

## Evidence for Thermal 3,5-Sigmatropy of 7-Vinylnorcaradienes

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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 benzenorcaradienes (**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 reactions<sup>1</sup> but in only one case has the process been studied in isolation and evidence for a concerted reaction been obtained.<sup>2</sup> The process may operate in another fairly simple case<sup>3</sup> but in other molecules where such rearrangement might have occurred it was not observed.<sup>4</sup> 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<sub>2</sub>Me)<sup>5</sup> was converted into the sensitive aldehyde (**4**; R = CHO) by reduction (LiAlH<sub>4</sub>) and oxidation (CrO<sub>3</sub>·2pyridine, CH<sub>2</sub>Cl<sub>2</sub>) 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<sub>6</sub>D<sub>6</sub> was monitored by Fourier transform <sup>1</sup>H 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  $\pi^4s + \sigma^2s + \pi^2a$ , 8-electron process [see (**6**)]. Such

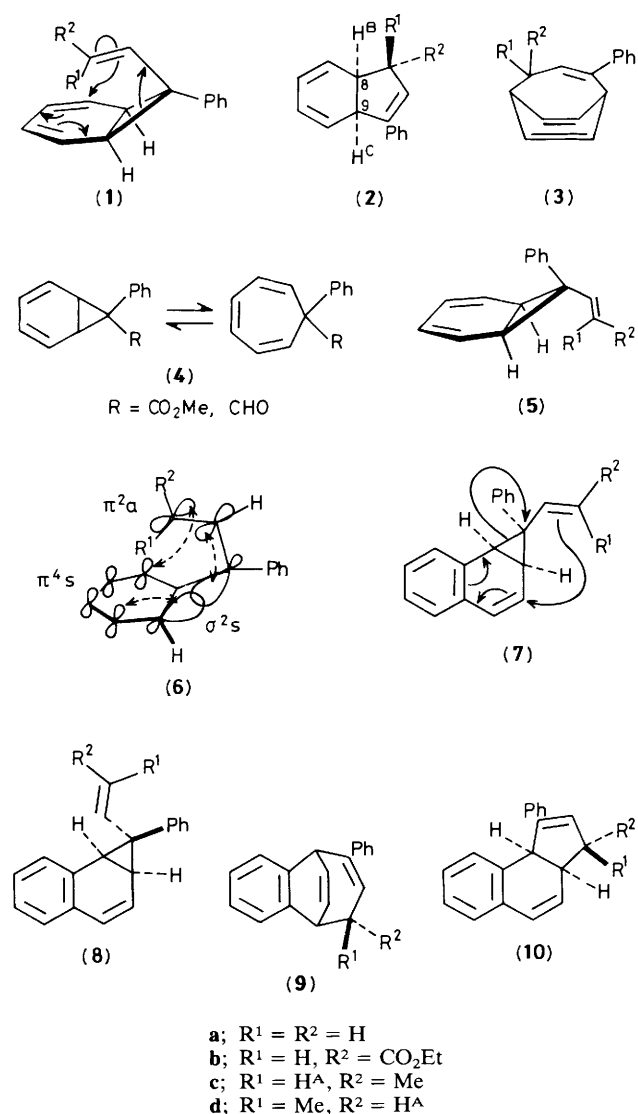
rearrangement necessarily involves the *endo*-vinyl isomers (**1**) with the consequence that an (*E*)-substituent on the vinyl group ends up in the *exo* position in the dihydroindenes (**2**). On the other hand if conversion of (**1**) into (**2**) were an example of vinylcyclopropane to cyclopentene rearrangement<sup>6</sup> 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,<sup>8</sup> 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 AgNO<sub>3</sub>-SiO<sub>2</sub> 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**). † 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<sup>B</sup> at *ca.* 0.5 p.p.m. to higher field in (**2c**) than (**2d**) suggests a *cis*-relationship of the Me group and H<sup>B</sup> in (**2c**); introduction of a Me group shields a *cis*-vicinal proton in cyclopentanes, and related effects in cyclohexanes are well known.<sup>9</sup> In addition the known<sup>10a,b</sup> *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,<sup>10a,c</sup> and the close agreement between

‡ 400 MHz <sup>1</sup>H N.m.r. spectra.

§ By reduction (LiAlH<sub>4</sub>, Et<sub>2</sub>O), tosylation of the resulting alcohol (tosyl chloride, pyridine, 0–5 °C, 14 h), and further reduction (LiAlH<sub>4</sub>, tetrahydrofuran, 20 °C to reflux).

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



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

Compound	H <sup>A</sup>	H <sup>B</sup>	H <sup>C</sup>
(2c)	2.89, dqt (8.5—9.0, 7, 2)	2.56, ddd (12, 8.5, 5.5)	4.13, dm (12.0)
(2d)	2.97, dqd (8.0, 7.0, 3.0)	3.13, dddd (12.7, 8.0, 5.8; 1.4)	4.09, dm (12.7)
<i>des</i> -Ph (2c)	2.71, quintet of q (7.0, 2.0)	2.51, ddd (11.5, 7.0, 4.5)	3.64, dm (11.5)
<i>des</i> -Ph (2d)	2.87, dqt (8.0—8.5, 7.0, 2)	3.01, dddd (12.5—13.0, 8.5, 5.0, 1.5)	3.56, dm (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*-vinyl norcaradienes (1) to the virtual exclusion of their *exo*-isomers (5). Since (1) and (5) would be

expected to interconvert freely under the reaction conditions<sup>11</sup> 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.<sup>12</sup> 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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