

## A Simple Entry to the *cis*-Bicyclo[3.3.0]octa-2,6-diene System

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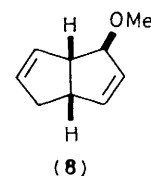
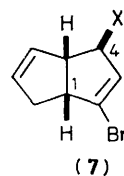
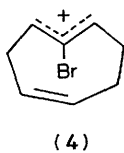
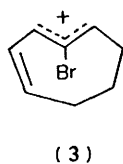
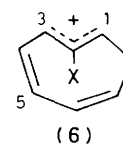
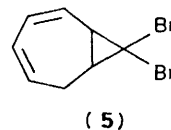
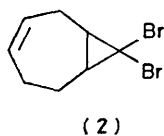
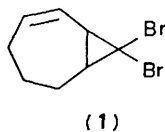
8,8-Dibromobicyclo[5.1.0]octa-2,4-diene (**5**) is converted into the *cis*-bicyclo[3.3.0]octa-2,6-diene (**7**; X = OMe or OH) by treatment with AgClO<sub>4</sub>-MeOH or AgClO<sub>4</sub>-aq. acetone, respectively; the corresponding *exo*-monobromide (**14**; X = H, Y = Br) is similarly converted into (**8**) by AgClO<sub>4</sub>-MeOH.

The reaction of *exo*-8-bromobicyclo[5.1.0]octane with silver(I) perchlorate in methanol is well known to lead to 3-methoxy-*trans*-cyclo-octene, apparently by a process involving concerted halide ion removal, disrotatory cyclopropyl-allyl rearrangement, and solvolysis by methanol.<sup>1</sup> Dibromides (**1**) and (**2**) both react with AgClO<sub>4</sub>-MeOH to give *trans*-cyclo-octenes; this has been explained in the same way, with loss of the *exo*-halogen and methanolysis of *trans,trans*-allyl cations (**3**) and (**4**) respectively.<sup>2,3</sup>

It was therefore of interest to examine the behaviour of the related dibromide (**5**) under the same conditions, with

a view to intercepting the ion (**6**; X = Br), which may formally be regarded as a homotropylium ion with a *trans,trans*-arrangement of bonds C(3)-C(4) and C(1)-C(8) about the allylic fragment C(1)-C(3).

Treatment of (**5**) with AgClO<sub>4</sub>-MeOH for 18 h at 25 °C led to a single major product (75%) which we have characterised as (**7**; X = OMe). The ring structure of (**7**; X = OMe) and the stereochemistry at the 4-position were established by reduction of the compound with lithium in *t*-butanol-tetrahydrofuran to (**8**), which was identical to an authentic

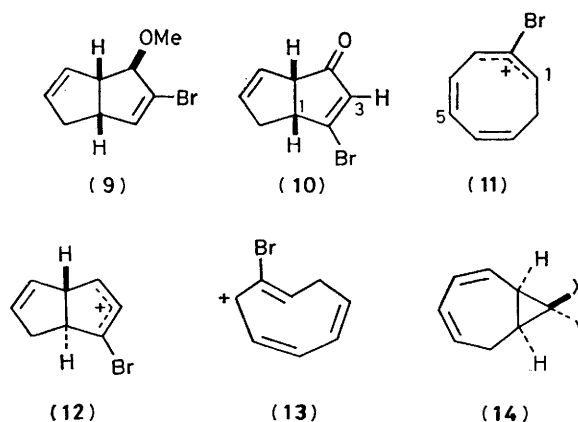


sample.<sup>4</sup> The <sup>1</sup>H n.m.r. spectrum of (7; X = OMe)<sup>†</sup> revealed the presence of three olefinic protons and decoupling experiments indicated that the proton resonating at δ 5.82 (t, *J* 2.5 Hz) was not coupled to either of the other olefinic protons (at δ 5.58); it was, however, coupled to 1-H and 4-H. This was consistent with structure (7; X = OMe) but did not rule out (9), as in this ring system 1,2- and 3,4-couplings in the fragment >C<sup>4</sup>H-C<sup>3</sup>H=C<sup>2</sup>H-C<sup>1</sup>H< are both *ca.* 2.5 Hz, *i.e.* of the same order as allylic couplings.<sup>4</sup> Circumstantial support for structure (7; X = OMe) was obtained by measuring the n.m.r. spectrum in the presence of Eu(fod)<sub>3</sub> (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato), when the signal at δ 5.82 (3-H) underwent a downfield shift greater than that of 1-H (δ 3.52) but less than that of 5-H (δ 3.21). The structure was confirmed by treatment of (5) with silver(i) perchlorate in aqueous acetone to produce (7; X = OH), followed by oxidation with manganese dioxide in dichloromethane to give (10). The proton at C-3 in (10) appeared as a doublet (*J* 2.5 Hz) at δ 5.8, whereas a proton at C-2 would have been expected to appear at δ *ca.* 7 by comparison with a series of cyclopentenones and cyclohexenones.<sup>5</sup>

According to extensive precedent,<sup>1-3</sup> (5) could react by removal either of the *exo*-halogen to give (6; X = Br), or of the *endo*-halogen to give (11). Electrocyclic closure of the ion (11) between carbons 1 and 5 before solvolysis could formally produce the bicyclo[3.3.0]octane skeleton, but the expected conrotatory process would lead to a *trans*-ring junction as in (12). The *cis*-bicyclo[3.3.0]octane system has been reported from the 'disallowed' thermal disrotatory closure of cyclo-octatetraene dications,<sup>6</sup> but homotropylium ions related to (11) are reported to be trapped by halide or acetate ions as cyclo-octatriene derivatives rather<sup>7</sup> than as bicyclo[3.3.0]octanes.<sup>‡</sup> The corresponding conrotatory closure of ion (6; X = Br) would lead to the required *cis*-stereochemistry about the ring junction, but the *transoid*-geometry about the C(2)-C(3) bond would seem to preclude this process on grounds of strain. The *cis*-bicyclo[3.3.0]octane system could result from the *trans*- to *cis*-conversion of the C(2)-C(3) bond in (6; X = Br), followed by conrotatory ring closure of the resulting cation (13). However, there is considerable evidence<sup>1,2</sup> that solvolysis of 'ions' produced in this reaction system is concerted with ring opening, or at least follows very rapidly; it would seem surprising, then, that (6; X = Br)

<sup>†</sup> [δ (CCl<sub>4</sub>) 5.82 (t, *J* 2.5 Hz, 1H), 5.58 (br. s, 2H), 3.94 (m, 1H), 3.52 (m, 1H), 3.25 (s, 3H), 3.21 (m, 1H), and 2.46 (complex, 2H).]

<sup>‡</sup> Photochemical closure of the homotropylium ion does lead to the *cis*-bicyclo[3.3.0]octane skeleton (P. A. Christensen, Y. Y. Huang, A. Meersters, and T. S. Sorensen, *Can. J. Chem.*, 1974, **52**, 3424).



should have a sufficient lifetime to isomerise before being trapped by methanol. Alternative pathways for the transformation of (5) into the stable<sup>8</sup> bicyclo[3.3.0]octane system, perhaps involving (13), need to be considered.

However, support for the loss of *exo*- rather than *endo*-bromine from (5) came from the reactions of the corresponding monobromides (14; X = H, Y = Br) and (14; X = Br, Y = H) with silver(i) perchlorate in methanol. The monobromides were obtained as a *ca.* 1:1 mixture by reaction of cycloheptatriene with CH<sub>2</sub>Br<sub>2</sub> and LiN(SiMe<sub>3</sub>)<sub>2</sub> in pentane,<sup>9</sup> and were separated by column chromatography. Treatment of the *endo*-isomer (14; X = Br, Y = H) with silver(i) perchlorate in methanol led to several products which did not include (8). However, similar treatment of *exo*-isomer (14; X = H, Y = Br) led to a single major product which was shown to be identical to (8) obtained above.

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