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

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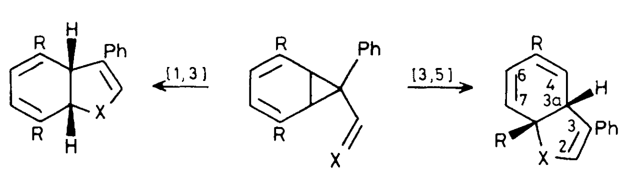
The 7-formylnorcaradiene (**1**; X = O, R = Me) rearranges at 40 °C to the dihydrobenzofuran (**4**; X = O, R = Me) and the 7-vinylnorcaradiene (**1**; X = *E*-$CHCO_2Et$, R = Me) rearranges to the dihydroindene (**9**), evidence for 3,5- rather than 1,3-sigmatropy in both processes.

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 3,5- rather 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.

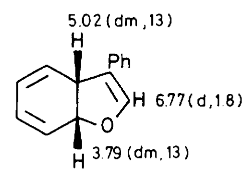
Thermolysis of (**1**; X = O, R = H)[1] in degassed C_6D_6 at 80 °C provided an equilibrium mixture of starting aldehyde and dihydrobenzofuran (**2**) in which the latter predominated (88%). Although the sensitivity of (**2**) prevented its isolation in pure form, the assigned structure is consistent with i.r. absorption at 1629 cm^{-1} (enol ether) and the δ-values (C_6D_6) 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 (CD_3CN) gave diphenylacetaldehyde in agreement with earlier observations on 7-formylcycloheptatriene.[4]



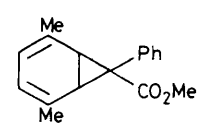
(**5**) (**1**) (**4**)

Scheme 1

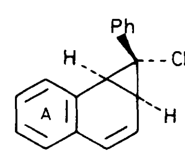
Rate measurements for the conversion of (**1**; R = H, X = O) into (**2**) at 65.5 °C in C_6D_6 (k 8.8 × 10^{-5} s^{-1}) and CD_3CN (k 11.0 × 10^{-5} s^{-1}) indicate little increased polarity in going to



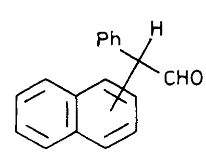
(**2**)



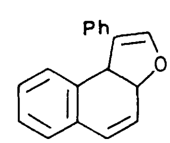
(**3**)



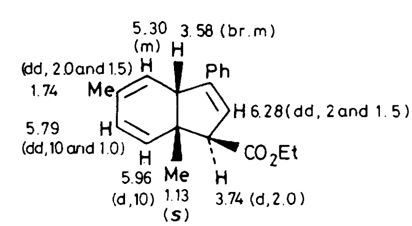
(**6**)



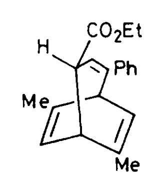
(**7**)



(**8**)



(**9**)



(**10**)

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 Et_3N (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–CH_2Cl_2 (medium pressure Hg-lamp, Pyrex filter) gave one main product (**3**) (43% yield) which, after reduction to the corresponding alcohol ($LiAlH_4$, Et_2O, 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 C_6D_6 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, C_6D_6) [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*-$CHCO_2Et$, 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 ($CDCl_3$) [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 earlier[1] 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]

Received, 3rd November 1987; Com. 1600

References

1 P. J. Battye and D. W. Jones, *J. Chem. Soc., Chem. Commun.*, 1986, 1807.
2 See refs. 1—3 in ref. 1.
3 S. Masamune, S. Tadaka, and R. Seidner, *J. Am. Chem. Soc.*, 1969, **91**, 7769; J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, 1968, **90**, 5041.
4 R. Grigg, R. Hayes, and A. Sweeney, *J. Chem. Soc., Chem. Commun.*, 1971, 1248.
5 (a) C. L. Wilson, *J. Am. Chem. Soc.*, 1947, **69**, 3002; D. A. Armitage and C. L. Wilson, *ibid.*, 1959, **81**, 2437; H. Hiraoka, *Tetrahedron*, 1973, **29**, 2955; D. E. McGreer and J. W. McKinley, *Can. J. Chem.*, 1973, **51**, 1487; H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Am. Chem. Soc.*, 1973, **95**, 2155; (b) E. Wenkert, M. E. Alonso, B. L. Buckwalter, and E. L. Sanchez, *ibid.*, 1983, **105**, 2021; M. E. Alonso, P. Jano, M. I. Hernandez, R. S. Greenberg, and E. Wenkert, *J. Org. Chem.*, 1983, **48**, 3047; P. R. Brook, A. J. Duke, T. G. Griffiths, S. M. Roberts, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, 1977, **60**, 1528.
6 C. G. F. Bannerman, J. I. G. Cadogan, I. Gosney, and N. H. Wilson, *J. Chem. Soc., Chem. Commun.*, 1975, 618; P. J. N. Brown, J. I. G. Cadogan, I. Gosney, and A. Johnstone, *ibid.*, 1981, 1035.