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.

Acknowledgment. The authors express their gratitude to the Research Service Department of the Stamford Laboratories for the infrared, ultraviolet, Raman, mass, and NMR spectra and the microanalyses.

STAMFORD, CONN.

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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).

reagent from this bromide was treated with 4-nonanone to give 4-methyl-6-propylundecan-6-ol. This alcohol was dehydrated with sulfuric acid and the resulting mixture of olefins was hydrogenated (platinum dioxide/ethanol) to give a small yield of 4-methyl-6-propylundecane, n_D^{24} 1.4262. The gas chromatogram of the product contained only one symmetrical peak and its mass spectrum contained a "parent" peak for $C_{15}H_{32}$ and was otherwise consistent with the structure assigned.

7-Tridecyn-6-one. An ether solution of hexanoic anhydride was added very slowly below −25° to an ether solution of heptynemagnesium bromide (from 1-heptyne and butylmagnesium bromide). The Grignard reaction was worked up in the usual manner to give a 17% yield of 7-tridecyn-6-one, b.p. 60–65°/0.2 mm.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.40; H, 11.70.

1-Octynoic acid. Reaction of heptynemagnesium bromide with excess Dry Ice in an autoclave gave a 53% yield of 1-octynoic acid, b.p. 144°/15 mm., n_D^{22} 1.4560 (lit.[4] b.p. 148–149°/19 mm., n_D^{13} 1.4634).

Ozonization of 1-heptyne trimer. A 1-heptyne trimer fraction (8.64 g., 30 mmoles, b.p. 117–123°/0.1 mm., n_D^{25} 1.4898) was dissolved in 100 ml. of *n*-pentane and ozonized at −78° in a stream of air containing 2% ozone. Uptake of ozone was practically quantitative for the first equivalent (about 27 mmoles). Twenty-five milliliters of methanol was added at this point and ozonization was continued until 57.5 mmoles had been absorbed. Ozone uptake during the second equivalent ranged from 75% down to 25%. The ozonide solution was poured into 100 ml. of water. The pentane was distilled, 8 ml. of 30% hydrogen peroxide solution was added, and the solution was refluxed for 1 hr. The cooled mixture was extracted thoroughly with ether. The ether extract was washed successively with the following solutions: 5% sodium bicarbonate, 5% sodium carbonate, and 5% sodium hydroxide, leaving a neutral ether fraction. The sodium bicarbonate and sodium carbonate washes were combined, acidified, and extracted with ether (acid fraction I). The sodium hydroxide wash was acidified and extracted with ether (acid fraction II). All three ether fractions were washed with water, dried, and fractionated. The products were analyzed by infrared and gas chromatography.

The neutral fraction yielded 1.43 g. of methyl hexanoate, b.p. 65–70°/15 mm., n_D^{24} 1.4047 (lit.[5] b.p. 52–53°/15 mm., n_D^{23} 1.4038), and a fraction (1.43 g.,b.p. 70–115°/1 mm., n_D^{24} 1.4697) which, from infrared and gas chromatographic analysis, was estimated to consist of about 20% triamylbenzenes, 60–80% of the α,β-unsaturated ketone, 7-tridecyn-6-one, and small amounts of hexanoic acid and two unknown constituents. However, the analysis (C, 80.40, 80.50; H, 12.03, 11.91) agreed very well with that for pure 7-tridecyn-6-one (C, 80.35; H, 11.41), indicating that most of this fraction was the ketone. Attempts to prepared a solid oxime of the ketone were unsuccessful. The pure ketone was isolated by treating it with Girard's T Reagent[6] and subsequently recovering it from the separated complex.

Distillation of acid fraction I showed it to be 98% hexanoic acid (2.68 g., b.p. 75–80°/15 mm., n_D^{24} 1.4151; lit.[7] b.p. 205°/760 mm., n_D^{25} 1.4164). A small amount (about 50 mg.) of higher-boiling material remaining in the pot consisted of a mixture of three acids, one of which had the same relative retention time as 1-octynoic acid. Acid fraction II (1.03 g., n_D^{24} 1.4203) was found to be about 90% hexanoic acid along with 10% of five other unidentified higher boiling acids, none of which was 1-octynoic acid. These other acids were probably intermediate breakdown products of the ozonization of the heptyne trimers.

The above analysis indicates that the over-all recovery of products from the ozonization was about 75% and that the products comprised about 75% hexanoic acid and its methyl ester, 20% 7-tridecyn-6-one, 5% triamylbenzenes, and traces of higher boiling acids, possibly including 1-octynoic acid.

Chromic acid oxidation of heptyne trimer. A solution of 7.1 g. (0.07 mole) of chromium trioxide in 10 ml. of water was added with stirring to a warm (55–60°) solution of 5 g. (0.017 mole) of the same heptyne trimer fraction used in the preceding experiment in 50 ml. of glacial acetic acid over a period of 1 hr. The solution was stirred overnight at room temperature. Most of the acetic acid was removed under vacuum at 40°, and the liquid remaining was warmed with 175 ml. of 2*N* sulfuric acid for 1 hr. The cooled solution was diluted with 280 ml. of saturated sodium chloride solution and then extracted with ether. The ether extract was washed with 5% sodium bicarbonate solution until basic and with water until neutral and dried over anhydrous sodium sulfate. The ether was removed and the resulting liquid was put through the gas chromatograph. Only one peak was obtained, which had the same shape and relative retention time as a synthetic sample of 7-tridecyn-6-one.

The sodium bicarbonate and water washings from the above procedure were combined, acidified, and extracted with ether. The ether extract was dried and the ether was removed. The gas chromatogram of the resulting liquid contained three peaks, identified as acetic acid, hexanoic acid, and 1-octynoic acid.

Chromic acid oxidation of 7-tridecyn-6-one. Two grams of 7-tridecyn-6-one was treated with chromium trioxide in glacial acetic acid under the same conditions as used in the oxidation of heptyne trimer. The product was analyzed by gas chromatography. Although most of the starting ketone remained, small amounts of 1-octynoic acid and hexanoic acid were formed.

Gas chromatography. All gas chromatography was performed on a Podbielniak Chromacon gas chromatography apparatus, series 9475-3V. Stainless steel columns 6-ft. long and 1/4-in. in diameter were packed with about 17 g. of 30–60 mesh acid-washed Chromosorb diatomaceous silica containing 30% absorbed stationary phase. Three different columns were used in this work: A, containing Apiezon L high vacuum grease; B, containing Dow-Corning high vacuum silicone grease; and C, containing didecylsebacate. Column temperatures between 150° and 250° were used and the helium carrier gas flow rate was about 25 cc. per min. Column loadings of 10 to 20 μl were generally used. In Table I are listed the relative retention times (relative to benzene as internal standard) of the compounds studied.

Hydrogenation of linear acetylene polymers. The mixtures of linear dimers and trimers of 1-butyne, 1-pentyne, and 1-heptyne were hydrogenated to the saturated hydrocarbons in absolute ethanol over platinum dioxide in a Parr apparatus for 2 hr. under 40 p.s.i.g. of hydrogen. The filtered solutions were then freed of alcohol and the resulting products were analyzed by infrared and gas chromatography. The trimer fractions usually contained some aromatic products which, of course, went through the above procedure unchanged. These aromatic trimers were easily identified in the analysis of the hydrogenated products by gas chromatography.

Partial hydrogenation of 1-heptyne dimer. A 0.4-g. sample of 1-heptyne dimer in 50 ml. of absolute ethanol was hydrogenated at atmospheric pressure over 0.1 g. of Lindlar's catalyst.[8] After 24 hr. 48.5 cc. of hydrogen (S. T. P.) had been absorbed; calcd. for 1 mole uptake, 46.6 cc. of hydrogen (S. T. P.) The catalyst was filtered and the ethanol was removed. The pale yellow liquid remaining (0.4 g., n_D^{24} 1.4580) had infrared bands at 733, 898, and 975 cm.$^{-1}$ but no longer contained bands at 955 and 2220 cm.$^{-1}$

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(4) C. Moureu, *Ann. chim.*, [8], **7**, 553 (1906).

(5) P. Heinanen, *Suomen Kemistilehti*, **16B**, 14 (1943).

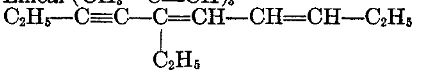
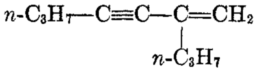
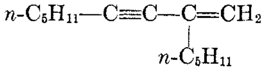
(6) A. Girard, *Helv. Chim. Acta*, **19**, 1095 (1936).

(7) L. T. C. Scheij, *Rec. trav. chim.*, **18**, 183 (1899).

(8) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

TABLE I

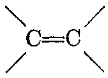
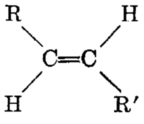
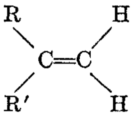
RELATIVE RETENTION TIMES OF MONOALKYLACETYLENE OLIGOMERS AND THEIR DEGRADATION PRODUCTS

Compound	Column	Temp.	Rel. Ret. Time
1,3,5-Trimethylbenzene	A	175	2.8
1,2,4-Trimethylbenzene	A	175	3.2
Linear $(CH_3—C≡CH)_3$	A	175	2.5
 $C_2H_5—C≡C—C(C_2H_5)=CH—CH=CH—C_2H_5$	A	175	6.1
1,3,5-Triethylbenzene	A	175	6.8
	C	175	6.6
1,2,4-Triethylbenzene	A	175	7.8
	C	175	7.4
5-Ethyldecane	A	175	4.5
	C	175	4.0
 $n\text{-}C_3H_7—C≡C—C(n\text{-}C_3H_7)=CH_2$	A	175	2.6
$n\text{-}C_3H_7—C≡C—CH=CH—n\text{-}C_3H_7$	A	175	3.9
1,3,5-Tri-*n*-propylbenzene	A	200	7.2
	B	175	6.9
1,2,4-Tri-*n*-propylbenzene	A	200	7.8
	B	175	8.3
Linear $(n\text{-}C_3H_7—C≡CH)_3$	A	200	7.8–8.2 (unresolved)
6-*n*-Propyldodecane	A	200	5.5
	B	175	5.7
4-Methyl-6-*n*-propylundecane	A	200	4.5
	B	175	4.6
 $n\text{-}C_5H_{11}—C≡C—C(n\text{-}C_5H_{11})=CH_2$	A	200	4.3
	A	250	3.6
$n\text{-}C_5H_{11}—C≡C—CH=CH—n\text{-}C_5H_{11}$	A	200	7.0
	A	250	4.6
6-Methyltridecane	A	250	4.2
n-Tetradecane	A	250	4.9
Linear $(n\text{-}C_5H_{11}—C≡CH)_3$	A	250	15.5 (unresolved)
	B	250	6.8 (unresolved)
1,3,5-Tri-*n*-amylbenzene	B	250	4.6
1,2,4-Tri-*n*-amylbenzene	B	250	5.2
Hydrogenated linear $(n\text{-}C_5H_{11}—C≡CH)_3$	B	250	5.4 (sh.)
			6.2
			6.9 (sh.)
$n\text{-}C_5H_{11}—C≡C—CO_2H$	B	175	1.5
$n\text{-}C_5H_{11}—CO_2H$	B	175	1.8
$n\text{-}C_5H_{11}—C≡C—CO—n\text{-}C_5H_{11}$	B	175	9.3

RESULTS AND DISCUSSION

The reaction of monoalkylacetylenes in the presence of nickel-carbonyl-phosphine catalysts yields either aromatic or linear oligomers or mixtures of both in varying ratios depending upon the monomer used.[1] It was relatively easy to identify, characterize, and quantitatively determine the 1,2,4- and 1,3,5-trialkylbenzenes in the trimer fractions by infrared and gas chromatographic analysis. Identification of the linear oligomers presented a more difficult problem. Nevertheless, a partial structure proof of certain linear dimers and trimers was carried out in the hope that a knowledge of the detailed structure of these nonaromatic products might give clues regarding the mechanism of their formation.

From their ultraviolet and infrared spectra, these nonaromatic products were shown[1] to be linear Nieuwland-type condensation polymers[9] of monoalkyl acetylenes—substituted vinyl acetylenes, butadienyl acetylenes, hexatrienyl acetylenes, etc. The presence of the following structural features could be ascertained from their infrared spectra:

Grouping	Infrared band (cm.$^{-1}$)
$R—C≡C—R'$	2220–2240 (weak)
 (conj.)	1600–1625
	950–975
	890–895

Bands for *cis* symmetrically disubstituted double bonds in the neighborhood of 690–730 cm.$^{-1}$ were never found and it was impossible to assign a band to the trisubstituted double bond grouping, although the latter must be present in the trimers and higher oligomers. It was possible to distinguish

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(9) J. A. Nieuwland and R. R. Vogt, *The Chemistry of Acetylene*, Reinhold, New York, 1945.

between the dimers and the higher oligomers by the position of their *trans*-disubstituted olefin band.[10] In the dimers it occurs at 956 ± 4 cm.$^{-1}$ and in the trimers, tetramers, *etc.*, at 970 ± 5 cm.$^{-1}$ (see Table II). This shift is attributed to conjugation of the terminal olefin group with a triple bond in the dimers and a double bond in the higher oligomers. This shift does not occur in the terminal vinylidene band.

Identification of the linear dimers was a relatively simple problem, since a total of only three structural and geometrical isomers is possible. These are the *trans* (I) and the *cis* (II) products of the head-to-head condensation of the two monomers and the terminal vinylidene product (III) resulting from head-to-tail condensation. Gas chromatography showed that the dimer products of 1-butyne, 1-pentyne, and 1-heptyne each contained only two components. Their infrared spectra were consistent with mixtures of I and III. It was also possible to correlate quantitatively the relative concentrations of I and III, as determined from the relative peak areas in their gas chromatograms, with the relative intensities of their 955- and 895-cm.$^{-1}$ infrared bands, respectively. The component with lower relative retention time and hence lower boiling point was always the branched isomer (III). Proof of the structures of the dimers of 1-heptyne was established by catalytic hydrogenation. The two hydrogenated components obtained occurred in the same relative molar ratio (by gas chromatography) as the two original dimers. Uptake of three moles of hydrogen would convert I or II to *n*-tetradecane (IV. R = *n*-C_5H_{11}) and III to 6-methyltridecane (V. R = *n*-C_5H_{11}). The identity of the hydrogenated 1-heptyne dimers to a mixture of IV and V (R = *n*-C_5H_{11}) was shown by their having the same relative retention times, boiling points, and refractive indices as mixtures of the known compounds. Hydrogenation of the 1-heptyne dimers at atmospheric pressure over Lindlar's catalyst formed the expected dihydro derivatives, shown by infrared to be a mixture of *cis,trans*-tetradeca-6,8-diene and 6-methylene-*cis*-tridec-7-ene.

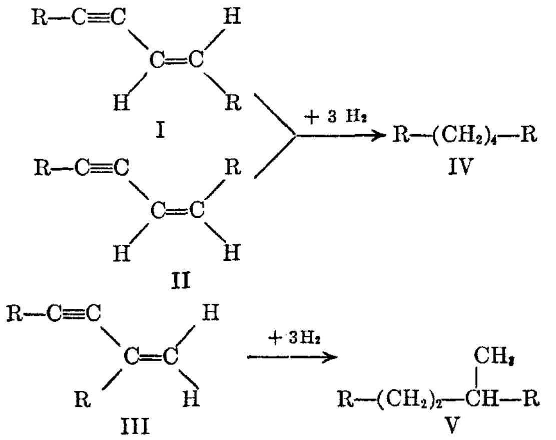
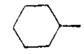
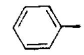
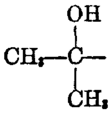
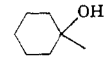
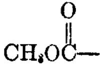


TABLE II

Position of the *trans* Terminal Olefin Band in Linear Acetylene Polymers $(R{-}C{\equiv}CH)_n$

R	*trans* RHC=CHR′ Band in $(R{-}C{\equiv}CH)_2$, cm.$^{-1}$	*trans* RHC=CHR′ Band in $(R{-}C{\equiv}CH)_{3,4,5\ldots}$, cm.$^{-1}$
CH_3—	956	973
C_2H_5—	953	967
n-C_3H_7—	955	970
n-C_4H_9—	958	976
n-C_5H_{11}—	957	975
	957	—
	—	965
 $CH_3{-}C(OH)(CH_3){-}$	—	965
	960	—
$(C_2H_5)_2NCH_2$—	955	975
$CH_3O{-}CH{=}CH$—	—	965
 $CH_3OC({=}O){-}$	958[a]	—

[a] L. Skatteböl, *Acta Chem. Scand.*, **13**, 198 (1959).

As for the linear trimers of monoalkyl acetylenes, the problem is more complex. There are now four possible structural isomers (VI–IX), each of which can exist in at least two different geometrical isomers; this results in a total of twelve possible isomers. A complete proof of structure involves the establishment of the following points: (1) the number of structural isomers present; (2) the nature of the terminal olefin groups—*i.e.*, whether they are *trans, cis*, or vinylidine groups; (3) the position of the alkyl substituent on the middle double bond—*i.e.*, whether it is adjacent to the triple bond, the double bond, or both; and finally (4) the configuration about the middle double bond.

To determine the over-all structures, the trimer fractions of 1-butyne, 1-pentyne, and 1-heptyne were catalytically hydrogenated and analyzed by gas chromatography. Before hydrogenation, the linear trimer peaks were not completely resolved from those of the aromatic components in these mixtures. After hydrogenation, a perfect separation was achieved, the saturated alkanes having much lower retention times than the aromatics, which were not hydrogenated.

Complete hydrogenation of the four possible linear trimers VI–IX, with an uptake of four moles of hydrogen, would yield a total of only three saturated hydrocarbons, X (from VI and VII), XI (from VIII), and XII (from IX). The hydrogenated 1-butyne trimer gave only one nonaromatic peak, while the hydrogenated 1-pentyne and 1-heptyne

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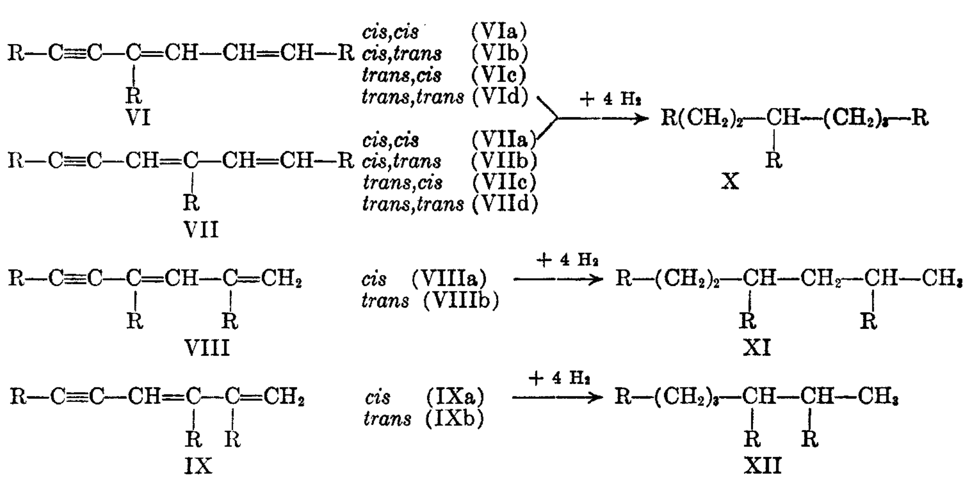
[10] For a detailed discussion of the infrared spectra of conjugated vinylacetylenes, see J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).



$R{-}C{\equiv}C{-}\underset{R}{C}{=}CH{-}CH{=}CH{-}R$ VI: *cis,cis* (VIa), *cis,trans* (VIb), *trans,cis* (VIc), *trans,trans* (VId)

$R{-}C{\equiv}C{-}CH{=}\underset{R}{C}{-}CH{=}CH{-}R$ VII: *cis,cis* (VIIa), *cis,trans* (VIIb), *trans,cis* (VIIc), *trans,trans* (VIId)

$\xrightarrow{+\,4\,H_2} R(CH_2)_2{-}\underset{R}{CH}{-}(CH_2)_3{-}R$ X

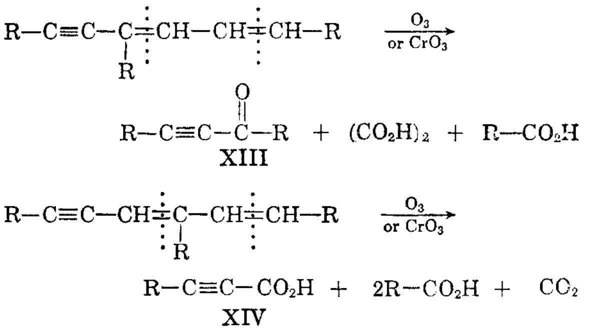
$R{-}C{\equiv}C{-}\underset{R}{C}{=}CH{-}\underset{R}{C}{=}CH_2$ VIII: *cis* (VIIIa), *trans* (VIIIb) $\xrightarrow{+\,4\,H_2} R{-}(CH_2)_2{-}\underset{R}{CH}{-}CH_2{-}\underset{R}{CH}{-}CH_3$ XI

$R{-}C{\equiv}C{-}CH{=}\underset{R}{C}{-}\underset{R}{C}{=}CH_2$ IX: *cis* (IXa), *trans* (IXb) $\xrightarrow{+\,4\,H_2} R{-}(CH_2)_3{-}\underset{R}{CH}{-}\underset{R}{CH}{-}CH_3$ XII

trimers each gave two nonaromatic peaks, the one with higher retention time being larger. Evidently, not all of the possible structural isomers VI–IX were present. Several of the possible saturated hydrocarbons X–XII were synthesized and compared with the hydrogenated trimers. Synthetic 5-ethyldecane (X. $R = C_2H_5$) was identical chromatographically with the hydrogenated linear product of 1-butyne trimer. Synthetic 6-propyldodecane (X. $R = n\text{-}C_3H_7$) and 4-methyl-6-propylundecane (XI. $R = n\text{-}C_3H_7$) were found to have retention times on two different columns identical with the larger and smaller components, respectively, of the hydrogenated linear 1-pentyne trimer mixture. By analogy, the two hydrogenated linear 1-heptyne trimers were also assumed to have structures X ($R = n\text{-}C_5H_{11}$) and XI ($R = n\text{-}C_5H_{11}$). There was no evidence for the presence of the third structure XII among any of the hydrogenated linear trimers. It may thus be concluded that structure IX was not included among the linear trimers.

Infrared analysis of the linear trimers of 1-pentyne and 1-heptyne helped to further limit the number of structures. As mentioned above, of the three possible terminal olefin groupings, bands for only the *trans* terminal olefin at 975 cm.$^{-1}$ and the vinylidine group at 895 cm.$^{-1}$ were observed in these products. All *cis* terminal olefin structures (VIa, VIc, VIIa, VIIc) could then be excluded. In addition, the ratio of the 975- to 895-cm.$^{-1}$ band intensities in the infrared was proportional to the relative concentrations of the hydrogenated products, X to XI (where $R = n\text{-}C_3H_7$ or $n\text{-}C_5H_{11}$), determined chromatographically, supporting the assumption that structure IX was not present, and narrowing down the possible structures to VIb, VId, VIIb, VIId, VIIIa, and VIIIb. The linear 1-butyne trimer contained only the 975-cm.$^{-1}$ *trans* band which limits the possibilities for this product to structures VIb, VId, VIIb, and VIId.

In order to establish the location of the central R group in the linear trimers, a linear trimer mixture was partially degraded by ozonization and chromic acid oxidation. As double bonds can be selectively cleaved in the presence of triple bonds by ozone[11] and by chromium trioxide in acetic acid,[12] it was hoped that the two double bonds in the linear trimers could thus be cleaved, leaving the acetylenic fragments intact. An acetylenic ketone (XIII) would be the expected product if the R group were on the carbon adjacent to the triple bond and an acetylenic acid (XIV) would result from those isomers having R substitution adjacent to the terminal double bond, *e.g.*,



$R{-}C{\equiv}C{-}\underset{R}{C}{=}CH{-}CH{=}CH{-}R \xrightarrow[\text{or } CrO_3]{O_3} R{-}C{\equiv}C{-}\overset{\overset{O}{\|}}{C}{-}R + (CO_2H)_2 + R{-}CO_2H$ XIII

$R{-}C{\equiv}C{-}CH{=}\underset{R}{C}{-}CH{=}CH{-}R \xrightarrow[\text{or } CrO_3]{O_3} R{-}C{\equiv}C{-}CO_2H + 2R{-}CO_2H + CO_2$ XIV

A sample of the trimer mixture from 1-heptyne was ozonized in pentane-methanol at −78° until two equivalents of ozone had been absorbed. After oxidative decomposition of the ozonide and separation of the products by extraction, fractionation, and gas chromatography, a 75% yield of products was obtained comprising about 75% hexanoic acid and its methyl ester, 20% 7-tridecyn-6-one (XIII. $R = n\text{-}C_5H_{11}$), 5% triamylbenzenes (present in the original 1-heptyne trimer mixture), and traces of higher boiling acids, possibly including 1-octynoic acid (XIV. $R = n\text{-}C_5H_{11}$).

The linear 1-heptyne trimers were also oxidized with chromium trioxide in acetic acid. The product mixture contained about 70% hexanoic acid, 25% 7-tridecyn-6-one, and 5% 1-octynoic acid. The two acetylenic products in these reactions were identified by comparison with authentic synthesized

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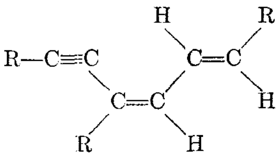
(11) F. Bohlmann and H. Sinn, *Ber.*, **88**, 1869 (1955).

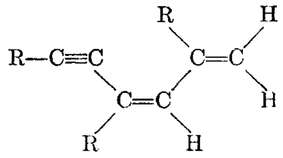
(12) H. K. Black and B. C. L. Weedon, *J. Chem. Soc.*, 1785 (1953).

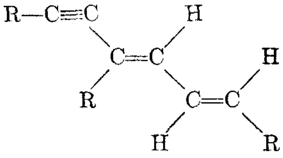
samples using infrared and gas chromatography. However, it was found that treatment of the ketone product, 7-tridecyn-6-one, under the same oxidizing conditions produced small amounts of 1-octynoic acid. Therefore, most of this acid probably resulted from attack on the ketone degradation product rather than direct oxidation of the original 1-heptyne trimer.

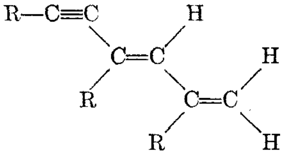
The occurrence of linear 1-heptyne trimer structures with the central R group adjacent to the triple bond (VI and VIII) is amply demonstrated by these degradation studies. Structures with the central R group adjacent to the terminal double bond (VII and IX), although not completely ruled out, must be present in very small amounts if indeed they do occur. It seems reasonable to assume that this applies generally to the linear trimers—*i.e.*, that structures with the central R group adjacent to the triple bond predominate.

Having ruled out all structures but VIb, VId, VIIIa and VIIIb, we are finally left with the problem of establishing the stereochemistry about the central double bond—*i.e.*, distinguishing between the two pairs of isomers VIb, VIIIa and VId, VIIIb. This has not been accomplished, primarily because samples of the pure isomers have not been isolated; they are not readily separated from one another and from the aromatic trimers even by gas chromatography. Comparison of the ultraviolet spectra of the pure isomers with compounds of known structure or total synthesis of one of the stereoisomers and direct comparison would readily complete the structure proof. In a number of related reactions in which metal catalyzed additions to an acetylenic bond occur[8,13] the product is always that which would result from a *cis* addition. The absence of *cis* terminal olefin groups in these oligomers demonstrates that the incorporation of the terminal olefinic monomer unit must occur solely by a *cis* addition to the triple bond.[14]

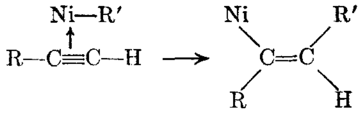

VIb

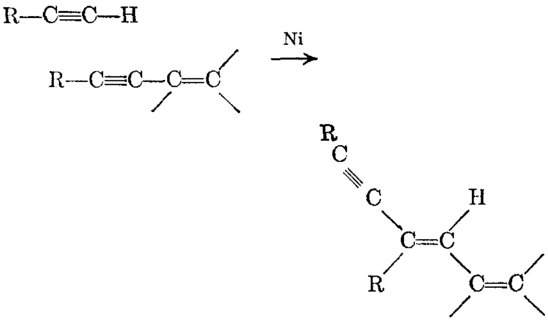

VIIIa


VId


VIIIb

If we assume that the central monomer unit is also introduced by a *cis* addition to its triple bond, two general schemes for this can be written, designated as (1) and (2) below:


(1)


(2)

In (1) the central monomer unit is introduced *intact* by *cis* addition of the catalyst-polymer chain to its triple bond, resulting in structures VIb and VIIIa. In scheme (2) the *cis* condensation of the third monomer unit across the triple bond of the central monomer unit already contained in the polymer chain gives structures VId and VIIIb for the linear trimers. The essential difference between (1) and (2) is that the former involves insertion of each additional acetylene monomer as a unit whereas in the latter the R—C≡C— and the H— are introduced successively from two different acetylenes. It follows that scheme (1) requires one hydrogen transfer per polymer chain while (2) requires one hydrogen transfer per monomer unit added.

The evidence appears to favor structures VIb and VIIIa and thus scheme (1). These structures would seem more likely to be alternative products to the closely related cyclization to aromatic derivatives,[1] as the 1 and 6 carbon atoms in the conjugated system approach one another very closely in certain conformations of VIb and VIII a. Reasonable bonding distances between these carbon atoms cannot be achieved in VId and VIIIb. This same argument may be used to explain our failure to obtain the other linear 1-butyne trimer structure (VIIIa. R = C_2H_5). Presumably, in the case of the 1-butyne trimer (which is about 80% aromatic), the R group is so small that formation of the symmetrical 1,3,5-triethylbenzene is greatly favored over VIIIa. It is also more difficult to assign a specific role to the Ni catalyst in scheme (2), which is analogous to a base-catalyzed condensation reaction. Scheme (1), on the other hand, is very similar to propagation mechanisms proposed[15] for the polymerization of olefins by Ziegler-Natta catalysts. In this reaction, however, the initiation and termination steps prob-

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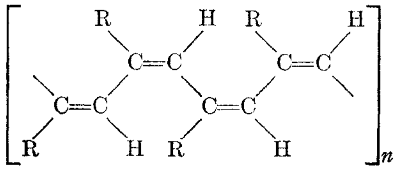
[13] E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 48 (1951).

[14] An alternate possibility, of course, is that the metal complex may catalyze *cis, trans* isomerization of the terminal double bond. This can be ruled out, however, as *cis*-2-butene is not converted to the *trans* isomer by $Ni(CO)_2(Ph_3P)_2$ in cyclohexane under conditions suitable for the polymerization of propyne or 1-butyne.

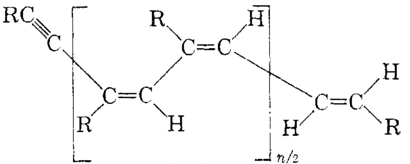
[15] See, for example, G. Natta, *J. Inorg. Nuclear Chem.*, **8**, 589 (1958); W. L. Carrick, A. G. Chasar, and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 5319 (1960); P. Cossee, *Tetrahedron Letters*, No. **17**, 12 (1960).

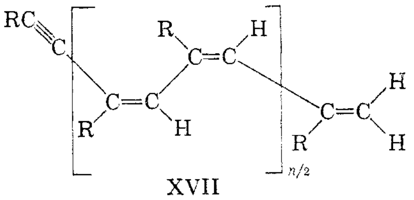
ably involve metal hydride intermediates. In addition to the above objections, structures VId and VIIIb and scheme (2) appear to be unlikely in view of the results of kinetic and deuterium isotope studies which will be reported in future papers in this series.

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


XV

The infrared bands for the terminal monomer units (R—C≡C—, *trans*—CH=CHR and —CR=CH_2) decrease in intensity as the number of monomer units in the chain increases. However, the position and intensity of the double bond band at 1625 cm.$^{-1}$ does not change in the higher oligomers. In their studies on the linear high polymers of 1-hexyne, Natta *et al.*[16] have assigned a band at the same place to the double bonds in the polymer resulting from the stereospecific head-to-tail coupling of monomer units by *cis* additions to the triple bonds (structure XV) in the manner of scheme (1) above. It would then appear that the higher oligomers formed in this reaction are most likely to be mixtures of structures XVI and XVII. If this latter assumption is valid, it has great significance with regard to the mechanism of formation of these linear products. Studies of both the catalyst activation and polymerization processes will be presented in later papers, where more detailed mechanisms for these reactions will be considered.


XVI


XVII

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

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

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

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

E. C. COLTHUP AND L. S. MERIWETHER

Received June 5, 1961

The polymerization of HC≡C—$(CH_2)_n$—C≡CH ($n = 2$-5) with dicarbonylbis(triphenylphosphine)nickel $Ni(CO)_2(Ph_3P)_2$ in refluxing cyclohexane yields both low and high molecular weight polymer products containing linear conjugation (n = 2-5) and aromatic fused ring structures (n = 3, 4 only), the latter resulting from a novel cyclization reaction. Copolymerization with monoalkylacetylenes affords analogous products.

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

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

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

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

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

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