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POLYYNES

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I. INTRODUCTION

Polyacetylenes or polyynes are compounds of general formula $R-[C\equiv C]_n-R'$, the molecules of which are made up of carbon atoms linked together by alternating single and triple bonds.

This class of compounds attracted the attention of research workers long ago. As early as 1885 Baeyer [1] tried to obtain compounds containing a large number of acetylenic bonds and consisting solely of carbon atoms. He suggested that these compounds would possess characteristic properties, being "explosive diamonds".

From propiolic acid, Baeyer was able to obtain, *via* butadiynedicarboxylic acid, butadiyne itself, which shows a great tendency to polymerise. When he tried to prepare octatetrayne, he was unable to isolate even the corresponding dicarboxylic acid, since it is immediately converted into an insoluble black mass. The instability of such compounds led Baeyer to formulate his strain theory.

Baeyer's work on the synthesis of polyacetylenic compounds was followed by a considerable break, with only isolated papers appearing. Comparatively recently, interest in this class of compounds has been rearoused; the active development of the chemistry of acetylene created the preconditions for the synthesis of polyacetylenic compounds; thus butynediol and hexynediol, the starting materials for the preparation of diynes and triynes have become readily available.

An important stimulus to the resumption of work in this field was the discovery of representatives of this group of compounds in Nature. In 1935 Vil'yams *et al.* [2] isolated from the essential oil of *Lachnophyllum gossypinum* a crystalline substance having the structure

$$CH_3-CH_2-CH_2-C\equiv C-C\equiv C-CH=CH-COOCH_3 .$$

This discovery resulted in a systematic study of polyacetylenic compounds by the schools of Jones in England and of Bohlmann in Germany.

At the present time polyynes containing up to 10 conjugated triple bonds in the molecule have been synthesised. Great effort has been required to investigate the properties of such compounds, the lifetimes of most of which are measured in seconds under ordinary conditions. During recent years interesting electrical and magnetic properties have been discovered in the polyynes.

The present survey covers work on the synthesis of polyynes from the simplest members of the polyynes series to polymers, and including macrocyclic compounds containing triple bonds. Work on the synthesis of natural polyacetylenic compounds is not considered in the review, since this would make it too long. Readers can obtain a detailed idea of these papers from the exhaustive reviews of Bohlmann[3], Jones[4], and Sörensen[5].

II. SYNTHESIS OF POLYYNES

Let us consider briefly the main methods for synthesising polyynes, which paved the way for broad investigations in this field.

In 1870 Glaser[6] observed that the copper derivative of phenylacetylene is smoothly oxidised by atmospheric oxygen to diphenylbutadiyne:

$$2C_6H_5C{\equiv}C{-}Cu \xrightarrow{O_2} C_6H_5C{\equiv}C{-}C{\equiv}C{-}C_6H_5.$$

Oxidative dehydrocondensation is still, in various versions, the main reaction of polyacetylenic synthesis.

Another important reaction was discovered by Cadiot and Chodkiewicz[7], who showed that monosubstituted acetylenes react with 1-bromoacetylenes in the presence of catalytic quantities of cuprous salts to give high yields of diacetylenic compounds:

$$RC{-}C{\equiv}CH + Br{-}C{\equiv}C{-}R \xrightarrow{Cu^+} R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

A classic method for obtaining a triple bond is the dehydrohalogenation of 1,1- or 1,2-dihalogenated compounds with strong bases[8]. Jones employed this method to synthesise polyynes, for example[9]:

$$CH_3CHCl{-}[C{\equiv}C]_4{-}CHClCH_3 \xrightarrow{NaNH_2} CH_3{-}[C{\equiv}C]_5{-}CH_3.$$

Variation and combination of these fundamental methods have made it possible to synthesise many polyacetylenic hydrocarbons.

1. Buta-1,3-diyne (Diacetylene)

The simplest member of the polyyne series is butadiyne, which was first obtained by Baeyer[1] in low yield by the decarboxylation of its dicarboxylic acid. A more convenient route for the synthesis of butadiyne is the oxidation of metal derivatives of acetylene. Straus and Kollek[10] oxidised cuprous acetylide with cupric chloride. Since both hydrogen atoms of acetylene can be replaced by copper, oxidation can result in the repeated doubling of the carbon chain of acetylene right up to the formation of macromolecular products. Butadiyne is an intermediate product in this reaction; polymeric compounds are the main products.

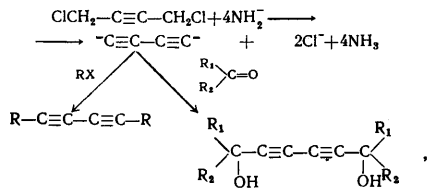
Schlubach and Wolf[11] obtained a 5% yield of butadiyne by oxidising sodium acetylide with air in liquid ammonia (in the presence of ferric oxide as catalyst).

Since this procedure does not give satisfactorily yields (owing to the fact that the butadiyne which is formed immediately reacts with sodamide), these workers attempted to effect oxidation with other agents, of which potassium permanganate proved to be the best, giving yields of 35% of butadiyne. In addition, 17.6% of a polymer was formed, representing more far reaching oxidative condensation of the sodium derivative of butadiyne formed in the reaction. The polymer is a black product, similar in appearance to coal, which does not burn in the flame of a burner.

A more convenient method for synthesising butadiyne was discovered by Keyssner[12] and developed by Johnson[13]. It consists in the dehydrochlorination of 1,4-dichlorobut-2-yne, which is readily obtainable from the corresponding diol. The nature of the alkaline reagent was found to play an important part. Use of aqueous solutions of caustic alkalis $Ca(OH)_2$ and K_2CO_3 makes possible a 60% yield of butadiyne.

Butadiyne decomposes rapidly close to its boiling point, and therefore it can be stored only at temperatures below -25°.

If dehydrohalogenation is carried out with sodamide in liquid ammonia, the disodium derivative of butadiyne is formed, and this can then react with alkyl halides to yield symmetrical conjugated butadiyne hydrocarbons and with ketones to give glycols



where R = C_2H_5, C_4H_9, $CH_2{=}CHCH_2$; $R_1 = C_6H_5CH{=}CH$; $R_2 = CH_3$.

Attempts to make disodiobutadiyne react with ethylene oxide, propylene oxide, and epichlorohydrin were unsuccessful. There is obviously no analogy here between the behaviour of sodium acetylide and the corresponding derivatives of butadiyne.

Such a difference may be assumed to be due to the greater acidity of butadiyne, which on the one hand diminishes the reactivity of its anion as a nucleophilic reagent towards carbonyl compounds, and on the other diminishes the possibility of reaction with ketones in the enolic form, which are acids.

It is interesting that Mansfield and Whiting[14], in an investigation of the relative strength of several unsaturated acids, in particular of acetylenic acids, established that the latter are stronger than their ethylenic and saturated analogues. The dissociation constants ($10^5 K$) these acids[15] are compared in Table 1.

Introduction of a second acetylenic bond into the acid molecule increases the dissociation constant, but the further increase in acidity of a polyacetylenic acid is insignificant.

Before Jones's work, only four monosubstituted butadiynes had been obtained.

$$\underset{(I)}{HOCR_1R_2C{\equiv}C{-}C{\equiv}CH};\quad \underset{(II)}{R_1{-}C{\equiv}C{-}C{\equiv}C{-}R_2}$$

$$\underset{(III)}{RC{\equiv}C{-}C{\equiv}CH}$$

TABLE 1.

R	RC≡C–COOH	RCH=CH–COOH	RCH_2CH_2COOH
CH_3	246	5.6	1.5
$CH_3(CH_2)_3$	140	1.5	1.4
Ph	590	8.6	2.3
H	1400	5.5	1.2

2-Methylhexa-3,5-diyn-2-ol (I: $R_1 = R_2 = CH_3$) was prepared by Zal'kind and Aizikovich[16] by heating the glycol (II: $R_1 = R_2 = CH_3CHOH$) with alkaline reagents.

Penta-1,3-diyne (III: $R = CH_3$) was prepared by Schlubach and Wolf from sodium acetylide and methylene iodide or prop-2-ynyl bromide[17]. They also synthesised phenylbutadiyne[18].

Jones[19] synthesised monosubstituted butadiynes by dehydrohalogenation of 1,4-dichlorobut-2-yne with sodamide in liquid ammonia. With three moles of the sodamide the main product is the monosodium derivative of butadiyne; addition of a halide yields the corresponding substituted butadiyne. Thus methyl iodide gave the extremely unstable penta-1,3-diyne (III: $R = CH_3$).

Hexa-1,3-diyne and octa-1,3-diyne (III: $R = C_2H_5$ and C_4H_9) were prepared from the corresponding bromides in 45% yield.

Allyl bromide probably forms hept-1-ene-4,6-diyne (III: $R = CH_2{=}CHCH_2$), which was not identified owing to its ease of decomposition.

Carbonyl compounds also react with the monosodium derivative of butadiyne. Thus acetone gave 2-methylhexa-3,5-diyn-2-ol (I: $R_1 = R_2 = CH_3$); with benzophenone, butyraldehyde, and formaldehyde the corresponding alcohols were obtained.

It was found that in all these reactions an appreciable quantity of the corresponding diacetylenic glycols was formed. These are of considerable interest, since they enable us to pass to triacetylenic compounds.

But a more convenient and simpler method of obtaining diacetylenic glycols is the oxidative condensation of acetylenic alcohols, a reaction used by Zal'kind and Aizikovich[20,21]. They employed air as oxidising agent, and carried out the dimerisation in the presence of cuprous chloride

$$2HO{-}CMe_2C{\equiv}CH + O_2 \xrightarrow{CuCl,\ NH_4Cl} HO{-}CMe_2C{\equiv}C{-}C{\equiv}C{-}CMe_2OH.$$

Jones and Boden[22] improved this method by carrying out the reaction at a higher temperature (~55°). However, rise in temperature results in resinification of the compounds obtained.

Zal'kind[20] made a fundamental improvement in this method by using pure oxygen for the oxidation, which increased the rate of condensation, since oxygen acts as an acceptor for the hydrogen evolved in the reaction. In the case of 2-methylbut-3-yn-2-ol it was shown that the rate of dimerisation is increased approximately sixfold compared with oxidation by air.

The early work on the oxidative dimerisation of acetylenic alcohols[23] was carried out in a solution of the complex of NH_4Cl and cuprous chloride at pH 3 before addition of the acetylenic compound. The pH can be varied by adding hydrochloric acid or ammonia; at pH > 5 copper derivatives of the acetylenes are usually precipitated, but the oxidative dimerisation takes place smoothly.

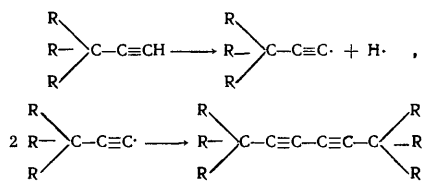
Zal'kind[20] found that reaction occurs also in concentrated ammoniacal solution, but an alkaline solution (cuprammonium, a strong base) in several cases breaks down the reaction products, which affects the yield.

The reaction can also be carried out at higher acidities without appreciable diminution in the reaction velocity or the yield. Acidity does not prevent oxidative dimerisation, but different products can be formed depending on the medium[24]. Thus the following products can be formed, depending on the pH, by the oxidative dehydrocondensation of hex-2-en-5-yn-4-ol:

$$CH_3CH{=}CH{-}CH(OH){-}C{\equiv}CH \xrightarrow{pH\ 6.5;\ 93\%} [CH_3CH{=}CHCH(OH)C{\equiv}C]_2$$
$$\downarrow\ pH1;\ 81\%$$
$$[CH_3CH(OH)CH{=}CH{-}C{\equiv}C]_2.$$

Several investigations have been made of the mechanism of oxidative dehydrocondensation.

Zal'kind and his collaborators[25] consider that the process starts with the breakdown of the acetylenic compound into radicals, which then recombine to form a diacetylenic derivative:



They assume that the formation of diacetylenic compounds takes place more readily the stronger the positive inductive effect of the groups or atoms in the vicinity of the triple bond. The hydrogen evolved in the reaction is either used up in hydrogenating part of the initial acetylene or else is oxidised by atmospheric oxygen to water. The role of copper salts and of atmospheric oxygen remains obscure in this mechanism.

In the case of the conversion of propyne into hexadiyne in the presence of cuprous chloride and atmospheric oxygen Mkryan and Papazyan[26] showed that formation of the diacetylenic compound is a result of interaction of the monosubstituted acetylenic derivative with the partly oxidised catalyst.

Klebanskii *et al.*[27] consider that the formation of diacetylenic compounds in aqueous solution takes place by an ionic–radical mechanism. First of all, acetylide ions are formed. If the reaction is carried out in acid medium, as in the oxidation of acetylenic compounds in the presence of cuprous chloride and atmospheric oxygen, for example, the acetylide ion may result from secondary dissociation of the complex anion $[R{-}C{\equiv}C(CuCl.NH_4Cl)]^-$ which is formed. The acetylide ions are then oxidised by cupric ions to radicals, which recombine to yield a molecule of the diacetylenic derivative. The whole process can be represented by the following equations:

$$2Cu^+ + {}^1/_2O_2 + H_2O \longrightarrow 2Cu^{2+} + 2OH^-,$$
$$R{-}C{\equiv}CH \rightleftharpoons R{-}C{\equiv}C^- + H^+,$$
$$R{-}C{\equiv}C^- + 2Cu^{2+} \longrightarrow R{-}C{\equiv}C\cdot + Cu^+,$$
$$R{-}C{\equiv}C\cdot + \cdot C{\equiv}C{-}R \longrightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

Clearly, formation of a diacetylenic compound in the presence of cuprous salts cannot take place in the absence of oxygen. The use of cuprous salts and also of atmospheric oxygen is not essential, as has been confirmed experimentally in the case of the reaction of monosubstituted derivatives of acetylene with cupric salts. In this case ammonia or an amine (pyridine, triethylamine) must be added to combine with the protons liberated in the reaction:

$$2Cu^{2+}+2R-C\equiv CH \longrightarrow 2Cu^{+}+R-C\equiv C-C\equiv C-R+2H^{+}.$$

This is unnecessary with cuprous salts, since hydroxide ions are formed as a result of the oxidation of univalent copper to the bivalent state.

2. Hexa-1,3,5-triyne (Triacetylene)

Grignard *et al.*[28] reported, without going into details, the synthesis of 1-iodo- and 1-phenyl-hexa-1,3,5-triyne.

Hunsmann[29] observed the formation of hexatriyne as a side-product in the electrical cracking of methane. The hexatriyne was isolated in the form of its addition product with acetone, 2,9-dimethyldeca-3,5,7-triyne-2,9-diol:

$$HO(CH_3)_2C-(C\equiv C)_3-C(CH_3)_2OH\ .$$

This same worker described the synthesis of hexatriyne from dichlorohexadiyne[29].

Schlubach and Franzen[30] found that reaction of the Grignard reagent from phenylacetylene with 1-iodo-2-phenylacetylene in the presence of cobaltous chloride yields diphenylbutadiyne. If, however, the starting materials are two moles of the Grignard reagent and diiodoacetylene, diphenylhexatriyne is formed, but another reaction also takes place:

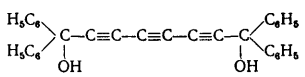
$$2C_6H_5C\equiv C-MgBr + IC\equiv CI \rightleftarrows C_6H_5C\equiv CI + BrMgC\equiv CMgBr\ .$$

Boden[31] obtained 1,6-diphenylhexa-2,4-diyne-1,6-diol, from which, after preliminary treatment of the diol with thionyl chloride and subsequent elimination of hydrogen halide with alcoholic alkali, he obtained diphenylhexatriyne:

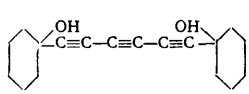
$$C_6H_5CHCl-C\equiv C-C\equiv C-CHCl-C_6H_5 \rightarrow C_6H_5-C\equiv C-C\equiv C-C\equiv C-C_6H_5.$$

In comparison with the extremely unstable hexatriyne, the diphenyl derivative is quite stable, remaining unchanged in air and in the light, and melting at 95°.

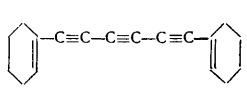
Kuhn and Zahn[32] described the tetraphenyloctatriynediol



Bohlmann[33] obtained diphenyl- and dicyclohexenyl-hexatriynes, using 1,6-dichlorohexa-2,4-diyne as starting material for the synthesis of hexatriyne, and sodamide for the dehydrochlorination. At the instant of formation hexatriyne condenses with ketones and aldehydes. Thus cyclohexanone yields bis-(1-hydroxycyclohexyl)hexatriyne



Elimination of water from this diol gives dicyclohex-1-enylhexatriyne:



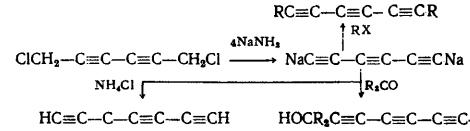
With benzophenone a good yield of 1,1,8,8-tetraphenylocta-2,4,6-triyne-1,8-diol was obtained, which was also prepared by Kuhn[32].

Diphenylhexa-2,4-diyne-1,6-diol was converted into diphenylhexatriyne by the series of reactions

$$C_6H_5CH(OH)-C\equiv C-C\equiv C-CH(OH)C_6H_5 \rightarrow$$
$$\rightarrow C_6H_5CHCl-C\equiv C-C\equiv C-CHClC_6H_5 \rightarrow$$
$$\rightarrow C_6H_5-C\equiv C-C\equiv C-C\equiv C-C_6H_5.$$

All these compounds are relatively stable.

Jones *et al.*[34] applied to the synthesis of triacetylenic compounds the method previously worked out for obtaining butadiyne:



When an excess of sodamide is used, a disodium derivative is obtained, which can be converted into a disubstituted hexatriyne or a triacetylenic alcohol. The isolation of hexatriyne is considerably more complicated than its synthesis, since this substance is very unstable, and polymerises even at -50°.

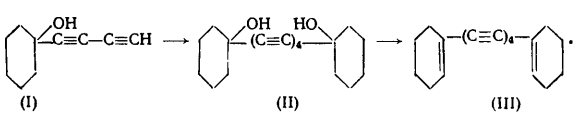
Diphenylhexatriynes are far more stable than the aliphatic hexatriynes[35,36].

3. Octa-1,3,5,7-tetrayne (Tetraacetylene)

Until 1951 the sole tetraacetylenic derivative was the very unstable dicarboxylic acid described by Baeyer and Landsberg[1].

Dimethyl- and diphenyl-octatetrayne were synthesised by Schlubach and Franzen[37]. A 78% yield of the former was obtained by the reaction of pentadiynylmagnesium bromide with cuprous chloride. The instability of the decatetrayne and the impossibility of studying its properties compelled these workers to synthesise diphenyloctatetrayne, which proved to be a quite stable compound melting at 113°.

Substituted tetraynes were also synthesised by Bohlmann[38] by the oxidative dimerisation of diacetylenic compounds. Thus bis-(1-hydroxycyclohexyl)octatetrayne was prepared by condensing butadiynylsodium with cyclohexane to form 1-butadiynylcyclohexanol (I), which on oxidation in air in the presence of cuprous chloride yielded the tetraacetylenic alcohol (II), elimination of water from which gave dicyclohex-1-enyloctatetrayne (III):



The diol (II) is a relatively stable compound melting at 151° without decomposition. The hydrocarbon (III) obtained from it is also stable, and is yellow, with m.p. 127°.

Condensation of butadiyne with formaldehyde yields penta-2,4-diynol (IV), a very unstable product with a tendency to polymerise. Dimerisation converts (IV) into the

extraordinarily reactive deca-2,4,6,8-tetrayne-1,10-diol (V), which in the light is instantly transformed into an insoluble dark blue substance:

$$\underset{\text{(IV)}}{HOCH_2{-}C{\equiv}C{-}C{\equiv}CH} \longrightarrow \underset{\text{(V)}}{HOCH_2{-}(C{\equiv}C)_4{-}CH_2OH}.$$

Jones *et al.*[34] prepared substituted tetraynes (VI) by oxidative dimerisation with atmospheric oxygen in the presence of cuprous chloride and ammonium chloride:

$$\underset{\text{(VI)}}{R{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}R}.$$

In this way a good yield of deca-2,4,6,8-tetrayne (VI: R = CH_3) was obtained from penta-1,3-diyne.

These workers[34] synthesised tetraacetylenic glycols. It is interesting that they were able to obtain from 2-methylhexa-3,5-diyn-2-ol a quantitative yield of the corresponding diol [VI: R = $(CH_3)_2COH$] only on replacing air by oxygen in the oxidative dimerisation. In a similar manner a low yield of the diol (VI: R = CH_3CH_2CHOH) was obtained from the secondary alcohol. Unsubstituted octatetrayne was obtained by Jones[39] as a solution in heptane by synthesising it as follows:

$$HOCH_2(C{\equiv}C)_3CH_2OH \longrightarrow ClCH_2(C{\equiv}C)_3CH_2Cl \rightarrow H(C{\equiv}C)_4H.$$

Examination of the ultraviolet spectrum of the heptane solution confirms the formation of octatetrayne by this method.

4. Deca-1,3,5,7,9-pentayne (Pentaacetylene)

A solution of decapentayne was obtained by Jones[39] by the series of reactions

$$HOCH_2{-}(C{\equiv}C)_4CH_2OH \xrightarrow[C_5H_5N]{SOCl_2} ClCH_2{-}(C{\equiv}C)_4{-}CH_2Cl \xrightarrow{NaNH_2} H{-}(C{\equiv}C)_5{-}H.$$

This method cannot be used to add on further ethynyl groups, since the yield of the hydrocarbons falls rapidly with increasing number of acetylenic bonds, in the sequence: butadiyne (60%), hexatriyne (50%), octatetrayne (12%), decapentayne (3%). Moreover, the latter hydrocarbons were not isolated in the pure form because of their great instability.

It was noted above that the diphenyl derivatives of octatetrayne are more stable than the dimethyl derivatives. An attempt was made to prepare a phenylated decapentayne.

Schlubach and Franzen[40] synthesised 1,10-diphenyldeca-1,4,6,9-tetrayne-3,8-diol from phenylpropiolaldehyde and butadiynylenedimagnesium dibromide:

$$C_6H_5{-}C{\equiv}C{-}CH(OH){-}C{\equiv}C{-}C{\equiv}C{-}CH(OH){-}C{\equiv}C{-}C_6H_5.$$

The diol was converted into the dichloride, and the latter treated with alcoholic alkali. Chromatographic purification resulted in the isolation of diphenyldecapentayne, a dark yellow compound which is comparatively stable to light and heating.

Bohlmann[41] found that a still more stable pentayne could be obtained by introducing a t-butyl group as substituent:

$$\underset{\text{(I)}}{(CH_3)_3C{-}C{\equiv}C{-}CHO} + BrMgC{\equiv}C{-}C{\equiv}C{-}MgBr \longrightarrow$$

$$\longrightarrow \underset{\text{(II)}}{(CH_3)_3C{-}C{\equiv}C{-}CH(OH){-}C{\equiv}C{-}C{\equiv}C{-}CH(OH){-}C{\equiv}C{-}C(CH_3)_3} \longrightarrow$$

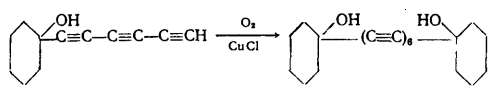
$$\longrightarrow \underset{\text{(III)}}{(CH_3)_3C{-}C{\equiv}C{-}CHCl{-}C{\equiv}C{-}C{\equiv}C{-}CHCl{-}C{\equiv}C{-}C(CH_3)_3} \longrightarrow$$

$$\longrightarrow \underset{\text{(IV)}}{(CH_3)_3C{-}(C{\equiv}C)_5{-}C(CH_3)_3}.$$

A good yield of the decapentayne (IV) was obtained. It melts without decomposition at 129°–130°.

5. Dodeca-1,3,5,7,9,11-hexayne (Hexaacetylene)

Bohlmann[33] obtained 1,12-bis-(1-hydroxycyclohexyl)-dodecahexayne by condensing hexatriyne with cyclohexanone and then dimerising the 1-hexatriynylcyclohexanol thus formed:



Unfortunately, this diol could not be obtained in the pure form, since it is converted into an insoluble black polymer even in the dark at 0°. Bohlmann considers[33] that the synthesis of compounds having a larger number of conjugated triple bonds is impossible, since, owing to the increasing energy content of such substances, they tend to pass into compounds containing less energy. This view was held also by Jones, who remarked that, as new members of the polyyne series are obtained, it becomes more and more difficult to isolate them owing to their poor solubility and increasing instability. But a little later this barrier was surmounted: these same workers obtained higher polyyne homologues containing stabilising substituents in the molecule.

Being now convinced of the extreme instability of tetradecahexayne, obtained by the oxidative dimerisation of heptatriyne[39], Jones worked out a synthesis of diphenyldodecahexayne[42] starting from phenylhexatriyne:

$$PhC{\equiv}C{-}C{\equiv}C{-}C{\equiv}CH \xrightarrow[O_2]{CuCl} Ph(C{\equiv}C)_6Ph.$$

Diphenyldodecahexayne proved to be very stable in comparison with the dimethyl analogue.

Bohlmann[41] obtained the di-t-butylhexayne by the following reactions:

$$(CH_3)_3C{-}C{\equiv}C{-}CHO + BrMgC{\equiv}CCH_2OMgBr \rightarrow (CH_3)_3C{-}C{\equiv}C{-}CHOHC{\equiv}C{-}CH_2OH \xrightarrow{SOCl_2}$$

$$\longrightarrow (CH_3)_3C{-}C{\equiv}C{-}CHCl{-}C{\equiv}C{-}CH_2Cl \xrightarrow{NaNH_2} (CH_3)_3C{-}(C{\equiv}C)_2{-}C{\equiv}CH \xrightarrow[CuCl,\ NH_4Cl]{O_2}$$

$$\longrightarrow (CH_3)_3C{-}(C{\equiv}C)_6{-}C(CH_3)_3.$$

The resulting 2,2,15,15-tetramethylhexadecahexayne was very stable, fusing at 140° and being converted into a black mass.

6. Tetradeca-1,3,5,7,9,11,13-heptayne (Heptaacetylene)

2,2,17,17-Tetramethyloctadeca-3,5,7,9,11,13,15-heptayne was obtained by Bohlmann[41] as follows:

$$(CH_3)_3C{-}(C{\equiv}C)_2{-}CHO + BrMgC{\equiv}C{-}C{\equiv}CMgBr \rightarrow (CH_3)_3C{-}(C{\equiv}C)_2CH(OH){-}(C{\equiv}C)_2{-}$$

$$-CH(OH){\cdot}(C{\equiv}C)_2{-}C(CH_3)_3 \xrightarrow{SOCl_2}$$

$$\longrightarrow (CH_3)_3C{-}(C{\equiv}C)_2CHCl{-}(C{\equiv}C)_2{-}CHCl{-}(C{\equiv}C)_2{-}C(CH_3)_3 \xrightarrow{NaHCO_3}$$

$$\longrightarrow (CH_3)_3C{-}(C{\equiv}C)_7{-}C(CH_3)_3.$$

This compound is remarkably stable to light and heat, being converted into an insoluble black mass only on being heated above 150°.

7. Hexadeca-1,3,5,7,9,11,13,15-octayne (Octaacetylene)

Diphenylhexadecaoctayne $C_6H_5-(C\equiv C)_8-C_6H_5$ was obtained by Jones[42] in ~0.5% yield from phenyloctatetrayne. It is extremely unstable and sensitive to light, a black product resembling coal being precipitated even from dilute solutions. The fact that the substance was the diphenyloctayne was confirmed by elemental analysis and the ultraviolet spectrum.

A more stable product was the di-t-butyl derivative, which was synthesised by Jones[42] as follows:

$$(CH_3)_3C-C\equiv C-CHO + BrMgC\equiv C-CH(OMgBr)C\equiv CH \longrightarrow$$
$$\longrightarrow (CH_3)_3C-C\equiv C-CH(OH)-C\equiv C-CH(OH)-C\equiv CH \xrightarrow[C_5H_5N]{SOCl_2}$$
$$\longrightarrow (CH_3)_3C-C\equiv C-CHCl-C\equiv C-CHCl-C\equiv CH \xrightarrow{NaNH_2}$$
$$\longrightarrow (CH_3)_3C-(C\equiv C)_3-C\equiv CH \xrightarrow[C_5H_5N]{Cu(CH_3COO)_2} (CH_3)_3C-(C\equiv C)_8-C(CH_3)_3.$$

The most difficult stage in the synthesis was oxidation of the tetrayne to the octayne. Attempts to carry out oxidative condensation under ordinary conditions were unsuccessful because of the extremely low solubility of its copper derivatives.

By using Eglinton's method[43] (oxidation with a pyridine solution of copper acetate), Jones obtained an octayne which was, like its lower homologues, a stable compound.

8. Eicosa-1,3,5,7,9,11,13,15,17,19-decayne (Decaacetylene)

The introduction of t-butyl substitutents as end-groups in polyynes made it possible to synthesise higher members of this series. However, they are difficult to prepare and the yields are low primarily because of the instability of the intermediate products.

The t-butyldecayne was synthesised by Jones[44] by the following scheme:

$$(CH_3)_3C-CHCl-C\equiv CCH_2Cl \rightarrow (CH_3)_3C-CCl=CH-C\equiv CH + (CH_3)_3C-(C\equiv C)_2H,$$
$$(CH_3)_3-C(C\equiv C)_2H \xrightarrow[Me_2NHCO]{EtMgBr} (CH_3)_3C-(C\equiv C)_2CHO \xrightarrow{BrMgC\equiv C-CH(OMgBr)C\equiv CH}$$
(I)
$$\longrightarrow (CH_3)_3C-(C\equiv C)_2CH(OH)-C\equiv C-CH(OH)C\equiv CH,$$
(II)
$$\xrightarrow[C_5H_5N]{SOCl_2} (CH_3)_3C-(C\equiv C)_2CHCl-C\equiv CCHClC\equiv CH \xrightarrow{KOH+Al_2O_3}$$
(III)
$$\longrightarrow (CH_3)_3C-(C\equiv C)_5H \xrightarrow[C_5H_5N]{(CH_3COO)_2Cu} (CH_3)_3C-(C\equiv C)_{10}-C(CH_3)_3.$$
(IV) (V)

The main difficulties were met in synthesising 6,6-dimethylhepta-2,4-diynal (I), the stage involving conversion of the glycol (II) into the dichloride also taking place with difficulty; the pentayne (IV) was obtained in 17% yield. It is noteworthy that the use of copper acetate enables the dichloride (III) to be directly converted into the decayne (V) in 24% yield.

The decayne was isolated as pinkish yellow crystals stable for several days in air and in light at room temperature. When heated it is converted into a coal-like substance.

III. PROPERTIES OF POLYYNES

1. Stability of Polyynes

It follows from the above data that the stability of polyynes drops sharply as the number of acetylenic links in the chain increases. Thus hexatriyne is considerably less stable than butadiyne, while octatetrayne cannot be isolated at all as a pure compound.

Polyynes are usually sensitive to light in the solid state, but are more stable in solution. This probably depends on the density of packing of the polyyne molecules in the crystal lattice. X-Ray structure data have shown that the linear molecules in decatetrayne or butadiynedicarboxylic acid are distant 3.8–4 Å from one another in the crystals. Interaction between the chains, resulting in the formation of insoluble network structures, is then possible.

The stability of polyynes is greatly increased by replacing the terminal hydrogen atoms by alkyl or aryl radicals. The volume and the configuration of the substituents also affect the stability. Thus unsubstituted hexatriyne decomposes explosively at -10°, decatetrayne is stable up to 50°, and bis-(1-hydroxycyclohexyl)octatetrayne fuses without decomposition at 151°. The greatest stabilising effect is shown by t-butyl end-groups. This has been explained[44] by the ability of bulky end-groups having cylindrical symmetry to keep the rodlike polyyne chains a sufficient distance apart.

At the same time, the possibility of attack on a terminal hydrogen atom, for example by free radicals, is eliminated in the disubstituted acetylenes.

From a comparison of Stuart models of the molecules of dimethyldodecahexayne (tetradecahexayne) and of the di-t-butyl derivative (see Fig. 1), Bohlmann[41] concluded that, in the former case, the straightened parallel polyyne chains can approach one another, whereas in the latter case the presence of the bulky t-butyl substituents prevents the parallel chains from coming closer than to within 3 Å. It is only at high temperatures that closer approach of the chains is possible, and that polymerisation of the polyyne can occur.

It is interesting to compare the melting points (or decomposition points) of the methyl- and t-butyl-polyynes (see Table 2).

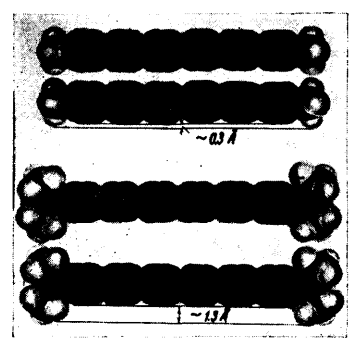


Fig. 1.

TABLE 2.

n	Methyl, m.p., °C	t-Butyl, m.p., °C
2	64°	130°–132°
3	128°	70°
4	decomposes at 80°	99°–100°
5	decomposes at – 5°	129°–130°
6	decomposes at – 5°	140°
7	–	decomposes at 150°
8	–	decomposes at 130°
10	–	decomposes at 100°

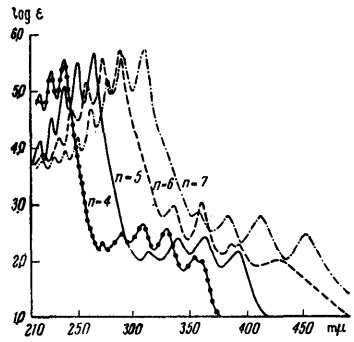


Fig. 2.

The stability of the di-t-butyldecayne and the high yield (40%) at the last stage make one confident that higher members of the series can be obtained.

2. Absorption Spectra of Polyynes

On comparing the infrared absorption spectra of a series of phenylated polyynes $C_6H_5-(C\equiv C)_n-C_6H_5$, (I), we note[42] that the hydrocarbons (I: n = 2–4, 6) absorb in the range characteristic of the phenyl group (3070, 1660, 1490, 1445, 920, and 680 cm^{-1}). Furthermore, the characteristic frequency of the C≡C bond (2200 cm^{-1}) is observed in all the hydrocarbons, its intensity increasing with increase in n.

Variation in frequency (cm^{-1}) with n

(I: $n = 2$)	(I: $n = 3$)	(I: $n = 4$)	(I: $n = 6$)
2200	2200	2205	2180, 2166

The positions of the absorption maxima of the bands due to the diphenyl polyynes are listed in Table 3.

Bands of medium intensity (A–D) increase in intensity from ϵ = 200 to ϵ = 500–20 000 with retention of the fine structure. The bands due to the diphenylpolyynes are somewhat less intense than those of the aliphatic polyynes. As in the aliphatic series, the intensity of the bands increases with n, although not to such a great extent, since the mean intensity of the bands is less.

The absorption spectra show the same pattern in the t-butylpolyynes. Fig. 2 shows the comparative absorption spectra of the di-t-butylpolyynes[45].

Bands of medium intensity occur in the visible range, and coincide in intensity with the lower homologues of the polyyne series. These results support the assumption that the intensity of absorption in this region is independent of the length of the polyyne chain[44]. High-intensity bands are more intense, as was to be expected, in the higher homologues.

Compared with the dimethylpolyynes, the simple di-t-butylpolyynes exhibit a more complicated fine structure in the long-wave region than is observed with polyynes containing one or more ethynyl groups.

It is interesting to compare the absorption spectra of the polyynes $[Bu^t(C\equiv C)_nBu^t]$ with those of the polyenes, as was done by Bohlmann[41]. The former show a considerable shift in the maxima towards shorter wavelengths compared with the corresponding polyenes. Table 4 collates the chief absorption maxima of the two series of hydrocarbons.

The reason for the different positions of the maxima must be sought in the different bond lengths and in differences in the π-electron layers. The doubling of the number of π electrons in the polyynes compared with the polyenes increases the probability of a transition, and hence the intensity of absorption is doubled.

The spectra are also influenced by differences in structure. According to Kuhn[46], the zigzag configuration of the *trans*-polyenes should lower the theoretical absorption intensity by about 25%. This does not occur with the completely straight polyyne chains. Finally, the sharpness of the bands in the polyynes is due to the rigidity of the molecule: the more inflexible the molecule, the more distinct the fine structure and the sharper the maxima[47]. The spectra of the diphenylpolyynes differ still more from those of the diphenylpolyenes[48].

The widely held view in the literature that acetylenic compounds absorb at shorter wavelengths than the corresponding ethylenic compounds applies here to the lower

TABLE 3.

n	A		B		C		D	
	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$
2	3270	27.8	3060	31.0	2880	22.0	—	—
3	3580	20.2	3300	30.3	3120	23.0	—	—
4	3970	21.2	3670	34.0	2415	33.8	3180	27.3
6	4600	8.75	4240	17.7	3920	17.4	3610	25
8	5090	4.45	4660	9.6	4300	12.3	3950	33

TABLE 4.

n	Polyyne		Polyene	
	λ_{max}, Å	ε	λ_{max}, Å	ε
2	< 2000	—	2260	22 500
3	2170	119 000	2630	51 500
4	2430	276 000	2960	64 000
5	2650	442 000	3260	72 500
6	2900	500 000	3600	82 200*

* In benzene.

members of the series. The absorption coefficient of the first few bands of the diphenylpolyynes is surprisingly low, and falls still more with increase in conjugation, which is contrary to what would be expected.

3. Reactions of Polyynes

The present section compares the chemical properties of acetylene and its higher polyyne homologues due to the presence and number of conjugated triple bonds. The peculiar position occupied by acetylenic hydrocarbons among organic compounds is due to their specific reactivity.

The anomalous reactivity of acetylenic compounds can be explained as follows. The electronic structure of the acetylenic bond differs from that of the ethylenic bond in that the σ bond is formed from two *sp* hybrid orbitals. The reactivity of an unsaturated system is determined solely by the π electrons, which are readily displaced, with the formation of reactive polar forms. It would appear that the C≡C bond, formation of which involves two pairs of π electrons, should exhibit a tendency to electrophilic reactions.

Physicochemical data have shown that the π electrons of a triple bond are less mobile than those of a double bond. This is evident, for example, from the ultraviolet spectra[50]. It is obvious that the energy of the π bond forms part of the total energy of the C≡C bond. Estimation of this quantity[49] taking into account the coulombic repulsion showed that the energy of an acetylenic π bond is 15–20% greater than that of an ethylenic π bond. Here the steric factor must also be taken into account: the formation of π complexes, which occurs in the electrophilic reactions of a double bond, is hardly possible with the triple bond, since the electrons are diffused throughout the molecule.

The nucleophilic reactivity of an acetylenic bond and the acidity of the acetylenic hydrogen are explained by the lack of symmetry of the electron distribution.

Formation of each electronic link involves a shift in electron density towards the middle of the bond. The magnitude of this shift is greater for each σ bond than for a π bond. Whereas with the olefines the displacement is roughly symmetrical, the acetylenes show an unsymmetrical effect. The C≡C grouping contains electrophilic carbon atoms even in the ground state.

In the polyynes this effect becomes stronger as the number of triple bonds increases, since each conjugated bond influences the neighbouring bond. There results a tendency for the π electrons to be displaced towards the centre of the molecule, which can be represented by a cumulene type of mesomeric structure:

$$-C\equiv C-C\equiv C-C\equiv C^{\delta+} \longleftrightarrow -\underbrace{(C=C)_n}=C=\overset{+}{C}-.$$

This makes clear the ease of occurrence of nucleophilic reactions in polyynes. Any electron donor would weaken this effect.

(a) Hydrogen replacement reactions. Owing to the electron-acceptor character of the triple bond, the elimination of hydrogen as a hydride anion is probably excluded. Rupture of a ≡C—H bond with the formation of free radicals was postulated by Zal'kind[25] purely hypothetically to explain the formation of diynes from monoacetylenic hydrocarbons.

A very characteristic reaction of unsubstituted acetylenic hydrocarbons is the splitting off of hydrogen as a proton. Acetylene itself is a weak C-acid of strength comparable with that of N-acids of the phthalimide type. No work has been done on the comparative acidity of acetylene and the polyynes; it may be supposed that an increase in the number of C≡C groups will strengthen the acid properties. This follows from Mansfield's observation[14] that introduction of a second C≡C group into the molecule of propiolic acid results in an appreciable increase in the dissociation constant. Introduction of a larger number of triple bonds only slightly increases the acidity.

Acetylides from polyynes are considerably less soluble than copper acetylide from acetylene[42]. Replacement of hydrogen by alkali metals (Li, Na) takes place more readily with butadiyne than with acetylene. Whereas acetylene can be condensed with ketones in the presence of KOH in anhydrous medium, with butadiyne this reaction takes place in aqueous solution, which is undoubtedly associated with the increased acidity of the hydrogen atom in the polyyne[49]:

$$R-C\equiv CH+O=C\begin{matrix}R_1\\R_2\end{matrix} \longrightarrow R-C\equiv C-\underset{\displaystyle OH}{\overset{\displaystyle R_1}{\underset{|}{\overset{|}{C}}}}-R_2.$$

(b) Nucleophilic addition reactions. Olefines react with nucleophilic reagents only if they are polarised by an electron-acceptor substituent; such polarisation is not required with an acetylenic bond.

A typical example is the formation of vinyl ethers[51]:

$$HC\equiv CH \xrightarrow[OH^-]{ROH} H_2C=CHOR.$$

Addition takes place still more readily to butadiyne; methanol forms 1-methoxybut-1-en-3-yne[50], which is of interest for preparative purposes:

$$HC\equiv C-C\equiv CH \xrightarrow{CH_3OH} HC\equiv C-CH=CHOCH_3.$$

Triynes and tetraynes undergo nucleophilic addition still more rapidly[52]. Owing to the great difference in rates of addition in this case, ethers of monoenols can be isolated. Decatetrayne, for example, yields a mixture of *cis*- and *trans*-isomers of the enol ether:

$$CH_3(C\equiv C)_4CH_3 \longrightarrow CH_3(C\equiv C)_3-CH=C\begin{matrix}OCH_3\\CH_3\end{matrix}.$$

Like alcohols, amines react particularly readily with polyynes[53]. Hydrocyanic acid adds on readily to polyynes in the presence of cyanide ions[54]:

$$CH_3(C\equiv C)_4CH_3 \xrightarrow[CN^-]{HCN} CH_3(C\equiv C)_3-CH=C\begin{matrix}CN\\CH_3\end{matrix}.$$

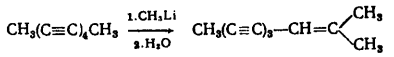
Complex catalysts are required for acetylene to undergo this reaction.

With polyynes the Michael type of addition is possible. Thus sodiomalonic ester adds on to polyynes[54]:

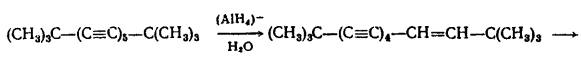
$$CH_3(C\equiv C)_4CH_3 \xrightarrow{^-CH(COOR)_2} CH_3(C\equiv C)_3-CH=C\begin{matrix}CH_3\\CH(COOR)_2\end{matrix}.$$

Lithium alkyls have not been observed to add on either to acetylene or to butadiyne, at least three conjugated

acetylenic bonds being required; thus decatetrayne instantly adds on methyllithium, yielding after hydrolysis substituted polyenynes[49]:

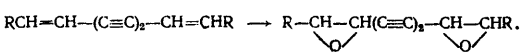


Lithium aluminium hydride reacts similarly. Addition of this reagent is possible only with polyynes[49]. The tetrayne reacts very rapidly, whereas the triyne reacts very slowly. Since the reaction involves ultimately partial hydrogenation of one triple bond, this route can be utilised for the synthesis of polyenynes:



This example shows especially clearly that the rate of nucleophilic addition is higher with polyynes.

(c) Electrophilic addition reactions. Typical electrophilic addition reactions take place more slowly with acetylenes than with olefines (by a factor of about 10). This is especially noticeable with oxidative reactions. Even a polyenyne reacts slowly with peracids, forming a partly epoxidised derivative[52]:



The triple bond reacts only with the peracid present in a large excess.

Acetylenes are ozonised far more slowly than are olefines.

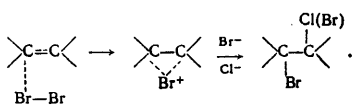
Reaction with hydrogen halides is very slow, this appearing especially clearly on passing from acetylene to polyynes, when the rate of nucleophilic addition reactions increases tenfold, while electrophilic addition shows the reverse order[53]. Thus acetylene reacts very slowly with hydrogen halides, while octatetrayne does not react at all[55].

The addition of water (in the presence of acids) takes place in a similar manner. Although butadiyne is converted comparatively rapidly into a ketone, hexatriyne reacts slowly. Tetraynes do not react at all[56]. The stable di-t-butylpentayne can be heated with concentrated H_2SO_4 at 50° for 1 h without apparent reaction.

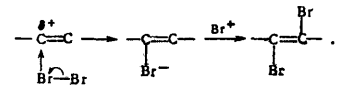
From these examples it is clear that the reactivity in electrophilic addition drops rapidly with increasing number of conjugated triple bonds.

Halogens react with olefines by electrophilic addition. Bromination is very rapid even in the dark. Acetylene reacts with bromine in the dark extremely slowly, butadiyne somewhat more rapidly. Bromine adds on still more rapidly to triynes and tetraynes[56].

An electrophilic mechanism for the halogenation of olefines is confirmed by the fact that bromination in the presence of chlorine results in the formation of compounds containing both chlorine and bromine:

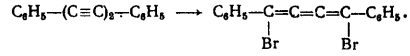


The reaction with decatetrayne under the same conditions yields only bromides, which supports a mechanism of nucleophilic addition:

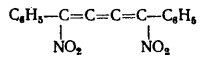


(d) Radical reactions. The addition of bromide to the polyyne series under the influence of light obeys different laws. Decyne reacts with bromine 40 times as rapidly in the light as in the dark[49]. Diynes and tetraynes react with bromine more rapidly solely on account of the greater number of triple bonds[55].

Schlubach[40] showed that in the diphenylpolyynes the addition of bromine takes place at the ends of the chain:



Schlubach and Rott[57] found that nitrogen dioxide in ethereal solution reacts similarly, and with diphenylacetylenes it was possible to isolate dinitro-derivatives having a cumulene structure:

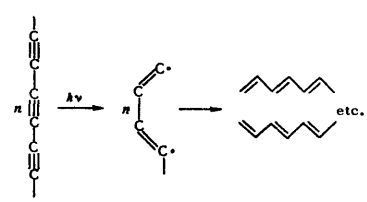


(e) Catalytic hydrogenation. A triple bond is hydrogenated to a double bond more readily than olefines are hydrogenated to alkanes. A comparison of the rates of hydrogenation of mono-, di-, and tetra-acetylenic compounds showed[55] that the reaction velocity increases linearly in proportion to the number of conjugated triple bonds. The mechanism of the catalytic hydrogenation of acetylenes probably consists in the preliminary dissociation of the hydrogen molecules into free radicals (atoms) on the surface of the catalyst. Atomic hydrogen adds on rapidly at a triple bond.

(f) Polymerisation of polyynes. Acetylene is converted by ultraviolet irradiation into a macromolecular product[58], butadiyne and benzene being formed as by-products.

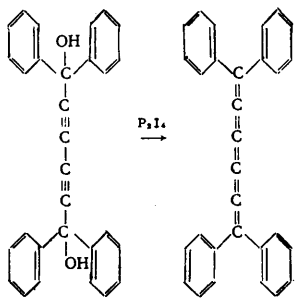
Polyynes undergo polymerisation especially readily. The tetrayne is converted after a few seconds into an insoluble black polymer. Diynes and triynes polymerise more slowly, the products being brown to red in colour.

Bohlmann[49] has put forward a hypothetical mechanism for this reaction. Under the influence of light the electron pairs are parted, and the resulting radicals recombine to form large rings of aromatic character:



(g) Formation of cumulenes from polyynes. Reduction of polyacetylenic alcohols can yield compounds with conjugated double bonds of allene type, cumulenes.

For example, the action of phosphorus diodide on 1,1,6,6--tetraphenylhexa-2,4-diyne-1,6-diol, prepared from benzophenone and butadiynylenedimagnesium dibromide, yields tetraphenylhexapentaene[59]:



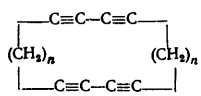
Cumulenes are also extremely unstable, and the same methods are used for their stabilisation as in the synthesis of polyynes, namely the introduction of phenyl and t-butyl substituents[60]. A heptaene and a nonaene have been synthesised[60] by introducing the latter substituents at the ends of the cumulene chain.

According to Kuhn[59], the mechanism of the formation of cumulenes from acetylenic glycols in the presence of phosphorus diiodide consists in replacement of hydroxyl by iodine with subsequent spontaneous elimination of the iodine and rearrangement to a cumulene structure. Replacement of the hydroxyls by chlorine atoms (by the action of HCl) in the presence of reducing agents (of the type of vanadous or chromous chloride) enabled the yield of cumulenes to be sharply increased[59].

Cumulenes (like polyynes) consist of rigid, immobile "rods" of carbon atoms[59].

IV. MACROCYCLIC COMPOUNDS CONTAINING CONJUGATED ACETYLENIC BONDS

Eglinton[61] and independently Sondheimer[62] found that the oxidative dimerisation of the alkadiynes $HC\equiv C-(CH_2)_n-C\equiv CH$ yields, in addition to linear products $H[C\equiv C-(CH_2)_n-C\equiv C]_mH$, cyclic compounds:



Eglinton[63] showed that the cupric ion is an oxidant for acetylenic hydrocarbons. The reaction is carried out in aqueous medium at pH 6, monoacetylenes giving a 50% yield of $\alpha\gamma$-diynes. Half of the ethynyl compound is converted into insoluble copper(I) acetylide:

$$4R-C\equiv CH + 2Cu^{2+} \longrightarrow R-C\equiv C-C\equiv C-R + 2RC\equiv C-Cu + 4H^+.$$

The acetylide can be converted into the $\alpha\gamma$-diyne with an excess of cupric ions, or by oxidation with oxygen and other oxidising agents.

In order to prepare cyclic compounds from diynes, the reaction must be effected in homogeneous solution and at great dilution, in order to avoid formation of the linear polymer:

$$HC\equiv C-(CH_2)_n-C\equiv C-[C\equiv C-C-(CH_2)_n-C\equiv C]_m-C\equiv C-(CH_2)_nC\equiv CH\ .$$

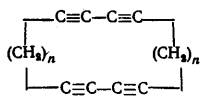
The formation of cyclic compounds is favoured by the rigidity of the tetratomic system $C-C\equiv C-H$.[64]

The most suitable medium for the reaction is a mixture of pyridine and methanol, in which all the components are soluble. At the same time the pyridine combines with the acid evolved in the reaction. For preparative purposes it is more convenient to use an excess of copper acetate. Sometimes the formation of an insoluble reddish brown acetylide is observed during the reaction.

When atmospheric oxygen in the presence of cuprous chloride was used as oxidant, the diynes (I)

$$HC\equiv C-(CH_2)_n-C\equiv CH$$
(I)

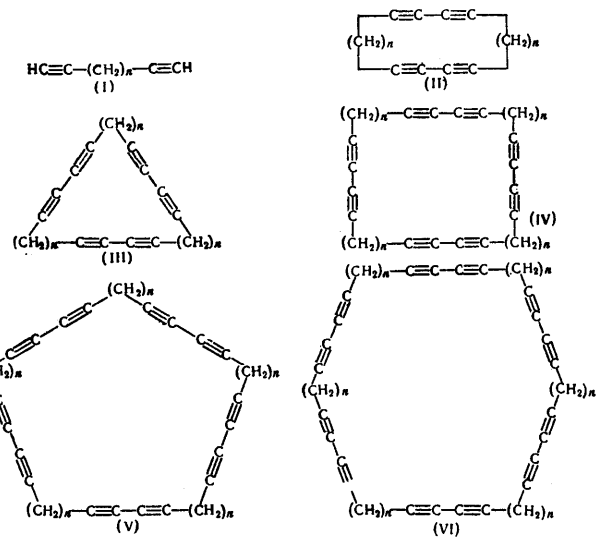
with n = 2 and 6 did not yield cyclic products, whereas with copper acetate mainly cyclic products were formed:



where n = 4 and 5.

This fact indicates that cyclisation is favoured by a homogeneous medium.

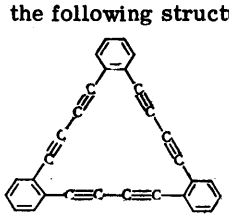
When Sondheimer also employed this oxidant[65], the diyne (I) gave not only cyclic dimers (II) but also cyclic trimers (III), tetramers (IV), pentamers (V), hexamers (VI), and still higher cyclic polyynes (see Scheme 1).



Scheme 1

Here n = 2–5. When n = 2, a linear product is formed at the same time.

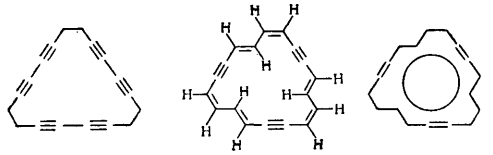
By the oxidative polymerisation of o-diethynylbenzene, Eglinton[66] obtained a 30% yield of a crystalline substance to which, on the basis of an elemental analysis and infrared spectroscopic data, the following structure is assigned†:



† See, however, Chem. and Ind., 699 (1959); Proc. Chem. Soc., 231 (1959) (Ed. of Translation).

At -5° this substance is stable for several months, but it decomposes explosively on being heated or on standing at room temperature.

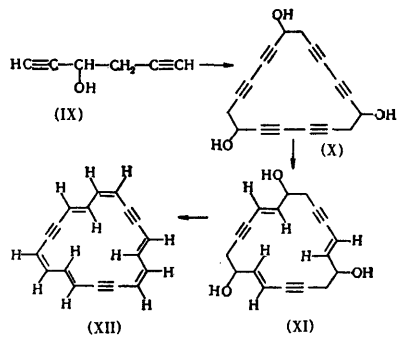
It is noteworthy that, in the presence of potassium t-butoxide, cyclic acetylenes rearrange into fully conjugated cycloalkenynes[67]. Thus cyclooctadeca-1,3,7,9,13,15-hexayne (VII) is converted into cyclooctadeca-*cis*-1,7,13,*trans*--3,9,15-hexaene-5,11,17-triyne:



(VII) (VIII) (VIIIa)

The hydrocarbon (VIII) contains 18 conjugated π electrons. In this compound the conditions of Hückel's rule are satisfied [the presence of $(4n + 2)$ conjugated π electrons][68], although, of course, not all the carbon–carbon bonds are equivalent here, as is required for maximum stability of aromatic compounds. As was to be expected, compound (VIII) is quite stable, remaining unchanged for several days under normal conditions.

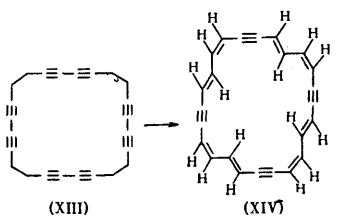
The conjugated hexaenetriyne (XII) was also obtained by a different route[67]:



(IX) (X) (XII) (XI)

The cyclic polyol (X) was obtained by oxidation of compound (IX) (with copper acetate in pyridine), and from it was obtained, after dehydration with potassium bisulphate in a boiling mixture of acetic anhydride and acetic acid, the required hexaenetriyne (XII).

Similarly, cyclotetracosa-1,3,7,9,13,15,19,21-octayne on treatment with a t-butoxide gave a cyclic product with a conjugated 24-membered ring, cyclotetracosa-1,3,7,9,13,-15,19,21-octaene-5,11,17,23-tetrayne[67]:



(XIII) (XIV)

The octaenetetrayne molecule cannot be planar because of the presence of four double bonds having a *cis*-configuration.

Partial hydrogenation of the octaenetetrayne on a palladium catalyst resulted in a compound which decomposed on being heated. On the basis of analytical and infrared spectroscopic data, this compound is assigned the structure cyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene. The infrared spectrum and the colour indicate that all twelve double bonds form part of one chromophoric system, and as a result *trans*-addition of hydrogen takes place.

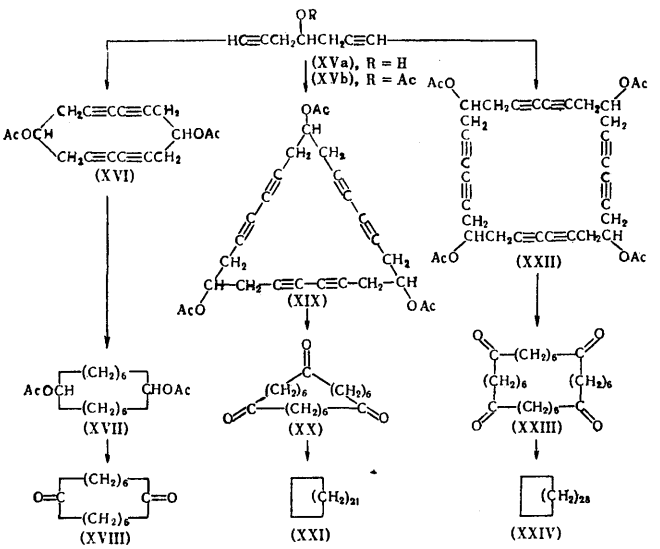
Cyclotetracosadodecaene is a 24-π-electron system which, in contrast to the cyclooctadecanonaene synthesised earlier[69], does not satisfy Hückel's rule. Therefore the cyclotetracosadodecaene is far less stable than the latter compound.

Later Sondheimer[70] and his collaborators prepared oxygen-containing cyclic polyynes. The starting material chosen was hepta-1,6-diyn-4-ol (XVa). Oxidation was effected with oxygen in the presence of cuprous chloride in aqueous alcohol acidified with hydrochloric acid. An insoluble crystalline product was isolated (exploding on being heated to 235°), which from its elemental analysis and infrared spectrum (the presence of α-diacetylene and the absence of terminal ethynyl groups) was one of the two possible stereoisomers of diacetyl cyclotetradeca-3,5,10,12-tetrayne-1,8-diol (XVI).

Chromatography on aluminium oxide of the reaction mixture after removal of (XV) yielded three different crystalline products: triacetyl cycloheneicosa-3,5,10,12,17,19--hexayne-1,8,15-triol (XIX) (probably a mixture of two possible stereoisomers) and tetraacetyl cyclooctacosa-3,5,10,12,17,19,24,26-octayne-1,8,15,22-tetraol (XXII).

In addition to these, an acyclic product was obtained, which was not investigated; its infrared spectrum showed its molecule to be linear and to contain acetylenic bonds.

The structure of the cyclic compounds obtained was demonstrated by hydrogenating them to the corresponding cyclic hydrocarbons (see Scheme 2).



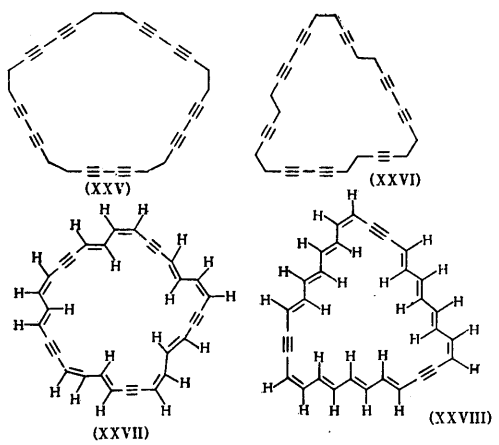
Scheme 2

Hepta-1,6-diyn-4-ol (XVa) is the principal diyne from which, under conditions of oxidative dehydrocondensation (oxygen, cuprous chloride, ammonium chloride, aqueous ethanol), are obtained the more complicated compounds (XIX) and (XXII) as well as the cyclic dimers (XVI). This result indicates that no substantial difference exists between the two methods of obtaining cyclic polyynes. The

solubility is of fundamental importance. The carbinol (XVa) is more soluble in aqueous ethanol than are the hydrocarbons described earlier. If the carbinol (XVa) is replaced by its acetate (XVb) in the oxidative dehydrocondensation (atmospheric oxygen in the presence of CuCl + + NH_4Cl), the main product is the cyclic dimer (XVI). This is obviously due to the acetate being less soluble than the carbinol (XVa) in aqueous ethanol. If, however, (XVb) is oxidised with copper acetate, the main product is the cyclic trimer (XIX).

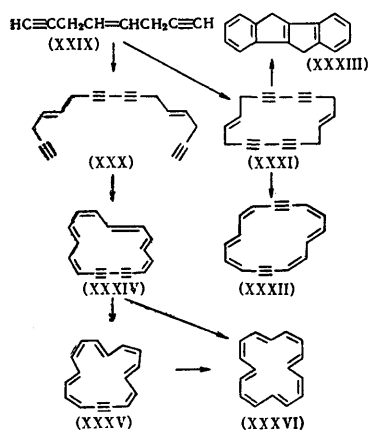
Recent papers by Sondheimer and his coworkers[71,72] describe syntheses of conjugated cyclic systems.

The formation may be noted of cyclotriaconta-1,3,7,9,-13,15,19,21,25,27-decaene-5,11,17,23,29-pentayne (XXVII) from the 1,3,7,9,13,15,19,21,25,27-decayne (XXV) by treatment with a t-butoxide (see Scheme 3).



Scheme 3

Here (XXVII) represents a monocyclic system containing thirty π electrons, which obeys Hückel's rule and is extremely stable.



Scheme 4

Oxidative condensation of oct-*trans*-4-ene-1,7-diyne (XXIX) with atmospheric oxygen in the presence of cuprous chloride, ammonium chloride, and ethyl alcohol containing dilute hydrochloric acid yielded the linear hexadeca-*trans*-4,*trans*--12-diene-1,7,9,15-tetrayne (XXX) and the cyclic dimer cyclohexadeca-*trans*-1,*trans*-9-diene-4,6,12,14-tetrayne (XXXI). Treatment of the cyclic dimer (XXXI) with potassium ethoxide in benzene results in a mixture of isomers, to which the structure (XXXII) is attributed. In addition, an appreciable yield of the indenoindene (XXXIII) is formed.

Oxidative condensation of the linear dimer (XXX) with copper acetate leads to the formation of a new cyclic compound (XXXIV), partial hydrogenation of which gives compounds to which the structures (XXXV) and (XXXVI) are attributed.

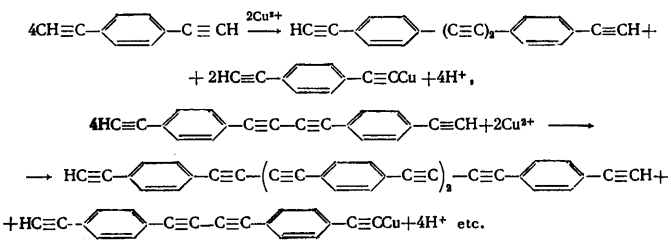
In concluding this survey of work on the synthesis of macrocyclic polyynes, we may note that, in the oxidation of diynes of the type $HC{\equiv}C-(CH_2)_n-C{\equiv}CH$, linear polymeric products are obtained as well as the interesting and theoretically important products. The yield of linear polymers drops sharply with increase in n and in the dilution of the reactants (in the case of oxidation with copper acetate). At high dilutions the yield of linear products is practically zero (see Scheme 4).

V. SYNTHESIS OF POLYYNES BY THE OXIDATIVE DEHYDROPOLYCONDENSATION OF DIYNES

In 1960 Hay[73] extended oxidative dehydrocondensation to *m*- and *p*-diethynylbenzenes. He used atmospheric oxygen as oxidant, in the presence of catalytic quantities of cuprous chloride in pyridine.

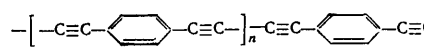
m-Diethynylbenzene yielded a polymer which was soluble in chlorobenzene and in nitrobenzene. Its infrared spectrum showed the presence of ≡CH end-groups (3290 cm^{-1}), their number indicating a molecular weight of 7000. The polymer was stable at room temperature, but decomposed at 180° with the evolution of hydrogen and methane.

Oxidation of *p*-diethynylbenzene gave a yellow product insoluble in organic solvents. At the same time[74-76] a polymer of *p*-diethynylbenzene was obtained by oxidative dehydropolycondensation with bivalent copper. It is obvious that oxidation of *p*-diethynylbenzene produces a mixture of polyynes and copper(I) acetylides:



Further oxidation of the reaction mixture (for example with aqueous potassium ferricyanide) results in the formation of polyynes having the structure $[-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$. The main reaction product is a powder insoluble in organic solvents; a soluble product of low molecular weight, bis--*p*-ethynylphenylbutadiyne, was also isolated[74]. The infrared spectrum of the latter compound is identical with that of the insoluble portion[75] of the product of oxidative dehydropolycondensation of *p*-diethynylbenzene. A similar polymer was obtained by Kotlyarevskii *et al.*[77], who used as oxidant air in the presence of cuprous chloride and ammonium

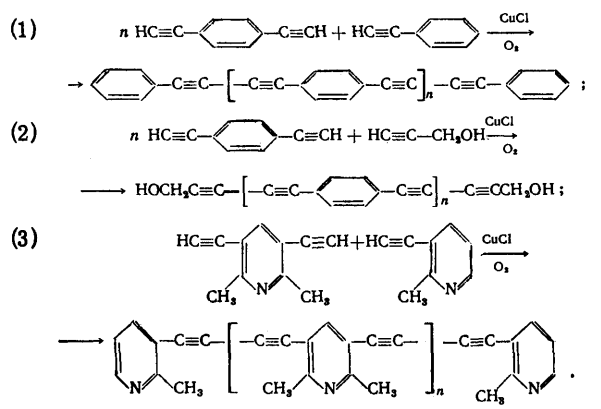
chloride. The sample contained 4.2% of chlorine, which was explained by the presence of the terminal group



Interesting results were obtained[75] in the oxidation of acetylene. When acetylene is passed into an ammoniacal solution of copper nitrate, an insoluble black powder is formed which is clearly a mixture of polyynes and copper acetylides. Further oxidation with potassium ferricyanide yielded a substance having a higher carbon content (up to 98%). The sample contained a small amount of copper. The X-ray diffraction pattern of polyacetylene contains a relatively strong interference band corresponding to a period of 3.85 Å, which can be attributed to the intermolecular distance in an ordered set of parallel linear $[C{\equiv}C]_n$ molecules. On heat treatment, no carbonisation or graphitisation is observed. It is only on heat treatment at 2300° that graphite is formed. But a graphitic structure can be obtained on prolonged boiling of ignited samples of polyacetylene in concentrated hydrochloric acid.

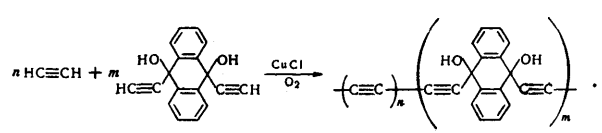
The use of stronger oxidising agents (hydrogen peroxide) and also oxidation by Eglinton's method[61] give cross-linked structures.

In order to obtain soluble polymers containing conjugated triple bonds, experiments were made on the oxidative dehydrocopolycondensation of (1) *p*-diethynylbenzene with phenylacetylene, (2) *p*-diethynylbenzene with propargyl alcohol, and (3) 3,5-diethynyl-2,6-dimethylpyridine with 3-ethynyl-2-methylpyridine[76]. Formation of the following products was to be expected:



By varying the amounts of the reactants it was possible to isolate soluble (in addition to insoluble) products of oxidative dehydrocopolycondensation, whose structures were confirmed by the infrared spectra and X-ray examination.

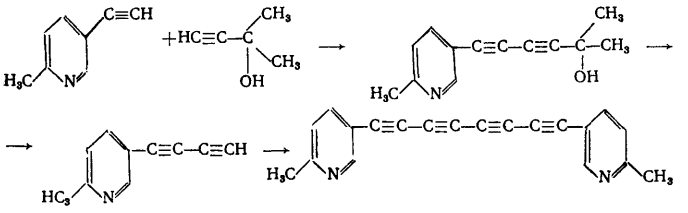
The oxidative dehydrocopolycondensation of acetylene and 9,10-diethynyl-9,10-dihydroanthrahydroquinone also yielded a soluble product[80]:



It is obvious that the introduction of bulky substituents forces apart the rigid linear polyacetylene molecules, facilitating penetration of solvent molecules.

Kotlyarevskii *et al.*[78,79] obtained a product of the oxidative dehydropolycondensation of 9,10-diethynyl-9,10-dihydroanthrahydroquinone together with other diynes. They also effected the synthesis of pyridylpolyynes by building up the acetylenic chain by the oxidative condensation of pyridylacetylenes with 2-methylbut-3-yn-2-ol and decomposing the resulting alcohols into monopyridyldiacetylenes and acetone[80].

Dipyridylpolyacetylenes are obtained by the oxidative dimerisation of monopyridylacetylenes:



Properties of the Polyacetylenes Obtained

The insoluble products of the oxidative dehydropolycondensation of acetylenes (acetylene, *p*-diethynylbenzene, diethynylpyridine, etc.) are characterised by a narrow electron paramagnetic resonance (EPR) signal, typical of conjugated systems, with 10^{16}–10^{19} unpaired electrons per gramme of the substance. Soluble products of the oxidative cocondensation of acetylenes give no EPR signals, which is consistent with the assumption that the concentration of unpaired electrons increases as the chain becomes longer[81–83]. An exception is provided by the polymer obtained by the simultaneous oxidation of acetylene and 9,10-diethynyl-9,10-dihydroanthrahydroquinone[76]. The soluble reaction product in this case contains 2.2×10^{17} unpaired electrons per gramme.

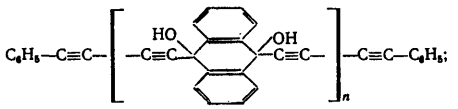
Preliminary data on the heat treatment of the resulting polyacetylenes showed that a rapid rate of heating produces explosive decomposition of the specimens. Such decomposition can be avoided by heating more slowly. The electrical properties of the products are usually improved. For example, the magnetic susceptibility of the polymer of *p*-diethynylbenzene ($10^6\chi = 0.2$) is increased tenfold when a specimen is heated to 200°.[77]

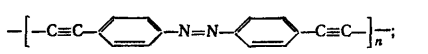
The electrical resistivity of a sample of polyacetylene obtained by oxidising acetylene with potassium ferricyanide is $\rho \simeq 10^6\ \Omega\ cm^{-1}$. With rise in temperature ρ falls, which may be explained by the accumulation of crystalline copper as a result of thermal dissociation and the separation of terminal copper atoms from the polyacetylene. However, the resistivity continues to decrease even at higher temperatures (above 2000°), when the copper has vaporised from the specimen, and this can be explained by the increase in length of the polyacetylene chains during pyrogenic synthesis due to thermal dissociation and separation of copper with subsequent recombination of the resulting free radicals[74].

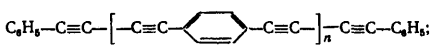
The thermo-e.m.f. of the initial polyacetylene specimen has a negative sign and a value of 1.38×10^4 mV deg^{-1}. At 1300° and 1500° α has a positive sign, and varies with temperature according to a characteristic curve having a maximum at 2300°, which corresponds to the temperature at which polyacetylene changes into graphite.

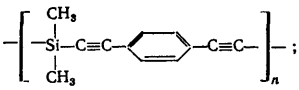
The measurements of ρ and α for the polyacetylene indicate that the sample was an n-type semiconductor in which copper atoms acted as donors. The observed change in sign of the thermo-e.m.f. corresponds to the transition of the polyacetylene to a p-type semiconductor, in which positive holes act as current carriers. Such a transition is linked with thermal dissociation involving the elimination of copper and hydrogen atoms from the carbon chain and is probably due to the acceptor properties of the terminal carbon atoms.

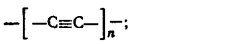
Some of the polyacetylenes which have recently been synthesised[84] display a high photoelectric sensitivity in modulated light, among them being the polymers

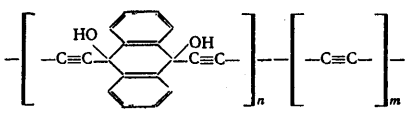












The considerable photosemiconductor sensitivity detected in these polymers suggests possible ways of synthesising photosensitive polymers.

In his interesting work on the synthesis of polydimethyleneacetylene, Bailey[85] chose as starting material 1-bromo-4-chlorobut-2-yne. With an excess of magnesium a Grignard reagent is readily formed, which on standing yields a mixture of soluble and insoluble polydimethyleneacetylenes:

$$Cl{-}CH_2{-}C{\equiv}C{-}CH_2{-}Br \longrightarrow Cl{-}CH_2{-}C{\equiv}C{-}CH_2MgBr,$$
$$ClCH_2C{\equiv}CCH(CH_2C{\equiv}CCH_2)_xCH_2C{\equiv}CCH_3 .$$

The molecular weight of the soluble part was 1500. Hydrogenation of polydimethyleneacetylene yielded a linear polymethylene. It is interesting that the softening point of the polydimethyleneacetylene was 550°, that of polymethylene being 65°–90°.

Papers have recently appeared on the synthesis of polyynes by the oxidative dehydropolycondensation of 4,4′-diethynylbiphenyl[86] and of bis-p-butadiynylphenyl ether[87].

It is evident from this review that the polyacetylenes represent a very interesting class of organic compounds.

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INORGANIC CYCLIC SILICON-CONTAINING COMPOUNDS AND THEIR ORGANIC DERIVATIVES

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INTRODUCTION

The growth of the chemistry of macromolecular organic derivatives of inorganic elements has been due to their valuable technical properties, which have ensured their wide use in various fields of technology and life. Of particular interest are polymers consisting of inorganic main chains substituted by organic groups; these are structurally intermediate between organic and inorganic compounds. The production of polymers containing inorganic chains has been little studied. It is difficult, and in most cases actually impossible, to adapt or use for the production of polymers containing inorganic chains the usual methods for the production of organic polymers.

The widely used polymerisation of unsaturated organic compounds cannot be used for the production of polymers containing inorganic chains, because there are no corresponding reactive unsaturated monomers. No attempts to polymerise monomers containing the P=O bond have yet been successful.