*The Catalytic Cyclic Polymerisation of Butadiene.**

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[Reprint Order No. 5056.]

The dimerisation of butadiene to *cyclo*octa-1 : 5-diene is catalysed by bistriphenylphosphinedicarbonylnickel^0 in the presence of acetylene. Complexes of nickel carbonyl with trimethyl or triphenyl phosphite catalyse the dimerisation without added acetylene, but are more active in the presence of acetylene. Trimers and tetramers of butadiene are also formed, consisting in part of compounds containing 12- and 16-membered rings, respectively. Small amounts of compounds formed from both butadiene and acetylene have been detected.

The remarkable ability of certain complexes derived from nickel carbonyl to polymerise acetylenic compounds to aromatic compounds was described by Reppe and Schweckendiek (*Annalen*, 1948, **560**, 104). In particular, the disubstituted complex bistriphenylphosphinedicarbonylnickel^0 $(Ph_3P)_2Ni(CO)_2$ catalysed the polymerisation of acetylene to benzene and styrene under extremely mild conditions, and of propargyl alcohol which similarly led to a mixture of 1 : 2 : 4- and 1 : 3 : 5-trishydroxymethylbenzene. Further examples of this catalytic trimerisation of ethynyl compounds have been provided by Rose and Statham (*J.*, 1950, 69) and by McKeever and Van Hook (U.S.P. 2,542,551); one case of the successful polymerisation of a disubstituted acetylene, but-2-yn-1 : 4-diol, is recorded by

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* Part of this work has been described in B.P. 701,106 and B.P. Appl. 27,070/51, and was read at a Chemical Society symposium on February 5th, 1953 (*Chem. and Ind.*, 1953, 239).

Kleinschmidt (U.S.P. 2,542,417) who obtained hexahydroxymethylbenzene by using the monosubstituted complex $(Ph_3P)Ni(CO)_3$.

Reppe and Schweckendiek also claimed that complexes of triphenylphosphine with certain metal halides, *e.g.*, $(Ph_3P)_2NiBr_2$ and $(Ph_3P)_2CuCl$, in addition to the nickel carbonyl complexes, catalysed the polymerisation of vinyl compounds, with or without acetylene, to give derivatives of dihydro-, tetrahydro-, or hexahydro-benzenes. More recently, however, acetylene has been found to react with acrylonitrile and methyl acrylate in the presence of $(Ph_3P)_2Ni(CO)_2$ to give the open-chain compounds 1-cyanohexa-1 : 3 : 5-triene and methyl hepta-2 : 4 : 6-trienoate, respectively (Cairns, Engelhardt, Jackson, Kalb, and Sauer, Abstr. Papers presented at the 120th Meeting Amer. Chem. Soc., Sept. 1951, p. 14M; *J. Amer. Chem. Soc.*, 1952, **74**, 5636; Kalb and Sauer, U.S.P. 2,540,736).

A new cyclic polymerisation catalysed by substituted nickel carbonyls has now been discovered. An attempt was made to prepare *cyclo*hexa-1 : 4-diene by Diels–Alder addition of acetylene to buta-1 : 3-diene in the presence of $(Ph_3P)_2Ni(CO)_2$ as catalyst. From the products of reaction in benzene solution at 120°, two readily distillable compounds were obtained. The minor fraction was identified as 4-vinyl*cyclo*hex-1-ene, the normal product of thermal dimerisation of butadiene (see Reed, *J.*, 1951, 685). The chief product, amounting to from three to four times the quantity of vinyl*cyclo*hexene, was substantially pure *cis-cis-cyclo*octa-1 : 5-diene. In further experiments *cyclo*octadiene was obtained in 30—40% yields with about 10% yields of vinyl*cyclo*hexene at butadiene conversions of 50—70% in a reaction time of 4 hr. It was established by infra-red examination of samples of the recovered solvent after careful fractional distillation that no *cyclo*hexa-1 : 4-diene (b. p. 89°; Wooster, U.S.P. 2,182,242) was formed in the reaction.

*cyclo*Octa-1 : 5-diene has been recognised as a by-product of the non-catalytic thermal dimerisation of butadiene (Foster and Schreiber, *J. Amer. Chem. Soc.*, 1948, **70**, 2303; Ziegler, *Angew. Chem.*, *A*, 1947, **59**, 177), forming an increasing proportion of the dimer fraction as the temperature is increased, *e.g.*, 2·2% at 120° to 10·6% at 270°, although the yield of dimer relative to high polymer simultaneously falls from 93% to 57% (Ziegler and Wilms, *Annalen*, 1950, **567**, 1, see also Hillyer and Smith, *Ind. Eng. Chem.*, 1953, **45**, 1133). Reduction of the eight-membered ring dimer of 2-chlorobutadiene, 1 : 6-dichloro-*cyclo*octa-1 : 5-diene (Brown, Rose, and Simonsen, *J.*, 1944, 101; Cope and Schmitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3056), with sodium in liquid ammonia also gives *cyclo*octa-1 : 5-diene (Cope and Bailey, *ibid.*, 1948, **70**, 2305; Cope, Stevens, and Hochstein, *ibid.*, 1950, **72**, 2510) but the overall yield is only 9·6% in a tedious preparation.

The *cyclo*octadiene prepared by this catalytic method was identical with previous preparations, as shown by the close similarity of its Raman spectrum with that reported by Goubeau (*Annalen*, 1950, **567**, 214) for Ziegler and Wilms's compound, the preparation of the crystalline silver nitrate adduct described by Cope, Stevens, and Hochstein (*loc. cit.*), and the formation of only succinic acid by ozonolysis. The compound readily gave *cyclo*octene on semi-hydrogenation but was best characterised by formation of a mono-adduct with 2 : 4-dinitrobenzenesulphenyl chloride (see Kharasch and Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724). The diene contained, however, a small amount of an impurity that could not be removed by fractionation. This was indicated by the slightly higher refractive index and lower m. p. than were obtained by previous workers, and by absorption in the infra-red at 765 $cm.^{-1}$ which could not be eliminated completely even by purification of the diene through the silver nitrate adduct. On hydrogenation, a sample of the diene, n_D^{20} 1·4950, absorbed 2·09 mols. of hydrogen to give *cyclo*octane of m. p. 11°, indicating 98·5% purity (Cope and Hochstein, *ibid.*, 1950, **72**, 2515). The possible nature of the impurity is discussed later.

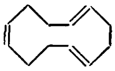
The conditions governing formation of *cyclo*octadiene in this catalytic reaction were examined in some detail. Experiment showed that the phosphine–carbonyl complex was inactive in the absence of acetylene, at least at temperatures below 130°, and the complex was recovered unchanged. At temperatures above 130°, extensive formation of vinyl*cyclo*hexene occurs by purely thermal dimerisation, and catalytic activity leading to *cyclo*octadiene was therefore generally sought in the range 100—120°, at which temperatures the thermal dimerisation of butadiene in solution was shown to be practically negligible.

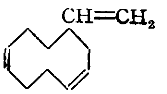
It follows that the vinyl*cyclo*hexene produced in the catalytic reaction is itself formed catalytically. No *cyclo*octadiene was formed in experiments in which the acetylene was replaced by other ethynyl compounds.

The reaction was extremely sensitive to poisons, the nature of which still remains obscure; extreme cleanliness was absolutely essential for a successful preparation. A decline in yield of *cyclo*octadiene was found in successive runs starting with a clean (sand-blasted) autoclave and new free-space packing until finally it was difficult even to achieve the normal initial catalyst promotion with acetylene and no dimers were formed at all. The use of a glass-lined autoclave partly overcame this poisoning effect, besides facilitating experimental manipulation, but it was not invariably effective. Traces of water and formaldehyde completely inhibit the *cyclo*octatetraene reaction (McKinley, *Ind. Eng. Chem.*, 1952, **44**, 995; Canale and Kincaid, U.S.P. 2,613,231), and in the present reaction it was desirable to add a little calcium carbide to the reaction mixture to ensure complete dryness. Small quantities of other drying agents such as alumina and silica gel appeared to inhibit the reaction, and ethylene oxide and phosphoric oxide gave very much reduced yields of *cyclo*octadiene.

Care was taken to exclude oxygen by repeated purging with nitrogen. Experiments showed that whereas the thermal decomposition of $(Ph_3P)_2Ni(CO)_2$ to triphenylphosphine, nickel, and carbon monoxide was comparatively slow at 140° in boiling xylene in an inert atmosphere, a markedly more rapid decomposition occurred in the presence of oxygen, giving triphenylphosphine oxide. Under comparable conditions, triphenylphosphine was only slowly oxidised to the oxide, showing that the complex itself was attacked directly by oxygen. In an attempt to inhibit polymerisation of the butadiene to high polymer, a small quantity of an antioxidant (generally 2 : 5-di-*tert.*-butyl-1 : 4-benzoquinone) was added to the reaction mixture, but the remarkably beneficial results recorded for similar additions of antioxidants to *cyclo*octatetraene preparations (Barnes, U.S.P. 2,579,106) were not observed. The usual solvent was benzene, but toluene, acetonitrile, *cyclo*hexane, and tetrahydrofuran gave comparable results. The erratic results obtained in this reaction parallel similar experiences recorded in the polymerisation of acetylene to *cyclo*octatetraene (see Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, 1949, p. 189).

This synthesis of *cyclo*octadiene led to the accumulation of a quantity of a dark brown oil remaining after the removal of the dimers from the reaction products. Distillation of the oil gave an intense blue liquid, b. p. 105—115°/20 mm., from which a fraction, b. p. 113°/120 mm., n_D^{20} 1·5111, analysing as a butadiene trimer, $C_{12}H_{18}$, was obtained on re-distillation. This fraction amounted to about 5% of the *cyclo*octadiene. Hydrogenation showed the presence of three double bonds and hence a monocyclic ring structure. The hydrogenated trimer partly crystallised, yielding 30—35% of *cyclo*dodecane (Ruzicka, Plattner, and Wild, *Helv. Chem. Acta*, 1946, **29**, 1611). This result establishes the formation from butadiene of a twelve-membered ring trimer, presumably the symmetrical *cyclo*-dodeca-1 : 5 : 9-triene (I). Distillation of the liquid part of the hydrogenated trimer gave a substance, b. p. 100—110°/14 mm., n_D^{20} 1·4708—1·4829, mainly 1·473—1·479. This high refractive index strongly suggests the presence of isomers of *cyclo*dodecane containing other large ring structures, probably ethyl*cyclo*decane derived from the trimer 8-vinyl-*cyclo*deca-1 : 5-diene (II) and diethyl*cyclo*octane isomers derived from corresponding divinyl*cyclo*octenes [*e.g.* (III)]. An attempt to synthesise ethyl*cyclo*decane was unsuccessful since *cyclo*decanone on treatment with ethyl-lithium gave solely the lithium salt of the enol of the ketone. A tendency of ketones of medium ring size to react in this way was observed with *cyclo*octanone (Cope and Fenton, *J. Amer. Chem. Soc.*, 1951, **73**, 1195), and appears to become complete with the ten-membered ring homologue.


(I)



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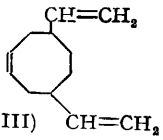


(III)

It was established that no octahydrodiphenyl, obtained in low yield by Alder and Rickert (*Ber.*, 1938, **71**, 372) by heating vinyl*cyclo*hexene and butadiene, was present by comparison of the infra-red spectrum of the hydrogenated trimer with that of di*cyclo*hexyl.

The formation of these monocyclic butadiene trimers of medium ring size was surprising, especially as nine- to twelve-membered rings have always been the most difficult to prepare (for review, see Prelog, *J.*, 1950, 420). Moreover, although Reppe, Schlichting, and Meister (*Annalen*, 1948, **560**, 93) originally believed that the $C_{10}H_{10}$ and $C_{12}H_{12}$ hydrocarbons formed during the polymerisation of acetylene to *cyclo*octatetraene contained ten- and twelve-membered rings respectively, recent work (Craig and Larrabee, *J. Amer. Chem. Soc.*, 1951, **73**, 1191; Cope and Fenton, *loc. cit.*; Withey, *J.*, 1952, 1930) has shown that it is most unlikely that compounds with rings greater than eight-membered are formed in the reaction.

The compound responsible for the blue coloration of the trimer became concentrated in the later fractions on redistillation, making it probable that the compound is a substituted azulene. This is supported by its stability in air and by ultra-violet analysis, although the concentration of the compound was too low to allow a definite conclusion.

Nickel carbonyl and the fully substituted derivative $Ni(PCl_3)_4$ (Wilkinson, *Nature*, 1951, **165**, 514) were inactive in the reaction. Triphenylphosphine, although readily available to the original German investigators (see B.I.O.S. Surveys Report No. 32, H.M.S.O., London, 1951. p. 18), is tedious to prepare in the laboratory and a more easily obtainable tervalent phosphorus compound was therefore sought as a ligand to replace one or two of the carbonyl groups of nickel carbonyl. Phosphorus trifluoride replaces up to three of the carbonyl groups of nickel carbonyl without altering the character of the complex (Chatt, *J.*, 1951, 3061) and through the courtesy of Dr. Chatt samples of his complexes roughly corresponding to $(PF_3)_2Ni(CO)_2$ were made available. Only one experiment (of five) was successful in producing a trace of *cyclo*octadiene, but this also gave a small amount of a new compound derived from both acetylene and butadiene (see below). Trimethyl and triphenyl phosphites replaced two carbonyl groups with extreme ease in cold ether solution, giving respectively the complexes $[(MeO)_3P]_2Ni(CO)_2$ as a moderately stable liquid if kept cold, and $[(PhO)_3P]_2Ni(CO)_2$ as a crystalline solid.

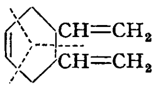
These complexes exhibited considerably greater catalytic activity than those of phosphine, and the catalyst life, as measured by the time during which the complexes catalysed the very exothermic acetylene polymerisation, was up to ten times as long. It was discovered that both phosphite complexes catalysed the formation of *cyclo*octadiene in the *absence of acetylene*, giving a product with physical constants agreeing with those quoted by Ziegler *et al.* and by Cope *et al.* (*locc. cit.*). The *cyclo*octadiene : vinyl*cyclo*hexene ratio, amounting at best to 2 : 1, was never as great in these experiments as with the acetylene-promoted phosphine catalyst. The triphenyl phosphite complex, to which most attention was directed, functioned without promotion at as low a temperature as 100°, but the conversion of the butadiene was never more than 50% in experiments lasting 48 hours, and considerable quantities of undistillable high polymer were always formed. The inclusion of calcium carbide and the antioxidant appeared to have no effect in experiments with the phosphite–carbonyl catalysts and they were therefore generally omitted. This is probably the most convenient procedure for the preparation of quantities of very pure *cyclo*octadiene.

It was established that pretreatment of the phosphite complexes with acetylene produced a markedly more active catalyst, and *cyclo*octadiene : vinyl*cyclo*hexene ratios of 5 : 1 were obtained at 100°, but the *cyclo*octadiene again had a high refractive index. Furthermore, it was occasionally possible to isolate a substantial quantity of distillable compounds boiling above the b. p. of *cyclo*octadiene, which was not obtained from experiments conducted in the absence of acetylene. The butadiene trimer was obtained (although now colourless) and shown by hydrogenation to *cyclo*dodecane to contain about 30—35% of *cyclo*dodeca-1 : 5 : 9-triene. In one experiment, a small amount of even higher-boiling material was isolated, which analysed as a butadiene tetramer, with the remarkably high refractive index n_D^{20} 1·5472. Hydrogenation indicated four double bonds, and from the hydrogenated product, 5% of *cyclo*hexadecane was separated as white needles, m. p. 57°

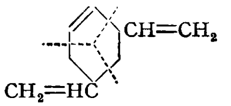
(Ruzicka and Giacomello, *Helv. Chim. Acta*, 1937, **20**, 548). A small part of the butadiene tetramer is thus present as *cyclo*hexadeca-1 : 5 : 9 : 13-tetraene.

The acetylene-promoted phosphite–carbonyl complexes also led to formation of small amounts of the compound of b. p. just above that of *cyclo*octadiene that had been observed in the successful phosphorus trifluoride experiment. By distillation of appropriately bulked fractions from a number of experiments, a compound $C_{10}H_{14}$, b. p. 169°, n_D^{20} 1·4860, was isolated, which was therefore derived from two molecules of butadiene and one molecule of acetylene. On hydrogenation 3 mols. of hydrogen were absorbed to give a saturated hydrocarbon $C_{10}H_{20}$, showing that the compound was cyclic and contained three double bonds.

Infra-red examination showed the presence of two vinyl groups and one *cis*-1 : 2-disubstituted ethylene linkage, all unconjugated, which was confirmed by lack of reaction with maleic anhydride and dimethyl acetylenedicarboxylate. The compound was therefore almost certainly one of the isomers of divinyl*cyclo*hexene [(IV)—(VI), the dotted lines show the components]. Complete characterisation was not attempted, but the physical properties of the saturated hydrocarbon suggest that it was 1 : 2-diethyl*cyclo*hexane indicating structure (IV) for the compound $C_{10}H_{14}$. Whatever the isomer, it is noteworthy that it is formed from two molecules of butadiene both reacting in the 1 : 2-position, whereas in vinyl*cyclo*hexene and *cyclo*octadiene at least one of the butadiene molecules has reacted in the 1 : 4-position. The four-membered ring dimer of butadiene, *trans*-1 : 2-divinyl*cyclo*butane, formed from two molecules of butadiene reacting in the 1 : 2-position (Reed, *loc. cit.*), was not detected in any of the products of this catalytic reaction.



(IV)



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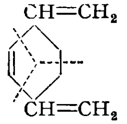

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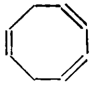


(VII)

The impurity responsible for the high refractive indices of the *cyclo*octadiene made with the acetylene-promoted catalysts was shown by ultra-violet analysis to be only partly accounted for by styrene (b. p. 144°; n_D^{20} 1·5434), which has a strong absorption band in the infra-red at 770 cm.$^{-1}$ and not at 765 cm.$^{-1}$. This was clearly demonstrated by comparison of the infra-red spectra of a pure specimen of *cyclo*octadiene containing 2% of styrene and the impure *cyclo*octadiene. Hydrogenation of a large sample of impure *cyclo*octadiene, followed by careful fractionation, led to the isolation of only ethyl*cyclo*hexane and *cyclo*octane. Hence, the impurity must have an eight-membered ring structure, and therefore *cyclo*octa-1 : 3 : 6-triene (VII) formed by reaction of one molecule of butadiene and two molecules of acetylene, or its isomerisation product, *cyclo*octa-1 : 3 : 5-triene, seem most likely to be present. Both, but especially (VII), show considerable absorption at about 765 cm.$^{-1}$ (Cope and Hochstein, *loc. cit.*; Cope, Haven, Ramp, and Trumbell, *J. Amer. Chem. Soc.*, 1952, **74**, 4868).

Early attempts to extend the cyclic polymerisation catalysed by the acetylene-promoted phosphine–carbonyl complex to substituted butadienes gave disappointing results. Isoprene, piperylene, 1 : 4- and 2 : 3-dimethylbutadiene, and 1- and 2-methoxybutadiene gave very small quantities of compounds comprised of one molecule of the diene and two or three molecules of acetylene (see Experimental). These compounds readily absorbed oxygen, and their constitutions were not established. Later, it was found that isoprene and piperylene gave substantial quantities of dimers with the acetylene-promoted phosphite–carbonyl complex but the products were not investigated in detail. Propene and *iso*butene failed to react, and vinylacetylene reacted uncontrollably giving high polymer and tar.

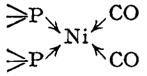
A wide variety of complexes derived from carbonyls and metal salts has been examined in the butadiene reaction, generally with acetylene added as promoter. All the results have been negative. Acetylene alone did not react with the cobalt carbonyl complexes $[Ph_3PCo(CO)_3]_2$ and $[(PhO)_3PCo(CO)_3]_2$ or the iron carbonyl complex $(Ph_3P)_2Fe(CO)_3$, the first two being completely insoluble in all solvents, and the last so extremely stable that it was invariably recovered unchanged. The iron carbonyl–butadiene complex $C_4H_6Fe(CO)_3$ (Reihlen, *Annalen*, 1930, **482**, 161) was also extremely stable and non-catalytic in the butadiene polymerisation. Other inactive complexes included cobalt and iron nitrosocarbonyls and iron carbonyl iodide and their substituted derivatives, *e.g.*, $Ph_3PCo(NO)(CO)_2$, $(PhO)_3PCo(NO)(CO)_2$, $(Ph_3P)_2Fe(NO)_2$, and $(PhO)_3PFe(CO)_3I_2$. Butadiene did not polymerise with any metal halide derivative. The square-planar complexes of nickel halides and tri-*n*-propylphosphine (see Jensen, *Z. anorg. Chem.*, 1936, **229**, 265) generally gave highly exothermic reactions on being heated with acetylene leading to voluminous black polymers or tar, but the addition of butadiene to the reacting system gave no distillate product. A solution of the red complex $(Pr_3P)_2NiBr_2$ was converted into a deep blue liquid on treatment in solution with butadiene alone at 120°, but no butadiene polymerisation occurred.

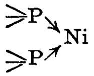
The Reppe complexes $(Ph_3P)_2NiBr$ and $(Ph_3P)_2CuCl$ did not react. Complexes of the nickel cation which polymerise acetylene to *cyclo*octatetraene such as nickel cyanide (Reppe) and especially the nickel acetonylacetone complex (Cope and Estes, *J. Amer. Chem. Soc.*, 1950, **72**, 1128) which also readily interpolymerises acetylene and mono- and di-substituted acetylenes (Cope and Campbell, *ibid.*, 1951, **73**, 3537; 1952, **74**, 179; Cope and Smith, *ibid.*, p. 5136) failed to polymerise butadiene, and attempts to interpolymerise acetylene and butadiene led to only *cyclo*octatetraene. The carbonyls of chromium, molybdenum, and tungsten formed much high polymer but no distillable products from butadiene above 90°.

Other ligands were sought to replace some of the carbonyl groups of nickel carbonyl. Thus, *o*-phenanthroline forms chelate complexes with iron, cobalt, and nickel carbonyls (Hieber *et al.*, *Ber.*, 1932, **65**, 1082, 1090) but the isolated nickel derivative $Ni(CO)_2$–*o*-phenanthroline was found to be unstable in air. A preparation *in situ* was therefore devised in which nickel carbonyl and the base were heated with acetylene and butadiene, a procedure well adapted to the use of other bases, such as pyridine, which give very unstable pyrophoric substitution products. A series of experiments with a number of different types of organic nitrogen bases with butadiene and acetylene gave small amounts of *cyclo*octadiene, but large quantities of vinyl*cyclo*hexene, suggesting that these complexes catalyse the formation of the six-membered ring dimer of butadiene.

It is concluded that the catalytic cyclic polymerisation of butadiene to large-ring compounds is a specific property of nickel^0 compounds, possessing the partial structure (VIII).

(VIII)





(IX)

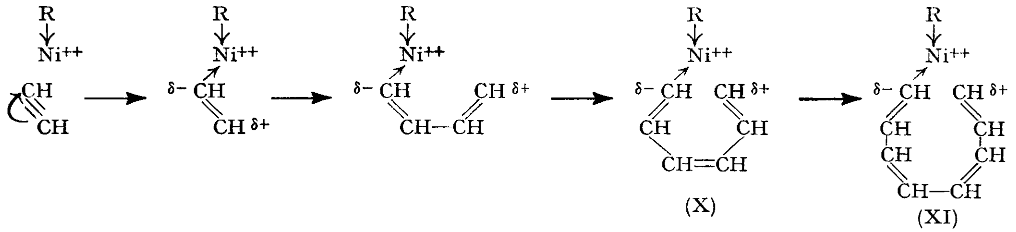
These compounds are not, of course, the active catalysts in the polymerisation but are converted into a soluble, electrophilic nickel complex by initial reaction with the unsaturated compound probably resulting in removal of one or both of the residual carbonyl groups (*e.g.*, IX). Variations in properties of the resulting complex then reside in the effects of the remaining ligands.

A theory of the mechanism by which butadiene is polymerised by the nickel carbonyl derivatives should embrace the related cyclic polymerisations of acetylene catalysed by the carbonyl derivatives which give benzene and styrene, and by the nickelous cation complexes which lead to *cyclo*octatetraene and related higher compounds. Although the formation of *cyclo*octatetraenes appears to be an exclusive property of the nickelous cation complexes, considerable quantities of aromatic products are also formed (see especially Cope and Estes, *loc. cit.*).

The interpolymerisation of acetylene with but-2-yne and diphenylacetylene to give 1 : 2-disubstituted *cyclo*octatetraenes led to the conclusion that the association of acetylene with the catalyst is through an electron pair of the triple bond (Cope and Campbell, *loc. cit.*; Cope and Smith, *loc. cit.*). This idea can be readily extended to butadiene, one double bond providing the electron pair for association to the catalyst and the other taking part in the polymerisation.

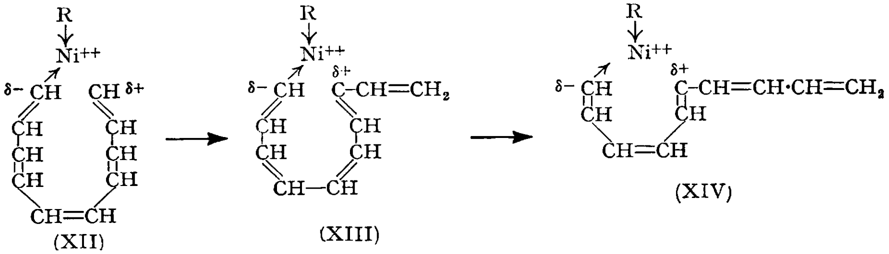
A partial picture of these cyclic polymerisation processes involves a steady successive build-up of the eventual ring system around the nickel atom by addition of units of either acetylene or butadiene, followed by the final break away of the nearly formed ring in a final cyclisation step. The characterisation of the 1-phenylbuta-1 : 3-diene present in the pentamer fraction from *cyclo*octatetraene preparations as the *cis*-isomer (Craig and Larrabee, *loc. cit.*; Cope and Fenton, *loc. cit.*) provides strong evidence for such a ring complex. More complete understanding is precluded by lack of evidence as to the actual nature of the active nickel complex.

In the *cyclo*octatetraene synthesis, a succession of anionoid attacks by the acetylene on the cationoid complex, R ⟶ Ni^{++} (where R is the co-ordinated group giving a soluble complex), leads to the sequence :



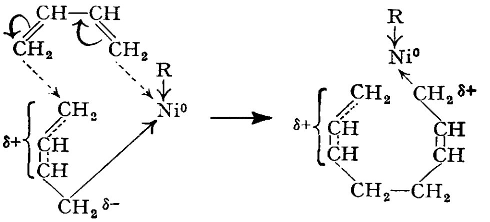
(X) (XI)

The intermediate complexes are mesomeric zwitterions which decompose by cyclisation, re-forming the initial complex and the *cyclo*polyolefin, *e.g.*, benzene from (X) and *cyclo*octatetraene from (XI). It is evident that further addition of acetylene must lead to isomerisation of the complex, presumably by successive 1 : 3-shifts in the conjugated double bond system. This is represented in the case of (XII) by changes to (XIII) and (XIV), precursors of vinyl*cyclo*octatetraene and *cis*-1-phenylbutadiene, respectively, and it is noteworthy that 1 : 2-divinylbenzene, which would require isomerisation at both ends of the carbon chain, is not formed. An analogous series of intermediates may be envisaged from complexes of $nickel^0$ but whereas the acetylene tetramer precursor (XI) appears to



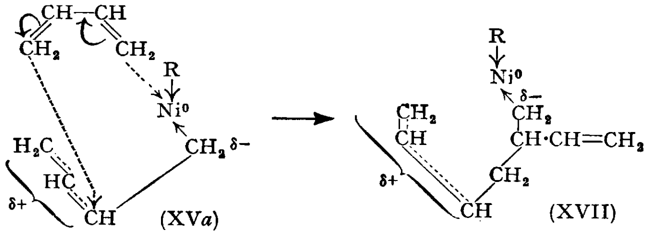
(XII) (XIII) (XIV)

be stable with Ni^{++}, the corresponding Ni^0 complex must isomerise readily to give styrene instead of *cyclo*octatetraene. In the polymerisation of butadiene, initial anionoid attack on the cationoid nickel complex gives the zwitterion (XV), and a further molecule of



(XV) (XVI)

butadiene the complex (XVI), which gives *cyclo*octadiene by cyclisation and breakaway from the nickel catalyst. The formation of vinyl*cyclo*hexene involves the reaction of the second molecule of butadiene at the allylic position of the initial intermediate (XV*a*) to give (XVII):



(XV*a*) (XVII)

Repetition of this process leads to complexes from which *cyclo*dodecatriene and vinyl*cyclo*decadiene, etc., could be formed. The formation of the large-ring compounds from butadiene, whilst underlining the remarkable cyclising properties of substituted nickel derivatives, is probably made possible by the absence of the conjugated double-bond system that is formed in complexes built up from acetylene, thus preventing substantial ring-contraction by isomerisation.

These schemes predict that the higher acetylene polymers should consist initially of a ring with one conjugated side-chain, whereas the higher butadiene polymers should contain rings with several vinyl side-chains.

No evidence of the formation of any compound with an open-chain structure has been forthcoming either in work on the polymerisation of acetylene or this work with butadiene, although such compounds would easily have been detected by their much lower refractive indices, especially in the fully hydrogenated derivatives. This suggests that the only method whereby the built-up carbon chain can become detached from the catalyst is by reaction at the other end of the chain, as indicated in the scheme. If this cyclisation does not occur, and presumably it becomes more difficult as the length of the chain increases, the complex may then initiate the long-chain polymerisation of butadiene, thus resulting in the formation of the large quantities of high polymer which always accompany the distillable polymers.

EXPERIMENTAL

Pressure Equipment.—Reactions involving the use of acetylene under pressure were studied in a unit comprising a stirred 1-l. autoclave, with electrical space heating, to which liquids could be introduced from a 250-c.c. storage vessel, and acetylene and nitrogen or other gases added through separate delivery pipes. All the parts were made of standard 250-atm. equipment, the acetylene lines being fitted with steel wire to decrease their volume. Copper-containing materials were excluded and all unfilled spaces packed with steel gauze. Valves in contact with acetylene were of the push-pull type and all were fitted with extended spindles for remote control from behind a brick wall. The acetylene supply was drawn from specially packed cylinders of 60 cu. ft. capacity containing no free space at the top, and a special non-return valve was incorporated immediately above the cylinder (Reppe, *Chem. Ing. Tech.*, 1950, **22**, 279). All operations were conducted within the limits of conditions laid down by Home Office Regulations (S.R. & O., 1947, No. 805).

Catalytic Polymerisation of Butadiene with Acetylene-promoted $(Ph_3P)_2Ni(CO)_2$ (with P. HARRISON).—A solution of the complex $(Ph_3P)_2Ni(CO)_2$ (10·0 g.), 2 : 5-di-*tert*.-butyl-1 : 4-benzoquinone (0·2 g.), and calcium carbide (5 g.) in benzene (200 c.c.) was heated in the autoclave under an initial pressure of 7 atm. of acetylene and 3 atm. of nitrogen until promotion of the complex occurred, generally in the range 120—130° (indicated by a sudden temperature rise of about 15—20°). The mixture was then cooled to 120—130°, and butadiene (250 c.c., 176 g.) added during 2 hr. After further heating at 120—130° (generally for 2 hr.) during which time further acetylene was admitted to restore the pressure, the mixture was allowed to cool overnight. The reaction mixture was freed from unreacted butadiene (30—70 g.) by releasing the pressure through cooled receivers and slightly warming the liquid product, filtered from acetylene polymer and calcium carbide, and flash-distilled at 150°/15 mm. Final fractionation of the distillate at atmospheric pressure to remove the solvent and then under reduced pressure gave vinyl*cyclo*hexene (9—15 g.), b. p. 77°/144 mm., and *cyclo*octadiene (35—55 g.), b. p. 95—97°/144 mm., n_D^{20} 1·4945—1·4960 (Found: C, 88·9; H, 11·1. Calc. for C_8H_{12}: C, 88·9; H, 11·1%).

In a reaction time of 8·5 hr., *cyclo*octadiene (62 g., 44%) and vinyl*cyclo*hexene (17 g., 10·5%) were obtained at a butadiene conversion of 85%. Reduction of the amount of catalyst to 1 g. gave no product.

cyclo*Octa*-1 : 5-*diene*.—The hydrocarbon was characterised as 2-*chloro*cyclo*oct*-5-*enyl* 2 : 4-*dinitrophenyl sulphide*, m. p. 112—113° (cf. Kharasch and Buess, *loc. cit.*) (Found : C, 48·8; H, 4·4. $C_{14}H_{15}O_4N_2SCl$ requires C, 49·0; H, 4·4%), after crystallisation from methanol–ethanol. Ozonolysis gave pure succinic acid, m. p. and mixed m. p. 186—187° [diphenacyl ester, needles (from alcohol), m. p. and mixed m. p. 151°].

cyclo*Octene*.—The dimer (10·94 g.) was shaken in hydrogen at room temperature and pressure in ether (60 c.c.) in the presence of pre-reduced palladium–barium sulphate (3 g.; 5% Pd). Absorption ceased abruptly after 1·07 mol. had been absorbed (2600 c.c. at 20°/760 mm. Calc. for one mol. of hydrogen, 2440 c.c.). After removal of catalyst and solvent, the residue was distilled giving *cyclo*octene (9·8 g.), b. p. 144—145°, n_D^{20} 1·4700, characterised as 2-*chloro*-cyclo*octyl* 2 : 4-*dinitrophenyl sulphide*, which crystallised from benzene–alcohol as needles, m. p. 140° (Found : C, 48·8; H, 4·8; Cl, 10·1. $C_{14}H_{17}O_4N_2SCl$ requires C, 48·8; H, 4·9; Cl, 10·3%), alone or mixed with a specimen made from authentic *cyclo*octene. The *cyclo*octene was further characterised by oxidation with potassium permanganate in acetone at 0—10° (Reppe, Schlichting, Klager, and Topel, *Annalen*, 1948, **560**, 1) to suberic acid, m. p. and mixed m. p. 140·5° (diphenacyl ester, m. p. and mixed m. p. 102—103°, and di-*p*-bromophenacyl ester, m. p. and mixed m. p. 143°).

cyclo*Octane*.—*cyclo*Octadiene (14·3 g.) in methanol (30 c.c.) was hydrogenated to completion at 50 lb./sq. in., Raney nickel catalyst (*ca.* 3 c.c.) being used. Removal of catalyst and solvent gave *cyclo*octane (12·1 g.), b. p. 67—68°/50 mm., m. p. 11°.

Butadiene Trimer.—The bulked residues from 15 runs (82·3 g.) were distilled (19 mm.) to give *cyclo*octadiene (18 g.), b. p. 45—47°, and liquid fractions, b. p. 60—105° (8 g.), b. p. 105—115° (16 g.), and b. p. 115—130° (16 g.) (intense blue). Refractionation of the latter fractions gave the *butadiene trimer* (13 g.), b. p. 112—114°/20 mm., n_D^{20} 1·5111 (Found : C, 89·1; H, 11·1. $C_{12}H_{18}$ requires C, 88·9; H, 11·1%).

cyclo*Dodecane*.—Hydrogenation (Adams catalyst) of the trimer (11·5 g.) in methyl acetate (35 c.c.) to completion (4795 c.c. at 20°/760 mm Calc. for 3 mol. of hydrogen : 5100 c.c.), followed by removal of catalyst and solvent, and cooling to −10°, gave crude *cyclo*dodecane (4·8 g.), which was filtered off and recrystallised from methanol–methyl acetate, forming needles (3·2 g.), m. p. 61° (Found : C, 85·7; H, 14·4. Calc. for $C_{12}H_{24}$: C, 85·6; H, 14·4%). The liquid part of the hydrogenated trimer was distilled at 144 mm. to give the following saturated hydrocarbon fractions : b. p. 100—101°, n_D^{20} 1·4708 (0·68 g.); b. p. 101—102°, n_D^{20} 1·4728 (1·08 g.); b. p. 102—103°, n_D^{20} 1·4741 (1·56 g.); b. p. 103—106°, n_D^{20} 1·4757 (1·40 g.); b. p. 106—108°, n_D^{20} 1·4787 (1·47 g.); and b. p. 108—110°, n_D^{20} 1·4829 (0·4 g., almost completely solidified on cooling to 0°).

Catalytic Polymerisation of Butadiene with Acetylene-promoted $[(MeO)_3P]_2Ni(CO)_2$.—A solution of the complex $[(MeO)_3P]_2Ni(CO)_2$ (10 g.) in benzene (250 c.c.), di-*tert*.-butylbenzoquinone (0·2 g.), and butadiene (150 c.c., 106 g.) was heated in the autoclave under an initial pressure of 6 atm. of acetylene and 3 atm. of nitrogen. After promotion of the catalyst, the temperature was maintained at 120° for 3 days, butadiene (150 c.c.) being added at the beginning of the second and the third day. Acetylene was added occasionally during the experiment, resulting in slight rises in temperature (thus showing continued activity of the catalyst). After cooling, the reaction product was steam-distilled to separate distillable products from high polymer. Final fractionation at 144 mm. gave vinyl*cyclo*hexene (38 g.), b. p. 74—78°, *cyclo*octadiene (49 g.), b. p. 95—96°, n_D^{20} 1·4971, and a fraction (4 g.), b. p. 98—120°. In other similar experiments, up to 30 g. of trimer have been obtained from a single run by prolonging the steam-distillation of the crude products. Hydrogenation as before gave 30—35% yields of *cyclo*dodecane.

cyclo*Hexadecane*.—By very prolonged (8 hr.) steam-distillation of the products of a reaction catalysed by acetylene-promoted $[(MeO)_3P]_2Ni(CO)_2$, a heavy oil (8·2 g.) was isolated. Distillation gave butadiene trimer, b. p. 56—80°/0·8 mm. (4·4 g.), and tetramer, b. p. 93—98°/0·8 mm., n_D^{20} 1·5472 (2·4 g.), 98—108°/0·8 mm., n_D^{20} 1·5468 (1·0 g.). On hydrogenation in ethyl acetate (20 ml.) with Adams catalyst, the tetramer fraction, b. p. 93—98°/0·8 mm. (2·2 g.), absorbed 1037 c.c. (Calc. for 4 mol. of hydrogen, 977 c.c.). Removal of catalyst and solvent, followed by cooling to −50°, led to the separation of crude *cyclo*hexadecane, which was filtered off and recrystallised from methyl acetate–methanol, forming white needles (0·1 g.), m. p. 57° (Found : C, 85·6; H, 14·3. Calc. for $C_{16}H_{32}$: C, 85·6; H, 14·4%).

Catalytic Polymerisation of Butadiene with Acetylene-promoted $[(PhO)_3P]_2Ni(CO)_2$.—A solution of $[(PhO)_3P]_2Ni(CO)_2$ (10 g.), di-*tert*.-butylbenzoquinone (0·2 g.), and butadiene (250 c.c., 176 g.) in benzene (200 ml.) was heated under an initial pressure of 7 atm. of acetylene and 3 atm. of nitrogen for 2·5 days at 110°, acetylene being added intermittently. The products were worked up by steam-distillation and finally fractionated at 144 mm. to give vinyl*cyclo*hexene (26 g.), *cyclo*octadiene (7·9 g.), b. p. 90—93°; b. p. 93—96°, n_{D}^{20} 1·4931 (36·7 g.); b. p. 96—97°, n_{D}^{20} 1·4951 (60·1 g.); b. p. 97—100°, n_{D}^{20} 1·4945 (12·3 g.); and material, b. p. 100—110°, n_{D}^{20} 1·4909 (4·1 g.); and b. p. 110—124°, n_{D}^{20} 1·4852 (6·6 g.). In other runs, butadiene trimer (10—30 g.) was also obtained.

Catalytic Polymerisation of Butadiene with Non-promoted $[(PhO)_3P]_2Ni(CO)_2$.—A solution of $[(PhO)_3P]_2Ni(CO)_2$ (10 g.) and di-*tert*.-butylbenzoquinone (0·2 g.) in benzene (200 ml.) was heated under an initial pressure of 3 atm. of nitrogen for 4 days at 100°. Steam-distillation and fractionation at 144 mm. gave vinyl*cyclo*hexene (32 g.) and pure *cyclo*octadiene (63·7 g.), b. p. 97°, n_{D}^{20} 1·4935, n_{D}^{25} 1·4912, m. p. −69·5.

*Divinyl*cyclo*hexene*.—Fractions having b. p. 98—120°/144 mm. from a number of experiments with acetylene-promoted phosphite–nickel carbonyl catalysts were bulked and fractionated to give *divinyl*cyclo*hexene*, b. p. 108—109°/144 mm. (169°/760 mm.), n_{D}^{20} 1·4860 (Found : C, 89·4; H, 10·5. $C_{10}H_{14}$ requires C, 89·6; H, 10·4%).

*Diethyl*cyclo*hexane*.—Divinyl*cyclo*hexene (2·5 g.) was hydrogenated to completion in methyl acetate (15 c.c.) in the presence of Adams catalyst (1510 c.c. were absorbed. Calc. for 3 mol. of hydrogen, 1560 c.c.). The catalyst and solvent were removed and the residue distilled to give diethyl*cyclo*hexane, b. p. 173—175°, n_{D}^{20} 1·4495 (Found: C, 85·5; H, 14·4. Calc. for $C_{10}H_{20}$: C, 85·6; H, 14·4%). Buck *et al.* (*J. Inst. Pet.*, 1948, **37**, 399) gives b. p. 177°, n_{D}^{20} 1·4471, for (presumably *cis*-) 1 : 2-diethyl*cyclo*hexane.

Reaction of Acetylene with Substituted Butadienes catalysed by $(Ph_3P)_2Ni(CO)_2$.—A solution of the complex $(Ph_3P)_2Ni(CO)_2$ (5 g.) in benzene (100 ml.) with di-*tert*.-butylbenzoquinone (0·2 g.) and calcium carbide (5 g.) was heated under an initial pressure of 6—7 atm. of acetylene and 3 atm. of nitrogen until promotion of the catalyst occurred. The substituted butadiene was then added (1 hr.) to the mixture at 120—130°, and heating continued for 3—4 hr. The reaction product was then filtered, flash-distilled, and fractionated, giving results collected in the Table.

Trialkyl and Triaryl Phosphite Complexes of Nickel Carbonyl.—Stoicheiometric quantities of nickel carbonyl and the phosphite ligand were mixed in ether solution (compare Rose and Statham, *loc. cit.*). The theoretical quantity of carbon monoxide was evolved briskly and after slight warming to complete the reaction, the ether was removed on a warm-water bath, finally under slight vacuum. The resulting *complexes*, obtained in nearly quantitative yields, were stored under nitrogen at −10°. The triphenyl phosphite complex was obtained as colourless needles, m. p. 95°, from light petroleum (b. p. 40—60°)–ether (Found: C, 62·2; H, 4·2; P, 8·4; Ni, 7·7. $C_{38}H_{30}O_8P_2Ni$ requires C, 62·1; H, 4·1; P, 8·4; Ni, 8·0%).

Products from the reaction of acetylene with substituted butadienes.

	Products,			Analysis, Found, %			Analysis, Required, %	
Diene	wt., g.	b. p./mm.	n_{D}^{20}	C	H	Formula	C	H
1-Methoxybutadiene	4·0	67°/10	1·5149	80·1	8·6	$C_5H_8O + 2C_2H_2$	79·4	8·8
(25·5 g.)	1·0	78°/10	1·5225	79·9	8·5	$C_5H_8O + 3C_2H_2$	81·5	8·6
2-Methoxybutadiene	1·4	65—67°/10	1·5282	82·0	8·6	—	—	—
(30·0 g.)	3·0	70°/10	1·5375	82·3	8·5	—	—	—
2 : 3-Dimethylbutadiene	4·0	47—48°/10	1·4930	89·8	10·2	$C_6H_{10} + C_2H_2$	88·9	10·1
(109 g. in 2 expts.;	1·9	50—52°/10	1·5044	90·1	10·2	$C_6H_{10} + 2C_2H_2$	89·6	10·4
products bulked)						$C_6H_{10} + 3C_2H_2$	90·0	10·0
1 : 4-Dimethylbutadiene	1·0	48—49°/10	—	89·8	10·1	$(C_6H_{10})_2$	87·8	12·2
(31 g.)	2·0	50—59°/10	—	90·2	9·9	—	—	—
Isoprene (42·5 g.)	3·5	44—46°/10	1·5080	89·9	10·1	$C_5H_8 + C_2H_2$	88·2	11·8
						$C_5H_8 + 2C_2H_2$	90·0	10·0
						$C_5H_8 + 3C_2H_2$	90·4	9·6
Piperylene (44·3 g.)	3·9	44—45°/10	1·5010	89·8	10·2	$(C_5H_8)_2$	88·2	11·8

Triphenyl Phosphite Complex of Cobalt Carbonyl (G. H. WHITFIELD).—A filtered ethereal solution of cobalt carbonyl (30 g.) was treated with an ethereal solution of triphenyl phosphite (138 g.) at room temperature. Carbon monoxide was rapidly evolved (4300 c.c. Calc. for 2 mol. 4200 c.c. at 18°), and the mixture was finally warmed under reflux to complete the reaction. The complex $[(PhO)_3PCo(CO)_3]_2$ (66·5 g.) was obtained as silky brown needles, m. p. 173° (decomp.), totally insoluble in common organic solvents.

Complexes of Cobalt Nitrosocarbonyl.—(a) *With triphenylphosphine.* A solution of cobalt nitrosocarbonyl (5 g.) in ether (25 c.c.) was treated with triphenylphosphine (7·6 g.) in ether (15 c.c.) and warmed; carbon monoxide was evolved, and final distillation of the ether gave the *complex* $Ph_3PCo(NO)(CO)_2$, maroon prisms, m. p. 125° (decomp.), from light petroleum (b. p. 60—80°) (Found: C, 59·8; H, 3·6; N, 3·5; P, 7·3. $C_{20}H_{15}O_3NPCo$ requires C, 59·0; H, 3·7; N, 3·4; P, 7·6%).

(b) *With triphenyl phosphite* (G. H. WHITFIELD). No reaction occurred between cobalt nitrosocarbonyl and triphenyl phosphite in boiling ether. A solution of cobalt nitrosocarbonyl (11·5 g.) and triphenyl phosphite (20·6 g.) in ether (100 c.c.) was heated under an initial pressure of 50 atm. of carbon monoxide for 5 hr. at 120°. Removal of the solvent from the residue followed by recrystallisation from methanol gave the *complex* $(PhO)_3PCo(NO)(CO)_2$ (19·6 g.) as orange rhombic prisms, m. p. 55° (Found: N, 3·1. $C_{20}H_{15}O_6NPCo$ requires N, 3·1%). Alternatively, excess of pure dry nitric oxide was passed slowly over the complex $[(PhO)_3P)_2Co(CO)_3]_2$ (27 g.) at 100° in an apparatus previously swept with nitrogen. After 2 hr., the nitrosocarbonyl complex was extracted with ether, filtered, and finally crystallised from methanol (16·1 g.).

Triphenyl Phosphite Complex of Iron Tetracarbonyl Iodide (G. H. WHITFIELD).—A solution of iron tetracarbonyl iodide (20 g.) in ether (200 c.c.) was treated at 20° with a solution of triphenyl phosphite (15 g.) in ether (50 c.c.). After 2 hr., 1150 c.c. of carbon monoxide had been evolved (Calc. for 1 mol., 1130 c.c. at 18°/760 mm.) and large purple prisms of the *complex* $(PhO)_3PFe(CO)_3I_2$ were deposited (28 g.), m. p. 115° (decomp.) (Found: P, 4·1. $C_{21}H_{15}O_6PI_2Fe$ requires P, 4·4%).

Triphenyl Phosphine Complex of Iron Nitrosocarbonyl.—Iron nitrosocarbonyl (2 g.) (Hieber, F.I.A.T. Review of German Science, 1939—1946, Inorganic Chemistry, Part II, p. 129) in ether (10 c.c.) was treated with triphenylphosphine (6 g.) in ether (20 ml.), and warmed. The *complex* $(Ph_3P)_2Fe(NO)_2$ (4·2 g.) was recrystallised from benzene, forming black plates, m. p. 195—198° (decomp.) (Found: C, 67·4; H, 4·5. $C_{36}H_{30}O_2N_2P_2Fe$ requires C, 67·6; H, 4·7%).

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[*Received, January* 23*rd*, 1954.]