

**Action of Magnesium on Dibromocyclo-octanes and -nonanes.  
A Novel Transannular Elimination Reaction**

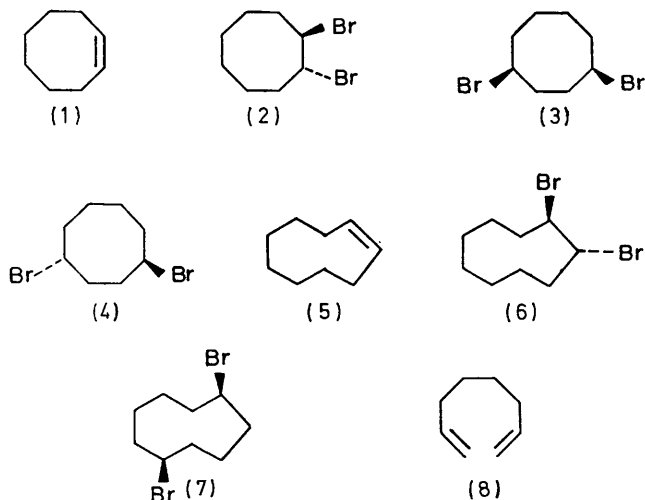
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*Summary* *cis*-Cyclo-octene and *cis*-cyclononene, respectively, are obtained as the main products when *cis* (or *trans*)-1,4-dibromocyclo-octane and *cis*-1,5-dibromocyclononane are treated with magnesium in ether.

WE have found that the addition of bromine to *cis*-cyclo-octene (**1**) in dichloromethane solution at  $-10^{\circ}$  gave *trans*-1,2-dibromocyclo-octane (**2**; 73%) and two transannular adducts, *cis*- and *trans*-1,4-dibromocyclo-octanes (**3** and **4**;

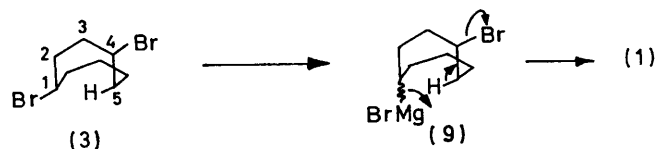
14% and 8%, respectively†). Addition of bromine to *cis*-cyclononene (5) under the same conditions gave *trans*-1,2-dibromocyclononane‡ (6, 48%) and *cis*-1,5-dibromocyclononane (7, 34%). Detailed evidence for the structures of these products will be presented elsewhere.<sup>1</sup> We now report that when the transannular adducts (3, 4, and 7) were treated with magnesium in boiling ether solution, the major products obtained were the original *cis*-cycloalkenes (1 and 5).



*cis*-1,4-Dibromocyclo-octane (3) was heated, under reflux, with an excess of magnesium turnings in ether solution for 2 h. After aqueous work-up, g.l.c. examination of the products revealed a major component, two minor components, two trace components, and no starting material (3). The major component, which was obtained in *ca.* 40% yield, was identified (g.l.c., n.m.r., i.r., m.s.) as *cis*-cyclo-octene (1) and the two minor components, each of which was obtained in *ca.* 10% yield, were identified as octa-1,7-diene (8) and cyclo-octane. It was not possible to isolate the trace components in sufficient quantities and in a pure enough state to enable them to be identified. The same products were obtained, and in approximately the same yields, when *trans*-1,4-dibromocyclo-octane (4) was treated with magnesium under the same reaction conditions.

The conversion of *cis*- and *trans*-1,4-dibromocyclo-octanes (3 and 4) into octa-1,7-diene (8), which is analogous to the reported conversion<sup>2</sup> of *cis*- and *trans*-1,4-dibromocyclohexanes into hexa-1,5-diene, is evidence for the orientation of the bromo-substituents in (3) and (4). The other minor component, cyclo-octane, possibly results from the protonation of the bis-Grignard reagent derived from (3) or (4). However, the formation of *cis*-cyclo-octene (1) as the major product of the reaction between magnesium and *cis*- or *trans*-1,4-dibromocyclo-octane (3 or 4) is more

unexpected and is an example of what we believe to be a novel transannular elimination reaction. Examination of molecular models reveals that (3) can readily take up the conformation illustrated in the Scheme. The reaction can then proceed, possibly *via* an intermediate Grignard reagent (such as 9), by a mechanism involving a 1,5-proton shift as indicated. As both *cis*- and *trans*-1,4-dibromocyclo-octanes (3 and 4) are converted into *cis*-cyclo-octene (1) at comparable rates, it is unlikely that the initial attack of magnesium on 3 or 4 is concerted with the subsequent internal elimination process.



SCHEME

*cis*-1,5-Dibromocyclononane (7) reacted with magnesium under the same conditions to give a mixture of C<sub>9</sub> hydrocarbons. The main product which was again the corresponding *cis*-cycloalkene, *i.e.* *cis*-cyclononene (5) was obtained in 35% yield. Cyclononane and *cis*-bicyclo[4,3,0]-nonane<sup>3</sup> (10) were each obtained in 10% yield, and smaller quantities of two other products were detected by g.l.c. The formation of (5) is a further example of the transannular elimination reaction and the formation of (10) is evidence for the orientation of the bromo-substituents in (7).



Finally, the action of magnesium on *trans*-1,2-dibromocyclo-octane and -nonane (2 and 6, respectively) was investigated. When an ethereal solution of *trans*-1,2-dibromocyclo-octane (2) was heated, under reflux, with an excess of magnesium turnings for 3 h, *cis*-cyclo-octene (1) was obtained in over 80% yield. A small quantity of cyclo-octane was also obtained, but no *trans*-cyclo-octene could be detected in the products. However, under similar conditions, *trans*-1,2-dibromocyclononane (6) gave an 85% yield of a mixture consisting of two parts of *cis*-cyclononene (5) and one part of *trans*-cyclononene (11). Treatment of *trans*-1,2-dibromocyclo-decane and -dodecane also leads<sup>4</sup> to mixtures of the corresponding *cis*- and *trans*-cycloalkenes.

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† At  $-95^{\circ}$ , the yields of (2), (3), and (4) were 51, 26, and 12%, respectively. Other workers (P. W. Henniger, L. J. Dukker, and E. Havinga, *Rec. Trav. chim.*, 1966, **85**, 1177) previously reported that while treatment of (1) with bromine in dichloromethane solution at  $0^{\circ}$  gave (2) almost exclusively, transannular adducts (*ca.* 20%) were obtained at  $-100^{\circ}$ .

‡ This compound is assumed to be the *trans*-isomer by analogy with the 1,2-bromine adducts of *cis*-cyclo-octene (A. C. Cope and H. E. Johnson, *J. Amer. Chem. Soc.*, 1957, **79**, 3889) and *cis*-cyclodecene (M. Havel, M. Svoboda, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1969, **34**, 340).

<sup>1</sup> M. S. Baird, C. B. Reese, and M. R. D. Stebles, manuscript in preparation.

<sup>2</sup> C. A. Grob and W. Baumann, *Helv. Chim. Acta*, 1955, **38**, 594.

<sup>3</sup> K. E. Blanchard and P. von R. Schleyer, *J. Org. Chem.*, 1963, **28**, 247.

<sup>4</sup> J. Sicher, M. Havel, and M. Svoboda, *Tetrahedron Letters*, 1968, 4269.