

BICYCLIC ALLENES : GENERATION AND TRAPPING OF

6,7-BENZOBICYCLO[3.2.1]OCTA-2,3-DIENE

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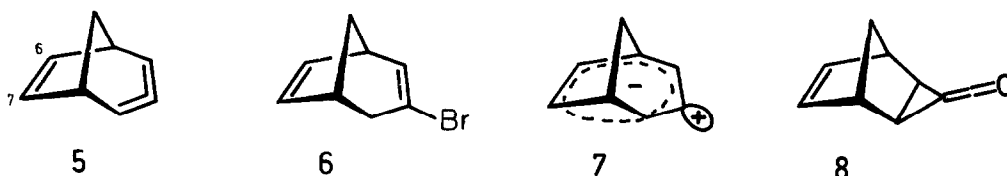
*SUMMARY:* Treatment of 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,3-diene (9) with potassium tert.-butoxide produces the strained bicyclic allene (10) which is trapped by 1,3-diphenylbenzo[c]furan (DBI) to give five isomeric cycloadducts. In the absence of DBI, allene (10) gave rise to enol ether (18) by addition of tert.-butanol.

The synthesis and isolation or trapping of highly strained molecules, such as cyclic allenes, has been an area of extensive research during the past twenty years<sup>1</sup>. Molecular models suggest that the allene linkage can be incorporated in only nine-membered or larger rings without distortion. If the ring size is decreased below this, it becomes necessary to deform allene linkage in order to close the ring. Two deformations will be facilitate ring closure. The first consists of bending the allene group at C<sub>2</sub>, the second deformation would retain the linear C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> linkage, but requires one of the methylene groups to be twisted to form a more nearly planar allene<sup>2</sup>. Seven and eight-membered rings are evidently large enough to accomodate the strain and deformation caused by the allene linkage. Recently, Balci and Jones<sup>3</sup> provided experimental evidence that 1,2-cyclohexadiene and 1,2-cycloheptadiene are both chiral and that racemization of (1) efficiently competes with cycloaddition with 1,3-diphenylbenzo[c]furan (DBI). More recently, these results were also supported by ab initio MCSCF calculation on 1,2-cyclohexadiene<sup>4</sup>. These calculations predict that (1)



is strongly bent and chiral (C<sub>2</sub>-symmetry) and undergoes facile racemization via a species best described as a diradical (2). Zwitterions (3) and (4) are electronically excited states of (2). Wentrup et al.<sup>5</sup> recently succeeded in isolating 1,2-cyclohexadiene in a matrix at 170° K and observing its IR spectrum.

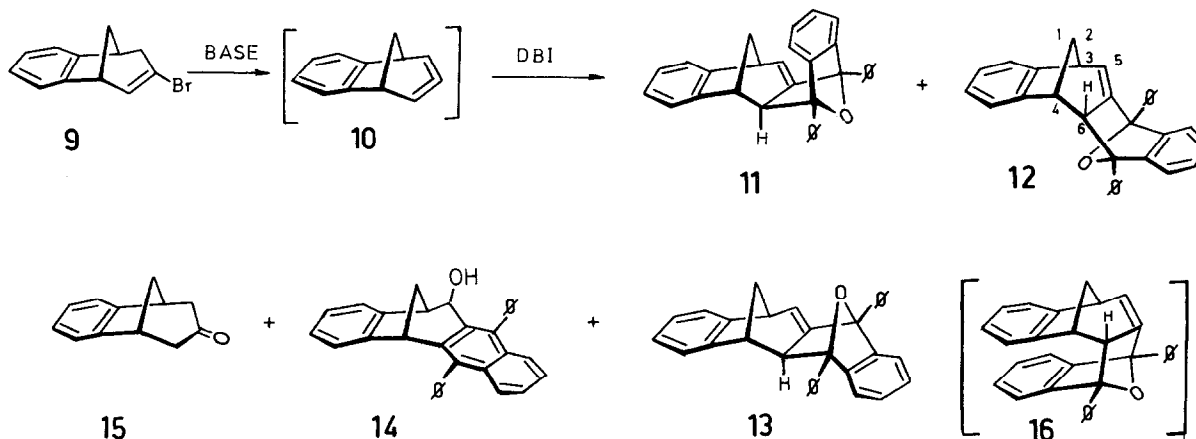
Moreover, the strained bicyclic allene (6) was generated by base-promoted dehydrobromination of (5), and trapped with DBI. The formation of optically active products from dehydrobromination with an optically active base was inferred to the intermediacy of a twisted allene structure<sup>6</sup>. According to a report by Bergman and Rajadbyaksha<sup>7</sup>, (5) gives with base in the absence of a trapping agent the acetylenic compound (17) in 29 % yield. The authors suggested the bishomoaromatic species (7), as a plausible precursor of (17). The following year, Klump and van Dijk<sup>8</sup> reported the same product from photolysis of (8).



The latter results prompted us an investigation of the fate of the allene (6) when the remote double bond in (5) is deactivated by benzosubstitution.

To this end, we prepared 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,3-diene (9) by a published method<sup>9</sup> and subjected it to dehydrobromination with potassium tert.-butoxide (4.0 equiv., 6h reflux) in the presence of 1.0 equiv. of DBI. Indeed, five products, (11-15) were isolated after repeated column chromatography (Alumina, Grade III, eluting with petroleum ether/toluene 9:1) in yields of 18%, 17%, 8%, 12%, and 16%, respectively.

Structural assignments were made on the basis of spectral data and extensive double resonance experiments. The formation of (11), (12), and (13)<sup>10</sup> is most reasonably explained by the intermediacy of the strained allene (10) which is trapped by DBI. There are four possible cycloadducts. Inspection of Dreidings models indicate that isomer (16), which was not found among the products, would be unstable due to strong steric interaction of the two benzene rings. We there-



fore believe that it underwent facile isomerization to the less strained alcohol (14)<sup>11</sup>. Ketone (15) ought to stem from addition of tert.-butanol to allene (10) followed by hydrolysis. Its spectral data matched those reported in the literature<sup>9</sup>.

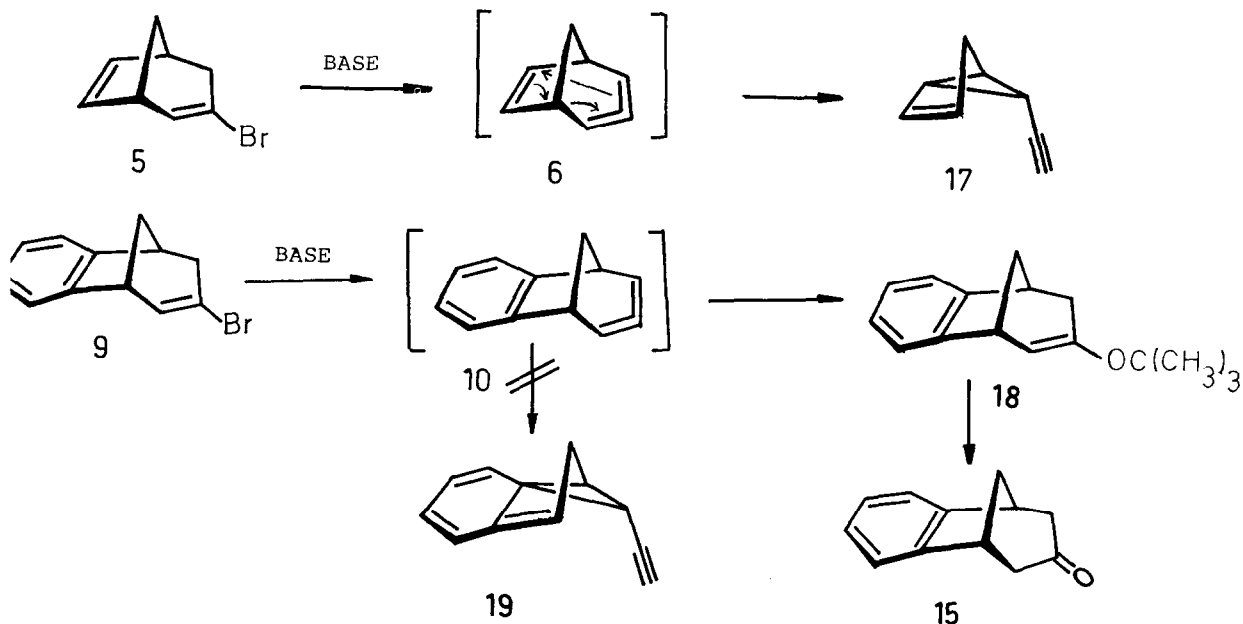
In the absence of DBI, enol ether (18) was formed as the sole product in high yield. It was identified by means of its spectral data<sup>12</sup> and its ready hydrolysis to the ketone (15) with dilute HCl.

1-Bromocyclohexene and 1-bromocycloheptene<sup>13</sup> form by the dehydrobromination reactions tricyclic hydrocarbons arising from dimerization of intermediate 1,2-cycloalkadienes. In contrast, reaction of (9) with base did not give any hydrocarbon as dimerization product. This is probably due to the high reactivity of (10), which was trapped by tert.-butanol before to reach the necessary concentration for dimerization.

On the basis of our results we can conclude that the dehydrobromination of (9) gives rise to the strained bicyclic allene (10) which unlike (6) does not isomerize further to a ring-opened alkyne in the absence of trapping agent because involvement of the remote double bond in (10) is impeded by the stability of the aromatic ring.

An alternative mechanism could be envisioned that might rationalize our results as well. Dehydrobromination of (9) might yield bicyclic alkyne which cyclo-adds with DBI. Base-promoted isomerization of the double bonds in cycloadducts would then give the observed adducts (11-13).

Further investigations are under way that might yield unequivocal evidence concerning the intermediate involved in the dehydrobromination of (9).



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## REFERENCES AND NOTES

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- 10) a) (11) : m.p. 231-232<sup>o</sup> C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS) ; δ 0.1 (A-part of AB-System) H<sub>2</sub>; 1.75 (B-part of AB-System, doublet of triplet) H<sub>1</sub>; 3.3 m, H<sub>3</sub>, H<sub>4</sub>, and H<sub>5</sub> ; 6.1 dd H<sub>6</sub>; 7.0-7.95 m, 18 H, aromatic protons; J<sub>1,2</sub>: 10.4 Hz, J<sub>1,3</sub> ≈ J<sub>1,4</sub> ≈ 4 Hz, J<sub>2,3</sub>: 7.7 Hz, J<sub>5,6</sub>: 2.9 Hz ; IR (CDCl<sub>3</sub>) 3060, 3030, 2930, 12860, 1600, 1500, 1445, 1335, 1310, 1105, 980 cm<sup>-1</sup>, Mass, m/e 424 (M<sup>+</sup>), 406, 329, 319, 309.
- b) (12) : m.p. 176<sup>o</sup> C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS) ; δ 2.15 m, H<sub>1</sub> and H<sub>2</sub> ; 3.25 m, H<sub>3</sub>; 3.45 t, H<sub>5</sub> ; 3.75 m, H<sub>4</sub> ; 5.65 dd, H<sub>6</sub> ; 6.3-7.9 m, 18 H, aromatic protons ; J<sub>1,2</sub>: 5.4 Hz, J<sub>5,6</sub>: 2.7 Hz, J<sub>4,5</sub>: 3.8 Hz ; IR (CHCl<sub>3</sub>) 3060, 3020, 2950, 2860, 1600, 1495, 1465, 1460, 1445, 1360, 1310, 1020, 990 cm<sup>-1</sup> ; Mass, m/e 424 (M<sup>+</sup>), 406, 331, 329, 319, 309, 250.
- c) (13) : m.p. 211<sup>o</sup> C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS) δ 1.4 (A-part of AB-System) H<sub>2</sub> ; 1.9 (B-part of AB-System, triplet of doublet) H<sub>1</sub>; 2.6 d, H<sub>5</sub> ; 3.05 d, H<sub>4</sub> ; 3.25 dd, H<sub>3</sub> ; 6.1 dd, H<sub>6</sub> ; 6.9-7.8 m, 18 H aromatic protons ; J<sub>1,2</sub>: 9.6 Hz, J<sub>1,3</sub>: 3.6 Hz, J<sub>1,4</sub>: 3.5 Hz, J<sub>3,6</sub>: 7 Hz, J<sub>5,6</sub>: 2.45 Hz, J<sub>1,5</sub> ≈ J<sub>2,3</sub> ≈ J<sub>2,4</sub> ≈ 0 ; IR (KBr) 3060, 2950, 2890, 1600, 1500, 1480, 1455, 1335, 1315 cm<sup>-1</sup>.
- 11) (14) : m.p. 220<sup>o</sup> C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS); δ 2.0 br. s, OH ; 2.25 (B-part of AB-System) dt, H<sub>1</sub>; 2.7 (A-part of AB-System) d, H<sub>2</sub>; 3.35 m, H<sub>3</sub> ; 4.1 d, H<sub>4</sub> ; 4.85 d, H<sub>5</sub> ; 6.9-7.6 m, 18 H aromatic protons; IR (KBr) 3580, 3310, 3060, 2975, 2930, 1600, 1490, 1470, 1440, 1405, 1375, 1030, 1010, 995 cm<sup>-1</sup>, Mass, m/e 424 (M<sup>+</sup>), 406, 347, 329, 302, UV (EtOH) ; λ 208 (ε 74450), 242 (ε 96800), 270 (ε 9150), 276 (ε 9468), 290 (ε 9361), 330 (319). UV spectrum establish clearly the presence of naphthalene system.
- 12) (18) : colorless liquid ; <sup>1</sup>H-NMR (CCl<sub>4</sub>/TMS) ; 1.15 s, 9H methyl protons ; 1.6-2.7 m, 4H methylene protons; 3.25 m, 2H bridge head protons; 5.25 d, 1H olefinic proton; 6.8-7.2, 4H aromatic protons, IR (CCl<sub>4</sub>) 3065, 2980, 2950, 1640, 1470, 1390, 1320, 1255, 1175 cm<sup>-1</sup>.
- 13) a) A. T. Bottini, L.J. Cabral, Tetrahedron Lett., (1977), 615-618.  
b) A. T. Bottini, K. A. Frost II, B.R. Anderson, V. Dev, Tetrahedron, 29, 1975-1981, (1973).

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