

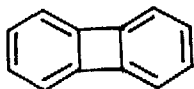
BENZO[3,4]CYCLOBUTA[1,2-d]TROPONE

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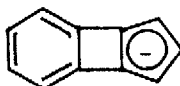
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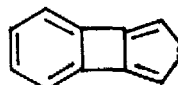
During recent years, a considerably amount of attention has been devoted to the synthesis of aromatic analogues of biphenylene 1, in which one benzenoid ring is replaced by another $(4n + 2)\pi$ electron system. Compounds which have been prepared include the norbiphenylene anion 2,¹ benzo[3,4]cyclobuta[1,2-c]thiophene 3,² benzo[3,4]cyclobuta[1,2]tropylium cation 4,³ and benzo[3,4]cyclobuta[1,2-c]tropone 5.⁴ Much of the interest in these ring systems centres



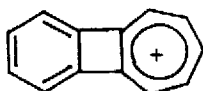
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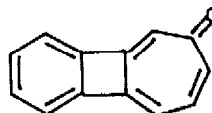
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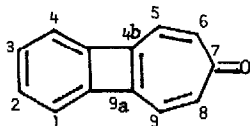


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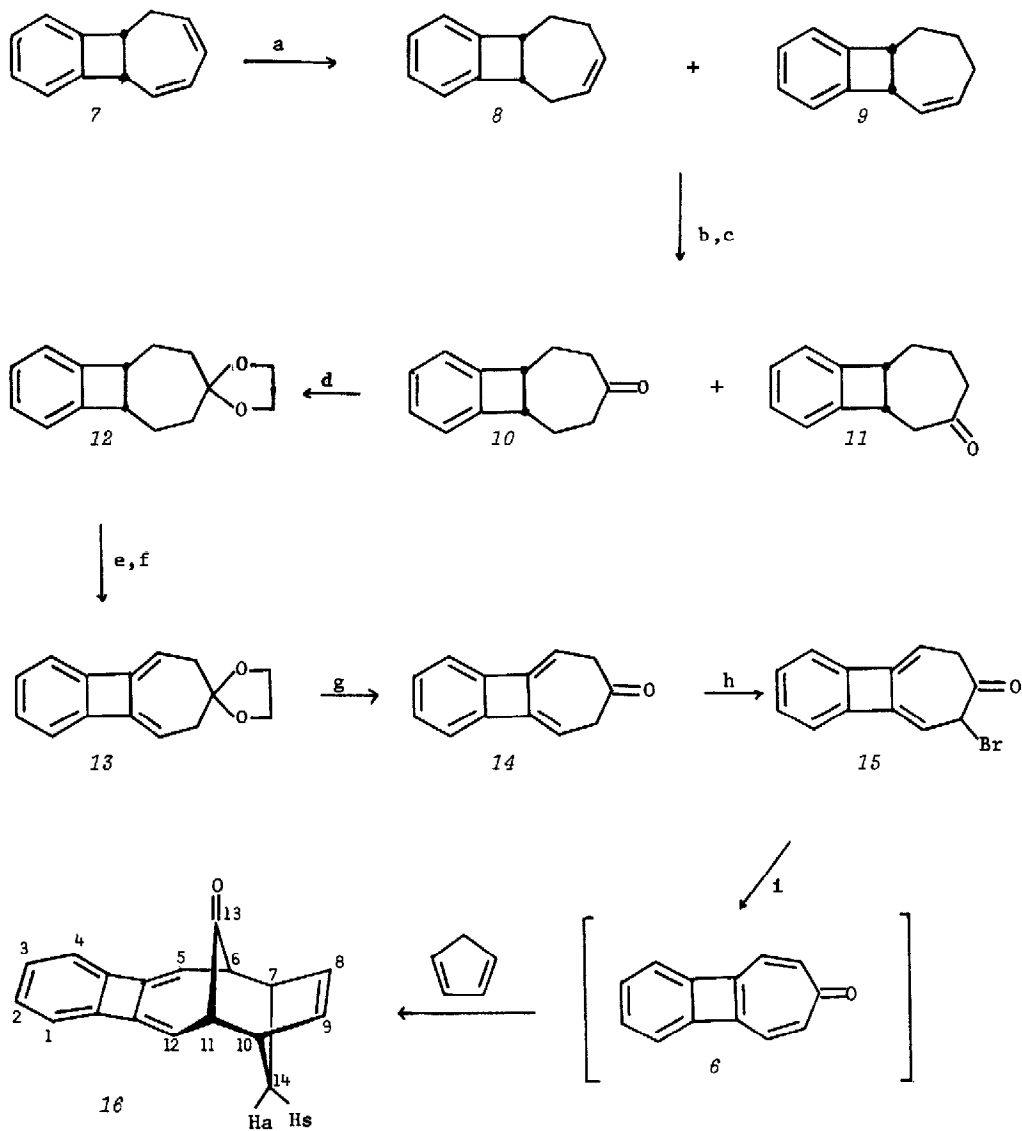
around the question of the extent of π -electron delocalization, and hence on the degree of antiaromatic and paramagnetic character of the central 4-membered ring. Of particular interest in this regard is benzo[3,4]cyclobuta[1,2-d] tropone 6, which possesses a formal benzocyclobutadienoid double bond. The high π -bond character of the 4b-9a bond can in principle be



6



6a



SCHEME

Reagents: a H_2 , 10% Pd-C b B_2H_6 , THF c $H_2Cr_2O_7$
d 1,2-ethanediol, TsOH e NBS, $BaCO_3$, CCl_4 f DBN, DMF, 100°
g 3M $HClO_4$, THF, 20° h NBS, CCl_4 i Et_3N , CH_2Cl_2 , 0°

dissipated by π -electron delocalization in the 7-membered ring, as in *6a*. It has been concluded that tropone itself is essentially polyolefinic in character, with little or no contribution from the analogous dipolar structure,⁵ and we regard *6* as an important system in which to test the ability of the tropone ring to behave as an aromatic system. Information regarding the chemical reactivity and spectroscopic properties of *6* is thus highly desirable. Although we are not fully able to supply such information at this stage, we nevertheless wish to report the generation and trapping of *6*.

Controlled hydrogenation of the benzyne-cycloheptatriene adduct *7*⁶ gave a mixture, consisting chiefly of alkenes *8*⁷ and *9*,⁶ which was subjected to hydroboration-oxidation, and gave, after careful chromatography over alumina, ketones *10*,⁷ m.p. 87-8°, and *11*,⁷ m.p. 75-6° as the main products. These ketones could be distinguished on the basis of their $\{H\}^{13}C$ nmr spectra (measured at 67.89 MHz). The spectrum of *10* shows 7 sets of chemically equivalent carbon atoms at $\delta_{CDCl_3}^{TMS}$ 24.1, 43.0, 46.5, 122.1, 127.6, 146.9 and 211.6, while that of *11* shows the presence of 13 non-equivalent carbon atoms at $\delta_{CDCl_3}^{TMS}$ 23.8, 28.1, 41.9, 43.8, 45.1, 47.2, 122.1, 122.2, 127.5, 127.7, 146.6, 146.8 and 211.5.⁸ Ketone *10* was converted into the acetal *12*, m.p. 126°, which on double bromination-dehydrobromination gave the diene-acetal *13*, m.p. 86-7°, 1H nmr $\delta_{CCl_4}^{TMS}$ 7.08 (s, 4H, aromatic), 5.46 (t, J 4Hz, 2H, vinyl), 3.83 (s, 4H, acetal methylene) and 2.63 (d, J 4Hz, 4H, methylene). Hydrolysis gave the dienone *14*,⁷ m.p. 123-4°, $\delta_{CDCl_3}^{TMS}$ 7.22 (s, 4H, aromatic), 5.65 (t, J 4Hz, 2H, vinyl) and 3.48 (d, J 4Hz, methylene). The overall yield for the *7* \rightarrow *14* conversion was c 2%. Attempts to introduce the final double bond into *14* have been fraught with difficulty and frustration. A number of model reactions which smoothly converted 3,5-cycloheptadienone into tropone under mild conditions failed when applied to the sensitive dienone *14*. Prolonged reaction of *14* with NBS in refluxing CCl_4 , however, gave a crude product containing the monobromide *15*, as well as c 50% unchanged dienone *14*. Treatment of this product with bases alone has so far not yielded any recognizable product. However, addition of triethylamine to a mixture of the crude bromination product and cyclopentadiene in CH_2Cl_2 at 0° afforded the 6 + 4 cycloadduct *16*,⁷ m.p. 150-1° in c 20% yield (based on dienone *14*): $\nu_{max}^{CCl_4}$ 1725 cm^{-1} , $\lambda_{max}^{cyclohexane}$ 243 (log ϵ 4.60), 324 (3.79), 339 (3.76) nm, 1H nmr $\delta_{CDCl_3}^{TMS}$ 7.19 (s, 4H, aromatic), 6.03 (br s, 2H, H_8, H_9), 5.75 (d, J 7Hz, H_5, H_{12}), 3.33 (m, 2H, H_6, H_{11}), 2.90 (m, 2H, H_7, H_{10}), 2.53 (d, J 11.5Hz, 1H, H_{14a}) and 1.61 (very br m, 1H, H_{14b}). The 1H nmr spectrum is very similar in the high field region to that of the tropone-cyclopentadiene adduct,⁹ and hence we assign the stereochemistry

shown. We therefore conclude that benzo[3,4]cyclobuta[1,2-d]tropone **6** is formed and trapped in this reaction. The adduct **16** is rapidly formed at 0°, while the analogous tropone adduct⁹ is formed only relatively slowly at room temperature. This indicates qualitatively that **6** is much more reactive than tropone in the $\pi_6 + \pi_4$ cycloaddition reaction.

The structures **17** and **18**, which obviate the necessity of a benzocyclobutadienoid double bond, may also be considered for the dehydrobromination product of **15**. Both **17** and **18** could



conceivably also give rise to the cycloadduct **16**, in view of the known reactions of oxyallyl systems¹⁰ and cyclopropanones¹¹ with dienes. A decision regarding the electronic structure of benzo[3,4]cyclobuta[1,2-d]tropone must await its isolation and spectral examination. We are continuing our efforts to isolate **6** and its derived hydroxytropylium cation.

References and Footnotes

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