Evidence for Thermal 3,5-Sigmatropy of 7-VinyInorcaradienes

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7-Phenyl-7-vinylcycloheptatrienes rearrange *via* their *endo*-norcaradiene valence tautomers (**1**; **a**—**d**) to give the dihydroindenes (**2**; **a**—**d**) and the Cope products (**3**; **a**—**c**); dihydroindene formation is stereospecific, and strongly inhibited in the benzonorcaradienes (**7**; **b**—**d**) in agreement with 3,5-sigmatropy rather than vinylcyclopropane-cyclopentene rearrangement.

3,5-Sigmatropic shifts have occasionally been proposed as steps in complex rearrangement reactions¹ but in only one case has the process been studied in isolation and evidence for a concerted reaction been obtained.² The process may operate in another fairly simple case³ but in other molecules where such rearrangement might have occurred it was not observed.⁴ We describe rearrangement of the 7-vinylnorcaradienes (1) to give the 8,9-dihydroindenes (2) and bicyclo[3.2.2]nonatrienes (3) and evidence that formation of the dihydroindenes involves 3,5-sigmatropy (1; arrows) rather than simple vinylcyclopropane rearrangement.

The readily prepared mixture of equilibrating cycloheptatriene and norcaradiene isomers (4; $R = CO_2Me)^5$ was converted into the sensitive aldehyde (4; R = CHO) by reduction (LiAlH₄) and oxidation (CrO₃·2pyridine, CH₂Cl₂) of the resulting alcohol. Wittig and Wadsworth–Emmons reactions then gave the vinylnorcaradienes (1). These also exist in equilibrium with their cycloheptatriene valence tautomers and this provides for easy interconversion of the *endo*-vinylnorcaradienes (1) and their *exo*-isomers (5).

Rearrangement of (1a) to give (2a) and (3a) (ratio *ca.* 3:2) in degassed C_6D_6 was monitored by Fourier transform ¹H n.m.r. measurements between 65 and 91 °C. Rearrangement followed good first order kinetics. Formation of (3a): k (75 °C) = $1.05 \times 10^{-4} \text{ s}^{-1}$; $\Delta H^{\ddagger} = 21.9 \pm 0.6 \text{ kcal mol}^{-1}$, $\Delta S^{\ddagger} = -14.3 \pm 1.6 \text{ cal mol}^{-1} \text{ K}^{-1.}$ Formation of (2a): k (75 °C) = $1.40 \times 10^{-4} \text{ s}^{-1}$; $\Delta H^{\ddagger} = 22.4 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^{\ddagger} = -12.3 \pm 1.3 \text{ cal mol}^{-1} \text{ K}^{-1}$. The negative activation entropies observed for the formation of both (2a) and the Cope rearrangement product (3a) suggest concerted processes for the formation of both products.

Formation of dihydroindene (2a) from (1a) could occur via a 3,5-sigmatropic shift (1; arrows). In the *endo*vinylnorcaradiene depicted in (1) the vinyl group is well positioned to function as the *antara* component in a thermally allowed $\pi^{4}s + \sigma^{2}s + \pi^{2}a$, 8-electron process [see (6)]. Such

 ± 1 kcal = 4.18 kJ; activation parameters calculated for 78 °C.

rearrangement necessarily involves the *endo*-vinyl isomers (1) with the consequence that an (E)-substituent on the vinyl group ends up in the *exo* position in the dihydroindenes (2). On the other hand if conversion of (1) into (2) were an example of vinylcyclopropane to cyclopentene rearrangement⁶ one might expect either the *endo* (1) or the *exo* (5) isomer to participate (but see ref. 7). As a consequence of this, and the non-stereospecificity of simple vinylcyclopropane to cyclopentene rearrangement,⁸ conversion of (1) into (2) via such a process would be expected to be non-stereospecific.

The rearrangement stereochemistry was first explored using the ester (1b). At 80 °C (1b) rearranged to a 86:14 mixture of (2b) and (3b); rearrangement was *ca.* 12 times faster than for (1a) and was stereospecific.[‡] The *cis* ring-junction and exo-directed ethoxycarbonyl group in (2b) was established by its conversion into (2c). The (E)- and (Z)-alkenes (1c) and (1d) prepared through Wittig reaction on (4; R = CHO) were readily separated by AgNO₃-SiO₂ chromatography. Thermolysis of (1c) at 75 °C gave the *exo*-Me compound (2c) and the Cope product (3c) and no trace of the *endo*-Me isomer (2d) which was the only product of the slower rearrangement of the (Z)-alkene (1d). \ddagger The high field spectra of (2c) and (2d) (Table 1) establish that both are *cis*-8,9-dihydroindenes (J_{BC}) ca. 12 Hz). The appearance of H^B at ca. 0.5 p.p.m. to higher field in (2c) than (2d) suggests a cis-relationship of the Me group and H^{B} in (2c); introduction of a Me group shields a cis-vicinal proton in cyclopentanes, and related effects in cyclohexanes are well known.9 In addition the known^{10a,b} des-phenyl derivatives of (2c) and (2d) were prepared from the des-phenyl derivative of (2b) and its C-1 epimer.§ The configuration of the latter des-phenyl derivatives was firmly established chemically, 10a,c and the close agreement between

^{‡ 400} MHz ¹H N.m.r. spectra.

[§] By reduction (LiAlH₄, Et₂O), tosylation of the resulting alcohol (tosyl chloride, pyridine, 0-5 °C, 14 h), and further reduction (LiAlH₄, tetrahydrofuran, 20 °C to reflux).



Table 1. Selected 400 MHz n.m.r. data: δ value, multiplicity (*J* values in Hz).

Compound	HA	Нв	H^{C}
(2c)	2.89, dqt	2.56, ddd	4.13, dm
	(8.5 - 9.0, 7, 2)	(12, 8.5, 5.5)	(12.0)
(2d)	2.97, dqd	3.13, dddd	4.09, dm
. ,	(8.0, 7.0, 3.0)	(12.7, 8.0, 5.8; 1.4)	(12.7)
des-Ph(2c)	2.71, quintet of q	2.51, ddd	3.64, dm
	(7.0, 2.0)	(11.5, 7.0, 4.5)	(11.5)
des-Ph (2d)	2.87, dqt	3.01, dddd	3.56, dm
	(8.0-8.5, 7.0, 2)	(12.5–13.0, 8.5, 5.0, 1.5)	(12.5)

the high field spectra of (2c) and (2d) and their respective *des*-Ph derivatives (Table 1) fully confirms our stereochemical assignments. The observed rearrangement stereochemistry implicates the *endo*-vinylnorcaradienes (1) to the virtual exclusion of their *exo*-isomers (5). Since (1) and (5) would be

expected to interconvert freely under the reaction conditions¹¹ the rearrangement stereochemistry strongly suggests 3,5- rather than 1,3-sigmatropy.

To provide further evidence we sought to thermolyse the benzo-derivatives (7) of (1). In these, 3,5-sigmatropy e.g.. (7; arrows) should be inhibited by the accompanying aromaticity loss whereas vinylcyclopropane rearrangement might be expected to proceed as readily in (7) as in (1). The exo-vinylbenzonorcaradienes (8) proved more accessible than the desired endo-vinyl isomers (7). However, interconversion of such isomers via o-quinonoid cycloheptatriene intermediates was as expected very easy.¹² Thermolysis of (8b) at 90 °C (6 h) resulted in quantitative conversion into the Cope product (9b) of (7b) and no detectable dihydroindene (10b) which however became available by thermolysis of (9b) at higher temperature (200 °C, 7.4 h). The benzo-derivative (8c) gave only the Cope rearrangement product (9c) on heating (102 °C, 65 min). Heating the (Z)-isomer (8d) at 102 °C for 110 min gave mostly the endo-vinyl isomer (7d) and heating to 130 °C (37 h) was required to cause Cope rearrangement to (9d) (91%) which was accompanied by the dihydroindene (10d) (9%).[‡] Although the origin of (10d) is obscure the predominating trend is clear. 2,3-Benzo-fusion powerfully inhibits the rearrangement leading to dihydroindenes. This observation strongly favours 3,5-sigmatropy as the process responsible for the formation of dihydroindenes (2) from the norcaradienes (1).

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