Isolation and Thermal Rearrangement of a 4a*H*-Benzocycloheptene

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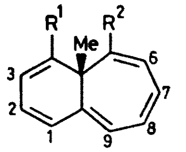
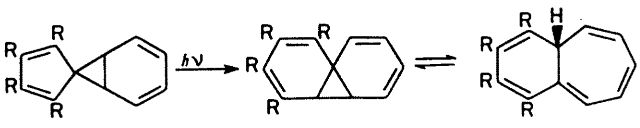
Summary The 4a*H*-benzocycloheptene (**1b**) rearranges at 140 °C to the 7*H*-benzocycloheptene (**12**); a pathway is suggested which involves valence tautomerism to a bisnorcaradiene intermediate, followed by a [1,5] shift of the ester group.

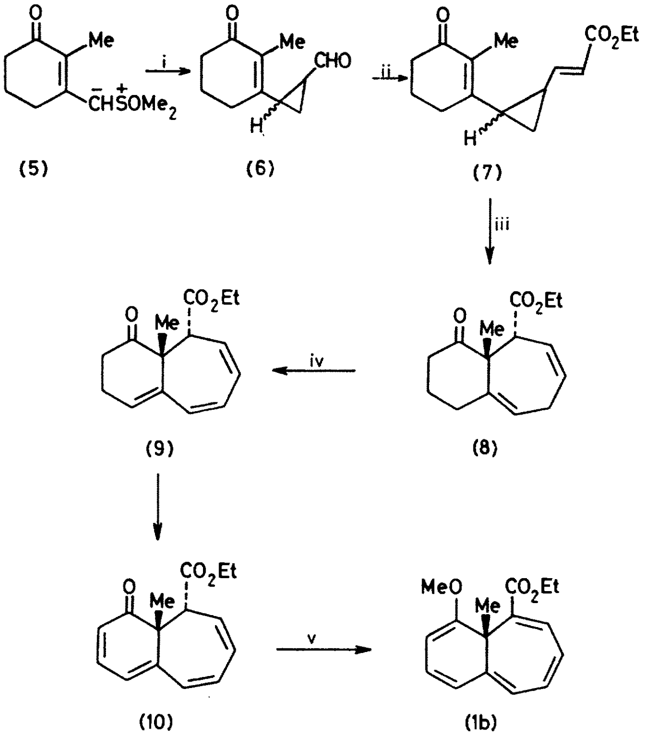
As part of an investigation of the synthesis and chemistry of bicyclic polyenes bearing bridgehead substituents, we have undertaken the preparation of 4a-methyl-4a*H*-benzocycloheptene (**1a**) and its derivatives. 4a*H*-Benzocycloheptenes (**2**) bearing a hydrogen atom at the bridgehead position have been implicated as intermediates in the thermal and photochemical rearrangements of spironorcaradienes (**3**) and of 'bisnorcaradienes' (**4**),[1] but no 4a*H*-benzocycloheptenes have so far been isolated. We report here the synthesis of the 4a*H*-benzocycloheptene ester (**1b**) and the investigation of its thermal rearrangement.



(**1**) a; $R^1 = R^2 = H$
b; $R^1 = OMe$, $R^2 = CO_2Et$



(**3**) (**4**) (**2**)



SCHEME 1. Reagents: i, $CH_2{=}CHCHO$; ii, $Ph_3\overset{+}{P}\bar{C}HCO_2Et$; iii, 140 °C; iv, DDQ; v, NaH then $MeOSO_2F$.

The construction of the carbon skeleton was based on a route previously described by Marino and Kaneko[2] for the preparation of other fused seven-membered ring systems, the key step being the thermal rearrangement of a divinylcyclopropane (Scheme 1). The oxosulphonium ylide (**5**) was prepared (40%) from 3-chloro-2-methylcyclohex-2-enone[3] and dimethyloxosulphonium methylide in tetrahydrofuran. It reacted with acrolein to give a mixture of the *cis*- and *trans*-cyclopropanecarbaldehydes (**6**) (81%), which with triphenylphosphonium ethoxycarbonylmethylide gave the unsaturated esters (**7**) (94%). The minor component, the *cis*-acrylic ester, rearranged spontaneously at 20 °C to the bicyclic ester (**8**); the *trans*-ester was quantitatively converted into (**8**) by heating in xylene. This bicyclic ester was dehydrogenated to the tetraenone (**10**) (59%) by heating it with an excess of dichlorodicyanobenzoquinone (DDQ) in a mixture of dioxan and acetic acid; the trienone (**9**) (15%) was also isolated from this reaction.

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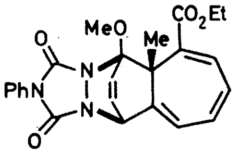
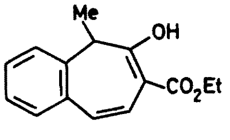
The tetraenone-ester (**10**) is an oil, b.p. 75—80 °C at 0·03 mmHg, with analytical and spectral data in agreement with the proposed structure. The extended conjugation is indicated by the u.v. spectrum, which has maxima at 265 (ϵ 1·26 × 10^4) and 400 nm (2·35 × 10^4). The carbonyl absorptions in the i.r. spectrum are at 1725 and 1665 cm^{-1}. In the ^{1}H n.m.r. spectrum, the 4a*H*-methyl group is at δ 1·28 and H-5 appears as a doublet (*J* 8·6 Hz) at δ 4·51.

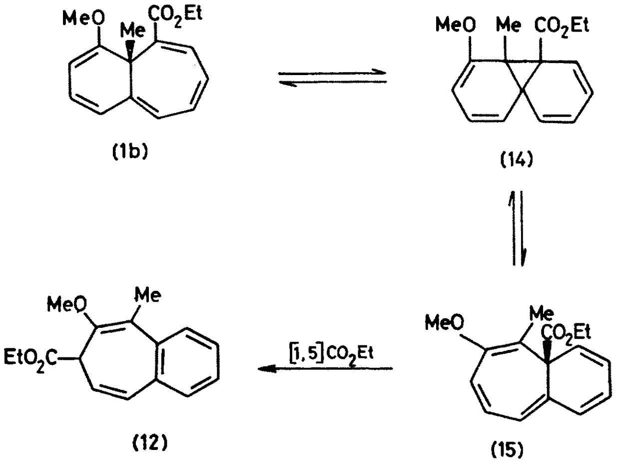


(**11**)



(**13**)

Addition of sodium hydride to a solution of the tetraenone (**10**) in dimethoxyethane at −10 °C produced the turquoise-coloured enolate anion. This was alkylated with methyl fluorosulphonate to give the enol ether (**1b**) as a red oil (70%), b.p. 70—75 °C at 0·02 mmHg, ν_{max} 1695 and 1640 cm^{-1}, λ_{max} 282 (ϵ 3·97 × 10^4) and 425 nm (9·03 × 10^3). The n.m.r. spectrum contains signals for the bridgehead methyl group at δ 0·86 and for the *O*-methyl group at δ 3·62. The compound gave a Diels–Alder adduct (70%), m.p. 161—163 °C, with *N*-phenyltriazolinedione at 0 °C, to which the structure (**11**) was assigned. The pentaene showed no tendency to undergo photochemical rearrangement: it could be recovered after irradiation under a variety of conditions. It was also unchanged after being heated in toluene, but in xylene at 140 °C it slowly rearranged to give a mixture of products from which a major component was isolated (42%) as an oil by layer chromatography. This compound was assigned the 7*H*-benzocycloheptene structure (**12**). It shows a carbonyl absorption at 1725 cm^{-1} and, in the ^{1}H n.m.r. spectrum, a *C*-methyl signal at δ 2·10 and an *O*-methyl signal at δ 3·63. Four aromatic hydrogen signals appear as a multiplet at δ 7·2—7·6 and the single hydrogen at C-7 as a doublet (*J* 7·1 Hz) at δ 3·41. The remaining skeletal hydrogen atoms give signals at δ 6·73 (H-9, d, *J* 9·5 Hz) and 6·38 (H-8, dd, *J* 7·1 and 9·5 Hz). Further support for the proposed structure is provided by its hydrolysis with $NaHSO_4$ in aqueous dioxan to the β-oxoester (**13**), m.p. 39—41 °C.



Scheme 2

A reasonable route for the thermal conversion of (**1b**) into (**12**) is shown in Scheme 2. The pentaene is proposed to undergo valence tautomerism to the bisnorcaradiene (**14**), which can then open in the alternative way to give the benzocycloheptene (**15**) with an ethoxycarbonyl group at the bridgehead. In accordance with the known tendency of alkoxycarbonyl groups to undergo sigmatropic migration,[4] a [1,5] shift then gives the observed product (**12**).

This reaction sequence accords with earlier proposals[1] of equilibria between 4a*H*-benzocycloheptenes and bisnorcaradienes. Such a reaction must occur in preference to thermal sigmatropic shifts of the bridgehead methyl group in (**1b**), and provides a further illustration of the reluctance of this group to undergo thermal migration.

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