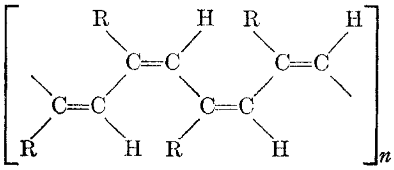
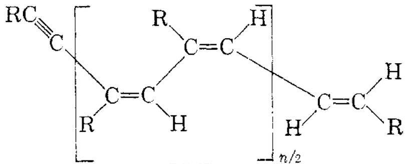
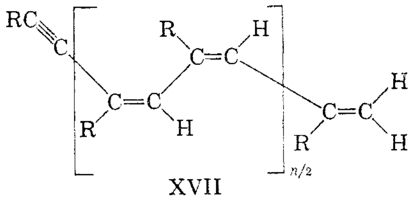
ably involve metal hydride intermediates. In addition to the above objections, structures VId and VIIIb and scheme (2) appear to be unlikely in view of the results of kinetic and deuterium isotope studies which will be reported in future papers in this series.

No detailed structural work has been done on the linear tetramers, pentamers, hexamers, and higher oligomers of the monoalkylacetylenes. Analysis of their infrared spectra and gas chromatograms suggests, however, that these higher oligomers may also each consist of only a pair of isomers. The small number of isomers can be rationalized by assuming a stereospecific and nonrandom incorporation of nonterminal monomer units. Structural differences would then appear only in the terminal olefinic monomer unit.

The infrared bands for the terminal monomer units (R—C≡C—, *trans*—CH═CHR and —CR═CH$_2$) decrease in intensity as the number of monomer units in the chain increases. However, the position and intensity of the double bond band at 1625 cm.$^{-1}$ does not change in the higher oligomers. In their studies on the linear high polymers of 1-hexyne, Natta *et al.*[16] have assigned a band at the same place to the double bonds in the polymer resulting from the stereospecific head-to-tail coupling of monomer units by *cis* additions to the triple bonds (structure XV) in the manner of scheme (1) above. It would then appear that the higher oligomers formed in this reaction are most likely to be mixtures of structures XVI and XVII. If this latter assumption is valid, it has great significance with regard to the mechanism of formation of these linear products. Studies of both the catalyst activation and polymerization processes will be presented in later papers, where more detailed mechanisms for these reactions will be considered.


XV


XVI


XVII

Acknowledgment. The authors wish to thank the Research Service Department for the infrared and elemental analyses.

STAMFORD, CONN.

---

[16] G. Natta, G. Mazzanti, G. Pregaglia, and M. Peraldo, *Gazz. Chim. Ital.*, **89**, 465(1959).

[CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Polymerization of Acetylenes by Nickel-Carbonyl-Phosphine Complexes. III.[1] Polymers from Terminal-Unconjugated Diacetylenes[2]

E. C. COLTHUP AND L. S. MERIWETHER

Received June 5, 1961

The polymerization of HC≡C—(CH$_2$)$_n$—C≡CH ($n = 2$–5) with dicarbonylbis(triphenylphosphine)nickel Ni(CO)$_2$(Ph$_3$P)$_2$ in refluxing cyclohexane yields both low and high molecular weight polymer products containing linear conjugation (n = 2–5) and aromatic fused ring structures (n = 3, 4 only), the latter resulting from a novel cyclization reaction. Copolymerization with monoalkylacetylenes affords analogous products.

In the first paper in this series,[3] we reported the results of a study of the polymerization of a wide variety of mono- and disubstituted acetylenes with dicarbonylbis(triphenylphosphine)nickel. This paper presents the results of an extension of this reaction to terminal unconjugated diacetylenes.

In the only previous attempt to polymerize terminal unconjugated diacetylenes, Stille and Frey[4] obtained red to black soluble polymers from the reaction of 1,6-heptadiyne with Ziegler-type catalysts, while 1,7-octadiyne and 1,8-nonadiyne gave cross-linked polymers with the same catalysts. Chemical and physical evidence suggested a struc-

---

[1] Paper II in this series: L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5163 (1961).

[2] Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 1960.

[3] L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961).

[4] J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **83**, 1697 (1961).

TABLE I

POLYMERIZATION OF DIACETYLENES WITH $Ni(CO)_2(Ph_3P)_2$ IN REFLUXING CYCLOHEXANE[a]

Acetylene	Wt., G.	Concn., Moles/L.	Catalyst Concn. (Moles/L.)	Reaction Time, Hr.	% Acetylene Reacted[b]
1,5-Hexadiyne	2.0	0.60	0.006	1½	100
1,6-Heptadiyne	23.0	1.67	.011	3	100
1,6-Heptadiyne	46.0	1.67	.011	2½	95
1,7-Octadiyne	26.5	1.67	.011	2	95
1,8-Nonadiyne	20.2	1.17	.010	2	100
1-Heptyne + 1,5-hexadiyne, 1:1	3.6, 3.0	0.52, 0.52	.007	3	70
1-Pentyne + 1,6-heptadiyne, 1:1	10.2, 13.8	1.31, 1.31	.014	3	100
1-Heptyne + 1,6-heptadiyne, 1:1	4.8, 4.6	0.54, 0.54	.006	3	100
1-Heptyne + 1,7-octadiyne, 1:1	12.0, 13.3	0.82, 0.82	.011	3	100
1-Heptyne + 1,8-nonadiyne, 1:1	9.5, 11.4	0.76, 0.73	.014	2	100
1-Pentyne + 1,6-heptadiyne, 9:1	10.2, 1.08	2.28, 0.26	.009[c]	3	100
1-Pentyne + 1,7-octadiyne, 20:1	15.0, 1.1	2.23, 0.11	.008[c]	2½	100
1-Pentyne + 1,7-octadiyne, 100:1	15.0, 0.21	2.25, 0.024	.008[c]	3	90
1,6-Heptadiyne + 1,7-octadiyne, 1:1	4.6, 5.1	0.54, 0.52	.006	3	100

[a] All experiments were carried out in a nitrogen atmosphere. [b] Based on the disappearance of the monomer C≡C—H bands at 2130 cm.$^{-1}$ in infrared. [c] These experiments were run in refluxing acetonitrile using dicarbonylbis[tris(2-cyanoethyl)phosphine]nickel as catalyst.

ture for poly-1,6-heptadiyne containing a polymer backbone of alternating single and double bonds with a cyclic repeating six-membered ring resulting from the stereospecific heat-to-tail coupling of acetylene groups.

This polymer appears to be structurally unrelated to the products obtained from 1,6-heptadiyne in the present work.

EXPERIMENTAL

Materials. The following research grade acetylenes were obtained from the Farchan Research Laboratories: 1-pentyne, 1-heptyne, 1,6-heptadiyne, 1,7-octadiyne, 1,8-nonadiyne; these were used without further purification. 1,5-Hexadiyne was synthesized according to the procedure of Pomerantz *et al.*[5] Dicarbonylbis(triphenylphosphine)nickel and dicarbonylbis[tris(2-cyanoethyl)phosphine]nickel were prepared by published methods.[6,7] "Spectro" grade cyclohexane and acetonitrile were obtained from Eastman.

Procedure. The following procedure was used in all of the polymerization experiments listed in Table I. The acetylene monomer (or mixture of monomers), solvent, and nickel complex were mixed at room temperature and were then heated in a nitrogen atmosphere at reflux (about 80°) until the reaction was over (2–3 hr.). The product isolation procedure depended on the solvent used in the reaction. When acetonitrile was used, petroleum ether (b.p. 30–60°) was added to the cooled reaction mixture and it was then washed thoroughly with 10% aqueous hydrochloric acid and finally with water. The petroleum ether layer was separated, dried, and the petroleum ether was removed from the polymer product. When present, the lower molecular weight products were separated from the high polymer by vacuum fractionation.

Products. The analytical data on the reaction products are summarized in Table II. These products were identified from their infrared, ultraviolet, and mass spectra and in a few cases by elemental analysis and oxidative degradation to compounds of known structure. Linear acetylene polymers were identified by infrared bands at 1625–1650 (double bond stretch), 970–980 (indicative of *trans* configuration of hydrogen atoms about a double bond) and 890–900 cm.$^{-1}$ (indicative of a vinylidine $H_2C{=}CR$— group) and by ultraviolet absorption in the 250–300-mμ region with high absorptivities. The 1,2,4-trisubstituted aromatic groupings were distinguished by infrared absorption in the 1600–1625 (double bond stretch), 1500–1525 (half ring stretching, half ring contracting), 860–880 (isolated hydrogen bending) and 800–820 cm.$^{-1}$ (two adjacent hydrogens bending) regions, and by ultraviolet absorption between 260 and 280 mμ with $a = 10$–15. The relative amounts of conjugated linear polyene and aromatic groupings in the high polymers could be estimated by comparison of the intensities of the 970–980 cm.$^{-1}$ and 800–820 cm.$^{-1}$ bands in their infrared spectra. The molecular weights of the oligomers were readily determined from the "parent peaks" in their mass spectra. The concentration of different molecular weight species in a mixture of oligomers could also be approximately ascertained from their mass spectra. The instruments used in this work have been described previously.[3]

Potassium permanganate oxidation of 1,3-bis(5-indanyl)-propane. The procedure of Bucher[8] was used. A solution of 7.2 g. of 1,3-bis(5-indanyl)propane in a mixture of 50 ml. of pyridine and 25 ml. of water was heated on a steam bath in a 3-l. flask provided with a reflux condenser. During the course of 30 min., 61.6 g. of powdered potassium permanganate was added, the flask being shaken after each addition of potassium permanganate to keep the mixture in a pasty condition. Water was added as necessary (about 100 ml.). The heating and shaking were continued until all the potassium permanganate had been reduced (about 1 hr.). The pyridine was then steam distilled and the manganese dioxide was filtered from the water solution. The water solution was acidified with concentrated sulfuric acid to *p*H 1.5 and then continuously extracted with ether. Four grams of trimellitic acid (37%) was isolated from the ether layer, m.p. 215–216° dec. (reported[9] m.p. 218°). A mixed melting point with an authentic sample of trimellitic acid showed no depression. The infrared spectrum was identical with that of the known compound.

Potassium permanganate oxidation of 5-propylindane and 5-amylindane. Three grams of 5-propylindane (from the copolymerization of 1-pentyne with 1,6-heptadiyne) was

---

(5) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Research Natl. Bur. Standards*, 52, 51 (1954).

(6) J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

(7) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, 81, 4200 (1959).

(8) J. E. Bucher, *J. Am. Chem. Soc.*, **32**, 374 (1910).

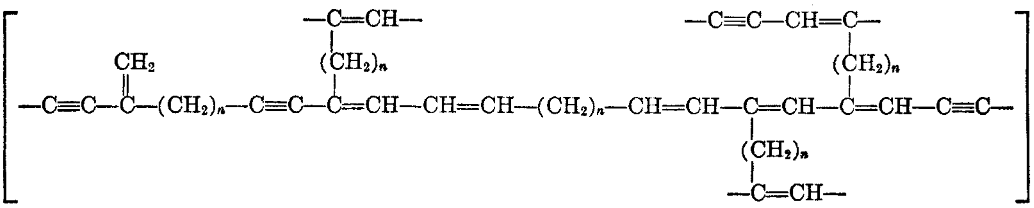
(9) W. Schultze, *Ann.*, **359**, 129 (1908).

oxidized with 17.7 g. of potassium permanganate by the same procedure as above to yield 1 g. of trimellitic acid, m.p. 215–216° dec. A similar yield of trimellitic acid was obtained from the permanganate oxidation of 5-amylindane.

Potassium permanganate oxidation of reaction product of 1-heptyne and 1,7-octadiyne, 1:1. The viscous product (15 g.) from a copolymerization of equimolar amounts of 1-heptyne and 1,7-octadiyne was immediately oxidized by the above procedure without prior work-up. The benzenetricarboxylic acid, obtained in poor yield (1 g.), had an infrared spectrum showing it to consist of about 80% trimellitic acid and 20% trimesic acid.

RESULTS AND DISCUSSION

In Table I are listed the experiments performed with unconjugated terminal diacetylenes, including homopolymerization and copolymerization with monosubstituted monoacetylenes. The products of these reactions are described in Table II. In most cases the catalyst was dicarbonylbis(triphenylphosphine)nickel, the monomer to catalyst ratio was in the range of 100:1 to 300:1, and the reactions were carried out in refluxing cyclohexane under a nitrogen atmosphere. Three of the experiments were run in refluxing acetonitrile with dicarbonylbis[tris(2-cyanoethyl)phosphine]nickel, but no significant difference was noted in the nature of the products from these two different catalysts. The reactions exhibited an induction period of about twenty min. duration, after which quantitative conversion of monomer (based on disappearance of the terminal acetylene bands in the infrared) usually occurred in two to three hours. However, the presence of unchanged terminal ethynyl groups was noted in a few of the polymer products.

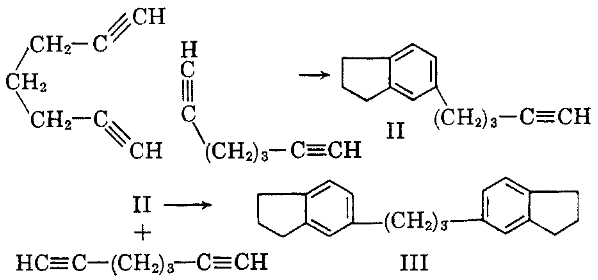


$$\left[-C{\equiv}C-\overset{\substack{CH_2\\ \|}}{C}-(CH_2)_n-C{\equiv}C-\overset{\substack{-C{=}CH-\\ |\\ (CH_2)_n\\ |}}{C}{=}CH-CH{=}CH-(CH_2)_n-CH{=}CH-\underset{\substack{|\\ (CH_2)_n\\ |\\ -C{=}CH-}}{C}{=}CH-\overset{\substack{-C{\equiv}C-CH{=}C-\\ |\\ (CH_2)_n\\ |}}{C}{=}CH-C{\equiv}C-\right]$$

I

Hompolymers. High molecular weight homopolymers were obtained from the whole series of diacetylenes examined, $HC{\equiv}C-(CH_2)_n-C{\equiv}CH$ ($n = 2$–5). A yellow cork-like, high melting (m.p. > 300°), presumably highly cross-linked polymer was the only product from 1,5-hexadiyne. No solvent for it could be found, and a satisfactory mineral oil mull could not be prepared for an infrared spectrum. The coupling of acetylene groups probably was exclusively linear in this polymer, whose structure might be represented as I ($n = 2$), with a completely random arrangement of monomer units in the polymer structure. Its insolubility and rigidity may be attributed to the presence of rather short alkylene chains between the groups of conjugated double and triple bonds.

The next higher homolog, 1,6-heptadiyne, formed two types of polymeric products, (1) a 75–80% yield of viscous, undistillable brown tar, which was soluble in hydrocarbon solvents such as benzene and cyclohexane, but formed a hard film after standing for several days in the air, finally hardening to a resin; and (2) a 20–25% yield of the aromatic trimer, 1,3-bis(5-indanyl)-propane (III). This latter product arose from a novel type of catalytic cyclization reaction in which two triple bonds from one diacetylene monomer reacted with one triple bond of a second monomer molecule to form the indane ring system. The structure of III was proven by the virtual identity of its infrared and ultraviolet spectra with those of a sample of 5-ethylindane and by its permanganate oxidation to trimellitic acid. The corresponding dimer product, 5-(4-pentynyl)indane (II), which is presumably the intermediate in the formation of III, was not isolated, although a small lower-boiling fraction obtained in one experiment may have contained some of this dimer. Since quantitative disappearance of the terminal ethynyl groups was observed in the reaction, this initially formed dimer must have reacted at the remaining acetylene group to give either III or high polymer.



From its infrared spectrum, the tarry higher polymer of 1,6-heptadiyne was found to contain both 1,2,4-trisubstituted aromatic and linear conjugated groupings. This product could have resulted either from the random polymerization of the diyne in both a cyclic and linear manner to give a polymer structure such as IV ($n = 3$), or the preformed dimer (II) may have further polymerized in a linear fashion to give products (V) analogous to those obtained from monoalkylacetylenes.[1] A formulation such as V ($n = 3$) would seem to be favored for this product because of its high aromatic content and good solubility, the latter suggesting a relatively low molecular weight ($m < 20$) and little cross-linking. The general tendency to resinify in these polymers is probably due to the oxidative cross-

TABLE II

Products of the Polymerization of Diacetylenes

Acetylene	Product or Fraction	M.P. or B.P./Mm.	Weight G.	Infrared Bands[a] (cm.$^{-1}$)	Mass Spectrum (principal mass peaks)[b]	Other Data
1,5-Hexadiyne	Cork-like polymer	>300° dec.	1.2			
1,6-Heptadiyne	1) 1,3-Bis(5-indanyl)propane, $(C_7H_8)_3$	180°/0.2	5	820 (s), 870 (s), 1500, 1600	276	Calcd. for $C_{21}H_{24}$: C, 91.3, H, 8.69; Found: C, 91.5, H, 8.87 Ultraviolet spectrum—λ_{max} at 278 (a = 12.95), 273 (a = 12.33), 269 and 264 mμ (cyclohexane).
	2) Polymeric pot residue	—	15	820, 975	Not volatile	Dark brown viscous resin which hardens on standing. Soluble in hydrocarbon solvents.
1,6-Heptadiyne	1) $(C_7H_8)_2$ (?)	85°/0.1	2	820, 870, 975 (w)		
	2) 1,3-Bis(5-indanyl)propane	180°/0.2	8.4	820, 870	276	
	3) Polymeric pot residue	—	25	820, 870, 975	Not volatile	Forms a hard film after standing several days in the air. Soluble in hydrocarbon solvents.
1,7-Octadiyne	Rubbery high polymer	ca. 250° dec.	40[c]	815 (w), 975, 1510, 3300 (w)	Not volatile	Swells in hydrocarbon solvents but only portion dissolves. Ultraviolet spectrum of soluble portion—λ_{max} at 278 (a = 2.05) and 268 (a = 2.43) mμ (cyclohexane)
1,8-Nonadiyne	Rubbery high polymer	ca. 250° dec.	25[c]	895, 975	Not volatile	Swells in hydrocarbon solvents but does not dissolve. Thorough removal of solvent leaves yellow-brown powder
1-Heptyne + 1,5-hexadiyne, 1:1	Viscous liquid containing $(C_7H_{12})_2$, $(C_7H_{12})_3$ along with high polymers	Polymerized on heating	5	820 (w), 895, 975	192, 277, 278, 288	Rapidly forms a brittle film on surface in air and solidifies to resin in a few days.
1-Pentyne + 1,6-heptadiyne, 1:1	1) Pale yellow liquid, mostly 5-propylindane	66–67°/0.55	2.0	820, 870	136 (3%), 160 (96%), 204 (0.5%)	n_D^{25} 1.5165
	2) Yellow liquid, mostly 5-propylindane	41°/0.1	0.5	820, 870	136 (0.5%), 160 (92%), 204 (5%)	n_D^{25} 1.5153
	3) Orange liquid, $(C_5H_8)(C_7H_8)$ + $(C_5H_8)_3$	70°/0.15	0.5	820 (w), 870 (w), 975, 2220 (w)	136 (1%), 160 (18.5%), 204 (57%)	n_D^{25} 1.5004
	4) Red liquid	65°/0.05	0.5	820 (w), 870 (w), 975 (s) 2220 (w)		n_D^{25} 1.5120
	5) Pot residue of higher polymers	—	20		Not volatile	
1-Heptyne + 1,6-heptadiyne, 1:1	1) $(C_7H_{12})_2$ + 5-Amylindane	80–85°/0.2	6.4	820 (s), 870 (s), 895, 975	188 (78%), 192 (1%), 276 (9%), 278 (2%), 284 (1%), 288 (9%), 384 (0.2%)	
	2) $(C_7H_{12})_3$	100–120°/0.2	1.0			
	3) 1,3-Bis(5-indanyl)propane	180°/0.2	0.8			
	4) Polymeric pot residue		0.9			
1 Heptyne + 1,7-octadiyne, 1:1	1) Yellow oil containing 3% $(C_7H_{12})_2$, 72% $(C_7H_{12})(C_8H_{10})$, 21% $(C_7H_{10})_3$, 2% $(C_7H_{12})_2(C_8H_{10})$, 1% $(C_7H_{12})(C_8H_{10})_2$ and 1% $(C_8H_{10})_3$		0.5	810, 830, 870, 892, 975	192 (3%), 202 (72%), 278, 288 (21%), 298 (2%), 308 (1%), 318 (1%)	Extracted from the rubbery polymer which formed on standing.

TABLE II (*continued*)

Acetylene	Product or Fraction	M.P. or B.P./Mm.	Weight G.	Infrared Bands[a] (cm.$^{-1}$)	Mass Spectrum (principal mass peaks)[b]	Other data
	2) Viscous brown oil which rapidly solidifies to a rubbery polymer.		20	810, 830, 870, 895, 975		Swells in hydrocarbon solvents.
1-Heptyne + 1,8-nonadiyne, 1:1	Dark brown viscous liquid containing $(C_7H_{12})_2$, $(C_7H_{12})(C_9H_{12})$, $(C_7H_{12})_3$, $(C_7H_{12})_2(C_9H_{12})$ and higher polymers		18.5	895, 975	192 (13%), 216 (32%), 288 (52%), 312 (2%)	Forms a surface film in air.
1-Pentyne + 1,6-heptadiyne, 9:1	1) Yellow liquid containing (C_5H_8)-(C_7H_8), $(C_5H_8)_3$, $(C_7H_8)_3$ and higher polymers		5	820, 870, 895, 975	160, 204, 276	
	2) Yellow-brown solid polymer		2	820, 870	Not volatile	Soluble in benzene, insoluble in petroleum ether.
1-Pentyne + 1,7-octadiyne, 20:1	Orange gummy mixture containing $(C_5H_8)_2$, $(C_5H_8)_3$, $(C_5H_8)_4$, $(C_5H_8)_5$ and higher polymers		10	895, 975	136 (50%), 204 (41%), 272 (5%), 340 (4%)	Completely soluble in benzene and petroleum ether
1-Pentyne + 1,7-octadiyne, 100:1	Red-orange liquid containing 14% $(C_5H_8)_2$, 68% $(C_5H_8)_3$, 8% $(C_5H_8)_4$ and 10% $(C_5H_8)_5$		12	895, 975	136 (14%), 204 (68%), 272 (8%), 340 (10%)	
1,6-Heptadiyne + 1,7-octadiyne, 1:1	Brown viscous oil containing $(C_7H_8)_3$, $(C_7H_8)_2(C_8H_{10})$, $(C_7H_8)(C_8H_{10})_2$, $(C_8H_{10})_3$ and higher polymers		8	820, 870, 905, 975 (w)	276 (35%), 290 (40%), 304 (16%), 318 (2%)	

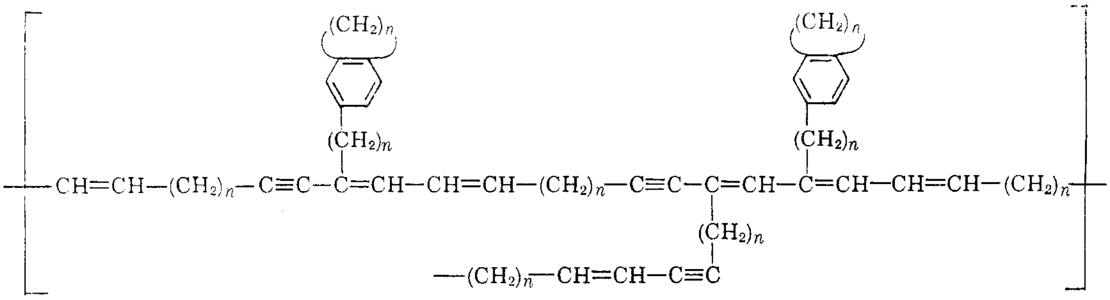
[a] (s) = strong, (w) = weak. [b] Percentages are based on the relative peak heights and refer only to that part of the material with mol. wt. <400. [c] Contains occluded solvent.

linking of the linear unsaturated portions on standing in the air.

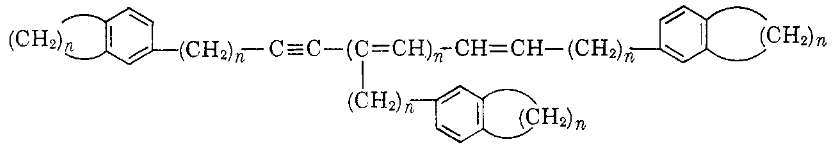
1,7-Octadiyne homopolymerized to a high molecular weight rubbery polymer which swelled in hydrocarbon solvents, but only a small part dissolved. Its infrared spectrum indicated the presence of both 1,2,4-trisubstituted aromatic and linear conjugated groupings as well as a small amount of residual terminal acetylenic groups. This polymer contained a lower proportion of aromatic structures than the high polymers of 1,6-heptadiyne. Its structure is probably best described by IV (n = 4) with some crosslinking and a few 5-hexynyl substituents on the linear conjugated chains. The rubbery character of this polymer may be attributed to the longer polyalkylene chains. No volatile low molecular weight products corresponding to those from 1,6-heptadiyne were isolated from this reaction. However, the soluble portion of the high polymer had an ultraviolet spectrum very similar to that of a substituted tetralin, suggesting that small amounts of 1,4-bis(6-tetralyl)butane or products of structure V (n = 4) had been formed. The tendency to aromatize to the condensed ring system is clearly much less in the case of 1,7-octadiyne than with 1,6-heptadiyne.

The reaction with 1,8-nonadiyne yielded an insoluble rubbery high polymer. Its infrared spectrum contained bands for linear conjugated chains but no evidence of aromatic groupings, indicating a structure resembling I (n = 5). Separation of the terminal ethynyl groups by a chain of five methylene groups is sufficient to completely inhibit intramolecular cyclization. Hence the tendency to form aromatic products among these nonconjugated terminal diacetylenes is primarily a function of the number of methylene groups separating the two ethynyl groups, reaching a maximum at n = 3 (1,6-heptadiyne).

Copolymers. A study of the copolymerization of this series of unconjugated terminal diacetylenes with monoalkylacetylenes has also been made with a view to preparing (1) a series of low molecular weight products such as 5-alkylindanes, 6-alkyltetralins, and 1:1 and 2:1 linear coupling products and (2) high molecular weight linear copolymers containing high proportions of monoalkylacetylenes and correspondingly small amounts of the diacetylenes. Earlier studies[3] had demonstrated that similarly substituted monoacetylenes would readily copolymerize with this catalyst to give products analogous to those formed by the pure monomers. Thus it was anticipated that both oligomeric products and high polymers would result from copolymerizations of monoalkylacetylenes with these diacetylenes. Since only low molecular weight products resulted from the homopolymerization of monoalkylacetylenes,[3] it was additionally surmised that small amounts of difunctional terminal diacetylenes added to these reactions might couple to-



IV



V

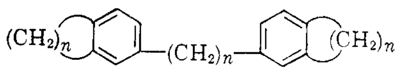
gether the short monoalkylacetylene chains to form high molecular weight polymers having unsaturated portions separated by short polymethylene chains.

Each of the four diacetylenes, $HC{\equiv}C{-}(CH_2)_n{-}C{\equiv}CH$ ($n = 2$–5), was treated in turn with an equimolar amount of 1-heptyne. The reaction with 1,5-hexadiyne produced a dark brown undistillable liquid copolymer, containing both aromatic and conjugated linear structures. A mass spectrum of the freshly prepared product did show the presence of dimers and trimers of 1-heptyne, but the bulk of the reactants, including all of the diacetylene, appeared to have formed higher polymers.

The product of the 1:1 reaction of 1,6-heptadiyne and 1-heptyne was more stable and was readily fractionated to give a large amount of the 1:1 adduct along with 1-heptyne dimers and trimers and 1,6-heptadiyne trimer. The mass spectrum of the mixture before distillation was consistent with the isolated yields. The 1:1 adduct was identified as 5-amylindane from its infrared spectrum and by permanganate oxidation to trimellitic acid. A second experiment in which 1-pentyne was substituted for the 1-heptyne gave a similar result except that the yields of 5-propylindane and the 1-pentyne dimers and trimers were much lower.

The 1:1 copolymerization of 1-heptyne with 1,7-octadiyne produced a viscous brown oil which rapidly hardened to a rubbery high polymer. An infrared spectrum of the oil had bands for 1,2,4- and 1,3,5-trisubstituted benzene rings and linear conjugated systems, the latter being in higher concentration. Permanganate oxidation of a fresh sample of this oil produced a 4:1 mixture of trimellitic and trimesic acids. The small amount of yellow oil extracted from the rubbery high polymer consisted mainly of the 1:1 adduct along with smaller amounts of 1-heptyne dimers and trimers and traces of higher oligomers. The results of the permanganate oxidation of the whole reaction product, as well as the absence in this fraction of terminal acetylene absorption in the infrared, suggest that the 1:1 adduct may be 6-amyltetralin. The 1:2 and 2:1 adducts could have either aromatic or linear structures.

Finally, an attempt was made to form mixed diacetylene coupling products by the reaction of equimolar quantities of 1,6-heptadiyne and 1,7-octadiyne. The product of this reaction, a viscous oil which did not harden on standing in the air, was highly aromatic. Although conclusive evidence is lacking, this product mixture probably contains aromatic diacetylene trimers of general structure VI where any combination of n = 3 or 4 is possible.



VI

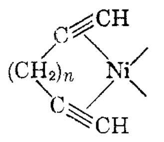
The higher incidence of 1,6-heptadiyne in the lower molecular weight products is consistent with its greater tendency than 1,7-octadiyne to form these fused ring aromatic structures.

In order to achieve the second objective of the copolymerization studies—the formation of high polymers of monoalkylacetylenes by incorporating small amounts of diacetylenes—a series of reactions of 1-pentyne with 1,6-heptadiyne and 1,7-octadiyne at molar ratios of mono- to diacetylene of 9:1 down to 100:1 was investigated. At the moderate ratios of 9:1 and 20:1 some higher polymers were formed. Better results were obtained with 1,7-octadiyne than with 1,6-heptadiyne since no aromatic material resulted with the former. However, at a 100:1 ratio of 1-pentyne to 1,7-octadiyne, the product mixture was virtually the same as that obtained in the homopolymerization of 1-pentyne, consisting only of low polymers. It appears that the presence of the diacetylene does not affect the number of monoacetylene molecules that will react in a linear fashion before polymerization stops. This is in the range of two to ten for the lower alkylacetylenes. Therefore, the use of mono- to diacetylene ratios much in excess of 10:1 would be of no further advantage. This is consistent with the observation that fairly high concentrations (greater than 5–10 mole per cent) of added diacetylenes are necessary to significantly increase the average molecular weight of polymers of monoalkylacetylenes.

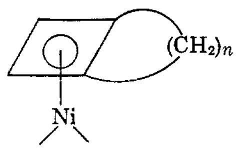
CONCLUSIONS

The four terminal unconjugated diacetylenes included in this study may polymerize with nickel-carbonyl-phosphines in two different ways: (1) by linear condensation and (2) by intramolecular aromatization. Each ethynyl group can react independently of the other to form linear acetylene polymers regardless of the number of carbon atoms lying between. In this respect their behavior is analogous to that of a monoalkylacetylene. However, these monomers differ greatly in their ability to undergo intramolecular aromatization, cyclization decreasing in the order 1,6-heptadiyne > 1,7-octadiyne >> 1,5-hexadiyne, 1,8-nonadiyne. Analogous results are obtained in copolymerizations with monoalkylacetylenes. This suggests that during the cyclization reaction both ends of the diacetylene chain must be coordinated to the nickel catalyst. An examination of molecular models lends support to this since only in 1,6-heptadiyne and to a lesser degree in 1,7-octadiyne can the two acetylene groups assume a conformation in which they can both coordinate by π-bonds to the nickel atom and, at the same time, the two penultimate carbon atoms are sufficiently close for bond formation.

The nature of these intermediate nickel-diacetylene complexes is unknown. Two types of π-bonded structures are possible, VII, in which the diacetylene is acting as a bidentate chelating ligand, and VIII, in which the two acetylene groups are coordinated as a π-cyclobutadiene group.



VII



VIII

There have been no transition metal complexes reported containing a chelating unconjugated diacetylene ligand, although many examples of chelating unconjugated diene complexes are known.[10] Several π-cyclobutadiene complexes of transition metals have recently been reported,[11] and their occurrence as intermediates in acetylene polymerization reactions has been postulated by several workers.[12]

It would appear that the most likely mechanism for the cyclization reaction would involve attack by another acetylene group on the intermediate nickel complex (VII or VIII). Once formed, the product could then dissociate from the catalyst complex. The linear polymerization of the diacetylenes probably proceeds by the same mechanism as that suggested for the linear polymerization of monosubstituted acetylenes in the preceding paper.[1] Further experiments with deuterium-labeled acetylenes are underway to test these conclusions.

Acknowledgment. The authors are grateful to the Research Service Department of the Stamford Laboratories for the infrared, ultraviolet and mass spectra and the microanalyses, and to Dr. G. W. Kennerly for helpful discussions.

STAMFORD, CONN.

---

(10) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959); J. Chatt, L. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957); R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959); G. Winkaus and G. Wilkinson, *Chem. & Ind.* (*London*), 1083 (1960); G. N. Schrauzer and H. Thyret, *J. Am. Chem. Soc.*, **82**, 6420 (1960).

(11) R. Criegee and R. Schröder, *Ann.*, **623**, 1 (1959); C. D. Ninetzescu, M. Avram, and E. Marica, *Ber.*, **92**, 1088 (1959); L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

(12) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956); J. C. Sauer and T. L. Cairns, *J. Am. Chem. Soc.*, **79**, 2659 (1957); M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **82**, 6255 (1960).