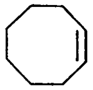
Action of Magnesium on Dibromocyclo-octanes and -nonanes. A Novel Transannular Elimination Reaction

By M. S. BAIRD, C. B. REESE,* and M. R. D. STEBLES
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

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*-cyclooctene (**1**) in dichloromethane solution at −10° 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.[1] 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**).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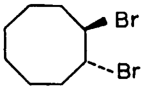

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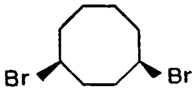

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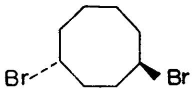

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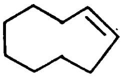
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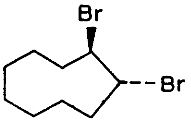

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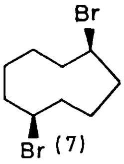

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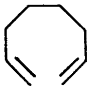
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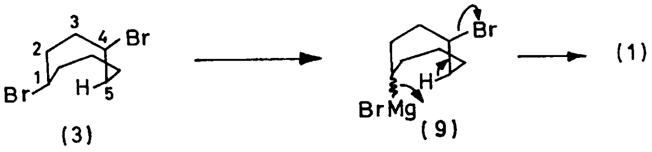
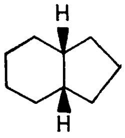
cis-1,4-Dibromocyclo-octane (**3**) was heated, under reflux, with an excess of magnesium turnings in ether solution for 2 h. After aqueous work-up, g.l.c. examination of the products revealed a major component, two minor components, two trace components, and no starting material (**3**). The major component, 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[2] 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_9 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[3] (**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**).



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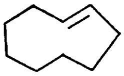
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Finally, the action of magnesium on *trans*-1,2-dibromocyclo-octane and -nonane (**2** and **6**, respectively) was investigated. When an ethereal solution of *trans*-1,2-dibromocyclo-octane (**2**) was heated, under reflux, with an excess of magnesium 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[4] to mixtures of the corresponding *cis*- and *trans*-cycloalkenes.

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† At −95°, 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° gave (**2**) almost exclusively, transannular adducts (*ca.* 20%) were obtained at −100°.

‡ 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).

[1] M. S. Baird, C. B. Reese, and M. R. D. Stebles, manuscript in preparation.

[2] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, 1955, **38**, 594.

[3] K. B. Blanchard and P. von R. Schleyer, *J. Org. Chem.*, 1963, **28**, 247.

[4] J. Sicher, M. Havel, and M. Svoboda, *Tetrahedron Letters*, 1968, 4269.