14. *Macrocyclic Compounds. Part II.*[1] *Synthesis of Macrocyclic Hydrocarbons Containing Triple Bonds, Double Bonds, and Benzene Nuclei.*

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Several macrocyclic compounds with C_{11}—C_{30} rings and containing one or more acetylene, diacetylene, ethylene, or phenylene groups in the macrocyclic chain have been synthesized either by condensation between a sodium acetylide and a primary halide or by oxidative coupling of terminal acetylenes in the final cyclization step. Most of the compounds have the unsaturated groups separated by two methylene groups, and can be isomerized by alkali. The extremely unstable *m*-octa-3′,5′-diynylenebenzene could be isolated at low temperatures; it is the smallest ring system known (C_{11}) which contains a diacetylene group.

Cyclopentacosane has been obtained for the first time.

MACROCYCLIC acetylenes containing conjugated diyne systems have been used extensively by Sondheimer and his co-workers as intermediates[2] in the preparation of macrocyclic "aromatic" compounds containing closed polyene chromophores, such as cyclo-octadecanonaene.[3] We have been interested in the spectroscopic behaviour of open polyene chromophores which are incorporated in a macrocyclic compound so that a particular geometrical shape is imposed on them by the ring-size. Such studies are related to the study of "overtone"-bands (*cis*-peak, etc.) in the electronic spectra of the geometrical isomers of acyclic polyenes.[4]

It was hoped that some of the macrocyclic non-conjugated poly-ynes described in the preceding paper[1] might serve as intermediates in the preparation of macrocyclic polyenes of this kind. However, treatment with potassium t-butoxide under the gentle conditions (90° and lower) used by Sondheimer[2] was without effect on practically all of them; under more drastic conditions (160—200°) *o*-polymethylenebenzenes were formed from the cyclic diynes, in analogy with the aromatization effected by Eglinton, Raphael, and Willis.[5] The only compound which responded to gentle alkali-treatment, although it did not give well-defined products, contained acetylenic bonds separated by two CH_2 groups, as also do Sondheimer's intermediates.

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[1] Part I, preceding paper.

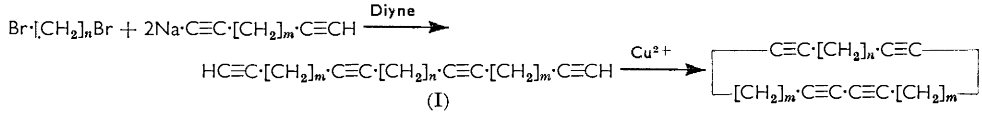
[2] Sondheimer *et al.*, *J. Amer. Chem. Soc.*, 1959, **81**, 1771, 4755; 1960, **82**, 754; 1961, **83**, 1259.

[3] Sondheimer and Wolovsky, *Tetrahedron Letters*, 1959, No. 3, 3.

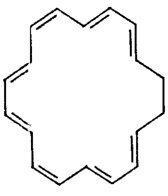
[4] Zechmeister, *Chem. Rev.*, 1944, **34**, 267; Dale, *Acta Chem. Scand.*, 1954, **8**, 1235; 1957, **11**, 265, 971.

[5] Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1960, 247.

In the present paper we report the synthesis of a variety of macrocyclic hydrocarbons containing this structural feature: acetylenic bonds separated from another unsaturated system by two CH_2 groups. For steric reasons, mainly concerning valency angles, it was considered that the 18-membered ring would have the ideal size. The 18-membered cyclo-octadeca-1,5,7,11-tetrayne (II; $m = 2$, $n = 6$) was therefore synthesized by the following steps, the first involving use of an excess of diyne in liquid ammonia:



$$\mathrm{Br{\cdot}[CH_2]_{\mathit{n}}Br + 2Na{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{m}}{\cdot}C{\equiv}CH} \xrightarrow{\text{Diyne}} \underset{\text{(I)}}{\mathrm{HC{\equiv}C{\cdot}[CH_2]_{\mathit{m}}{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{m}}{\cdot}C{\equiv}CH}} \xrightarrow{\mathrm{Cu^{2+}}} \begin{bmatrix}\mathrm{C{\equiv}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\equiv}C} \\ \mathrm{[CH_2]_{\mathit{m}}{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}[CH_2]_{\mathit{m}}}\end{bmatrix} \text{(II)}$$

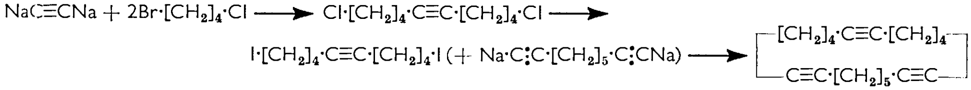


(III)

The intermediate octadeca-1,5,13,17-tetrayne (I; $m = 2$, $n = 6$), m. p. 43°, was obtained in 37% yield when a 14% excess of free hexadiyne was added to suppress the concentration of the disodium salt, which would lead to polymers or cyclic compounds (when no excess was used, the yield was only 16%). The final oxidative coupling by means of cupric acetate in pyridine[6] gave the cyclo-octadecatetrayne, m. p. 58—60°, in 30% yield. The triple bonds in this compound are separated by only two CH_2 groups, and it was hoped that alkali-treatment would lead to the conjugated cyclo-octadecaoctaene (III). In fact, there was a reaction in the presence of potassium t-butoxide even at room temperature, but it has not yet been possible to control the reaction to obtain well-defined isomerization products.

A second aim was to complete the series of cycloalkanes. After our syntheses of cyclononadecane[1] the next missing link was the 25-membered ring. The acceptable yield in the above reaction led us to adapt it for the synthesis of cyclopentacosa-1,8,10,17-tetrayne (II; $m = 5$, $n = 7$). The intermediate pentacosa-1,8,17,24-tetrayne (I; $m = 5$, $n = 7$), m. p. 29°, was obtained in 44% yield by using a 60% excess of free nonadiyne, and oxidative coupling gave the cyclopentacosatetrayne, m. p. 35°, in 8% yield. Complete hydrogenation finally yielded cyclopentacosane, $C_{25}H_{50}$; its melting point, 52—54°, fits well into the cycloalkane series,[6] which is hereby complete up to and including the 30-membered ring. The intriguing melting point behaviour of this series will be discussed in the following paper.[7]

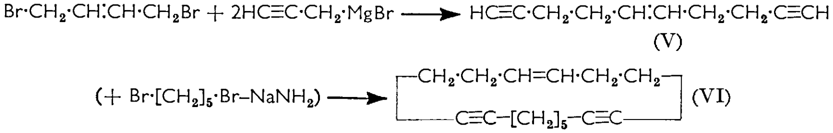
Another possible synthetic route to the 25-membered ring was abandoned when a model reaction with easily available starting materials gave only a negligible yield of cyclononadeca-1,7,13-triyne (IV), m. p. 58°, the first known cyclic triyne, in the following reaction steps:



$$\mathrm{NaC{\equiv}CNa + 2Br{\cdot}[CH_2]_4{\cdot}Cl \longrightarrow Cl{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}[CH_2]_4{\cdot}Cl \longrightarrow I{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}[CH_2]_4{\cdot}I\ (+\ Na{\cdot}C{\vdots}C{\cdot}[CH_2]_5{\cdot}C{\vdots}CNa) \longrightarrow} \begin{bmatrix}\mathrm{[CH_2]_4{\cdot}C{\equiv}C{\cdot}[CH_2]_4} \\ \mathrm{C{\equiv}C{\cdot}[CH_2]_5{\cdot}C{\equiv}C}\end{bmatrix} \text{(IV)}$$

An analogous attempt to prepare cycloheptadeca-1,6,11-triyne failed completely.

For the synthesis of intermediates for macrocyclic polyenes, it was thought that the presence of one double bond between two triple bonds might direct the isomerization more cleanly to the desired polyene. A 15-membered ring containing two triple bonds and one double bond (VI) was therefore prepared by the following steps:



$$\mathrm{Br{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2Br + 2HC{\equiv}C{\cdot}CH_2{\cdot}MgBr \longrightarrow \underset{\text{(V)}}{HC{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}CH}}$$

$$\mathrm{(+\ Br{\cdot}[CH_2]_5{\cdot}Br{-}NaNH_2) \longrightarrow} \begin{bmatrix}\mathrm{CH_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2} \\ \mathrm{C{\equiv}C{-}[CH_2]_5{-}C{\equiv}C}\end{bmatrix} \text{(VI)}$$

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[6] Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1959, **81**, 4600.

[7] Part III, Dale, following paper.

It is of interest that, whereas the open-chain product (V) was a liquid mixture of the *cis*- and the *trans*-olefin, the cyclized product (VI) contained only the *cis*-isomer. The *trans*-configuration in this case seems to be unsuitable sterically for ring formation. Reaction with potassium t-butoxide, in the hope of producing the conjugated cyclopentadecapentaene (cf. Sondheimer *et al.*[8]), was again uncontrollable.

We therefore incorporated benzene nuclei into the macrocyclic chain, to stabilize the unsaturated systems and prevent intramolecular addition[9] or whatever secondary reactions occur in the polyenes during alkali-isomerization. The annexed chart shows the compounds prepared and the reactions used.

The isomerization method was tried out on the terminal diacetylenes (VII) and gave readily the expected dibutadienylbenzenes, which, however, were so autoxidizable that it was preferred to methylate the diacetylenes (VII) and isomerize the resulting compounds (VIII) to the more stable and crystalline conjugated open-chain polyenes, to be used as references for spectral comparisons with the cyclic polyenes obtained later.

The disodium salt of the terminal diynes (VII) gave, with 1,5-dibromopentane, the three isomeric cyclic compounds (XI; $n = 5$) in moderate yields. As the macro-ring size (*o*-, 15 carbon atoms; *m*-, 16; *p*-, 17) was smaller than 18 carbon atoms, considered to be sterically ideal for the incorporation of a polyene system, it may not be surprising that the alkali-isomerization, although controllable, was very much slower and that the resulting polyenes were liquid. Three analogous macrocyclic diynes, which are not isomeric, but all contain 18 carbon atoms in the big ring (XI; *o*-, $n = 8$; *m*-, $n = 7$; *p*-, $n = 6$) were therefore prepared, and their isomerization was more rapid and well-defined. The isomerization of these compounds, the isolation of the polyenic compounds, and a detailed discussion of the spectral properties will be reported later.

In one case, in addition to the cyclic " monomer " (XI; *o*-, $n = 5$), the cyclic " dimer " (IX) with a 30-membered macro-ring, was also isolated. It was spectrally indistinguishable from the monomer.

The terminal diynes (VII) were then oxidatively coupled and gave the high-melting cyclic " dimers " (XII), whose ultraviolet spectra are superpositions of normal dialkylbenzene and dialkyldiacetylene spectra; the latter contribution disappears on hydrogenation.

In the case of the *meta*-isomer the cyclic " dimer " was formed only in concentrated solution at higher temperatures (90—100°) but in low yield (2%). Along with it, a similar amount of the cyclic " monomer " (X) was obtained, and the higher yield (12%) in dilute solution at 70° accounts for the absence of dimer. The monomer was extremely unstable and polymerized in a few seconds, even in the dark, to an insoluble red polymer the moment the solvent was eliminated, but it could be isolated by crystallization at −80°.

The tension caused by the fact that the 11-membered ring is too small to allow the six carbon atoms of the diacetylene group to form a linear arrangement is also reflected in the ultraviolet and infrared spectra, which are different from those of the dimer although, in general, monomers can hardly be distinguished spectrally from the corresponding dimers. The weak ultraviolet bands at 306, 317, and 331 mμ of the monomer (absent in the dimer) might invite discussion, but it remains to be proved that they are not caused by a strongly absorbing (isomeric ?) impurity. The monomer was further characterized by isolation of *m*-octamethylenebenzene {bicyclo[8,3,1]tetradeca-1(14),10,12-triene} after catalytic reduction; this compound may also be strained, as a non-planar aromatic ring is indicated by the lack of the typical vibrational structure of *meta*-disubstituted benzenes.

All the other acetylenic compounds were also quantitatively hydrogenated, primarily as an aid in determining their structure, but in some cases also to provide a derivative

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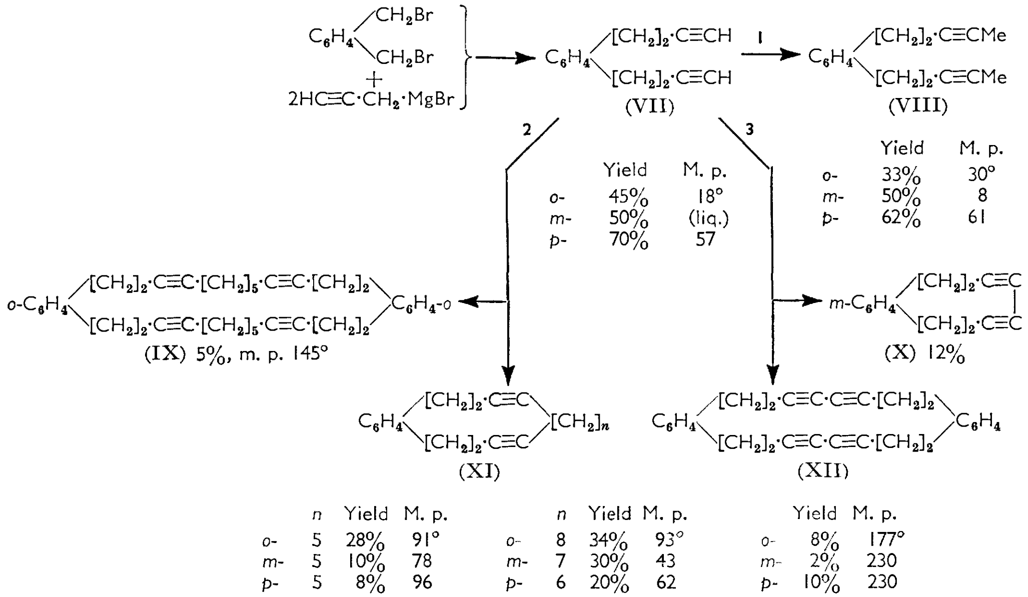
[8] Sondheimer *et al.*, *J. Amer. Chem. Soc.*, 1960, **82**, 755; 1961, **83**, 1686.

[9] Amiel and Sondheimer, *Chem. and Ind.*, 1960, 1162; Sondheimer and Gaoni, *J. Amer. Chem. Soc.*, 1961, **83**, 4863.

stable enough to support a Rast determination of the molecular weight without decomposition; the obtained polymethylenebenzenes and the dibenzo-analogues are new compounds.



Reagents: 1, $NaNH_2$–NH_3–MeI. 2, $NaNH_2$–NH_3–Br·$[CH_2]_n$·Br. 3, Cu^{2+}.

EXPERIMENTAL

Octadeca-1,5,13,17-*tetrayne* (I; $m = 2$, $n = 6$).—Hexa-1,5-diyne (0·25 mole) was added to a suspension of sodamide (0·22 mole) in liquid ammonia (1 l.), and the mixture stirred for 4 hr. Then 1,6-dibromohexane (0·1 mole) was introduced slowly, and stirring continued for 3 days. After evaporation of the ammonia, the residue was taken up in ether and water added. The organic layer was separated, washed with water, dried, and evaporated. Distillation gave a solid fraction (8·75 g., 37%), b. p. 100—125°/10^{-2} mm., and a residue (8 g.). The distillate recrystallized from ethanol, giving *octadeca*-1,5,13,17-*tetrayne* (7·8 g.), m. p. 42—44°, $\lambda_{max.}$ for terminal acetylene at 3·0, 4·68, and 15 μ. On a platinum dioxide catalyst the tetrayne absorbed 8·0 mol. of hydrogen, to give n-octadecane, m. p. 27—28°.

When no excess of hexa-1,5-diyne was used with respect to either sodamide or dibromohexane, the yield was only 16% and the distillation residue increased correspondingly. On the other hand, the use of too large an excess presents no advantage here as the volatile hexadiyne cannot be easily recovered.

Pentacosa-1,8,17,24-*tetrayne* (I; $m = 5$, $n = 7$).—As above, nona-1,8-diyne (96 g., 0·8 mole) was added to sodamide (0·5 mole) in liquid ammonia (1 l.), and 1,7-dibromoheptane (0·2 mole) was introduced. The reaction time was 7 days. Distillation gave first unchanged nona-1,8-diyne (58 g.), b. p. 30°/0·1 mm., then the tetrayne (29·3 g., 44%), b. p. 180—200°/10^{-3} mm., and a residue (11·5 g.). Recrystallization from ether–ethanol (1 : 20) gave *pentacosa*-1,8,17,24-*tetrayne* (37%), m. p. 27·5—29° (Found: C, 89·1; H, 10·6. $C_{25}H_{36}$ requires C, 89·2; H, 10·8%). As above it absorbed 7·8 mol. of hydrogen, to give n-pentacosane, m. p. 53—54°.

Cyclo-octadeca-1,5,7,11-*tetrayne* (II; $m = 2$, $n = 6$).—Octadeca-1,5,13,17-tetrayne (2·1 g.) was added in 1 hr. to a stirred solution of cupric acetate (5 g.) in pyridine (500 ml.) at 75° (cf. Sondheimer[6]). Chromatography on alumina of the coupled product gave *cyclo-octadeca*-1,5,7,11-*tetrayne* (30%), m. p. 58—59·5° (from methanol) (Found: C, 91·4; H, 8·4. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%), $\lambda_{max.}$ (in hexane) 216, 227, 242, 256 mμ (ε 340, 395, 375, 230). As above, 7·4 mol. of hydrogen were absorbed, giving cyclo-octadecane, m. p. 72·5—74°.

Cyclopentacosa-1,8,10,17-*tetrayne* (II; $m = 5$, $n = 7$).—Pentacosa-1,8,17,24-tetrayne (5 g.)

was slowly added in 4 hr. to the cupric acetate–pyridine solution at 90—100°. The mixture was left for 2 days at room temperature, then worked up, and the coupling product was chromatographed on alumina; it gave one crystalline fraction (0·4 g.), m. p. 33—34°. Recrystallization from ethanol–propanol gave the *cyclopentacosa*-1,8,10,17-*tetrayne*, m. p. 35—35·5° (Found: C, 90·1; H, 10·1. $C_{25}H_{34}$ requires C, 89·75; H, 10·25%). The infrared spectrum showed the absence of terminal acetylene and presence of diacetylene bands at 4·42 and 4·62 μ. In cyclohexane the tetrayne had $\lambda_{max.}$ 216, 227, 241, 255 mμ (ε 410, 450, 410, 260). It absorbed 7·75 mol. of hydrogen, as above, giving *cyclopentacosane*, m. p. 52—54° (from propanol) [Found: C, 85·5; H, 14·2%; *M* (Rast), 389 ± 7. $C_{25}H_{50}$ requires C, 85·6; H, 14·4%; *M*, 350]. A mixed m. p. with n-pentacosane was 47—50°. The infrared spectrum was very similar to those of other cycloalkanes of comparable size.

Cyclononadeca-1,7,13-*triyne* (IV).—1-Bromo-4-chlorobutane was prepared from tetrahydrofuran by treatment first with hydrogen chloride and then with phosphorus tribromide.[10] 1,10-Dichlorodec-5-yne, b. p. 100—104°/10^{-2} mm., was obtained from this compound in one step by using disodium acetylide in liquid ammonia (30% yield), or in two steps by letting it first react with monosodium acetylide to give 1-chlorohex-5-yne [10] (70% yield), whose sodium salt with another mol. of bromochlorobutane gave the same dichlorodecyne [11] (33% yield). 1,10-Di-iododec-5-yne, b. p. 134—142°/10^{-2} mm., was obtained in 50% yield from this compound by treatment with potassium iodide in refluxing acetone.[11] The final cyclization was performed according to the general procedure between the disodium salt of nona-1,8-diyne in liquid ammonia and the 1,10-di-iododec-5-yne. After a reaction time of 3 days a yield of only 1% of a crystalline substance was obtained; this had b. p. 144—180°/10^{-2} mm., m. p. (from methanol) 57—58·5°; its infrared spectrum showed absence of terminal acetylene and indicated presence of disubstituted acetylene (bands at 7·35 and 7·50 μ).

Attempt to Prepare Cycloheptadeca-1,6,11-*triyne*.—1,8-Dichloro-oct-4-yne was obtained in 30% yield in one step (cf. a much lower yield in a two-step reaction [12]) from 1-bromo-3-chloropropane and disodium acetylide in liquid ammonia. Treatment with potassium iodide in acetone [12] converted it in 70% yield into 1,8-di-iodo-oct-4-yne, b. p. 94—108°/10^{-3} mm. The final reaction with the disodium salt of nona-1,8-diyne gave no cyclic product; all fractions contained terminal acetylene groups.

cis-*Cyclopentadec*-1-*ene*-5,12-*diyne* (VI).—Dec-5-ene-1,9-diyne (V) was prepared according to Sondheimer and his co-workers,[8] but from *cis*-1,4-dibromobut-2-ene (instead of the *trans*-isomer), and propargylmagnesium bromide. A mixture of *cis*- and *trans*-isomers was obtained, which was used directly, as the disodium salt, in a reaction with 1,5-dibromopentane in liquid ammonia. The product distilled at 90—110°/10^{-3} mm. and gave after crystallization from ethanol impure cyclopentadec-1-ene-5,12-diyne, m. p. 63—72°, in 14% yield (Found: C, 89·9; H, 9·9. Calc. for $C_{15}H_{20}$: C, 89·9; H, 10·1%). The infrared spectrum showed no terminal acetylene bands; it showed strong bands at 7·42 and 7·50 (disubstituted acetylene), 3·33 and 6·05 (C=C), and 10·34vw (*trans*-band), and 14·45vs μ (*cis*-band). The impurity may be a linear product with vinyl end groups (formed by loss of hydrogen bromide) as bands are found at 11·0 μ (and 10·05 μ); it cannot be an isomeric cyclic product because the hydrogenation product, although it has the correct infrared spectrum of cyclopentadecane, is also impure and melts at 54—63·5° (lit., 62°).

Dibut-3′-*ynylbenzenes* (VII; *o*-, *m*-, and *p*-).—Propargylmagnesium bromide [8] (1 mole) was prepared in ether (500 ml.); αα′-dibromoxylene [13] (0·5 mole) was added quickly with vigorous stirring, and the stirring continued overnight. The mixture was then poured on ice, the aqueous phase acidified with hydrochloric acid, the organic layer separated, and the aqueous layer extracted twice with ether. The combined extracts were dried (Na_2SO_4) and evaporated. The residue was distilled at reduced pressure. To obtain analytically pure samples, the diyne was precipitated from ethanol as its silver salt; the salt was filtered off, washed with ethanol, and decomposed by 5N-hydrochloric acid. The liberated diyne was extracted with ether, dried, and distilled. All three isomers passed over at 90—95°/10^{-3} mm.

o-*Dibut*-3′-*ynylbenzene*, obtained in 45% yield, had m. p. 17—18° (Found: C, 92·0; H, 7·85. $C_{14}H_{14}$ requires C, 92·3; H, 7·7%), $\lambda_{max.}$ 3·03, 4·68, and 15·5 (C≡CH) and 3·25, 3·30, 6·20, 6·66,

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[10] Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1294.
[11] Baker, Kierstead, Linstead, and Weedon, *J.*, 1954, 1804.
[12] Baker, Linstead, and Weedon, *J.*, 1955, 2218.
[13] Atkinson and Thorpe, *J.*, 1907, **91**, 1697.

and 13·22 μ (*o*-substituted benzene), and the ultraviolet spectrum expected for the aromatic part (*ortho*-disubstitution).[14]

The meta-*isomer* was obtained in 70% yield as a liquid (Found: C, 91·6; H, 7·7%). The spectrum contained the same acetylenic bands, and bands typical for *meta*-substituted benzene at 3·30, 6·19, 6·27, 6·70, 12·68, and 14·23 μ. The ultraviolet spectrum was normal for a *meta*-substituted benzene.[14]

The para-*isomer* was obtained in 70% yield, with m. p. 55—57° (Found: C, 92·4; H, 7·9%). The spectrum showed the same acetylenic bands, and bands for *para*-substituted benzene at 3·30, 6·56, 12·1, and 12·4 μ. The ultraviolet spectrum was typical for a *para*-disubstituted benzene.[14]

Dipent-3′-ynylbenzenes (VIII; *o*-, *m*-, and *p*-).—Dibut-3-ynylbenzene (0·1 mole) was added to a suspension of sodamide (0·2 mole) in liquid ammonia (500 ml.). An hour later, methyl iodide or bromide (0·2 mole) was added, and the mixture stirred overnight. The ammonia was then evaporated and the residue taken up in ether. The ether solution was washed with water, dried (Na_2SO_4), and evaporated. The residue in all three cases distilled at 130—140°/10^{-3} mm. When the infrared spectrum showed the presence of traces of terminal acetylene, the substance was shaken vigorously with a concentrated solution of Nessler's reagent, extracted with hexane, and redistilled.

o-*Dipent-3′-ynylbenzene* was obtained in 33% yield by using methyl iodide, and melted at 30°. It had the expected aromatic bands at 3·30, 6·20, 6·66, and 13·25 μ and not the three typical C≡CH bands; instead there is a very weak band at 4·48 (disubstituted acetylene) and a new band at 7·22 μ (Me).

The meta-*isomer* was obtained in 50% yield by using methyl bromide, and melted at 8°. Aromatic bands were at 3·30, 6·20, 6·27, 6·70, 12·8, and 14·3 μ, and the methyl band was at 7·25 μ. The acetylenic band at 4·48 μ was hardly visible, but strong bands [15] at 7·5 μ are, as in all these acetylenes, present.

The para-*isomer*, obtained by using methyl iodide (45% yield) or bromide (62% yield), had m. p. 61° (from methanol) (Found: C, 91·3; H, 8·6. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%) and aromatic bands at 3·30, 6·55, and 12·6 μ in addition to bands at 4·48 and 7·22 μ.

" (*Trideca-3,10-diynylene*)*benzenes* " (XI; $n = 5$; *o*-, *m*-, and *p*-).—A solution of dibut-3-ynylbenzene (0·1 mole) in ether (50 ml.) was added rapidly to a stirred suspension of sodamide (0·2 mole) in liquid ammonia (1 l.). An hour later 1,5-dibromopentane (0·1 mole) in ether was introduced, and the mixture stirred for 3 days under condenser cooled in solid carbon dioxide. The ammonia was then evaporated, and the residue taken up in ether, washed with water, dried (Na_2SO_4), and recovered. The residue distilled at 140—160°/10^{-3} mm. The infrared and ultraviolet spectra of these compounds and the following three of general structure (XI), as well as their hydrogenation products were normal [14,15] and substantiated the appropriate aromatic system and acetylenic bonds; no terminal acetylene or methyl group was indicated.

The *ortho*-isomer, *benzocyclopentadec-1-ene-5,12-diyne*,* was obtained in 16% yield; with a reaction time of seven days the yield increased to 28% of crude and 20% of pure product; it had m. p. 87—91° [Found: C, 91·15; H, 8·8%; *M* (Rast), 270 ± 7. $C_{19}H_{22}$ requires C, 91·1; H, 8·9%; *M*, 250]. Hydrogenation over platinum dioxide was complete after the absorption of 3·9 mol., and the resulting *benzocyclopentadecene* * melted at 12—13° (Found: C, 88·4; H, 11·4. $C_{19}H_{30}$ requires C, 88·3; H, 11·7%). From the crude oily residue after the evaporation of the ether extract from the cyclization reaction crystals separated. Recrystallized from benzene, they had m. p. 144—145° (yield 4·5%) and proved to be 1,2:16,17-*dibenzocyclotriaconta-1,16-diene-5,12,20,27-tetrayne* (IX) (Found: C, 90·9; H, 8·7. $C_{38}H_{44}$ requires C, 91·1; H, 8·9%). The ultraviolet and infrared spectra were identical with those of the cyclic monomer. The mol. weight could not be determined in camphor because of decomposition. Hydrogenation as above in dioxan at 25°/1 atm. gave *dibenzotriaconta-1,16-diene*, m. p. 110—111° (Found: C, 88·35; H, 11·5. $C_{38}H_{60}$ requires C, 88·3; H, 11·7%); the ultraviolet spectrum was unchanged and typical for an *ortho*-disubstituted benzene. Mol. weight determination (in camphor) gave 505 ± 6 (calc., 517).

The *meta*-isomer, *bicyclo*[13,3,1]*nonadeca-1(19),15,17-triene-4,11-diyne*, obtained in 10%

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* Naming of the *ortho*-isomers follows I.U.P.A.C. Rule A-23.5.

[14] Tunnicliff, Brattain, and Zumwalt, *Analyt. Chem.*, 1949, **21**, 890.

[15] Mannion and Wang, *Spectrochim. Acta*, 1961, **17**, 990.

yield, had m. p. 77—78° (Found: C, 91·1; H, 8·7%; *M*, 267 ± 6). Hydrogenation caused absorption of 4·3 mol. of hydrogen, and the resulting *bicyclo*[13,3,1]*nonadeca*-1(19),15,17-*triene* melted at 0—2° (Found: C, 87·9; H, 11·5%).

The *para*-isomer, *bicyclo*[13,2,2]*nonadeca*-1(18),15(19),16-*triene*-4,11-*diyne*, was obtained in 8% yield, with m. p. 95—96° (Found: C, 90·7; H, 8·9%; *M*, 258 ± 12). Hydrogenation ceased after the absorption of 4·2 mol. of hydrogen; the resulting *bicyclo*[13,2,2]*nonadeca*-1(18),15(19),16-*triene* melted at 10—12° (Found: C, 87·95; H, 11·3%).

Benzocyclo-octadec-1-*ene*-5,15-*diyne* (XI; *o*-, $n = 8$).—This *compound*, obtained as above (reaction time 7 days) from *o*-dibut-3-ynylbenzene and 1,8-dibromo-octane in 34% yield, had b. p. 160—180°/10^{-3} mm. and m. p. 92—93° (Found: C, 90·5; H, 9·7. $C_{22}H_{28}$ requires C, 90·35; H, 9·65%). Hydrogenation gave benzocyclo-octadecene * m. p. 14—15°(Found: C, 87·8; H, 11·7. $C_{22}H_{36}$ requires C, 87·9; H, 12·1%).

Bicyclo[15,3,1]*heneicosa*-1(21),17,19-*triene*-4,13-*diyne* (XI; *m*-, $n = 7$).—Prepared as above (7 days) from *m*-dibut-3-ynylbenzene and 1,7-dibromoheptane in crude yield of 30%, this *diyne* had b. p. 150—160°/10^{-3} mm. Recrystallization from methanol gave 16% of pure product, m. p. 42·5—43·5° (Found: C, 90·3; H, 9·3. $C_{21}H_{26}$ requires C, 90·6; H, 9·4%).

Bicyclo[14,2,2]*eicosa*-1(19),16(20),17-*triene*-4,12-*diyne* (XI; *p*-, $n = 6$).—This *compound*, obtained as above (7 days) from *p*-dibut-3-ynylbenzene and 1,6-dibromohexane in 20% yield, had b. p. 125—160°/10^{-3} mm., m. p. 60·5—62° (Found: C, 90·8; H, 9·3. $C_{20}H_{24}$ requires C, 90·85; H, 9·15%).

o-, m-, *and* p-*Compounds* (XII).—These compounds were prepared by oxidative coupling of the dibut-3-ynylbenzenes (VII) in dilute pyridine solution, usually at 70°, in the presence of cupric acetate,[6] and were isolated by chromatography on alumina. Besides the cyclic "dimers" (XII), which were first eluted, compounds of higher molecular weight were obtained in low yields; they were not further examined. Only in the case of the *meta*-isomer was a fraction eluted before the dimer; it proved to be the very unstable cyclic monomer (see below).

The *ortho*-isomer, (XII), 1,2:11,12-*dibenzocycloeicosa*-1,11-*diene*-5,7,15,17-*tetrayne*, was obtained in 8% yield, with m. p. 177° (Found: C, 93·5; H, 6·6. $C_{28}H_{24}$ requires C, 93·3; H, 6·7%). The infrared spectrum showed diacetylene bands at 4·40, 4·60, and 7·45 μ (α-CH_2),[15] and bands typical for an *ortho*-disubstituted benzene at 3·30, 6·20, 6·66, and 13·3 μ. The compound (in cyclohexane) had $\lambda_{max.}$ 215(sh), 244, 258, 265, 273 mμ (ε 31,000, 1200, 1040, 770, 630). Hydrogenation as above gave *dibenzocycloeicosa*-1,11-*diene*, m. p. 66° [Found: C, 89·0; H, 10·5%; *M* (Rast), 385 ± 5. $C_{28}H_{40}$ requires C, 89·3; H, 10·7%; *M*, 377], whose infrared spectrum showed no acetylenic absorption, though the aromatic bands remained at 3·30, 6·20, 6·30, 6·67, 13·4 μ; there were ultraviolet maxima (in hexane) at 212, 260, 266, 273 mμ (ε 23,200, 470, 630, 570).

The *meta*-isomer (XII), *tricyclo*[21,3,1,$1^{10,14}$]*octacosa* - 1(27),10,12,14(28),23,25 - *hexaene* - 4,6,17,19-*tetrayne*, was not obtained at 70° and only in 2% yield in concentrated solution at 90—100°; it melted at 230° (Found: C, 93·3; H, 6·7%), gave bands at 4·40 and 4·60 (diacetylene), at 7·37 and 7·46 (α-CH_2), and at 3·28, 6·20, 6·28, 6·70, 12·52, and 14·1 μ (*m*-disubstituted benzene), and $\lambda_{max.}$ (in dioxan) 243, 257, 268(sh), 272(sh) mμ (ε 1200, 980, 450, 360). Hydrogenation as above was complete after absorption of 7·4 mol. and gave the *hexaene*, m. p. 80° (Found: *M*, 329 ± 7). The unstable cyclic monomer is described separately below.

The *para*-isomer (XII), *tricyclo*[20,2,2,$2^{10,13}$]*octacosa* - 1(25),10,12,22(26),23,27 - *hexaene* - 4,6,16,18-*tetrayne* was formed in 10% yield; it had m. p. 230° (Found: C, 93·4; H, 6·8%), $\lambda_{max.}$ 4·40 and 4·60 (diacetylene) and at 3·30, 6·57, and 12·4 μ (*p*-disubstituted benzene), and $\lambda_{max.}$ (in dioxan) 215, 221, 243, 257, 265, 273 mμ (ε 17,600, 15,800, 1050, 930, 730, 585). It absorbed 8·9 mol. of hydrogen, to give the *hexaene*, m. p. 42° (Found: C, 88·9; H, 10·3%; *M*, 378 ± 17), whose infrared spectrum showed no acetylenic absorption, though aromatic bands remained at 3·30, 6·57, and 12·45 μ, and $\lambda_{max.}$ (in hexane) were at 215, 222, 225, 261, 266, 268, 275 mμ (ε 23,600, 24,600, 20,800, 750, 1080, 950, 1090).

Bicyclo[8,3,1]*tetradeca*-1(14),10,12-*triene*-4,6-*diyne* (X).—When the oxidation product of *m*-dibut-3′-ynylbenzene was chromatographed on alumina, a substance was eluted with benzene–hexane before the "dimer"; it was faintly yellow in solution, but when the solvent had evaporated it polymerized in a few seconds even at 20°, to give a bright-red insoluble film. Chromatography was best performed in darkness at 0°, with a fraction collector. Every fifth fraction was evaporated to dryness, and all fractions between the first and the last that gave

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* Naming of the *ortho*-isomers follows I.U.P.A.C. Rule A-23.5.

the red polymer were cautiously concentrated together at room temperature. Dilution with methanol and addition of water at −80° precipitated a faintly yellow powder which was filtered off quickly and stored at −80°. The yield was 12% when the oxidative coupling was performed in dilute solution at 70°, and only 2% at 90—100°. When placed on a hot stage the substance immediately became red below 90° and exploded above 90°; after having become red it did not explode any more above 90°. An infrared spectrum of a solution in CCl_4 showed bands at 3·32, 3·42, 3·50, 4·49, 6·24, 6·28, 6·72, 6·91, 6·99, 7·45, 7·54, 7·80, 8·16, 8·63, 9·20, 9·58, and 10·80 μ. The ultraviolet spectrum (in hexane) showed a broad shoulder at 240—270 mμ (ε ~600) and maxima at 306, 317, and 331 mμ (ε 380, 355, and 310). Hydrogenation in solution as above gave a liquid which after filtration through alumina and distillation in a tube corresponded analytically and spectrally to the *triene* [Found: C, 89·2; H, 10·4%; *M* (Rast), 208. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%; *M*, 188], and gas chromatography showed it to be homogeneous. The infrared spectrum showed the aromatic bands at 3·30, 6·20, 6·28, 6·72, 12·6, 14·0, and 14·3 μ. The ultraviolet spectrum (in hexane) showed a band with one maximum at 266 mμ (ε ~240) and only indications of shoulders on each side.

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