Persistence of Stereoselectivity in the Thermal Cyclizations of 5-Alkenylcyclohexa-1,3-dienes; a Novel Route to Some Functionalized Bridged Tricyclic Rings

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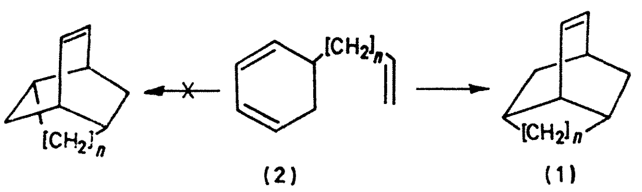
Summary Heating of 5-pent-4-enylcyclohexa-1,3-diene at 210° leads to predominantly tricyclo[5,3,1,$0^{3,8}$]undec-9-ene, along with minor amounts of the epimeric tricyclo[5,2,2,$0^{1,5}$]undec-8-enes which are probably formed through a competing sequence involving the intermediate 1-pent-4-enylcyclohexa-1,3-diene; ketones corresponding in their skeletal structure to the tricyclic hydrocarbons have been obtained by heating α-pyrone with hepta-1,6-dien-3-one.

THE identification of molecules of C_s symmetry (**1**; n = 0—2) as the sole tricyclic products of the thermal reactions of 5-alkenylcyclohexa-1,3-dienes[1] (**2**; n = 0—2) prompted the investigation of the thermal behaviour of 5-pent-4-enylcyclohexa-1,3-diene[2] (**3a**).



(2) (1)

n = 0 - 2

The diene (**3a**) was prepared by a sequence involving coupling of the Grignard reagent (**4**) with 3-bromocyclohexene to produce the diene† (**5**) (74%), b.p. 40° at 0·5 mmHg. A fourfold excess of the diene (**5**) was brominated (*N*-bromosuccinimide) to give a mixture of bromides in 91% yield which were treated with dimethylamine (100°; 4 h; 78% yield of amines), followed by oxidation (30% H_2O_2, MeOH). Pyrolysis of the amine oxides at 105—120° afforded the diene (**3a**) and the isomer (**6a**) in 68% yield based on the amine percursors.‡

Heating compound (**3a**), (>99·9% pure by g.l.c.) at 210° (21 h; 40—80 mmHg) gave three isomeric tricyclic products,§ (**7a**) (21·4%) yield, (**8a**) (5·9% yield), and (**9a**) (72·7% yield), m.p. 41—43°.**

Tricyles (**7a**) and (**8a**) were epimers as hydrogenation of either olefin gave tricyclo[5,2,2,$0^{1,5}$]undecane (**10**). The epimers were most likely formed in a sequence involving a [1,5] sigmatropic shift[4] of hydrogen from the diene (**3a**) followed by an intramolecular Diels–Alder reaction of the intermediate (**6a**). Indeed, the isomers (**7a**) and (**8a**) were obtained in ratios essentially identical to those achieved from the thermal reaction of (**3a**) by heating (**6a**) under the same conditions!

The formation of (**9a**) from the direct cyclization of (**3a**) is a further example of the remarkable stereoselectivity in the thermal Diels–Alder reactions of 5-alkenylcyclohexa-1,3-dienes.

Ready entry into the bridged tricyclic ring systems (**7**), (**8**), and (**9**) was achieved by generating the ketone (**3b**) under conditions in which it is thermally labile. Heating α-pyrone (**11**) and the dienone (**12**) in molar ratio 2·33 : 1 (50 h, 227—232°; 102 mmHg) produced a mixture of the isomeric ketones (**7b**), (**8b**), and (**9b**) (separated by g.l.c.) in the ratio 43 : 11 : 37 and a conjugated ketone (**6b**) (3%).¶ When this ketone (prepared independently in 40% yield by condensing 1-diethylaminobuta-1,3-diene (**13**) with the ketone (**12**) and treating the resulting adduct with dilute acid[5]) was heated at 227°, the ketones (**7b**) and (**8b**) were obtained in the ratio 79 : 21. Hence, compound (**6b**) is a likely intermediate in the sequence leading from (**11**) and (**12**) to the epimeric ketones (**7b**) and (**8b**). Wolff–Kishner reduction of the individual ketones (**7b**), (**8b**), and (**9b**) gave the corresponding hydrocarbons (**7a**), (**8a**), and (**9a**) which were identical to the products of the thermal reorganization of (**3a**).

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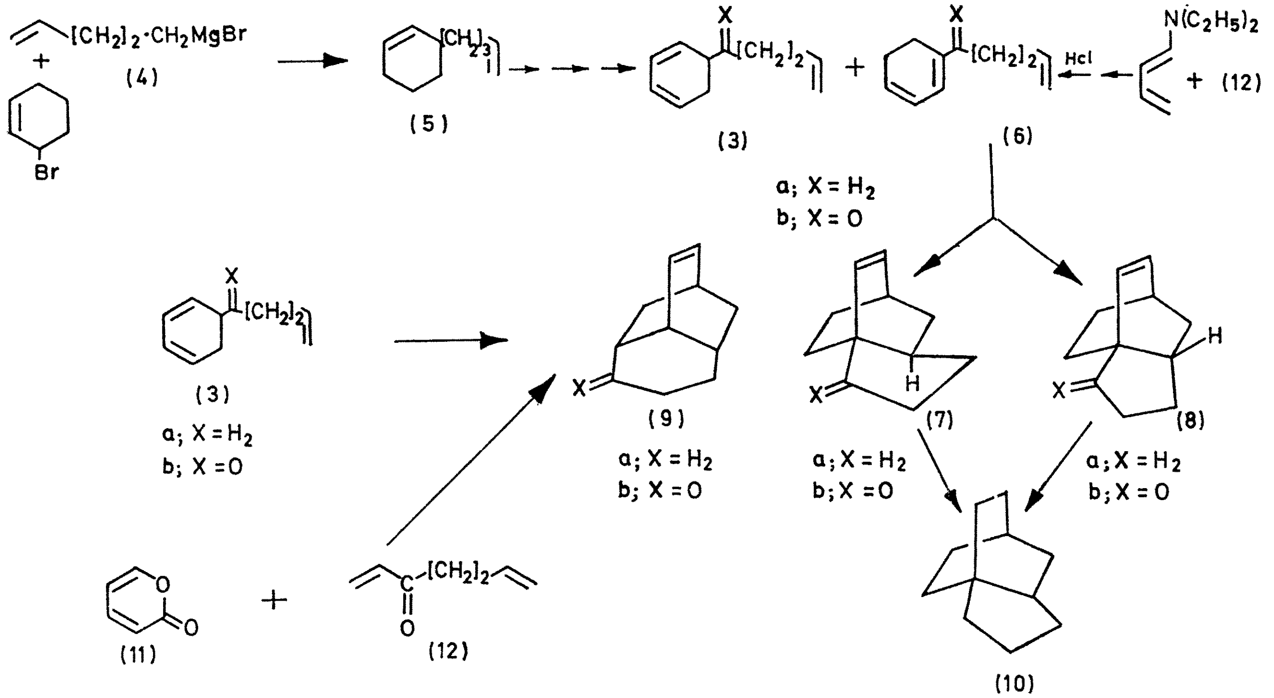
† Satisfactory elemental analyses and/or mass spectral data were obtained for all new compounds.

‡ The isomers (**3a**) and (**6a**) were formed in ratios varying from 1·86 to 2·76 : 1 and were separated by g.l.c. on a 2 m column containing 10% 1,2,3-tris(cyanoethoxypropane) on 60—80 mesh Chromosorb W after being distilled (47° and 2 mmHg).

§ Confirmation of the structure of compound (**9a**) has been obtained by relating dihydro-(**9a**) to tricyclo[5,3,1,$0^{3,8}$]undecane which has been prepared by a modification of a route employed[3] for a related system. We tentatively assign structure (**7a**) to the major epimer. This assignment will be discussed in detail in the full paper.

** 300 MHz n.m.r. and i.r. spectra were consistent with the tricyclic structures (**7**)—(**9**) and are available from the author.

¶ Disproportionation products of (**6b**) were also formed. The semicarbazones of (**7b**), (**8b**), and (**9b**) had m.p.s. of 235–236° (decomp.), 229·5° (decomp.), and 215–216° (decomp.), respectively.



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