The emulsion so formed was broken by extraction with ether (discarded). The aqueous solution was made alkaline with 50 ml. of cold 20% sodium hydroxide solution. The oil so liberated was taken up in ether and the etheral solution was dried with anhydrous potassium carbonate and filtered. Ethereal hydrogen chloride was then added. The precipitate was crystallized from ethyl acetate–absolute ethanol and gave 2.3 g. (40% yield), m.p. 144–146°.

1,6-Dipyrrolidinohexane.—A solution of 5.4 g. (0.025 mole) of 1,6-dipyrrolidino-2,4-hexadiyne (XXVI) in 50 ml. of absolute ethanol containing 1 g. of Raney nickel (wet with water) was hydrogenated at an initial pressure of 60 p.s.i.g. The pressure dropped by 6.3 p.s.i.g. within 20 min. and an additional 3.5 hr. was required to complete the reaction (pressure drop of 8.4 p.s.i.g.). The nickel was removed by filtration. Distillation gave 2.7 g. of product, b.p. 151–156° at 6.5 mm. Redistillation provided 1.7 g., b.p. 144–146° at 4.5 mm. (lit.,[22] b.p. 148–149° at 4 mm.).

The dihydrochloride had m.p. 235–238° dec. (lit.,[22] m.p. 238–239°).

Acknowledgment.—The authors express thanks to Air Reduction Co., N. Y., for generous samples of acetylenic carbinols; to Messrs. W. L. Brown, G. M. Maciak, H. L. Hunter, R. M. Hughes, and Alfred Brown of the Lilly Research Laboratores, Indianapolis, for the analytical work; and to Eli Lilly and Co. for financial support.

[22] A. P. Phillips, *J. Am. Chem. Soc.*, **77**, 1693 (1955).

Hydridic Reducing Agent–Group VIII Metal Compound. A New Catalyst System for the Polymerization of Acetylenes and Related Compounds. I

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A new catalyst system for the polymerization of acetylenic compounds is described. The system consists of an hydridic reducing agent such as sodium borohydride, plus a salt or complex of a Group VIII metal, *i.e.*, nickel chloride. This system polymerizes acetylene itself to linear, *trans* high molecular weight polyacetylene. Monosubstituted acetylenes are polymerized largely to dimers and trimers. These reactions proceed smoothly, rapidly, and in good yield. Olefinic compounds such as ethylene, butadiene, and allene are also polymerized by these catalyst systems.

Reppe[1] has reported the catalytic preparation of a number of aromatic products from acetylene and monosubstituted acetylenes, using catalysts such as $(R_3P)_2Ni(CO)_2$. The literature contains a number of other references to the use of diphosphine nickel dicarbonyl catalysts for the aromatization of acetylenes.[2] More recently the scope of these catalysts for linear oligomerization, as well as aromatization of substituted acetylenes has been discussed.[3–5] Franzus[6] has demonstrated the aromatization of acetylene compounds by the use of Ziegler-Natta type catalysts. Natta and coworkers[7] have prepared linear high polymers of acetylene and monosubstituted acetylenes, using catalyst systems such as $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$.

Chatt[8] has described the preparation of stable phosphine–platinum–acetylene complexes by the reduction of the corresponding bis(phosphine)-platinum dichloride complexes with powerful reducing agents such as hydrazine. The present work involves the use of a cocatalyst system composed of an hydridic reducing agent, such as sodium borohydride, plus a compound of a Group VIII metal.[9] This co-catalyst system brings about the polymerization of acetylene to a linear, black product, totally unlike cuprene, and similar to the polyacetylene described by Natta and co-workers. The same cocatalyst system also brings about the polymerization of many substituted acetylenes, to dimers, trimers, tetramers, and higher polymers. Trimeric products may be (a) aromatized, *i.e.*, three acetylene groups may fuse to form a substituted benzene ring, or (b) may be linear instead. These reactions are truly catalytic, and high turnover numbers of substrate are observed. For example, in the presence of a several-fold molar excess of reducing agent, one mole of a co-catalyst such as $(Bu_3P)_2NiCl_2$ can cause the polymerization of several thousand moles of phenylacetylene in a few minutes. Olefinic compounds such as ethylene, butadiene, and allene are also polymerized by these catalyst systems.

Experimental

Chemicals.—The acetylene derivatives used were all purchased from Farchan Research Laboratories. In most

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[1] W. Reppe, *Ann.*, **560**, 104 (1948).

[2] See, for example, J. Rose and F. Statham, *J. Chem. Soc.*, 69 (1950); R. Kleinschmidt, U. S. Patent 2,542,417 (1951).

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

[4] L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5163 (1961).

[5] E. C. Colthup and L. S. Meriwether, *J. Org. Chem.*, **26**, 5169 (1961).

[6] B. Franzus, R. J. Canterino, and R. A. Wickliffe, *J. Am. Chem. Soc.*, **81**, 1514 (1959).

[7] G. Natta, G. Mazzanti, and R. Corradini, *Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* [8], **25**, 3 (1958); see also Australian Patent 219,925, July 8, 1956.

[8] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[9] For a preliminary communication, see also L. B. Luttinger, *Chem. Ind.* (London), 1135 (1960). Also M. L. H. Green, M. Nehme, and G. Wilkinson, *ibid.*, 1136 (1960).

cases, they were used as received. Matheson acetylene was purified immediately before use by passing through a train consisting, successively, of a Dry Ice–acetone trap, concd. sulfuric acid, a potassium hydroxide column, and finally a column of activated alumina. Mass spectroscopy indicated that the effluent gas was about 99.96% pure acetylene. All the inorganic transition metal salts such as nickel chloride were reagent grade. Sodium and potassium borohydride were purchased from Metal Hydrides, Inc., and were approximately 95–98% pure. All solvents used were C.P., reagent, or spectro grade. Tributylphosphine was purchased from Westvaco. Triphenylphosphine was Eastman White Label. These were used as received. Tris(2-cyanoethyl)phosphine, obtained in this laboratory,[10] was recrystallized before use to free it of oxide and polymer; m.p. 97° (lit. 98°). (The melting point of this and all other compounds listed below, are uncorrected.)

Bis(triphenylphosphine)nickel dichloride was prepared by the method of Venanzi.[11]

Bis(tri-*n*-butylphosphine)nickel dichloride was prepared by Jensen's procedure.[12] M.p. found 47–48°; lit. 48–49°.

Bis[tris(2-cyanoethyl)phosphine] nickel Dichloride.—Recrystallized tris(2-cyanoethyl)phosphine (13.2 g.) was dissolved in reagent grade acetone. Anhydrous nickel chloride (5.2 g.) was added. A deep wine-red color developed in the solution. The mixture was stirred. After 2-hr., bluish crystals began to settle. These were filtered off, washed with acetone, and dried; m.p. 176–180°.

Anal. Calcd. for $C_{18}H_{24}N_6P_2NiCl_2$: C, 41.88; H, 4.65. Found: C, 41.54; H, 4.74.

Bis[tris(2-cyanoethyl)phosphine] nickel Dibromide.—This was prepared exactly like the chloride. It was a green solid.

Diiodoacetylene was supplied by Dr. V. Galasyn of this laboratory.[13] It was recrystallized immediately before use; m.p. 75–78°(lit. 78–82°).[14]

Procedure.—The apparatus used for most experiments consisted of a three- or four-necked flask fitted with a gas inlet for prepurified nitrogen, a thermometer, and a double or triple reflux condenser. When gaseous acetylenes were being investigated, the top condenser was a cold finger filled with a Dry Ice–acetone slurry and a second gas inlet was provided for the acetylene. Heating was accomplished, when necessary, with a mantle.

The experimental procedure with the less volatile acetylenes was as follows. The acetylene plus the solvent were deaerated with prepurified nitrogen for about 10 min. The reducing agent, *e.g.*, sodium borohydride, was then added. Stirring by the nitrogen stream was usually continued throughout the experiment, and a few minutes after addition of the reducing agent, the transition metal compound was also added. Little difference in results was noted if the transition metal compound was added before the reducing agent. Either could also be added before the acetylene. However, if the two catalyst components were mixed before the addition of the acetylene, a vigorous reaction occurred, resulting in the consumption of catalyst. For this reason, the acetylene was always added to the system before the two catalyst components were allowed to come into contact.

In the experiments with the gaseous acetylenes carried out at atmospheric pressure, the solution was first saturated with the acetylene gas, before addition of both catalyst components, and kept saturated by a rapid flow of the acetylene, so as to minimize loss of the catalyst components by their direct reaction with one another.

When the reaction was run in an autoclave it was found convenient to chill the autoclave containing the solvent to about −70°, and then add the catalyst components separately. At this temperature, little or no reaction between these compounds occurred during the short period of contact in the absence of substrate. The autoclave was then quickly sealed, and acetylene passed in.

In most cases, the reactants were allowed to remain in contact with one another for several hours, although it appeared that the reaction is usually over in 20 min. or less for most monosubstituted acetylenes. The gaseous acetylenes, which were in most instances bubbled continuously through solutions of the catalyst system, appeared to react for several hours.

Following separation from the rest of the reaction mixture, the reaction products were identified by (a) infrared analysis (disappearance of the triple bond and the triple bond C—H stretches of the monomers, development of product bands in the double bond regions, *i.e.*, bands at 895 and 975 cm.$^{-1}$ for the linear dimers and trimers of monoalkyl acetylenes); by (b) vapor phase chromatography against authentic samples of dimers, trimers, etc., obtained by other means[15]; by (c) mass spectrometry; and by (d) other methods, such as X-ray analysis in the case of linear polyacetylene, ultraviolet analysis in the case of the low polymers of acetylene, etc.

The results of a number of such experiments are summarized in Table I.

Results and Discussion

On addition of the final catalyst components to these systems, the color of the metal ion or complex in solution was usually discharged and a brown-to-black tinge rapidly developed in its stead. An exotherm usually occurred, sometimes immediately, often after an induction period of several minutes. The solubility of the transition metal compound in the system often appeared to be greatly increased by the presence of the acetylene plus the reducing agent.

Acetylene.—Perhaps the most remarkable of all these reactions were those of acetylene (experiments 1–4). The major reaction product in these experiments was a high molecular weight polymer of acetylene. The infrared spectrum of this material was virtually featureless, except for the presence, in most samples, of a strong band at about 1010 cm.$^{-1}$, ascribable to *trans* double bonds. This spectrum is almost identical with that reported by Natta[7] for a material believed to be a linear, *trans*, high polymer of acetylene. X-ray examination of the products of the present reactions revealed degrees of ordering ranging from completely amorphous to materials similar to those of Natta. As with Natta's products, colors ranged from brown to black, with the more ordered materials generally being darker and having a more pronounced infrared band in the 1010-cm.$^{-1}$ region. While some of the lighter colored products, featureless in the infrared and completely amorphous to X-rays, may be related to the well known random acetylene polymer cuprene, the darker material must have a different structure. In contrast to cuprene, which

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[10] See M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1103 (1959).

[11] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

[12] K. A. Jensen, *Z. Anorg. Chem.*, **229**, 265 (1936).

[13] See U. S. Patent 2,124,218, July 19, 1938.

[14] "Handbook of Chemistry and Physics," Chemical Rubber Co., 34th ed. (1952–1953).

[15] See ref. 4 for structure proofs and related information concerning the polymers obtained in these reactions.

TABLE I. POLYMERIZATION OF VARIOUS ACETYLENES IN THE PRESENCE OF NICKEL SALTS

Expt. No.	Acetylene	Molarity Acetylene	Molarity Reducing Agent	*trans* Metal Compound and Molarity	Solvent	Time of Reaction[c]	Exotherm Observed after Cat. Addn.	Products Infrared (cm.$^{-1}$)	Mass Spec.[b] a.	b.	c.	d.	e.	% Approximate Yields
1	Acetylene	Saturated	$NaBH_4$ 0.9[a]	$[P(CNE)_3]_2NiCl_2$[d] 0.019[a]	Ethanol	4.25 hr.	40°	1014	...	..	...	...	...	1 g.[e]
2	Acetylene	Saturated	$NaBH_4$ 0.44[a]	$[P(CNE)_3]_2NiCl_2$ 0.016[a]	Acetonitrile	5.5 hr.	9°	...	...	..	...	...	...	1 g.[e]
3	Acetylene	Saturated	KBH_4 0.19[a]	$[P(CNE)_3]_2NiCl_2$ 0.014[a]	Water	6 hr.	None	...	...	..	...	...	...	0.2 g.[e]
4	Acetylene	Init. press. of acetylene was ≈35 p.s.i. at −70°	$NaBH_4$ 0.26	$[P(CNE)_3]_2NiBr_2$ 0.016	Ethanol	24 hr.	...	...	...	..	...	...	...	1 g.[e]
5	Butyne-1	≈20 cc. of butyne-1 was absorbed during the course of the reaction	$NaBH_4$ 0.044[a]	$[P(CNE)_3]_2NiCl_2$ 0.010[a]	Ethanol	2.5 hr.	47° Almost explosive	895,975	...	..	69	23	6[f]	≈40
6	Pentyne-1	1.90	$NaBH_4$ 0.307	$NiCl_2$ 0.090	Ethanol	1 hr.	44°	895,975	...	26	64	9	0.4	40
7	Phenylacetylene	1.78	$NaBH_4$ 0.33	$(nBu_3P)_2NiCl_2$ 0.011	Acetonitrile	4.5 hr.	>55 Almost explosive	...	...	26	24	21	...	60
8	Phenylacetylene	1.68	$NaBH_4$ 0.031	$(nBu_3P)_2NiCl_2$ 0.00022	Acetonitrile	5.25 hr.	None	...	...	..	...	...	...	≈50
9	1,6-Heptadiyne	1.61	$NaBH_4$ 0.16	$(nBu_3P)_2NiCl_2$ 0.011	Acetonitrile	4 hr.	5°	...	...	..	...	...	...	15
10	1,7-Octadiyne	1.72	$NaBH_4$ 0.26	$[(CNE)_3P]_2NiCl_2$	Ethanol	1 hr.	25°	975,890 820,2120	...	..	...	...	...	90
11	3-Diethylamino-propyne-1	1.57	$NaBH_4$ 0.26	$[(CNE)_3P]_2NiCl_2$ 0.011	Ethanol	2 hr.	25°	975,1650 CH_2NR_2	...	..	...	...	...	62
12	Propargyl alcohol	3.9	KBH_4 0.053	$[(CNE)_3P]_2NiCl_2$ 0.0028	Water	10 min.	85°	1625 C=C 850 1,3,5 subst. benz. 810, 1,2,4 subst. benz.	...	..	...	...	...	26
13	Propargyl alcohol	4.21	KBH_4 0.25	$[P(CNE)_3]_2NiCl_2$ 0.015	Water	10 min.	75° Almost explosive	...	?	?	?	19	...	70–90
14	Hexyne-3	1.86	$NaBH_4$ 0.307	$NiCl_2$ 0.045	Butanol	100°/3 hr.	...	...	...	41	58	1.5	...	15
15	Diphenylacetylene	1.07	$NaBH_4$ 0.71	$[P(CNE)_3]_2NiCl_2$ 0.011	Acetonitrile	80°/4 hr.	...	...	...	..	...	...	...	1 ?
16	Heptyne-1	1.80	$NaBH_4$ 0.51	$NiCl_2$ 0.14	Ethanol	5 hr.	43°	895,975	...	15	73.5	10.5	...	45

[a] These are initial concentrations. Solubility of the acetylene in the solvent caused concentration changes during the course of the reaction. [b] Mass spec: a. monomer, b. dimer, c. trimer, d. tetramer, e. pentamer. [c] Except where otherwise noted, all experiments were carried out at 25°. [d] $(CNE)_3P$ = tris(2-cyanoethyl)phosphine. [e] Polyacetylene formed. [f] Mass spec. also showed about 2% hexamer in product.

may be described as a conglomeration of long chains, branches, crosslinks, etc., the present material is probably largely linear.

It proved to be very difficult to determine the physical properties of this polymer. Like Natta's product, it was insoluble in all solvents. This insolubility precluded any determination of molecular weight. Carbon and hydrogen analyses were usually low.

Emission spectroscopy established the presence of relatively large quantities of nickel and boron in some samples. In certain cases, these two elements accounted for about 7% of the total weight of polymer. The nickel–boron mole ratios found in these samples were very roughly 2:1, corresponding to the compound Ni_2B, a known product of the reaction between certain nickel salts and sodium borohydride in aqueous solution.[16] The presence of nickel boride in these polymers may be suggestive as to the polymerization mechanism. It was found that nickel and boron could be removed from these polymers by washing with hydrochloric acid.

Melting points could not be obtained for polyacetylene. Instead, a very slow decomposition was observed, becoming apparent, in some cases, as low as 130°, and not being complete even at 300°.

In attempts to free these materials from low molecular weight organic impurities, samples of polyacetylene were exhaustively and successively extracted with several solvents. The following features of their reactions with solvents are noteworthy: (a) a relatively small quantity of intensely colored (yellow to red) material is dissolved by nonpolar solvents, a point being reached where no more solvent extraction is apparent; (b) a marked, reversible swelling of polyacetylene by acetone can be demonstrated; (c) the polymer, after extraction with nonpolar solvents, can be extracted with acetone for an indefinite period of time, yielding yellow solutions. The polymer meanwhile grows progressively lighter in color (over a period of several weeks), the infrared band at 1010 cm.$^{-1}$ is usually lost, and the material tends to appear more amorphous to X-rays than before solvent extraction.

These facts suggest that polyacetylene slowly breaks down on extraction. It is to be expected that particles of "linear" polyacetylene would contain some largely amorphous regions, and that these regions might be sites for oxidative attack on the polymer chains. Polyene chains in a noncrystalline state would be expected to be prone to air oxidation. In linear polyacetylene, stability is conferred by relatively close packing of the chains, and possibly by resonance stabilization and interchain interactions as well. As chains become solvated, they may peel away from the main body of the polymer mass, and become more accessible to attack by oxygen dissolved in the solvent.

Experiment 4 was run in an autoclave, with the hope of obtaining higher yields. This hope was not realized, the quantity and ratio of products formed being about the same as in other experiments in similar solvents.

The colored solvent extracts of polyacetylene were shown by ultraviolet spectroscopy to contain conjugated polyenes having from three to perhaps a dozen double bonds. Investigation of these products was hampered by their relative instability, as well as by the relatively small quantities of material involved. Oxidation occurred rapidly in solution or on driving off solvent, even under relatively oxygen-free conditions, and led to insoluble residues.

Similar by-products of the high polymerization of acetylene were also reported by Natta and coworkers.[7,17] There was no indication of the formation of benzene or cyclooctetraene in any of these experiments.

Monosubstituted Acetylenes.—As shown in the table, catalytic polymerization reactions occurred with a number of monosubstituted acetylenes. Linear and aromatic products were obtained, the type of reaction product depending mainly on the acetylene used. However, variations in co-catalyst composition produced variations in dimer/trimer ratios for linear oligomers of a given acetylene such as heptyne-1. When linear products were formed, polymerizatoin to tetramer and higher homologues was sometimes observed, *e.g.*, in the polymerization of butyne-1 (experiment 5), but in most cases, the product consisted predominently of dimers and trimers.

A large proportion of these experiments involved heptyne-1 as substrate. This monomer gave reaction products which could easily be separated and identified.[4] However, unlike the products formed using the nickel carbonyl type catalysts, part of the product formed with the present catalyst systems, was often hydrogenated.

A similar reaction pattern was observed for the various alkyl acetylenes tried, *i.e.*, butyne-1, pentyne-1, and heptyne-1. The products formed from heptyne-1, when nickel compounds were used as catalysts, consisted mainly of linear dimers, trimers, and tetramers described elsewhere.[4] The same types of products were obtained with the other alkylacetylenes.

With phenylacetylene, the trimeric products formed were always associated with a dark tar of indefinite structure. In all the runs on phenylacetylene, the isolable products were largely the 1,3,5- and 1,2,4-triphenylbenzenes, plus an unknown compound, containing a *trans* terminal double bond, which is probably the linear trimer of

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(16) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, *J. Am. Chem. Soc.*, **75**, 199 (1953); H. I. Schlesinger and H. C. Brown, U. S. Patent 2,461,661 (February 15, 1949).

(17) E. Lombardi and L. Guiffre, *Atti. accad. Nazl. Lincei, Rende. Classe Sci. Fis. Mat. Nat.* [8], **25**, 70 (1958).

phenylacetylene. These results are similar to those obtained when phenylacetylene is polymerized with nickeldiphosphine dicarbonyl catalysts,[2–5] with one important exception, *i.e.*, with the present catalyst systems, dimers were also formed.

Phenylacetylene is a more reactive monomer than the alkyl acetylenes. While monoalkylacetylenes go mainly to linear products when nickel co-catalysts are used, phenylacetylene undergoes, in the main, the aromatization reactions.

As shown in experiment 8 at least 4000 moles of phenylacetylene can be trimerized per mole of nickel co-catalyst. The maximum catalyst efficiency attainable in this type of reaction is undoubtedly much higher.

1,6-Heptadiyne, (experiment 9), reacted largely by dimerization. The over-all yield was relatively low. No high polymer formation was observed here. In contrast, 1,7-octadiyne, (experiment 9), reacted at both functionalities to give a rubbery, sponge-like high polymer. This material was insoluble in all solvents tried and so was not amenable to molecular weight determination. An infrared mull showed the presence of the usual 975 and 890-cm.$^{-1}$ bands found in dimers and trimers of monosubstituted alkyl acetylenes, as well as suggestions of aromatic structures and double bonds.[3–5] A sharp band at 2120 cm.$^{-1}$ was due to terminal $-C\equiv CH$ groups, either in the polymer or in absorbed unreacted monomer. The contrasting behavior of 1,7-octadiyne and 1,6-heptadiyne is noteworthy. A similar difference in the behavior of these two diynes was observed with diphosphine–nickel–dicarbonyl catalysts.[5] These differences must reflect greater difficulty in ring-closure reactions for the longer-chain diyne compounds.

Experiments with propargyl chloride showed this substrate does not polymerize in these reactions. It has recently been demonstrated in this laboratory that propargyl chloride reacts with borohydride to give a quantity of propyne stoichiometric with the amount of catalyst initially present.[18] Similarly, propiolic acid also failed to polymerize. This substrate also failed to polymerize in the presence of tetrakis(phosphorus trichloride)nickel.[19] The inertness of propiolic acid toward these catalysts is particularly striking when the extremely high reactivity of its alkyl esters in such reactions is considered.

A base such as sodium borohydride catalyzes the dimerization of ethyl propiolate,[20] in contrast to the trimerization to aromatic products found when the hydridic reducing agent–Group VIII metal compound co-catalyst system is used. Ethyl propiolate is readily trimerized to aromatic products, even by a particularly sluggish co-catalyst system of this general type. In the various experiments with ethyl propiolate using these catalyst systems, there was no hint of the formation of cyclooctatraene derivatives as were formed in polymerizations of this substrate with another type of complex nickel catalyst.[19] These experiments did not involve simple base-catalyzed reactions.[20]

Experiment 11 showed that the aminoacetylene, 3-diethylaminopropyne-1, oligomerizes to dimer and trimer under typical reaction conditions.

Experiment 12 showed that under typical polymerization conditions, propargyl alcohol reacts with almost explosive violence. Infrared analysis indicated that the major products were the trisubstituted benzenes, of which the 1,3,5-isomer constituted 65%, and the 1,2,4-compound 35%. In experiment 13, the major products appeared to be linear compounds, although aromatic products were also formed in smaller quantities. While these differences may reflect changes in experimental conditions, analysis of the products of the propargyl alcohol reactions was very difficult, either in the infrared or by means of mass spectroscopy.

Disubstituted Acetylenes.—Under typical reaction conditions, hexyne-3 polymerizes to a much smaller extent than do monoalkyl acetylenes. Mass spectrometry showed a very high dimer/trimer ratio of 3:1 as well as extents of product hydrogenation which were very similar to those obtained in comparable experiments with heptyne-1. In experiment 14, hexyne-3 was run at a pot temperature of 100°. A 15% yield of polymeric products was obtained. Infrared analysis indicated the presence of an hydrogenated linear dimer, probably a tetrasubstituted butadiene (formed by partial hydrogenation of dimer). Some hexaethylbenzene (aromatic trimer) may also have been formed. The scope of the catalytic reaction thus embraces disubstituted acetylenes. Diphenylacetylene did not polymerize at room temperature. However, when the reaction was run at 78° (experiment 15), a small quantity of a white crystalline solid was obtained. This melted at about 400° and had an infrared spectrum compatible with hexaphenylbenzene (m.p. 426[21]). Diiodoacetylene did not react to give identifiable products, but instead appeared to decompose under the usual conditions of reaction, to give a considerable quantity of iodine.

Copolymerization of Acetylenes.—The scope of these reactions was also extended to copolymers (*cf.*, of heptyne-1 and pentyne-1). Reaction proceeded smoothly and in good yield. The presence of the copolymers, as well as of the heptyne and pentyne homodimers and homotrimers, was proved by mass spectrometry. The copolymers formed included trimers containing two heptyne residues and one pentyne residue, tetramers containing two heptyne residues, and tetramers containing three

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[18] Dr. J. S. Noland, personal communication.

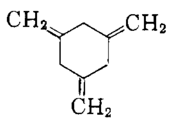
[19] J. R. Leto and M. F. Leto, *J. Am. Chem. Soc.*, **83**, 2944 (1961).

[20] Mrs. M. F. Leto, personal communication.

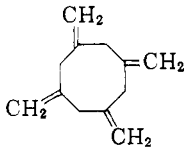
[21] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

heptyne and one pentyne residue. Heptyne dimer accounted for 23% of the product, pentyne trimer for 17%, pentyne tetramer for 1%, heptyne trimer for 11%, while the copolymers contributed as follows: $2C_71C_5$ trimer, 20%; $2C_52C_7$ tetramer, 3%; $3C_71C_5$ tetramer, 2%.

Polymerization of Olefins and Diolefins.—These catalyst systems have also been found capable of polymerizing olefins and diolefins. High molecular weight polyethylene has been obtained from ethylene. Butadiene yields oligomers such as trimer, tetramer, etc., as well as dimer and high polymer. Allene yields mainly trimer and tetramer, *i.e.*, trimethylenecyclohexanes and tetramethylenecyclooctanes, such as



and



These have infrared spectra almost identical with those recently reported for such compounds by Benson and Lindsey.[22]

Hydrogenation of Linear Polymers during the Course of the Catalytic Reactions.—In typical reactions of heptyne-1 and in other experiments where linear polymers were formed, these were found to be hydrogenated to various extents. Typically, dimers formed from heptyne-1 might be 90% hydrogenated with one or more moles of hydrogen. The source of the hydrogen appears to be the reducing agent used. The extent of hydrogenation depends on (a) the amount of, *e.g.*, borohydride present, smaller quantities giving less hydrogenation, (b) the extent of polymerization, the yields of hydrogenated products sometimes appearing to be greater at lower over-all extents of polymerization, *i.e.*, when more reducing agent is available to fewer polymer molecules, and (c) more specific factors, such as the transition metal compound used.

In typical heptyne-1 polymerizations, dimer and tetramer are hydrogenated to a considerably greater extent than trimer. An obvious possibility —that trimer (which usually constitutes well over half of the reaction product) is largely aromatic in nature and hence is hydrogenation resistant—can be ruled out in most cases because of the lack of aromatic bands in the infrared spectra of the products. A possible explanation for the anomalous behavior of trimer may be that the particular trimer isomers formed are sterically hindered with respect to hydrogenation (and possibly with respect to further reaction on the catalyst fragment to give tetramer, etc., as well). The experimental facts may be accommodated by the following formulation: almost all the isomeric dimers formed from heptyne-1 in these reactions may be hydrogenated (*cf.*, high extent of hydrogenation of dimer). Of the trimer formed, some isomers may be resistant to further addition of monomer and/or hydrogen. Dissociation of these species from the catalyst fragments therefore results in (unhydrogenated) trimer. On the other hand, those trimer isomers which can more easily add monomer (as well as hydrogen), do so to yield tetramers, etc., the latter polymers having on the average a higher extent of hydrogenation than the trimers.

The hydrogenation of linear reaction products occurs with pentyne-1 and probably with other monosubstituted acetylenes as well.

It was established by separate experiments that hydrogenation of the reaction products in these systems need not occur during the course of a polymer forming reaction, but may occur on the already elaborated polymer molecule, instead. This suggests that it should be possible to find reaction conditions such that little or no product hydrogenation will occur.

Small extents of dehydrogenation of reaction products were also observed in the mass spectra of many samples. While it has not been proved that dehydrogenation could not occur in the mass spectrometer, the available evidence suggests this reaction also occurred in the course of the polymerizations.

The behavior of pentyne-1 polymers is strikingly different from that of those derived from heptyne-1 with respect to dehydrogenation. Here, mass spectra revealed that almost all the tetramer formed was dehydrogenated to the extent of 1 mole of hydrogen per mole of tetramer.

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[22] R. E. Benson and R. V. Lindsey, *J. Am. Chem. Soc.*, **81**, 4247, 4250 (1959).