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STEREOSELECTIVE FORMATION OF CYCLIC BISALLENES FROM 5,5,10,10-TETRABROMOTRICYCLO[7.1.0.0.^{4,6}]DECANES

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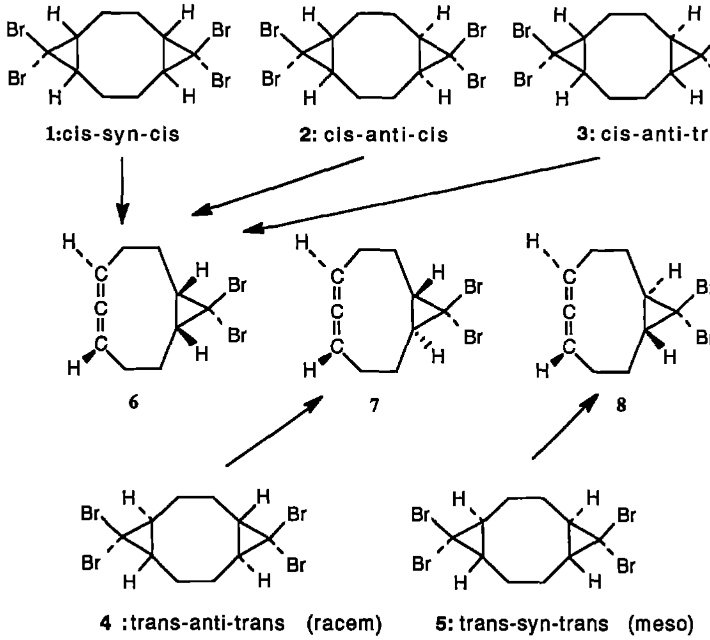
Abstract: The stereochemical outcome of the title conversions is predicted and tested. Within detection limits, the transformations of the stereoisomeric compounds 1, 2, 3, and 5 to the cyclic bisallenes 9 and 10 occur stereospecifically. 1 - 3 all yield meso compound 9; 5 gives rac-10. Isomer 4 is not yet available for analogous experiments.

Conrotatory ring openings of cyclopropylidenes (or their direct precursors) to yield allenes are well documented. Appropiate stereochemical information residing in the starting materials or the reagents can direct such processes[1-3], making them enantio- or diastereoselective. Skattebol prepared two monocyclic bis-allenes, 1,2,6,7-cyclodecatetraene and 1,2,9,10-cyclohexadecatetraene, from dibromocarbene adducts of the related cycloalkadienes with methyllithium[4]. In both cases only one diastereomer was isolated, and the cyclodecatetraene was shown to be meso-compound 9 by X-ray structure analysis[5]. Subsequent work from the present group showed that meso-9 is formed not only from cis-syn-cis-5,5,10,10-tetrabromo-tricyclo[7.1.0.0^{4,6}]decane (1) but also from cis-anti-cis-isomer (2). Similar ring expansions of dibromocarbene adducts to cis,cis-4,4,9,9-tetramethoxycyclodeca-1,6-diene and 4,4,10,10-tetramethoxy-cyclododeca-1,7-diene, however, led to mixtures of rac- and meso-forms of monocyclic bisallenes[7]. Thus, it seems reasonable to assume that the ring opening of tetrabromotricyclic compounds with a relatively small (eight-membered) central ring will be directed by strain and will therefore be highly stereoselective. We decided to test this hypothesis with the other stereoisomers of 1/2 and find out which would lead to rac-cyclodeca-1,2,6,7-tetraene (10). In addition, this study might be a model for developing reaction paths towards rac-cyclodeca-1,2,4,6,7,9-hexaene, a compound of some theoretical interest[8].

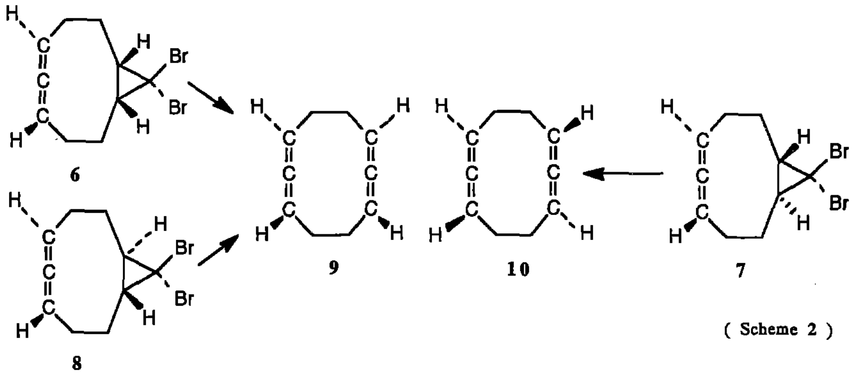
Stepwise allene formation by opening of the cyclopropane rings one at a time can be expected[7], and 10,10-dibromo-bicyclo[7.1.0]deca-4,5-dienes will be intermediates. There are three possible chiral isomers, 6 - 8 (Scheme 1). Stereochemistry alone determines that 1 and 2 can only give 6, and 4 can only lead to 7. Consideration of the least motion pathway makes very likely that 5 will be transformed into 8. 3 is the most strained of the isomers 1 - 5.

Strain relief and least motion movements seem to favour the opening of the trans-fused cyclopropane which will bring about the formation of 6.



(Scheme 1)

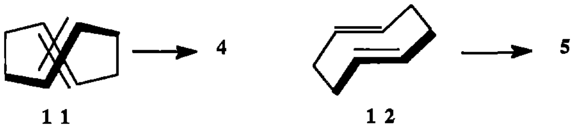
Going on with the second step (Scheme 2), a least motion path from 6 gives meso-bisallene 9 clearly. Similarly 7 must lead to rac-bisallene 10. A formation of 9 from 7 would necessitate a very complex multi-atom movement. The most favourable path from 8 is a little less obvious, but the formation of 9 as only or major product is very likely. Altogether then, these transformations seem most probable: 1, 2, 3, and 5 give meso-9, and only 4 is transformed into rac-10.



(Scheme 2)

The reactions of 1 and 2 with methyllithium are known[4,6], but as the yields are not very good the formation of a small amount of unknown 10 might have been overlooked. Compound 3 is available from cis,trans-1,5-cyclooctadiene by CBr_2 addition. Only KOtBu/$HCBr_3$ can be used for this purpose as the phase transfer catalytic process results in extensive trans/cis isomerization of the starting material[9]. Subsequent conversion of 3 with methyllithium gives meso-9 as predicted.

In principle, trans-anti-trans-tetrabromo-compound 4 and its trans-syn-trans isomer 5 could be prepared from the two conformers of trans,trans-1,5-cyclooctadiene, 11 and 12, respectively (Scheme 3). Constraint in the molecules does not permit interconversion of 11 and 12, and the twist conformer 11 is favoured over the chair conformer 12 energetically[10]. In a recent publication a method to make gram-amounts of relatively unstable 11 was described[11] whereas 12 has not been obtained as yet.



(Scheme 3)

Reaction of 11 with bromoform /KOtBu below 10°C yielded 4[12]. At higher temperatures partial formation of 3 was observable by ^{1}H-NMR spectroscopy. There are characteristic differences in the positions and multiplicities of the signals of 4 and 3: The lowest field multiplet of 4 appears around 2.47 ppm, whereas the respective, very complex multiplet of 3 stretches from 2.2 to 2.5. Subsequent conversion of 4 with methyllithium leads to a mixture of products in low yield. The lowest boiling fraction turned out to be extremely sensitive towards polymerization. It contained two components with mass spectroscopic mol peaks at m/e 132 and 146 (chemical ionization) for $C_{10}H_{12}$ and $C_{11}H_{14}$. Low yield and stability did not permit purification so that the rac-bisallene 10 had to be characterized in the mixture with $C_{11}H_{14}$ (present as a minor component being a methylated derivative of 10 presumably). - The CA-spectrum of the m/e 132 component showed daughter ions at M-1, M-2, M-3, and M-4 (naphthalene^{+}), 117 ($C_9H_9^{+}$), 104 ($C_8H_8^{+}$), and 91. The IR-spectrum had an allene absorption at 1945 cm^{-1}. In its 300 MHz-^{1}H-NMR spectrum, there was an olefinic multiplet at 5.1-5.3 ppm and a CH_2-multiplet between 2.0 and 2.3 ppm. Most importantly, there was no multiplet at 4.9-5.0 ppm which is characteristic of the meso-compound 9. The higher boiling fractions of the conversion of 4 apparently contained dimers of 10 (MS: m/e 264).

Once the NMR olefin signal of 10 was established, the conversions of 1 and 3 to 9 were reinvestigated: In both cases no indication of the formation of 10 traces could be found in the spectra of raw samples of 9. Thus, only 4 yielded 10, whereas the other isomers gave pure 9 within the detection limits of ^{1}H-NMR spectroscopy.

As stated above, the last missing tetrabromotricyclododecane isomer, trans-syn-trans (5) cannot be made from 12 as this is unobtainable hitherto. An approach along lines developed by Deyrup and Betkouski[13] was also in vain. These authors added one unit of CCl_2 selectively to the trans double bond of cis,trans-1,5-cyclooctadiene and then isomerized the other double bond photochemically in the presence of cuprous chloride. The process proved to be very inefficient as the desired isomerized alkene was formed in low yield and had to be isolated by preparative gas chromatography. For the formation of our allenes only the bromopolycyclic compounds are useful, and attempted photoisomerization of these might easily lead in other directions. In any case, we could not even find conditions for an effective selective dibromocarbene monoaddition: Sensitive cis,trans-1,5-cyclooctadiene was too easily biscyclopropanated or isomerized.

In conclusion then, we have shown that tricyclic dibromocarbene bisadducts do open to bisallenes stereospecifically if the molecule is constrained by a relatively small central ring.

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[12] m.p. 165°C. $C_{10}H_{12}Br_4$ (451.8), calc. C 26.58 H 2.68, found C 26.47 H 2.71. ^{1}H-NMR (300 MHz): δ 2.42 - 2.49 (m, 4H); 1.28 - 1.35 (m, 4H); 0.98 - 1.07 (m, 4H).

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