5 (8H, m)].



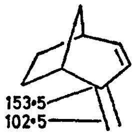
(1)



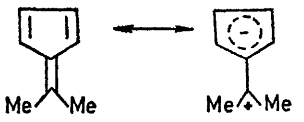
(2) (2a)



(3)



(4)



(5) (5a)

(6)

The most striking physical properties of (**2**) are its ^{13}C n.m.r. and u.v. spectra and its dipole moment.[3]

The ^{13}C n.m.r. chemical shifts of C-2 and C-9 in (**2**) are δ (Me_4Si) 144·5 and 110·3, respectively. Under identical conditions, the ^{13}C n.m.r. chemical shifts of C-2 and C-9 in (**4**) are δ (Me_4Si) 153·5 and 102·5, respectively, *i.e.*, it could be taken that the C-2 in (**2**) is more electronegative than that in (**4**) and the C-9 in (**2**) is more positive than that in (**4**).[4] This suggests that resonance contribution of (**2a**) is important in (**2**).

Measurement of the u.v. spectrum of (**2**) showed a broad absorption having fine structure at 243 nm (ε 12,000) (calculated[5] λ_{max} 232 nm). The olefin (**4**) has a spectrum with λ_{max} at 230 nm, and ϵ_{max} 5000. This bathochromic effect of 13 nm in (**2**) can be accounted for in a similar manner [*cf.* (**5**) ⟷ (**5a**)].

The dipole moment was found to be 0·59 D, which suggests a high degree of charge separation in (**2**).§

These data for (**2**) are in accord with a delocalized bishomofulvene-type resonance structure (**2a**).[6]

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§ The dipole moment was determined by measuring the dielectric constants and densities of solutions of varying molarity at 20° in benzene and extrapolating.

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[3] The same treatment has previously been applied to methylenenorbornadiene and methylenebicyclo[4,2,1]nona-2,4,7-triene; R. W. Hoffmann, R. Schuttler, W. Schafer, and A. Schweig, *Angew. Chem. Internat. Edn.*, 1972, **11**, 512; M. T. Reetz, R. W. Hoffmann, W. Schafer, and A. Schweig, *ibid.*, 1973, **12**, 81.

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[6] For a homoaromatic bishomocyclopentadienide anion (**6**), see J. M. Brown and J. L. Occolowitz, *Chem. Comm.*, 1965, 376; S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, 1967, **89**, 3656.