

cyclohexanone is reported to boil at 78–79° (11 mm.); n_D^{20} 1.4662; 2,4-dinitrophenylhydrazone, m.p. 145–146°.³⁰

Comparative Metalations of Triphenylmethane by Lithium-Biphenyl and by Lithium-Phenylcyclohexene.³¹—The relative kinetic basicities of the lithium adducts of biphenyl and of 1-phenylcyclohexene were compared by allowing each to react individually with triphenylmethane under identical conditions. Thus 0.060 mole of the hydrocarbon (either pure biphenyl or 1-phenylcyclohexene) was allowed to react with 0.050 g. atom of lithium pieces in 30 ml. of tetrahydrofuran at $28 \pm 1^\circ$. After 2 hr. of stirring the lithium had dissolved to form a blue-green (biphenyl) or red (phenylcyclohexene) solution. Then 15.30 g. (0.0625 mole) of triphenylmethane, dissolved in 120 ml. of tetrahydrofuran, was added in one portion. The solution was stirred at the same temperature for 16 hr. and then carbonated in the usual way. Customary work-up gave the following yields of triphenylacetic acid: (a) from biphenyl: 2.76 g. of acid (19.2%); m.p. 261–264°; neut. equiv. 289. (b) from phenylcyclohexene: 6.11 g. of acid (42.4%); m.p. 263–265°; neut. equiv. 290.

(30) A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1842 (1941).

(31) The following experiment was performed by Miss Deborah Drew, NSF undergraduate research assistant during the summer of 1961. The authors gratefully acknowledge her assistance in this and related studies.

Derivatives of Triphenylmethylithium.—Non-acidic derivatives of trityllithium, prepared by the lithium-biphenyl method, were 1,1,1-triphenylethane (treatment with methyl iodide), (80%) and 3,3,3-triphenylpropanol (treatment with ethylene iodide) (89%). In these reactions it was found convenient to steam distil the hydrolyzed reaction mixture to remove the biphenyl and hydrobiphenyls. The residue could then be purified readily by filtration and recrystallization of the collected solid.

Determination of "Soluble" Lithium-Biphenyl Ratios.—Under nitrogen 3.70 g. (0.024 mole) of biphenyl and 0.50 g. (0.072 g.-atom) of lithium in 55 ml. of tetrahydrofuran were stirred in a calibrated flask to form the blue-green solution. Aliquots were withdrawn periodically, hydrolyzed, and titrated with standard acid. After 16 hr. at room temperature the "soluble" lithium attained a constancy of 2.5 ± 0.05 equivalents: 1.0 equivalent of biphenyl.

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

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The scope of a new catalytic reaction for the polymerization of acetylenic compounds was investigated. The catalyst system consists of a Group VIII metal compound plus a hydridic reducing agent. Polymerization was achieved with six out of seven of the Group VIII metals tried, iron compounds failing to cocatalyze these reactions. No metals outside of Group VIII were cocatalysts. Silane and simple alkali hydrides function as reducing agent cocatalysts, but are far less effective than the alkali boro and aluminohydrides. Nonhydridic reducing agents, even very powerful ones such as hydrazine, show little or no cocatalytic action.

The first paper in this series¹ described a new catalyst system for the polymerization of acetylenic compounds. This system consists of a compound of nickel plus an hydridic reducing agent. A typical example is nickel chloride plus sodium borohydride.

We now report extension of the scope of this reaction. The effects of other transition metal compounds were studied. In addition, a number of other variables such as different reducing agent cocatalysts were also investigated. A number of fundamental aspects of these reactions were also examined.

Experimental

Materials.—The various inorganic salts used were all either reagent grade or the nearest readily available equivalents. Solvents were reagent grade or equivalent. The reducing agents, except for the rather pure complex hydrides (as described in the first paper in this series¹) were probably all contaminated by small quantities of oxidation products.

The acetylenes used in these experiments were in most cases obtained from The Farchan Chemical Company and were used as received.

Bis(tri-*n*-butylphosphine)palladium Dichloride was prepared by mixing 1.78 g. of palladous chloride and 8.5 g. of tri-*n*-butylphosphine in 50 ml. of water. After storage for a couple of weeks in a freezer, the mixture deposited brilliant yellow plates. These were recrystallized from ethanol and dried, m.p. 66° in exact agreement with Mann.²

Bis(triphenylphosphine)platinum Dichloride.—Platinum chloride (2.66 g.) was dissolved in concentrated, air-free hydrochloric acid. The system was kept air-free with a stream of prepurified nitrogen. The pH was brought up to 8 with potassium hydroxide. The volume was made up to 50 ml. with distilled water. Triphenylphosphine (5.2 g.) in 50 ml. of hot ethanol was added. A yellow precipitate was formed immediately, and the original deep brown to pink color of the solution was discharged. The mixture was stirred magnetically under nitrogen for 7 hr. It was then filtered, washed extensively with water, ethanol, and finally with dry ethyl ether, and then dried. The product was a fine white powder with a slight grayish tinge, m.p. 290–295° (lit.³ value 310°).

(2) F. G. Mann, *J. Chem. Soc.*, 1549 (1954).

(3) K. A. Jensen, *Z. anorg. Chem.*, **229**, 225 (1936).

(1) L. B. Luttinger, *J. Org. Chem.*, **27**, 1591 (1962).

TABLE I
 EFFECT OF CHELATION^a

Experiment number	Acetylene	Molarity of acetylene	Molarity of reducing agent	Transition metal compound and molarity	Solvent	Yield, %
120	Heptyne-1	1.51	0.26 NaBH ₄	0.016 Nickel chloride chelate of (CHE) ₂ PCH ₂ CH ₂ P(CNE) ₂	EtOH	43
121	Heptyne-1	2.88	0.66 NaBH ₄	0.09 (CNE) ₂ PCH ₂ CH ₂ P(CNE) ₂ plus 0.028 corresponding nickel chloride chelate	3:1 EtOH-CH ₃ CN	0
122	Ethyl propiolate	1.12	0.17 NaBH ₄	0.021 (CNE) ₂ PCH ₂ CH ₂ P(CNE) ₂ plus 0.0076 corresponding nickel chloride chelate	CH ₃ CN	47

^a All reactions run at room temperature.

All experimental details are the same as are given in paper I. Description of all products, their isolation, identification, etc., are given in ref. 15 of paper I.

Effect of Various Simple Phosphine Ligands.—The initial experiments in this series were carried out using nickeldiphosphine dihalides, (R₃P)₂NiX₂, as the transition metal components of the catalyst system. It was found that the tris(2-cyanoethyl)phosphine complex is more effective than either the tri-*n*-butylphosphine complex or the triphenylphosphine complex. The later two appear to be about equally active.

Effect of Chelation.—The effect of chelation of the transition metal is shown in Table I. Experiment 120 (substrate heptyne-1) shows the effect of a chelating ligand, (CNE)₂-PCH₂CH₂P(CNE)₂, on the ability of a transition metal cocatalyst to enter into the catalytic reaction.⁴ Such a chelated nickel atom is very tightly bound, and would be expected to be rather less active catalytically than the nickel atoms in analogous nonchelate complexes such as [(CNE)₃-P]₂NiCl₂. The slight solubility of this compound in the reaction medium resulted in a mild, comparatively slow reaction. No exotherm was observed in experiment 120; however, the yield and the products formed in this experiment were similar to those in comparable experiments with [(CNE)₃-P]₂NiCl₂. The effect of an excess of chelating agent, (CN)₂-PCH₂CH₂P(CNE)₂, is shown in experiment 121. Here, the formation of a second chelate ring around the nickel atom may be possible, and, in any case, the tendency of the first chelate ring to dissociate is suppressed. No polymerization of heptyne-1 occurred in this experiment. Presumably, the nickel atom in the catalytically active species, or in the precursor, is too tightly bound in chelate rings to permit reaction to occur. Experiment 122 shows that with a more active acetylene (ethyl propiolate) aromatization reactions will occur even in the presence of excess chelating agent.

Effect of the Anion in Phosphine Complexes.—Variation among the anions Cl⁻, Br⁻, CNS⁻ in phosphine complexes produced little change in the polymerization of heptyne-1.

Comparison of Cocatalytic Behavior of Nickel Chloride with That of the Corresponding Tris(2-cyanoethyl)phosphine Complex.—It was found that the complex [P(CH₂-CH₂CN)₃]₂NiCl₂ is a more effective cocatalyst than is nickel chloride itself under identical conditions. Greater catalytic effectiveness is shown by the greater product yield obtained.

Comparison of Cobalt and Nickel Salts. Aromatization of Heptyne-1 by Cobalt Salts.—A series of experiments on heptyne-1, utilizing a number of inorganic salts of nickel and cobalt, and carried out under identical conditions, established the following: (a) Cobalt and nickel chloride give the same product yields, but of the corresponding nitrates, the nickel salt is about 20% less effective. Nickel fluoride is about 25% less effective, with respect to product yield, than is the corresponding cobalt salt. It appears that cobalt

salts may be slightly more active catalytically toward heptyne-1 than the corresponding nickel compounds, but the differences are not very marked. Similar results were observed for acetylene itself. (b) As shown earlier,¹ the major products from the polymerization of heptyne-1 were usually linear polymers. However, in a number of cases aromatic products were also formed in substantial yields. The aromatic products consisted of the 1,3,5- and 1,2,4-triamylbenzenes. Appreciable yields of aromatic compounds from heptyne-1 occurred only when cobalt salts were used as cocatalysts. The products from one such experiment were analyzed by vapor phase chromatography and compared with a sample of mixed aromatic and linear reaction products from the polymerization of heptyne-1 with a nickel diphosphine-dicarbonyl catalyst (the presence of both linear and aromatic polymers in the latter sample had been established previously). Comparison of the vapor phase chromatography data of these two samples indicated that the product obtained with the cobalt catalyst contained 60% aromatic and about 20% linear polymers, with the balance consisting of unidentified compounds. Infrared spectroscopy of the products from this reaction gave qualitative agreement with this result.

In these experiments with cobalt salts, not only was aromatic trimer formed, but aromatization appeared to take place largely at the expense of dimer. Mass spectrometry showed that, as expected, relatively less trimer was hydrogenated when this fraction contained aromatic products than when only linear products were formed.

Comparison of the Effects of Anions in Inorganic Salts of Nickel and Cobalt.—Considering first the series of nickel salts, it was found that the effects of varying the anions are not large. Chloride and bromide gave about equal product yields, and these yields are about 20–25% greater than those obtained with the nitrate, the cyanide, and the iodide.

A number of other results due to specific anions were also noted. Thus, with nickel iodide, a larger quantity of tetramer was formed than when the corresponding fluoride or chloride were used. Nickel cyanide gave rise to relatively more dimer as compared to trimer than most of the other nickel and cobalt salts tested in this series of experiments.

Under the conditions employed in these experiments, the chlorides and nitrates were completely soluble in the solvent, while nickel bromide, nickel iodide, and nickel cyanide were not. Therefore, solubility differences alone cannot account for the variations in products and yields obtained with these salts.

With regard to the cobaltous salts, it was found that substantially the same yields were obtained with both the nitrate and the chloride. It was also found that cobalt fluoride is somewhat less effective than the chloride and nitrate.

Effect of Various Group VIII Transition Metal Compounds.—The nature of the products obtained from a given monomer, such as heptyne-1, has been found to depend on various factors, among which is the particular group VIII transition metal compound used. Table II summarizes the results obtained with a variety of such compounds, using heptyne-1 as substrate.

(4) Purified ethylene bis[(2-cyanoethyl)phosphine] was supplied by Dr. M. Grayson of this laboratory [see M. Grayson, P. T. Keough and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959)]. The chelate of this compound with nickel dichloride was supplied by Dr. L. S. Meriwether.

TABLE II
 EFFECT OF VARIOUS GROUP VIII TRANSITION METALS ON THE POLYMERIZATION OF HEPTYNE-1^a

Experiment number	Molarity of heptyne-1	Molarity of reducing agent	Transition metal compound and molarity	Solvent	Mass spec. ^b			Approximate yield, %
					A	B	C	
117	1.35	0.29 NaBH ₄	0.0094 PdCl ₂ (<i>n</i> -Bu ₃ P)	EtOH	42	48	...	25
118	1.71	0.58 NaBH ₄	0.076 Co(NO ₂) ₂ ·6H ₂ O	EtOH	13	86	1	60
119	1.50	0.30 NaBH ₄	0.014 RuCl ₃	CH ₃ CN	47	36	1	12
130	1.43	0.307 NaBH ₄	0.019 PtCl ₄ ·8H ₂ O	EtOH	54	44	2.5	35
131	1.43	0.307 NaBH ₄	0.03 OsCl ₃	EtOH	55	43	2.0	17
132	1.43	0.307 NaBH ₄	0.052 PdCl ₂	EtOH	62	36	2.0	8.6

^a All experiments carried out at room temperature. ^b A = dimer; B = trimer; C = tetramer.

In some cases [polymerizations with bis(tributylphosphine)palladium dichloride, with inorganic salts of ruthenium and cobalt (experiments 117, 118, 119), and in some cases, with nickel salts as well], the formation of higher molecular weight materials was indicated by (a) the very dark color of the products, suggesting longer conjugated chains, (b) the high viscosity of the products, which were sometimes pitch-like in consistency as compared with the far more mobile oils usually obtained with other catalysts, and (c) the fact that the vapor pressures of the samples analyzed by the mass spectrometer were considerably lower than those from other heptyne-1 polymerizations. Other effects due to the individual transition metals are discussed below.

Experiment 130 shows that platinum chloride is an effective cocatalyst for heptyne-1 polymerizations. A noteworthy feature of this reaction was the high dimer-trimer ratio of the polymers formed. This ratio was greater than unity (compare with paper I in this series¹). In other experiments with heptyne-1, only experiments 131, 132, and 119, in which osmium trichloride, palladous chloride, and ruthenium chloride, respectively, were the transition metal compound cocatalysts, showed heptyne dimer-trimer ratios greater than unity (a similar dimer-trimer ratio was also observed in an experiment in which diborane was used as reducing agent; see below). Experiment 131 shows that osmium trichloride has a somewhat lower order of catalytic activity in the heptyne-1 polymerization than nickel or platinum chlorides. A relatively large extent (5%) of dehydrogenation of trimer occurred in this experiment.

The results just described suggest that the formation of relatively larger quantities of dimer as compared with trimer is due to a quality common to the heavier metals in Group VIII, but not shared by the lighter ones (cobalt, nickel). This factor may be the greater size of the transition metal cation in those cases where larger quantities of dimer were formed or may be associated with the geometry of their reacting orbitals, particularly the greater ability of these orbitals in the heavier metals to penetrate into acetylenic ligands. Thus, it has been pointed out on theoretical grounds,⁵ as well as shown experimentally,⁶⁻⁹ that the heavier transition metals in the last transition series should and do form more stable organometallic compounds than the corresponding lighter elements in the rows above them.

Comparison of experiments 117 and 132 indicates that palladous chloride is a poorer catalyst for the polymerization of heptyne-1 than is bis(tri-*n*-butylphosphine)palladium dichloride. This is analogous to the results found with the corresponding nickel compounds. The catalytic activity of these two palladous compounds is lower than that of the corresponding nickel compounds.

Iron Compounds.—Experiments carried out under standard conditions showed that ferric chloride is not a cocatalyst for these reactions. It was further found that neither ferrous

chloride nor the ferrous *o*-phenanthroline complex are catalytically active even at a temperature of 75°. The reason for the failure of iron compounds in this reaction is not clear but may be related to the fact that iron salts are the most difficult of all the salts of Group VIII metals to reduce to the metallic state.

Effect of the Valence State of the Transition Metal.—It was found that cobaltous and cobaltic fluoride were almost equally effective cocatalysts in these reactions. Presumably, both salts are carried down to the same valence state in the course of the reactions.

Compounds of Transition Metals from Groups Other Than Group VIII as Cocatalysts.—Experiments performed under otherwise typical conditions showed that zinc chloride, manganous chloride, mercurous chloride, stannous chloride, mercuric chloride, titanium and zirconium tetrachlorides, silver nitrate, tungsten trioxide, sodium tungstate, sodium chromate, and chromic chloride will not function as transition metal cocatalysts for the polymerization of heptyne-1 and other monosubstituted acetylenes under otherwise typical reaction conditions.

These results indicate that polymerization of monosubstituted acetylenes by the catalyst systems under investigation is confined to the Group VIII metal compounds. It is noteworthy that in a number of these experiments catalysis failed to occur even upon extended heating at 75–80°.

Catalytic Effects of Various Reducing Agents. Potassium and Lithium Borohydrides and Lithium Aluminum Hydride.—It was found that potassium and lithium borohydrides are about as effective cocatalysts for these polymerizations as the sodium salt. In suitable solvents—*e.g.*, diglyme—lithium aluminum hydride is equally effective.

Simple Hydrides.—Lithium hydride was found to be ineffective as a cocatalyst for the polymerization of heptyne-1 and propargyl alcohol even at temperatures up to 103°. However, at still more elevated pot temperatures of the order of 150–160°, polymerization of heptyne-1 did occur. The proportion of trimer and tetramer was greater than that usually obtained from typical runs on this substrate using sodium borohydride as cocatalyst at room temperature. This may simply reflect dimer loss by evaporation in the course of this experiment. The reaction was found to be truly cocatalytic in the sense of this paper—*i.e.*, a transition metal salt such as nickel chloride was necessary in order to afford a significant extent of polymerization, even at this high temperature.

It was found that sodium hydride was about as effective as the lithium compound in these reactions.

Calcium hydride cannot serve as a cocatalyst for the polymerization of heptyne-1, even at a pot temperature of 160°. A more reactive acetylene, propargyl alcohol, did react at pot temperatures of the order of 140° to yield what appeared to be a mixture of 1,3,5- and 1,2,4-trisubstituted aromatic products. In control experiments carried out at the same temperature, no reaction occurred unless both components of the cocatalyst couple were present. These experiments show that calcium hydride possesses a feeble cocatalytic activity, weaker than that of sodium and lithium hydrides.

(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(6) L. B. Luttinger, unpublished results.

(7) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

(8) G. Calvin and G. E. Coates, *Chem. Ind.* (London), 160 (1958).

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

High Temperature Polymerization of Phenylacetylene.—At a pot temperature of 135° and in the presence of an active Group VIII metal compound, phenylacetylene is rapidly polymerized, even when a reducing compound cocatalyst has not been added. A typical phenylacetylene product mixture is formed, containing 1,3,5- and 1,2,4-triphenylbenzenes. No reaction occurs, even at considerably higher temperatures, unless the Group VIII cocatalyst component is present. In such systems, phenylacetylene itself may act to reduce the transition metal compound, and thus initiate polymerization. So far, this is the only case found of effective cocatalysis by a nonhydridic reducing agent, but it could almost certainly be extended at appropriately high temperatures to other acetylenic compounds as well. The experiments on heptyne-1 referred to earlier show that under roughly similar conditions, heptyne-1 cannot act as a catalytically effective reducing agent.

Silane(s).—Silane, as well as smaller quantities of its higher homologues, $\text{Si}_n\text{H}_{(2n+2)}$, was generated by the reaction of magnesium silicide with phosphoric acid in a separate vessel, effluent gas from which was led into the flask used for the attempted catalytic reactions. It was easily demonstrated (by reaction with air) that a silane-rich stream of gas could be generated continuously for hours by this means.

It was found that nickel salts did not act as cocatalysts with silane. The silane was not able to reduce the nickel salt to the catalytically active form, even at elevated temperatures. However, palladous chloride and nitrate were found to polymerize heptyne-1 in the presence of silanes in the temperature range 50–125°, depending on experimental conditions. Heptyne dimers and trimers were formed in small yields in these reactions, and a relatively small proportion of the products, particularly dimer, was hydrogenated. An unusually large extent of product dehydrogenation (10% of the dimer and 18% of the trimer) occurred in one of these experiments. These features may be consequences of the elevated reaction temperature, the use of a palladium cocatalyst, the weak reducing powers of silanes, and possibly of the low concentration of the latter in these systems as well.

Diborane.—Experiments with diborane indicated that this compound is an effective cocatalyst for heptyne-1 polymerization. A close relationship exists between this reagent and the borohydrides. It is of interest that the heptyne oligomers obtained from this reaction showed a dimer-trimer ratio greater than unity. Diborane was the only reducing agent tried that produced this effect with a metal from the first row of Group VIII as cocatalyst.

Hypophosphorous Acid.—It was found that, even at 80°, hypophosphorous acid is not an effective cocatalyst for the polymerization of heptyne-1. Presumably, a much stronger hydridic reducing agent is needed in order to afford reaction.

Nonhydridic Reducing Agents.—Formamidinesulfonic acid was found to be a feeble cocatalyst for the polymerization of monosubstituted acetylenes, giving rise to low yields of polymers at temperatures of the order of 70°. Sodium thiosulfate showed a cocatalytic activity similar to that of formamidinesulfonic acid, but was an even weaker cocatalyst. Hydrazine was found to be without cocatalytic properties, even at 70° and under a variety of experimental conditions.

Effect of Solvent on Reactions of Monosubstituted Acetylenes.—Most of the initial experiments were carried out in acetonitrile. Cyclohexane itself did not support reaction, but on the addition of 25% ethanol, catalysis occurred. These results suggest that the failure of reaction in an inert solvent is a consequence of the almost complete insolubility of one of the catalyst components (in this case the sodium borohydride) in the system. The results further suggest that the catalytic reaction is essentially homogeneous, proceeding to no measurable extent on the surface of undissolved catalyst.

Of all solvents tried (on heptyne-1), ethanol appeared to be generally the most favorable. Reactions of this solvent

tended to be more rapid and exothermic than those run in acetonitrile under similar conditions. Water was also found to be an adequate solvent for certain of these reactions. Thus an almost explosive reaction was obtained with propargyl alcohol, which is completely miscible with water. (On the other hand, acetylene is relatively insoluble in water. While polymerization of acetylene did occur in water, the yield was considerably poorer than that obtained in less polar solvents.) One of the remarkable features of the catalyst system under discussion is its effectiveness in solvents such as water. Other catalyst systems showing a formal similarity (such as the Ziegler-Natta catalyst systems) are often rendered totally inactive, even by traces of moisture. Diglyme as well as 17% diglyme-83% cyclohexane was also found to support reaction. The employment of solvents such as diglyme permits the use of certain very reactive hydridic reducing agents—e.g., lithium aluminum hydride.

Effect of Varying the Cocatalyst Concentrations and Ratios.—An experiment run in acetonitrile, using 0.12 *M* sodium borohydride, but in all other respects typical of runs described above, afforded little polymerization of heptyne-1. This concentration of borohydride represents, then, a rough lower limit of reducing agent cocatalyst concentration in the heptyne-1 polymerization reaction (lower concentrations of borohydride suffice to bring about the polymerization of the more reactive phenylacetylene). In this experiment, all the borohydride was in solution from the start, and the system was homogeneous throughout.

With regard to the concentration of transition metal compound required for these catalyses, it was found that, under otherwise typical conditions, rapid polymerization of heptyne-1 occurs when the solution is about 0.009 *M* in this component. Even smaller concentrations of transition metal cocatalyst suffice, e.g., in propargyl alcohol polymerizations.

It is of interest to compare this experiment with the one mentioned earlier, in which the concentrations of reducing agent cocatalyst were lowered to the point of little reaction. It is evident that a considerably smaller molar quantity of transition metal compound cocatalyst than reducing agent is necessary in order to affect polymerization.

Effect of Oxygen on Polymerization.—When an oxygen stream was substituted for nitrogen in a typical heptyne-1 experiment, a very large exotherm occurred immediately on mixing the reactants and the polymerization appeared to go more rapidly than in the absence of oxygen. Otherwise—(i.e., with respect to yield, product ratio, etc.)—results were very similar to those obtained in the absence of oxygen.

Effect of Reaction Temperature.—It was found that at 80°, relatively little hydrogenation of the product obtained from heptyne-1 occurred. This may mean that at such temperatures the polymers are stripped off the nickel atom before hydrogenation can take place. It may also suggest that at such temperatures hydrogen is lost to the system before hydrogenation can occur.

It was also found that the polymerization of heptyne-1 proceeds normally at 0°.

Lithium Aluminum Deuteride as Reducing Agent. Deuterium-containing Heptyne Polymers.—Use of lithium aluminum deuteride as reducing agent afforded heptyne polymers which were labeled with deuterium. Mass spectrometry of such reaction products showed that over 80% of the dimer and over 20% of the trimer had been deuterated (the true values may have been higher—i.e., mass spectroscopy cannot distinguish between products containing two additional deuterium atoms and those containing four additional hydrogen atoms). Infrared spectroscopy showed that, besides the double bond C—H stretch at about 3100 cm^{-1} , there was present a small band at about 2200 cm^{-1} which was due to double bond C—D. It was estimated that about 20% of the double bonds in the reaction product were deuterated in this reaction. These results should be com-

pared with the 50% over-all monodeuteration of products indicated by mass spectrometry. This work suggests that the reaction involves transfer of a hydride ion to the acetylenic substrate, presumably *via* the transition metal cocatalyst. A high dimer-trimer ratio was obtained in this experiment. This may, in part, be due to the use of a deuterated cocatalyst (a similar experiment, in which lithium aluminum hydride in diglyme was used, gave a lower dimer-trimer ratio).

Mechanism.—While it is not at present possible to give a detailed account of the mechanism of these reactions, the following is proposed as a working hypothesis, which is at least not in disagreement with the experimental evidence.

It is assumed that, at the start of the reaction, the group VIII transition metal ion is reduced to a lower valence state by the hydridic reducing agent, at the same time accepting a hydride ion from the latter, and so forming a transition metal hydride. In fact, it is suspected that the restriction of these catalyses to group VIII of the periodic table reflects the relatively great tendency on the part of the elements in this

group to form hydrides. Similarly, restriction of the effective cocatalysts to hydridic reducing agents indicates that it is the transfer of hydride ion from reducing agent to metal atom which is characteristic of the most favorable reaction paths.

The reduced transition metal species then forms complexes with acetylenes. In these complexes, the metal atom may act as a hydride transfer agent, thus permitting transfer of hydrogen from one acetylenic substrate molecule to another, two or more of which being in some way associated or complexed with the metal atom in question.

The complexes formed are probably π complexes—*i.e.*, they involve double bonding between the metal atom and the acetylenic triple bond itself.⁹ The transition state for the catalytic reaction probably involves a structure very similar to that of a π complex between a metal atom and one or more acetylenic molecules, *via* such triple bonds. In view of the limited information available it is probably not justifiable to carry speculation as to the details of the reaction mechanism any further at this time.

Pyrolysis of Cyanoformates. A New Synthesis of Nitriles

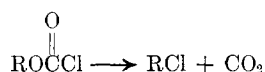
WILLIAM A. SHEPPARD

Contribution No. 790 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

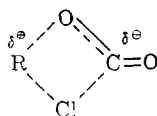
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The gas phase decomposition of alkyl cyanoformates, ROCCN, where R is CH₃, C₆H₅CH₂, and NCCH₂, gives carbon dioxide and the corresponding nitrile. In contrast to the relatively mild conditions employed in chloroformate decomposition, this reaction requires temperatures in the range of 700 to 800°. Ethyl cyanoformate decomposes above 400° to ethylene, hydrogen cyanide, and carbon dioxide. Possible mechanisms for these decompositions are considered.

The thermal decomposition of alkyl chloroformates leads to alkyl chlorides and carbon dioxide.¹



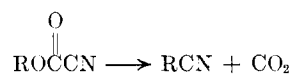
Chloroformates from primary alcohols generally decompose at a convenient rate in a temperature range of 150 to 250°, whereas those from tertiary alcohols are often too unstable for isolation at room temperature. At elevated temperatures, depending on the structure of the alkyl group, the competing elimination reaction can be significant. Recently, Lewis and co-workers^{1d} reported extensive kinetic, optical activity, and isotopic studies, including an examination of the effect of structure of the alkyl group, and concluded that the chloroformate decomposition substitution reaction was best explained by a polar transition state of the type:



(1) (a) A. R. Choppin, H. A. Frediani, and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **61**, 3176 (1939); A. R. Choppin and G. F. Kirby, Jr., *ibid.*, **62**, 1592 (1940); A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948); (b) S. T. Bowden, *J. Chem. Soc.*, 310 (1939); (c) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955); (d) E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1955 and 1961 (1961); E. S. Lewis, W. C. Herndon, and D. C. Duffey, *ibid.*, 1959.

and that the elimination reaction occurred by a polar mechanism.

As a new synthetic route to nitriles, the pyrolysis of cyanoformates appeared attractive. Methyl cyanoformate, prepared from methyl chloroformate



and sodium cyanide,² was passed through a heated tube at reduced pressure. However, it was found that no reaction occurred in the 200–300° region that is normal for decomposition of chloroformates, and a temperature of 700° was required to promote loss of carbon dioxide and formation of acetonitrile in a yield of 30 to 40%. Ethyl cyanoformate partly decomposed at 400° to ethylene, hydrogen cyanide, and carbon dioxide and no propionitrile was detected: complete decomposition occurred at 700°.

In order to explore the generality of this decomposition reaction, two new cyanoformates, benzyl and cyanomethyl, were prepared. Benzyl cyanoformate decomposed smoothly at 700° to benzyl cyanide in 50% yield. The conversion of cyanoformate to nitrile was higher for benzyl than for methyl but was also accompanied by an increase of by-products. Cyanomethyl cyanofor-

(2) W. Gluud, W. Nusler, and K. Keller, German Patent 592,539 (1934), *Chem. Abstr.*, **28**, 3417 (1934).