Preparation of Some Derivatives of *cis,trans*-Cyclo-octa-1,4-diene

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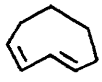
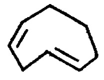
Summary Derivatives of *cis,trans*-cyclo-octa-1,4-diene, a previously undescribed system, have been prepared in good yield by the Ag$^+$-assisted solvolysis of *exo*-8-bromo- and 8,8-dibromo-bicyclo[5,1,0]oct-3-ene.

ALTHOUGH both *cis,trans*-cyclo-octa-1,3-diene[1] (**1**) and -1,5-diene[2] (**2**) are known compounds, we are not aware of any literature reports relating to the synthesis of *cis, trans*-cyclo-octa-1,4-diene (**3**) or any of its derivatives. We now report that when *exo*-8-bromobicyclo[5,1,0]oct-3-ene† (**4b**) was treated with an excess of silver perchlorate in acetone–water (95 : 5, v/v) solution,[5] *cis,trans*-cyclo-octa-1,4-dien-6-ol (**5**; R = H) was obtained.


(1)


(2)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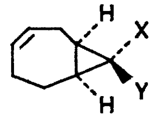
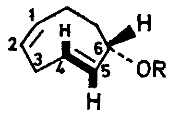


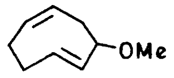
(4) a; X=Y=Br
b; X=Br,Y=H
c; X=H,Y=Br



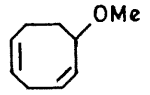
(5)

Compound (**5**; R = H) was isolated (73%) and identified by mass, i.r., and n.m.r. spectroscopy; it was further characterised as its analytically-pure acetate ester (**5**; R = Ac) and as its crystalline phenylurethane derivative (**5**; R = CONHPh), m.p. 98·5—99·5°. From its n.m.r. spectrum [τ 3·90 (m, 1H), 4·1—4·8 (m, 3H), 5·72 (dt, *J* 4·5 and 9 Hz, 1H), 6·24 (s, 1H), 6·8—8·75 (m, 6H)], (**5**; R = H) appears to be a pure diastereoisomer:[6] the relative configuration of the *trans*-double bond and the asymmetric carbon centre (C-6), indicated in formula (**5**), have been assigned on the assumption that the stereochemical course of hydrolysis of (**4b**) was the same as that of *exo*-8-bromobicyclo[5,1,0]octane.[6] *cis,trans*-Cyclo-octa-1,4-dien-6-ol (**5**; R = H) may be distilled (b.p. *ca.* 60°/2 mm) but with a low recoverable yield; it also appears to be unstable at room temperature.

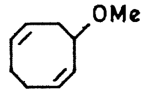
Treatment of *exo*-8-bromobicyclo[5,1,0]oct-3-ene (**4b**) with $AgClO_4$ in MeOH solution[5] gave an 84% yield of a colourless liquid, b.p. 40°/2 mm, consisting of 6-methoxy-*cis,trans*-cyclo-octa-1,4-diene (**5**; R = Me) (*ca.* 80%) and what is believed to be 4-methoxy-*cis,trans*-cyclo-octa-1,5-diene (**6**) (*ca.* 20%). After a solution of this material and a small quantity of iodine[1] in CCl_4 had been allowed to stand in the dark for 48 h, a virtually quantitative yield of a mixture of 6-methoxy-*cis,cis*-cyclo-octa-1,4-diene (**7**) (*ca.* 80%) and 4-methoxy-*cis,cis*-cyclo-octa-1,5-diene (**8**) (*ca.* 20%) was obtained. These isomeric *cis,cis*-compounds (**7** and **8**) were separated by g.l.p.c., and identified by comparison with the methanolysis products of *endo*-8-bromobicyclo[5,1,0]oct-3-ene (**4c**) (see below).



(6)



(7)



(8)

Pure 6-methoxy-*cis,trans*-cyclo-octa-1,4-diene (**5**; R = Me) was isolated from the crude methanolysis products of (**4b**) by g.l.p.c., and characterised by spectroscopic methods and elemental analysis; it was isomerized by a trace of iodine[1] in CCl_4 solution to its pure *cis,cis*-isomer (**7**). 6-Methoxy-*cis,trans*-cyclo-octa-1,4-diene is a colourless mobile liquid which slowly becomes viscous even at 0°; its n.m.r. spectrum‡ [Figure] again suggests that it is a pure diastereoisomer[6] with the relative configuration indicated in formula (**5**; R = Me).§

endo-8-Bromobicyclo[5,1,0]oct-3-ene¶ (**4c**) reacted only very slowly with $AgClO_4$–MeOH at 25°; however, when the reactants were heated under reflux for 1 h, a virtually

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† Reaction between cyclohepta-1,4-diene[3] and an excess of $CHBr_3$ and $KOBu^t$ in Bu^tOH solution gave 8,8-dibromobicyclo[5,1,0]oct-3-ene (**4a**), b.p. 92—98°/2 mm, (45%). A bis-dibromocarbene adduct, m.p. 111—111·5°, was obtained as a by-product in 10% yield. Treatment of 8,8-dibromobicyclo[5,1,0]oct-3-ene (**4a**) with dimsyl sodium in Me_2SO solution gave[4] *exo*-8-bromobicyclo[5,1,0]oct-3-ene (**4b**), b.p. 83—85°/3 mm, (77%).

‡ The low-field multiple at τ 3·94 in the n.m.r. spectrum of (**5**; R = Me) may be assigned to the resonance of 4-H: double-irradiation in the bis-allylic region at τ 7·31 caused this multiplet to collapse to a doublet (*J* 17 Hz), and had no effect on the double-doublet at τ 4·64. However, double-irradiation at τ 6·30 caused the latter signal, which may be assigned to the resonance of 5-H, to collapse almost to a doublet (*J ca.* 17 Hz). The low-field multiplet at τ 3·90 in the n.m.r. spectrum of (**5**; R = H) may, by analogy, also be assigned to the resonance of 4-H; indeed, this resonance signal for 4-H is a characteristic feature of the n.m.r. spectra of all the 6-substituted derivatives of *cis,trans*-cyclo-octa-1,4-diene examined.

quantitative yield of a mixture of 6-methoxy-*cis,cis*-cyclo-octa-1,4-diene (**7**) and 4-methoxy-*cis,cis*-cyclo-octa-1,5-diene (**8**), consisting mainly of the latter isomer, was obtained. These compounds were separated by g.l.p.c., and characterised by elemental analysis and the usual spectroscopic methods. Finally, reaction between 8,8-dibromobicyclo[5,1,0]oct-3-ene (**4a**) and AgClO$_4$–MeOH at 25° gave a high yield of a mixture of 5-bromo-6-methoxy-*cis,trans*- and -*cis,cis*-cyclo-octa-1,4-dienes (**9**) and (**10**), respectively. This mixture, which was richer in the *cis,trans*-isomer (**9**) (*ca.* 75%), was separated into its components by g.l.p.c. Compounds (**9**) and (**10**) were characterised by elemental analysis and spectroscopic methods; when it was heated or allowed to stand in CCl$_4$ solution at 25°, compound (**9**) was converted into compound (**10**).

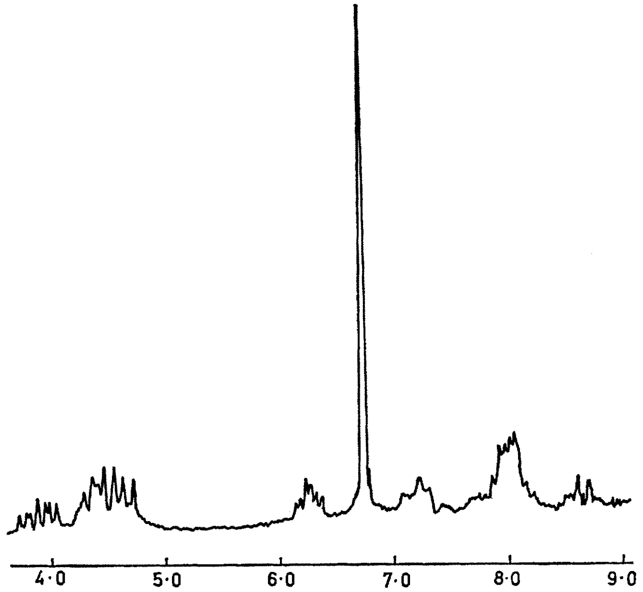
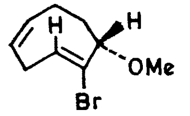
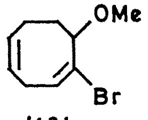


FIGURE. 100 *MHz n.m.r. spectrum of* 6-*methoxy*-cis,trans-*cyclo-octa*-1,4-*diene* (**5**; R = Me) *in* CCl$_4$ *solution.*



(**9**)



(**10**)

The preparation of the *cis,trans*-cyclo-octa-1,4-diene derivatives described here emphasizes the synthetic value of the AgClO$_4$-promoted ring-expansion reaction.[5] The results are also mechanistically interesting in that the disrotatory mode of ring-opening involving an *exo*-leaving group and leading to an intermediate *trans,trans*-allylic system,[8] which was favoured in the solvolysis of 8-halogenobicyclo[5,1,0]octane derivatives,[5] was still favoured in the solvolysis of 8-halogenobicyclo[5,1,0]oct-3-ene derivatives (**4**). Also, the solvolysis of (**4a**) and (**4b**) led predominantly to (*cis,trans*)-cyclo-octa-1,4-diene derivatives, whereas the solvolysis of (**4c**) led predominantly to a (*cis,cis*)-cyclo-octa-1,5-diene derivative.

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§ The resonance signal of the methine proton (τ 6·30, dt, *J* 5 and 9 Hz) of (**5**; R = Me) closely resembles that of the methine proton (τ 6·36, dt, *J* 5·5 and 9 Hz) of 3-methoxy-*trans*-cyclo-octene,[6] the methanolysis product of *exo*-8-bromobicyclo[5,1,0]octane.

¶ Reduction of (**4a**) with Zn–AcOH[7] at 65° gave a 71% yield of a mixture of *endo*-8-bromobicyclo[5,1,0]oct-3-ene (**4c**) (*ca.* 75%) and its *exo*-isomer (**4b**) (*ca.* 25%). The latter compound could be removed by treating the mixture with AgClO$_4$–MeOH at 25° for 1 h.

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