

eluent to give 190 mg (38%) of a white solid; mp 198–202 °C dec;  $^1\text{H}$  NMR  $\tau$  4.49 (s, 4 H), 5.99 (s, 4 H), 7.15 ( $A_2B_2$ , 8 H); mass spectrum mol wt 212. Anal. Calcd for  $C_{14}H_{16}N_2$ : C, 72.83; H, 4.83; N, 22.35. Found: C, 72.83; H, 4.90; N, 22.42.

**Conversion of Compound 5 to 12.** Compound 5 (50 mg, 0.15 mmol) was dissolved in 5 ml of glacial HOAc and heated at 120 °C for 1 h. The mixture was cooled and added to cold  $\text{NH}_4\text{OH}$ . The aqueous solution was extracted with chloroform ( $3 \times 50$  ml) and the combined extracts were dried over anhydrous  $\text{K}_2\text{CO}_3$ , filtered, and evaporated to dryness. The residue was examined using high-pressure liquid chromatography (HPLC) (column 0.5 m Dorasil A, 20%  $\text{CHCl}_3$ , 80% isooctane, Waters ALC 202 instrument) which revealed the presence of compound 12. Isolation by preparative HPLC afforded 40 mg (80%) of compound 12.

**X-Ray Data Collection.** The detailed data are available in the microfilm edition of this journal.<sup>8</sup>

**Registry No.**—3, 25887-95-0; 4, 59547-39-6; 5, 59547-40-9; 10, 59547-41-0; 12, 59547-42-1; *p*-bromoaniline, 106-40-1; ethylenediamine, 107-15-3.

**Supplementary Material Available.** A listing of all of the crystallographic data (8 pages). Ordering information is given on any current masthead page.

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- (8) See paragraph at end of paper regarding supplementary material.

## Bishomoaromatic Interaction in the Disrotatory Ring Opening of Cyclopropyl Carbenoids

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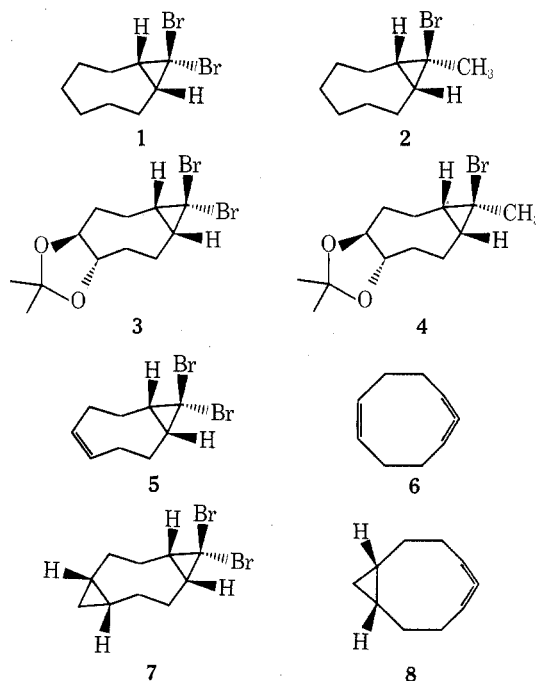
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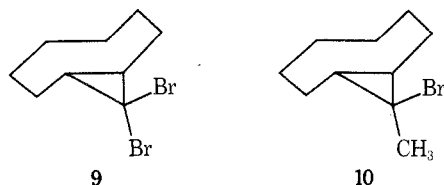
Treatment of 9,9-dibromo-*cis*-bicyclo[6.1.0]nonanes **1**, **3**, and **15** with butyllithium at  $-95$  °C leads to corresponding *endo*-lithio-*exo*-bromo derivatives which upon addition of methyl iodide can be alkylated, leading to the *endo*-methyl-*exo*-bromo derivatives **2**, **4**, and **16** respectively. Even the strained 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**9**) is converted in this way to 9-bromo-9-methyl-*trans*-bicyclo[6.1.0]nonane (**10**). However, in the presence of a double bond (**5**) or a cyclopropyl ring (**7**) at  $C_{4,5}$  the carbenoids generated with butyllithium at  $-95$  °C undergo a very rapid ring opening to the corresponding allenes. This result may be explained by assuming a bishomoaromatic interaction which favors a facile disrotatory ring opening of the carbenoids.

Geminal dihalo compounds have been shown to produce carbenoid species on reaction with organolithiums.<sup>1</sup> In the specific instance of 1,1-dibromocyclopropanes, the transient carbenes generally prove to undergo either ring opening to allenes<sup>2a-h</sup> or specific insertion in C-H bonds.<sup>3a-i</sup> At very low temperatures ( $-70$  to  $-105$  °C) the geminal dibromocyclopropanes can be easily lithiated to 1-bromo-1-lithiocyclopropanes. The latter behave like anions and are able to undergo alkylation reactions.<sup>4a-c</sup>

Our present research, directed toward the synthesis of nine-membered-ring systems via ring expansions, required the synthesis of 9-*exo*-bromo-9-*endo*-methyl-*cis*-bicyclo[6.1.0]nonane derivatives. To this end a recently described method of Hiyama et al.<sup>4a</sup> was employed, which permits the stereoselective *endo* methylation of cyclopropylidenes derived from geminal dibromocyclopropanes. Upon reaction of 9,9-dibromo-*cis*-bicyclo[6.1.0]nonane (**1**) with butyllithium at  $-95$  °C and subsequent treatment with excess of methyl iodide in THF, the desired 9-*exo*-bromo-9-*endo*-methyl-*cis*-bicyclo[6.1.0]nonane (**2**) was isolated in essentially quantitative yield. In a similar way, the acetonide of 4,5-*trans*-dihydroxy-9,9-dibromo-*cis*-bicyclo[6.1.0]nonane (**3**) was converted to the corresponding *endo*-methyl derivative (**4**) in 92% yield. However, on treatment of 9,9-dibromo-*cis*-bicyclo[6.1.0]non-4-ene (**5**) with butyllithium and methyl iodide under identical conditions, 1,2,6-cyclononatriene (**6**) was formed, as evidenced readily by its NMR and ir spectral data.<sup>5a-c</sup> Similar anomalous behavior was observed when a cyclopropyl-



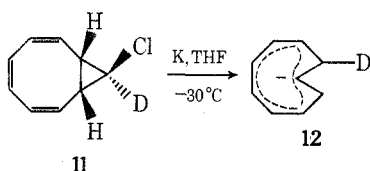
pane was annelated at  $C_{4,5}$ .<sup>6</sup> Upon treatment of 10,10-dibromo-*cis,cis*-tricyclo[7.1.0.0<sup>4,6</sup>]decane (**7**) with butyllithium-methyl iodide at  $-95$  °C only *cis*-bicyclo[7.1.0]deca-



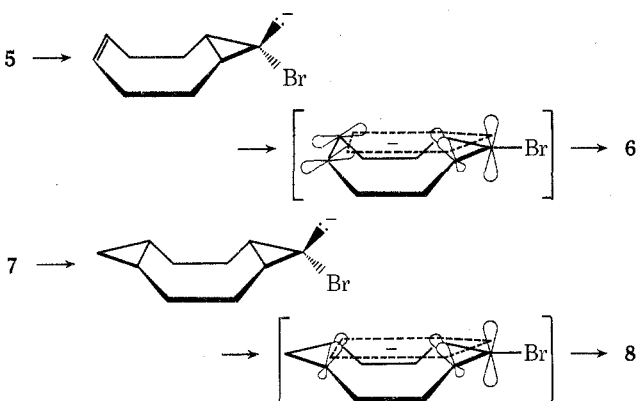
4,5-diene (8) was obtained. The strained 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (9) proved to be stable under the conditions described above and could be converted smoothly to 9-methyl-9-bromo-*trans*-bicyclo[6.1.0]nonane (10). Whereas the formation of allenes is a common reaction at elevated temperatures ( $> -30$  °C), its formation from 5 and 7 at such very low temperatures is rather surprising.

Relying on the ability of cyclopropylidenes to undergo alkylation reactions, they can be regarded as anions at such low temperatures. The preferred mode of ring opening of such species, leading to allenes, will be conrotatory based on orbital symmetry considerations.<sup>7a,b</sup> This has been confirmed by extended Hückel,<sup>8</sup> *ab initio*,<sup>9</sup> and MINDO/2<sup>10</sup> calculations.

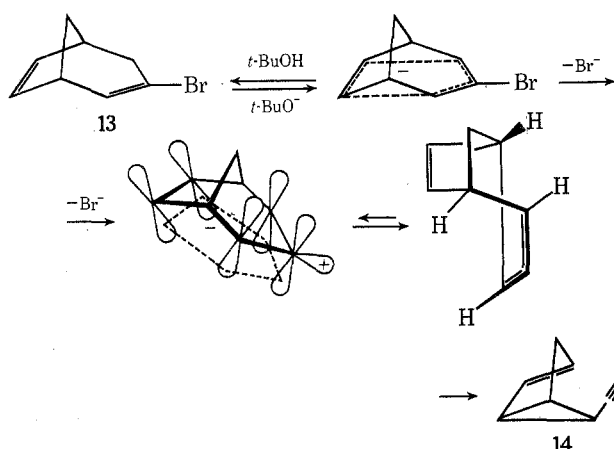
A representative example would be the stereospecific ring opening of 9-*endo*-deuterio-9-*exo*-chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (11) with potassium in THF, leading to the *trans,cis,cis,cis*-cyclononatetraenyl anion (12).<sup>11a,b</sup>



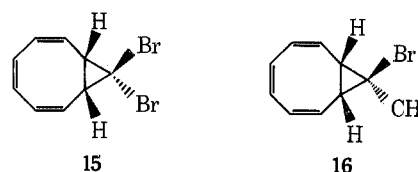
Based on steric considerations the conrotatory mode of ring opening seems to be an unfavorable process at very low temperatures for the carbenoids derived from 1, 3, 5, and 7, even for 9, in which the cyclopropane unit is annelated in a "favorable" *trans* configuration. This conrotatory mode of ring opening is restricted for 9 because the system has to pass through an initially strained *trans,trans* allylic geometry. The alternative way, *viz.*, a disrotatory movement, seems to be more attractive for systems 1, 3, 5, and 7, but in fact it is a forbidden process. Therefore it is most likely that the rapid mode of ring opening of 5 and of 7 is due to a bishomoaromatic



interaction<sup>12</sup> between the cyclopropylidene moiety and the double bond or the Walsh-type orbitals of the cyclopropane unit at C<sub>4,5</sub>, respectively. Extension of the electronic system of the cyclopropylidene by two electrons in this way leads to an aromatic transition state, favoring a disrotatory ring opening. Further evidence for this explanation can be quoted from recent literature on bicyclo[3.2.1]octa-2,6-diene systems.<sup>13a-d</sup> A particular example which is worth recording and which, by its nature, has close similarity to our cases is the base-catalyzed rearrangement of 3-bromobicyclo[3.2.1]octa-



2,6-diene (13) to *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (14).<sup>14</sup> In this reaction, the intermediacy of a homoconjugated carbene has been suggested. The model for the rapid ring opening of the cyclopropylidenes derived from 5 and 7 suggests an interaction through space over a relatively large distance. Therefore it became obvious to us that a further requirement might be some flexibility in the bicyclo[6.1.0]nonane skeleton which allows bending of the double bond (in 5) and of the cyclopropane (in 7) toward the cyclopropylidene system. An example in this series which does not meet this requirement is 9,9-dibromo-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (15), in which the double bond at C<sub>4,5</sub> is tightly fixed. Indeed, upon treatment of 15 with butyllithium and methyl iodide at  $-95$  °C only 9-*endo*-methyl-9-*exo*-bromo-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (16) was formed. Some experiments carried



out at higher temperatures showed that the lithiate derived from 15 was stable even up to  $-45$  °C. Above this temperature decomposition to an indefinable mixture of products took place. The lithiate derived from 1 proved to undergo ring opening at an appreciable rate at  $-40$  °C, leading to the corresponding allene.

### Experimental Section

**General.** The starting materials 1 and 5 were prepared by reaction of dibromocarbene with the appropriate olefins according to a known procedure.<sup>15</sup> 9,9-Dibromo-*trans*-bicyclo[6.1.0]nonane (9) was obtained from *trans*-cyclooctene<sup>16</sup> by reaction with bromoform and potassium *tert*-butoxide in pentane.<sup>2c</sup> 9,9-Dibromo-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (15) was prepared as indicated by Vogel.<sup>17</sup> Melting points were determined on a Mettler apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as an internal standard.

**9-*exo*-Bromo-9-*endo*-methyl-*cis*-bicyclo[6.1.0]nonane (2).** To a solution of 2.80 g (0.01 mol) of 1 in 15 ml of dry THF (distilled from LiAlH<sub>4</sub>) was added dropwise 4 ml of a 20% solution of butyllithium in hexane at  $-95$  °C (toluene-liquid nitrogen bath). After stirring for 10 min 1.5 ml of methyl iodide was added in one portion and after 1 h the mixture was gradually warmed to 0 °C. Then 100 ml of water was added and the product was extracted with ether. Workup and subsequent distillation gave 1.5 g (70%) of 2;<sup>21</sup> bp 118–121 °C (14 mm); NMR (CDCl<sub>3</sub>)  $\delta$  1.63 (s, 3, CH<sub>3</sub>), 1.60–2.20 (aliphatic and cyclopropane H). Anal. Calcd for C<sub>10</sub>H<sub>17</sub>Br: C, 55.30; H, 7.83. Found: C, 55.31; H, 7.89.

**4,5-*trans*-Dihydroxy-9,9-dibromo-*cis*-bicyclo[6.1.0]nonane Acetonide (3).** *cis,cis*-Cycloocta-1,5-diene was converted to 1,2-*trans*-dihydroxycyclooct-5-ene by reaction with performic acid and subsequent hydrolysis.<sup>18</sup> Reaction with acetone and anhydrous copper sulfate gave the acetonide.<sup>19</sup> To a solution of 21 g (0.12 mol) of the acetonide and 51 g (0.46 mol) of potassium *tert*-butoxide in 900 ml

of hexane was added dropwise with stirring at  $-15^{\circ}\text{C}$  a solution of 87.3 g (0.35 mol) of bromoform in 200 ml of hexane. Stirring was prolonged for an additional 2 h at ambient temperature, then 1 l. of water was added and the organic layer was separated. After washing, drying, and evaporation, the remaining dark oil was treated with cold 96% ethanol. The precipitated solid was recrystallized from a small volume of diisopropyl ether. This afforded 17 g (42%) of **3**: mp  $84-86^{\circ}\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.38 (s, 6,  $\text{CH}_3$ ), 3.40-4.20 [m, 2,  $-\text{CH}(\text{O})-\text{CH}(\text{O})-$ ]. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{Br}_2\text{O}_2$ : C, 40.67; H, 5.08. Found: C, 40.55; H, 5.01.

**4,5-trans-Dihydroxy-9-exo-bromo-9-endo-methyl-cis-bicyclo[6.1.0]nonane Acetonide (4)**. To a solution of 1.7 g (0.005 mol) of **3** in 10 ml of dry THF was added 2.2 ml of butyllithium solution and 0.7 ml of methyl iodide in a similar way as described for **2**. Workup afforded 1.22 g (92%) of **4** as a white solid; mp [ $(i\text{-Pr})_2\text{O}$ ]  $70-71^{\circ}\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.39 (s, 6,  $\text{CH}_3$ ), 1.63 (s, 3, endo  $\text{CH}_3$ ), 3.40-4.35 [m, 2,  $\text{CH}(\text{O})-\text{CH}(\text{O})-$ ]. Anal. Calcd for  $\text{C}_{13}\text{H}_{21}\text{BrO}_2$ : C, 53.98; H, 7.27. Found: C, 54.04; H, 7.10.

**Cyclonona-1,2,6-triene (6)**. To a solution of 2.80 g (0.01 mol) of **5** were added 0.011 mol of butyllithium and excess of methyl iodide at  $-95^{\circ}\text{C}$  as described for the synthesis of **7**. Workup gave an oil which, upon examination by TLC, proved to consist of one component besides some TLC immobile material (silica gel; pentane as eluent). Chromatography gave 0.98 g (81%) of **6**, identical with the compound prepared by other routes.<sup>5a,b</sup> NMR ( $\text{CDCl}_3$ )  $\delta$  5.20 (m, 2, allenic H), 5.55 (m, 2, olefinic H), 1.25-2.60 (m, 8, other H); ir (neat)  $\nu$   $1958\text{ cm}^{-1}$  (allene).

**10,10-Dibromo-cis,cis-tricyclo[7.1.0.0<sup>4,6</sup>]decane (7)**. This compound was prepared by treatment of bicyclo[6.1.0]non-4-ene<sup>20</sup> [NMR ( $\text{CDCl}_3$ )  $\delta$  5.58 (m, 2, olefinic H), 0.50-2.60 (m, 12, aliphatic and cyclopropyl H)] with bromoform and potassium *tert*-butoxide as described for **3**; yield 58%; bp  $83-85^{\circ}\text{C}$  (0.01 mm). Anal. Calcd for  $\text{C}_{10}\text{H}_{14}\text{Br}_2$ : C, 40.81; H, 4.67. Found: C, 40.53; H, 4.70.

**cis-Bicyclo[7.1.0]deca-4,5-diene (8)**. This compound was prepared in an identical way as described for **6** from 2.94 g (0.01 mol) of **7**. Workup and chromatography over a short column (silica gel; pentane as eluent) provided 0.89 g (67%) of the allene **8**: NMR ( $\text{CDCl}_3$ )  $\delta$  5.27 (m, 2, allenic H), 0.40-2.60 (m, 12, aliphatic ring H and cyclopropyl H); ir (neat)  $\nu$   $1960\text{ cm}^{-1}$  (allene). This compound proved to be thermolabile.

**9-Methyl-9-bromo-trans-bicyclo[6.1.0]nonane (10)**. A solution of 2.82 g (0.01 mol) of **9** in 20 ml of THF was treated at  $-95^{\circ}\text{C}$  with butyllithium and methyl iodide as described for **2**. Workup afforded 1.93 g (89%) of **10**: bp  $55-60^{\circ}\text{C}$  (0.1 mm); NMR ( $\text{CDCl}_3$ )  $\delta$  1.68 (s, 3,  $\text{CH}_3$ ), 1.65-2.40 (other H's). Anal. Calcd for  $\text{C}_{10}\text{H}_{17}\text{Br}$ : C, 55.30; H, 7.83. Found: C, 55.20; H, 7.81.

**9-endo-Methyl-9-exo-bromo-cis-bicyclo[6.1.0]nona-2,4,6-triene (16)**. A solution of 1.38 g (0.005 mol) of **15**<sup>17</sup> in 10 ml of THF was treated with butyllithium and methyl iodide as described for **2**. Workup in the usual way afforded an oil which upon separation of the compounds which had no TLC mobility (silica gel; petroleum ether as eluent), gave 0.89 g (84%) of **16**: NMR ( $\text{CDCl}_3$ )  $\delta$  1.61 (s, 3, endo  $\text{CH}_3$ ), 2.09 (s, 2, cyclopropane CH), 5.62-6.05 (m, 6, olefinic H). The compound proved to decompose upon distillation.<sup>22</sup>

**9-exo-Bromo-cis-bicyclo[6.1.0]nonane (17)**<sup>6</sup>. To 20 ml of a 1 M solution of dimethyl anion in  $\text{Me}_2\text{SO}$  was added with stirring 2.8 g (0.01 mol) of **1** at such a rate as to maintain the temperature at  $25-30^{\circ}\text{C}$ . After stirring for an additional 2 h, 150 ml of water was added and the product was extracted with ether. After washing, drying, and evaporation of the organic solvent the residue was distilled and afforded 1.1 g (55%) of **17**, bp  $105-110^{\circ}\text{C}$  (18 mm).

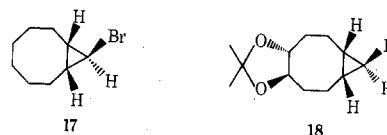
**4,5-trans-Dihydroxy-9-exo-bromo-cis-bicyclo[6.1.0]nonane Acetonide (18)**. A solution of dimethyl anion was prepared by dissolving 15 g (ca. 0.5 mol) of sodium hydride (80% dispersion in mineral oil) in 500 ml of  $\text{Me}_2\text{SO}$  ( $\text{CaH}_2$  dried). In 0.5 h was added dropwise with stirring at  $20^{\circ}\text{C}$  a solution of 60 g (0.17 mol) of **3** in 100 ml of THF. The mixture was stirred for about 2 h and poured into 4 l. of water. The product was extracted with ether. The oil which remained after washing, drying, and evaporation of the solvent was treated with 95% ethanol and afforded 21 g (45%) of **18**: mp (95% ethanol)  $66-67^{\circ}\text{C}$ ;

NMR ( $\text{CDCl}_3$ )  $\delta$  1.40 (s, 6,  $\text{CH}_3$ ), 0.60-2.55 (aliphatic and cyclopropyl H), 3.42-4.40 [m, 2,  $-\text{CH}(\text{O})-\text{CH}(\text{O})-$ ]. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{BrO}_2$ : C, 53.36; H, 6.91. Found: C, 52.44; H, 7.06.

**Registry No.**—**1**, 32644-18-1; **2**, 59474-03-2; **3**, 59474-04-3; **4**, 59474-05-4; **5**, 54809-08-4; **6**, 1502-42-7; **7**, 59474-06-5; **8**, 59493-11-7; **9**, 59531-26-9; **10**, 59531-27-0; **15**, 59474-07-6; **16**, 59474-08-7; **17**, 1551-94-6; **18**, 59474-09-8; butyllithium, 109-72-8; methyl iodide, 74-88-4; *cis,cis*-cycloocta-1,5-diene, 1552-12-1; bicyclo[6.1.0]non-4-ene, 4729-13-9.

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**5** only affords the allene **6** in this reaction. This reaction has been assumed to proceed via carbenoid species as intermediates. See C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Cardenas, and P. D. Gardner, *Chem. Ind. (London)*, 766 (1965).

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