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DIASTEREOMERIC MONOCYCLIC DIALLENES. THE STEREOCHEMISTRY OF FORMATION OF RACEMIC AND MESO-3,4,9,10-CYCLODECATETRAENE-1,7-DIONE

Roy Baker, P.J. Garratt, K.C. Nicolaou and F. Sondheimer

Chemistry Department, University College London,
20 Gordon Street, London WC1H OAJ

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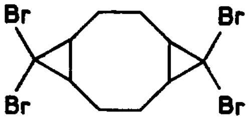
Dehmlow and Ezimora [1] have reported that treatment of either anti or syn-5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]decane (1) with CH$_3$Li gave 1,2,5,6-cyclodecatetraene, probably as the meso-diastereomer 2. They suggested that the formation of the meso, rather than a mixture of the racemic and meso forms of 1,2,5,6-cyclodecatetraene, might be controlled by the stereochemistry of the presumed intermediate 10,10-dibromo-cis-bicyclo[7.1.0]deca-4,5-diene (3). However, 3 can only exist in two enantiomeric forms, and the exo (4) and endo (5) compounds illustrated in their paper are, in fact, identical. Any control of stereochemistry, other than by asymmetric induction, cannot take place by a stepwise mechanism. The formation of the second allene function involves monorotation of either the 1,2 or 1,3 cyclopropane bonds [2] (or clockwise and anti-clockwise conrotation of these bonds), [3] and both modes of rotation have equivalent steric interactions. The influence of a remote optical centre in a flexible ring should be negligible, and almost equal amounts of racemic



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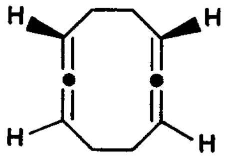

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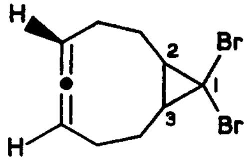

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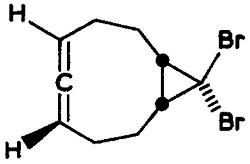

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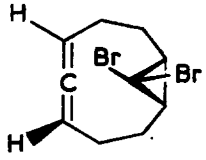

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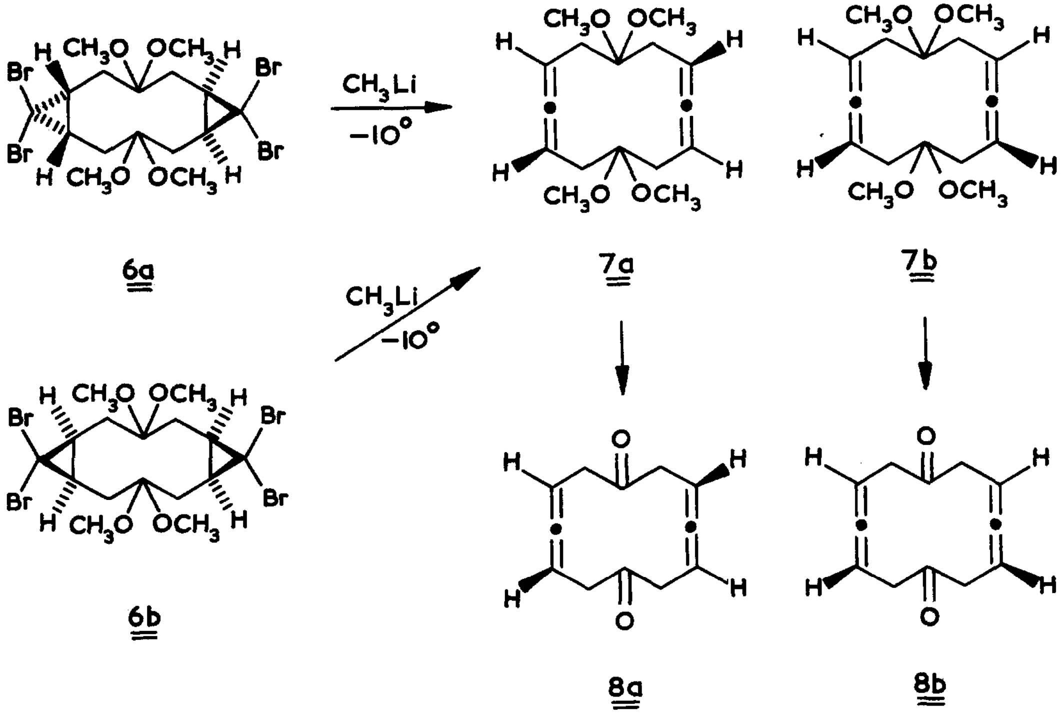
and *meso* diastereomers would be expected. Control of stereochemistry could only occur if the two cyclopropyl ring openings took place simultaneously. Such an event is unlikely, but we have investigated a system in which both *meso* and racemic diastereomeric diallenes are known to be formed in order to determine whether stereochemical control does occur.

6,6,12,12-Tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.$0^{5,7}$]dodecane (**6**), which had originally been obtained as an amorphous powder,[4] was subjected to slow crystallisation from CH_2Cl_2, when the crystalline *anti*-tetrabromide **6a** (mp 155-156°) was isolated in high yield.[5] The isomer **6a** showed only a single methoxyl resonance (τ 6.74) in the nmr spectrum (CD_2Cl_2),[6] and the stereochemical assignment was secured by a full X-ray crystallographic analysis.[7] The combined mother liquors from a large number of preparations of **6**, from which **6a** had been separated, were chromatographed on silica gel. Elution with pentane-Et_2O then gave $\sim$ 1% of the crystalline *syn*-tetrabromide **6b** (mp 148-149°).[5,8] Isomer **6b** showed resonance signals in the nmr spectrum ($CDCl_3$) at τ 6.70 (s, 6H, OCH_3), 6.74 (s, 6H, OCH_3), 7.75 (d, 4H, CH_2), 8.12 (m, 4H, CH_2), 8.90 (m, 4H, cyclopropane), consistent with the *syn* stereochemistry. A full X-ray crystallographic analysis is being carried out.

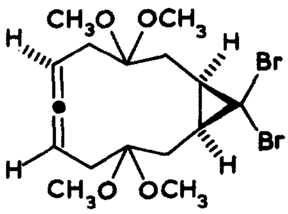


6a **7a** **7b**

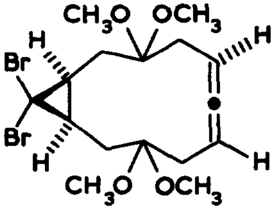
6b **8a** **8b**

The *anti*-tetrabromide **6a** was treated with CH_3Li at -10°, when a mixture of the racemic **7a** and *meso* **7b** diketals was obtained. Similar treatment of the *syn*-tetrabromide **6b** also gave a mixture of **7a** and **7b**, the composition of which (nmr) appeared to be identical with that obtained from isomer **6a**. The composition of the diallene mixture is thus the *same*, whether it is derived from the *syn* or the *anti*-tetrabromide.

The opening of the dibromocyclopropane ring by CH_3Li is believed to occur via the cyclopropyl carbene, followed by cleavage of the 2,3-bond by a monorotatory or conrotatory process.[2,3] In the case of 2,3-disubstituted dibromocyclopropanes, such as **6**, both conrotatory modes are equally favoured, and a racemic mixture of the two enantiomers **9a**, **9b** would be formed. Ring opening of the second dibromocyclopropane ring can now proceed to give either **7a** or **7b**. This mechanism is completely in accord with the lack of stereochemical control observed in these reactions. The presumption [1] that the observed formation of naphthalene by treatment of 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]deca-1,7-diene with CH_3Li involves *meso*-1,2,4,6,7,9-cyclodecahexaene, and thus supports the prediction of Woodward and Hoffman,[9] must be considered doubtful.



9a



9b

The identity of the two ketals **7a**, **7b** was made by treating isomer **6a** with CH_3Li at -10° in the presence of (-)sparteine, according to the method of Nozaki *et al*.[10] Chromatography of the product on silica gel gave the diastereomeric diketals **7a**, **7b**. The compound, mp 113-116°, was found to have $[\alpha]_D^{20}$ + 24.45 ± 0.05° (c 2.3 g/100 ml, *n*-hexane),[10] and therefore corresponds to the racemic isomer **7a**. On the other hand the compound, mp 86-87.5°, showed no optical activity and corresponds to the *meso* isomer **7b**. Hydrolysis of **7a** gave the optically active dione **8a** (mp 96-97°), $[\alpha]_D^{20}$ + 55.55 ± 0.05° (c, 0.88 g/100 ml, EtOH),[11] while hydrolysis of **7b** gave the optically inactive *meso* dione **8b** (mp 67-68°).

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REFERENCES

1 E.V. Dehmlow and G.C. Ezimora, *Tetrahedron Letters*, 4047 (1970).

2 W.R. Moore and J.B. Hill, *Tetrahedron Letters*, 4343, 4553 (1970).

3 W.M. Jones and J.W. Wilson, *Tetrahedron Letters*, 1587 (1965); J. Walbrick, J.W. Wilson, and W.M. Jones, *J. Am. Chem. Soc.*, **90**, 2895 (1968).

4 P.J. Garratt, K.C. Nicolaou and F. Sondheimer, *Chem. Commun.*, 1219 (1970).

5 Satisfactory microanalytical and mass spectral data have been obtained for this compound.

6 Compound **6a** was extremely insoluble in all solvent examined, and only the methoxyl signal was well resolved in the nmr spectrum.

7 R.W. Baker and P.J. Pauling, unpublished observations; *J. Chem. Soc. Perkin II*, in press.

8 The ratio of **6a**:**6b** formed in the reaction of 4,4,9,9-tetramethoxy-1,6-cyclodecadiene with $CHBr_3$ and KOtBu is estimated to be ~80:1.

9 R.B. Woodward and R. Hoffman, *The Conservation of Orbital Symmetry*, Verlag Chemie, 1970, p.63.

10. H. Nozaki, T. Aratami, T. Toraya and R. Noyari, *Tetrahedron*, **27**, 905 (1971).

11. The optical purity of this material is not known.