Rapid Circumambulation of the Formyl Group in 5-Formyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene

By Richard J. Bushby* and David W. Jones*

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

Summary 1,5-Sigmatropic formyl migration in 5-formyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene is rapid at 25 °C (k_{isom}. 90 s^{-1}); line shape analysis of ^{1}H n.m.r. spectra obtained between -20 and $+70$ °C shows migration is associated with an activation enthalpy of 13·2 $\pm$ 0·3 kcal mol^{-1} and an activation entropy of $-5·1$ $\pm$ 0·2 cal K^{-1} mol^{-1} (1 cal = 4·184 J).

1,5-Alkyl shifts in cyclopentadienes[1] commonly require temperatures above 330 °C and proceed with free energies of activation greater than 43 kcal mol^{-1}. In marked contrast we describe the temperature dependent ^{1}H n.m.r. spectrum of 5-formyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene (1) which shows that in this compound formyl migration is rapid (k, 90 s^{-1}) at 25 °C ($\Delta G^{\ddagger}$ 14·8 $\pm$ 0·3 kcal

mol^{-1}). The formyl group is thus the only simple organic group shown to surpass the 1,5-migratory aptitude of the trimethylsilyl group in 5-trimethylsilylcyclopentadiene ($\Delta G^{\ddagger}$ 15·45 kcal mol^{-1}).[1]
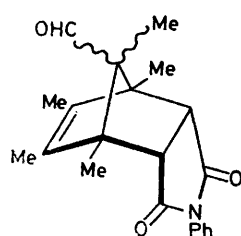
Pentamethylcyclopentadiene, conveniently prepared *via* electrocyclic ring-closure of the 3,4,5-trimethylhepta-3,5-dien-2-yl cation,[2] was converted into the alcohol (2) by the method of de Vries.[3] Although attempted oxidation of (2)
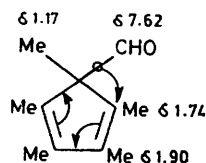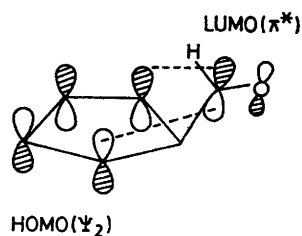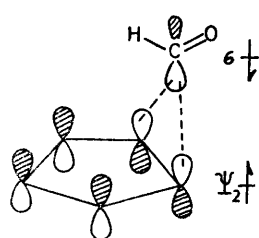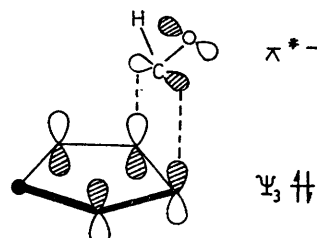

(1)
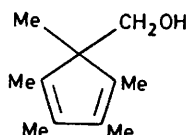
(2)

(3)

(4)

(5)

(6)

with CrO$_3$.2 pyridine–CH$_2$Cl$_2$ failed to give (1), the aldehyde was obtained (*ca.* 20%) by Pfitzner–Moffat oxidation of (2) (Me$_2$SO, C$_6$H$_{11}$N : C : NC$_6$H$_{11}$, pyridinium trifluoroacetate, 22 °C, 18 h) followed by careful short-column chromatography on Kieselgel G (Merck). The aldehyde showed ν_{max} (film) 1 715, 2 690, and 2 800 cm^{-1}, and the appropriate ^{1}H n.m.r. spectrum (CDCl$_3$) at −30 °C (Figure) apart from the temperature invariant ($< \delta$ 0·1) high field position (δ 7·62) of the aldehyde proton. This shielding could be attributed to the preferred location of the aldehyde proton over the diene system; in the *N*-phenylmaleimide adduct

(3) of (1) the aldehyde proton appears at normal shift (δ 9·55). The acetyl group in 5-acetyl-1,2,3,4,5-penta-methylcyclopenta-1,3-diene is also shielded (δ 1·48; CCl$_4$). The temperature variation observed in the ^{1}H n.m.r. spectrum of (1) is illustrated in the Figure. Line shape analysis† of spectra taken at 5 °C intervals between −20 and +70 °C yielded an activation plot (for 19 points) and the following activation parameters for the isomerisation process (1; arrows) at 25 °C: E_a 13·8 ± 0·3, $\Delta H^{\ddagger}$ 13·2 ± 0·3, and $\Delta G^{\ddagger}$ = 14·8 ± 0·3 kcal mol^{-1}; A = 10$^{12.6}$ s^{-1}, $\Delta S^{\ddagger}$ = − 5·1 ± 0·2 cal K^{-1} mol^{-1}. The higher field vinylic methyl signal (δ 1·74) is assigned to the methyl groups at C-1 and C-4 [see (1)] as in other 1,2,3,4,5-pentamethylcyclo-penta-1,3-dienes.[4] As the temperature is raised this signal broadens more rapidly than that at δ 1·90 (see Figure) in
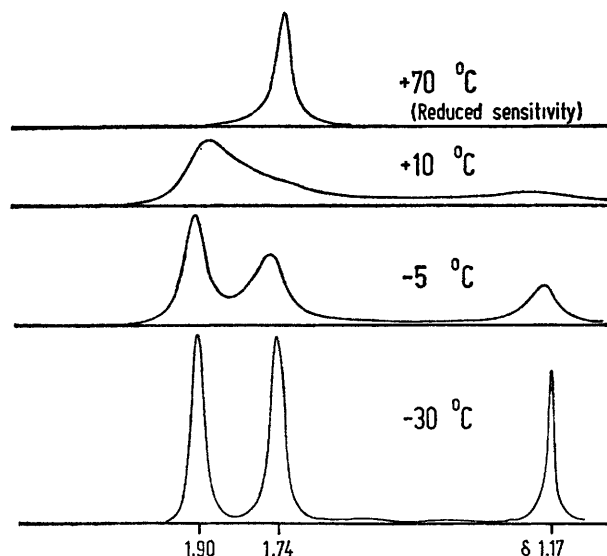

FIGURE. ^{1}H N.m.r. spectrum of (1) at different temperatures.

accordance with 1,5- rather than 1,3-formyl shifts. Under the same conditions 5-acetyl- and 5-ethoxycarbonyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene show temperature invariant ^{1}H n.m.r. spectra.[4] This confirms for the cyclopentadiene system the order of migratory aptitude CHO $\gg$ COMe or CO$_2$Me found in indenes[5] and cyclohexadienes.[6] For migration of the electropositive species MR$_3$ (M = Si, Sn, *etc.*) in cyclopentadienes and indenes a $\Delta\Delta G^{\ddagger}$ of 9 kcal mol^{-1} is observed.[1] For formyl migration in 1-formyl-1,3-dimethylindene $\Delta G^{\ddagger}$ is *ca.* 26 kcal mol^{-1}; $\Delta\Delta G^{\ddagger}$ for formyl migration in indenes and cyclopentadienes is therefore *ca.* 11 kcal mol^{-1}. The much easier migration of the formyl group than of alkyl groups can be attributed to secondary orbital interactions. The initial interaction between the HOMO of the diene system and the LUMO of the formyl group shown in (4) may be enhanced as reaction proceeds. Alternatively the rearrangement can be envisaged as involving interaction between a half-filled σ-orbital of the formyl radical and the cyclopentadienyl ψ_2 as in (5) whilst the degenerate cyclopentadienyl ψ_3

overlaps with the vacant π^*-orbital of the formyl group as in (6). Whilst this latter model of the secondary orbital interaction receives theoretical support,[7] and explains easy migration of other unsaturated groups[8] including a car-

banionic centre,[9] the nodal properties of the orbitals make it difficult to apply to the corresponding indenyl systems.

[1] C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
[2] R. S. Threlkel and J. E. Bercaw, *J. Organometallic Chem.*, 1977, **136**, 1.
[3] L. deVries, *J. Org. Chem.*, 1960, 1838.
[4] R. F. Childs and M. Zeya, *J. Amer. Chem. Soc.*, 1974, **96**, 6418, and references cited therein.
[5] D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Perkin I*, 1978, 1050.
[6] P. Schiess and P. Funfschilling, *Tetrahedron Letters*, 1972, 5195.
[7] N. Trong Anh, M. Elian, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1978, **100**, 110.
[8] M. F. Semmelhack, H. N. Weller, and J. Clardy, *J. Org. Chem.*, 1978, **43**, 3591, and references cited therein.
[9] G. Boche and D. Martens, *Chem. Ber.*, 1979, **112**, 175.