Thermal Rearrangement of 10,10-Dibromobicyclo[7,1,0]decane

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Summary *trans*-2,3-Dibromocyclodecene (**8**) is obtained by the action of heat on 10,10-dibromobicyclo[7,1,0]-decane (**7**).

ALTHOUGH the thermal rearrangement of halogenocarbene adducts of both cyclopentene[1] and cyclohexene[2] appears to involve the concerted transformation of a cyclopropyl to an allylic cation or related species, this is not the case for 8,8-dibromobicyclo[5,1,0]octane (**1**). (**1**) is stable below 240°, but is converted into *cis*-1-bromocyclo-octene (**2**) under more forcing conditions.[1] 9,9-Dibromobicyclo[6,1,0]-nonane (**3**) is slightly more susceptible to thermal rearrangement; when it is heated at 240° for 1 h, *cis*-2,3-dibromocyclononene (**4**) is obtained as the major product.[3] A study of the pyrolysis of *endo*- and *exo*-9-bromobicyclo[6,1,0]-nonanes suggests[3] that the rearrangement of (**3**) proceeds with fission of the *exo*-carbon–bromine bond and may therefore be concerted. However, examination of the products provides no evidence for an intermediate *trans*,-*trans*-allylic cation or related species.

In contrast to their pyrolytic reactions, when (**1**) and (**3**) are submitted to silver perchlorate assisted hydrolysis at 20°, they are rapidly converted[4] into the corresponding 2-bromo-*trans*-cycloalken-3-ols (**5** and **6**, respectively). It seems likely that the latter ring-expansion reactions proceed with cleavage of *exo*-carbon–bromine bonds and an outward disrotatory opening[5] of the cyclopropane rings as expected for concerted processes. We now report that *trans*-2,3-dibromocyclodecene (**8**) is the main thermal rearrangement product of 10,10-dibromobicyclo[7,1,0]-decane[6] (**7**), and thus that *cis*-cyclononene is the smallest cycloalkene, the dibromocarbene adduct of which appears to undergo a concerted *thermal* rearrangement involving cleavage of the *exo*-carbon–bromine bond and an outward disrotatory opening[5] of the cyclopropane ring.

When 10,10-dibromobicyclo[7,1,0]decane (**7**) was distilled at a sufficiently low pressure, the pure compound was obtained. However, when it was distilled at a pressure of 2 mm (bath temperature *ca.* 180°), the distillate (b.p. 120—125°) was contaminated with *ca.* 30% of a mixture of *trans*-2,3-dibromocyclodecene† (**8**, *ca.* 90%) and *cis*-2,3-dibromocyclodecene (**9**, *ca.* 10%). When (**7**) was heated at 156° for 5 min, it underwent 80% conversion into a mixture of (**8**, *ca.* 75%) and (**9**, *ca.* 25%); when it was heated at 185° for 5 min, it was completely converted into a mixture of (**8**, *ca.* 55%) and (**9**, *ca.* 45%).

cis-2,3-Dibromocyclodecene (**9**) appears to be the thermodynamically more stable isomer: when pure *trans*-isomer (**8**) was treated with lithium bromide in acetone solution for 48 h at 20° and then for 6 h under reflux, the recoverable 2,3-dibromocyclodecenes consisted of 90% of *cis*- and 10% of *trans*-isomer. It is therefore reasonable to conclude that *trans*-2,3-dibromocyclodecene (**8**) is the main initial product of thermal rearrangement of (**7**), and that *cis*-isomer (**9**) is obtained from (**8**) after further heating.

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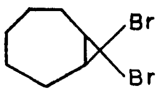
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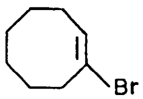
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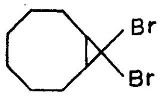
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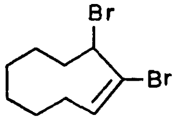
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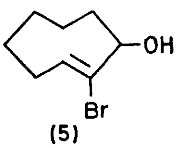
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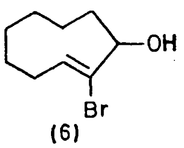
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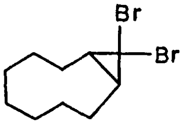
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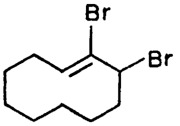
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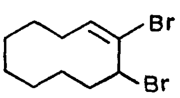
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† *trans*- and *cis*-2,3-Dibromocyclodecenes can be readily distinguished from the low-field regions of their n.m.r. spectra (CCl_4 solution). *trans*-Isomer (**8**): τ 3·65 (t, *J* 7·5 Hz, 1H, 1-H), 5·40 (t, *J* 7·5 Hz, 1H, 3-H); *cis*-isomer (**9**): τ 4·12 (dd, *J* 6 and 12 Hz, 1H, 1-H), 4·66 (dd, *J* 5 and 12 Hz, 1H, 3-H).

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