Positional Selectivity in the Rearrangement of 7-Formyl and 7-Vinyl Norcaradienes; Evidence for 3,5-Sigmatropy

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The 7-formyInorcaradiene (1; X = O, R = Me) rearranges at 40 °C to the dihydrobenzofuran (4; X = O, R = Me) and the 7-vinyInorcaradiene (1; X = E-CHCO₂Et, R = Me) rearranges to the dihydroindene (9), evidence for 3,5- rather than 1,3-sigmatropy in both processes.

We recently provided stereochemical and other evidence for the occurrence of a 3,5-sigmatropic shift in the conversion of 7-vinylnorcaradienes into dihydroindenes.¹ We now describe the related conversion of 7-formylnorcaradienes into dihydrofurans, together with the finding that for both reactions bond relocation on the cyclohexadiene ring occurs indicating 3,5rather than 1,3-sigmatropy (Scheme 1). These observations suggest that provided molecular geometry permits antarafacial use of a vinyl group,^{1,2} the 3,5-sigmatropic shift can compete favourably with Cope rearrangement.

Thermolysis of (1; X = O, R = H)¹ in degassed C₆D₆ at 80 °C provided an equilibrium mixture of starting aldehyde and dihydrobenzofuran (2) in which the latter predominated (88%). Although the sensitivity of (2) prevented its isolation in pure form, the assigned structure is consistent with i.r. absorption at 1629 cm⁻¹ (enol ether) and the δ -values (C₆D₆) and coupling constants appended to structure (2). These agree with the values reported for *cis*-8,9-dihydrobenzofuran (2; lacking Ph group), the *trans* isomer of which shows a coupling constant between the ring junction protons $J_{vic.} = 23.5$ Hz;³ compound (2) readily afforded a fully characterised adduct with *N*-phenylmaleimide. Thermolysis of the equilibrium mixture of (1; X = O, R = H) and (2) at 130 °C (CD₃CN) gave diphenylacetaldehyde in agreement with earlier observations on 7-formylcycloheptatriene.⁴



Rate measurements for the conversion of (1; R = H, X = O) into (2) at 65.5 °C in C₆D₆ ($k 8.8 \times 10^{-5} \text{ s}^{-1}$) and CD₃CN ($k 11.0 \times 10^{-5} \text{ s}^{-1}$) indicate little increased polarity in going to



the rearrangement transition state. The rearrangement in C_6D_6 was not appreciably affected by addition of either acetic acid (0.1 mol equiv.) or Et₃N (2 mol equiv.). Rearrangement of (1; X = O, R = H) into (2) therefore appears different from the well established conversion of acylcyclopropanes into dihydrofurans,⁵ most examples of which can only be formal 1,3-shifts and involve either high temperatures^{5a} or catalysis by acids or metals.^{5b}

To distinguish between 1,3- and 3,5-sigmatropy for the norcaradiene aldehyde into dihydrobenzofuran conversion, we prepared the symmetrically substituted dimethyl derivative (1; X = O, R = Me). This would give different single products via 1,3- and 3,5-sigmatropy (Scheme 1). Irradiation of methyl phenyldiazoacetate in p-xylene-CH2Cl2 (medium pressure Hg-lamp, Pyrex filter) gave one main product (3) (43% yield) which, after reduction to the corresponding alcohol (LiAlH₄, Et₂O, 20 °C) followed by Swern oxidation, gave (1; X = O, R = Me). Athough this compound was stable for several weeks at -40 °C, it rearranged slowly in C₆D₆ at 20 °C and equilibrium with (4; X = O, R = Me) was fully established after heating at 40 °C (30 min); the dihydrofuran (4) predominated in the mixture (94%) and was characterised by ¹H n.m.r. (400 MHz, C₆D₆) [1.43 (3H, s), 1.52 (3H, t, J 1.5 Hz), 3.76 (1H, m, H-3a), 5.71 (1H, m, H-4), 5.73 (1H, dd, J 10 and 1.5 Hz, H-6), 5.79 (1H, d J 10 Hz, H-7), 6.74 (1H, d, J 2 Hz, H-2)]. The dihydrobenzofuran (5; X = O, R = Me) which would have resulted from 1,3-sigmatropy was not detectable in the 400 MHz n.m.r. spectrum of the crude rearrangement product.

As expected from preferred 3,5-sigmatropy of 7-formylnorcaradienes, the benzo-derivative (6), for which 3,5-shift demands loss of aromaticity in ring A, rearranges only at higher temperature (160 °C, 240 min) and gives mainly the aldehydes (7) (80%), and only a little of the furan (8) (*ca.* 10%) and starting material. It is possible that (8) arises in this case *via* a formal 1,3-shift analogous to that prevailing for simple acylcyclopropanes.^{5a}

The bond relocation characteristic of 3,5-sigmatropy is also

found for rearrangement of 7-vinylnorcaradienes. Thus the alkene (1; X = E-CHCO₂Et, R = Me) rearranges cleanly over 90 min at 80 °C in benzene to give mainly the dihydroindene (9) (86%) as well as the Cope rearrangement product (10) (14%). The ¹H n.m.r. data (CDCl₃) [δ (multiplicity, *J* in Hz) appended to structure (9) clearly distinguish this structure from that which would have arisen *via* 1,3-sigmatropy.

The observations described here and earlier¹ provide clear examples of 3,5-sigmatropy. This process may explain the earlier observations that α -oxocarbenes add to benzenes to give either norcaradienes or dihydrofurans, and that the norcaradienes can be converted into furans by DDQ (DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone).⁶

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