722. *Macrocyclic Acetylenic Compounds. Part II.*[1] 1,2:7,8-*Dibenzocyclododeca*-1,7-*diene*-3,5,9,11-*tetrayne.*

By O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael.

The product of the oxidative coupling of *o*-diethynylbenzene (IV) has been shown to be the strained hydrocarbon (V), the properties of which are described. Reduction of this product is accompanied by extensive trans-annular interactions with the formation of unexpected products.

In previous communications[1,2] details were given of a modification of the conventional Glaser procedure for the oxidative coupling of ethynyl compounds which has the advantage that the synthesis of macrocyclic systems containing the $\alpha\gamma$-diyne unit can be performed under high-dilution conditions. Application of this method to *o*-diethynylbenzene (IV)

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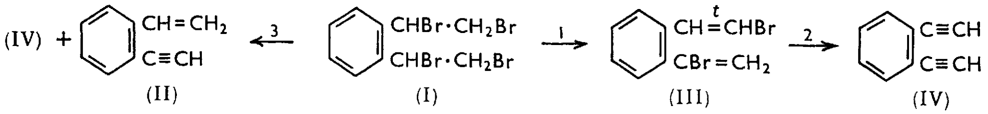
[1] Eglinton and Galbraith, *J.*, 1959, 889.

[2] Eglinton and Galbraith, *Chem. and Ind.*, 1956, 737.

furnished a hydrocarbon which was originally[3] tentatively assigned the unstrained "trimeric" formulation (VI). This paper now presents full details of the conclusive chemical evidence[4] which shows the substance to possess the extraordinary, highly-strained "dimeric" structure (V).

The starting material, *o*-diethynylbenzene (IV), had been previously prepared by Deluchat[5] but his route was adjudged unsatisfactory on several counts and was considerably modified. The precursor, *o*-divinylbenzene, was obtained by Halford and Weissman's procedure.[6] By treatment with bromine in carbon tetrachloride, the diene gave a single tetrabromide (I) in 75% yield, although *meso-* and racemic forms are theoretically possible. The *trans*-bromination of the first olefinic bond evidently exerts some stereochemical control over the addition of the second molecule of bromine to the remaining olefinic bond. Deluchat[5] had reported that treatment of the tetrabromide with potassium ethoxide gave largely naphthalene—in itself an interesting observation—while sodium ethoxide gave a mixture containing the desired hydrocarbon (IV), *o*-di-(1-bromovinyl)benzene, and 1-1'-bromovinyl-2-ethynylbenzene in unspecified yields. The use of more selective reagents seemed advisable. However, attempted dehydrobromination of the tetrabromide (I) with sodamide in liquid ammonia gave a mixture of two hydrocarbons, subsequently found to be 1-ethynyl-2-vinylbenzene (II) and *o*-diethynylbenzene (IV). When this mixture was coupled in high dilution by the action of cupric ion, the only identifiable crystalline product was the colourless hydrocarbon 1,4-di-*o*-vinylphenylbutadiyne in about 20% yield. Proof of this structure followed from the analytical and light-absorption data. Further, catalytic hydrogenation gave a benzenoid hydrocarbon, $C_{20}H_{26}$, having infrared absorption at 1378 cm.$^{-1}$ (C–Me). The formation of the enyne (II) implies that the sodamide is effecting debromination as well as dehydrobromination. There are a few precedents for this observation; sodamide, suspended in a hydrocarbon medium, was found by Bourguel[7] to generate styrene as well as phenylacetylene



Reagents: 1, Bu^{t}OK in Bu^{t}OH. 2, Bu^{t}OK in benzene. 3, $NaNH_2$ in NH_3.

from 1',1'-dibromoethylbenzene; 1',2'-dibromoethylbenzene, however, is said[8] to react normally with sodamide. The tetrabromide has a rather overcrowded molecule and steric factors may well be important. Attempts to isolate the *o*-diethynylbenzene (IV) from the mixture by both physical (distillation and chromatography) and chemical (selective bromination, and mercury-derivative formation) procedures were unsuccessful, and alternative dehydrohalogenating reagents were therefore examined.

Potassium t-butoxide (2 mol.) in t-butyl alcohol and dioxan at 7° rapidly eliminated 2 mol. of hydrogen bromide with the formation of the dibromo-diene (III; the establishment of this structure will appear in a further paper). Vigorous treatment of this product (III) with an excess of a solution of potassium t-butoxide in boiling benzene gave the required diyne (IV) in 70% yield [calc. from (I)]. Unexpectedly, sodamide in liquid ammonia was in this case also an unsatisfactory dehydrobrominating agent: the dibromodiene (III) gave the diyne (IV) in only 10% yield, the major portion being converted into a brown, bromine-containing polymer (the analogous α-bromostyrene gave phenylacetylene in only 45% yield under the same conditions, a polymeric residue again being formed). Anion-induced polymerisation involving the vinyl group may be the cause. The two-step

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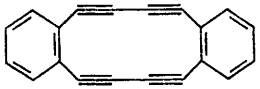
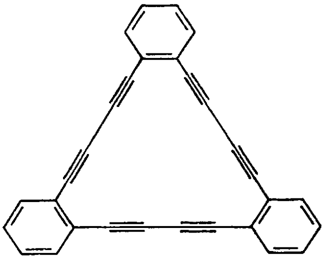
[3] Eglinton and Galbraith, *Proc. Chem. Soc.*, 1957, 350.
[4] Behr, Eglinton, and Raphael, *Chem. and Ind.*, 1959, 699.
[5] Deluchat, *Compt. rend.*, 1931, **192**, 1387.
[6] Halford and Weissman, *J. Org. Chem.*, 1952, 1646.
[7] Bourguel, *Ann. Chim.* (*France*), 1925, **3**, 191.
[8] Jacobs, *Org. Reactions*, Vol. V, p. 1.

potassium t-butoxide process is hence the preferred route to *o*-diethynylbenzene (IV). The yield over seven stages from *o*-xylene is 13%.



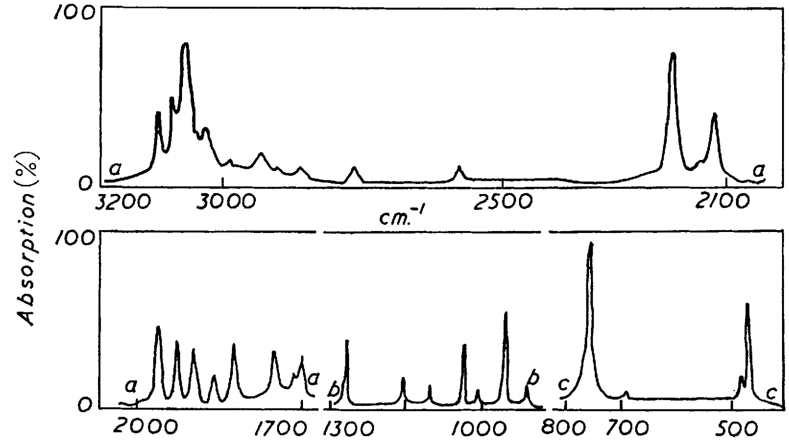
(V)



(VI)

The high-dilution procedure employed for the oxidative coupling of *o*-diethynylbenzene (IV) was similar to that described earlier.[1,2] As the diyne readily forms an insoluble yellow-brown copper salt a large volume of the powerful pyridine–methanol solvent pair is required to avoid loss by precipitation. The minimum of entraining solvent, ether, is employed for the same reason. The only substance that we were able to isolate from the reaction product was the yellow hydrocarbon (V). Reaction in more concentrated solution resulted only in lower yields of hydrocarbon (V) and the formation of insoluble copper derivatives and of polymeric material, there being no indication of the formation of any other hydrocarbon.

FIG. 1. *Infrared absorption of* 1,2:7,8-*dibenzocyclododeca*-1,7-*diene*-3,5,9,11-*tetrayne* (V): (*a*) 8·15 × 10^{-3}M-*solution in* CCl_4, 20 mm. *path* (NaCl; *grating*); (*b*) 2·14 × 10^{-2}M-*solution in* CS_2, 2 mm. *path* (NaCl; *grating*); (*c*) 3·80 × 10^{-3}M-*solution in* CS_2, 2 mm. *path* (KBr).



A number of structural possibilities for the hydrocarbon product had initially to be considered. Any non-cyclic polymer was put out of court immediately by the total absence of ethynyl absorption at 3300 cm.$^{-1}$. The possibility that an enyne rather than a diyne linkage was formed by the coupling[9] was improbable in view of the basic conditions employed;[1] further, the infrared spectrum (Fig. 1) showed no indication of such a structural feature. Again, the nuclear magnetic resonance spectrum showed only a single, slightly asymmetric peak corresponding to the absorption of the benzene hydrogen atoms (for this and the other nuclear magnetic resonance spectra, and for their interpretation, we thank Dr. N. Sheppard of Cambridge). This left for plausible consideration only a cyclic " polymeric " structure, of which (V) and (VI) are the first members. Obvious aspects of stereochemistry led to the initial belief that the rigidity of the *o*-diethynylbenzene unit

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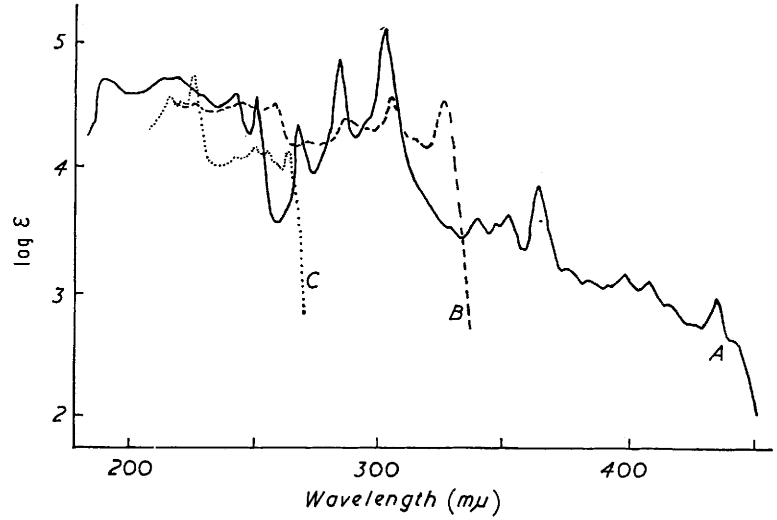
[9] Akhtar and Weedon, *Proc. Chem. Soc.*, 1958, 303.

would be maintained throughout the coupling reaction to produce the strainless cyclic " trimer " (VI).

The obvious step of molecular-weight determination to distinguish between the cyclic " dimer " and " trimer " proved difficult for some time because of the heat-lability and relative insolubility of the hydrocarbon. However, a determination by the thermistor-drop technique [10] (for which we express our thanks to Dr. V. M. Clark of Cambridge) gave a value in close agreement with the " dimer " formulation (V). This value was confirmed by an *X*-ray determination of the molecular weight involving determination of the dimensions of the unit cell [11] and the density of a crystal of greater purity than that originally examined.[3] A structural *X*-ray analysis of the hydrocarbon [11] has since conclusively shown the validity of the extraordinary strained " dimeric " structure (V) with its " pair of ' bowed ' diacetylenic linkages." The instability of the substance is doubtless a consequence of this strained system. The ultraviolet absorption (Fig. 2) of the hydrocarbon is remarkable for its wealth of fine structure, several of the well-defined peaks being spaced at intervals of *ca.* 2200 cm.$^{-1}$, evidently corresponding to the C≡C stretching frequency; the yellow colour of the hydrocarbon is a consequence of the continuance of the absorption bands into the visible region.

FIG. 2. *Ultraviolet absorption of*: *A*, *compound* (V); *B*, 1,4-*diphenylbuta*-1,3-*diyne*; *C*, o-*diethynylbenzene* (IV).



The infrared spectrum (Fig. 1) of the hydrocarbon clearly demonstrates the presence of the *o*-disubstituted benzene rings, there being only a single intense peak (753 cm.$^{-1}$, $\Delta\nu_{\frac{1}{2}}^{a} = 3{\cdot}5$ cm.$^{-1}$, $\varepsilon = 1530$) in the 750 cm.$^{-1}$ region. Under similar conditions, *o*-diethynylbenzene (IV), *o*-xylene, and tetralin had absorption maxima at 756 ($\Delta\nu_{\frac{1}{2}}^{a} = 5$ cm.$^{-1}$, $\varepsilon = 564$), 741 ($\Delta\nu_{\frac{1}{2}}^{a} = 4$ cm.$^{-1}$, $\varepsilon = 495$), and 742 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}^{a} = 5$ cm.$^{-1}$, $\varepsilon = 356$) respectively. There are four relatively weak ($\varepsilon = 10$—50) bands at 1270, 1163, 1109, and 1035 cm.$^{-1}$ which probably correspond to the in-plane C–H bending modes,[12] the triply bonded substituents being classified as weak acceptors. The pattern in the 1700—2000 cm.$^{-1}$ region, like the rest of the spectrum, is unusually simple and probably reflects the symmetry of the molecule; most of the peaks are readily accountable as summation bands of the out-of-plane C–H deformations at 1005, 947, 910, and 753 cm.$^{-1}$.[13] The main C–H

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[10] Iyengar, *Rec. Trav. chim.*, 1954, **73**, 789.

[11] Grant and Speakman, *Proc. Chem. Soc.*, 1959, 231.

[12] Katritzky and Jones, *J.*, 1959, 3670.

[13] (*a*) Whiffen, *Spectrochim. Acta*, 1955, **7**, 253; (*b*) Cava and Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.

stretching band at 3063 cm.$^{-1}$ is accompanied by several weaker peaks, which are probably combination bands (ref. 14*a*, page 65). The twin peaks at 2187 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}{}^{a}$ = 11 cm.$^{-1}$, ε = 36) and at 2116 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}{}^{a}$ = 14 cm.$^{-1}$, ε = 14) must originate from the diyne systems. Their intensities are unusual, the peak at 2187 cm.$^{-1}$ having almost the same ε as the ν_{C-H} at 3063 cm.$^{-1}$, whereas diphenyldiacetylene absorbs only weakly at 2216 ($\Delta\nu_{\frac{1}{2}}{}^{a}$ = 25 cm.$^{-1}$, ε = 3) and 2147 cm.$^{-1}$ ($\Delta\nu_{\frac{1}{2}}{}^{a}$ = 20, ε = 4).

To confirm the degree of unsaturation of the hydrocarbon (V) it was hydrogenated catalytically over palladium–charcoal under conditions which quantitatively converted 1,4-diphenylbutadiyne into 1,4-diphenylbutane. Absorption of hydrogen was extremely rapid but ceased when only 68% of the theoretical volume for 4 triple bonds had been taken up. From the product a crystalline hydrocarbon, $C_{20}H_{14}$, m. p. 300—302° (3%), was isolated very easily in spite of its low concentration because of its extreme insolubility. The ultraviolet absorption (Fig. 3) strongly resembled that of fluorene and the compound was speedily identified as the known "*trans*-fluorenacene" (5,11-dihydroindeno[1,2-*b*]-fluorene) (VII) by direct comparison with a genuine sample.[15] This correlation with a known compound first clinched the molecular size of the hydrocarbon (V) at a time when the above conclusive physical measurements were not yet available.

FIG. 3. *Ultraviolet absorption of*: *A*, *compound* (VII); *B*, *compound* (IX); *C*, *compound* (X); *D*, *compound* (VIII).

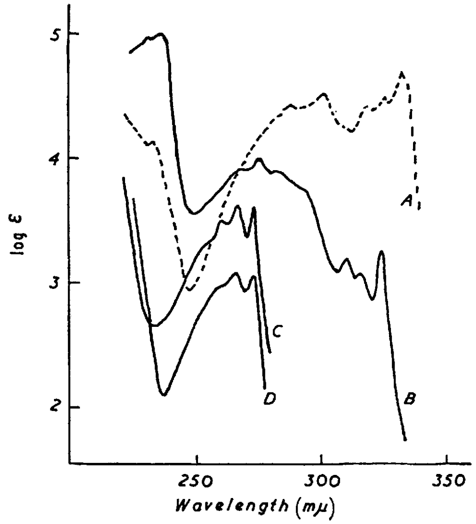
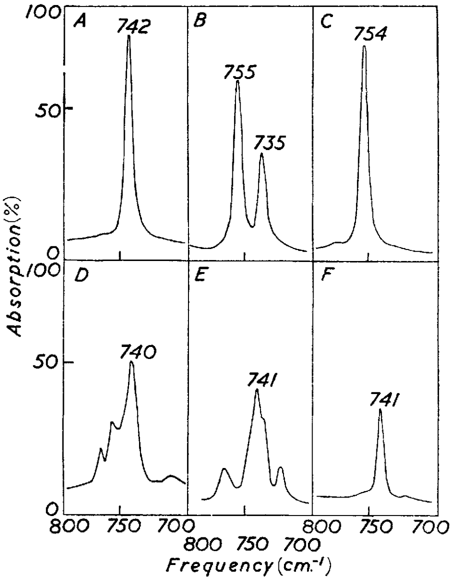


FIG. 4. *Infrared maxima for solutions* (*not equimolar*) *in* CS_2 *of*: *A*, o-*xylene*; *B*, 1,2:5,6-*dibenzocyclo-octa*-1,5-*diene*; [18b] *C*, 1,2:5,6:9,10-*tribenzocyclododeca*-1,5,9-*triene*; [18b] *D*, *compound* (VIII); *E*, *compound* (X), *m. p.* 120—122°; *F*, *compound* (X), *m. p.* 230—231°.



The main products of the catalytic hydrogenation were isolated by careful chromatography and crystallisation. The major hydrocarbon component, $C_{20}H_{24}$, m. p. 103—105° (50%), showed spectral characteristics [ultraviolet (Fig. 3), infrared (Fig. 4), and nuclear magnetic resonance] closely resembling those of tetralin and diethylbenzene and was undoubtedly the expected hydrogenation product (VIII). The second substantial constituent, a hydrocarbon $C_{20}H_{16}$, m. p. 117—119° (38%), was provisionally allotted the

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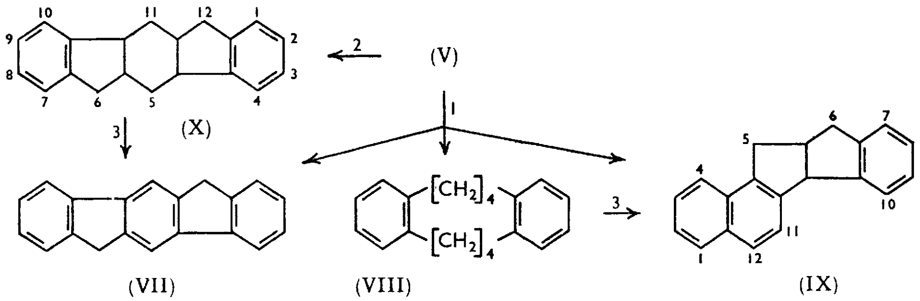
[14] (*a*) Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co., London, 1958, p. 77; (*b*) Dannenberg and Rahman, *Chem. Ber.*, 1955, **88**, 1405.

[15] Deuschel, *Helv. Chim. Acta*, 1951, 2463; sample kindly provided by Prof. L. Chardonnens, The University, Fribourg, Switzerland.

structure (IX) on the following grounds: The ultraviolet absorption (Fig. 3) was strongly suggestive of an αβ-disubstituted naphthalene, a contention further substantiated by the infrared [14] evidence (Fig. 5). The mass-spectrogram of its breakdown fragments was fully consistent with a structure containing benzindane, methylnaphthalene, and toluene residues (we are indebted to Dr. R. I. Reed of this Department for this information). It was found, very remarkably, that this naphthalene was the sole detectable product of the palladium-induced catalytic dehydrogenation at 320° of the hydrocarbon (VIII); that compound (IX) is formed under these circumstances suggests the thermodynamically more stable *cis*-fusion of the two five-membered rings.[16]



Reagents: 1, Pd–C,H_2. 2, Na in NH_3. 3, Pd–C, 300°.

The proportions of the above compounds in the product of hydrogenation of hydrocarbon (V) were conveniently assessed by gas–liquid chromatography [17] which also indicated traces of other substances not further investigated. Calculation of the hydrogen uptake derived from these found proportions amounted to *ca.* 70%, an excellent, if surprising, correlation with the 68% estimated earlier.

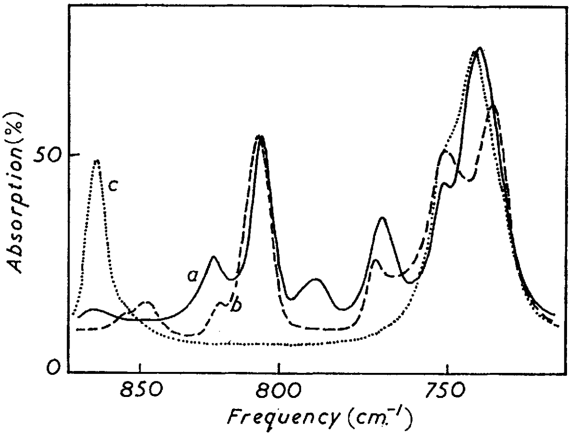


Fig. 5. *Infrared spectra* (0·5 *mm. path*) *of solutions in* CS_2 *of*: (*a*) *compound* (IX), 0·056M; (*b*) 1,2-*dimethylnaphthalene*, 0·028M, *and indane*, 0·028M; (*c*) 2,3-*dimethylnaphthalene*, 0·028M, *and indane*, 0·028M.

As we had already found that sodium–ammonia reduction of 1,4-diphenylbutadiyne had yielded roughly equal amounts of 1,4-diphenylbutane and *trans*-1,4-diphenylbut-2-ene, we examined the effect of this reducing agent on the hydrocarbon (V). Gas–liquid chromatography showed the product to be considerably more complex than that derived by catalytic reduction. Peaks corresponding to the hydrocarbon (VIII) (*ca.* 10%) and the " naphthalene " (IX) (*ca.* 10%) were apparent, but the two biggest peaks (*ca.* 20 and 50%) corresponded to two of the constituents observed only in traces in the gas–liquid chromatogram of the catalytic-hydrogenation mixture. These two major components

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[16] Cook and Linstead, *J.*, 1934, 946.

[17] Eglinton, Hamilton, Hodges, and Raphael, *Chem. and Ind.*, 1959, 955.

were isolated and proved to be isomeric hydrocarbons, $C_{20}H_{20}$, m. p.s 230—231° and 120—122°. The fact that both were smoothly dehydrogenated to the same " fluorenacene " (VII) suggested that they were two stereoisomers of structure (X). Their almost identical ultraviolet spectra (Fig. 3) resembled closely in their maxima those of 1,2-dimethylindane with double the relevant intensities. Further, the infrared spectra showed no *C*-methyl groups but clearly indicated *o*-disubstituted benzene rings (Fig. 4). Evidently additional factors, presumably of a steric nature, other than strain in an attached ring, are capable of seriously perturbing the " umbrella " C–H out-of-plane deformation mode[13b] (cf. A.P.I. project 44, spectra numbers 678, 1419, 1511, 1585, 1599, 1709). The nuclear magnetic resonance spectrum of the 120° isomer conclusively showed the absence of olefinic or methyl hydrogen; diffuse absorption, typical of rigid alicyclic systems occurred between $\sigma = 2$ and 4 (maximum at 2·7 corresponded to benzylic CH_2). A further indication of the close relationship of these two hydrocarbons was provided by the finding that the 120° compound appeared to be partly converted into the 230° hydrocarbon during gas–liquid chromatography, the degree of isomerisation being dependent on the contact time. However, we have been unable to effect this conversion under other circumstances.

The occurrence of extensive transannular reactions under reducing conditions of such mildness seems to be unprecedented and offers a wide field for speculation. Although paper schemes to account for the products may be readily devised, more concrete suggestions must await further experimental evidence.

EXPERIMENTAL

General.—The following conditions for the physicochemical measurements apply unless otherwise stated. M. p.s were measured on a Kofler hot stage and are corrected; ultraviolet spectra were generally measured on solutions in cyclohexane, by means of a Unicam S.P. 500 spectrophotometer; infrared survey measurements were recorded on a Perkin–Elmer Model 13 or 117, and precise measurements on a Unicam S.P. 100 prism-grating spectrometer (only significant peaks in the infrared region are reported). Nuclear magnetic resonance measurements, which are relative to cyclohexane as internal standard ($\sigma = +3{\cdot}9$), were kindly made on a Varian 40 Mc./sec. machine by Dr. N. Sheppard of the University Chemical Laboratories, Cambridge. Micro-Rast molecular-weight determinations were made[18a] on 1·0—1·3 mg. of substance in *ca.* 11 mg. of camphor; standard substances, *e.g.*, 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene[18b] and 1,4-diphenylbutane, gave results *ca.* 15% below the theoretical value. Other molecular-weight measurements,[10] kindly performed by Dr. V. M. Clark of Cambridge, were made in specially purified methylene chloride; standardisation with 1,4-diphenylbutane gave values *ca.* 4% low. Gas–liquid chromatograms[17] were run on a Pye " Argon " chromatograph with a 4 ft. column of 100—120 mesh Celite, with 5% Apiezon " L " as stationary phase, at *ca.* 220° and flow rates of *ca.* 30—50 ml./min. The relative amounts of eluates were based on measurement of peak areas, not weight standardisation, and the quantitative results therefore depend on uniform detector response. The alumina for chromatography was acid-washed, neutralised, and standardised according to Brockmann's method; Grade I was used. Light petroleum was of b. p. 40—60°.

o-*Divinylbenzene.*—A slight modification of the recorded route was used.[6] In the preparation of *o*-di(ethoxycarbonylmethyl)benzene from *o*-di(cyanomethyl)benzene, the pure nitrile was not isolated; this raised the overall yield from *o*-di(bromomethyl)benzene from 58% to 82%. It was also found unnecessary to purify the *o*-di-(2-hydroxyethyl)benzene before dehydration; thorough ether-extraction of the diol was important. Contrary to previous reports,[5] *o*-divinylbenzene was found to polymerise slowly to a viscous glass.

o-*Di*-(1′,2′-*dibromoethyl*)*benzene* (I).—Bromine (610 g.) in carbon tetrachloride (830 ml.) was added dropwise to a solution of *o*-divinylbenzene (250 g.) in carbon tetrachloride (250 ml.), cooled in ice and stirred with a vibro-mixer. After addition of about 85% of the bromine, no further reaction appeared to take place. When all the bromine had been added, one-third of

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[18] (*a*) Dr. A. Bernhard, Max-Planck-Institut, Mülheim/Ruhr; (*b*) we are indebted to Dr. F. G. Mann, F.R.S., for samples of these compounds.

the solvent was removed under reduced pressure and the residue left overnight at −10°. The resultant crystalline deposit was collected, the volume of solvent again reduced, and a further crop obtained. The crude crystalline product was washed with light petroleum to give the *tetrabromide* (565 g., 66%) as light pink crystals. These were recrystallised from light petroleum (b. p. 60—80°) to give colourless plates m. p. 72—74° (Deluchat[5] reports m. p. 71—74°) (Found: C, 26·85; H, 2·45; Br, 70·9. $C_{10}H_{10}Br_4$ requires C, 26·65; H, 2·40; Br, 70·9%). Further treatment of the residues from the mother-liquors with ethanol–ether, and cooling to −10° yielded additional tetrabromide (80 g., 9%) of satisfactory purity. The remaining mother-liquors appeared to contain partially brominated and polymeric material.

Treatment of the Tetrabromide (I) *with Sodamide in Liquid Ammonia.*—Sodium (6 g.) was converted into sodamide in liquid ammonia (200 ml.), ferric nitrate being used as catalyst.[19] The tetrabromide (17 g.) in ether (150 ml.) was added during 5 min. and the mixture left for 30 min. Excess of sodamide was decomposed with ammonium chloride (25 g.), and the ammonia allowed to evaporate. Ether-extraction afforded a dark oil from which, on distillation, was obtained a mixture of *o*-diethynylbenzene (IV) and 1-ethynyl-2-vinylbenzene (II) as a colourless liquid (4 g.), b. p. 60—64°/1 mm., n_D^{20} 1·5880, $\nu_{max.}$ (liquid film) 3275, 2100, 1825, 1620, 995, 915, and 763 cm.$^{-1}$. A Lassaigne test for bromine was negative. Several attempts were made to separate or to remove the *o*-diethynylbenzene by a preferential reaction. Addition of bromine lacked sufficient specificity, while chromatography on alumina in light petroleum achieved only partial separation. Addition of excess of potassium mercuri-iodide solution afforded a precipitate of mercury derivatives. That of 1-ethynyl-2-vinylbenzene could be extracted with benzene, as needles m. p. 115°, $\lambda_{max.}$ 242, 264, 278, and 292 mμ (log ε 4·72, 4·51, 4·62, and 4·63). The insoluble polymeric derivative containing *o*-diethynylbenzene units remained, but treatment with alkaline potassium cyanide proved unexpectedly ineffective in liberating the parent acetylene. The mercury derivative of phenylacetylene similarly prepared had $\lambda_{max.}$ 250, 258, 270, and 278 mμ (log ε 4·40, 4·63, 4·69, and 4·56).

Oxidative Coupling of the Above Reaction Product.—To a solution of cupric acetate (6 g.) in pyridine–methanol–ether (3 : 3 : 1; 350 ml.), heated under reflux, a solution of the product (1 g.) from the above reaction in ether (150 ml.) was added dropwise in 3 hr. under high-dilution conditions. After a further 3 hours' heating, the solution was evaporated to small volume, acidified, and extracted with ether. The neutral fraction afforded a sticky solid, extraction of which with light petroleum followed by chromatography on alumina yielded *di-*(o*-vinylphenyl*)*-butadiyne* as colourless needles (200 mg.), m. p. 104—105° (from methanol) [Found: C, 94·2; H, 5·5%; *M* (Rast) 252. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%; *M*, 254], $\nu_{max.}$ (mull) 2100, 1620, 995, 906, 768, and 752 cm.$^{-1}$, $\lambda_{max.}$ (in hexane) 242, 283, 300, 321, 344 mμ (log ε 4·88, 4·45, 4·54, 4·56, 4·47). It absorbed bromine more quickly than did diphenylbutadiyne, but the addition was not selective.

Hydrogenation of the hydrocarbon (313 mg.) over Adams's catalyst in ethyl acetate for 5 hr. resulted in the uptake of 272 ml. (theor. 317 ml.). The solution, after passage through alumina and distillation, gave 1,4-*di-*(o*-ethylphenyl*)*butane* (150 mg.), b. p. 180—190° (bath)/1 mm., n_D^{24} 1·5382 (Found: C, 90·0; H, 10·1. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%), $\nu_{max.}$ (film) 1378, 754 cm.$^{-1}$ and typical aromatic and aliphatic absorption.

1-1′-*Bromovinyl-*2-trans-2′*-bromovinylbenzene* (III).—Potassium (3·93 g., 0·1 g.-atom) was dissolved in t-butyl alcohol (250 ml.), dioxan (20 ml.) was added, and the solution cooled to *ca.* 15°. This solution was added dropwise to a vigorously stirred, ice-cooled solution of the tetrabromide (23·5 g., 52 mmoles) in dioxan (50 ml.), the temperature being kept below 7°; a pale brown precipitate was formed almost immediately. The solvents were then removed under nitrogen (55 mm., bath temp. 25—30°). The residue was treated with 1·5% hydrochloric acid and thoroughly extracted with ether. The extract was washed, dried (Na_2SO_4) and evaporated under reduced pressure, to give the *dibromo-compound* (15·0 g.) as a pale orange oil of satisfactory purity. The infrared spectrum and a gas–liquid chromatogram (177°) showed this material, which was used as such in the next experiment, to be almost pure. A portion, distilled, had b. p. 80° (bath)/4 × 10^{-4} mm., n_D^{22} 1·6385 (Found: C, 41·95; H, 3·1; Br, 55·25. $C_{10}H_8Br_2$ requires C, 41·7; H, 2·8; Br, 55·5%) [Deluchat[5] recorded b. p. 125—216°/2 mm., n_D^{23} 1·6366 for the dibromo-compound obtained by the action of sodium ethoxide on the tetrabromide (I)], $\nu_{max.}$ (film), 3040w, 1620sh, 1605m, 1218m, 935s, (*trans*-CH=CHBr), 901s ($C{=}CH_2$), 762s, 730m br. cm.$^{-1}$.

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[19] Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.

When sodium ethoxide in ethanol was used [5] in the dehydrohalogenation, the mixture being heated only briefly (1 min.), the product was less homogeneous. Attempts to carry the dehydrohalogenation (potassium t-butoxide) through to the diyne in one step were unsuccessful.

o-*Diethynylbenzene* (IV).—Potassium (6·32 g., 0·16 g.-atom) was dissolved in t-butyl alcohol (*ca.* 400 ml.). After the alcohol had been removed under reduced pressure, the potassium t-butoxide was dissolved in dry benzene (*ca.* 600 ml.) and the opalescent solution then heated under reflux with stirring (Hirshberg stirrer). A solution of 1-1′-bromovinyl-2-*trans*-2′-bromovinylbenzene (15·0 g., 52 mmoles) in dry benzene (100 ml.) was then added and the mixture stirred and heated for 4 hr. During the reaction, aliquot parts were removed and worked up and their infrared spectra inspected for the presence of absorption at 1650 cm.$^{-1}$ due to C=C; after 3·5 hr. this absorption had disappeared (continuing the reaction after the dehydrobromination was complete was detrimental to the yield). The mixture was cooled, ether (*ca.* 100 ml.) was added, and the whole shaken with dilute hydrochloric acid. The organic layer was washed, dried, and evaporated to give a dark red oil which was distilled at 80° (bath)/10^{-4} mm. Redistillation gave o-*diethynylbenzene* (4·6 g., 70%) as an almost colourless oil, b. p. 80—82°/14 mm. n_D^{20} 1·5900 (Deluchat [5] reported b. p. 80—82°/14 mm., $n_D^{17.5}$ 1·5915) (Found: C, 94·95; H, 5·0, $C_{10}H_6$ requires C, 95·2; H, 4·8%). On one occasion the compound decomposed violently on attempted distillation. $\lambda_{max.}$ (in hexane) were at 217, 222, 227, 251, 256, 264 mμ (log ε 4·54, 4·50, 4·71, 4·13, 4·10, 4·10), $\nu_{max.}$ (in CCl_4) at 3312s, 2107w, (in CS_2) 756 cm.$^{-1}$. *o*-Diethylbenzene was formed on hydrogenation of a small portion over palladium–charcoal (10%) in ethyl acetate and was identified by comparison of its infrared spectrum with spectrum number 1419 of API project 44.

1,2:7,8-*Dibenzocyclododeca*-1,7-*diene*-3,5,9,11-*tetrayne* (V).—Anhydrous cupric acetate (12·1 g., 67 mmoles) was dissolved in a mixture of dry pyridine (600 ml.), and methanol (600 ml.) and ether (100 ml.) were then added. *o*-Diethynylbenzene (1·97 g., 15 mmoles) in 1 : 1 pyridine–methanol (400 ml.) was added in 5·5 hr. to the copper acetate solution, the high-dilution technique [1] being used. The dark green solution was heated under reflux for a further 45 min., set aside overnight, and filtered through a sintered-glass funnel. It was then poured on to a stirred mixture of 50 v/v% sulphuric acid (700 ml.), ice (*ca.* 1 kg.), and ether (500 ml.), more ice being added to keep the temperature below 15°. Three layers were formed—the upper ether layer, a brown-green emulsion, and the aqueous layer. The last two were thoroughly extracted with ether, and the combined ether extracts washed with dilute sulphuric acid, water, and sodium carbonate solution, and dried (Na_2SO_4). The bulk of the solvent was removed under reduced pressure in a stream of nitrogen (bath temp. <30°), and the last 50 ml. were removed at room temperature. Benzene (40 ml.) was then added, the mixture warmed gently and filtered from an insoluble cream residue (*ca.* 100 mg.). The filtrate was immediately chromatographed on alumina (Type H; 190 g.). Elution of the bright yellow band with benzene (250 ml.) gave a dark orange solution of the hydrocarbon (842 mg., 43%, spectroscopic estimation based on the intensity of the 304 mμ absorption band). Slow crystallisation from benzene at *ca.* 0° yielded the pure *hydrocarbon* as canary-yellow needles [Found: C, 96·8; H, 3·55%; *M* (thermistor drop),[10] 245. $C_{20}H_8$ requires C, 96·75; H, 3·25%; *M*, 248], $\nu_{max.}$ (in CCl_4; grating spectrometer) 3112, 3085, 3063, 3026, 2187, 2116, 1953, 1920, 1889, 1852, 1816, 1747, 1698, (in CS_2) 1270, 1163, 1035, 947, 754, 692 (KBr prism) 476 cm.$^{-1}$, $\lambda_{max.}$ (in cyclohexane) 192, 215, 221, 244, 252, 269, 285, 304 mμ (log ε 4·68, 4·69, 4·69, 4·57, 4·55, 4·31, 4·84, 5·08) (in C_6H_6) 338, 346, 351, 362·5, 374·5 382·5, 392, 465, 415, 433 mμ (log ε 3·57, 3·53, 3·61, 3·83, 3·18, 3·08, 3·13, 3·07, 2·89, 2·92), $\lambda_{min.}$ (in cyclohexane) 204, 217, 237, 249·5, 260, 274·5, 292 (log ε 4·62, 4·68, 4·46, 4·24, 3·52, 3·91, 4·21), (in C_6H_6) 332, 342·5, 348·5, 356, 372, 379·5, 387, 402, 412·5, 428 mμ (log ε 3·41, 3·45, 3·50, 3·32, 3·15, 3·05, 2·99, 2·99, 2·88, 2·69) (Cary model 11; we are indebted to Dr. R. S. M. Smellie for this determination). The yellow colour and associated long-wave absorption (395—450 mμ) were established as characteristic features of the pure hydrocarbon by examination of successive fractions eluted from a benzene chromatogram of the hydrocarbon over alumina: the relative intensities of the peaks were found to be constant. Nuclear magnetic resonance measurements gave only one peak (with fine structure) at $\sigma = -1{\cdot}80$ (in dioxan), $\sigma = -1{\cdot}75$ (in CH_2Cl_2).

The best crystallisation solvent was benzene (solubility: 6 mg./ml. at 20°, 10 mg./ml. at 55°). The hydrocarbon is, however, moderately soluble in tetrahydrofuran and slightly soluble in ether, dioxan, carbon tetrachloride (2 mg./ml.), chloroform, methylene chloride (1 mg./ml.), ethyl acetate, n-hexane, cyclohexane (1 mg./100 ml.), and pyridine. The hydrocarbon is unstable in the crystalline state, decomposing explosively when ground (*e.g.*, during the preparation of a Nujol mull) or when heated above 80°. After a few days at room temperature, either in air or a vacuum, in the light or in the dark, the crystals, though unchanged in shape, are black, insoluble, and no longer give a distinct *X*-ray diffraction pattern. Storage in the solid state is feasible for several weeks at $-5°$, though it is better to store the compound as a benzene solution. It is more stable in pyridine than in benzene; for instance, a dilute solution of the hydrocarbon (*ca.* 1 mg./2 ml.) in pyridine darkened only slowly at 100°, whereas a similar solution in benzene at 80° charred after a few minutes. The density of the hydrocarbon was determined by flotation of a large crystal (*ca.* 5 mm. × 0·1 mm.; very small crystals were unduly sensitive to convection effects) in an aqueous solution of zinc chloride whose density was then measured. Adsorbed and dissolved air were removed from the crystal and the solution respectively at the water pump in 15 min. Found: $d_4^{19} = 1·283$ (from dioxan), 1·306 (from benzene). The dimensions of the unit cell were:[11] $a = 28·3$, $b = 3·87$, $c = 11·5$ Å ($\beta = 90°$); hence for four molecules of *M* 248 the required density is $d = 1·308$.

The isolation procedure described was superior to that involving the removal of the solvent under reduced pressure, acidification of the residue, and extraction with ether, as less of the product decomposed.

The hydrocarbon formed a 1 : 1 *complex* with trinitrofluorenone,[20] as red needles, m. p. 160° (decomp.) (from acetic acid) (Found: C, 70·5; H, 2·8; N, 7·7. $C_{20}H_8,C_{13}H_5N_3O_7$ requires C, 70·4; H, 2·4; N, 7·5%). Hexanitrosobenzene [21] in ethanol–acetic acid (4 : 1) did not form a complex.

Catalytic Hydrogenation of 1,2:7,8-*Dibenzocyclododeca*-1,7-*diene*-3,5,9,11-*tetrayne* (V).—A solution of the hydrocarbon (806 mg., 3·2 mmoles) in tetrahydrofuran (40 ml.) was added to 10% palladium–charcoal (1643 mg.; "Baker") which had been prehydrogenated under ethyl acetate, and the hydrogenation carried out in the usual manner. The uptake was 382 ml. (16·1 mmoles) of hydrogen (68%) after 5 hr., most of the hydrogen (60%) being taken up in the first 10 min. Evaporation of the solvent, together with the hot chloroform used for extraction of the catalyst, left an oil (564 mg.), trituration of which with ether yielded colourless crystals. This solid, after sublimation, at 210°/10^{-4} mm. was identified as "*trans*-fluorenacene" [5,11-dihydroindeno(1,2-b)fluorene] (VII), m. p. 300—302° (sealed tube; uncorr.) (Found: C, 94·3; H, 5·8. Calc. for $C_{20}H_{14}$: C, 94·45; H, 5·55%), $\nu_{max.}$ (KCl disc) 955m, 870m, 770s, 730s cm.$^{-1}$. Infrared and ultraviolet absorption spectra (in ether) were identical with those of a genuine sample;[15] the mixed m. p., 298—300°, was undepressed. The residual oil was chromatographed on alumina (40 g.).

(*a*) Elution with light petroleum (b. p. 60—80°) yielded a colourless oil (263 mg.), trituration of which with methanol–ether led to the deposition of 1,2:7,8-*dibenzocyclododeca*-1,7-*diene* (VIII) (*ca.* 100 mg.), which crystallised from ethanol in colourless needles, m. p. 103—105° [Found: C, 90·8; H, 8·95%; *M*, 224 (micro-Rast). $C_{20}H_{14}$ requires C, 90·85; H, 9·15%; *M*, 264], $\nu_{max.}$ (in CS_2) 765, 756, 740 cm.$^{-1}$ [no absorption near 1370 cm.$^{-1}$ (CH_3)], $\lambda_{max.}$ (in cyclohexane) 266·5, 274 mμ (log ε 2·91, 2·88), $\lambda_{min.}$ 237, 271 mμ (log ε 1·90, 2·72). Tetralin [22] has $\lambda_{max.}$ (in iso-octane) 267, 273 mμ (log ε 2·77, 2·77). The nuclear magnetic resonance spectrum showed bands with fine structure at $\sigma = -1·90$ (aromatic CH), $+2·37$ (benzylic CH_2), and $+3·45$ (saturated CH_2); 1,4-diphenylbutane and tetralin had similar absorption.

(*b*) Benzene–light petroleum (1 : 9) yielded an oil (146 mg.), which after trituration with ether–ethanol deposited crystals (*ca.* 30 mg.), recrystallisation of which from methanol gave a "*naphthalene derivative*," probably 5,6-*dihydrobenz*[e]*indeno*[1,2-a]*indene* (IX) as colourless plates, m. p. 117—119° [Found: C, 93·6; H, 6·5%; *M*, 235 (micro-Rast). $C_{20}H_{16}$ requires C, 93·7; H, 6·3%; *M*, 256]. The mass spectrogram showed peaks at mass numbers 91, 115, 141, 142, 166, and 256 (parent peak). Structure (IX) is consistent with this pattern in view of the known propensity for fission at benzylic carbons. Thus, the peaks at 115, 141, and 142 normally occur in the cracking pattern of a methylnaphthalene or a methylenenaphthalene ($C_{11}H_9$, 141) fragment. Mass numbers 91 and 166 probably represent the benzyl (C_7H_7, 91) and benzindane ($C_{13}H_{10}$, 166) fragments respectively. This product had $\nu_{max.}$ (in CS_2) 870, 804, 766, 749, 741, cm.$^{-1}$, $\lambda_{max.}$ (in cyclohexane) 236, 268, 275, 310, 316, 324 mμ (log ε 4·82, 3·75, 3·82, 3·03,

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[20] Newman and Lutz, *J. Amer. Chem. Soc.*, 1956, **78**, 1956.

[21] Bailey and Case, *Proc. Chem. Soc.*, 1957, 176; we are indebted to Dr. Bailey for a sample.

[22] API Project 44, No. 133.

2·92, and 3·09 respectively), $\lambda_{min.}$ 248 (log ε 3·37). 2,3-Benzindane[23] has $\lambda_{max.}$ (in EtOH) 322, 315, 310, 292, 285, 280, 276, 270, 264, 228 mμ (log ε 3·38, 3·03, 3·62, 3·65, 3·73, 3·70, 3·62, 3·54, and 4·99 respectively).

(*c*) Elution with benzene yielded a red oil (34 mg.), from which, on treatment with ether and very slow evaporation, a further small quantity of the dihydroindeno[1,2-*b*]-fluorene (VII) separated.

The gas–liquid chromatogram (214°; 40 ml./min.) of the crude reduction product showed that the hydrocarbons (VIII), m. p. 103° (R.T. 20 min.), and (IX), m. p. 117° (R.T. 35 min.), constitute 50% and 38% of the mixture respectively. Six other peaks were noted. The hydrocarbon (VII), m. p. 300°, which gave a broad peak (R.T. 47 min., 75 ml./min.) too weak to be measured, was estimated, from the amount isolated, to constitute at least 3% of the product.

The two low-melting products, (VIII) and (IX), are very soluble and tend to crystallise together, and consequently only relatively small amounts of pure material were isolated.

Sodium–Liquid Ammonia Reduction of 1,4-*Diphenylbuta*-1,3-*diyne* (*with* J. W. PURDIE).—A solution of the diyne (1·10 g., 5 mmoles) in dry tetrahydrofuran (50 ml.) was added slowly to a solution of sodium (920 mg., 40 milli-atom-equiv.) in liquid ammonia (300 ml.), the colour changing from blue through violet and red to a dull orange. More sodium (1·84 g.) was then added, the mixture becoming green, then blue. The volume was increased to 500 ml. with liquid ammonia, and the mixture stirred for 2 hr., after which dry ammonium chloride was added slowly until the colour changed to pale yellow. After evaporation of the ammonia the residue was treated with 6N-hydrochloric acid (50 ml.) and extracted with ether. The neutral fraction was chromatographed on alumina (grade III; 30 g.). Elution with light petroleum yielded a colourless oil, the infrared spectrum of which demonstrated the presence of non-conjugated ethylenic material, $\nu_{max.}$ (film) 966 cm.$^{-1}$ (*trans* C=C), $\lambda_{max.}$ (in cyclohexane) 260 mμ (log ε 2·77).

A portion of the oil (42 mg., 0·208 mmole) was hydrogenated in ethyl acetate over 10% palladium–charcoal, resulting in a hydrogen uptake of 0·114 mmole and the formation of 1,4-diphenylbutane [$\nu_{max.}$ (in Nujol) 745, 698 cm.$^{-1}$].

Sodium–Liquid Ammonia Reduction of 1,2:7,8-*Dibenzocyclodedeca*-1,7-*diene*-3,5,9,11-*tetrayne* (V).—A solution of the hydrocarbon [1·3 g., 5·2 mmoles, (spectroscopic estimation)] in tetrahydrofuran (100 ml.) was added slowly to a solution of sodium (1·70 g.) in liquid ammonia (300 ml.). More sodium (4·9 g.) was then added and the volume of the mixture increased to 750 ml. by addition of liquid ammonia. After 2 hours' stirring ammonium chloride (dried for 12 hr. at 120°; omission of this precaution gave rise to increased carbonyl absorption in the product) was added slowly, the blue solution becoming colourless. The ammonia was allowed to evaporate overnight and the residue then dissolved in 6N-hydrochloric acid (200 ml.) and extracted with ether. The extract was washed with saturated sodium carbonate solution, dried (Na_2SO_4), and evaporated. The residual yellow oil (1·367 g.), $\nu_{max.}$ (film) 1750s, 1700s cm.$^{-1}$ (carbonyl impurity) was chromatographed in benzene–light petroleum (1 : 1) on alumina (type O; 100 g.). Three fractions were obtained. Elution (*a*) with benzene–light petroleum (1 : 19; 400 ml.) yielded a colourless gum (821 mg., 3·3 mmoles), (*b*) with benzene–light petroleum (1 : 2; 300 ml.) yielded a yellow gum (150 mg.), $\nu_{max.}$ 970m cm.$^{-1}$, and (*c*) with ether (200 ml.) yielded a brown gum (160 mg.). Fractions (*b*) and (*c*) were not further examined.

Fraction (*a*) on hydrogenation over platinum oxide (190 mg.) in ethyl acetate containing one drop of perchloric acid absorbed only 2·28 ml. (0·1 mmole) after 85 min. The resulting gum (760 mg.) when triturated with ether deposited a precipitate (40 mg.) which after crystallisation from chloroform–ether furnished 4*b*,5,5*a*,10*b*,11,11*a*-*hexahydroindeno*[1,2-b]*fluorene* (X), α-*form*, as rectangular plates, m. p. 230—231° [Found: C, 92·4; H, 7·9%; *M* (thermistor drop) 245 (in $CHCl_3$). $C_{20}H_{20}$ requires C, 92·25; H, 7·75%; *M*, 260], $\nu_{max.}$ (in CS_2) 741 cm.$^{-1}$ [no absorption near 1370 cm.$^{-1}$ (C–CH_3)], $\lambda_{max.}$ (in cyclohexane) 260·5, 266·5, 273 mμ (log ε 3·18, 3·39, 3·41), $\lambda_{min.}$ 233, 262·5, 270 mμ (log ε 2·02, 3·15, 3·00). 1,2-Dimethylindane[24] (in iso-octane) has $\lambda_{max.}$ 260, 267, 273 mμ (log ε 2·90, 3·10, 3·16) $\lambda_{min.}$ 232, 264, 270 (log ε 1·52, 2·85, 2·63). The ethereal mother-liquor was concentrated and chromatographed on alumina (100 g.), and 50 ml. fractions were collected. Elution with light petroleum (b. p. 60—80°; 650 ml.) yielded crystalline and partially crystalline fractions (468 mg.). The combined fourth and fifth fractions were

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[23] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Chapman and Hall Ltd., London, 1951, No. 214.

[24] Entel, Ruof, and Howard, *Analyt. Chem.*, 1953, **25**, 1304.

recrystallised several times from methanol–ether, to give 4*b*,5,5*a*,10*b*,11,11*a*-*hexahydroindeno*-[1,2-b]*fluorene* (X), β-*form,* as long needles, m. p. 120—122° [Found: C, 91·9; H, 8·05%; *M* (thermistor drop), 259 (in $CHCl_3$), 246 (in CH_2Cl_2)], $\nu_{max.}$ (in CS_2) 769, 741, 735, 722 cm.$^{-1}$ [no absorption near 1370 cm.$^{-1}$ ($C-CH_3$)], $\lambda_{max.}$ (in n-hexane) 260·5, 267, 273·5 mμ (log ε 3·33, 3·45, 3·45), $\lambda_{min.}$ 234, 262·5, 271 mμ (log ε 2·47, 3·30, 3·19). Nuclear magnetic resonance showed bands at σ −1·65 (aromatic CH) and diffuse absorption between σ 2 and 4 with a maximum at σ 2·7. The benzylic methylene in tetralin and 1,4-diphenylbutane shows absorption at σ 2·7; the broad absorption regions are typical of rigid systems. Elution with increasing proportions of benzene, up to pure benzene, provided a further 155 mg. of semicrystalline material, which was not further examined. Gas–liquid chromatography (224°; 20 ml./min.) showed that the crude product, before alumina chromatography, contained α-isomer (R.T. 18 min., 21%), β-isomer (R.T. 16 min., 48%), 1,2:7,8-dibenzocyclododeca-1,7-diene (VIII) (R.T. 14 min., 8%), the "naphthalene" (IX) (R.T. 28 min., 7%), and at least four other minor components. Immediately after this chromatogram had been run, a pure sample of the β-isomer was chromatographed to determine the inherent degree of isomerisation. The proportions given are therefore corrected.

Isomerisation of β- *to* α-4*b*,5,5*a*,10*b*,11,11*a*-*Hexahydroindeno*[1,2-b]*fluorene* (XI).—During gas–liquid chromatography (4% Apiezon "L" on 100—120 mesh Celite at 214°) of the two hexahydrofluorenes (X) it was noted that the α-form gave one peak whereas the β-form gave two peaks, the retention time of the second peak of the β-form being the same as that for the α-form. Alteration of the flow rate of the carrier gas (100 ml./min. to 24 ml./min.) showed that the relative area of the second β-peak decreased as a function of retention time (from 10·5 min. to 30·5 min.). A later chromatogram run under identical conditions on an apparently similarly prepared column showed an α : β ratio different from that in the previous experiment. In all experiments crystalline samples of the highest purity were used. Attempts (KOH, ethylene glycol, 244°, 3 hr.; "Celite," 300°, 3 hr.) to isomerise the β(120°)- to the α(230°)-hydrocarbon were unsuccessful, the former compound being substantially unchanged.

Dehydrogenations.—(a) *General.* The following procedure (for details of which we are indebted to Professor V. Prelog, E.T.H., Zurich) was used for all the dehydrogenations. The hydrocarbon was placed in a tube (diameter *ca.* 7 mm.) which was sealed at one end. It was then covered with thoroughly dried, granular 15% palladium–charcoal,[25] and the tube was sealed under nitrogen. After total immersion in a silicone oil-bath at 320° for 2 hr., during which the tube was inverted to ensure the complete mixing of the components, the tube was cooled, opened and the product sublimed out at *ca.* 5 × 10^{-5} mm. The recovery in all cases was almost quantitative. Tetralin (5·2 mg.), on dehydrogenation with palladium-charcoal (43 mg.), gave crystalline naphthalene in high yield.

(b) *Dehydrogenation of the* β-*hexahydrofluorene* (X). The hydrocarbon (7·1 mg.) on dehydrogenation with palladium–charcoal (63 mg.), followed by sublimation at 230° (block), yielded indeno[1,2-b]fluorene (VII), m. p. and mixed m. p. 300—302°; infrared (KCl disc) and ultraviolet (ether) absorption spectra were identical with those of a genuine sample.[15]

(c) *Dehydrogenation of the* α-*hexahydrofluorene* (X). Similar treatment of this hydrocarbon (25 mg.) furnished indeno[1,2-*b*]fluorene (VII) of slightly lower purity.

(d) *Dehydrogenation of dibenzocyclododecadiene* (VIII). The hydrocarbon (6·9 mg.) was dehydrogenated with palladium–charcoal (70 mg.) for 5 hr.; sublimation at 230° then yielded gummy crystals (5·1 mg.), $\lambda_{max.}$ (in cyclohexane) 274, 280 mμ (log ε 3·59, 3·60), $\lambda_{min.}$ 257 mμ (log ε 3·58). Gas-liquid chromatography (214°, 40 ml./min.) showed that the product consisted of unchanged material (R.T. 23 min., 57%) and the "naphthalene" (IX), m. p. 117° (R.T. 39 min., 43%).

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[25] Newman and Zahm, *J. Amer. Chem. Soc.*, 1943, **65**, 1097.