Preparation of Cyclodeca-1,6-diyne-3,8-diol and its Dimethyl Ether

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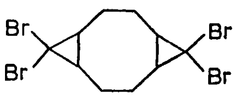
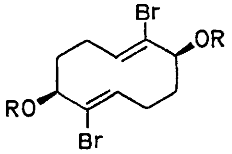
Summary The silver ion-promoted hydrolysis and methanolysis of the bis-dibromocarbene adduct of *cis,cis*-cyclo-octa-1,5-diene are described; the conversion of the major products into 3,8-dihydroxy- and 3,8-dimethoxy-cyclodeca-1,6-diynes, respectively, is also reported.

The only monocyclic ten-membered ring compounds containing two acetylenic groups which have been prepared previously[1,2] both contain hetero-atoms. We now report the synthesis of cyclodeca-1,6-diyne-3,8-diol (**5a**) and its dimethyl ether (**5b**), which we believe to be the first such ten-membered homocyclic diacetylenes to be described. Our interest in this work was stimulated by the possibility of (**5a**) being a precursor of *cis,cis*-cyclodeca-1,6-diene-3,8-diyne (**6**), which, in turn, is a potential precursor of the as yet unknown dehydro[10]annulene[3] and the isomeric bis-allene, cyclodeca-1,2,4,6,7,9-hexaene.[4] The latter systems are both of theoretical interest.


(1)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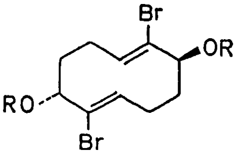
b; R = Me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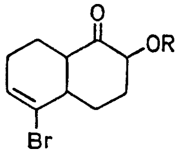
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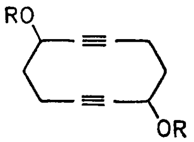
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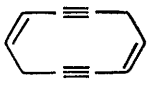
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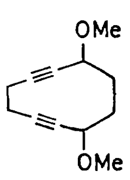
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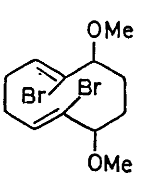
(8)

The bis-dibromocarbene adduct of *cis,cis*-cyclo-octa-1,5-diene (**1**) has been reported[5] not to be susceptible to Ag$^+$-catalysed acetolysis; however, treatment of it with silver sulphate in 98% sulphuric acid for 24 h at room temperature gave α-tetralone in over 50% yield.[6] We now report that when solid (**1**) was added over a period of 30 min to a cooled stirred solution of silver perchlorate in methanol and the reaction allowed to continue for a further 15 min at 20°, t.l.c. of the products revealed a major component, two minor components, and several other trace components. Separation of the products by chromatography on silica gel gave what are believed to be 2,7-dibromo-*cis*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (**2b**, 41%, m.p. 63·5—65°), 2,7-dibromo-*trans*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (**3b**, 6%, m.p. 160—162°), and the octalone derivative (**4b**, 9%, m.p. 101—102°). The structures assigned to the two *trans,trans*-cyclodeca-1,6-diene derivatives (**2b** and **3b**) are based on their elemental compositions, spectroscopic properties (see following communication[7] for a discussion of their ^{1}H n.m.r. spectra), and on their conversion into the corresponding cyclodeca-1,6-diyne derivatives (see below). However, while it is clear that these compounds are diastereoisomeric 2,7-dibromo-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-dienes,† the evidence for the lower-melting compound being the *cis*-dimethoxy-derivative (**2b**) is not conclusive (see following communication[7]).

Treatment of (**1**) with silver perchlorate in aqueous acetone (1:9; v/v) under the same conditions[8] gave what are believed to be 2,7-dibromo-*cis*-3,8-dihydroxy-*trans, trans*-cyclodeca-1,6-diene (**2a**, 42%, m.p. 155—157°) and the octalone alcohol (**4a**, 7%, m.p. 155°). None of the diastereoisomeric diol corresponding to the putative *trans*-dimethoxy-compound (**3b**) was isolated from the products. Treatment of (**2a**) with methyl iodide and barium oxide in dimethyl sulphoxide solution[9] gave the putative *cis*-dimethyl ether (**2b**).

When (**2b**) was treated with an excess of potassium t-butoxide in dimethyl sulphoxide solution[10] for 5 s at 20° and the crude products purified by extraction with aqueous silver nitrate solution, 3,8-dimethoxycyclodeca-1,6-diyne (**5b**) was obtained as a crystalline solid, m.p. 63·5—65°, in 29% yield. This compound was characterized on the basis

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† It follows from their very rapid reactions[10] with KOBu^t–Me$_2$SO to give diacetylenes that (**2b**) and (**3b**) each have two *trans*-double bonds. Supporting evidence (A. Shaw, Ph.D. Thesis, Cambridge University, 1971, p. 18) comes[7] from the comparatively high-field resonances ($>\tau$ 6) of their methine protons (3-H and 8-H).

of analytical data and its ^{1}H n.m.r. (CCl_4) [τ 6·15 (m, 2H), 6·73 (s, 6H), 7·3—8·3 (m, 8H)], i.r. [ν_{max} (Nujol) 2210 m, 2260 w cm^{-1}], and mass [M^+ at m/e = 192] spectra. The isomeric structure (**7**) for this diacetylenic compound may be excluded on the basis of spin-decoupling evidence.‡ This, in turn, confirms that the precursor of (**5b**) is a *trans,trans*-cyclodeca-1,6-diene and not a *trans,trans*-cyclodeca-1,5-diene derivative (**8**).

Finally, the diacetylenic diol (**5a**) was prepared from the bis-tetrahydropyranyl ether of (**2a**). Treatment of (**2**; R = C_5H_9O) with potassium t-butoxide in dimethyl sulphoxide solution under the above conditions, followed by removal of the protecting groups, gave cyclodeca-1,6-diyne-3,8-diol (**5a**). The latter compound was isolated as a crystalline solid, m.p. 154—155°, in 19·5% yield (based on **2a**).

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‡ Spin-decoupling evidence indicates that the diacetylene, m.p. 64–66°, obtained by the action of $KOBu^t$ in Me_2SO solution on the putative 2,7-dibromo-*trans*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (**3b**) is also a 3,8-dimethoxycyclodeca-1,6-diyne.

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