cyclobutene were prepared according to the method of Raasch, *et al.*[14]

A solution of 26 g. (0.46 mole) of potassium hydroxide in 100 ml. of ethanol was added dropwise to 80 g. (0.45 mole) of 1,4-dichloro-3,3,4-trifluorocyclobutene in 100 ml. of ethanol in a 500-ml. three-neck flask fitted with a reflux condenser, stirrer, and dropping funnel. During the addition, the reaction flask was cooled to 0° in an ice bath. A white precipitate of potassium chloride formed throughout the course of the addition. After the addition was complete, the reaction was stirred for 3 hr. The ethanol solution was washed several times with cold water. The crude product was dried over anhydrous magnesium sulfate and distilled to yield 78.5 g. (92% conversion) of 1-chloro-4-ethoxy-3,3,4-trifluorocyclobutene; b.p. 108.5°/628 mm.; $n^{25}\mathrm{D}$ 1.3838.

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Condensed Cyclobutane Aromatic Compounds. XXIV. The Mechanism of Thermal Rearrangement of the Linear Benzocyclobutadiene Dimer: Synthesis of 9,10-Benzocyclobutenoanthracene[1]

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The thermal isomerization of the linear benzocyclobutadiene dimer to 1,2,5,6-dibenzocycloöctatetraene proceeds *via* a two-stage process. The initial *o*-quinodimethane type intermediate has been intercepted in the form of adducts with several dienophiles. The *p*-benzoquinone adduct has been transformed into a hydrocarbon which is identical with the direct adduct of anthracene with benzocyclobutadiene.

It has been reported that the linear benzocyclobutadiene dimer (I)[3] undergoes rearrangement to 1,2,5,6-dibenzocycloöctatetraene (II) on heating for several hours at 150–155°, or even during the slow determination of its melting point (133°).[4,5]

The path originally envisaged[4,5] for this reaction involved the concerted cleavage of the two central benzocyclobutenoid bonds of I to give isomer II directly. An alternative two-step mechanism would consist of cleavage of one of the benzocyclobutene systems of I to give an unstable *o*-quinoid intermediate (III), followed by rearrangement of III to the octatetraene II. Confirmation of this latter mechanism now has been obtained by the trapping of the transient intermediate III by various dienophiles.[6] The trapping of *o*-quinoid intermediates in this manner has ample analogy in a number of other recent investigations.[7]

Three Diels–Alder adducts (IV, V, and VI) were prepared by heating dibenzotricycloöctadiene (I) with solutions of maleic anhydride, N-phenylmaleimide, and *p*-benzoquinone, respectively. It was found that the additions occurred slowly even at temperatures as low as 80–110°. In the reaction with benzoquinone, which was studied the most carefully, it was found that in boiling toluene (110°) and in the presence of about four equivalents of benzoquinone, adduct VI was obtained in 47% yield along with a 37% yield of dibenzocycloöctatetraene (II). Clearly, it appears that the intramolecular rearrangement of III to II occurs so readily that this process competes favorably with the bimolecular reaction of III with the quinone.[8] The Diels–Alder products of III have been assigned tentatively the configurations resulting from maximum overlap of the intermediates in the transition state (Alder rule), as shown in Chart I.

Although the thermal decomposition of benzocyclobutene[9] and the naphthocyclobutenes[10] to *o*-quinoid hydrocarbons, as evidenced by adduct formation, has been observed at high temperatures (200° and above) benzocyclobutene itself is known to be quite stable at 150°.[11] On the other hand, 1,2-diphenylbenzocyclobutene reacts slowly with maleic anhydride even at room temperature[12]; the ease of ring cleavage in this unusual case may most likely be attributed to resonance stabilization of the open quinomethane form by the phenyl groups. Indeed, the recently reported hydrocarbon VII has been isolated as the stable quinoid structure[7c] rather than as a closed benzocyclobutene derivative (VIIa), undoubtedly because *the fusion of an additional small ring to the four-membered ring of benzocyclobutene destabilizes the benzocyclobutenoid form relative to the corresponding open o-quinoid form.* The ready thermolysis of dibenzotricycloöctadiene may be viewed as another example of this principle, since

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[2] Alfred P. Sloan Fellow, 1958–1962.

[3] 3,4,7,8-Dibenzotricyclo$[4.2.0.^{2,5}]$octadiene-3,7.

[4] M. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 257 (1959).

[5] M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).

[6] Similar results and conclusions have been reached concerning this reaction in another independent study: M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, in press. We thank Professor Nenitzescu for his friendly communication of these results to us prior to publication.

[7] For example, see: (a) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959); (b) I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1795 (1960); (c) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

[8] (a) A related set of competing reactions involving diphenyl-*o*-quinodimethane and 1,4-naphthoquinone has been recorded: M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960). (b) The possibility that the octatetraene II is in equilibrium with the closed quinoid form III was discounted by refluxing II overnight in benzene with N-phenylmaleimide, when II was recovered quantitatively. Under these conditions (see Experimental), I gives an adduct.

[9] F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, **15** (1962).

[10] M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).

[11] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

[12] F. R. Jensen and W. E. Coleman, *ibid.*, **80**, 6149 (1958).

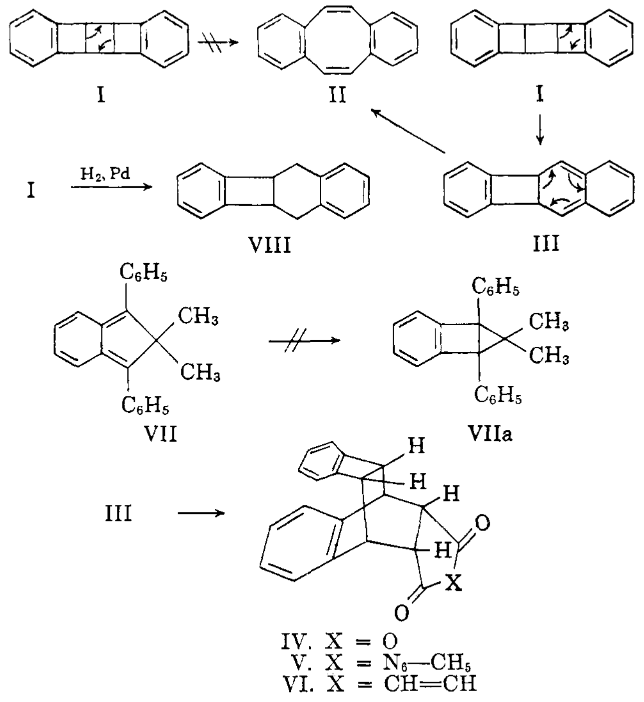
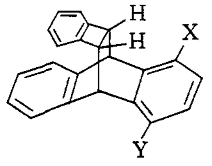


CHART I

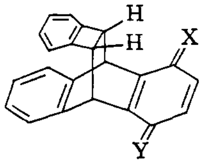
the presence of the central cyclobutane ring in I adds considerable additional strain to the two benzocyclobutenoid units of the molecule. Further evidence of this strain in I was observed when it was found that I underwent hydrogenolysis at room temperature in the presence of palladium to give 5,5a,9b,10-tetrahydrobenzo[*b*]biphenylene (VIII),[13] m.p. 130–131°. Under these conditions benzocyclobutene itself does not undergo hydrogenolysis.[14]

Since, as a result of the studies outlined above, benzoquinone adduct VI was readily available, the conversion of VI into 9,10-benzocyclobutenoanthracene (IX) was investigated. The route first attempted was analogous to the original classic synthesis of trypticene from the benzoquinone–anthracene adduct.[15] Adduct VI was aromatized by acid to the corresponding hydroquinone X, which was oxidized directly in excellent yield to the yellow quinone XI by chromic acid in the form of Jones Reagent.[16] Many unsuccessful attempts were made to convert quinone XI to hydrocarbon IX *via* a characterizable dioxime (XII) and diamine (XIII). In one such sequence (see Experimental section) quinone XI reacted with hydroxylamine hydrochloride in ethanol to give, in good yield, a green crystalline substance tentatively assigned the structure XIV.[17] The amorphous residue from this reaction, when subjected to further oximination, followed by reduction, diazotization, and deamination gave a very small quantity of a hydrocarbon, m.p. 167–170°, having the correct composition for IX. A far better synthesis of this same hydrocarbon was found in the sodium borohydride reduction of adduct VI to an apparently homogeneous diol (XV) in 94% yield, followed by dehydration of diol XV to IX (25% yield) with phosphorus trichloride in phosphorus oxychloride. Two syntheses of trypticene by similar routes have been reported[18,19] starting from the benzoquinone–anthracene adduct.

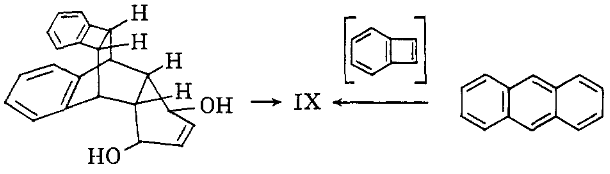
When attempts were made to generate benzocyclobutadiene in the presence of anthracene at room temperature, only the usual "angular" benzocyclobutadiene dimer was isolated. The desired Diels–Alder reaction took place, however, in refluxing dimethylformamide. The 9,10-benzocyclobutenoanthracene obtained in this manner in 33% yield was identical with the hydrocarbon, m.p. 167–170°, described above. The synthesis of IX from entirely unrelated precursors thus provides confirmation for the proposed structures of the adducts of dibenzotricycloöctadiene.



IX. X = Y = H
X. X = Y = OH
XIII. X = Y = NH_2
XIV. X = NO; Y = OEt



XI. X = Y = O
XII. X = Y = NOH



XV

Experimental[20]

Adduct of Dibenzotricycloöctadiene with Maleic Anhydride (IV).—A solution of hydrocarbon I (0.204 g.) and maleic anhydride (1.0 g.) in toluene (1 ml.) was heated on the steam bath for 12 hr. After evaporation of the solvent and removal of excess maleic anhydride by sublimation, the crude adduct (0.261 g.) was crystallized from methanol to give the pure product (0.141 g., 47%), m.p. 255–256°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.01; H, 4.60.

Adduct of Dibenzotricycloöctadiene with N-Phenylmaleimide (V).—A solution of hydrocarbon I (0.104 g.) and N-phenylmaleimide (0.87 g.) in benzene (1 ml.) was heated on the steam bath for 10 hr. After evaporation of the benzene, the residue was crystallized from cyclohexane–petroleum ether to yield colorless crystals (0.066 g., 35%), m.p. 255–256°.

Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.86; H, 5.29; N, 3.82.

Adduct of Dibenzotricycloöctadiene with *p*-Benzoquinone (VI). A solution of hydrocarbon I (7.00 g.) and sublimed *p*-benzoquinone (15 g.) in toluene (80 ml.) was refluxed for 5 hr. After cooling, the product was precipitated by the addition of methanol, filtered, and dried. Excess benzoquinone was removed by washing with a large quantity of hot water. Partial sublimation of the dried residue at 100° *in vacuo* removed dibenzocycloöctatetraene (2.60 g., 37%). The remaining adduct (5.01 g., 47%) formed pale yellow crystals from benzene–cyclohexane. The

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(13) M. Avram, I. G. Dinulescu, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 555 (1962).

(14) Benzocyclobutene is reduced very slowly in the presence of palladium to give, as the only product, bicyclo[4.2.0]octane: M. P. Cava and M. J. Mitchell, unpublished experiments.

(15) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942).

(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **39** (1946).

(17) We have obtained compounds of this type from trypticenequinone as well. The results of a study of the reaction of hydroxylamine with the latter quinone will be reported at a later date.

(18) A. C. Craig and C. F. Wilcox, Jr., *J. Org. Chem.*, **24**, 1619 (1959).

(19) W. Theilacker, V. Berger-Brose, and K. H. Beyer, *Chem. Ber.*, **93**, 1659 (1960).

(20) Analyses were carried out by Schwarzkopf Laboratories, Woodside, N. Y., and by Midwest Microlab, Indianapolis, Ind. Melting points are uncorrected.

compound begins to melt at *ca.* 210°, resolidifies (rearrangement to hydroquinone X), and finally decomposes above 280°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59, H, 5.16. Found: C, 85.01; H, 5.56.

Conversion of Benzoquinone Adduct VI to the Corresponding Quinone (XI).—A mixture of benzoquinone adduct VI (1.150 g.) and acetic acid (35 ml.) containing a few drops of 40% hydrobromic acid was refluxed for 1 hr. Dilution of the reaction mixture with water precipitated the crude hydroquinone X, which was further purified by solution in methanol and precipitation with water. The resulting grey microcrystalline powder (1.045 g., 91%) had no definite melting point, but decomposed at 270–280°. This substance was not further characterized, but was oxidized directly to the corresponding quinone as follows. To a solution of the hydroquinone (1.045 g.) in pure acetone (150 ml.) was added a chromic acid solution in the form of Jones Reagent[16] until the solution was clearly orange from an excess of oxidant. Dilution of the reaction mixture with water gave a yellow precipitate of quinone XI (1.036 g., 99%). The quinone was purified by silica gel chromatography (methylene chloride) and crystallization from methylene chloride–petroleum ether to give small bright yellow crystals, m.p. 267–269°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.08; H, 4.37.

Borohydride Reduction of Benzoquinone Adduct VI to Diol XV.—Finely powdered benzoquinone adduct VI (1.105 g.) was placed in a polyethylene bottle together with benzene (25 ml.) and methanol (25 ml.). Powdered sodium borohydride (2.0 g.) was added and the mixture was allowed to stand at room temperature for 0.5 hr. with occasional swirling, during which time the adduct went into solution. The resulting colorless solution was warmed with dilute hydrochloric acid and then extracted well with ether. The ethereal solution was extracted with 10% aqueous sodium hydroxide to remove phenolic products, then dried and evaporated to give crystals of diol XV (1.042 g., 94%), m.p. 198–202°. Crystallization from methanol gave the pure colorless diol, m.p. 205–208°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 83.51; H, 6.37. Found: C, 83.42; H, 6.69.

Catalytic Reduction of Dibenzotricycloöctadiene.—Hydrocarbon I (0.102 g.) was dissolved in dioxane and subjected to catalytic hydrogenation at room temperature and atmospheric pressure in the presence of palladium-on-charcoal catalyst. After 2-hr. one equivalent of hydrogen had been absorbed. The reaction product was worked up in the usual manner and the crystalline product (0.091 g., 88%) was isolated following chromatography on alumina (petroleum ether and benzene). Recrystallization from methanol gave pure tetrahydrobenzo[*b*]biphenylene (VIII), m.p. 130–131°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.26; H, 7.14.

After completion of our experiments, the synthesis of hydrocarbon VIII was described by an entirely different method.[13] A sample prepared by this procedure proved to be identical (infrared analysis) with compound described above.

9,10-Benzocyclobutenoanthracene (IX). A. From Anthracene.—To a boiling solution of anthracene (1.78 g.) in dimethylformamide (30 ml.) containing suspended zinc dust (1.5 g.) was added dropwise a solution of *trans*-1,2-dibromobenzocyclobutene (2.62 g.) in a minimal amount of dimethylformamide. The mixture was refluxed with stirring for 1 hr., then cooled, when anthracene (0.50 g.) separated and was removed by filtration. The filtrate was diluted with xylene and maleic anhydride (1.5 g.) was added. The solution was heated on the steam bath for 5 hr., the solvent was evaporated and the remaining solid was digested with excess hot aqueous sodium hydroxide to dissolve the maleic anhydride–anthracene adduct which had formed. The base-insoluble solid which remained was dissolved in benzene and filtered through alumina. Evaporation of the benzene gave material which was further purified by chromatography on alumina (cyclohexane) followed by several crystallizations from methanol. The pure hydrocarbon (0.935 g., 33%) formed white crystals, m.p. 168–170°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.08; H, 5.92.

B. From Diol XV.—Diol XV (0.153 g.) was refluxed with a mixture of phosphorus oxychloride (13 ml.) and phosphorus trichloride (0.8 ml.) for 3.5 hr., the solution was then poured onto ice and water and the resulting precipitate was filtered and dried. Chromatography on alumina in benzene gave white crystals (0.117 g., 25%), m.p. 158–162°. Pure hydrocarbon IX, m.p. 167–170°, was obtained after removal of a small amount of a volatile impurity by sublimation followed by crystallization from benzene–methanol. This substance was identical by infrared comparison with a sample obtained from anthracene (method A).

C. From Quinone XI.—Pure quinone XI (1.190 g.) was refluxed on the steam bath with a solution of hydroxylamine hydrochloride (2.5 g.) in ethanol (70 ml.). The quinone slowly dissolved and after 0.5 hr. it was replaced by a copious crystalline precipitate. This precipitate, which was removed by filtration, formed fine pale green needles (0.759 g.), m.p. 260–270° dec. Elemental analysis agreed best with its formulation as a mononitroso monoethoxy derivative of 9,10-benzocyclobutenoanthracene (*i.e.*, XIV).

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.38; H, 5.40; N, 3.84.

The filtrate from the above nitroso compound was diluted with water and the amorphous precipitate was dissolved in ethanol and refluxed for 2 hr. with potassium acetate (0.100 g.) and hydroxylamine hydrochloride (1.0 g.). The product of this treatment was precipitated by dilution with water, filtered, and then refluxed for 5 hr. with a solution of sodium sulfide nonahydrate (2.0 g.) in ethanol (50 ml.). The reaction mixture was diluted with water (100 ml.) and the ethanol was removed by distillation. The crude precipitated diamine was removed by filtration and digested with a mixture (15 ml.) of equal parts of acetic acid and 32% hypophosphorous acid, the insoluble residue being discarded. The acid extract was cooled to −10° and sodium nitrite (0.300 g.) was added. The solution was allowed to stand at room temperature for 2 hr., then it was diluted with water and kept overnight. The precipitated solid was removed by filtration and dissolved in benzene. After extraction with aqueous base to remove phenols, the benzene solution was dried, concentrated and chromatographed on alumina. There were obtained directly white crystals of hydrocarbon IX (0.064 g.), m.p. 163–167°. After crystallization from ethanol the pure product (m.p. 167–170°) was identical in infrared spectrum with material obtained by method A and method B described above.

Acknowledgment.—The support of this work by the National Science Foundation is gratefully acknowledged.