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HOMO-1,4-ADDITION TO CYCLO-OCTA-1,4-DIENE AND CYCLOHEPTA-1,4-DIENE

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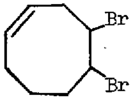
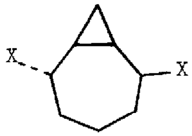
Summary Cyclo-octa-1,4-diene and cyclohepta-1,4-diene give the bicyclic derivatives IIa-b and IVa-b on reaction with Br_2-CCl_4 or I_2-$AgClO_4$-MeOH respectively. Cyclo-octa-1,4-diene also undergoes homo-1,4-addition in the Prevost reaction with I_2-AgOAc or I_2-AgOCOPh in benzene.

There have been two recent reports of the preparation of 1,4-dienes by homo-1,4-elimination from α,α'-difunctionalised cyclopropanes.[1,2] Van Tamelen had earlier recognised the possibility of the reverse reaction, homo-1,4-addition to a 1,4-diene. Treatment of cyclohexa-1,4-diene with Br_2-CCl_4 or with I_2 and silver benzoate in the Prevost reaction led, however, only to 1,2-adducts.[3]

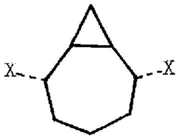
Reaction of cyclo-octa-1,4-diene with Br_2-CCl_4 is reported to give a crystalline dibromide, which was formulated as (I), largely on the basis of its catalytic reduction to cyclo-octane by three mol.equiv. of hydrogen.[4] However, examination of the n.m.r. spectrum of the crystals in CCl_4 [τ 5.10 (br.t., J = ca. 4 Hz, 1H), 5.28 (dt, J = 11, 3 Hz, 1H), 7.69 (br.dd, J = 13, 5 Hz, 1H), 7.96 (dt, J = 13, 5.5 Hz, 1H), 8.0 - 8.5 (complex, 6H), 9.1 (2H)], readily showed that this was not the case. On this basis the compound was reassigned



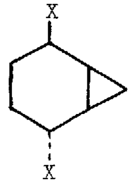
(I)



(II)



(III)



(IV)

(a) X = Br
(b) X = OMe
(c) X = OCOMe
(d) X = OCOPh

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(b) X = OMe
(c) X = OCOMe

as (IIa).+ Confirmation of this was obtained from the 220 MHz spectrum of the crystals in C_6D_6 solution, when the signals in the cyclopropane region were separated into two sets [τ 9.49 (q, J = 5.75 Hz, 1H)), 9.54 (td, J = 8.75, 5.75 Hz, 1H)], in agreement with a cis-disubstituted cyclopropane. Compound (IIa) gave only cyclo-octa-1,4-diene on reduction with Na-l.NH_3, Li-Bu^tOH-THF or $LiAlH_4$-Et_2O; however, reduction with $NaBH_4$ in 70% aqueous-dioxan[1] did give cis-bicyclo[5.1.0]octane as a minor component, together with the diene (ca. 1:2).

Reaction of (IIa) with silver perchlorate in methanol gave the diether (IIb) (56%); (IIb) was also obtained (57%) when cyclo-octa-1,4-diene was added to iodine (1 mol.equiv.) and silver perchlorate (2 mol.equiv.) in methanol. In an analogous manner, reaction of (IIa) with silver acetate or silver benzoate in benzene gave the diacetate (IIc) and dibenzoate (IId) respectively*; treatment of cyclo-octa-1,4-diene with I_2-AgOAc (1:2) and I_2-AgOCOPh (1:2) in benzene[5] also gave (IIc) and (IId), though minor monocyclic products were also observed in each case.

In view of these homo-1,4-additions to cyclo-octa-1,4-diene, the reactions of other 1,4-dienes were investigated. N.M.R. studies of the reactions of cyclohexa-1,4-diene and cyclonona-1,4-diene with Br_2-CCl_4 were consistent with 1,2-addition and showed no cyclopropane signals.‡ However, cyclohepta-1,4-diene apparently gave both 1,2-adduct and (IVa) [τ 5 - 5.5 (complex 2H), 7.3 - 8.4 (complex, 6H), 9 - 9.6 (complex 2H)]. Reaction of cyclohepta-1,4-diene with silver perchlorate-I_2 in methanol also gave the homo-1,4-adduct, (IVb) (56%), while treatment with silver acetate - I_2 in benzene led to (IVc) as the major product.

1. L. Birladeanu, D.L. Harris and S. Winstein, J.Amer.Chem.Soc., 1970, 92, 6387.
2. T. Hanafusa, S. Imai, K. Ohkata, H. Suzuki and Y. Suzuki, J.C.S.Chem.Comm., 1974, 73.
3. E.E. Van Tamelen, J.Amer.Chem.Soc., 1955, 77, 1704; G.E.McCasland and E.C. Horswill, J.Amer.Chem.Soc., 1954, 76, 1654.
4. W.O. Jones, J.Chem.Soc., 1954, 312.
5. C.V. Wilson, Organic Reactions, 1957, 9, 332.

+In addition to (IIa), a minor component characterised as (I) was also observed.

*Minor products, probably the isomers (IIIc) and (IIId) were also obtained.

‡A similar result was observed in the reaction of cyclohexa-1,4-diene with I_2-AgOBz, confirming Van Tamelen's chemical study.