

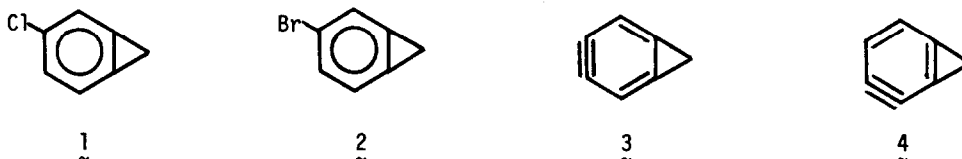
SYNTHESIS OF 3-CHLORO- AND 3-BROMOBENZOCYCLOPROPENE

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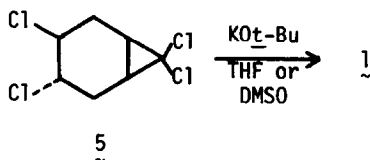
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It has been demonstrated that 7,7-dichlorobicyclo[4.1.0]hept-3-enes are excellent precursors to benzocyclopropenes.<sup>1-4</sup> We report here an application of this method to the synthesis of the functionalized benzocyclopropenes 1 and 2, potential precursors to cyclopropabenzynes 3 and 4.



The starting material 5, m.p. 77°-78°C, was prepared in 63% yield by chlorination of 7,7-dichlorobicyclo[4.1.0]hept-3-ene.<sup>5</sup> The presence of seven distinct signals in the <sup>13</sup>C NMR spectrum establishes the stereochemistry.

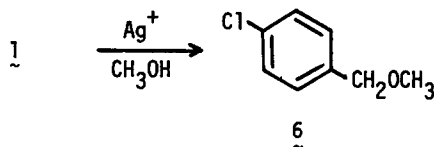
Reaction of 5 with KOt-Bu (6 equiv.) in THF at room temperature for 18 hours gave 1 in 61% yield. Purification was achieved by bulb to bulb distillation at 0.02 mm Hg. In dimethyl



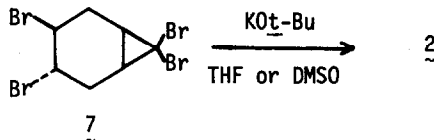
sulfoxide, the yield of 1 was 45%. Spectral data for 1 are: NMR (d-CHCl<sub>3</sub>) δ 3.30 (s, 2H) and 7.20 (narrow multiplet, 3H); IR (neat) 1665 cm<sup>-1</sup> (aromatic double bond); UV λ<sub>max</sub><sup>C<sub>2</sub>H<sub>5</sub>OH</sup> 273 (ε=910), 278 (ε=1100), and 285 (ε=910) nm. Since this result conflicts with the recent report of Kumar, Tayal, and Devaprabhakara,<sup>6</sup> who reported that 5 gives 2-chlorobenzocyclopropene upon treatment with KOt-Bu in DMSO, the position of the halogen was established unequivocally by <sup>13</sup>C NMR spectroscopy as follows: when subjected to single frequency off resonance decoupling, three of the aromatic carbons were singlets, one was a clear doublet, indicating bonding to a proton which is isolated from the other protons, and the doublets for the remaining two aromatic

carbons showed extra lines due to second-order transitions resulting from bonding to adjacent coupled protons.

The silver ion catalyzed methanolysis<sup>7</sup> of 1 gave 6, identical in all respects with an authentic sample prepared by methanolysis of *p*-chlorobenzylbromide.



Compound 2 was prepared by treating 7 with  $\text{KOt-Bu}$  in THF or DMSO in 46% and 40% yields, respectively. Spectral data: NMR ( $d\text{-CHCl}_3$ )  $\delta$  3.12 (s, 2H) and 6.79-7.15 (m, 3H); IR (neat)



$1660\text{ cm}^{-1}$ ; UV  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$  273 ( $\epsilon=1020$ ), 278 ( $\epsilon=1190$ ), and 285 ( $\epsilon=1000$ ). The location of the bromine was established by  $^{13}\text{C}$  NMR spectroscopy as described previously for 1.

We are currently investigating the generation of the benzyne 3 and 4.

#### Acknowledgment

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