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## Cyclobutene-Fused Aromatic Molecules\*

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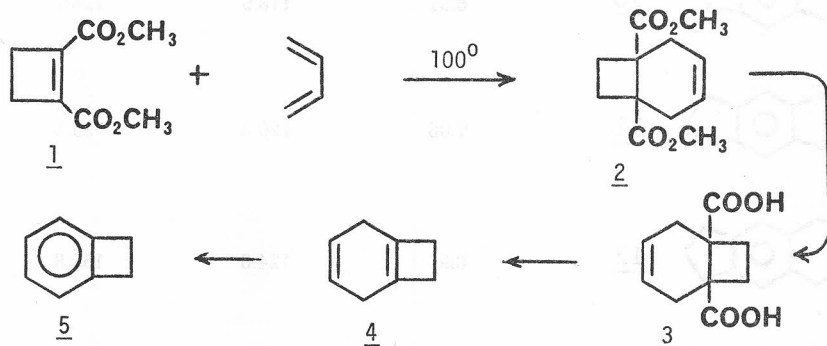
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The Diels-Alder cycloaddition of dimethyl-1,2-cyclobutenedimethylcarboxylate to a 1,3-diene results in the formation of an adduct which can subsequently be decarboxylated and dehydrogenated to provide a cyclobutene-fused benzenoid system. The use of appropriate dienes has led to the preparation of a series of para- and meta- bis-annulated benzenes. Variations in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR and in the UV spectra are found to be a function of the size of the annelated rings as well as their relative orientation.

A similar approach has been employed in a preparation of the very elusive tricyclobutabenzene which may represent the missing link between 1,5,9-cyclododecatriene and 6-radialene. Tricyclobutabenzene is a stable crystalline material (mp 141–142 °C) whose physical properties are quite consistent with higher homologs. An X-ray structure of its perfluoro analog shows no evidence for any bond alternation.

A double-barreled application of the Diels-Alder approach has led to the synthesis of naphtho[b,e]dicyclobutene. The physical properties of this molecule are also compared to higher homologs.

Recently there have appeared several methods for the large scale preparation of benzocyclobutene. Although these procedures allow for straightforward, high yield synthesis of the parent compound, they are not readily adapted to various substituted derivatives. We have developed a new route to benzocyclobutene which lends itself well to the synthesis of molecules in which one or two additional small rings are fused to the benzene nucleus.<sup>1</sup>



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When butadiene is heated in a combustion tube with dimethyl-cyclobutene-1,2-dicarboxylate (*1*) for 48 hours at 100 °C, the Diels-Alder adduct *2*, may be obtained in 73% yield. Although both ester functions in *2* are of the neopentyl type, hydrolysis to the corresponding diacid *3* may be readily accomplished by refluxing overnight with potassium hydroxide in aqueous methanol. Treatment of this diacid with one equivalent of lead tetraacetate in dimethylsulfoxide containing two equivalents of pyridine gives a product which is mainly the diene *4* contaminated with a small amount of benzocyclobutene (*5*). If the amounts of lead tetraacetate and pyridine are doubled, a 57% yield of benzocyclobutene may be obtained directly. The substitution of 1-vinylcyclobutene into the above sequence provides benzo[1,2:3,4]-dicyclobutene (*7*)<sup>2</sup> while the substitution of 1,2-dimethylenecyclobutane into the same sequence provides benzo[1,2:4,5]dicyclobutene (*9*). Utilizing various dienes in this fashion, a series of para and meta-bisannulated benzenes can be readily prepared.<sup>3</sup>

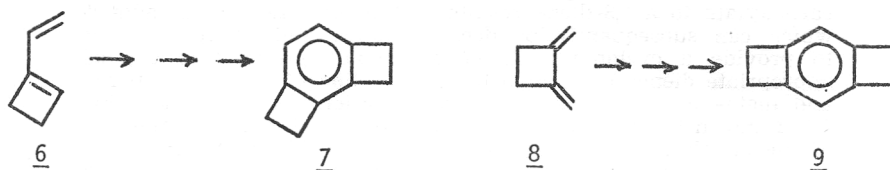


Table I shows the NMR spectral data for a series of para-bisannulated benzenes.<sup>4</sup> It may be seen that the chemical shift of the unsubstituted aromatic

TABLE I

NMR Data for the Unsubstituted C-H of Benzo-[1,2:4,5]dicycloalkenes. (In ppm downfield from TMS)

	Ar-H	Ar-C	$J^{13}\text{C-H}$
<u>9</u>	6.64	117.3	160.2 Hz
<u>10</u>	6.91	118.9	158.7
<u>11</u>	7.08	120.0	155.1
<u>12</u>	6.91	124.8	153.8
<u>13</u>	6.74	134.1	152.3

carbon moves upfield with increasing strain from a value of 134.1 ppm for compound 13 to 117.3 ppm for compound 9. At the same time the C—H coupling constant for this unsubstituted aromatic C—H bond increases steadily from a value of 152.3 Hz for 13 to 160.2 Hz for 9. Both of these trends may be satisfactorily explained by invoking a rehybridization theory set forth by Streitwieser and by Finnigan some years ago.<sup>5</sup> It was claimed that for small ring fused benzocycloalkenes the bridgehead carbon rehybridizes to use orbitals of higher p-character in bonding to the small ring. This would cause the orbital used in bonding to the adjacent unsubstituted aromatic carbon to become higher in s-character as the size of the fused ring is decreased from six carbons to four. This effect would then demand that this neighboring carbon contribute an orbital higher in p-character to preserve the C—C bond order. Such rehybridization would therefore leave the aromatic C—H bond enriched in s-character and polarized toward carbon (see Figure 1.). Such polarization might explain the higher field shift of this carbon atom with decreasing size of the fused rings on benzene. Also consistent with this model is the observed increase in the aromatic C—H coupling constant. Such polarization should result in

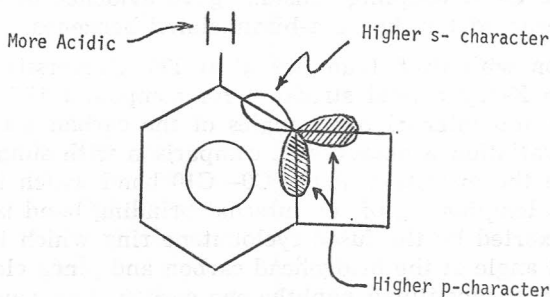
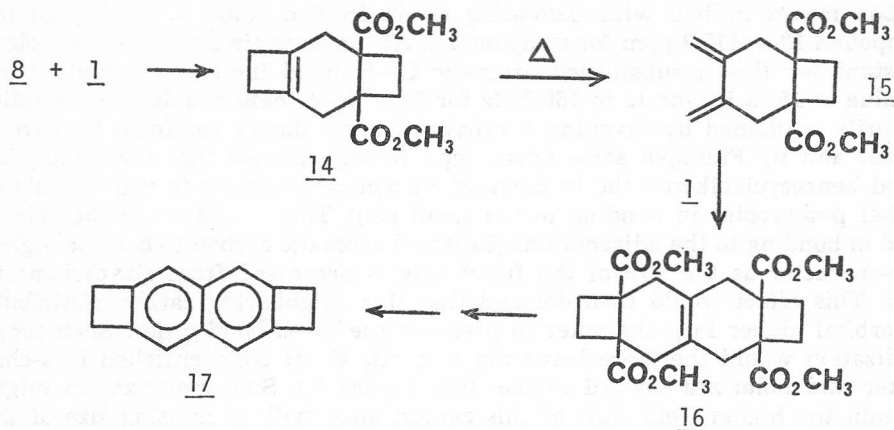


Figure 1.

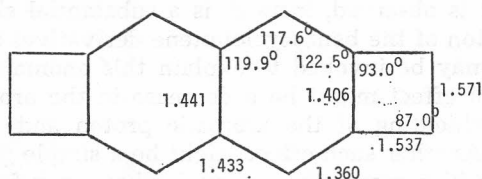
an increase in the acidity of the aromatic proton and therefore a lower field chemical shift. What is observed, instead, is a substantial shift to higher field for the aromatic proton of the benzocyclobutene derivatives 9 and 10. A variety of different effects may be invoked to explain this anomalous high field chemical shift. One such effect might be a decrease in the aromatic ring current leading to lesser deshielding of the aromatic proton and therefore a higher field chemical shift. Another such effect might be a simple geometric distortion of the benzene ring which moves the proton further away from the deshielding ring current. A third explanation could be simple, local anisotropy effects associated with the proton in relation to its immediate environment.

In the course of preparing the para-bisannelated system 9 it was noticed that intermediate 14, upon pyrolysis in the injection port of a gas chromatograph, afforded the ring opened diene 15. If this compound is reacted with an additional equivalent of the dienophile 1 the tetracyclic tetraester 16 may be prepared. Hydrolysis of the four ester groups in the normal fashion afforded the corresponding tetracarboxylic acid which could then be treated with lead tetraacetate to effect decarboxylation and aromatization to afford naphthodicyclobutene 17.<sup>6</sup> It was found that the employment of dichlorodicyanobenzoquinone (DDQ) facilitated the final oxidation step. Examination of the carbon-13



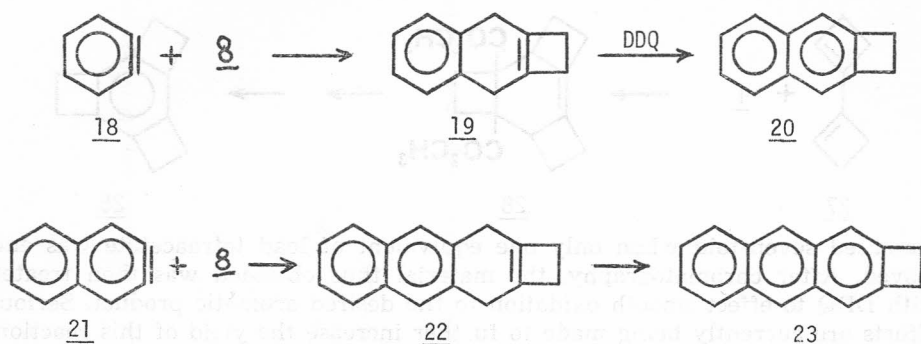
and proton chemical shifts of the unsubstituted aromatic carbon of compound 17 as well as the C—H coupling constant gave evidence of the same effects that had been observed for the para-bisannelated benzenes.

In cooperation with Prof. Ivan Bernal at The University of Houston, we have obtained an X-ray crystal structure for compound 17.<sup>7</sup> Figure 2. shows the bond lengths and internal bond angles of the carbon framework for this molecule. Little variation is observed in comparison with simple unsubstituted naphthalene with the exception of the C9—C10 bond which is lengthened by over 0.02 Å. This lengthening of the internal bridging bond is explained by a pinching effect exerted by the fused cyclobutene ring which tends to open up the internal bond angle at the bridgehead carbon and pinch closed the internal bond angle at the unsubstituted naphthalene carbon thus causing C9 and C10 to move further away from each other. This same pinching effect has been observed in an X-ray crystal structure of benzo[1,2,4,5]dicyclobutene.<sup>8</sup>

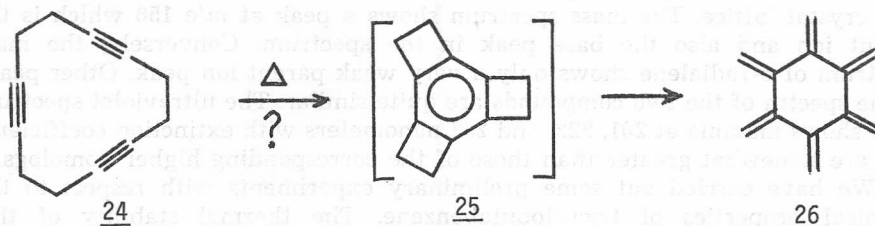


To further explore the utility of the Diels-Alder reaction in the preparation of cyclobutene-fused aromatic molecules, we subjected the previously prepared dienes to cycloaddition with benzyne.<sup>9</sup> Thus the reaction of 1,2-dimethylenecyclobutane (8) with benzyne led to the formation of the expected [2 + 4] adduct 19. Further oxidation of this species with DDQ led to naphtho[b]cyclobutene (20) in good yield. When 1-vinylcyclobutene (6) was employed in the same sequence, naphtho[a]cyclobutene could similarly be prepared. In like fashion, the corresponding cyclobutene-fused anthracenes could be synthesized by the reaction of 2,3-dehydronaphthalene (21) with dienes such as 6 and 8.

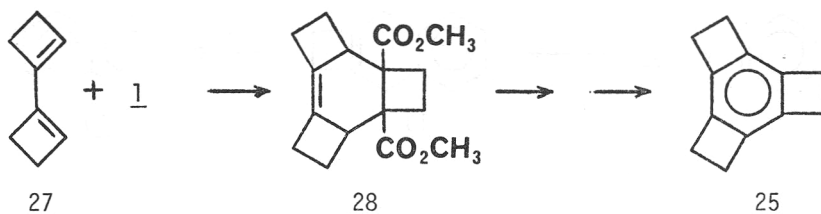
Let us now turn our attention to the Diels-Alder preparation of trisannelated benzenes. Before outlining the synthesis of tricyclobutabenzene, however,



let us consider why this molecule is currently of such great theoretical interest. Recently there have been several reports on the preparation of 6-radialene (26) utilizing high temperature reaction conditions. In one instance pyrolysis of 1,5,9-cyclododecatriyne (24) at 650 °C has led to the isolation of 6-radialene and it has been suggested that this isomerization may occur via the intermediacy of tricyclobutabenzene.<sup>10</sup> Thus far, however, all attempts to isolate tricyclobutabenzene in this reaction have been unsuccessful. The perfluoro analog of 25 has been prepared by a cyclotrimerization reaction and it is a stable crystalline material (mp 135—136 °C) which shows no evidence for any bond alternation in the central ring.<sup>11</sup>



The key to the successful employment of our benzocyclobutene synthesis for the preparation of 25 is the availability of the appropriate diene 27. Several years ago Lüttke and Heinrich worked out an elegant preparation of this diene by the copper chloride promoted coupling of 1-cyclobutenyl magnesium bromide.<sup>12</sup> We were able to reproduce their synthesis of this diene and subsequently treated it with the cyclobutene diester 1 at 120 °C for 12 hours to provide a 47% yield of adduct 28 as a mixture of two epimers. These epimers were detected by gas chromatography as well as by the appearance of two separate methyl ester peaks in the NMR. It proved unnecessary to separate these species and the mixture was simply hydrolyzed by treatment with potassium hydroxide in refluxing aqueous methanol. Subsequent acidification afforded a nearly quantitative yield of the corresponding dicarboxylic acid. Treatment of this diacid with lead tetraacetate in dimethylsulfoxide led to a mildly exothermic reaction accompanied by copious gas evolution. The temperature was maintained at 25—40 °C and, after the gas evolution had ceased (ca. 15 min), the reaction mixture was hydrolyzed and extracted with ether. After chromatography on silica gel eluting with hexane, 2.2 mg of tricyclobutabenzene was obtained as a white crystalline solid with a melting point of 141—142 °C.<sup>13</sup> It was found that the yield of tricyclobutabenzene could be



increased seven-fold when only one equivalent of lead tetraacetate was employed. After chromatography, the material thus obtained was then treated with DDQ to effect smooth oxidation to the desired aromatic product. Serious efforts are currently being made to further increase the yield of this reaction.

Examination of the physical properties of tricyclobutabenzene show this molecule to be a normal delocalized aromatic system with features that are consistent with previously prepared higher homologs. The chemical shift of the benzylic proton appears at 3.12 ppm, a value nearly identical to that reported for benzocyclobutene itself. The carbon-13 chemical shift of the aromatic carbon appears at 138.5 ppm while the benzylic carbon appears at 129.6 ppm. Again these values are very closely analogous to those of benzocyclobutene. It is interesting to note that the melting point of tricyclobutabenzene is nearly 50 °C higher than tricyclopentabenzene in which each of the fused rings contains an additional methylene unit. This higher melting point is attributed to the greater planarity of 25 and therefore its tighter packing in a crystal lattice. The mass spectrum shows a peak at  $m/e$  156 which is the parent ion and also the base peak in the spectrum. Conversely, the mass spectrum of 6-radialene shows only a very weak parent ion peak. Other peaks in the spectra of the two compounds are quite similar. The ultraviolet spectrum of 25 shows maxima at 201, 222, and 262 nanometers with extinction coefficients that are somewhat greater than those of the corresponding higher homologs.

We have carried out some preliminary experiments with respect to the chemical properties of tricyclobutabenzene. The thermal stability of this molecule was determined by observing its disappearance in the gas chromatograph as a function of the temperature of the injection port. Comparison with an internal standard showed that at 325 °C, 100% of tricyclobutabenzene remained. At 345 °C, 50% of 25 was found to still be present and at 380 °C only 10% was observed. Tricyclobutabenzene reacts slowly with trifluoroacetic acid at room temperature and readily with bromine at 0 °C. Due to the small amounts of material presently available, the products of these reactions have not yet been determined. We are continuing to investigate the chemistry of this intriguing molecule.

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### SAŽETAK

#### Ciklobuten kondenziran s aromatskim molekulama

R. P. Thummel

Diels-Alderova cikloadicija dimetil-1,2-ciklobutendikarboksilata u 1,3-dien daje adukt koji se može dekarboksilirati i dehidrogenirati, dajući ciklobuten kondenziran s benzenoidnim sustavom. Upotreba odgovarajućih diena dovodi do pripreve niza para- i meta-bis-aneliranih benzena. Za varijacije u  $^1\text{H}$   $^{13}\text{C}$  NMR- i UV-spektrima nađeno je da su funkcije veličine aneliranih prstena i njihove relativne orijentacije.

Sličan postupak uporabljen je pri preparaciji vrlo teško dostupnog triciklobutabenzena koji možda predstavlja most između 1,5,9-ciklododekatrina i 6-radialena. Tricklobutabenzen stabilan je kristalan materijal (t. t. 141–142 °C) čija su fizikalna svojstva prilično skladna s višim homolozima. Za njegov perfluoro-analog nije prema studiju X-zrakama nađena nikakova alternacija veza.

Nafto [b,e]diciklobuten sintetiziran je primjenom Diels-Alderova pristupa i njegova su svojstva uspoređena s višim homolozima.

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