Thermal Rearrangements of Benzobicyclononatrienes (1,4-Propeno-1,4-dihydronaphthalenes) to Benzobarbaralanes; Intramolecular Diels–Alder rather than Intramolecular Ene Reactions

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The rearrangement of (**1**) to (**2**) involves the sequence (**1**) → (**4**) → (**7**) → (**8**) → (**2**) rather than the intramolecular ene process (**1**; arrows) earlier proposed; other examples of this process and the walk rearrangement of type (**4**) → (**7**) are described.

The benzobicyclononatriene (**1**) isomerises to the benzobarbaralane (**2**) and the dihydrobenzindene (**3**) (ratio 2.5 : 1 after 140 h at 230 °C). It has been proposed[1] that (**2**) is formed by an intramolecular ene reaction (**1**; arrows)[1] and that (**3**) arises *via* the Cope rearrangement product (**4**) of (**1**) by vinylcyclopropane-cyclopentene rearrangement (**4**; arrows). Our interest in the 3,5-sigmatropy exhibited by certain 7-vinylnorcaradienes[2] and our observation of an intramolecular Diels–Alder reaction (IDAR) in 5-vinyl-5*H*-benzocycloheptenes,[3] *e.g.* (**5**; arrows), led us to consider other mechanisms for the conversion of (**1**) into (**2**) and (**3**). Alternative routes to (**2**) include: (a) Cope rearrangement of (**1**) to (**4**), followed by electrocyclic ring-opening of (**4**) to (**6**) and IDAR (**6**; arrows) to give (**2**); (b) walk rearrangement of (**4**) to (**7**), which after ring-opening to (**8**) undergoes IDAR to (**2**); (c) the intermediate (**7**) of mechanism (b) could arise by Cope rearrangement involving the aromatic ring and C(2)–C(3) double bond of (**1**); (d) the intermediate (**8**) of mechanism (b) could arise by a 1,5-vinyl shift in (**6**); (e) direct conversion of (**1**) into (**2**) could involve thermal di-π-methane rearrangement with either C(7)–C(2) or C(8)–C(2) bridging. There is a precedent for a thermally induced di-π-methane rearrangement.[4]

To distinguish between these possibilities we have studied thermolysis of the benzonorcaradienes (**9**)—(**12**). These were prepared from the known ester (**13**; X = H, Y = CO_2Et)[5] or the related deuteriated compound (**13**; X = D, Y = CO_2Et) prepared from N_2CDCO_2Et[6] and naphthalene. These esters were reduced ($LiAlH_4$) and the resulting alochols oxidised to aldehydes using the Swern procedure. Wittig and Wadsworth–Emmons reactions then afforded the compounds (**9**)—(**12**).

Although (**9**)—(**12**) exist predominantly as *exo*-isomers, *exo–endo* isomerisation *via o*-quinonoid isomers like (**6**) was expected to be rapid[2] and to allow conversion into products of type (**1**) by Cope rearrangement. Indeed, heating (**9**) at 103 °C (30 h)† resulted in quantitative conversion into the Cope rearrangement product (**14**). Upon further heating at 200 °C, (**14**) gave a mixture of (**15**), the dihydrobenzindene (**16**), and the benzocycloheptatriene (**17**). The relative proportions of (**14**), (**15**), (**16**), and (**17**) are time dependent. After 2 h (**17**) is the major product (15% of mixture), and (**15**) and (**16**) are less abundant (each 8—9%); the residue (68%) is unchanged (**14**). After 16 h heating, little (**14**) remains and the benzobarbaralane (**15**) is the major product [ratio (**15**) : (**17**) = 6.6]. This result suggested that (**17**) was an intermediate in the formation of (**15**), and isolated (**17**) was shown to give (**15**) at 203 °C (19 h) [ratio (**15**) : (**17**) *ca.* 6.5 : 1]. The existence of the equilibrium (**15**) ⇌ (**17**) was shown by heating (**15**) at 203 °C (12 h), when a similar mixture of (**15**) and (**17**) was obtained. This ready interconversion and the assignment of (*E*)-configuration to the exocyclic double bond in (**17**) (J_{AB} 16 Hz) led to the tentative assignment of C(9) stereochemistry shown in (**15**). This was confirmed by observation of nuclear Overhauser enhancement (n.O.e.) between the CH_2 protons and the alkenic proton(s) in the alcohol (**18**) derived from (**15**) and of a similar n.O.e. in the dihydro-derivative of (**18**). Mechanisms (a) and (c) would have given the C(9) epimer of (**15**) and are

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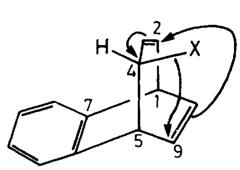
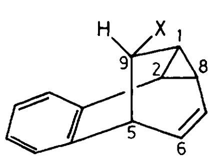
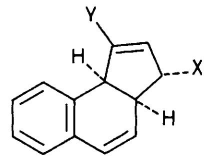
† Samples of (**9**)—(**12**) in degassed C_6D_6 were heated in sealed tubes and rearrangements followed using 90 or 400 MHz ^1H n.m.r. spectra.



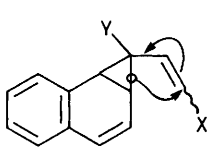
(1) X = Y = H
(14) X = CO_2Et, Y = H
(27) X = Me



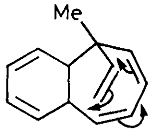
(2) X = H
(15) X = CO_2Et
(18) X = CH_2OH
(19) X = CO_2Me
(28) X = Me



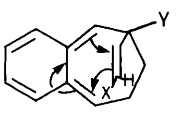
(3) X = Y = H
(16) X = CO_2Et, Y = H



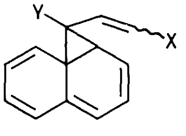
(4) X = Y = H
(9) X=(*E*)-CO_2Et, Y = H
(10) X=(*E*)-CO_2Me, Y = D
(11) X=(*E*)-Me, Y = H
(12) X=(*Z*)-Me, Y = H



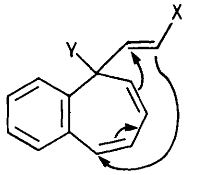
(5)



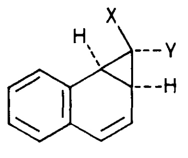
(6) X = Y = H



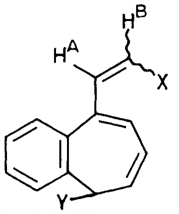
(7) X = Y = H



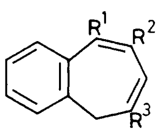
(8) X = Y = H
(21) X = CO_2Me, Y = D
(22) X = CO_2Me, Y = H



(13)



(17) X=(*E*)-CO_2Et, Y = H
(20) X=(*E*)-CO_2Me, Y = D
(23) X=(*E*)-CO_2Me, Y = H
(29) X=(*Z*)-Me, Y = H



(24) R^3 = CO_2Et, R^1 = R^2 = H
(25) R^1 = CO_2Et, R^2 = R^3 = H
(26) R^2 = CO_2Et, R^1 = R^3 = H

therefore unlikely. Further evidence was sought by thermolysis of (**10**). This afforded benzobarbaralane (**19**) with the original deuterium equally distributed between C(2) and C(5). This observation is consistent with mechanism (b), where D-scrambling could accompany interconversion of (**20**) and (**21**) if 1,5-H(D) migration is fast compared to IDAR. That the 1,5-H shift is faster than IDAR was shown by heating (**22**) (prepared by Wadsworth–Emmons reaction of a known[7] aldehyde) at 150 °C (45 min). A 12.5 : 1 mixture of (**23**) and (**19**) was obtained. The course of rearrangement of (**10**) is not consistent with mechanism (d) or with a di-π-methane rearrangement involving C(8)–C(2) bridging which would have localised D at C(6) and C(8) respectively. An intramolecular ene reaction with CO_2R migration (**14**; arrows) would also have localised D at C(8). Di-π-methane rearrangement with C(7)–C(2) bridging, followed by a reverse Diels–Alder reaction and D-scrambling by 1,5-H(D) shifts of the type interconverting (**20**) and (**21**), is inconsistent with faster formation of (**17**) than (**15**).

The failure of (**6**) and its derivatives to undergo intramolecular Diels–Alder reaction [mechanism (a)] is consistent with a failure to trap related *o*-quinodimethanes in both intermolecular[5,8a] and intramolecular[8b] reactions. This is associated with very low equilibrium concentrations of *o*-quinodimethanes related to (**6**), as well as the facility of other reactions of their much more abundant valence tautomers, such as (**4**). There appears to be little evidence for thermal walk rearrangement of the type (**4**) → (**7**)[9] although the related photo-reaction[9,10] is better established. The thermal process may be more common than hitherto believed. Thus although (**13**; X = H, Y = CO_2Et) is reported[5] to give (**24**), our investigation of this thermolysis at 250 °C (3 h) using 400 MHz ^1H n.m.r. spectra indicated the formation of (**25**) (16.4%) produced *via* walk rearrangement as well as (**24**) (47.5%), (**26**) (13.1%), and starting material (23%).

Thermolysis of the (*E*)-alkene (**11**) at 100 °C gives the Cope rearrangement product (**27**), which at a higher temperature (230 °C, 31 h) gives mainly the benzobarbaralane (**28**). In agreement with the inhibition of Cope rearrangement by a (*Z*)-methyl group on one of the double bonds,[11] compound (**12**) rearranges slowly at 160 °C (38 h) to give the C(4) epimer of (**27**) (39%) and the product, (**29**), of walk rearrangement and 1,5-H shift (61%). Evidently, the (*Z*)-methyl group also strongly inhibits IDAR, as the C(9) epimer of (**28**) is not observed on heating to 230 °C. At this temperature small quantities of (**28**) itself are produced. These observations provide a good precedent for a thermal walk rearrangement of the type (**4**) → (**7**).

That mechanism (b) is also appropriate for rearrangement of the parent compound (**1**) was indicated by the thermolysis of (**1**) deuteriated at C(4) and C(2).‡ The ^{1}H n.m.r. spectrum of the product (**2**) indicated the absence of protons at C(9) and 50% D at C(2) and C(5). These observations rule out the intramolecular ene mechanism and support mechanism (b).

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‡ Prepared by treatment of (**1**) with KOBu^t in $(CD_3)_2SO$ (60 °C, 4 h), *cf.* ref. 12.