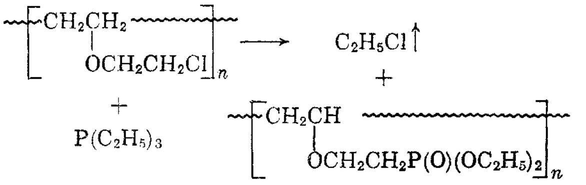
oration of the ethyl ether from the upper layer left a viscous oil and some salt. This was discarded. Removal of the volatiles from the lower layer left 74.5 g. of a soft, tacky, yellow polymer. This product was dissolved in 200 ml. (194 g., 1.16 moles) of triethyl phosphite and the mixture refluxed. Nitrogen was slowly bubbled into the solution and the gaseous stream passed through a Dry Ice–trichloroethylene trap. Refluxing was continued for 1 week until no further ethyl chloride evolved:



(b) *Isolation.* When 25.1 g. of the reaction mixture was heated *in vacuo* (1 hr. at 160° finally) 14.0 g. of polymer was recovered (96%). It still had the odor of triethyl phosphite and therefore the following isolation method was employed. A 44.5-g. portion of the reaction mixture was mixed with 100 ml. of water. The cloudy dispersion of triethyl phosphite in water clarified upon the addition of 5 drops of concd. hydrochloric acid. After standing for 24 hr. to ensure complete hydrolysis of the triethyl phosphite, the solution was extracted with two portions of dichloromethane, the extract dried, and the solvent evaporated. The residue, 23.7 g., (90%) was an orange, slightly mobile oil at room temperature and was quite tacky. It dissolved readily in cold water but precipitated as a gum above 40°. Upon cooling below 40° the gum redissolved.

STAMFORD, CONN.

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

The Polymerization of Acetylenes by Nickel-Carbonyl-Phosphine Complexes. I. Scope of the Reaction[1a]

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The polymerization of thirty-five different mono- and disubstituted acetylenes with dicarbonylbis(triphenylphosphine)-nickel [$Ni(CO)_2(Ph_3P)_2$] catalyst in an inert solvent at reflux has been attempted. Primarily aromatic products were obtained from monosubstituted acetylenes with lower alkyl, aryl, vinyl, $HOCH_2$—, $C_2H_5O_2C$—, R—CO—, and R—O— substituents; monosubstituted acetylenes with higher alkyl, cyclohexyl, $HOCH_2CH_2$—, CH_3—CH(OH)—, $(CH_3)_2C(OH)$—, 1-hydroxycyclohexyl, and $(C_2H_5)_2$ NCH_2—substituents yielded linear low polymers. Unreactive were most disubstituted acetylenes, disubstituted conjugated diacetylenes, and monosubstituted acetylenes with *tert*-butyl-, HO_2C—, amide, nitrile, and halogen substituents.

The trimerization of acetylenes to aromatic compounds in the presence of nickel-carbonyl-phosphine complexes was discovered by Reppe and Schweckendiek.[1b] They obtained from the reaction of acetylene with $Ni(CO)_2(Ph_3P)_2$ ($Ph = C_6H_5$) in acetonitrile a product consisting of 88% benzene and 12% styrene. With the same catalyst in refluxing benzene, propargyl alcohol gave a quantitative yield of 1,2,4- and 1,3,5-trimethylolbenzene, but 2-butyne-1,4-diol failed to aromatize, suggesting that at least one acetylenic hydrogen must be present in the monomer. Rose and Statham[2] reported the isolation of only 1,2,4-triphenylbenzene and only 1,3,5-tris(α-hydroxybenzyl)benzene from the trimerization of phenylacetylene and phenylethynylcarbinol, respectively, with the same catalyst. These authors failed to isolate products from 3-methyl-1-butyne-3-ol, 3-diethylamino-1-butyne, benzoylacetylene and phenylpropiolic acid. However, a U. S. patent issued to McKeever and Van Hook[3] describes the preparation of tris(1-methyl-1-hydroxyethyl)benzene and tris(isopropenyl)benzene from 3-methyl-1-butyne-3-ol and isopropenylacetylene, respectively, using $Ni(CO)_3(Ph_3P)$, $Ni(CO)_2(Ph_3P)_2$ or $Ni(CO)_2(Ph_3As)_2$ as catalysts. In another U. S. patent Kleinschmidt[4] describes the preparation of hexamethylolbenzene from 2-butyne-1,4-diol using $Ni(CO)_2(Ph_3P)_2$ as catalyst, and more recent patents describe the formation of 1,2,4-trivinylbenzene from vinylacetylene,[5] hexakis(trifluoromethyl)benzene from bis(trifluoromethyl)acetylene[6] and of *o*-divinylbenzene from the copolymerization of acetylene and divinylacetylene.[7] Sauer and Cairns,[8] in attempting to test the possible formation of a cyclobutadiene intermediate, succeeded in copolymerizing acetylene and butyne-2 to *o*-xylene, but they obtained no *p*-xylene.

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[1] (a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 11–16, 1960. (b) W. Reppe and W. J. Schweckendiek, *Ann.*, 560, 104 (1948).

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

[3] C. H. McKeever and J. O. Van Hook, U. S. Patent 2,542,551 (Feb. 20, 1951).

[4] R. F. Kleinschmidt, U. S. Patent 2,542,417 (Feb. 20, 1951).

[5] Brit. Patent 824,417 (Dec. 2, 1959).

[6] J. F. Harris, Jr., U. S. Patent 2,923,746 (Feb. 2, 1960); J. F. Harris, Jr., R. J. Harder, and G. N. Sausen, *J. Org. Chem.*, 25, 633 (1960).

[7] A. C. Cope and C. T. Handy, French Patent 1,213,148 (March 29, 1960).

[8] J. C. Sauer and T. L. Cairns, *J. Am. Chem. Soc.*, 79, 2659 (1957).

TABLE I

RESULTS OF SUCCESSFUL POLYMERIZATIONS OF MONOSUBSTITUTED ACETYLENES WITH $Ni(CO)_2(Ph_3P)_2$ CATALYST

Acetylene	Concn., Moles/ L.	Catalyst Concn., Moles/ L. × 10^3	Sol- vent[a]	Temp. and Time/Hr.	Product	Yield, %	M.P. or B.P./Mm.	n_D^{25}	Calcd.	Found[b]	Ultraviolet Spectrum, in Cyclohexane λ_{max} (mμ)	a^c
CH_3—C≡CH	2.74	6.2	B	160[d]/6	Linear dimers	4	85/760	1.4920	mol. wt. 80	80 (M, 100%)	—	
					Mixture of 60% 1,2,4- and 40% 1,3,5-trimethylbenzene	30	105–110/20	1.5060	mol. wt. 120	120 (M, 100%)	—	
					Linear trimers	15	145–150/20	1.5267	mol. wt. 120	120 (M, 100%)	—	
C_2H_5—C≡CH	2.39	7.1	B	180[e]/24	Linear dimers	2.0	90–100/760	1.4838	mol. wt. 108 162	108 (M, 73%) 162 (M, 13%)	—	
					1,2,4- and 1,3,5-Triethylbenzene and linear trimers	19.8	55/0.6	1.5000	mol. wt. 162	162 (M, 90%)	—	
					Linear trimers and tetramers	1.5	60–80/0.6	1.5062	mol. wt. 162 216	162 (M, 22%) 216 (M, 73%)	—	
					Linear tetramers and pentamers	7.4	80/0.5	1.5131	mol. wt. 216 270	216 (M, 65%) 270 (M, 17%)	—	
					Linear tetramers and pentamers	3.5	85–95/0.5	1.5231	mol. wt. 216 270	216 (M, 32%) 270 (M, 62%)	—	
					Linear pentamers and hexamers (plus trace of heptamers)	5.0	100–105/0.5	1.5291	mol. wt. 270 324	270 (M, 45%) 324 (M, 29%)	—	
n-C_3H_7—C≡CH	1.43	4.5	B	80/8	Linear dimers	10.6	25–28/0.4	1.4610	C 88.24 H 11.76 mol. wt. 136	88.10 11.89 136 (M, 91%)	—	
					Linear dimers and aromatics	2.4	28–82/0.4	1.4850			—	
					1,2,4- and 1,3,5-Tripropylbenzene and linear trimers	31.3	82/0.4	1.4962	C 88.24 H 11.76 mol. wt. 204	88.55 12.18 204 (M, 95%)	—	
					Linear trimers	5.9	82–86/0.5	1.4985		—	—	
					Linear trimers and tetramers (plus traces of pentamers and hexamers)	11.8	86/0.5	1.5015	C 88.24 H 11.76 mol. wt. 204 mol. wt. 272	87.78 12.12 204 (M, 91%) 272 (M, 5%)	—	
n-C_4H_9—C≡CH	2.0	6.2	80% H, 20% B	71/6	Linear dimers	5.9	50–60/0.1	1.4650	mol. wt. 164	164 (M, 100%)	—	
					Linear + aromatic trimers and trace of tetramers	57	80–90/0.1	1.4893	mol. wt. 246 328	246 (M, 99%) 328 (M, 1%)	—	
n-C_5H_{11}—C≡CH	2.0	8.0	B	82/5	Linear dimers	15	80/0.5	1.4596	C 87.42 H 12.58 mol. wt. 192	87.37 12.90 192 (M, 100%)	225 233	63.3 60.0
					Linear + aromatic trimers and trace of tetramers	48	145/0.5	1.4858	C 87.42 H 12.58 mol. wt. 288	87.49 13.02 288 (M, 100%)	260 (sh.) 268 279 320 (sh.)	37.0 42.4 32.2 —

TABLE I (*continued*)

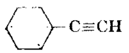
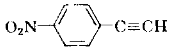
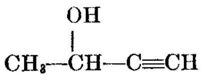
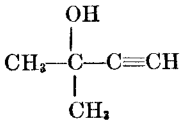
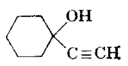
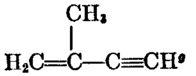
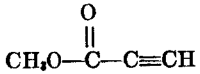
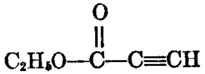
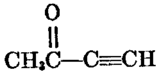
Acetylene	Concn., Moles/ L.	Catalyst Concn., Moles/ L. × 10^3	Solvent^{a}	Temp. and Time/Hr.	Product	Yield, %	M.P. or B.P./Mm.	n_D^{25}	Calcd.	Found^{b}	Ultraviolet Spectrum, in Cyclohexane λ_{max} (mμ)	a^{c}
	0.33	5.2	B	80/5	Linear dimers	28	80–90/0.5	—	—	—	229	—
$C_6H_5—C≡CH$	0.47	3.9	E	78.5/1	Linear trimer	32	109	—	C 94.08 H 5.92 mol. wt. 306	94.14 6.14 316 (CB)	250 281 316 337	85.6 71.1 44.7 31.0
$C_6H_5—C≡CH$	0.62	5.2	C	81.5/1	Linear trimer	37	109	—	—	—	—	—
$C_6H_5—C≡CH$	0.64	5.2	B	75/0.5	Linear trimer	32	109	—	—	—	—	—
$C_6H_5—C≡CH$	2.39	2.5	B	80/3	1,2,4-Triphenylbenzene	∼20	100	—	—	—	251 275 (sh.)	110.0 78.7
					Linear trimer	∼50	109	—	—	—	—	—
					1,3,5-Triphenylbenzene	∼0.7	170	—	—	—	251	171.0
	0.31	7.8	B	80/6	Tris(*p*-Nitrophenyl)benzene (?)	19	257–259	—	C 65.30 H 3.33 N 9.5	65.56 3.57 9.7	—	—
$HOCH_2—C≡CH$	6.25	39.0	B	80/6	Mixture of 65% 1,2,4-trimethylolbenzene and 35% 1,3,5-trimethylolbenzene	65	220–230/0.1	—	—	—	215 264 274 (sh.) (in ethanol)	60.0 1.9 1.2
 $CH_3—CH(OH)—C≡CH$	0.95	5.2	H	69/8	Mixture containing linear dimer (?)	17	142.5–143/760	1.4315		—	252 (in ethanol)	92.7
$HO—CH_2CH_2—C≡CH$	0.69	5.2	H	69/8	Linear dimers (?)	21	145–147/760	1.4482		—	265 276 (sh.) (in ethanol)	32.3 25.5
					Tris(β-hydroxyethyl)benzenes (?)	38	130–140/0.1	—		—	—	
 $CH_3—C(OH)(CH_3)—C≡CH$	0.79	5.2	B	80/8	Linear trimer	63	141–142	—	C 71.43 H 9.52 mol. wt. 252	71.71 9.70 228 (CB)	258 (sh.) 266 276 (in ethanol)	35.0 40.2 29.6
	0.54	5.2	B	80/8	Linear dimer	58	90–91	—	C 77.42 H 9.67 mol. wt. 248	77.53 9.64 269, 237 (CB)	271 282 (in ethanol)	69.2 53.4
$(C_2H_5)_2N—CH_2—C≡CH$	1.0	14.0	B	80/0.5	Linear dimer	8	108–111/0.1	1.4780	mol. wt. 222	222 (M)	—	
					Linear trimer (+ trace of tetramer)	32	162–163/0.1	1.4962	mol. wt. 333 444	333 (M) 444 (M, trace)	—	
$H_2C=CH—C≡CH$	2.3	12.5	H	$110^{f}/1$	1,2,4-Trivinylbenzene	39		—		—	—	

TABLE I (*continued*)

Acetylene	Concn., Moles/ L.	Catalyst Concn., Moles/ L. × 10³	Sol-vent[a]	Temp. and Time/Hr.	Product	Yield %	M.P. or B.P./Mm.	n_D^{25}	Calcd.	Found[b]	Ultraviolet Spectrum, in Cyclohexane λ_{max} (mμ) a[c]
 $H_2C{=}\overset{CH_3}{\overset{\vert}{C}}{-}C{\equiv}CH$[e]	3.9	10.0	B	56–85/3.5	1,2,4-Tris(isopropenyl)-benzene	10	60–70/0.1	1.5551	—	—	229 101 260 73.6
$CH_3O{-}CH{=}CH{-}C{\equiv}CH$[g]	2.0	6.3	C	83/3	Linear dimer + linear trimer + 1,3,5-tris(β-methoxy-vinyl)benzene	10	150–160/0.1	—	mol. wt. 164 246	164 (M, 37%) 246 (M, 47%)	267 82.0 (other peaks at 230, 295, 310, 330 mμ)
 $CH_3O{-}\overset{O}{\overset{\Vert}{C}}{-}C{\equiv}CH$	0.90	0.9	B	35–65/1	1,2,4-Tris(carbmethoxy)-benzene	78	96–99	—	—	—	Identical with known
 $C_2H_5O{-}\overset{O}{\overset{\Vert}{C}}{-}C{\equiv}CH$	0.90	0.9	B	25–65/0.5	1,2,4-Tris(carbethoxy)benzene	89	145/0.2	1.5037	C 61.22 H 6.17	60.99 6.20	Identical with known
					1,3,5-Tris(carbethoxy)benzene	6	135–136	—	C 61.22 H 6.17	61.38 6.33	Identical with known
$C_6H_5OCH_2{-}C{\equiv}CH$	1.27	12.7	B	80/3	1,2,4- and 1,3,5-Tris(phenoxy-methyl)benzene	63[h]	—	—	—	—	—
$C_2H_5O{-}C{\equiv}CH$	1.6	11.0	C	81/1	1,2,4-Triethoxybenzene	29	150/6	1.5034	C 68.57 H 8.57 mol. wt. 210	68.84 8.70 210 (M)	—
 $CH_3\overset{O}{\overset{\Vert}{C}}{-}C{\equiv}CH$	0.84	8.4[i]	A	80/2	1,3,5-Triacetylbenzene	80[h]	—	—	—	—	—

[a] A = acetonitrile, B = benzene, C = cyclohexane, E = absolute ethanol, H = *n*-hexane. [b] M = mass spectrometric method; the percentages represent the approximate amounts of compounds of the given molecular weight in the sample, as estimated by comparison of relative peak height. CB = cryoscopic benzene method. [c] a = absorptivity at indicated wave length. [d] Reaction was run in a 300-ml. stainless steel rocking autoclave at 280 p.s.i.g. A pressure drop of 140 p.s.i.g was observed. [e] Reaction was run in a 300-ml. stainless steel rocking autoclave at 215 p.s.i.g. A pressure drop of 75 p.s.i.g was observed. [f] Reaction was run in a 300-ml. stainless steel rocking autoclave at 35 p.s.i.g. [g] β-Naphthol (1 g.) added as free radical polymerization inhibitor. [h] Yield based on percent disappearance of monomer by infrared analysis of reaction solution. Product identification was also by infrared only; product was not isolated. [i] Catalyst in this reaction was dicarbonylbis[tris(2-cyanoethyl)phosphine]nickel.

The only report of the linear polymerization of an acetylene with a nickel-carbonyl-phosphine catalyst is the paper of Cairns and co-workers[9] who copolymerized acetylene and acrylonitrile to 2,4,6-heptatrienenitrile.

The general confusion associated with the scope and products of this reaction as well as the unusual nature of the catalysis prompted us to undertake a detailed examination of the reactions of acetylenes with nickel-carbonyl-phosphine complexes. This paper presents the results of a broad survey of the scope and products of the reaction. The acetylene monomers studied fall into three general classes: (1) those that form primarily aromatic trimers; (2) those that yield principally linear oligomers; and (3) unreactive acetylenes.

EXPERIMENTAL

Materials. Most of the acetylene compounds were available in this laboratory or obtained commercially. They were purified until their melting points or boiling points and refractive indices agreed with the literature values.

The following compounds were prepared by published methods: *p*-nitrophenylacetylene,[10] cyclohexylacetylene,[11] *t*-butylacetylene,[12] cyanoacetylene,[13] propiolamide,[13] ethoxyacetylene,[14] propargyl acetate,[15] and 1,3,5-triphenylbenzene.[16]

Dicarbonylbis(triphenylphosphine)nickel, $Ni(CO)_2(Ph_3P)_2$, was prepared by the method of Rose and Statham.[2] The complex was successfully stored for long periods without decomposition in a freezer at −30°.

Analytical or pure grade solvents were used throughout the experiments. Melting points are uncorrected.

Procedure. The procedure followed was to dissolve the acetylene compound and the catalyst in about a 250:1 mole ratio in a suitable inert solvent—*e.g.*, benzene, cyclohexane, ethanol—and reflux the solution for from one to 24 hr. The solvent was removed and the liquid products were separated by vacuum fractionation and the solid products were isolated by crystallization. A number of the products were very high-boiling liquids or low-melting solids, which made their purification difficult and sometimes impossible. The reactions with propyne, 1-butyne, and 2-butyne could not be carried out under the usual reflux conditions because of their low boiling point. A 300-ml. stainless steel autoclave was used for these reactions.

Infrared spectra were determined on the neat liquids and on mineral oil mulls of the solids on a Perkin-Elmer Model 21 infrared spectrophotometer. Ultraviolet spectra were obtained in cyclohexane or ethanol solution on a Cary Model 11 ultraviolet spectrophotometer. Mass spectra were obtained with a Consolidated Electrodynamics Model 21-103C mass spectrometer with heated inlet. NMR spectra were determined on a Varian Model 4300B high resolution NMR spectrometer.

RESULTS AND DISCUSSION

In Table I are listed the successful polymerization reactions of monosubstituted acetylenes with dicarbonylbis(triphenylphosphine)nickel. Attempts to polymerize the following monosubstituted acetylenes were unsuccessful: *t*-butylacetylene, propargyl chloride, propargyl acetate, 5-chloro-1-pentyne, propiolic acid, propiolamide, and cyanoacetylene.

Disubstituted acetylenes were generally inert in this reaction, the following compounds failing to polymerize: 2-butyne, 3-hexyne, diphenylacetylene, 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 1,4-dichloro-2-butyne, 2-butyne-1,4-diol diacetate, acetylenedicarboxylic acid, diethyl acetylenedicarboxylate, 2,7-dimethyl-3,5-octadiyne-2,7-diol, 1,8-dimethoxy-1,7-octadiene-3,5-diyne, and 1,4-bis(1-hydroxycyclohexyl)buta-1,3-diyne. However, 2-butyne-1,4-diol did polymerize, as previously reported,[4] to hexamethylolbenzene, m.p. 302°, in 78% yield. The attempted trimerization of 2-butyne-1-ol produced a mixture from which 80% of the starting material and 18% of an amorphous brown solid, m.p. 155–165°(with charring), were recovered. The infrared spectrum of this brown solid suggested that it might contain a trimethyltrimethylolbenzene.

The solutions of the acetylene and the catalyst in the solvent were pale yellow. Either during the heating up period or a few minutes after commencing to reflux, the solutions of the more reactive acetylenes—*e.g.*, phenylacetylene—would suddenly turn dark red to brown. This was accompanied by a violent exotherm which sometimes carried the reaction mixture out of the reflux condenser. After refluxing for a short while, the solutions of the less reactive acetylenes—*e.g.*, 1-heptyne—gradually changed from yellow to red and finally to dark brown without evidencing an exotherm. In some of the unsuccessful experiments the solution remained pale yellow during the refluxing period; in others, the solutions turned dark red or dark brown while refluxing, even though only unreacted monomer was recovered from the reaction.

In most cases the monomer reacted quantitatively even though product isolation was seldom greater than 30–40% because of tar formation. The original nickel complex was never recovered from a successful reaction; instead, depending upon reaction conditions, triphenyl phosphine or its oxide and nickel metal or a nickel salt (oxide, hydroxide, *etc.*) were isolated. Most of the carbon monoxide was lost from the reaction in the gas phase. However, some of the carbon monoxide may have been incorporated into the acetylene polymers, for traces of carbonyl-containing products were frequently obtained.

The polymer products included the aromatic trimers, 1,2,4- and 1,3,5-trisubstituted benzenes, and

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(9) T. L. Cairns, V. L. Engelhardt, H. L. Jackson, G. H. Kalb, and J. C. Sauer, *J. Am. Chem. Soc.*, **74**, 5636 (1952).

(10) V. B. Drewsen, *Ann.*, **212**, 150 (1882).

(11) R. Ya. Levina and A. A. Potapova, *J. Gen. Chem. (U.S.S.R.)*, **7**, 353 (1937).

(12) M. P. Ivitsky, *Bull. soc. chim.*, [4], **35**, 357 (1924).

(13) C. Moureu and J. C. Bongrand, *Ann. chim.*, **14**, 47 (1920).

(14) I. N. Nazarov, *Zhur. Obsh. Khim.*, **28**, Vol. 2, 460 (1958).

(15) L. Henry, *Ber.*, **6**, 729 (1873).

(16) A. F. Odell and C. W. Hines, *J. Am. Chem. Soc.*, **35**, 81 (1913).

linear Nieuwland-type condensation polymers,[17] substituted vinylacetylenes, butadienylacetylenes, hexatrienylacetylenes, *etc.*, having the general formulas $R—C{\equiv}C–(CR{=}CH)_n–CH{=}CHR$ and $R—C{\equiv}C–(CR{=}CH)_n–CR{=}CH_2$, where n ranges from 0 to about 8–10. This is the first report of the formation of linear homopolymers of substituted acetylenes using nickel-carbonyl-phosphine catalysts. However, we have been able to show that some of the acetylene trimers previously reported to be aromatic are in fact linear substituted butadienylacetylenes. The determination of the structures of some of these linear polymers are described in paper II of this series.[18]

Alkyl acetylenes. The polymerization of monoalkyl acetylenes with nickel-carbonyl-phosphine catalysts has not been previously reported. These monomers have yielded the greatest variety of linear products, with polymers up to heptamers definitely identified and chains of up to perhaps twenty monomer units indicated from the experiments. The series of normal alkyl acetylenes from propyne to 1-heptyne was studied intensively.

The yield of aromatic polymer in the products decreased from about 65% with propyne to less than 5% with 1-heptyne, although the total conversion to polymers in this series was almost constant. The proportion of 1,2,4- to 1,3,5-trisubstitution fell in the range of 50–50 to 65–35% in favor of the unsymmetrical product with no trend observed through the series. Among the linear products, the trimers (not the dimers) were formed in greatest amount, with the yields of dimers, tetramers, pentamers, hexamers, *etc.*, falling off in that order. The yield of linear polymers above trimers was greatest from 1-butyne and 1-pentyne, approaching 50% of the product in the case of 1-butyne; 1-heptyne gave only a trace of tetramer. The operation of a steric effect in the reaction was evident in the conversion of cyclohexylacetylene only to a linear dimer and the failure of *t*-butylacetylene to polymerize at all. The decrease in proportion of aromatic product with increasing length of alkyl chain suggests that the aromatization reaction has greater steric requirements than the linear polymerization.

Attempts to polymerize 2-butyne and 3-hexyne with nickel-carbonyl-phosphine catalysts failed even under forcing conditions.

Aryl acetylenes. The trimerization of phenylacetylene in the presence of dicarbonylbis(triphenylphosphine)nickel was first reported[2] to produce only 1,2,4-triphenylbenzene. In a reinvestigation of this reaction, Overberger and Whelan[19] have shown that this product, m.p. 109°, is not 1,2,4-triphenyl benzene, which has two forms, melting at 100° or 119–120°, and suggest that it may be a "complex of 1,2,4-triphenylbenzene with a related phenylacetylene derivative." In a recent communication, Booth and Rowe[20] claim that the 109° substance is a molecular complex of 1,2,4-triphenylbenzene with the dimer, *trans*-1,4-diphenylbutenyne. They arrive at this conclusion from the results of X-ray, infrared, and NMR investigations. However, they fail to report the molecular weight of their material; both Rose and Statham[2] and we found that the molecular weight of this product corresponded to a trimer of phenylacetylene.

Our first attempts to repeat the trimerization[2] yielded only the 109° product in 30–40% yield, regardless of the solvent employed (see Table I). However, when the reaction was scaled up in benzene and when the crude gummy product was allowed to crystallize very slowly under petroleum ether (b.p. 30–60°), a 70% yield of an intimate mixture of three different crystalline compounds was obtained, which were separable by hand picking with tweezers. Approximately 1% of the material was rectangular platelets which on recrystallization melted at 170°. These were identified as 1,3,5-triphenylbenzene by comparison of infrared spectra and mixed melting point with a known sample.[16] About 30% of the material was pale yellow needles of m.p. 109°, whose infrared and ultraviolet spectra are virtually identical with those of the 109° product isolated by Overberger and Whelan,[19] which is presumably the same product obtained by Rose and Statham.[2] The remainder of the material (about 70%) was identified as 1,2,4-triphenylbenzene by comparison of its infrared and ultraviolet spectra and mixed melting point (100°) with an authentic sample prepared by a slight modification of the Rose and Statham synthesis.[2] It is not clear why some of the 1,2,4-compound was not isolated in earlier experiments.

The ultraviolet spectrum of the 109° trimer is consistent only with a phenyl-substituted polyunsaturated system, as it has bands out at much longer wave lengths than the cyclic trimers. Its infrared spectrum shows the presence of a *trans* terminal disubstituted double bond (band at 965 $cm.^{-1}$), although no triple bond absorption at about 2220 $cm.^{-1}$ was found. On the other hand, the Raman spectrum contains a strong band at 2210 $cm.^{-1}$, which, as this band is absent in the infrared spectrum, is indicative of a fairly symmetrically disubstituted acetylene. The proton magnetic resonance spectrum of this compound in deuterochloroform at 40 mc. and 9340 gauss is complex, containing a sharp peak at −287.6 c.p.s. plus a group of about 20 peaks centered at about −298.3 c.p.s. (assigning 0 shift to tetramethylsilane). The two aromatic isomers, 1,2,4- and 1,3,5-tri-

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[17] J. A. Nieuwland and R. R. Vogt, *The Chemistry of Acetylene*, Reinhold, New York, 1945.

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

[19] C. G. Overberger and J. M. Whelan, *J. Org. Chem.*, **24**, 1155 (1959).

[20] G. Booth and J. M. Rowe, *Chem. & Ind.*, 661 (1960)

phenylbenzene, have a sharp peak at −288.0 c.p.s. plus a group of about twelve peaks centered at about −302.0 c.p.s. and a sharp peak at −311.0 c.p.s. plus a group of nine peaks centered at about −299.8 c.p.s., respectively, relative to the same internal standard. These spectra have not been completely analyzed but it appears that the principal peaks represent the protons on the phenyl substituents. The 109° isomer is clearly a unique compound and not a combination involving one of the aromatic products. From all of the above evidence plus the chemical reactivity of the 109° compound toward olefin reagents, we conclude that it is a triphenylbutadienylacetylene. By analogy with linear trimers of monoalkylacetylenes, whose structures have been determined,[18] the compound is probably the unreported 1,3,6-triphenyl-1-hexyne-3,5-diene.

In an attempt to study the effect of *para* substitution on the polymerization of phenylacetylene, *p*-nitrophenylacetylene was synthesized and treated with the catalyst in refluxing benzene. A dark solid formed during the reaction which, after washing repeatedly with dimethylformamide, yielded a tan powder, m.p. 257–259°, for which no solvent could be found. Its infrared spectrum and microanalysis indicated that it was probably a tris(*p*-nitrophenyl)-benzene.

The only diarylacetylene tried was diphenylacetylene which failed to react and was recovered almost quantitatively.

Acetylenic alcohols. In general, acetylenic alcohols have been found to react quite readily with nickel-carbonyl-phosphine catalysts to give both aromatic and linear products.

The trimerization of propargyl alcohol[1] was repeated and the reported products, 1,2,4- and 1,3,5-trimethylolbenzene, were obtained in good yield as a 65–35% mixture. Surprisingly, propargyl acetate failed to polymerize and was recovered unchanged. From 3-butyne-2-ol there was obtained 17% of a colorless liquid, b.p. 142.5–143°, with a menthol odor. Vapor phase chromatography showed that this product was a mixture of two compounds in a 2:1 ratio, whose infrared spectrum showed bands for secondary hydroxyl, ether, and *trans* double bond structures. The ultraviolet spectrum is consistent with a vinylacetylene structure, suggesting that one of these compounds is the linear dimer. The second compound may be a cyclization product of the dimer. The reaction of 3-butyne-1-ol gave two products, a 21% yield of a colorless liquid, b.p. 145–147°, also with a menthol odor, and 38% of a yellow liquid, b.p. 130–140°/0.1 mm., with a burnt sugar odor. The lower boiling material had bands in the infrared at 975 and 1610 cm.$^{-1}$ and an ultraviolet spectrum (a_{266} = 32), all of which are consistent with a linear dimer structure. The yellow liquid appears to be a linear trimer from its infrared spectrum (bands at 975 and 2220 cm.$^{-1}$). There was considerable charring in the pot during product distillation in the last two experiments.

The reaction of 2-methyl-3-butyne-2-ol is reported in the patent literature[3] to give tris(1-methyl-1-hydroxyethyl)benzene, a white crystalline solid, m.p. 140–142°. Only the analysis is given. The reaction was repeated and gave a white crystalline solid of like melting point. Molecular weight determination and analysis agree with the trimer. The infrared spectrum, however, contains no aromatic bands; conjugated unsaturation (1605 cm.$^{-1}$), *trans* double bond (965 cm.$^{-1}$), and tertiary alcohol (bands in 1150–1180 cm.$^{-1}$ region) are present. The ultraviolet spectrum is consistent with a triene or butadienylacetylene. The compound decolorizes bromine in carbon tetrachloride and potassium permanganate in water or acetone very slowly and forms a black mass in concentrated sulfuric acid. Catalytic hydrogenation over platinum dioxide at atmospheric pressure yielded a dihydrocompound, m.p. 157° (Calcd. for $C_{15}H_{26}O_3$: C, 70.87; H, 10.24. Found: C, 70.82; H, 10.27), and hydrogenation over platinum dioxide in a Parr apparatus (45 p.s.i.g. of hydrogen) produced a tetrahydrocompound, which had lost one molecule of water, m.p. 152.5–153.5° (Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.30; H, 10.91). The above evidence supports the conclusion that the trimer of 2-methyl-3-butyne-2-ol, m.p. 140–142°, is a linear polymer, probably 2,9-dimethyl-6-(1-hydroxy-1-methylethyl)3,5-decadiene-7-yne-2,9-diol.

The polymerization of 1-ethynylcyclohexane-1-ol produced a white crystalline solid of m.p. 90–91°. Analysis and molecular weight determination showed it to be a dimer. Its infrared and ultraviolet spectra agree with a linear dimer structure and the Raman spectrum had a strong triple bond absorption at 2210 cm.$^{-1}$ The compound also decolorized bromine in carbon tetrachloride and potassium permanganate in acetone. Catalytic hydrogenation over platinum dioxide produced a partially hydrogenated compound, m.p. 150°. The dimer of 1-ethynylcyclohexane-1-ol is 1,4-bis(1-hydroxycyclohexyl)-1-butene-3-yne.

As in the case of the alkyl acetylenes, the acetylenic alcohols show a rapidly decreasing tendency to aromatize and a greater tendency to form linear polymers as the bulk of the hydroxyalkyl substituent increases. The formation of higher linear polymers appears to be limited, although linear tetramers, pentamers, *etc.*, may have been present among the reaction products from some of the monomers but were decomposed during distillation.

Among the group of disubstituted acetylenic alcohols investigated, only 2-butyne-1,4-diol aromatized readily while 2-butyne-1-ol gave a small yield of product. Colors were obtained with the other acetylenic diols, indicating complex formation, but only starting material was recovered even when refluxing *o*-xylene was used as solvent. Apparently they are too highly hindered to aromatize. Just as with propargyl alcohol, the diacetate of 2-butyne-1,4-diol was unreactive. Acetylation appears to inhibit the polymerization of acetylenic alcohols.

Acetylenic acids, esters, amides, nitriles, and ketones. The behavior of this group of acetylene derivatives in the Reppe aromatization reaction has not been previously reported. Propiolic acid did not react and acetylene dicarboxylic acid yielded mostly propiolic acid by decarboxylation, except for a small amount of brown solid (which was not mellitic acid) that formed in one experiment.

Methyl and ethyl propiolate reacted more vigorously than any other acetylenes tried. Methyl propiolate aromatized in 78% yield to 1,2,4-tris-(carbmethoxy)benzene; the ethyl ester gave predominantly 1,2,4-tris(carbethoxy)benzene (89%) along with a small amount of 1,3,5-tris(carbethoxy)-benzene (6%). Solutions of the acetylenic ester and catalyst in benzene at room temperature became cherry red and the exothermic reaction occurred in some experiments at temperatures as low as 35–40°. The benzenetricarboxylic acid esters were identified by comparison of their infrared spectra with those of authentic samples. When a solution of diethyl acetylenedicarboxylate and nickel complex was heated to reflux in cyclohexane, the solution turned dark brown but no exotherm was observed. Most of the monomer was recovered from the reaction mixture, but a small residue containing some ethyl mellitate remained. Jones and Whiting[21] obtained an 18% yield of ethyl mellitate from the "carbonylation" reaction of diethyl acetylenedicarboxylate with nickel carbonyl and acetic acid in aqueous ethanol at 65–70°.

Propiolamide and cyanoacetylene were not polymerized by dicarbonylbis(triphenylphosphine)-nickel in refluxing benzene. Starting monomer was recovered from both systems.

Methyl ethynyl ketone (1-butyne-3-one) trimerized in the presence of dicarbonylbis[tris(2-cyanoethyl)phosphine]nickel[22] in refluxing acetonitrile to 1,3,5-triacetylbenzene in good yield. Product identification was made only by comparison of the infrared spectrum with that of a known sample.

It is not immediately apparent why the acetylenic esters and ketones aromatize readily while the acids, amides and nitriles are unreactive. The carboxylic acid group may serve to decompose the nickel complex. The nitrogen atoms in amide and nitrile groups may inhibit catalysis by coordination with the nickel. However, as nitrile-containing solvents and catalysts do not interfere, other factors must be involved.

Vinylacetylenes. Vinylacetylenes have been found to polymerize readily. A 39% yield of 1,2,4-trivinylbenzene[6] was obtained from the reaction of a benzene solution of vinylacetylene with the catalyst in an autoclave at 110°. The reported aromatization of isopropenylacetylene[3] (2-methyl-1-butene-3-yne) was confirmed; however, the isolated yield of 1,2,4-tris(isopropenyl)benzene, the only isomer obtained (judging from its infrared spectrum), was poor (10%) because of the great tendency of the product to polymerize on distillation.

Methoxyvinylacetylene (1-methoxy-1-butene-3-yne) polymerized in low yield to a product which analyzed in infrared for a mixture of mostly linear dimers, linear trimers, and 1,3,5-tris(2-methoxyvinyl)benzene. The mass spectrum showed that the sample contained 37% dimers and 47% trimers.

Acetylenic halides. The polymerization of three acetylenic halides, propargyl chloride, 5-chloro-1-pentyne and 1,4-dichloro-2-butyne, was attempted, but in each case, the catalyst was decomposed and all failed to react. The presence of a halogen on the monomer, even far removed from the triple bond, as in the pentyne derivative, seems to destroy the catalyst system.

Acetylenic ethers and amines. Ethoxyacetylene reacted vigorously with dicarbonylbis(triphenylphosphine)nickel in refluxing cyclohexene to form 1,2,4-triethoxybenzene in 29% yield. Phenyl propargyl ether was successfully aromatized to a mixture of 1,2,4- and 1,3,5-tris(phenoxymethyl)benzene.

Diethylaminopropyne (1-diethylamino-2-propyne) reacted smoothly to give an 8% yield of the linear dimer, *trans*-1,6-bis(diethylamino)-2-hexene-4-yne, 32% of a linear trimer, probably *trans*-1,8-bis-(diethylamino)-5-diethylaminomethyl-2,4-octadiene-6-yne, and a trace of tetramer. These results demonstrate that the presence of a basic amino group on the monomer does not inhibit polymerization.

Conjugated diacetylenes. The polymerization of several disubstituted conjugated diacetylenes was attempted, unsuccessfully. The reactions of unconjugated diacetylenes are described in Paper III of this series.[23]

Copolymers. It is possible to copolymerize two different acetylenes as long as the difference in their structure or reactivity is not too great. Mixtures of 1-pentyne plus 1-heptyne and 1-pentyne plus phenylacetylene formed a wide range of copolymers as well as the usual homopolymers. The copolymerization of 2-butyne with an excess of acetylene under conditions similar to those reported by Sauer and Cairns[8] produced a mixture of products which by infrared and vapor phase chromatographic analysis was shown to consist of 43% ben-

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(21) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 48 (1950).

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

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

zene, 50% *o*-xylene, 3.5% styrene, and 3.5% prehnitene (1,2,3,4-tetramethylbenzene).

On the other hand, no copolymers were formed by mixtures of 1-pentyne plus ethyl propiolate, phenylacetylene plus ethyl propiolate, 1-heptyne plus propargyl alcohol, acetylene plus 2-butyne-1,4-diol, and phenylacetylene plus 2,5-dimethyl-3-hexyne-2,5-diol. Great differences between the relative polymerization rates of the monomers are probably responsible for these failures to form mixed polymers.

CONCLUSIONS

Considerably more information has been obtained on the scope of the Reppe "aromatization" reaction than was previously available in the literature and some discrepancies have been resolved. In addition to aromatic polymers, a new class of linear oligomers of monosubstituted acetylenes is formed. The reaction is quite general for monosubstituted acetylenes, including alkyl, aryl, and vinyl acetylenes, acetylenic alcohols, esters, ketones, ethers, and amines. Inert are acetylenic acids, amides, nitriles, halides, and certain highly hindered acetylenes, as well as all disubstituted acetylenes except 2-butyne-1,4-diol and 2-butyne-1-ol. Copolymers can be produced from similar monomers. Qualitatively, the general order of reactivity of monosubstituted acetylenes is: acetylenic esters, ethers, and ketones, vinylacetylenes > arylacetylenes > acetylenic alcohols > higher alkylacetylenes > lower alkylacetylenes, acetylene ≫ acetylenic acids, halides, and certain other derivatives. The more reactive monomers usually form aromatic products, the less reactive generally giving a large proportion of linear polymers.

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The Polymerization of Acetylenes by Nickel-Carbonyl-Phosphine Complexes. II. Proof of Structure of the Linear Low Polymers of Monosubstituted Acetylenes[1a]

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The structures of the linear dimer and trimer products from the polymerization of several monoalkyl acetylenes with dicarbonylbis(triphenylphosphine)nickel $Ni(CO)_2(Ph_3P)_2$ have been determined by hydrogenation to saturated hydrocarbons of known structure and by partial degradation with ozone and chromium trioxide. The mechanistic significance of the formation of only certain linear isomers is discussed.

The first paper in this series[1b] dealt with the scope of the polymerization reaction with a wide variety of substituted acetylenes. The polymer products included both aromatic compounds and a series of linear low polymers. In this paper the structure determinations of several linear dimers and trimers of the monoalkylacetylenes will be described.

EXPERIMENTAL

6-Methyltridecane. Reaction of the Grignard reagent from heptyl bromide with 2-heptanone yielded 6-methyltridecan-6-ol. Dehydration of this alcohol with sulfuric acid and hydrogenation of the resulting olefins (platinum dioxide/ethanol) gave 6-methyltridecane, b.p. 67–70°/1 mm., n_D^{25} 1.4273.

Anal. Calcd. for $C_{14}H_{30}$: C, 84.76; H, 15.25. Found: C, 84.70; H, 14.95.

5-Ethyldecane. Reaction of the Grignard reagent from amyl bromide with 3-heptanone yielded 5-ethyldecan-5-ol. Dehydration of this alcohol with sulfuric acid and hydrogenation of the resulting olefins (platinum dioxide/ethanol) gave 5-ethyldecane, b.p. 82–83°/14 mm., n_D^{25} 1.4219.

Anal. Calcd. for $C_{12}H_{26}$: C, 84.61; H, 15.39. Found: C, 84.86; H, 15.01.

4-Nonanol. Reaction of the Grignard reagent from amyl bromide with butyraldehyde gave 4-nonanol, b.p. 190–195° (lit.[2] b.p. 192–193°).

4-Nonanone. The oxidation of 4-nonanol with sodium dichromate in glacial acetic acid at 10° afforded a 79% yield of 4-nonanone, b.p. 187–190° (lit.[3] b.p. 187–188°).

6-Propyldodecane. Reaction of the Grignard reagent from hexyl bromide with 4-nonanone, followed by dehydration of the 6-propyldodecan-6-ol and hydrogenation (platinum dioxide/ethanol) of the resulting olefins yielded 6-propyldodecane, b.p. 120–121°/12 mm., n_D^{25} 1.4308.

Anal. Calcd. for $C_{15}H_{32}$: C, 84.81; H, 15.19. Found: C, 85.21; H, 15.16.

4-Methyl-6-propylundecane. Passing anhydrous hydrogen bromide through refluxing 2-methylpentan-1-ol for 30 hr. gave a 52% yield of 2-methyl-1-bromopentane. The Grignard

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(1)(a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 11–16, 1960. (b) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961).

(2) M. Pexsters, *Chem. Zentr.*, **I**, 1398 (1907).

(3) M. Guerbet, *Compt. rend.*, **154**, [I], 1357 (1912).