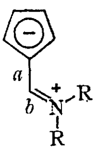
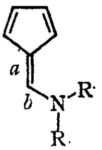
# Rotational Isomerism of Fulvene Derivatives

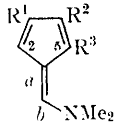
By A. P. DOWNING, W. D. OLLIS, and I. O. SUTHERLAND

(*Department of Chemistry, The University, Sheffield*)

THE 6-dialkylaminofulvenes are conveniently represented by the canonical forms (Ia) and (Ib) and although this representation necessarily has some shortcomings, it nevertheless does focus attention upon the extent to which rotation about the bonds *a* and *b* is inhibited by the requirements of electron delocalisation. These considerations encouraged investigation of the temperature-dependence of the nuclear magnetic resonance (n.m.r.) spectra of the fulvenes (II—V) and from the results (see Table) it is possible to discuss the magnitudes of the free-energy barriers to rotation about bonds *a* and *b*.


(Ia)


(Ib)



(II) $R^1 = R^2 = R^3 = H$
(III) $R^1 = R^2 = H$; $R^3 = CHO$
(IV) $R^1 = R^2 = CHO$; $R^3 = Me$
(V) $R^1 = R^2 = CHO$; $R^3 = H$

Restricted rotation about bond *b* would be associated with non-equivalence of the two *N*-methyl groups in the compounds (II—V) and restricted rotation about bond *a* would result in non-equivalence of symmetrically placed identical groups or protons on the cyclopentadienyl residue. The n.m.r. spectra (see Table) of the compounds (II—V)[1] showed two singlets due to non-equivalent *N*-methyl groups at low temperatures and these singlets coalesced at higher temperatures. Analysis[2,3] of the line shapes of the coalescing signals and the calculation of exchange rates over a wide temperature range gave Arrhenius parameters for the exchange process associated with rotation about bond *b*. The effect of suitably placed electron-withdrawing substituents (CHO) in the compounds (III, IV, and V) is as expected. It would be predicted [see canonical form, (Ia)] that such substituents would increase the double-bond character of bond *b*. The effect of this increase is clearly reflected by increases in $E_a$ and $\Delta G_0\ddagger$ for the compounds (III, IV, and V) as compared with compound (II). The values of $\log_{10}A$ (see Table) correspond to a positive entropy of activation in all cases. This is an interesting but anticipated consequence of the requirement that the transition state for the bond *b* rotational process is *less* dipolar than the ground state; the dipole moment of 6-dimethylaminofulvene is 4·5D,[1] in comparison with fulvene, 1·2D.[4] The relatively less dipolar transition-state associated with bond *b* rotation can be considered in relation to the diagram (Ib) but detailed consideration of the geometry of the transition state is not possible: the nitrogen atom could, for example, have either a planar or pyramidal configuration.

Our results in relation to bond *a* rotational processes reveal an interesting situation. Thus the n.m.r. spectrum (dimethyl sulphoxide solution) of compound (V) shows two narrow multiplets due to the protons in positions 2 and 5 but these signals are substantially unaltered when the

TABLE

*Nuclear magnetic resonance data and activation parameters for the fulvenes* (II), (III), (IV), *and* (V)

| Compound | Solvent | $\Delta\nu_{AB}$[a] (c./sec. ± 0·1 c./sec.) | $T_c$ (° C ± 2°) | $E_a$[b] (kcal./mole) | $\log_{10}A$[b,c] | $\Delta G_0\ddagger$[b] (kcal./mole) |
|---|---|---|---|---|---|---|
| (II) | $CDCl_3$–$C_6F_6$ | 6·50 (−50°) | −17 | 15·1 ± 1·0 | 14·1 ± 0·6 | 13·5 ± 0·1 |
| (III) | $C_2HCl_5$ | 8·70 (2°) | 51 | 20·9 ± 1·6 | 15·3 ± 1·0 | 17·9 ± 0·3 |
| (IV) | $C_2HCl_5$ | 8·70 (0°) | 72 | 27·3 ± 1·9 | 18·5 ± 1·0 | 20·3 ± 0·2 |
| (V) | $C_2HCl_5$ | 8·15 (44°) | 96 | 26·5 ± 2·0 | 16·8 ± 1·1 | 21·5 ± 0·3 |

[a] $\Delta\nu_{AB}$ is the separation of the *N*-methyl signals in c./sec. at the indicated temperature. In all cases $\Delta\nu_{AB}$ was slightly temperature-dependent below the temperature range in which it was affected by the exchange process. This was taken into account in the calculation of exchange rates.

[b] Errors are for 90% confidence limits.

[c] Rate constants, and therefore *A*, are based upon $sec.^{-1}$ units.

temperature is raised to 160°. This means that the free-energy barrier to rotation about bond *a* in this 6-dimethylaminofulvene (V) is greater than 24·7 kcal./mole. at 160°. This opinion is based upon a minimum observable line-broadening of 1 c./sec. Compound (V) with its two formyl substituents is the most favourable case we have so far studied for reduction of the free-energy barrier to rotation about bond *a*. It is clear, therefore, that the bond *a* rotational barrier in 6-dimethylaminofulvenes is higher (>24·7 kcal./mole.) than the corresponding barrier (18·0—19·4 kcal./mole.) for rotation about the intercyclic bond of pentatriafulvenes (calicenes).[5] These results are presumably relevant to a recent theoretical study.[6]

Previous studies of the n.m.r. characteristics of fulvenes[7] have been mainly concerned with spectral analysis. In addition the n.m.r. spectrum of 6-dimethylaminofulvene (II) has just been reported[8] but no indication is given that non-equivalence of the *N*-methyl groups has been looked for or detected. The relation of our results* to earlier studies on the rotational isomerism of amides[3,9] and vinylogous amides[10] will be appreciated.

(*Received, December 15th*, 1966; *Com.* 994.)

---

* Details of the interpretation of the n.m.r. spectra of compounds (II–V) will be given in a full paper.

[1] K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Annalen.*, 1963, **661**, 52.

[2] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228; F. A. L. Anet, *J. Amer. Chem. Soc.*, 1964, **86**, 458; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, 1959.

[3] L. W. Reeves, *Adv. Phys. Org. Chem.*, 1965, **3**, 187.

[4] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 1949, **17**, 264.

[5] A. S. Kende, P. T. Izzo, and W. Fulmor, *Tetrahedron Letters*, 1966, 3697.

[6] M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, 1965, **21**, 3423.

[7] D. Meuche, M. Neuenschwander, H. Schaltegger, and H. V. Shlunegger, *Helv. Chim. Acta*, 1964, **47**, 1211; M. Neuenschwander, D. Meuche, and H. Schaltegger, *ibid.*, p. 1022; W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, 1964, **86**, 3118; Y. Kitahara, I. Murata, K. Shirahata, S. Katagiri, and H. Azumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 780; H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*. 1965, **48**, 959; A. S. Kende, P. T. Izzo, and P. T. McGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 3359.

[8] M. L. Heffernan and A. J. Jones, *Austral. J. Chem.*, 1966, **19**, 1813.

[9] M. J. Rogers and J. C. Woodbury, *J. Phys. Chem.*, 1962, **66**, 540; A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, 1965, **42**, 3320.

[10] H. E. A. Kramer, *Z. phys. Chem. (Frankfurt)*, 1964, **43**, 292, 349; 1965, **44**, 82; *Annalen.*, 1966, **696**, 15, 28.