Very Rapid Formyl Shifts in 1-Formylindenes; Strict Stereospecificity and Exclusive 1,5-Sigmatropy

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Summary Rapid formyl migration establishing an equilibrium between (**1**) and (**4**) is revealed by trapping, transfer of non-equilibrium spin, and racemisation experiments; racemisation of (**11**) is twice as fast as its conversion into (**3**), and interconversion of (**2**) and (**9**) is stereospecific in accord with the exclusive occurrence of 1,5,-sigmatropy.

Although many examples of apparent 1,5-acyl shifts are known,[1] evidence for the concerted nature of the process is sparse[1a,c] and in some cases two-step mechanisms have been proposed.[1e] We provide an example of very rapid 1,5-formyl migration together with strong evidence for the concerted nature of the process.

When heated the 1-formylindene (**1**) is cleanly converted into the 2-isomer (**7**); the reaction presumably involves 1,5-formyl shift to the transient isoindene (**4**) which gives (**7**) by 1,5-hydrogen shift. In agreement the intermediate (**4**) is trapped as the adduct (**8**; X = H)† on heating (**1**) with *N*-phenylmaleimide. Although conversion of (**1**) into (**7**) is slow below 200 °C (k 3·66 × 10^{-5} s^{-1} at 170 °C in Ph_2O) the

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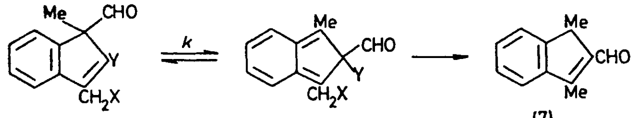
† Two adducts are formed, the major having the *endo-anti*-configuration.

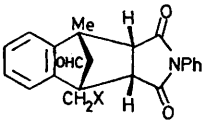
adduct (**8**; X = H) was obtained (78% yield) by heating (**1**) with *N*-phenylmaleimide at 80 °C (70 h). Thus in (**4**) reverse formyl shift to (**1**) is more rapid than the 1,5-hydrogen shift giving (**7**) so that at temperatures below *ca.* 150 °C the formyl group is shuttled over C(1), C(2), and C(3) of the indene nucleus without noticeable formation of (**7**). This process exchanges the environments of the methyl groups in (**1**) as shown by n.m.r. experiments on transfer of non-equilibrium spin.[2] At 150 °C a second radio-frequency equal to the resonance frequency of the tertiary methyl group causes a 62% decrease in the intensity of the vinylic methyl signal; as expected the effect diminishes with temperature and the power of the second radio-frequency. The remarkably rapid formyl migration thus indicated (*k*, *ca.* 0·1 s^{-1} at 150 °C) was confirmed by preparation of (**1**) in optically active form‡ and observing its racemisation *via* the symmetric isoindene (**4**). Racemisation of (**1**) in Ph$_2$O solution in the temperature range 50—80 °C yielded the following rate data [10^{-5} k/s^{-1} (T/°C)], 2·42 (50), 6·47 (60), 20·4 (70), and 47·08 (80), $\Delta H^{\ddagger} = 22{\cdot}08 \pm 0{\cdot}75$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11{\cdot}41 \pm 2{\cdot}21$ cal K^{-1} mol^{-1}. The low activation enthalpy and *negative* activation entropy support a concerted formyl shift rather than possible two-step mechanisms involving initial cleavage of the indenyl–formyl bond. To rule out homolysis or heterolysis to other than strongly interacting radical or ion pairs the optically active aldehyde (**2**) was prepared. After 3 h heating in boiling benzene (**2**) was cleanly converted into a mixture of (**2**) and (**9**) in which the latter predominated (73%). Based on the initial rate of isomerisation of (**2**) to (**9**) essentially all the (**2**) present had undergone rearrangement yet separation of the mixture gave (**2**) with its optical activity unchanged ([α]$_D$ + 123°). Moreover, when the product (**9**) ([α]$_D$ −65·1°) was heated at 80 °C (3·5 h) the isomer (**2**) reclaimed had lost no optical activity. Even after heating a mixture of (**2**) and (**9**) for 48 h [*ca.* 100 half-lives for the (**2**) → (**9**) conversion] the recovered isomers each retained ⩾95% of their respective optical activities. In accord with intervention of the asymmetric isoindene (**5**) in this interconversion the optically active adduct (**8**; X = OMe)† was obtained in the presence of *N*-phenylmaleimide. However the rate of trapping was much less than the rate of interconversion of (**2**) and (**9**) so that although the near-perfect asymmetric induction in the equilibrium (**2**) ⇌ (**9**) argues strongly for a concerted process, the co-occurrence of 1,5- and 1,3-shifts§ was still a possibility. To exclude the latter the optically active deuterium-labelled dialdehyde (**11**) was prepared; racemisation of (**11**) should proceed at *ca.* twice its initial rate of conversion into (**3**) if each act of racemisation involves formation of the isoindene (**6**), but racemisation will be faster than this if it is in part due to 1,3-formyl shifts. Sutherland's modification of the Prins reaction[3] applied to 1-methoxycarbonyl-1,3-dimethylindene gave the formate (**12**) which by reduction with LiAlD$_4$ and oxidation of the resulting diol, first with MnO$_2$, and then with CrO$_3$–pyridine–CH$_2$Cl$_2$, gave (**11**). Samples of (**11**) were heated in degassed diglyme at 120 °C and racemisation followed to *ca.* 40% and deuterium exchange to *ca.* 20%. First-order plots (for 5 points) derived from polarimetric and n.m.r. measurements on chromatographically purified mixtures of (**11**) and (**3**) gave a racemisation rate constant ($k_{\text{rac.}}$) of $5{\cdot}46 \pm 0{\cdot}26 \times 10^{-5}$ s^{-1} and a rate constant for the conversion of (**11**) into (**3**) ($k_{\text{exch.}}$) of $2{\cdot}82 \pm 0{\cdot}05$ s^{-1}. The $k_{\text{rac}}/k_{\text{exch.}}$ ratio of $1{\cdot}94 \pm 0{\cdot}13$ rules out an important racemisation route other than isoindene formation and together with the observed asymmetric induction provides convincing evidence that the extremely easy racemisation of (**1**) proceeds solely by 1,5-sigmatropic formyl migration to the isoindene (**4**).



(1) X = Y = H
(2) X = OMe, Y = H
(3) X = H, Y = CDO

(4) X = Y = H
(5) X = OMe, Y = H
(6) X = H, Y = CDO

(7)



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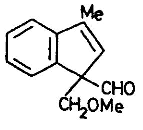
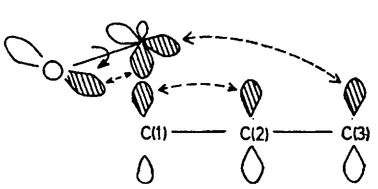


(9)



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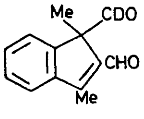

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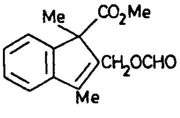

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‡ Carbonation of 1,3-dimethylindenyl-lithium gave 1-carboxy-1,3-dimethylindene which was resolved *via* its quinine salt, and converted into (**1**) ([α]$_D$ + 135°) by reduction to the alcohol (LiAlH$_4$ at −15 °C) followed by oxidation (CrO$_3$–pyridine–CH$_2$Cl$_2$).

§ For migrating π-systems the 1,3-shift could be a thermally 'allowed' ${}_{\pi}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ process as pictured in (**10**); alternatively the concerted-forbidden pathway could be followed (*cf.* ref. 4).

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[2] *Cf.* I. Calder, P. J. Garratt, and F. Sondheimer, *Chem. Comm.*, 1967, 41, and cited references.

[3] J. J. S. Bajorek, R. Battaglia, G. Pratt, and J. K. Sutherland, *J.C.S. Perkin I*, 1974, 1243.

[4] J. A. Berson, *Accounts Chem. Res.*, 1972, **5**, 406.