mixture was allowed to stir for 5 min. Ethanethiol, distilled from CaH_2, was syringed into the cooled (0 °C) reaction mixture. A 1.6:1 mixture of II and I (0.77 g, 3.8 mmol) was syringed into the reaction and heated for 2.5 h at 140–147 °C.

The reaction mixture was cooled, poured into 150 ml of ice water, and extracted with petroleum ether to remove any unreacted II The aqueous layer was acidified with 4 N HCl and extracted with ether (3 × 50 ml). The organic layers were combined, washed with NaCl solution, dried over anhydrous $MgSO_4$, and filtered, and the volatile solvents removed by evaporation under reduced pressure in a hood. Sublimation yielded white needles, mp 69–71 °C (lit. 69.2–70.2 °C).[2] 1,2-Dihydro-5-naphthol: IR (CCl_4) -OH, br, 3600–3400; C=C, 1600 cm^{-1}. NMR δ 7.03–6.55 (br m, 4 H); 6.00 (dt, 1 H), J = 8, 4 Hz; 1.90 (br s, 1 H), 2.75 (t, 2 H), J = 8 Hz; 1.38–1.17 (br m, 2 H).

Acknowledgments. This work was supported by the National Science Foundation (MPS-73-05015-A-02). We thank Professors S. Welch and H. Rappoport for suggestions.

Registry No.—I, 60578-56-0; II, 60573-57-1; III, 39677-53-7; IV, 60573-58-2; V, 60573-59-3; VI, 30448-78-3; VII, 52178-91-3; VIII, 60573-60-6; IX, 4242-13-1; *p*-methoxyacetophenone, 100-06-1; 2-(4′-methoxyphenyl)-4-penten-2-ol, 60573-61-7; 2-anisaldehyde, 135-02-4; 1-(2′-methoxyphenyl)-3-buten-1-ol, 24165-67-1; 3-anisaldehyde, 591-31-1; 1-(3′-methoxyphenyl)-3-buten-1-ol, 24165-65-9; 4-anisaldehyde, 123-11-5; 1-(4′-methoxyphenyl)-3-buten-1-ol, 24165-60-4; 2-(4′-methoxyphenyl)-1,4-pentadiene, 60573-62-8; 1,2-dihydro-5-naphthol, 1429-22-7.

Supplementary Material Available. Plots of observed chemical shifts of protons of IV and V (2 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Small Ring Bis-Annelated Benzenes

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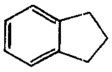
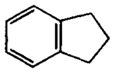
Benzocyclobutene has been prepared by a three-step route involving first the Diels–Alder addition of butadiene to dimethyl cyclobutene-1,2-dicarboxylate. The resulting diester adduct may be hydrolyzed to the corresponding dicarboxylic acid which upon treatment with 2 equiv of lead tetraacetate undergoes bisdecarboxylation and aromatization of the six-membered ring. By substituting different dienes into this scheme, a series of bis-annelated benzene isomers in which the benzene portion was fused to a four- or five-membered ring has been prepared. The ultraviolet and 100-MHz ^1H NMR spectra of these molecules have been reported. In the para-fused series, the chemical shift of the aromatic proton ortho to the fused ring is found to shift upfield with increasing strain. The shift is attributed to a perturbation of the aromatic ring current rather than to inductive effects due to rehybridization at the bridgehead carbon atoms. A shift to longer wavelength absorption in the UV is observed for the para-fused systems as compared to the meta-fused ones. The extinction coefficient is found to increase as the system becomes more symmetrical and more planar.

In 1930 Mills and Nixon proposed that the five-membered ring of indan might sufficiently distort the geometry of the benzene portion of this molecule so that Kekulé resonance form **1a** would be preferred over **1b** and thus partial double bond fixation might result.[1] Since that time these predictions have been shown to be ambiguous[2] while a theoretical treatment has even been presented which favors structure **1b** over **1a**.[3] Nevertheless, more recent calculations using the CNDO/2 technique[4] as well as an extended Hückel treatment[5] both support a preferred structure in which the bridging bond is lengthened for strained benzocycloalkenes.

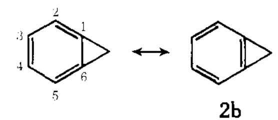


1a



1b

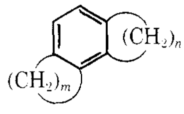
There are two fundamental devices whereby one can hope to induce bond localization in an otherwise aromatic molecule: the incorporation of steric strain and the demands of an electronic environment. The latter approach is demonstrated in molecules such as phenanthrene and triphenylene where some bond alteration in the central ring results from the fusion of two or three benzene rings meta to one another. The incorporation of steric strain into an aromatic molecule as a probe of bond localization offers the advantage of not electronically perturbing the cyclic π system. Various structural and spectroscopic studies on the benzocyclopropene[6] and benzocyclobutene system have sought to delineate any bond fixation. X-ray crystallographic data are available for naphthocyclopropene[7] and one derivative of benzocyclopropene.[8] Both studies are inconclusive in that they find the 1,2, the 5,6, and the 1,6 bonds all to be shorter than the C–C bond length of benzene (1.39 Å). Thus there appear to be three adjacent short bonds, making it difficult to say anything definite about bond localization in these systems.



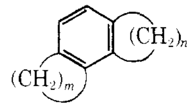
2a 2b

Efforts to delineate the effects of fusing a small ring onto the benzene nucleus have led to the presentation of a good deal of chemical, physical, and theoretical data. Vaughn has reported on the behavior of benzocycloalkenes toward electrophilic reagents.[9] Streitweiser points out the increased acidity of benzene protons ortho to a small fused ring.[10] He explains this observation by invoking substantial changes in hybridization at the bridgehead carbons. This viewpoint is corroborated by the earlier metalation studies of Finnegan.[11] Rieke has used the Streitweiser model to explain changes in half-wave reduction potentials[12] and in spin densities[13] of various fused naphthalene systems. Molecular orbital interpretations have provided reasonable correlations with possible hybridization effects.[14,15] Similar theoretical treatments have also been applied to discussions of proton[4,16] and carbon-13[17] NMR data.

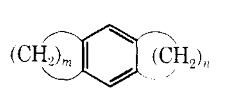
If one assumes that the fusion of a small ring onto the benzene nucleus tends to orient the double bonds such that one of the two Kekulé forms is favored, then it follows that the fusion of two small rings meta to one another would certainly enhance this effect. Thus as the size of the annelated rings is decreased, one resonance form (**3a** or **3b**) should be preferred over the other. When the two small rings are fused para to one another as in **4**, both resonance forms are identical where *m* = *n*. Any localizing effect of the fused rings must therefore cancel out.



3a



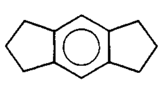
3b



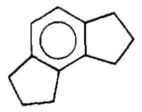
4

The triscycloalkenobenzenes where the fused rings contain from five to eight carbons have been known for some time. A study of their various physical properties has led to the conclusion that when one or more five-membered rings or three six-membered rings are fused to the benzene nucleus, one observes a considerable distortion of the ring current or magnetic anisotropy.[18] A determination of the ionization potentials, UV spectra, and charge-transfer spectra for a series of cycloalkenobenzenes, biscycloalkenobenzenes, and triscycloalkenobenzenes has aided in the investigation of the effect of strain on the π-electron sextet in the ground state as well as higher energy states.[19] In 1960, Cava and co-workers prepared benzo[1,2:4,5]dicyclobutene (**16**)[20] and an x-ray crystal structure of this molecule showed the angles of the benzene ring to be substantially perturbed while the bond lengths of the six-membered ring did not vary significantly.[21] In a preliminary report, we described the preparation of the meta-fused isomer, benzo[1,2:3,4]dicyclobutene (**18**), and pointed out some interesting differences between **16** and **18**.[22] This paper will investigate further the properties of meta and para bis-annelated benzenes.

Synthesis of Bis-Annelated Benzenes. Our synthetic objective was to prepare all the bis-annelated benzene isomers in which the benzene portion was fused to a four- or five-membered ring. Of the six possible meta and para isomers, three had been previously reported. Both benzo[1,2:4,5]dicyclopentene[23] (**5**) and benzo[1,2:3,4]dicyclopentene[24] (**6**) have been prepared by cyclizations involving Friedel–Crafts type ring closures. We successfully prepared **5** by the published route but had difficulties in the early stages of the syntheses of **6**. It was therefore decided to prepare **6** by an application of our general Diels–Alder approach. Cava and co-workers prepared benzo[1,2:4,5]dicyclobutene (**16**) by the thermal extrusion of two molecules of sulfur dioxide from the corresponding disulfone.[20] Anticipating some possible difficulties with the pyrolysis step, we chose to prepare **16** utilizing our cycloaddition route.

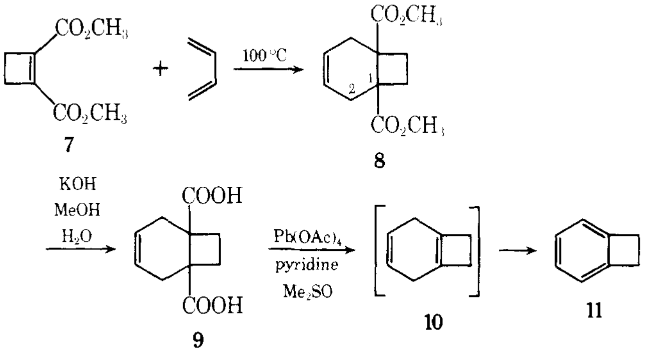


5



6

We have recently developed a new approach to the synthesis of benzocyclobutene which is proving most useful in the preparation of annelated derivatives.[25] When butadiene is sealed in a combustion tube with dimethyl cyclobutene-1,2-dicarboxylate for 2 days at 100 °C, the Diel–Alder adduct, **8**, may be obtained in 73% yield.[26] Although both ester functions in **8** are of the neopentyl type, hydrolysis to the corresponding diacid, **9**, may be readily accomplished by refluxing overnight with potassium hydroxide in aqueous methanol. Treatment of **9** with 1 equiv of lead tetraacetate in dimethyl sulfoxide containing 2 equiv of pyridine[27] gives a product which is mainly bicyclo[4.2.0]octa-1(6),3-diene (**10**) contaminated with a small amount of benzocyclobutene (**11**). If the amounts of lead tetraacetate and pyridine are doubled, a 57% yield of **11** may be obtained directly. Under similar oxidizing conditions, 1,4-cyclohexadiene was converted smoothly into benzene.



When dienes **12–15** are substituted for butadiene in the Diels–Alder sequence, the bis-annelated benzenes **16–19** can be obtained. The initial cycloadducts from **14** and **15** show a

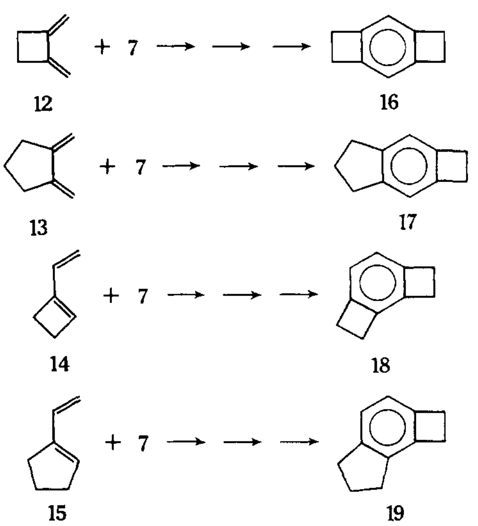
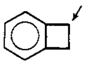
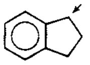
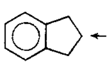
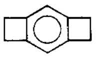
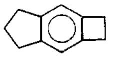
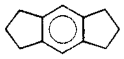
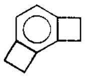
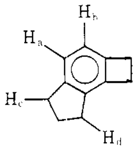
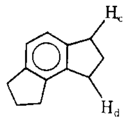
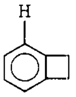
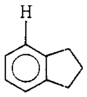
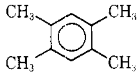
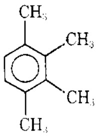
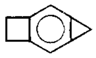


Table I

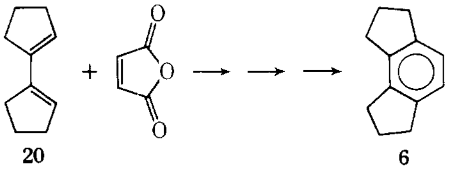
		UV absorption data, nm			¹H NMR chemical shifts, δ ($CDCl_3$)				
Compd[e]		λ_{max} (95% EtOH) (ε)			Ar–H				$J_{C(Ar)-H}$[a]
	**16**	276 (4570)	280 (5125)	286 (3890)	6.64	2.99			159.9
	**17**	276 (4070)	280 (4380)	286 (3752)	6.91	3.08	2.86	2.00	158.2
	**5**	277 (3665)	281 (3785)	287 (3797)	7.08		2.85	2.05	155.4
	**18**	266 (1360)	269 (1370)	275 (1540)	6.88	3.14			161.0
	**19**	267 (972)	271 (879)	276 (1037)	H_a 7.07 H_b 6.80	3.12	H_c 2.85 H_d 2.77	2.03	J_{CH_a} = 156.8 J_{CH_b} = 159.4
	**6**	268 (1008)	272 (870)	277 (1066)	6.95		H_c 2.82 H_d 2.74	1.99	156.9
	**11**	259 (1380)	265 (2110)	271 (2070)	6.76[b]	3.17			162[c]
	**1**	259 (889)	266 (1224)	273 (1357)	7.07[b]		2.90	2.04	155.5[c]
	**21**	268 (712)	273 (654)	278 (727)	6.90		CH_3 2.19		154.0
	**22**	267 (301)	272 (244)	276 (235)	6.88		1,4-CH_3 2.24 2,3-CH_3 2.17		156.1
	**23**[d]	284 (1000)	287.5 (1000)	294 (631)	6.85	3.08			

[a] In hertz, experimental error ±1.0 Hz. [b] Reference 17. [c] Reference 34. [d] Reference 31. [e] Registry no. are, respectively, 1610-51-1, 60582-10-7, 495-52-3, 58436-35-4, 50582-11-8, 1076-17-1, 694-87-1, 496-11-7, 95-93-2, 488-23-3, 57867-58-0.

mixture of two products by VPC and NMR. This product mixture could be explained by competing exo and endo modes of Diels–Alder addition which should provide a molecule which is epimeric at the tertiary carbon, C-2. This mixture could be carried through the sequence and had apparently no serious influence on any of the subsequent steps. The hydrocarbon products were readily purified by column chromatography on silica gel by elution with ether–hexane.

Dienes 12 and 13 were prepared by established procedures.[28] We have recently reported the synthesis of 1-vinylcyclobutene (**14**).[22] The addition of vinylmagnesium bromide to cyclobutanone provided 1-vinylcyclobutanol in 66% yield. When this alcohol was heated in the presence of a small amount of iodine crystals, dehydration occurred and 1-vinylcyclobutene was distilled from the mixture in 72% yield. In a similar manner, we have prepared 1-vinylcyclopentene.

Benzo[1,2:3,4]dicyclopentene (**6**) was synthesized by the addition of 1,1′-dicyclopentenyl (**20**) to maleic anhydride,[29]



20 **6**

followed by hydrolysis, decarboxylation, and aromatization under the conditions previously described.

Properties of Bis-Annelated Benzenes. In Table I are compiled some of the spectral properties of the series of bis-annelated benzenes and several related model compounds.

The ¹H NMR chemical shifts were assigned without difficulty. For all molecules except **19** the aromatic peak appeared as a singlet. For **19** an AB quartet was observed with $J = 7.5$ Hz in good agreement with similar ortho couplings.[16] The upfield doublet was assigned to the proton ortho to the four-membered ring based on a recent reassignment of the chemical shifts of benzocyclobutene.[17] The downfield doublet corresponds well with the analogous resonance of indan.

Whether or not the molecule was symmetrical, the cyclobutene ring protons in all cases appeared as a sharp singlet. In the meta-fused cyclopentene systems, however, two overlapping triplets were observed for the benzylic protons in the five-membered ring. The downfield triplet was assigned to the less hindered exterior methylene in accordance with observations made for prehnitene (**22**).[30] In all cases the coupling between cyclopentene methylene protons was 7–7.5 Hz.

A significant trend is evidenced for the aromatic chemical shift of the para-fused series: **16, 17, 5.** With increasing strain the signal moves to higher field, in good accord with assignments for benzocyclobutene and indan. The recently prepared cyclopropa[4,5]benzocyclobutene (**23**) does not correlate with this trend, exhibiting an aromatic resonance at δ 6.85.[31] In the light of observations by other groups,[16,17] this inconsistency is not unexpected. Consider, for example, the ortho proton of benzocyclopropene which appears at δ 7.15, considerably downfield from what one might expect based only on strain arguments.

It is well known that as the number of alkyl substituents on a benzene ring is increased, the chemical shift of the aromatic protons moves to higher field as a result of shielding due to simple inductive effects.[32] These shifts are also influenced by distortions of the benzene ring geometry caused by steric interactions between the substituent groups. In the series **16**, **17**, **5**, the inductive effect of the fused rings should remain nearly constant.

A theory has been put forth to explain the enhanced acidity of the aryl positions adjacent to a fused strained ring.[11] It is claimed that for bridgehead carbons "the atomic orbitals used to construct the strained ring have higher p character. Hence, the remaining orbital has higher s character. The ortho-carbon is thus bound to an orbital of higher electronegativity". As the size of the fused ring is decreased the electronegativity of this ortho carbon should increase. The expected effect of this would be to decrease shielding of the attached proton, shifting the resonance to lower field. What is observed for the series **16**, **17**, **5** as well as for indan and benzocyclobutene is instead a shift to *higher field*.

A sensitive probe of hybridization is the ^{13}C–H coupling constant. Increase in this coupling constant may be taken as an indication of increasing s character of the carbon orbital used in forming the bond.[33] In Table I are recorded the values of $J(^{13}\text{C–H})$ measured by examining the carbon-13 satellites of the aromatic peak in the ^{1}H NMR spectra. For the series of compounds **16**, **17**, **5** as well as the series **18**, **19**, **6** the coupling constant is seen to increase as the size of the fused rings decreases. This observation lends support to the above argument for rehybridization with increasing s character of the ortho C–H bond. There still exists, however, an apparent dichotomy in the correlation between increased shielding at the ortho carbon and increase in $J(^{13}\text{C–H})$. This inconsistency has been pointed out by Günther[34] and more recently by Kitching.[17]

The NMR behavior of strained benzocycloalkenes can be explained by postulating that two electronic effects are operating simultaneously. It has been well documented that there is a localized electronegativity effect which seemingly results from changes in hybridization of the aromatic carbon atoms due to increasing strain.[10–15] The increased shielding of the aromatic protons, however, may be caused by a perturbation of the ring current resulting in a decrease in the diamagnetic anisotropy of the molecule. It is noteworthy that the position of fusion of two small rings to the benzene nucleus is of importance in determining the magnitude of this effect. In the most strained examples of **16** and **18**, the deshielding is more pronounced for the para-fused isomer. In the higher homologues, however, this difference is less well defined and even reversed for **5** and **6**.

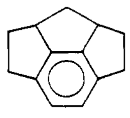
These same two opposing effects are reflected to a lesser degree in the chemical shifts of the benzylic protons. As expected, the cyclobutenyl protons resonate at lower field than the cyclopentenyl ones since they are bonded by orbitals having more s character. Anisotropic deshielding effects are much less strongly felt at benzylic positions owing to the increased distance of the protons from the aromatic ring. Nevertheless the decrease in the cyclobutenyl chemical shift for the series **11**, **17**, **16** is in line with increased shielding which might result from partial disruption of the aromatic ring current. Once again the meta isomers appear to be less sensitive to this sort of anisotropic perturbation.

For the ethanol solution ultraviolet spectra of the compounds listed in Table I, a broad absorption band may be observed in which at least three vibrational bands can be detected. The λ_{max} and extinction coefficients for these bands have been recorded and two important trends are evidenced.

In considering durene (**21**) and prehnitene (**22**), the λ_{max} are very similar indicating that for unstrained systems the substitution pattern of 1,2,3,4 vs. 1,2,4,5 has little influence on the electronic properties of the molecule. The meta-fused isomers **18**, **19**, and **6** all correspond well with the tetramethylbenzenes. For the para-fused isomers, however, a consistent shift of 9–11 nm to longer wavelength is observed. Such shifts previously have been attributed to increased strain. Our data indicate that it is the position at which this strain is introduced into the benzene ring which is critical in perturbing the electronic nature of the molecules. From the longest wavelength 0–0 band, it can be deduced that the energy separation between the ground and first excited state of para-fused benzenes is less (~3.5 kcal/mol) than that for meta-fused benzenes. Such a difference may be due to a less stable ground state or a more stable excited state. Again the data for **23** are out of line with its higher homologues with the shift being in the direction of still longer wavelength.

The extinction coefficients for durene are 2–3 times greater than those for prehnitene. A similar increment is observed when comparing para- to meta-fused bis-annelated benzenes. An increment in extinction coefficient is also observed as the size of the fused rings is decreased. Such changes have often been associated with increased strain.

We have suggested that increased strain in the series **5**, **17**, **16** may perturb the magnetic anisotropy of the aromatic ring. It is not evident, however, that such strain should directly influence the allowedness of an electronic transition (ϵ). Arnold has put forth an explanation for the higher extinction coefficient of indan over tetralin.[35] He claims that out-of-plane vibrations in the less planar tetralin system provide for poorer overlap between electronic states leading to a less likely transition. Thus the magnitude of the extinction coefficient is more strongly linked to the planarity of the ground state than to the strain inherent in the molecule. The case is well illustrated by comparing **6** (ϵ 1066) with the much more highly strained **24** (ϵ 470).[24,36] The lower extinction coefficient for **24** can be explained by the lack of planarity or puckered conformation imposed by the additional fused ring.[37]



24

Experimental Section

Dimethyl sulfoxide was distilled under vacuum from lithium aluminum hydride. Pyridine was distilled from barium oxide. Just prior to use, lead tetraacetate was recrystallized from acetic acid and dried under vacuum, protected from oxygen and light. Proton magnetic resonance spectra were obtained on a Varian Associates T-60 or XL-100[38] spectrometer and chemical shifts are reported in parts per million downfield from Me_4Si. Infrared spectra were obtained on a Beckman IR-4250 spectrometer. Ultraviolet spectra were obtained on a Cary 14 spectrometer. All melting points are uncorrected.

Dimethyl Bicyclo[4.2.0]oct-3-ene-1,6-dicarboxylate (8). In a heavy wall glass tube were placed 3.93 g (0.023 mol) of dimethyl cyclobutene-1,2-dicarboxylate (**7**),[39] 0.04 g of hydroquinone, and 6 ml (excess) of condensed butadiene. The tube was sealed and heated in an oil bath to 100 °C for 48 h. The tube was then cooled and opened and the crude product was flash distilled to provide 3.76 g (73%) of **8**, bp 67–69 °C (0.03 mm): NMR (CCl_4) δ 5.98 (d of d, 2 H, C=CH–), 3.60 (s, 6 H, CO_2CH_3), 2.6–2.1 (m, 6 H), and 1.7 ppm (m, 2 H); IR (thin film) 2930, 1705, 1410, 1130, 1095, 1065 and 985 cm^{-1}.

Bicyclo[4.2.0]oct-3-ene-1,6-dicarboxylic Acid (9). To a solution of 3.66 g (15.9 mmol) of diester **8** in 55 ml of methanol was added a solution of 5.6 g (0.10 mol) of potassium hydroxide in 5 ml of water. The mixture was refluxed overnight, poured into 200 ml of water, and acidified with concentrated hydrochloric acid. The aqueous solution was extracted with ether and the extracts were dried over sodium sulfate. Filtration, removal of solvent, and drying under vacuum provided 2.48 g (80%) of the diacid **9**, mp 149–151 °: NMR (Me_2SO-d_6) δ 11.5 (broad s, 2 H, COOH), 6.0 (m, 2 H, C═CH–), 2.6–2.1 (m, 6 H), and 1.8 ppm (m, 2 H); IR (KBr) 2950, 1708, 1410, 1300, 1254, 1152, and 1095 cm^{-1}.

Bicyclo[4.2.0]-octa-1(6),3-diene (10). To a solution of 0.196 g (1.0 mmol) of **9** and 0.158 g (2.0 mmol) of freshly distilled pyridine in 5 ml of dry Me_2SO under nitrogen was added 0.488 g (1.1 mmol) of lead tetraacetate. An exothermic reaction was observed and the reaction mixture was stirred at room temperature for 3 h. The mixture was then poured into 15 ml of water and extracted five times with ether. The ether solution was dried over potassium carbonate and filtered, and the solvent removed on the rotary evaporator to afford 40.3 mg of crude product. Analysis by VPC (10 ft × 0.25 in 10% Carbowax 6000 on Chromosorb W 60/80 at 113 °C and 30 ml/min) showed **10** at 8.4 min (77%) and benzocyclobutene (**11**) at 12.2 min (23%). The assignments were verified by NMR (CCl_4) δ 7.0 (m, ArH of **11**), 5.65 (s, C═CH of **10**), 3.15 (s, $ArCH_2$ of **11**), and 2.50 ppm, (s, allylic CH_2 of **10** which are coincidently equivalent).

Benzocyclobutene (11). To a solution of 1.96 g (10 mmol) of **10** and 3.16 g (40 mmol) of pyridine in 30 ml of dry Me_2SO under nitrogen was added 9.76 g (22 mmol) of lead tetraacetate. An exothermic reaction was observed with considerable gas evolution. The temperature was maintained at 35 °C with ice bath cooling. After stirring for 3.5 h, the reaction mixture was poured into 120 ml of water and extracted five times with ether. The ether solution was dried over potassium carbonate and filtered, and the solvent removed on the steam bath by distillation through a Vigreux column. Bulb-to-bulb distillation of the residue afforded 0.591 g (57%) of **11** which showed a single major peak by VPC (10 ft × 0.25 in Carbowax 6000 on Chromosorb W 60/80 at 125 °C and 30 ml/min): NMR (CCl_4) δ 6.96 (m, 4 H) and 3.14 ppm (s, 4 H); IR (thin film) 2925, 1745, 1463, 1440, 1117, and 785 cm^{-1}.

1-Vinylcyclobutanol. Vinylmagnesium bromide was generated according to the procedure of Seyferth.[40] A dry, three-neck, 250-ml flask under a nitrogen atmosphere was equipped with a mechanical stirrer, dry ice condenser, and small addition funnel. The apparatus was charged with 7.29 g (0.30 mol) of magnesium metal and 25 ml of dry THF. In the addition funnel was placed a solution of 37.5 g (0.350 mol) of vinyl bromide in 75 ml of dry THF and about 2 ml of this solution was added to the flask with very rapid stirring to initiate the reaction. After initiation, the remaining vinyl bromide was added slowly to maintain a gentle reflux. Once all the magnesium had been consumed, the mixture was cooled to 35 °C and a solution of 14.0 g of cyclobutanone in 30 ml of dry THF was added slowly. The dry ice condenser was replaced by a normal condenser and the solution was refluxed for 90 min. After the flask was cooled to 35 °C, 40 ml of saturated ammonium chloride was added dropwise with additional cooling and vigorous stirring to effect hydrolysis of the magnesium salts. These salts were collected by suction filtration and washed well with anhydrous ether. The combined filtrate was dried over magnesium sulfate and filtered and the solvent removed on the rotary evaporator. Distillation afforded 12.89 g (66%) of 1-vinylcyclobutanol: bp 67–68 °C (45 mm) [lit.[41] bp 49–50 °C (15 mm)]; NMR (CCl_4) δ 6.3–4.9 (ABX pattern, 3 H, CH_2═CH–), 4.0 (broad s, 1 H, OH), and 2.2–1.4 ppm (m, 6 H, –CH_2–); IR (thin film) 3360, 2290, 1246, 1150, and 920 cm^{-1}.

1-Vinylcyclobutene (14). In a 15-ml round-bottom flask were placed 6.45 g (0.066 mol) of 1-vinylcyclobutanol and 0.40 g of iodine crystals. The mixture was distilled at atmospheric pressure with magnetic stirring through a Claisen-type distillation head equipped with a 3-in. Vigreux section. After removal of water from the distillate, VPC analysis (Carbowax 20M, 70 °C) showed about 30% unreacted alcohol. This diene–alcohol mixture (4.73 g) was combined with 0.20 g of iodine crystals and redistilled through the same stillhead to afford 3.78 g (72%) of 1-vinylcyclobutene which showed only a single peak by VPC: bp 82 °C (760 mm); NMR (CCl_4) δ 6.5–4.9 (ABX pattern, 3 H, CH_2═CH–), 5.83 (m, 1 H, C═CH), and 2.5 ppm (m, 4 H, –CH_2–); IR (thin film) 3045, 2920, 1574, 984, 903, 846, and 767 cm^{-1}.

Bis-annelated benzenes were prepared following the procedures described above for benzocyclobutene. Details concerning amounts of reagents, yields, and physical properties of the intermediates and final products are given below.

Benzo[1,2:4,5]dicyclobutene (16). The reaction of 3.16 g (0.04 mol) of 1,2-dimethylenecyclobutane[28a] with 6.48 g (0.04 mol) of **7** at 80 °C for 20 h gave a product which appeared to contain a good deal of polymer. The ether-soluble portion was chromatographed on 60/200 mesh silica gel eluting with 5:95 ether/petroleum ether to provide 1.58 g (16%) of solid diester adduct, mp 137–142 °C: NMR (CCl_4) δ 3.66 (s, 6 H, CO_2CH_3), 2.6–2.0 (m, 10 H), and 1.7 ppm (m, 2 H); IR (thin film) 2878, 2864, 1742, 1436, 1288, 1125, and 1094 cm^{-1}. Hydrolysis of 1.46 g (5.8 mmol) of the diester with 2.28 g (40 mmol) of KOH in 2 ml of water and 30 ml of methanol provided 1.21 g (93%) of the corresponding dicarboxylic acid,[42] mp 86–89 °C: NMR (Me_2SO-d_6) δ 2.5 (broad s, 4 H, cyclobutenyl H), 2.3 (m, 6 H), and 1.7 ppm (m, 2 H); IR (KBr) 3000, 1710, 1405, 1332, and 1290 cm^{-1}. Treatment of 1.11 g (5.0 mmol) of the dicarboxylic acid with 4.88 g (11 mmol) of lead tetraacetate in 20 ml of dry Me_2SO containing 1.20 g (15 mmol) of pyridine afforded 0.40 g (60%) of crude **16**, mp 90–95 °C. Recrystallization from methanol gave a pure sample of **16**: mp 100–101 °C (lit.[24] mp 101 °C); NMR ($CDCl_3$) δ 6.64 (s, 2 H, ArH) and 2.99 ppm (s, 8 H); IR (KBr) 2930, 1451, 1308, 1215, and 875 cm^{-1}; UV (95% ethanol) 276 nm (ϵ 4570), 280 (5125), and 286 (3890).

4,5-Cyclopentenobenzocyclobutene (17). The reaction of 3.16 g (0.034 mol) of 1,2-dimethylenecyclopentane[28b] with 5.71 g (0.034 mol) of **7** at 80 °C for 20 h gave 3.97 g (45%) of the Diels–Alder adduct after chromatography on 100 g of 60/200 mesh silica gel, eluting with 1:3 ether/hexane: NMR (CCl_4) δ 3.65 (s, 6 H, CO_2CH_3), 2.6–2.1 (m, 14 H), and 1.5 ppm (m, 2 H); IR (thin film) 2855, 1725, 1440, 1325, and 1270 cm^{-1}. Hydrolysis of 3.40 g (12.8 mmol) of the diester with 5.8 g (102 mmol) of KOH in 4 ml of water and 50 ml of methanol provided 2.55 g (85%) of the corresponding dicarboxylic acid,[42] mp 145–150 °C: NMR (Me_2SO-d_6) δ 2.5 (m, 4 H), 1.9 (m, 2 H), and 1.55 ppm (m, 2 H); IR (KBr) 3000, 1730, 1424, 1295, 1177, and 900 cm^{-1}. Treatment of 1.18 g (5 mmol) of the dicarboxylic acid with 4.88 g (11 mmol) of lead tetraacetate in 20 ml of dry Me_2SO containing 1.98 g (25 mmol) of pyridine afforded 0.148 g (20%) of **17** after chromatography on silica gel eluting with hexane, mp 32–33 °C: NMR ($CDCl_3$) δ 6.91 (s, 2 H, ArH), 3.08 (s, 4 H), 2.86 (d of t, 4 H) and 2.00 ppm (quintet, 2 H); IR (thin film) 2960, 2930, 1475, 1331, 1210, and 875 cm^{-1}; UV (95% ethanol) 276 nm (ϵ 4070), 280 (4380), and 286 (3752).

Benzo[1,2:3,4]dicyclobutene (18). The reaction of 2.21 g (27.6 mmol) of 1-vinylcyclobutene with 4.70 g (27.6 mmol) of **7** at 110 °C for 13 h gave a crude product which upon analysis by VPC (5 ft × 0.25 in. 1.5% OV-101 on Chromosorb G 100/120 at 180 °C and 30 ml/min) showed very little starting material and two unresolved peaks at longer retention time. This material was chromatographed on 230 g of 60/200 mesh silica gel, eluting with 1:3 ether/hexane, to provide 4.15 g (60%) of the Diels–Alder adduct: NMR (CCl_4) δ 5.5 (m, 1 H, C═CH), 3.64 (s, 3 H, CO_2CH_3), 3.62 (s, 3 H, CO_2CH_3), and 2.8–1.4 ppm (m, 11 H); at 100 MHz the singlet at 3.62 ppm was resolved into two lines; IR (thin film) 2960, 1745, 1736, 1440, and 1126 cm^{-1}. Hydrolysis of 4.00 g (16 mmol) of the diester with 5.6 g (100 mmol) of KOH in 5 ml of water and 50 ml of methanol provided 3.07 g (86%) of the corresponding dicarboxylic acid:[42] NMR (Me_2SO-d_6) δ 9.77 (broad s, 2 H, COOH), 5.60 (m, 1 H, C═CH), and 3.3–1.5 ppm (m, 11 H); IR (KBr) 3000, 1705, 1412, 900, and 414 cm^{-1}. Treatment of 1.11 g (5 mmol) of the dicarboxylic acid with 4.88 g (11 mmol) of lead tetraacetate in 20 ml of dry Me_2SO containing 1.98 g (25 mmol) of pyridine afforded 70 mg of product after chromatography on 38 g of silica gel eluting with 1:4 ether/hexane. This material was shown to be 50% pure by VPC (10 ft × 0.125 in 10% Carbowax 20M on Chromosorb W 60/80 at 100 °C and 30 ml/min). Pure **18** was isolated by preparative VPC, mp 36–36.5 °C: NMR ($CDCl_3$) δ 6.88 (s, 2 H, ArH) and 3.14 ppm (s, 8 H); IR (thin film) 3030, 2972, 2928, 1447, 1423, 1248, and 823 cm^{-1}; UV (95% ethanol) 266 nm (ϵ 1360), 269 (1370), and 275 (1540); mass spectrum (70 eV) *m/e* (rel intensity) 130 (100), 129 (44), 128 (36), 115 (49), and 51 (17). Anal. Calcd for $C_{10}H_{10}$: *m/e* 130.0783. Found: *m/e* 130.0782.

3,4-Cyclopentenobenzocyclobutene (19). The reaction of 5.5 g (0.058 mol) of 1-vinycyclopentene with 7.14 g (0.042 mol) of **7** at 80 °C for 12 h gave 6.69 g (60%) of the Diels–Alder adduct after chromatography on silica gel, eluting with 1:9 ether/hexane: NMR (CCl_4) δ 5.75 (m, 1 H, C═CH), 3.66 (s, 6 H, CO_2CH_3), and 2.9–1.4 ppm (m, 14 H); IR (thin film) 2880, 2825, 1745, 1440, 1240, and 790 cm^{-1}. Hydrolysis of 6.51 g (0.024 mol) of the diester with 7.5 g (0.134 mol) of KOH in 6 ml of water and 35 ml of methanol provided 5.52 g (97%) of the corresponding dicarboxylic acid:[42] NMR (Me_2SO-d_6) δ 10.0 (broad s, 2 H, COOH), 5.8 (m, 1 H, C═CH), and 2.7–1.1 ppm (m, 14 H); IR (KBr) 2960, 1700, 1440, 1410, and 1300 cm^{-1}. Treatment of 5.2 g (0.022 mol) of the dicarboxylic acid with 19.5 g (0.044 mol) of lead tetraacetate in 75 ml of dry Me_2SO containing 7.66 g (0.097 mol) of pyridine afforded 4.52 g of crude product which was determined to be 8.3% pure by VPC (8 ft × 0.25 in. 10% Carbowax 20M on Chromosorb W60/80 at 135 °C and 30 ml/min) giving an overall yield of

12%. Chromatography on silica gel eluting with hexane provided a pure sample of **19:** NMR ($CDCl_3$) δ 7.07 (d, 1 H, J = 7.5 Hz), 6.80 (d, 1 H, J = 7.5 Hz), 3.12 (s, 4 H), 2.85 (t, 2 H), 2.77 (t, 2 H), and 2.03 ppm (quintet, 2 H); IR (thin film) 2950, 2860, 1465, 1448, 1432, 1312, 1243, 1230, and 813 cm^{-1}; UV (95% ethanol) 267 nm (ϵ 972), 271 (879), and 276 (1037).

Benzo[1,2:3,4]dicyclopentene (6). The reaction of 12.3 g (0.092 mol) of 1,1′-dicyclopentenyl[43] with 9.0 g (0.092 mol) of maleic anhydride at 75 °C for 12 h gave an essentially quantitative yield of the Diels–Alder adduct. A sample recrystallized from hexane gave mp 102–103 °C (lit.[29] mp 102–103 °C). Hydrolysis of the diester with 41.1 g (0.73 mol) of KOH in 75 ml of water and 250 ml of methanol gave 20.89 g (90%) of the corresponding dicarboxylic acid, mp 198–208 °C: NMR (Me_2SO-d_6) δ 12.0 (broad s, 2 H) and 3.2–1.4 ppm (m, 16 H); IR (KBr) 3040, 2960, 1710, 1425, 1245, and 423 cm^{-1}. Treatment of 20.0 g (0.08 mol) of diacid with 78.0 g (0.176 mol) of lead tetraacetate in 200 ml of dry Me_2SO containing 27.8 g (0.352 mol) of pyridine afforded 1.57 g (12%) of **6** after chromatography on silica gel eluting with 3:7 ether/petroleum ether, mp 39–40 °C (lit.[24] mp 40–42 °C: NMR ($CDCl_3$) δ 6.95 (s, 2 H, ArH), 2.82 (t, 4 H), 2.74 (t, 4 H), and 1.99 ppm (quintet, 4 H); IR (thin film) 2960, 2900, 1470, 1315, 1200, and 800 cm^{-1}; UV (95% ethanol) 268 nm (ϵ 1008), 272 (870), and 277 (1066).

Benzo[1,2:4,5]dicyclopentene (5). The procedure of Arnold and co-workers[23] was followed. Starting with 23.6 g (0.2 mol) of indan, 7.05 g (25% overall yield) of **5** was obtained, mp 53–55 °C (lit.[23] mp 52–54 °C): NMR ($CDCl_3$) δ 7.08 (s, 2 H, ArH), 2.85 (t, 8 H), and 2.05 ppm (quintet, 4 H); IR (KBr) 2920, 1485, 1440, 1320, 1210, and 865 cm^{-1}; UV (95% ethanol) 277 nm (ϵ 3665), 281 (3785), and 287 (3797).

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Registry No.—**7,** 1128-10-5; **8,** 37490-84-9; **9,** 60582-12-9; **10,** 38325-66-5; **12,** 14296-80-1; **13,** 20968-70-1; **14,** 58436-36-5; **15,** 28638-58-6; **20,** 934-02-1; butadiene, 106-99-0; vinyl bromide, 593-60-2; cyclobutanone, 1191-95-3; 1-vinylcyclobutanol, 17202-79-8; tricyclo[6.2.0.0$^{3.6}$]dec-1(8)-ene-3,6-dicarboxylate dimethyl ester, 60582-13-0; tricyclo[6.2.0.0$^{3.6}$]dec-1(8)-ene-3,6-dicarboxylic acid, 60582-14-1; tricyclo[6.3.0.0$^{3.6}$]undec-1(8)-ene-3,6-dicarboxylate dimethyl ester, 60582-15-2; tricyclo[6.3.0.0$^{3.6}$]undec-1(8)-ene-3,6-dicarboxylic acid, 60582-16-3; tricyclo[6.2.0.0$^{4.7}$]dec-1-ene-4,7-dicarboxylate dimethyl ester, 58436-37-6; tricyclo[6.2.0.0$^{4.7}$]dec-1-ene-4,7-dicarboxylic acid, 58436-38-7; tricyclo[6.3.0.0$^{4.7}$]undec-1-ene-4,7-dicarboxylate dimethyl ester, 60582-17-4; tricyclo[6.3.0.0$^{4.7}$]undec-1-ene-4,7-dicarboxylic acid, 60582-18-5; maleic anhydride, 108-31-6; tricyclo[7.3.0.0$^{4.8}$]dodec-8-ene-2,3-dicarboxylate dimethyl ester, 60619-05-8; tricyclo[7.3.0.0$^{4.8}$]dodec-8-ene-2,3-dicarboxylic acid, 60582-19-6; indan, 496-11-7.

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