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ADDITION OF BROMINE TO MEDIUM-RING ALLENES AND ACETYLENES

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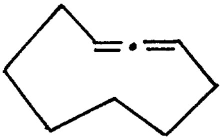
Although transannular reactions are relatively common in medium-ring chemistry,[1] reports relating to the transannular addition of bromine to medium-ring unsaturated hydrocarbons have not been numerous. We have recently shown[2] that, like *cis*-cyclodecene,[3] *cis*-cyclo-octene and *cis*-cyclononene react with bromine to give both 1,2- and transannular adducts. In the light of these results, our finding[4] that the reaction between bromine and cyclonona-1,2-diene (1) gave a mixture of *cis*-1,4- and *cis*-2,3-dibromocyclononenes (2 and 3, respectively), with the transannular product (2) predominating, did not call for much comment. However, we now report that no transannular adducts can be detected in the products of the reactions between bromine and cyclo-octa- and cyclodeca-1,2-dienes (4 and 5, respectively).

Cyclo-octa-1,2-diene[5] (4) was generated *in situ*[6] by treating 8,8-dibromobicyclo[5,1,0]-octane (6) with methyl lithium in ether solution at -78°. The excess of methyl lithium and any other carbanionoid species present were discharged by adding pivalic acid until the reaction solution became slightly acidic. Then a solution of bromine in carbon tetrachloride was added until a slight orange-red colour persisted; 0.8 molecular equivalents (based on 6) of bromine were consumed. Examination (n.m.r., t.l.c.) of the products after work-up revealed the presence of only one bromine adduct of (4), namely *cis*-2,3-dibromocyclo-octene (7); the latter compound (57%, based on 6) was isolated in a pure state by silica gel chromatography.



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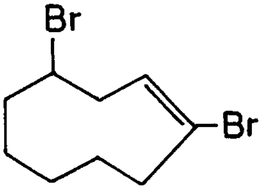

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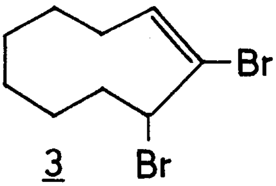

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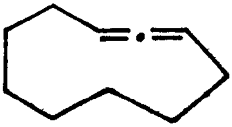

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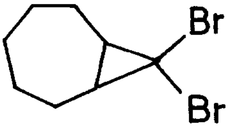

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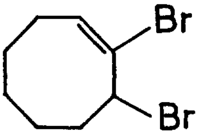

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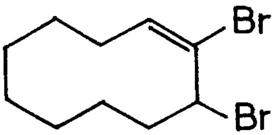
Reaction between cyclodeca-1,2-diene[7] (5) and a stoicheiometric amount of bromine in carbon tetrachloride solution at -10^0 gave a 95% yield of a mixture of *cis*- and *trans*-2,3-dibromocyclodecenes (8 and 9, respectively) with the *cis*-isomer as by far the major product (>95%). No transannular adduct could be detected, even in a trace amount.

Thus the general behaviour of medium-ring allenes towards the addition of bromine does not correspond to that of *cis*-cycloalkenes of the same ring-size. Indeed, cyclonona-1,2-diene (1) behaves anomalously in that it reacts with bromine to give a transannular adduct (2). The rationalization of these results is not obvious, but it must be concluded that only the cationoid intermediate formed by the attack of bromine on cyclonona-1,2-diene (1) can take up a conformation which favours the occurrence of a transannular hydride shift.



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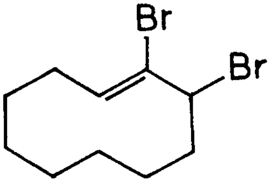

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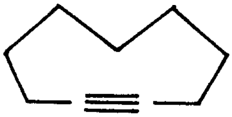

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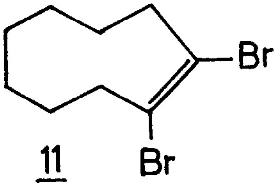

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Finally, the reaction between cyclononyne (10) and bromine in carbon tetrachloride solution at -10^0 was studied. Examination of the crude products (g.l.c.) after the addition of nearly one molecular equivalent of bromine revealed the presence of only one dibromo-compound. The latter compound was isolated in 55% yield by silica gel chromatography and was characterized as cis-1,2-dibromocyclononene (11) on the basis of its spectroscopic properties. The reaction between bromine and cyclo-octyne has similarly been reported[8] to give 1,2-dibromocyclo-octene[9] in 76% yield, but the nature of the by-products, if any, has not been described.

The results of the present investigation clearly demonstrate that transannular products are by no means necessarily formed in addition reactions between bromine and medium-ring unsaturated hydrocarbons.

Acknowledgement

One of us (A.S.) thanks the S.R.C. for the award of a research studentship.

References and Footnotes

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3. M. Havel, M. Svoboda, and J. Sicher, Coll. Czech. Chem. Commun. 34, 340 (1969).
4. M.S. Baird, C.B. Reese, and A. Shaw, Tetrahedron 27, 231 (1971).
5. E.T. Marquis and P.D. Gardner, Tetrahedron Letters, 2793 (1966).

6. Cyclo-octa-1,2-diene (1) dimerizes too rapidly at room temperature to permit its ready isolation.[5] The following reaction was carried out: 8,8-dibromobicyclo [5,1,0]octane (6) was treated with an excess of methyl lithium in ether solution at -78°C, the products were then neutralized with pivalic acid and allowed to warm up to room temperature. The dimer of (1) was isolated from the products in good yield.
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9. Although the authors[8] formulated this product as the *cis*-isomer, they described it simply as 1,2-dibromocyclo-octene.