579. *Poly-cyclotrimerisation of Alkadiynes and Cycloalkadiynes on Complex Metal Catalysts*

By A. J. Hubert and Johannes Dale

On $[Co(CO)_4]_2Hg$, non-conjugated alkadiynes give, in addition to polymers, dimers containing one aromatic nucleus and one triple bond. On Ziegler catalysts, terminal non-conjugated diacetylenes give also mainly polymers and, in addition, two types of dibenzenoid trimers: a dumb-bell type αω-di-(3,4-alkylenephenyl)alkane and a barrel-shaped cage type 3,3′:5,5′-dialkylene-(αω-diphenylalkane). A third type of trimer, 1,3,5-trimethyl-2,4,6-triprop-1′-ynylbenzene, is obtained from the conjugated hexa-2,4-diyne. Macrocyclic non-conjugated alkadiynes give on Ziegler catalysts, also by cyclotrimerisation, insoluble polymers with unusual swelling properties.

Monoacetylenic compounds can be trimerised to benzene derivatives or polymerised to conjugated polyenes in the presence of a great variety of complex metal catalysts, such as metal-carbonyl complexes and Ziegler-type catalysts. For the cyclic trimerisation * cobalt carbonyl complexes [1] have proved particularly useful, but Ziegler catalysts also give benzene derivatives in high yield, especially when the acetylene is disubstituted.[2-4] Monosubstituted acetylenes and acetylene itself trimerise [2,3] or polymerise [2,5,6] on Ziegler catalysts depending on the conditions, and the same is true on nickel carbonyl–phosphine complexes.[7]

Only recently has some work been published on the behaviour of diacetylenic compounds on such catalysts. Stille and Frey [8] found that terminal unconjugated alkadiynes (I) gave polymers on Ziegler catalysts, but the " cyclo-polymerised " structure (II) proposed by them seems doubtful in the light of our results (see below). On the other hand, Colthup and Meriwether [9] obtained oligomers and polymers from the same alkadiynes on nickel carbonyl–triphenylphosphine complexes, and the " poly-cyclotrimerised " structures (III) deduced by them are in agreement with our results on Ziegler catalysts. Finally, disubstituted conjugated diacetylenes have been trimerised to triethynylbenzene derivatives on cobalt carbonyl complexes by Hübel and Merényi; [10] only in the case of the unsubstituted butadiyne does the second triple bond enter into reaction to give polymers.

The purpose of the present work was to compare the reactions of open-chain diynes with those of macrocyclic diynes [11] on $[Co(CO)_4]_2Hg$ and Ziegler-type catalysts. In particular, if the triple bonds of cycloalkadiynes were close in space, interesting intramolecular reactions may be envisaged.

The results showed that the course of the reaction depended strongly not only on the type of diyne and catalyst, but also on the conditions. In the presence of $[Co(CO)_4]_2Hg$ in dioxan solution the terminal alkadiynes (I, n = 4 and 5) gave small quantities of volatile oligomers together with dark tarry, soluble polymers. The most volatile constituent was isolated and showed infrared and ultraviolet absorption characteristic of 1,2,4-trisubstituted benzenes, as well as infrared bands for terminal acetylene; it therefore must have the dimer structure (IV). With n = 2 only a viscous tar was obtained. The methylated alkadiyne, undeca-2,9-diyne, on the other hand, gave in 1-molar solution exclusively an

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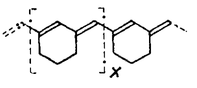
* The earlier literature has been surveyed in refs. 1, 3, and 4.

[1] Hübel and Hoogzand, *Chem. Ber.*, 1960, **93**, 103.
[2] Smith, B.P. 802,510/1958.
[3] Lutz, *J. Amer. Chem. Soc.*, 1961, **83**, 2551.
[4] Hoover, Webster, and Handy, *J. Org. Chem.*, 1961, **26**, 2234.
[5] Natta, Pino, and Mazzanti, Ital. P. 530,753/1955.
[6] Watson, McMordie, and Lands, *J. Polymer Sci.*, 1961, **55**, 137.
[7] Meriwether, Colthup, Kennerly, and Reusch, *J. Org. Chem.*, 1961, **26**, 5155; Meriwether, Colthup, and Kennerly, *ibid.*, 5169.
[8] Stille and Frey, *J. Amer. Chem. Soc.*, 1961, **83**, 1697.
[9] Colthup and Meriwether, *J. Org. Chem.*, 1961, **26**, 5169.
[10] Hübel and Merényi, *Chem. Ber.*, 1963, **96**, 930.
[11] Dale, Hubert, and King, *J.*, 1963, 73.

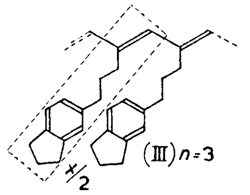
insoluble polymer. High dilution was necessary to obtain oligomers, and, in addition to some unchanged monomer, a liquid was isolated by distillation in 44% yield. Higher-boiling liquids and 8% of an insoluble polymer were also obtained. The dimer structure (V) was assigned to the low-boiling liquid based on its typical ultraviolet spectrum; the infrared spectrum was of course of little help as neither the benzene ring nor the triple bond carry hydrogen atoms. The higher-boiling fractions had very similar infrared and ultraviolet spectra, which suggests that also in the polymers the reaction has proceeded by cyclotrimerisation, and not by polyene formation.

$HC{\equiv}C\cdot[CH_2]_n\cdot C{\equiv}CH$

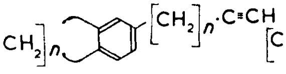
(I)



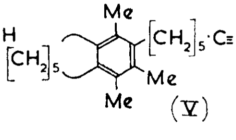
(II)*n* = 3



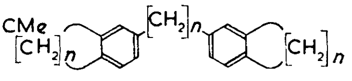
(III)*n* = 3



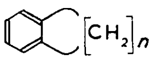
(IV)



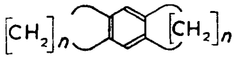
(V)



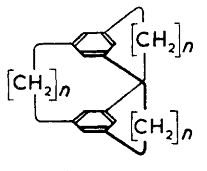
(VI)*n* = 2-6



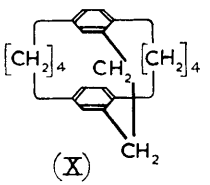
VII



(VIII)



(IX)*n* = 5-7



(X)

The cycloalkadiynes (XIII; *n* = 5, 6, and 7) under the same conditions were completely transformed into brittle, insoluble polymers.

In the presence of Ziegler-type catalysts prepared from titanium tetrachloride and triethylaluminium (Al/Ti from 0·5 to 2) the terminal alkadiynes (I) gave at moderate concentrations mostly soluble and insoluble polymers together with a little volatile material. The yield of the main oligomer, which proved to have the trimer structure (VI) already demonstrated for the oligomer formed from hepta-1,6-diyne (*n* = 3) on nickel–carbonyl–phosphine catalysts,[9] was increased by working at higher dilution. Thus, hexa-1,5-diyne gave 2% of the crystalline trimer (VI; *n* = 2), m. p. 85°, at normal concentration, and 13% at high dilution. It is noteworthy that even this strained benzocyclobutene system is formed with ease. The tetralin system (*n* = 4) is the most favoured; with longer chains the yield drops off and approaches zero when *n* = 7. The structural proof rests in all cases on molecular-weight determinations and the presence of infrared bands typical for 1,2,4-trisubstituted benzene rings. The ultraviolet spectrum provides *a priori* a less stringent argument as the intensity of the long-wavelength band at 250—280 mμ was found to increase strongly with diminishing size of the fused saturated ring (Figure 1); thus, the 1-alkyl-3,4-benzocyclobutene chromophore (*n* = 2) absorbs about five times stronger than the 1-alkyl-3,4-benzocycloheptene chromophore (*n* = 5) and simple 1,2,4-trialkylbenzenes.[12] At the same time there is a marked increase in resolution of the vibrational structure. *A posteriori*, therefore, the ultraviolet spectrum may be a valuable diagnostic

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[12] Dale, *Chem. Ber.*, 1961, **94**, 2821.

for such fused systems. A completely analogous trend has been found[13-15] in the simple 1,2-benzocycloalkenes (VII) both for the intensity (Table 1) and the vibrational structure. Throughout this whole 1,2-disubstituted benzene series the extinction lies much lower than the extinction per benzene ring in the 1,2,4-trisubstituted series represented by (VI). This has its origin in the primary effect of the different substitution pattern of the two series, which by induction disturbs the electronic symmetry of the benzene ring to a differing extent, whereby the basically forbidden $A_{1g} \longrightarrow B_{2u}$ transition becomes more or less "allowed."[16] Still another series, which now lies on an over-all higher intensity level because of its inherent substitution pattern, is represented by the 1,2:4,5-bispolymethylenebenzenes (VIII)[17,18] (Table 1).

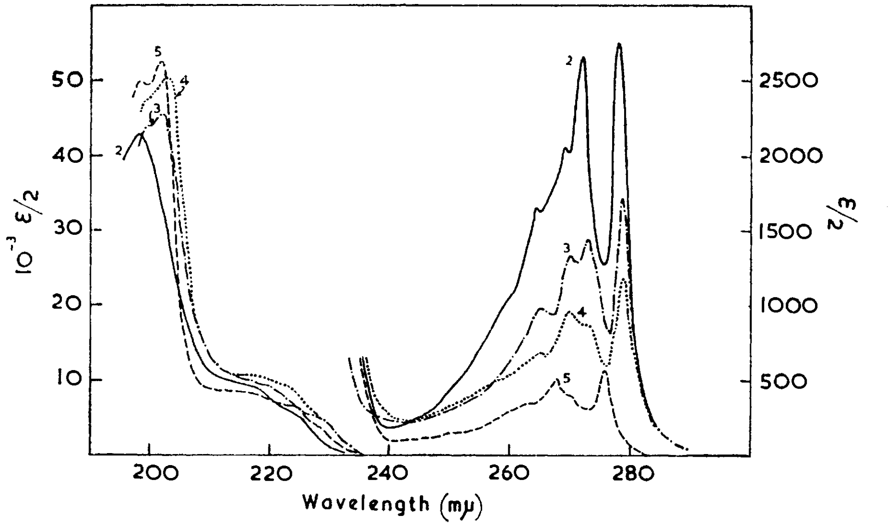

FIGURE 1. Ultraviolet spectra (in hexane) of αω-di-(3,4-alkylenephenyl)alkanes (VI). The appropriate n is marked on the curves and the ordinate is the extinction per aromatic nucleus. The molar extinction curve of 1,2,4-tri-n-propylbenzene[12] is on this scale almost indistinguishable from the curve $n = 5$

TABLE 1

Ultraviolet absorption intensity ($\varepsilon_{\text{max.}}$ at 260—290 mμ) of benzocycloalkenes (VII) and the derivatives (VI) and (VIII)

n	(VI)	(VII)	(VIII)
2	2750 × 2	1900[14]	5100[18]
3	1720 × 2	1500[15]	3850[17]
4	1170 × 2	620[15]	1950[17]
5	560 × 2	280[15]	—
6	—	330[15]	—
Alkyl substituted benzene	1,2,4-Pr^n_3[12] 490	1,2-Me_2 260	1,2,4,5-Me_4[17] 700

The question arises why the deformation of a benzene ring by the fusion with a small ring increases the intensity and accentuates the vibrational structure of the forbidden benzene transition, when the opposite effect, decreased intensity and disappearance of the

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[13] Huisgen, Rapp, Ugi, Walz, and Mergenthaler, *Annalen*, 1954, **586**, 1.
[14] Cava and Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.
[15] Moore, Marcus, Fenton, and Arnold, *Tetrahedron*, 1959, **5**, 179.
[16] Sklar, *Rev. Mod. Phys.*, 1942, **14**, 232; *J. Chem. Phys.*, 1942, **10**, 135.
[17] Marcus, Lauer, and Arnold, *J. Amer. Chem. Soc.*, 1958, **80**, 3742.
[18] Cava, Deana, and Muth, *J. Amer. Chem. Soc.*, 1960, **82**, 2524.

structure, is observed when the deformation is caused by steric interaction of bulky substituents in *ortho*-position.[19] It seems necessary here to distinguish between two different types of ring distortion: (1) twisting perpendicular to the plane, and (2) angular deformation in the plane.

The first case is encountered with bulky *ortho*-substituents; from molecular models it is seen that an out-of-plane twisting is easier and more tension-releasing than opening of angles. Thus, the hexagonal symmetry of a plane projection of the ring is roughly preserved, and the band whose weakness is due to this symmetry (Figure 2a) remains weak, especially since there should be no polarisation component perpendicular to the plane (Figure 2b). Further, as suggested before,[12] the non-planarity diminishes π-orbital overlap, which may explain the extra reduction of intensity, and the coexcitation of low-frequency deformation vibrations perpendicular to the plane blur the structure.

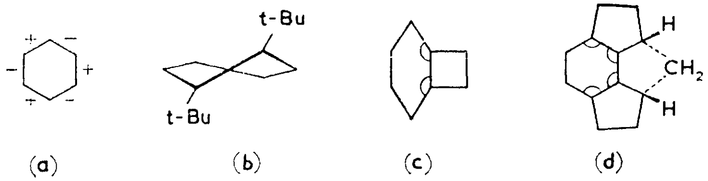


FIGURE 2

In the second case, the CCC-angles at the joints with the small ring should tend to open and deform the hexagon (Figure 2c) so that in the excited state the centre of negative charge does not coincide any longer with the centre of positive charge, thus making the " forbidden " transition " allowed." Perpendicular deformation of the benzene plane is unlikely as this can only increase the strain in and near the small ring, and the vibrational structure will be preserved, or even exalted, as a consequence of this increased rigidity. It is of interest that even a six-membered ring ($n = 4$) strains the aromatic nucleus, as seen on molecular models and reflected in the high absorption intensity (Table 1).

The two factors can be seen to co-operate in an interesting series of 1,2,3,4-tetrasubstituted benzenes reported by Rapoport and Smolinsky.[20] The extinction at 260—280 mμ, which is 290 for 1,2,3,4-tetramethylbenzene, is increased by the fusion of two five-membered rings in the 1,2- and the 3,4-position to 800—900, which is lower than for indane (VII; $n = 3$), presumably because the angle deformation by one ring is partly counteracted by the other (Figure 2d). However, the benzene ring has no reason to be non-planar and the spectrum has several extremely sharp peaks. A methylene group introduced between the two five-membered rings (Figure 2d) forms such a short link on one side that now the benzene ring must become warped, and accordingly the vibrational structure is completely lost, but the intensity stays relatively high (ε 470) because enough angle strain remains to distort the hexagonal symmetry. Finally, when one of the fused five-membered rings is transformed into a six-membered ring, more angle strain is relieved (ε 325), but the aromatic nucleus remains twisted and the absorption band has no structure.

In addition to the dumb-bell type trimers (VI), melting below 90°, a second type of trimer was isolated in much smaller yield ($<1\%$) and only when the chain was long enough ($n = 5$, 6, and 7); dilution had no effect on the yield. These compounds had very high melting points (260, 181, and 217°, respectively) and were shown to have the dibenzenoid barrel-shaped cage-structure (IX) by the ultraviolet and infrared spectra, which were typical for 1,3,5-substituted aromatic compounds, and by the n.m.r. spectrum, which showed only one type of aromatic proton and an anomalous chemical shift of those CH_2-protons which can be on the inside between the two aromatic nuclei, and therefore are influenced by the

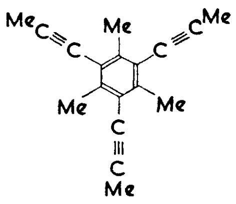
[19] Krüerke, Hoogzand, and Hübel, *Chem. Ber.*, 1961, **94**, 2817; Hoogzand and Hübel, *Angew. Chem.*, 1961, **73**, 680; *Tetrahedron Letters*, 1961, 637.

[20] Rapoport and Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 1171.

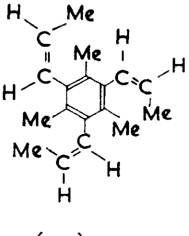
two aromatic ring currents. The general cage-structure (IX) is not completely novel as a similar unsymmetrical cage-compound (X) has been synthesised by Cram and Reeves,[21] although by a much less direct route.

On the basis of the present results it seems justified to assume that also the polymers are generally formed by poly-cyclotrimerisation. In fact, to the extent that the quality of the infrared spectra of the polymers permits bands to be observed (Experimental section), these are the same as in the oligomers and no new absorptions occur, except sometimes broad bands at 3, 6·2, and 10—12 μ, attributable to adsorbed water and oxides of aluminium and titanium. The arguments given by Stille and Frey [8] for the cyclo-polymerised structure (II) in the case of hepta-1,6-diyne are anyway not compelling. On the contrary, they report data which can be taken as strong evidence against it; thus, the absorption intensity in the ultraviolet and visible (ε 120 per monomer unit) is much too low for a polyene system, and the unexplained maxima at 270 and 280 mμ are identical in position and close in intensity (ε 1830 per monomer) to those observed here for the 1,2,4-trisubstituted benzene chromophore (1·5 monomers). It is important that after heating or after hydrogenation they found that only this absorption remained, and that hydrogenation was very slow. Also, the reported infrared band at 1605 cm.$^{-1}$ may well be aromatic or water absorption instead of polyene. Any polymer structure should give glutaric acid on ozonolysis, even alkyl-substituted benzenes,[22] but the high absorption of chlorine is more difficult to understand. Of course, the colour shows that polyene structures are originally present to some extent, and we believe that the coloured polymer may approach the structure (III) suggested by Colthup and Meriwether [9] for the polymer obtained on nickel carbonyl–phosphine complexes. Probably the initial easy formation of indane units of type (IV; $n = 3$) is succeeded in part by the polyene-type polymerisation such as observed for monosubstituted acetylenes.[5,6]

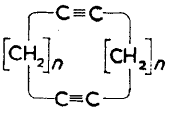
The behaviour of conjugated acetylenes on Ziegler catalysts does not seem to have been investigated. Hexa-2,4-diyne was therefore studied systematically and found to polymerise readily giving soluble or insoluble polymers depending on conditions. In addition, a crystalline sublimable substance, m. p. 225°, was isolated in yields up to 5%; it was shown to have the structure of an aromatic trimer. The infrared spectrum showed the presence of acetylenic bonds (4·46 and 4·86 μ), and the n.m.r. spectrum the presence of only two types of methyl-groups in the ratio 1 : 1, thus favouring a symmetrical trimethyltripropynylbenzene structure (XI). The ultraviolet spectrum (Figure 3) was very characteristic, and



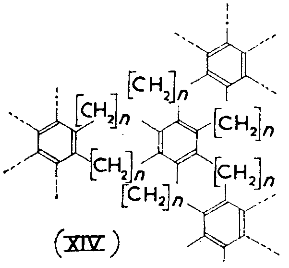
(XI)



(XII)



(XIII)



(XIV)

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[21] Cram and Reeves, *J. Amer. Chem. Soc.*, 1958, **80**, 3094.

[22] Bailey, *Chem. Rev.*, 1958, **58**, 925.

a comparison with the spectra of phenylacetylene[23] and the diethynylbenzenes[24] (see Experimental section) showed that the intense band at 245 mμ lies closer to the intense band at 227 mμ for the *ortho*- and at 228 mμ for the *meta*-isomer, than to the intense band for the *para*-isomer at 271 mμ, even without correcting for the red-shift due to the methyl-groups. As the 1,2,4-isomer should resemble the *para*-isomer in containing through-conjugated *para*-linked acetylenic groups, while the 1,3,5-isomer should resemble the *meta*-isomer in having no through-conjugated groups, the symmetrical structure seemed again the most probable. Recently, the unsymmetrical 1,2,4-isomer, m. p. 156°, was obtained,[10] together with the symmetrical one, on cobalt carbonyl complexes; it has in fact additional strong absorption at 290 mμ.

Catalytic hydrogenation of the trimer (XI) stopped sharply after absorption of three moles of hydrogen, even at 50°, and 110 atm. on platinum dioxide, and the liquid triolefin (XII) could be isolated. Infrared absorption at 14·4 μ shows that the double bonds have *cis*-configuration. The reason for the strong selectivity is no doubt the increased steric hindrance to further adsorption on the catalyst created by the necessary twist of the *cis*-prop-1-enyl groups out of the aromatic plane. This is reflected in the ultraviolet spectrum (Figure 3) which shows a structureless weakened main band at a wavelength position (220 mμ) which is even shorter than for styrene[25] (248 mμ).

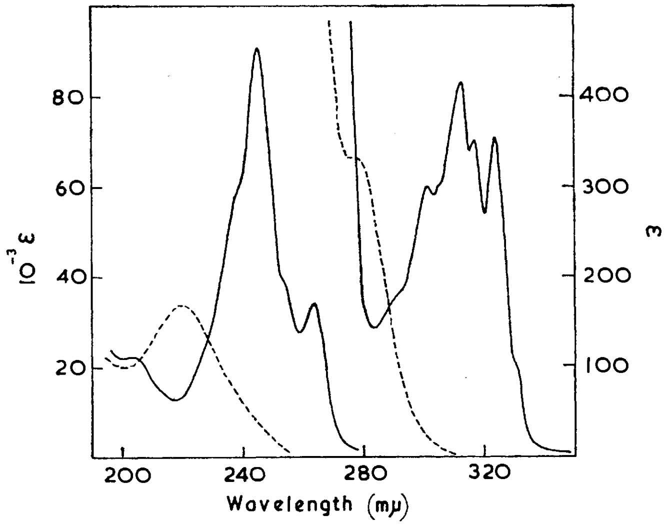

FIGURE 3. Ultraviolet spectra (in hexane) of 1,3,5-trimethyl-2,4,6-triprop-1-ynylbenzene (XI) (full line) and of 1,3,5-trimethyl-2,4,6-tri-*cis*-prop-1-enylbenzene (XII) (broken line)

A small amount of a second crystalline, but unstable yellow substance, m. p. 265°, was obtained once, but attempts to purify and identify it have failed.

The macrocyclic alkadiynes (XIII) were transformed on Ziegler catalysts in most cases rapidly and completely into brittle insoluble polymers (Table 2). Only cyclododeca-1,7-diyne ($n = 4$) and, using high dilution, cyclotetradeca-1,8-diyne ($n = 5$) gave partly soluble polymers, but defined oligomers could not be isolated. Extraordinary swelling

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[23] Morton, Hassan, and Calloway, *J.*, 1934, 883; Rumpf and Gillois, *Bull. Soc. chim. France*, 1955, 1348.

[24] Behr, Eglinton, Galbraith, and Raphael, *J.*, 1960, 3614; Chodkiewicz, Cadiot, and Willemart, *Compt. rend.*, 1957, **245**, 2061.

[25] Dale, *Acta Chem. Scand.*, 1957, **11**, 971.

properties were observed[26] for the insoluble polymers; the swelling is almost instantaneous and highest for benzene, but occurs also for all other solvents tried. The solvent can be easily recovered from the swollen paste by heating, leaving the polymer powder unchanged, and the process can be repeated indefinitely. The degree of swelling is a maximum when $n = 5$ (Table 2), and it can be exalted by using dilute solutions, much catalyst compared with diyne, a high Al : Ti ratio in the catalyst, and rapid addition of the diyne (Table 2). The infrared spectrum cannot prove that the structure is that of a poly-cyclotrimerised network (XIV), as the infrared-active C–C stretching of a hexa-alkylated benzene would be expected to fall in the region for CH_2-scissoring at 7 μ, but there are no bands in the double-bond region (6 μ), and the ultraviolet spectrum of a soluble fraction from the high-dilution experiment showed typical high-intensity aromatic absorption at 206 mμ with a shoulder at 232 mμ. It is felt that the reason for the maximal swelling for $n = 5$ might be that the particular conformational homogeneity of cyclotetradeca-1,8-diyne[11] directs the reaction more completely to essentially two-dimensional net-works (XIV) than in the other cases, leaving only relatively few cross-links between these " planes."

EXPERIMENTAL

Preparation of Diacetylenic Compounds.—The preparation of the acylic terminal diacetylenes and the macrocyclic diacetylenes has been described in Part I.[11] The conjugated diacetylene, hexa-2,4-diyne, was prepared from 1,4-dichlorobut-2-yne and methyl iodide.[27]

Undeca-2,9-diyne was synthesised in the following manner: Nona-1,8-diyne (0·1 mole) was added to a well-stirred suspension of sodamide (0·2 mole) in liquid ammonia (500 ml.). After 1 hr., methyl iodide (0·2 mole) was added dropwise and the stirring continued overnight. The ammonia was then evaporated and the residue extracted with ether. The ether solution was washed with water, dried, and distilled, giving a 50% yield of crude diyne. Traces of terminal acetylenes were removed by shaking the liquid with Nessler's reagent; by extraction with ether, the mercuric salts of terminal acetylenes remain insoluble. The infrared spectrum (liquid film) showed after this treatment the complete absence of bands characteristic of –C≡CH.

Experiments with $[Co(CO)_4]_2Hg$ *as Catalyst.*—*Undeca*-2,9-*diyne*. A concentrated solution of the diyne (1·6 g. = 0·011 mole) and the catalyst (0·15 g.) in dioxan (10 ml.) was heated on a water-bath for 2 hr. The precipitated polymer was filtered off and washed with a hydrochloric acid–dioxan mixture to eliminate most of the catalyst. The brittle polymer (1·8 g.) was insoluble in all solvents and did not melt or decompose below 350°.

To ensure high dilution, a solution of the diyne (14·8 g., 0·1 mole) and the catalyst (1·5 g.) in dioxan (250 ml.) was added in small portions (2·5 ml. every hr.) to a large volume (750 ml.) of boiling dioxan. After evaporation of the dioxan, the catalyst was decomposed with hydrochloric acid and the residue taken up in hexane. After filtration through alumina, the solvent was evaporated leaving a colourless oil. Distillation gave a first fraction (6·7 g.), b. p. 40—50°/0·01 mm., which proved to be the starting material; then a second fraction (2·75 g.), b. p. 160—170°/0·005 mm., whose infrared spectrum did not yield much information, but whose ultraviolet maxima (in hexane) at 206, 225sh, 265sh, 271, and 278 mμ (ε 44,700, 11,000, 260, 280, 240, assuming *M*, 296) indicated that it consisted mainly of 1,2,4-*trimethyl*-3-*oct*-6′-*ynyl*-5,6-*pentamethylenebenzene* (V); a third fraction (2·05 g.), b. p. 170—250°/0·005 mm.; and a fourth fraction (1·0 g.), b. p. >250°. The last two fractions had infrared and ultraviolet spectra similar to those of the third fraction. The residue (0·5 g.) was insoluble in hexane.

Octa-1,7-*diyne*. A solution of the diyne (5 g.) and $[Co(CO)_4]_2Hg$ (0·5 g.) in dioxan (50 ml.) was refluxed for 2 hr. After distillation of the solvent and unchanged octadiyne, a higher-boiling fraction was obtained (0·1 g. = 2%), leaving a dark brown tar (1 g. = 20%). The distilled liquid showed infrared bands (liquid film) at 3·02 and 4·70 μ (–C≡CH) and at 3·33, 6·18, 6·34, 6·64, 10·95, and 12·10 μ (1,2,4-substituted benzene) and must therefore be 1-*hex*-5′-*ynyl*-3,4-*tetramethylenebenzene* (IV; $n = 4$) (Found: *M*, 202, 205. $C_{16}H_{20}$ requires *M*, 212); $\lambda_{max.}$ (in hexane) 202, 218, 222sh, 264, 270, 273sh, and 278 mμ (ε 48,700, 10,000, 9200, 460, 645, 570, and 745).

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[26] Hubert, Dale, and Hargitay, U.S. Pat. Appl., 1962, Ser. No. 247,808.

[27] Allan, Jones, and Whiting, *J.*, 1955, 1862.

Nona-1,8-*diyne.* Under the same conditions as above only a 0·1% yield of a volatile oil was obtained. Its ultraviolet spectrum was identical with that given above (ε_{278} 500); it must therefore be 1-*hept*-6′-*ynyl*-3,4-*pentamethylenebenzene* (IV; $n = 5$).

Hexa-1,5-*diyne.* Under the above conditions only unchanged diyne and a viscous black tar were obtained.

Cycloalkadiynes (XIII; $n = 5, 6, 7$). These diynes were converted completely into brittle, insoluble, and infusible polymers even at high dilution. No interesting swelling properties (cf. below) were observed.

Experiments with Ziegler Type Catalysts.—*Hexa*-1,5-*diyne.* A solution of triethylaluminium (21 mmoles) in benzene (10 ml.) was added under nitrogen to a solution of titanium tetrachloride (19 mmoles) in benzene (40 ml.). To this catalyst was added quickly a solution of the hexadiyne (5 g., 64 mmoles) in benzene (50 ml.). The reaction was very exothermic, and after 5 min. the solution was poured into ethanol, whereby a polymer (4·2 g.) was precipitated and filtered off; it was partially (2·2 g.) soluble in benzene. The filtrate was evaporated and the residue extracted, first with hexane to give a crystalline substance, m. p. 82—84: (0·1 g. = 2%), and then with benzene to give a pasty mass (0·4 g.).

The yield of the crystalline substance was improved by working with dilute solutions: $AlEt_3$ (42 mmoles) was added to a solution of $TiCl_4$ (34 mmoles) in benzene (300 ml.). To this well-stirred catalyst solution was then added dropwise under nitrogen over 2 hr. a solution of the hexadiyne (6 g., 77 mmoles) in benzene (250 ml.). The mixture was worked up as above to yield a benzene-soluble polymer (4·6 g.) and hexane-soluble crystals (1·0 g.). The crystals were sublimed to give pure 3,4:3′,4′-*bisethylenebibenzyl* (VI; $n = 2$) (0·8 g., 13%), m. p. 84—86° (Found: C, 92·1; H, 7·7%; *M*, 245. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%; *M*, 234). The infrared spectrum (KBr disc) showed the absence of bands for $-C\equiv CH$ and the presence of bands at 3·32, 6·27, 6·31, 11·28, and 12·07 μ (1,2,4-substituted benzene); a strong band at 6·79 μ may either be aromatic stretching or scissoring of strained CH_2. Ultraviolet maxima (in hexane) were at 198, 216sh, 264, 269, 272, and 278 mμ (ε 85,600, 19,400, 3260, 4120, 5330, and 5490).

Hepta-1,6-*diyne.* To a solution of $AlEt_3$ (135 mmoles) and $TiCl_4$ (90 mmoles) in benzene (1 l.) was added dropwise over 3—4 min. a solution of the diyne (33 g.) in benzene (50 ml.). Working up gave a deep red-brown polymer (23·7 g.), insoluble in benzene, and a soluble part which in part (5·7 g.) distilled at 150—210°/0·1 mm. Redistillation gave a first fraction (0·7 g.), b. p. 80—90°/0·1 mm., having infrared spectral bands at 6·10, 10·07, 10·38, and 11·00 μ, an intermediate fraction (0·6 g.), and a main fraction (2·8 g.), b. p. 180—195°, having infrared bands typical for 1,2,4-substituted benzene. This latter liquid proved to be 1,3-*di*-(3,4-*trimethylenephenyl*)*propane* (VI; $n = 3$) (9%). A background absorption in the ultraviolet spectrum below ~300 mμ indicated the presence of an impurity; it could be removed by ozonisation in pentane at 20° and subsequent passage through alumina. A concentrated solution of the purified substance in pentane finally crystallised at −70°, and had m. p. 41—43° (Found: C, 90·7; H, 9·0%; *M*, 279. $C_{21}H_{24}$ requires C, 91·25; H, 8·75%; *M*, 276); $\lambda_{max.}$ (in hexane) 202, 217sh, 227sh, 265, 270, 273, and 279 mμ (ε 91,400, 19,800, 11,800, 1980, 2660, 2870, and 3440); infrared spectrum (KBr disc) showed aromatic absorption at 3·35, 6·19, 6·33, 6·70, 11·20, 11·48, 12·10, and 12·25 μ. A non-distillable fraction, soluble in hexane, gave essentially the same i.r. spectrum as the distilled trimer, while a fraction, insoluble in hexane and soluble in benzene, in addition showed broad absorption at 3—3·5, 6·2, and 11—12 μ; the same was true for the coloured benzene-insoluble polymer.

Octa-1,7-*diyne.* In the same manner as above, this diyne (50 g.) gave a yellow polymer (26 g.), soluble in benzene but insoluble in hexane, whose infrared spectrum showed only broad peaks at ~3, 6·2, and ~10·3 μ on an absorbing background, and an oil (25 g.) which was soluble in hexane. It could be partially distilled to give a liquid (8·9 g.), b. p. 220°/0·1 mm., from which crystals were obtained in pentane. These proved to be 1,4-*di*-(3,4-*tetramethylenephenyl*)-*butane* (VI; $n = 4$) (13%), m. p. 65: (Found: C, 90·6; H, 9·4%; *M*, 316. $C_{24}H_{30}$ requires C, 90·5; H, 9·5%; *M*, 318); the infrared spectrum (KBr disc) showed aromatic absorption at 3·35, 6·20, 6·35, 6·66, 10·88, 11·01, 11·42, 11·58, 12·06, and 12·33 μ; $\lambda_{max.}$ (in hexane) were at 203, 217, 223sh, 265, 270, 273sh, and 279 mμ (ε 100,800, 20,600, 18,000, 1380, 1930, 1750, and 2340).

Nona-1,8-*diyne.* The diyne (50 g.) was treated as before to give an insoluble polymer (~30 g.) and a soluble portion from which distilled a fore-fraction (0·8 g.) below 200°/0·1 mm., showing by gas-chromatography the presence of at least 10 different compounds, and a main fraction (4·2 g.), distilling above 200°, mainly at 250°/0·1 mm. The residue (16·7 g.) was a viscous oil. The high-boiling fraction was treated with pentane; an insoluble residue (0·47 g.) was recrystallised in hexane to give *tetracyclo*[9,9,5,$1^{3,19}$,$1^{9,13}$]*heptacosa*-1,3(26),9,11,13(27),19-*hexaene* (IX; n = 5) (1%), m. p. 260° (Found: C, 89·4; H, 10·0%; *M*, 369. $C_{27}H_{36}$ requires C, 89·9; H, 10·1%; *M*, 360). Infrared bands (KBr disc) typical for 1,3,5-trisubstituted benzene were at 3·33, 6·24, 11·31, and 14·20 μ. Ultraviolet maxima (in hexane) were at 199, 204sh, 217sh, 260, 264sh, 266, 269, 273, and 276 mμ (ε 96,500, 67,500, 15,100, 340, 385, 450, 405, 405, 260). The n.m.r. spectrum (in CS_2) showed signals at δ −6·38 (6 aromatic H), −2·4 (12 α-CH_2), −1·5 (12 β-CH_2), and −0·66 γ-CH_2). The pentane solution precipitated another kind of crystal (1·2 g.), m. p. 77°, after recrystallisation 81°, which proved to be 1,5-*di*-(3,4-*pentamethylenephenyl*) *pentane* (VI; n = 5) (Found: C, 90·1; H, 10·0%; *M*, 339); infrared bands (KBr disc)3·34, 6·21, 6·35, 6·67, 11·18, and 12·25 μ; $\lambda_{\max.}$ (in hexane) 198, 202, 218sh, 225sh, 263sh, 268, and 276 mμ (ε 100,000, 105,000, 17,000, 13,000, 685, 1000, and 1130). The n.m.r. spectrum (in CS_2) showed signals at δ −6·76 (2 aromatic H), −6·74 (4 aromatic H), −2·6 (12 α-CH_2), and −1·6 (12β- + 6γ-CH_2). The yield (2·5%) may in reality be higher as the mother-liquor gave a crystal mixture which could not be further separated.

A *high-dilution experiment* was performed by adding to a similar catalyst solution in petrol (b. p. 40—60°) at reflux a solution of the nonadiyne (50 g.) in petrol (500 ml.) in small portions (∼6 ml., 80 times) *via* a Soxhlet so that each portion became diluted with ∼100 ml. of solvent before encountering the catalyst. Working up gave a polymer (15 g.), insoluble in hexane–benzene, and a soluble part which by distillation gave a trimer fraction (8·7 g.) and a viscous residue (2·4 g.). Crystallisation of the distillate gave an unchanged yield (0·5 g.) of the cage-trimer (IX), m. p. 260°, and a much higher yield (5·9 g.) of the dumb-bell trimer (XI), m. p. 75—78°, leaving an oil (2·3 g.).

Deca-1,9-*diyne*. From this diyne (46 g.) was obtained a polymer (43 g.), insoluble in hexane and in benzene, and a soluble portion from which a fraction (1·6 g.) distilled above 200°/0·1 mm., leaving a hexane-soluble residue (5 g.). The distillate was treated with pentane to yield crystals (90 mg.) of *tetracyclo*[10,10,6,$1^{3,21}$,$1^{10,14}$]*triaconta*-1,3(29),10,12,14(30),21-*hexaene* (IX; n = 6) (0·2%), m. p. 180—181° (Found: C, 89·45; H, 10·3%; *M*, 390. $C_{30}H_{42}$ requires C, 89·5; H, 10·5%; *M*, 402); infrared bands (KBr disc) 3·35, 6·25, 11·31, and 13·95 μ; $\lambda_{\max.}$ (in hexane) 199, 203, 218sh, 223sh, 260, 266, and 273 mμ (ε 96,100, 89,100, 17,500, 14,700, 300, 375, and 320). The pentane-soluble part (1·5 g., ∼3%) could not be crystallised, but contains probably more of the trimer just described ($\nu_{\max.}$ 6·24, 11·3, and ∼14·0 μ) together with a trimer of type (VI) ($\nu_{\max.}$ 6·66 and 12·2 μ).

Undeca-1,10-*diyne*. To a smaller volume (250 ml.) of a catalyst solution of the same concentration was added as before the diyne (20 g.). An insoluble polymer (17·1 g.) was obtained, together with a soluble portion which on distillation gave almost no high-boiling oil and very little residue (∼0·5 g.). The distillate yielded only a little of a solid (70 mg.), m. p. 210°, after recrystallisation m. p. 215—217°, which proved to be *tetracyclo*[11,11,7,$1^{3,23}$,$1^{11,15}$]*tritriaconta*-1,3(32),11,13,15(33),23-*hexaene* (IX; n = 7) (0·3%) (Found: C, 89·5; H, 10·2%; *M*, 349. $C_{33}H_{48}$ requires C, 89·1; H, 10·9%; *M*, 445); infrared bands (KBr disc) 3·33, 6·22, 11·39, and 14·23 μ; $\lambda_{\max.}$ (in hexane) 200, 203, 218sh, 260, 266, 269sh, and 273 mμ (ε 110,300, 105,300, 18,300, 355, 460, 400, and 400).

Undeca-2,9-*diyne*. With the above catalyst type this diyne gave in most cases insoluble, but also partially soluble polymers. However, the infrared spectra resemble strongly those of the starting material and cannot furnish much information about the structure, as the benzene nuclei which may form do not carry hydrogen.

Diphenylbutadiyne. This diyne gave under the above conditions a mixture of insoluble and soluble titanium-containing polymers, which could not be further characterised or satisfactorily purified.

Hexa-2,4-*diyne*. This conjugated diyne gave on treatment with the same type of catalyst as above, a sublimable crystalline substance besides soluble and brittle insoluble polymers, the relative yields depending on the conditions. In the presence of only $TiCl_4$ there was no reaction even at 80° for 12 hr. The diyne was recovered to some extent when the ratio Al : Ti was either very high (5) or low (0·5) at 20°. When the ratio catalyst : diyne was high (∼1), only an infusible red polymer containing titanium was obtained after 1 hr. at 30°. With a normal Al : Ti ratio (=1) and a small catalyst : diyne ratio (0·03) at high temperature (80° for 1 hr.) led mainly to a soluble, vitreous polymer. Between these extremes the yield of the crystalline substance was always low (0·2 to 5%); the best conditions for its formation are the following.

The catalyst solution was prepared from $AlEt_3$ (4 mmoles) and $TiCl_4$ (4 mmoles) in benzene (100 ml.), the diyne (5 g. = 64 mmoles) added, and the mixture heated at 40° for 1—2 hr. After destruction of the catalyst with methanol, the solvents were evaporated. The brown tarry residue was extracted with benzene, the benzene solution was filtered through a column of active alumina, and the column washed with benzene. The benzene was evaporated and the residue extracted with hexane, leaving an insoluble powder; the hexane solution contained a vitreous polymer.* The hexane-insoluble powder was sublimed *in vacuo* to give the crystalline 1,3,5-*trimethyl*-2,4,6-*triprop*-1′-*ynylbenzene* (XI) (5%), m. p. 225° (Found: C, 92·2; H, 7·4%; *M*, 268. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%; *M*, 234); infrared bands (KBr disc) 3·43, 3·50, 4·46, 4·86, 6·93, 7·05, 8·57, 9·82, 10·62, 13·4, and 13·8 μ; $\lambda_{max.}$ (in cyclohexane) 204, 245, 264, 301, 313, 317, and 324 mμ (ε 22,300, 90,400, 34,200, 300, 415, 345, and 350). The n.m.r. spectrum (in CS_2) showed two lines of equal intensity in the region for methyl groups at δ −2·86 (aromatic CH_3) and −1·74 (acetylenic CH_3).

Catalytic hydrogenation in a micro-apparatus [28] on Raney nickel in xylene (chosen because of its low vapour pressure) was followed quantitatively; the absorption stopped after 3·08 moles of hydrogen had been consumed. When benzene was used as solvent, subsequent distillation *in vacuo* permitted the isolation of 1,3,5-*trimethyl*-2,4,6-*tri*-cis-*prop*-1′-*enylbenzene* (XII) as a liquid (Found: C, 89·8; H, 9·8. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%). Typical infrared bands (liquid film) for *cis*-double bonds were at 3·32, 6·05, and 14·4 μ; no bands for *trans*-double bonds were found. Ultraviolet maxima (in hexane) were at 220 and 275 mμ (ε 34,400 and 330).

Exactly the same *cis*-triolefin was obtained by hydrogenation on PtO_2 in butanol; 3·27 moles of hydrogen were absorbed.

Further hydrogenation was extremely slow, and even after one night at 50° and 110 atm. on PtO_2, no defined products were obtained; the average composition corresponded to more than 2 remaining double bonds per molecule, and the mixture absorbed 1·8 moles of bromine per molecule.

Ultraviolet Spectra of m- *and* p-*Diethynylbenzenes*.—Samples of these compounds,[29] needed for spectral comparison, were kindly sent us by Dr. A. S. Hay, General Electric Research Labs., Schenectady, New York. The *meta*-isomer had maxima (in hexane) at 218, 228, 241, 247, 253, 272, 286, 288, and 296 mμ (ε 28,800, 38,500, 17,600, 17,600, 12,400, 3070, 330, 340, and 310). The *para*-isomer had maxima (in hexane) at 210, 215, 259, 271, 282, and 292 mμ (ε 24,000, 23,600, 34,600, 41,300, 1890, and 1070).

Cycloalkadiynes (XIII; *n* = 4, 5, 6, 9).—To a catalyst solution prepared from triethylaluminium and titanium tetrachloride in a solvent, usually benzene, was added quickly, if not otherwise stated, a 20% solution of the diyne in the same solvent. The temperature rose to about 40° and a considerable increase of viscosity was observed. After about 10 min., the viscous mixture was poured into methanol. The precipitated polymer was filtered off and washed (ethanol and methanol) until it became white, then dried at 100° to give a yellowish infusible powder. The polymers swell rapidly in organic solvents, and the degree of swelling depends strongly on the structure of the diyne and the preparative conditions (Table 2). The swelling was determined as the volume of solvent which 1 g. of polymer can absorb without becoming fluid. For a particular polymer of cyclotetradeca-1,8-diyne (*n* = 5), this value was 35—40 ml. with benzene (Table 2), 25—30 ml. with chloroform and ethanol, and 20—25 ml. with hexane, cyclohexane, and decalin. Swelling occurs also with acetone, methanol, mineral oil, etc. The bulk density of a swelling powder was 0·4—0·5; non-swelling powders are often more fluffy. The solvent can be easily recovered by heating, leaving the original powder unchanged, and the process can be repeated indefinitely. Analysis showed that some catalyst remains in the polymer (*n* = 5) (Found: C, 86·2; H, 10·9; ash, 0·6%). The infrared spectrum (*n* = 5) showed bands (KBr disc) at 3·44, 6·85, and ~14 μ (CH_2), but also at 7·40 μ ($\cdot C{\equiv}C{\cdot}CH_2\cdot$), and at ~9·35 and ~10·4 μ (catalyst?).

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* Further elution of the column with much benzene gave a coloured polymer. In one case a yellow powder, m. p. 265° (decomp.), was eluted after the trimer. Ultraviolet maxima (in cyclohexane) were at 280, 291, 370, and 388 mμ [ε (calc. per monomer) 17,000, 36,000, 970, 1210]. It could not be sublimed, and decomposed on renewed passage on alumina.

[28] Ogg and Cooper, *Analyt. Chem.*, 1949, **21**, 1400.

[29] Hay, *J. Org. Chem.*, 1960, **25**, 637.

In the case of cyclododeca-1,7-diyne ($n = 4$) a polymer fraction (17%), soluble in benzene but insoluble in methanol, and a liquid volatile fraction (17%) were also obtained. The polymer showed only infrared bands typical for CH_2.

A high-dilution experiment was carried out with cyclotetradeca-1,8-diyne: to a catalyst solution (210 mmole of $AlEt_3$ and 190 mmole of $TiCl_4$ in 1 l. of benzene) was added dropwise over 8 hr. a solution of the diyne (6 g. = 32 mmole) in benzene (0·5 l.). The coloured polymer (7·8 g.) precipitated by methanol could not be washed free of catalyst, but a fraction (1 g.) could be extracted with benzene; it was slightly yellow, softened at about 100—120°, was insoluble in ethanol and acetone, and fixed bromine; its ultraviolet spectrum (in cyclohexane) had maxima at 206 and 323sh mμ [ε (calc. per 1·5 monomers) 25,500, 6000]. The benzene-insoluble polymer was hard and brittle and did not swell in organic solvents.

TABLE 2

Poly-cyclotrimerisation of cycloalkadiynes (XIII) on Ziegler catalysts

n	Diyne (mmole/l.)	$AlEt_3$ (mmole/l.)	$TiCl_4$ (mmole/l.)	Solvent	Yield of insol. polymer (%)	Swelling (ml. benzene/ g. polymer)
4	55	210	190	Benzene	75	5
5	140	17	17	,,		25—30
	140	170	170	,,	103	35—40
	280	340	340	,,		30—40
	55	68	68	,,		50—60
	140	85	170	,,		20—25
	140	340	170	,,		50—60
	220[a]	72	108	,,	80	20—30
	180[b]	300	450	,,	50	15
	140	170	170	Hexane–benzene 7 : 1		40
	140	170	170	Heptane		35—40
	180	1150	1150	,,	100	0
	110	210	190	1-Methylnaphthalene	105	20
6	114	170	170	Benzene		10—15
9	40	80	80	,,	100	2

[a] Addition of diyne during 15 min. [b] Addition of diyne during 8 hr.

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