dryness leaving a crystalline residue. Recrystallization from benzene–petroleum ether afforded 0.36 g. of the ketoaldehyde **18**, m.p. 135–139°, identical to the compound obtained previously by comparison of infrared spectra.

**3-Methoxy-17-acetyl-18-norestra-1,3,5(10),16-tetraene (20). A. From the Ketoaldehyde 18.**—Potassium hydroxide (15.6 g.) and the ketoaldehyde **18** (26.0 g.) were added to 780 ml. of water. The flask was then evacuated and about 30 ml. of water was distilled. The mixture was then heated at reflux in a nitrogen atmosphere with stirring for a total of 5 hr. The material in the flask quickly changed to an oil and then slowly began to crystallize. The solution was cooled, was treated with excess acetic acid, and was filtered with a generous water wash. The air-dried material, 24.0 g., was chromatographed on 450 g. of acid-washed alumina. A total of 13.4 g. of material, eluted with 50% benzene–petroleum ether, was recrystallized from methanol to yield 7.6 g. of product, m.p. 166–169°, and 4.55 g., m.p. 163–168°. Recrystallization of a portion of this material led to a pure sample of **20**, m.p. 168–169°; $[\alpha]_D$ +112°; $\lambda_{max}$ 5.99 μ; $\lambda_{max}$ 231 mμ (ε 13,900).

*Anal.* Calcd. for $C_{20}H_{25}O_2$: C, 81.04; H, 8.16. Found: C, 81.08; H, 8.31.

Following elution of 5.8 g. of semicrystalline mixture with 10% ethyl acetate in benzene there was obtained 3.7 g. of crystalline material by washing the column with ethyl acetate. Recrystallization from acetone–petroleum ether provided 1.45 g. of material, m.p. 169–173°. Pure **3-methoxy-17ξ-acetyl-18-norestra-1,3,5(10)-trien-16ξ-ol (19)** was obtained by recrystallization from acetone–ether, m.p. 172–174°; $[\alpha]_D$ +64°; $\lambda_{max}^{KBr}$ 2.90, 5.98 μ.

*Anal.* Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.39; H, 8.11.

**B. From the Hydroxy Ketone 19.**—A solution of 0.10 g. of the hydroxy ketone **19** and 30 ml. of dioxane containing 5 ml. of 10% aqueous potassium hydroxide was heated at reflux under nitrogen for 20 hr. The solution was cooled and diluted with water yielding 90 mg. of crystals. These were dissolved in benzene and chromatographed on 10 g. of silica. Crystalline material (80 mg.), eluted at 5% ethyl acetate in benzene, was recrystallized from methanol to give 40 mg. of the unsaturated ketone **20**, m.p. 161–164°, identical in the infrared to the previously obtained material.

This dehydration was also effected by heating at reflux for 7 hr. a solution of 0.31 g. of the hydroxy ketone **19**, 1 g. of benzoic acid, and 0.875 ml. of triethylamine. Isolation of the product by ether extraction and chromatography yielded 0.11 g. of the unsaturated ketone **20** and 0.15 g. of starting material **19**. Partial dehydration could also be effected by sublimation.

**3-Methoxy-17-acetyl-18-norestra-1,3,5(10)-trien-20-one (21).** A solution of 0.175 g. of the unsaturated ketone **20** in 30 ml. of ethanol containing 0.40 g. of 5% palladium on charcoal was stirred in an atmosphere of hydrogen. One equivalent of hydrogen was taken up in 15 min. The catalyst was filtered and the solution was concentrated to dryness. The product was recrystallized from petroleum ether, yielding 55 mg. of pure saturated ketone **21**, m.p. 125–126°; $\lambda_{max}$ 5.86 μ.

*Anal.* Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.47; H, 8.81.

This material was identical in the infrared to a sample of the *dl*-material.[14,15]

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# Condensed Cyclobutane Aromatic Compounds. XXV. The Thermal Decomposition of 1,2,5,6-Tetrabromo-3,4,7,8-dibenzotricyclo[4.2.0.0$^{2,5}$]octadiene

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The thermal decomposition of 1,2,5,6-tetrabromo-3,4,7,8-dibenzotricyclo[4.2.0.0$^{2,5}$]octadiene (I) yields not 5,10-dibromobenzo[*b*]biphenylene (II), as previously believed, but rather 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI). The proof of structure of VI is described, and the mechanism of its formation from I is discussed. Spectral evidence confirming the structure of I is presented.

The reaction of excess potassium *t*-butoxide with α,α,α′,α′-tetrabromo-*o*-xylene has been reported to give a mixture of the colorless 1,2,5,6-tetrabromo-3,4,7,8-dibenzotricyclo[4.2.0.0$^{2,5}$]octadiene (I, m.p. 214°) and the yellow 5,10-dibromobenzo[*b*]biphenylene (II, m.p. 222–223°). Structure I was assigned to the colorless tetrabromide on the basis of two reactions: (1) catalytic reduction of I gave 1,2,5,6-dibenzocyclooctadiene (III) in high yield, and (2) dibromide II was formed in 35.8% yield when tetrabromide I was refluxed in ethanolic sodium iodide solution for two weeks.[1] More recently, the direct thermal conversion of I into II by refluxing a solution of I in *o*-dichlorobenzene for four hours has been claimed.[2] The product from this reaction was described as orange-brown needles, m.p. 222–223°.

Since it has been found that the hydrocarbon 3,4,7,8-dibenzotricyclo[4.2.0.0$^{2,5}$]octadiene (IV) forms an adduct (V) with *N*-phenylmaleimide at moderate temperatures,[3,4] we investigated the reaction of this dienophile with tetrabromide I in nitrobenzene at 200°. No Diels–Alder adduct was obtained, but a brown crystalline substance, $C_{16}H_8Br_2$, m.p. 222–225°, was isolated in 64% yield. This compound was not identical with yellow dibromide II by the criteria of mixture melting point and infrared comparison; we have assigned to it the structure of 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI). The same brown dibromide VI, in impure form, was the only product isolable by us from attempts to reproduce the reported conversions of I into biphenylene II[1,2]; however, when a little phenol was added to scavenge the elemental bromine which was otherwise present, the pyrolysis of I in *o*-dichlorobenzene proceeded very cleanly, giving pure VI in 92% yield.

As expected on the basis of the assigned structure, dibromide VI shows a marked similarity to the known dichloro analog (VII)[5,6] in both its infrared and ultraviolet absorbtion spectra (see Experimental section). Furthermore, like VII, VI was reduced catalytically by palladium on charcoal in the presence of triethylamine to give 4*b*,5,9*b*,10-tetrahydro-7*H*-indeno[2,1-*a*]indene (VIII)[7] in high yield. Finally, dibromide VI

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[1] F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. **20**, 7 (1959).

[2] W. Baker, J. W. Barton, J. F. W. McOmie, and R. J. G. Searle, *J. Chem. Soc.*, 2633 (1962).

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[4] M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, **19**, 309 (1963).

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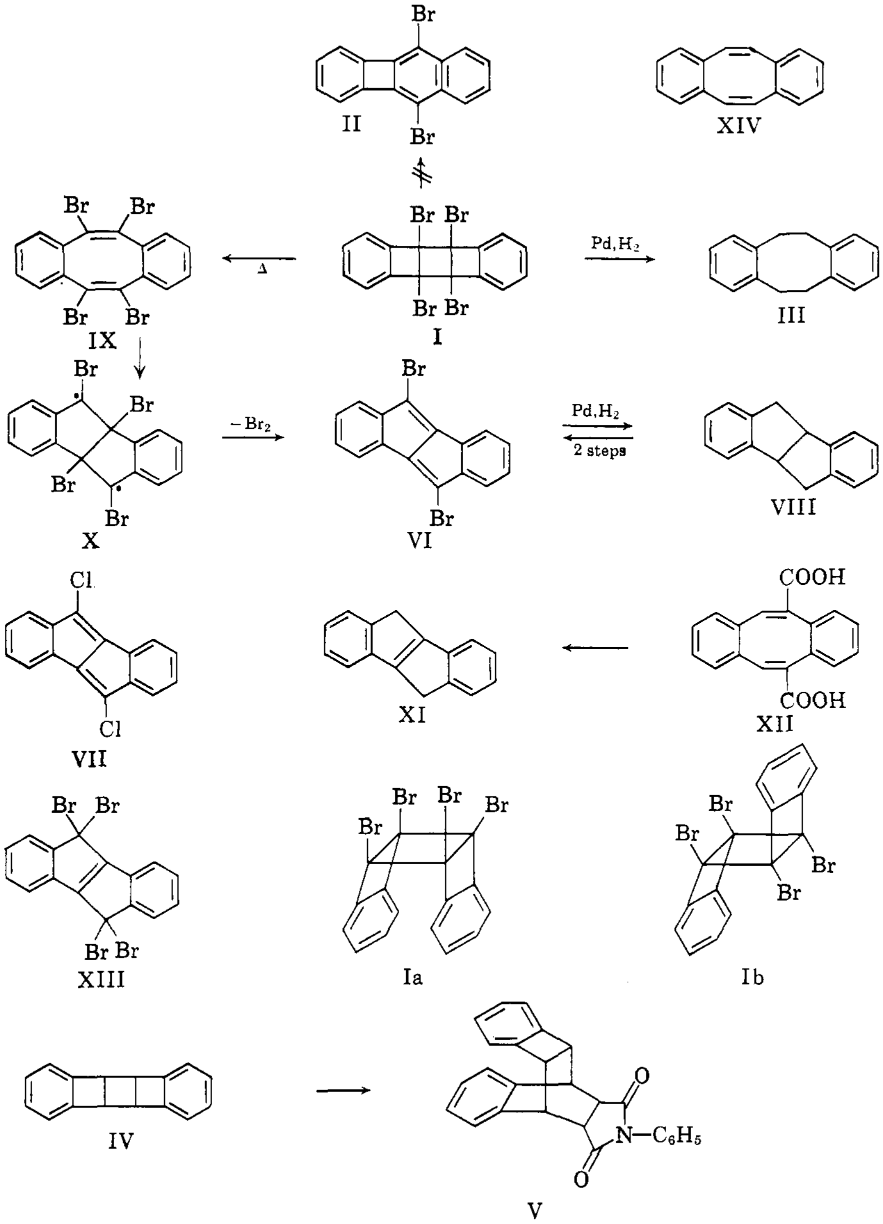
[6] S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940).

[7] C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).



was synthesized from hydrocarbon VIII (15% over-all yield) by reaction of VIII with *N*-bromosuccinimide, followed by treatment of the crude bromination product with sodium acetate.

The mechanism of the pyrolytic formation of VI from I deserves some comment. It seems likely that, by analogy with the behavior of the parent hydrocarbon (IV),[8,9] tetrabromide I may decompose thermally to a cyclooctatetraene derivative (IX). In the case of the open tetrabromide (IX), all four bromines are forced into very close proximity with each other due to the tub structure of the central ring; indeed, it is impossible to construct a molecular model (Leybold type) of IX because of this proximity effect. Steric factors may, therefore, favor a decoupling of the π-electrons of the central bonds of IX and rearrangement to the diradical X. The diradical would then afford the observed product VI and elemental bromine. The formation of free bromine during the pyrolysis of I in *o*-dichlorobenzene may be observed visually. The formation of a central pentalane nucleus in the pyrolysis of a dibenzocyclooctatetraene is not without analogy: hydrocarbon XI has been found to be one of the thermal decarboxylation products of diacid XII.[10]

The finding that the alledged conversion of tetrabromide I into biphenylene II does not occur considerably weakens the structure proof of I. However, the catalytic reduction of I to octadiene III,[1] which we have confirmed, eliminates the pentalane structure XIII and leaves only the octatetraene IX and the *syn* and *anti* isomers Ia and Ib for possible consideration. In both structures Ia and IX the aromatic rings lie over each other, and the protons of each ring should be shielded by π-electrons of the overlying ring. This effect is clearly discernible in the n.m.r. spectrum (deuteriochloroform solution) of the model compound, dibenzocyclooctatetraene (XIV), which shows aromatic protons shifted upfield to 2.92 τ. In contrast, the unshielded aromatic protons of dibenzotricyclooctadiene (IV), which is known to possess the *anti* configura-

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

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

(10) L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

tion,[11] appear at 2.72 $\tau$. This value is almost identical with that (2.75 $\tau$) found for the protons of tetrabromide I, which, therefore, most likely has the *anti* configuration Ib. Final confirmation of this structure must await the results of an X-ray crystallographic analysis of I which is now in progress.

In conclusion, the reported conversions of tetrabromide I into biphenylene II appear to be in error, the actual transformation product of I being pentalene derivative VI. It must be emphasized, however, that the results reported here cast no doubt on the constitution of authentic biphenylene II as obtained by the potassium *t*-butoxide transformation of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene.

## Experimental[12]

**Attempted Preparation of a Diels–Alder Adduct from Tetrabromide I.** — 1,2,5,6 - Tetrabromo - 3,4,7,8 - dibenzotricyclo-$[4.2.0.0^{2,5}]$octa-3,7-diene (I, 520 mg., 1 mmole) was heated with 800 mg. (4.6 mmoles) of *N*-phenylmaleimide in 20 ml. of nitrobenzene at 200° for 2–3 min. The reaction mixture was allowed to cool slowly to room temperature and was then passed through a short column of grade III neutral alumina. Vacuum evaporation of the resulting solution gave a brown residue which was recrystallized from ethanol to give 230 mg. (64%) of 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI), brown crystals, m.p. 222–225° dec.; the infrared and ultraviolet spectra of the product were identical with those of a sample prepared from 4*b*,5,9*b*,10-tetrahydro-7*H*-indeno[2,1-*a*]indene (VIII → VI).

**Dehalogenation of Tetrabromide I with Sodium Iodide.**—A solution of 520 mg. (1 mmole) of tetrabromide I and 500 mg. (3.33 mmoles) of sodium iodide in 25 ml. of ethanol was refluxed for 17 days. The reaction mixture was evaporated to dryness *in vacuo*, and the residue was extracted with 1:5 benzene–cyclohexane. The residue was worked up to give 348 mg. of starting material. The benzene–cyclohexane extract was washed with 5% aqueous sodium bisulfite, dried over magnesium sulfate, and subjected to chromatography on a column (2 × 30 cm.) of grade I neutral alumina (Woelm) with 1:5 benzene–cyclohexane to give two fractions: (A) 750 ml., containing 78 mg. of starting material; and (B) 900 ml., containing 25.2 mg. (38.4% based on unrecovered starting material) of virtually pure 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI), which was crystallized once from absolute ethanol to give the pure product, m.p. 222–223°; the infrared spectrum of the pure material was identical with that of the sample isolated from the attempted Diels–Alder reaction (see preceding) and also with that of the sample prepared from 4*b*,5,9*b*,10-tetrahydro-7*H*-indeno[2,1-*a*]indene (VIII → VI, see following).

**Preparation of 5,10-Dibromo-7*H*-indeno[2,1-*a*]indene (VI). A. By Thermolysis of Tetrabromide I.**—A solution of 0.5 g. tetrabromide I in 50 ml. of *o*-dichlorobenzene was refluxed for 4 hr., cooled, and mixed with *ca.* 50 ml. of ether. The resulting solution was washed with water, 5% aqueous sodium bicarbonate, and 5% aqueous sodium bisulfite; it was dried over magnesium sulfate and evaporated to dryness *in vacuo*. The residue was taken up in 50 ml. of 1:5 benzene–cyclohexane and chromatographed with the same solvent on a column (4 × 20 cm.) of grade I neutral alumina (Woelm) to give fractions: (A) 450 ml., containing 35 mg. of crude starting material; (B) 500 ml., 24 mg. of VI, m.p. 205–206° (from ethanol); (C) 900 ml., 51 mg. of VI, m.p. 210–213°; (D) 400 ml., 55 mg. of VI, m.p. 180–185°; (E) 500 ml.; and (F) 350 ml. which were combined to give 70 mg. of VI, m.p. 176–18°. The yield of VI was 200 mg. (48%). Infrared analysis of samples A through F showed the presence of a small amount of impurity (*not* 5,10-dibromobenzo[*b*]biphenylene).

The thermolysis of tetrabromide I under the same conditions described earlier, but in the presence of 200 mg. of phenol (bromine scavenger), gave 333 mg. (92%) of virtually pure 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI), m.p. 218–221° (from benzene–methanol).

**B. From 4*b*,5,9*b*,10-Tetrahydro-7*H*-indeno[2,1-*a*]indene.**—A solution of 103 mg. (0.5 mmole) of 4*b*,5,9*b*,10-tetrahydro-7*H*-indeno[2,1-*a*]indene (VIII)[7] in 10 ml. of carbon tetrachloride was refluxed with 356 mg. (2 mmoles) of *N*-bromosuccinimide while a solution of 50 mg. of benzoyl peroxide in 10 ml. of 1:4 chloroform–carbon tetrachloride was added slowly from a Hershberg dropping funnel. When all of the peroxide solution had been added (3 hr.), the reaction mixture was cooled, filtered, and the filtrate was evaporated to an oil. The oil was mixed with 1.0 g. of sodium acetate and *ca.* 25 ml. of absolute ethanol and the resulting suspension was refluxed for 3 hr. The reaction mixture was evaporated to dryness *in vacuo*, the residue was extracted with 1:5 benzene–cyclohexane, and the extract was chromatographed on a column (40 mm. × 20 cm.) of grade I neutral alumina (Woelm). The eluate containing the first brown zone to leave the column was collected and evaporated to dryness; the residue was recrystallized from absolute ethanol to give 26 mg. (15%, based on VIII) of 5,10-dibromo-7*H*-indeno[2,1-*a*]indene (VI), m.p. 215–218°.

*Anal.* Calcd. for $C_{16}H_{18}Br_2$: C, 53.57; H, 2.24; Br, 44.39. Found: C, 53.29; H, 2.38; Br, 44.55.

The spectral properties of dibromide VI, *i.e.*, its absorption in the ultraviolet [$\lambda_{\max}^{\text{dioxane}}$ 278 mμ, log $\epsilon$ 4.70; 379 (3.84); 402 (4.16); 428 (4.47)] and its infrared absorption [$\nu_{\max}^{\text{KBr}}$ 6.19, 6.26, 6.34 (w); 7.03 (s); 7.49 (w); 8.32, 10.5, 13.5 μ (s)], compare favorably with those of the known dichloro analog (VII),[5,6] *i.e.*, in the ultraviolet [$\lambda_{\max}^{\text{dioxane}}$ 273 mμ, log $\epsilon$ 4.74; 382 (3.83); 397 (4.22); 423 (4.33)] and in the infrared [$\nu_{\max}^{\text{KBr}}$ 6.19, 6.27, 6.35 (w); 7.04 (m); 8.26, 10.3, 13.5 μ (s)].

**Hydrogenolysis of 5,10-Dibromo-7*H*-indeno[2,1-*a*]indene (VI).**—A suspension of 280 mg. (0.778 mmole) of dibromide VI in 5.0 ml. of triethylamine was hydrogenated at atmospheric pressure in the presence of 5% palladium on charcoal. The reaction mixture consumed 54.3 ml. (STP) of hydrogen, out of an expected 66.4 ml. (STP). The reaction was filtered, the filtrate was poured into water, and the resulting suspension was extracted with benzene. Chromatography of the benzene extract on grade I neutral alumina (Woelm) gave 151 mg. (94%) of 4*b*,5,9*b*,10-tetrahydro-7*H*-indene[2,1-*a*]indene, m.p. 104–105°, identical in its melting point and infrared spectrum with an authentic sample.[7]

**Hydrogenolysis of Tetrabromide I.**—A suspension of 200 mg. (0.384 mmole) of 1,2,5,6-tetrabromo-3,4,7,8-dibenzotricyclo-$[4.2.0.0^{2,5}]$octa-3,7-diene (I) in 30 ml. of 2% ethanolic triethylamine was hydrogenated at atmospheric pressure in the presence of 100 mg. of 10% palladium on charcoal for 1.5 hr. The reaction mixture absorbed 51.4 ml. (STP) of hydrogen which is 99% of the theoretical volume (6 moles of hydrogen per mole of tetrabromide). The reaction mixture was filtered, the filtrate was poured into water, and the resulting suspension was extracted with petroleum ether (b.p. 30–60°). The extract was passed through a short column of grade I neutral alumina and the eluate was evaporated to dryness *in vacuo* to give 78 mg. (97%) of dibenzo[*a*,*e*]cyclooctadiene (III), identical in its melting point and infrared spectrum with an authentic sample.[13]

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[12] Analyses were performed by A. Bernhardt, Mülheim. Melting points are uncorrected.

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