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# Advances in the Synthesis of α-Ethynylcarbonyl Compounds

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The methods of synthesis of α-ethynylcarbonyl compounds are discussed. Attention has been concentrated on the methods of synthesis of preparative value. Despite the practical approach employed, the review deals with a large number of studies devoted to methods of purely theoretical interest. The biliography includes 215 references.

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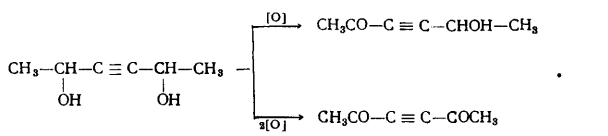
## I. INTRODUCTION

In recent years there has been a considerable growth of interest in the chemistry of ethynylcarbonyl compounds for two reasons. Firstly, ethynyl ketones contain several reaction centres in the molecule and therefore can be legitimately included amongst synthetically promising substances, and, secondly, many ethynyl ketones isolated from plant raw material have shown antibiotic properties. This is particularly important because, despite the application of wide-spectrum antibiotics discovered recently, there is an urgent need in clinical chemotherapy for new antibacterial preparations and continuous and intensive research in this field is necessary. The chemistry of acetylene has been developing very rapidly. Whereas acetylene itself, ethynyl alcohols, and acetylenic acids have been extensively reviewed, no reviews are as yet available on the methods of synthesis and the chemistry of ethynylcarbonyl compounds. In this sense the present review is essentially the first attempt to set out the principal information available on this problem. The data on which the review is based were selected from the standpoint of their practical value. Attention has been concentrated on the methods of synthesis of α-ethynylcarbonyl compounds which, in the authors' view, are the most interesting representatives of this class of compounds, and also on the assessment of these methods and the elucidation of the limits of their applicability. It should, however, be noted that the generally known and widely used methods of preparation of aliphatic ketones and aldehydes in most cases cannot unfortunately be extended to ethynyl compounds. On the other hand, among synthetic methods for the latter, many are exceptionally specific and there is no prospect of their general employment.

## II. OXIDATION OF ETHYNYL ALCOHOLS AND HYDROCARBONS

One of the most widely used synthetic methods for ethynylcarbonyl compounds is the oxidation of the corresponding primary and secondary carbinols and certain hydrocarbons. A wide variety of oxidising agents may be used for the oxidation of alcohols, but the presence in the ethynylcarbinol molecule of a group as reactive as the triple bond narrows considerably the range of acceptable oxidants. The application of vigorous oxidising agents such as, for example, potassium permanganate or nitric acid is undesirable because of the consequent disruption of the multiple bond by the agent.

Historically, the first oxidising agent employed was chromium trioxide $CrO_3$. Andre[1] was the first to employ chromium trioxide in acetic acid solution for the preparation of ethynyl ketones. Depending on the reactivity and the stability of the alcohol, this oxidising agent can be used in combination with various solvents at different temperatures. The nature of the solvent employed, the concentration of the reactants, and temperature have an appreciable effect on the reaction. Thus various aliphatic, aromatic, and heterocyclic ethynyl ketones have been obtained by the action of chromium trioxide in sulphuric acid[2-6]. Secondary diethynyl carbinols[7-12], vinylethynyl carbinols[6,13], acetylenic hydroxy-acids[14,15], and ethynyl glycols[2,16-18] are oxidised under similar conditions. It was noted that aliphatic glycols are oxidised with much greater difficulty than aromatic glycols[2]. Compared with diaroylacetylenes, the yields of the analogous aliphatic diketones are much lower, which is probably due to their low stability. Primary and secondary hydroxy-groups are oxidised. By selecting the reaction conditions and the starting material: : oxidant ratio, it is possible to achieve the oxidation of only one of the hydroxy-groups[2,19]:




Thus in the oxidation of hex-3-yne-2,5-diol by an equimolar amount of chromium trioxide in sulphuric acid at low temperatures the product was 2-hydroxyhex-3-yn-5-one. Using an excess of chromium trioxide, it is possible to convert the glycol into the corresponding diketone. To oxidise more unstable alcohols and glycols, less reactive solutions of chromium trioxide in acetone[20-22] or in acetic acid[23-26] are employed. Recently a chromium trioxide–pyridine complex was proposed for the oxidation of ethynyl

carbinols[27-29]. Owing to the mildness of the reaction conditions, the method gives good results; the replacement of pyridine by acetone as the solvent impairs the yields.

Very contradictory data have been published on the oxidation of primary ethynyl alcohol. Thus Jones and coworkers[30,31] showed that the oxidation of primary alcohols and glycols with chromium trioxide in acetone does not stop at the stage involving the formation of the carbonyl compound. The reaction takes place with formation of mono- and di-carboxylic acids, the yields of which vary from 20 to 40%.

At the same time Wille et al.[32], who oxidised propargyl alcohol by the same oxidising agent, and also Jacobs et al.[33], who oxidised 1-phenylpent-3-en-1-yn-5-ol, obtained the corresponding aldehydes in a yield of about 50%. These different results are associated with the different duration of contact between the reactants and their relative amounts.

The problem of the mechanism of the oxidation of various alcohols by chromium trioxide has been widely discussed. Two principal hypotheses concerning the oxidation mechanism have been put forward on the basis of numerous kinetic studies: Westheimer's so called "ether" mechanism[34] and the mechanism in which the dissociation of hydrogen as the hydride ion is postulated[35]. The above data clearly show the large scale of the application of chromium trioxide for synthetic purposes. However, a certain limitation of this method should also be noted: many highly unsaturated ketones, which are very sensitive to the acidity of the medium, cannot be obtained by this method. Potassium dichromate is less often used for the oxidation of alcohols[36].

In recent years new oxidising agents with a wide range of activity and high selectivity have been found. Among these, activated manganese dioxide obtained in 1948 and extensively used for the oxidation of a wide variety of different classes of compounds occupies a prominent place. Monoethynyl[37-39], vinylethynyl, and polyethynyl ketones[40-42], and ethynyl, vinylethynyl, and polyethynyl aldehydes[43-45] have been synthesised with the aid of activated manganese dioxide. Glycols[17,46] and esters of acetylenic hydroxy-acids[28] are oxidised less successfully. A characteristic feature of this reaction is the lack of sensitivity of the carbon framework, in particular the double and triple bonds, to the action of the oxidant. Because of the specificity of its action, activated manganese dioxide is justifiably regarded as the most convenient and almost irreplaceable dehydrogenating agent for the oxidation of highly unsaturated and extremely unstable hydroxy-compounds. The oxidation is carried out under a wide variety of conditions: with various solvents, in a fairly wide range of temperatures, and with different proportions of the components. It has been established empirically[47,48] that the polarity of the solvent has a very significant effect on the rate and mode of this reaction.

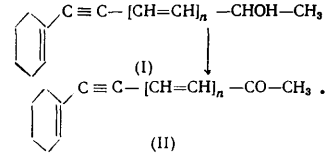
It is considered more desirable to employ chloroform, benzene, pentane, and ether than acetone, since the degree of deactivation of activated manganese dioxide is directly related to the polarity of the solvent employed. The most highly deactivating solvents are aliphatic alcohols, particularly tertiary alcohols; acetone and ethyl acetate also deactivate the oxidant, but much less. The duration and temperature of the reaction depend on the activity of the manganese dioxide, the substance to be oxidised, and the proportions of the components. To reduce its duration, the reaction is frequently carried out at an elevated temperature. The test substance : reactant weight ratio is usually varied in the range 1 : 5–1 : 20 and in some cases 1 : 50. According to many investigators, the ease of oxidation depends on the adsorbability of the given compound on the oxidant. Experimental confirmation has been obtained[40] for the earlier hypothesis of Ball et al.[50] that the more saturated compounds, which are less well adsorbed on the oxidant, should react at a lower rate. However, the degree of adsorption is scarcely the sole factor determining the rate of reaction.

Pratt proposed a free-radical mechanism for the oxidation by activated manganese dioxide[51,52]:

$$R_2CHOH + O{=}Mn{=}O \rightarrow R_2\dot{C}OH + HO{-}Mn{=}O \rightarrow$$
$$\rightarrow R_2\dot{C}{-}\dot{O} + HO{-}Mn{-}OH \rightarrow R_2CO + MnO + H_2O\ .$$

It must be particularly emphasised that the capacity for the selective oxidation of a hydroxyl activated by multiple bonds and an aromatic ring is one of the many specific features of manganese dioxide.

A less widely used synthetic method for ethynylcarbonyl compounds is based on the Oppenauer oxidation of ethynyl alcohols. On prolonged refluxing with aluminium t-butoxide in acetone–benzene solution, ehtynyl carbinols are converted into the corresponding ketones[53-56]:



(I) (II)

It has been noted that the ethynyl alcohols (I) with $n = 0$ react slowly with this oxidising agent. An increase in the number of double bonds has a favourable effect on the reaction and leads to an improvement of the yield of the ketones (II).

Nickel peroxide and manganese acetate are less widely used oxidising agents but give good results[57,58,59]. Nickel peroxide is more often used[57]; the reaction is carried out in a neutral medium, since in an alkaline medium primary alcohols are converted into acids. The yields of the desired products are fairly high.

A satisfactory result was obtained in the oxidation of ethynyl and vinyl alcohols by quinones[60]. Thus 1,5-diphenylpent-4-en-1-yn-3-ol mixed with *o*-chloranil in an alcoholic solution gives at room temperature the ethynyl vinyl ketone (III) in 91% yield:

$$Ph{-}C{\equiv}C{-}\underset{OH}{CH}{-}CH{=}CH{-}Ph \rightarrow Ph{-}C{\equiv}C{-}CO{-}CH{=}CH{-}Ph\ .$$
(III)

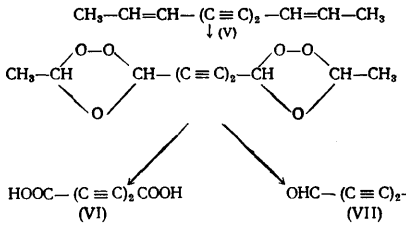
Together with the oxidation of the alcoholic group, ketones are also prepared by a method involving the dissociation of unsaturated compounds at the double bond. The double bond in vinylethynyl compounds is known to be oxidised by peracids much faster than the triple bond and the rate of oxidation increases with the number of substituents at the double bond. This feature was used to synthesise ethynyl ketones[61]. Acetylacetylene and vinylacetylacetylene have been synthesised by heating isopropenylacetylene and isopropenylvinylacetylene with hydrogen peroxide for 35–40 h at 35–45 °C in acetic acid and acetic anhydride. Sometimes monoacetates derived from the alcohols (IV) are formed together with the ketones:

$$R{-}C{\equiv}C{-}\overset{CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{CH_3COOH} R{-}C{\equiv}C{-}CO{-}CH_3 + R{-}C{\equiv}C{-}\overset{OOCCH_3}{\underset{|}{C}}{-}CH_3\ ,$$
(IV)

where R = H or $CH{=}CH_2$.

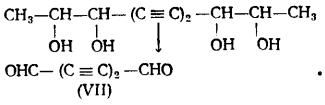
The double bond in enynes is also more sensitive than the triple bond to the action of ozone. This difference in the reactivities of the multiple bonds has been used for

preparative purposes [62]. It has been established that the reaction of dienediynes (V) with ozone takes place smoothly with formation of diozonides, the acid hydrolysis of which gives the acetylenic acids (VI) in 65% yield. At the same time the reductive dissociation of ozonides with zinc dust in water or dioxan makes it possible to obtain a good yield even of the highly unstable diethynyl dialdehyde (VII)

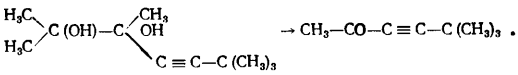


However, this method is more suitable for the synthesis of acetylenic acids than aldehydes.

One of the methods for the synthesis of aliphatic carbonyl compounds is the cleavage of the carbon chain of $\alpha$-glycols between the hydroxylated carbon atoms with lead tetra-acetate, sodium periodate, and periodic acid. This method has also been successfully used in the acetylenic series. Bohlmann and coworkers employed sodium periodate and periodic acid for the dissociation of diols. Thienylpropiolic aldehyde [63], $\alpha$-hexynal [64], and the diethynyl dialdehyde (VII) were obtained in this way [62]:

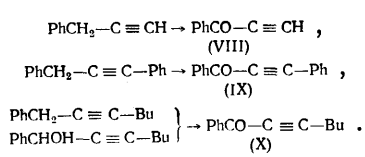


The oxidation of $\alpha$-glycols with lead tetra-acetate also takes place relatively easily [65]. It is sufficient to heat the diol for 2–3 h to 60–65 °C in glacial acetic acid with a 20% excess of the oxidising agent [66,67]:

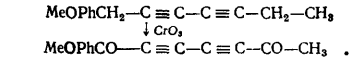


Depending on the structure of the initial glycol, it is possible to obtain by this method both aldehydes and ketones [68]. The method cannot be regarded as preparative, but it is very convenient for the identication and the demonstration of the structures of organic substances.

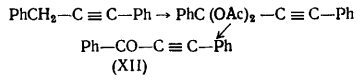
Iwai and Okajima [69-71] introduced the carbonyl group into acetylenic compounds by direct oxidation of the propargylmethylene group with selenium dioxide. Ethynyl ketones (VIII), (IX), and (X) were obtained by prolonged refluxing of the hydrocarbon with sublimed selenium dioxide in alcohol or in a 1 : 1 alcohol–dioxan mixture.



The reaction takes place more unambiguously and a smaller number of side products are formed when the propargylmethylene group is activated by other multiple bonds. By selecting the experimental conditions, the reaction can be stopped at the stage involving the formation of the carbinol [69,70]. On the other hand, there are indications in the literature that primary and secondary ethynyl alcohols can be oxidised to the corresponding ketones and aldehydes [71,72]. The yields of the required products vary in the range 5–27%. Despite its apparent simplicity, the method has not found wide application because of the toxicity of selenium dioxide and the difficulty of obtaining the initial acetylenic hydrocarbons. Together with selenium dioxide, chromium trioxide in acetic acid [73] and lead tetra-acetate [74] have been used to oxidise the propargylmethylene group:

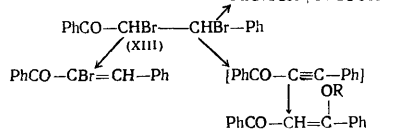


Benzylethynyl hydrocarbons exchange the hydrogen atom activated by the adjacent triple bond and the phenyl ring for the acetoxy-group on treatment with lead tetra-acetate. Thus the interaction of triphenylpropyne with lead tetra-acetate in acetic acid at 100 °C gave the diacetate (XI), which was hydrolysed to diphenylpropynone (XII) by refluxing with a solution of sodium carbonate:

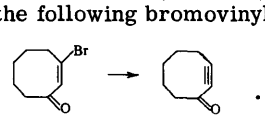


## III. THE DEHYDROHALOGENATION REACTION

The most widely employed method of synthesis of ethynyl compounds is dehydrohalogenation of halogeno-derivatives. However, in the series of ethynylcarbonyl compounds the application of this method is very limited because of the exceptional reactivity of the $\alpha$-ethynyl-carbonyl group. The triple bond of $\alpha$-ethynyl ketones, is highly activated by the adjacent carbonyl group and readily undergoes various nucleophilic addition reactions [75,76]. The dehydrohalogenation of dihalogeno-derivatives is performed using alcoholic solutions of alkalis or sodamide in liquid ammonia. These methods, with few exceptions, are unsuitable for the synthesis of ethynyl ketones. In 1904 Watson [77] attempted to prepare phenylbenzoylacetylene from dibromobenzylideneacetophenone and $\alpha$-bromobenzylidene-acetophenone. He found that, when the halogeno-ketone (XIII) is treated with alcoholic alkali, the reaction takes place in different ways depending on the conditions:



Under mild conditions, the reaction does not go to completion. Only one molecule of hydrogen bromide is dissociated from dibromobenzylideneacetophenone. After prolonged refluxing, the alcohol addition product, $\beta$-ethoxy-benzylideneacetophenone, was isolated. The reaction does not occur in water and, when attempts are made to split off hydrogen bromide with solid alkali, the molecule is cleaved into phenylacetylene and benzoic acid [78]. Under the action of potassium carbonate, it was possible to dehydrobrominate the following bromovinyl ketones [79]:



Dehydrohalogenation with pyridine and sodium acetate stops at the stage involving the formation of the mono-halogeno-derivative [80]. When the monobromo-ketones are treated with ammonia and primary or secondary amines,

the halogen is usually substituted by an amino-group. On the other hand, after dehydrochlorination of the β-chlorovinyl ketone (XIV) with sodamide in liquid ammonia, the ethynyl ketone (XV) was isolated[81]:

$$\underset{\text{(XIV)}}{R{-}CO{-}CH{=}CHCl} \rightarrow \underset{\text{(XV)}}{R{-}CO{-}C{\equiv}CH}\ .$$

R= ferrocenyl

Reactions involving addition to the triple bond can be avoided in certain cases when the dehydrohalogenation is carried out with a base in solvents such as benzene or acetone[78,82]. The use of triethylamine in benzene or in acetone permits the synthesis of dibenzoylacetylene from the dibromide (XVI)[82] in 82–95% yield and also from the monochloride (XVII)[83]:

$$\left.\begin{array}{l} ArCO{-}CHBr{-}CHBr{-}CO{-}Ar \\ \text{(XVI)} \\ Ar{-}CO{-}CCl{=}CH{-}CO{-}Ar \\ \text{(XVII)} \end{array}\right\} \longrightarrow ArCO{-}C{\equiv}C{-}CO{-}Ar\ .$$

It is noteworthy that Japanese chemists[84] succeeded in obtaining ethynyl phenyl ketone in the usual way by the dehydrochlorination of the dichloro-derivative with alcoholic alkali, the mixture being refluxed for 5 h. However, these results are somewhat doubtful.

Compounds with a protected carbonyl group are more successfully dehydrohalogenated. Claisen obtained the first ethynyl aldehyde as early as 1896 by the dehydrobromination of the dimethylacetal of dibromopropionaldehyde[85]:

$$R{-}CHBr{-}CHBr{-}CH(OR')_2 \xrightarrow[ROH]{KOH} R{-}C{\equiv}C{-}CH(OR')_2 \xrightarrow{H_3^+O} R{-}C{\equiv}C{-}CHO\ .$$

Subsequently this method became one of the principal procedures for the synthesis of α-ethynyl aldehydes[86–90]. The protective acetal group prevents side reactions and its removal by hydrolysis in an acid medium does not involve any special complications[91].

## IV. INTERACTION OF METAL ACETYLIDES AND IOTSICH REAGENTS WITH ACID DERIVATIVES

### 1. Reaction of Metal Acetylides and Iotsich Reagents with Acid Halides

Until the 1940's ethynyl ketones were obtained mainly by the condensation of alkali metal acetylides and acid halides. Thus in 1899 Nef[92] was the first to obtain phenylacetylacetylene and phenylbenzoylacetylene by the action of sodium phenylacetylide in ether on acetyl and benzoyl chlorides respectively:

$$R{-}COCl + NaC{\equiv}C{-}Ph \rightarrow R{-}CO{-}C{\equiv}C{-}Ph\ ,$$

where R = methyl or phenyl.

Later this reaction was extended to other acetylenic hydrocarbons and acid halides[93–96]. Sodium, potassium, and lithium acetylides were employed. Sodium phenylacetylide proved to be convenient for preparative purposes. In some cases acid bromides react under milder conditions than the corresponding acid chlorides[2,96,97]. It has been shown[93] that the reaction of sodium phenylacetylide with benzoyl chloride is complicated by side reactions. The ethynyl ketone formed reacts readily with a second molecule of acetylide, yielding the corresponding tertiary carbinol. For this reason, the method gives unsatisfactory yields of the desired products, which are contaminated by carbinols and halogeno-compounds. Good results were achieved only in the synthesis of relatively unreactive nitroarylethynyl ketones and similar compounds[98,99]:

$$m\text{-}NO_2C_6H_4COCl + NaC{\equiv}C{-}Ph \rightarrow m\text{-}NO_2C_6H_4CO{-}C{\equiv}C{-}Ph\ ,$$

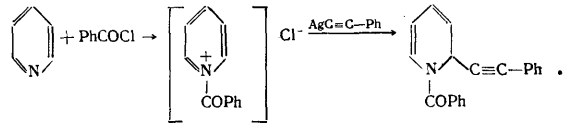
$$m\text{-}NO_2C_6H_4C{\equiv}C{-}COCl + NaC{\equiv}C{-}Ph \rightarrow m\text{-}NO_2C_6H_4C{\equiv}C{-}CO{-}C{\equiv}C{-}Ph\ .$$

The attempt to prepare the symmetrical ketone from sodium ethylacetylide and phenylpropiolic acid chloride was unsuccessful[100]. However, Chauvelier[24], who carried out this reaction with care, succeeded in synthesising 1,5-diphenylpenta-1,4-diyn-3-one, which was characterised as the hydrazone. In 1936 Kroeger and Nieuwland showed that the substitution of metal acetylides by the Iotsich reagent gives more satisfactory results[101]. It is best to employ ethynylmagnesium chloride derivatives; these are less reactive than the analogous bromides and iodides, which readily take part in secondary reactions[102–104]. The use of silver acetylides, which do not interact with the carbonyl group, excludes the possibility of the appearance of side products. By heating silver phenylacetylide with benzoyl chloride, Nef[92] obtained 1,3-diphenylprop-1-yn-3-one in a high yield. It is more convenient to carry out this reaction with silver derivatives soluble in carbon tetrachloride, chloroform, or benzene. In some cases the normal course of the reaction requires the addition of aluminium chloride[105]. The same paper describes the synthesis of halogenoethynyl ketones from silver acetylides and halogeno-carboxylic acid chlorides:

$$X{-}CH_2COCl + AgC{\equiv}C{-}R \rightarrow X{-}CH_2CO{-}C{\equiv}C{-}R,$$

where X = Cl or Br and R = $C_4H_9$ or $C_6H_{13}$.

The synthesis of these ketones from sodium acetylides results in very low yields. Silver acetylides are much more soluble in pyridine[106] but the reaction in this solvent mainly gives rise to the formation of *N*-acyl-2-alkynyl-2-dihydropyridine:




The possibility of preparing α-ethynyl ketones by the reaction of copper acetylides with acid halides is of some interest[107]. The authors determined the conditions under which the desired products are formed with very satisfactory yields (up to 45%):

$$PhCOCl + CuC{\equiv}C{-}Ph \rightarrow PhCOC{\equiv}C{-}Ph\ .$$

Organozinc and organocadmium compounds, which have found wide application in the synthesis of saturated and vinyl ketones, are more promising in this type of process. The attempts to extend this method to ethynyl ketones proved to be unsuccessful[108] and only in recent years has it been established[109] that phenyl- and vinyl-acetylenes form ethynylzinc iodides by the reaction with solutions of alkylzinc iodides. The reaction of ethynylzinc iodides with aliphatic and aromatic acid chlorides gives rise to the corresponding ethynyl ketones. The reaction involves considerable charring, which is reduced when ethynylzinc chlorides are employed. The yields of ketones reach 40–70%. Similar results were obtained with ethynylcadmium halides[110]. The ethynylcadmium halide reagent was obtained by the action of cadmium chloride on the ethylnylmagnesium halide derivative. The reagent thus formed reacts with mono- and di-carboxylic acid chlorides, giving rise to the formation of ethynyl ketones in 40–70% yield. Ethynyl ketones were obtained similarly from an ethynyllead reagent[111].

Recently Gavrilenko et al.[112] suggested that complex aluminium acetylides, which can be readily obtained from lithium, potassium, or sodium aluminium hydrides and monosubstituted acetylenes in tetrahydrofuran, diglyme [2-methoxyethyl ether (Ed. of Translation)], or pyridine, be used for the synthesis of ethynyl ketones:

$$MAlH_4 + RC{\equiv}CH \rightarrow \underset{\text{(XVIII)}}{MAl(C{\equiv}C{-}R)_4} + 4H_2 \ .$$

Under certain conditions, the complex acetylides (XVIII) are formed strictly selectively without the addition of lithium aluminium hydride to the triple bond. The interaction of complex aluminium acetylides with acid chlorides is carried out at 29–40°C and with acid anhydrides at 70°C:

$$MAl(C{\equiv}C{-}R)_4 \xrightarrow{R'COCl} R'CO{-}C{\equiv}C{-}R$$
$$MAl(C{\equiv}C{-}R)_4 \xrightarrow{(R''CO)_2O} R''CO{-}C{\equiv}C{-}R \ .$$

When the temperature is raised in excess of the above limits, charring becomes more extensive and the yields of ethynyl ketones, which even under optimum conditions are only 20–40%, are reduced. Thus this method is hardly likely to find wide application.

## 2. Interaction of Alkali Metal Acetylides and Iotsich Reagents with Acid Anhydrides

Although as early as 1899, Nef[92] indicated the possibility in principle of synthesising ethynyl ketones from sodium acetylides and acetic anhydride, it was not until 1936 that Kroeger and Nieuwland[101] made a detailed study of this reaction and demonstrated the advantage of anhydrides over acid chlorides. It was established that much better results are achieved, as with acid chlorides, when Iotsich reagents are employed instead of alkali metal acetylides. The relatively unreactive ethynylmagnesium chlorides are preferable to the bromides and iodides, which largely favour the occurrence of side reactions involving the formation of ethynyl carbinols:

$$(CH_3CO)_2O + R{-}C{\equiv}C{-}MgCl \rightarrow R{-}C{\equiv}C{-}CO{-}CH_3 \ .$$

The yields of ethynyl ketones in this reaction are in the range 40–80%. According to Nieuwland, more satisfactory results are obtained in reactions with alkylacetylenes when the anhydride is added to the Iotsich reagent at −25°C. When condensations of this kind are carried out in the range between −50° and −70°C, the yields of the desired products are improved[113–115]. When the reaction is carried out at room temperature, the reagents must be mixed in the reverse order (i.e. ethynylmagnesium halide must be added carefully to the anhydride) to prevent more completely the occurrence of side effects. This method was used successfully in the synthesis of ethynyl ketones with aliphatic substituents[113,114,116–118] and cycloalkyl-[119,120], silylethynyl-[115,121], and asymmetric vinylethynyl-carbonyl compounds[122].

The reaction of sodium acetylides with acid anhydrides yields the corresponding ketones, but there are many exceptions[123]. Symmetrical vinylethynyl ketones (XIX) were obtained in satisfactory yields from the anhydrides of cinnamic, crotonic, succinic, and maleic acids and sodium phenylacetylide[108,109]:

$$\begin{matrix} PhCH{=}CH{-}CO \\ \qquad\quad\ O \\ PhCH{=}CH{-}CO \end{matrix} + NaC{\equiv}C{-}Ph \rightarrow \underset{\text{(XIX)}}{PhCH{=}CH{-}CO{-}C{\equiv}C{-}Ph} \ .$$

The attempt to obtain the analogous ketones from the anhydride of acrylic acid and ethynylmagnesium chlorides or lithium acetylides was unsuccessful[124]. Either the starting materials were recovered unchanged or the yield of reaction products was unsatisfactory.

The use of lithium acetylides as the acetylenic component leads to the formation of tertiary ethynyl carbinols. The preferential formation of alcohols can be explained by the high solubility of the lithium complex in ether and its capacity for the ready formation of the ketone, the subsequent reaction of which with a second molecule of the acetylide no less readily gives rise to the ethynyl alcohol, which is undesirable in this case. However, in many studies it was noted that, when the condensation of lithium acetylides with acid anhydrides is carried out at temperatures of the order of −80°C, it is possible to stop the process at the stage where the carbonyl compound is formed[125]. The interaction of lithium acetylides with cyclic anhydrides of dicarboxylic aliphatic[126], alicyclic, and aromatic acids[127] leads to the formation of α-ethynyl keto-acids in high yields. The attempts to employ in this synthesis ethynylmagnesium bromides and the analogous ethynylmagnesium chlorides were unsuccessful.

In order to suppress the side reaction involving the formation of acetylenic hydroxy-acids, the condensation must be carried out at a temperature between −5° and 30°C.

## 3. Interaction of Nitriles, Amides, and Salts with Iotsich Reagents and Alkali Metal Acetylides

The method of preparation of saturated ketones from Grignard reagents and saturated nitriles is generally known. Ethynylmagnesium derivatives are much more reactive than the saturated and aromatic derivatives. However, even these yield the corresponding ethynyl ketones on reaction with aliphatic and aromatic acid nitriles and amides. Thus diphenylpropynone was obtained by the reaction of phenylethynylmagnesium bromide with benzonitrile[128]. On the other hand, Iotsich reagents do not react either with acetonitrile or acetamide[101]. The nitriles of substituted propiolic acid react fairly less readily with ethynylmagnesium compounds, giving high yields of diethynyl ketones[129]:

$$R{-}C{\equiv}C{-}CN + R'{-}C{\equiv}C{-}MgBr \rightarrow RC{\equiv}CC(=NMgBr)C{\equiv}CR' \xrightarrow{H_2O} RC{\equiv}CCOC{\equiv}CR' \ .$$

In a study of the reaction between a Grignard reagent and the nitrile of β-bromocrotonic acid, Boularand and coworkers showed that the reaction involves an elimination–addition mechanism[130]:

$$CH_3CBr{=}CH{-}CN \xrightarrow{RMgX} CH_3{-}C{\equiv}C{-}CN \xrightarrow{RMgX}$$
$$CH_3{-}C(R){=}CHCN + CH_3{-}C{\equiv}C{-}CO{-}R \ ,$$

where R = methyl or ethyl.

The use of aromatic organomagnesium compounds makes it possible to obtain as the sole reaction product arylated nitriles of the type $CH_3{-}C(Ar){=}CH{-}CN$. The reaction of β-mesityl-β-methoxyacrylonitrile with phenylmagnesium bromide involves a 1,2-addition mechanism with formation of benzoylmesitylacetylene[131].

In 1903 a method was proposed for the synthesis of saturated aldehydes from disubstituted formamides and Grignard reagents [132]. Later this method found fairly wide application for the syntheses of aldehydes of the ethynyl [63,133] and vinylethynyl series [134]:

$$R{-}C{\equiv}CMgBr + (CH_3)_2NCHO \rightarrow R{-}C{\equiv}C{-}CH\,N(CH_3)_2OMgBr \xrightarrow{H_2O+} R{-}C{\equiv}C{-}CHO\,.$$

The reaction of acetamides with ethynylmagnesium bromides yields the corresponding ethynyl ketones [135]. Anomalies were observed in this reaction. For example, Viguer [136], in his attempt to obtain tetrolic aldehyde from diethylformamide and propynylmagnesium bromide, obtained 4-diethylaminohepta-2,5-diyne by the reaction:

$$HCON(C_2H_5)_2 + CH_3C{\equiv}CMgBr \rightarrow CH_3C{\equiv}C{-}\underset{\displaystyle N(C_2H_5)_2}{\overset{\displaystyle OMgBr}{\overset{|}{\underset{|}{CH}}}}{-}N(C_2H_5)_2 \xrightarrow{CH_3C{\equiv}CMgBr} \rightarrow CH_3C{\equiv}C{-}\underset{\displaystyle N(C_2H_5)_2}{\overset{|}{CH}}{-}C{\equiv}C{-}CH_3\,.$$

As in the case where the Iotsich reagent is employed, the reaction of heptynyl-lithium bromide with acetamide does not yield ethynyl ketones, the acetylenic hydrocarbon being regenerated [101].

Vinylamino-ketones (XX) and vinylamino-aldehydes (XXI), which are vinylogues of carboxylic acid amides, react with Iotsich reagents via the following mechanism:

$$R{-}C{\equiv}CMgBr + \underset{R'}{\overset{R'}{>}}N{-}CH{=}CH{-}CO{-}R'' \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}CO{-}R'',$$

(XX)

$$R{-}C{\equiv}C{-}MgBr + \underset{Me}{\overset{Ph}{>}}N{-}CH{=}CH{-}CHO \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}CHO\,,$$

(XXI)

yielding vinylethynylcarbonyl compounds [137,138].

Salkind [139] established that aldehydes and ketones may be prepared by the reaction between Grignard reagents and anhydrous salts of formic and acetic acids. Later this reaction was used to synthesise ethynylcarbonyl compounds. Thus in the reaction with methylmagnesium iodide sodium phenylpropiolate is converted into phenylacetylacetylene [140]. A similar result was obtained in the reaction of an excess of methyl-lithium with free propiolic acid [141]. Phenylmagnesium bromide and phenyl-lithium do not enter into this reaction. In this case the yields of ketones are usually lower than when acid chlorides, amides, and nitriles are employed and therefore the reaction has not been used for preparative purposes.

## 4. Interaction of Iotsich Reagents and Ethynyl Derivatives of Alkali Metals with Esters

Usually the reaction of formic acid esters with Grignard reagents yields secondary alcohols. However, Gattermann [142], who used an excess of the ester, cooled the system intensively, and mixed the reagents in the reverse sequence, succeeded in driving the process towards the formation of aldehydes. Under similar experimental conditions, Iotsich reagents can be used successfully because of their relatively lower reactivity [143]. Formate esters react with equimolar amounts of alkali metal acetylides to form the corresponding aldehydes [144-146], but this synthesis is relatively inconvenient, since, even when the experimental conditions are rigorously maintained, ethynyl aldehydes are formed in a mixture with alcohols and the yield does not exceed 30%. Iotsich [146-149] made a fairly detailed study of the interaction between carboxylic acid esters and ethynylmagnesium derivatives:

$$CH_3COOC_2H_5 + R{-}C{\equiv}CMgBr \rightarrow R{-}C{\equiv}C{-}CO{-}CH_3 \xrightarrow{R{-}C{\equiv}CMgBr} \rightarrow (R{-}C{\equiv}C)_2C(OH){-}CH_3\,.$$

The primary reaction products are ketones. With ethyl acetate and higher carboxylic acid esters, ketones could not be isolated and therefore the sole reaction products were tertiary diethynyl alcohols [150-152]. Condensation of ethynylmagnesium compounds with ethyl benzoate also yields ethynyl carbinols [153]. Esters of acids with a triple bond, including the $\alpha$-position, behave similarly. Ethyl phenylpropiolate reacts in this way with methylmagnesium iodide, phenylmagnesium bromide [140], and tolylmagnesium bromide [154]:

$$PhC{\equiv}C{-}COOC_2H_5 + 2\,CH_3MgI \rightarrow PhC{\equiv}C{-}\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3\,.$$

On the other hand, Hurd [155], who started with ethyl phenylpropiolate and phenylmagnesium bromide, obtained 1,3-diphenylprop-1-yn-3-one in 85% yield. The interaction of ethyl cinnamate with sodium phenylacetylide gives rise to the ethynyl vinyl ketone (XXII) [156]:

$$PhCH{=}CH{-}COOC_2H_5 + PhC{\equiv}CNa \rightarrow \underset{(XXII)}{PhCH{=}CH{-}CO{-}C{\equiv}C{-}Ph}\,.$$

However, the formation of compound (XXII) has been inadequately demonstrated, since the analogous ketone obtained from cinnamic acid anhydride and sodium phenylacetylide differs sharply from it in its physical constants and chemical properties [109]. The reaction of oxalic esters with Iotsich reagents has been successfully used to synthesise the esters of ethynyl keto-acids [157]:

$$R{-}C{\equiv}C{-}MgBr + C_2H_5OOC{-}COOC_2H_5 \rightarrow R{-}C{\equiv}C{-}CO{-}COOC_2H_5\,.$$

The method of synthesis is simple and convenient, consisting in mixing the ethereal solutions of equimolar amounts of alkyl- or aryl-ethynylmagnesium bromides and oxalic acid esters at a temperature not exceeding 5°C. When the alkoxy-group in the ester becomes more complex, the yield of reaction products increases.

## 5. Synthesis of Ethynyl Ketals and Acetals and Their Hydrolysis to Ethynyl Ketones and Aldehydes

Chichibabin [158] and Bodroux [159] showed that the orthoformic ester reacts with organomagnesium derivatives to form acetals. This reaction is one of the best procedures for the preparation of aldehydes by the Grignard reaction and is superior as regards yields and the availability of the reactants to other methods of synthesis of aldehydes (from carboxylic acid esters, formic acid salts, amides, etc.). The orthoformic acid ester reacts smoothly with an equimolar amount of the Iotsich reagent, forming ethynyl acetals in yields of 75–80%: [143,160-162]

$$R{-}C{\equiv}CMgBr + HC(OR')_3 \rightarrow R{-}C{\equiv}C{-}CH(OR')_2 \xrightarrow{H_3^+O} R{-}C{\equiv}C{-}CHO\,.$$

In the decomposition of the organomagnesium complex either the acetal or the ethynyl aldehyde directly can be isolated, depending on the conditions. The reaction of

ethynylenedimagnesium dibromide with orthoformate constitutes a simple and convenient synthesis of the diacetal of butynedial[163]:

$$BrMgC{\equiv}C{-}MgBr + HC(OR)_3 \rightarrow \underset{(XXIII)}{(RO)_2HC{-}C{\equiv}C{-}CH(OR)_2} \xrightarrow{H^+} \underset{(XXIV)}{OHC{-}C{\equiv}C{-}CHO}.$$

Satisfactory results were obtained when the reaction was carried out in benzene. In ether the diacetal (XXIII) could be obtained only after refluxing for several days. The isolation of the acetylene–dialdehyde (XXIV) is difficult because of its low stability. Acetals of vinylethynyl aldehydes were synthesised by the same method[164]:

$$R{-}CH{=}CH{-}C{\equiv}CMgBr + HC(OR')_3 \rightarrow \underset{(XXV)}{R{-}CH{=}CH{-}C{\equiv}C{-}CH(OR')_2} \xrightarrow{H_2^+O} \rightarrow R{-}CH{=}CH{-}C{\equiv}C{-}CHO,$$

where R = H or alkyl.

In the hydrolysis of the acetals of vinylethynyl aldehydes (XXV) with 3% hydrochloric acid extensive charring is observed. Gusev and Kucherov showed[165,166] that the optimum conditions for the hydrolysis of the acetal (XXVI) of diacetylene-aldehyde are achieved by brief refluxing of compound (XXVI) with dilute hydrochloric acid in dioxan. The extreme lability of the aldehyde (XXVII) precludes its isolation in a pure form:

$$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C(OH){-}C{\equiv}C{-}C{\equiv}CH + HC(OR_3) \rightarrow \begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C{-}C{\equiv}C{-}CH(OR)_2 \rightarrow$$

$$\xrightarrow{KOH} \underset{(XXVI)}{HC{\equiv}C{-}C{\equiv}C{-}CH(OR)_2} \xrightarrow{H^+} \underset{(XXVII)}{HC{\equiv}C{-}C{\equiv}C{-}CHO}.$$

When lithium or sodium phenylacetylide was allowed to react with the acetal of $\alpha$-bromoacetaldehyde, the acetal of 4-phenylbut-3-ynal was obtained[167]:

$$PhC{\equiv}CLi + BrCH_2CH(OR)_2 \rightarrow PhC{\equiv}C{-}CH_2CH(OR)_2 \xrightarrow{H^+} PhC{\equiv}C{-}CH_2CHO.$$

Howk[168] proposed a single-stage catalytic synthesis of acetals and ketals from readily available starting materials—monosubstituted acetylenes and orthoformic esters:

$$R{-}C{\equiv}CH + HC(OR')_3 \xrightarrow{ZnX_2} R{-}C{\equiv}C{-}CH(OR')_2.$$

The suggested mechanism is as follows:

$$HC(OR)_3 + ZnX_2 \rightarrow [HC^+(OR)_2] + [ZnX_2OR^-]$$

$$HC{\equiv}CR'$$

$$\left[RO{-}\overset{H\ OR}{\overset{|\quad|}{C}}{-}\overset{+}{C}H{\equiv}CR'\right] + ZnX_2OR^- \rightarrow R'{-}C{\equiv}C{-}CH(OR)_2 + ZnX_2 + ROH.$$

The best catalysts proved to be zinc chloride, iodide, and nitrate, and also cadmium iodide. Orthoformate, orthoacetate, and orthovalerate were used as the ester components. The method of synthesis is simple, the yields of acetals and ketals varying in the range 15–80%.[169]

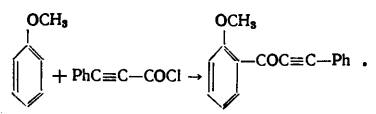
The acetal of tetrolic aldehyde can be obtained by treating diacetylene with ethanol and potassium hydroxide under the conditions of Favorskii's reaction[170]. When the reaction mixture is heated to 100°C, ethyl $\beta$-ethynylvinyl ether (XXVIII) is formed. The acetals are produced in appreciable amounts only at temperatures above 130°C and also when the amount of alcohol is increased. The acetal (XXIX) isomerises to the acetal of tetrolic aldehyde by the mechanism discovered by Favorskii for acetylenic hydrocarbons:

$$HC{\equiv}C{-}C{\equiv}CH{-} \begin{cases} \xrightarrow{100^\circ} \underset{(XXVIII)}{HC{\equiv}C{-}CH{=}CHOEt} \\ \xrightarrow{>130^\circ} HC{\equiv}C{-}CH_2{-}CH(OEt)_2 \xrightarrow{KOH} CH_3C{\equiv}C{-}CH(OR)_2. \\ \qquad\qquad (XXIX) \end{cases}$$

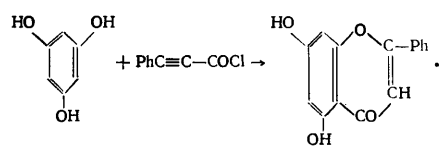
The hydrolysis of the acetals to aldehydes[91] by dilute inorganic acids causes extensive polymerisation. It has been found[171–173] that, when acetals of acetylenic aldehydes are heated with oxalic acid, it is possible to obtain aldehydes in yields of the order of 35%. Even better results are achieved when acetals are refluxed with aqueous tartaric acid with subsequent elimination using calcium chloride of the alcohol formed simultaneously. In this case the yield of tetrolic aldehyde rises to 55%.

## V. ACYLATION OF AROMATIC COMPOUNDS BY ACETYLENECARBOXYLIC ACID CHLORIDES UNDER THE CONDITIONS OF THE FRIEDEL–CRAFTS REACTION

The Friedel–Crafts reaction, discovered as early as 1877, is in important method for the preparation of aromatic ketones. Its detailed and extensive study established that acylation with aliphatic carboxylic acids, their chlorides, and anhydrides is possible for a wide variety of aromatic compounds—benzene and its homologues, naphthalene and its derivatives, and also a number of heterocycles. The Friedel–Crafts reaction with the chlorides of $\alpha\beta$-unsaturated acids has been less well investigated. Experiments have shown that the acylation of aromatic compounds by the chlorides of acetylenecarboxylic acids has many limitations. The first such synthesis, carried out by Gatterman, was the acylation of anisole with the chloride of phenylpropiolic acid[174]:



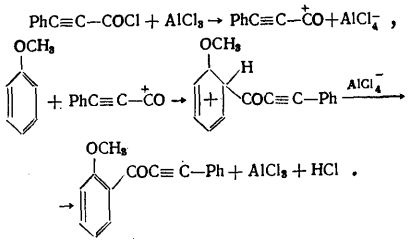
Seka and Prosche[175] also successfully employed the Friedel–Crafts condensation of phenylpropiolic acid and polyhydric phenols for the direct synthesis of hydroxyflavones:



The attempt to carry out this reaction with benzene did not result in the formation of ethynyl ketone[77]. The reported synthesis of tetradecylbenzoylacetylene under analogous conditions is doubtful[176].

The different behaviour of benzene, anisole, and phenols is probably associated with the electronic nature of the methoxy- and hydroxy-groups. If one remembers that the mechanism of this condensation includes a stage in which an acylcarbonium ion is formed with subsequent attack by the latter on the position in the benzene ring with the highest electron density then the promoting effect of HO and $CH_3O$ groups on the acylation process becomes understandable. Other substituents with a $+I$ effect,

leading to an increase of electron density in *ortho*- and *para*-positions, should have a similar effect:



This hypothesis is confirmed by the exceptional ease of the acylation of *p*-methylanisole with the chloride of phenylpropiolic acid[177]. It is interesting that the reaction with an excess of aluminium chloride leads to the formation of chlorination products only.

The above methods of synthesis of ethynyl ketones have not found extensive application.

## VI. HYDRATION OF POLYETHYNYL COMPOUNDS

The hydration of polyethynyl compounds has been investigated in fair detail. It is known[178,179] that in the presence of mercury(II) salts the addition of water to polyacetylenes takes place with participation of all the triple bonds and leads to the formation of a mixture of polyketones. However, as early as 1892, Griner[180] obtained by the hydration of hexa-2,4-diyne in the cold in the presence of aqueous sulphuric acid a substance to which he ascribed the structure of a β-ethynyl ketone (XXX):

$$CH_3C{\equiv}C{-}C{\equiv}C{-}CH_3 \rightarrow CH_3CO{-}CH_2C{\equiv}C{-}CH_3 .$$
(XXX)

Later Bohlmann et al.[181] established on the basis of the infrared spectra of the ketones and their hydrazones that the product of the addition of water to dimethyldiacetylene is an α-ethynyl ketone. Di-t-butylacetylene reacts with water slowly, probably due to steric hindrance. Under analogous conditions, the corresponding α-pentadiynyl ketone (XXXI) was obtained from octatriyne:

$$CH_3{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \xrightarrow[H_2SO_4]{H_2O} CH_3C{\equiv}C{-}C{\equiv}C{-}CO{-}C_2H_5 .$$
(XXXI)

When an attempt is made to hydrate tetra-acetylene, the latter breaks down completely. By hydrating asymmetric triacetylenes (XXXII), it is possible to form isomeric ethynyl ketones [(XXXIII) and (XXXIV)]:

$$(CH_3)_2CH{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \text{ (XXXII)} \rightarrow \begin{cases} (CH_3)_2CH{-}C{\equiv}C{-}CO{-}CH_2{-}CH_3 \text{ (XXXIII)} \\ (CH_3)_2CH{-}CH_2{-}CO{-}C{\equiv}C{-}CH_3 \text{ (XXXIV)} \end{cases} .$$

By analysing the NMR spectra of the hydration products of isopropylmethyldiacetylene, Petrov et al.[182] established that these are a mixture of compounds (XXXIII) and (XXXIV) with the latter predominating. It has been established chromatographically that the ketones (XXXIV) and (XXXIII) are formed in proportions of 9 : 1. Petrov et al. deduced a general rule governing the addition of water to asymmetric diacetylenes on the basis of the hyperconjugation effect of substituents, which varies in the series $CH_3 > CH(CH_3)_2 > C(CH_3)_3$.

The spreading of the hyperconjugation effect over a conjugated system, which determines the mode of addition, is respresented as follows:

$$CH_3{\rightarrow}C{\equiv}C{-}C{\equiv}C{-}CH(CH_3)_2 .$$

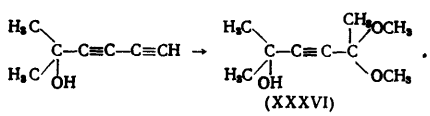
Consequently the hydration of isopropylmethyldiacetylene should involve preferentially the triple bond adjacent to the isopropyl group, since it is precisely this bond that has the highest electron density. Depending on the hydration conditions, diacetylenic hydrocarbons are capable of being converted into diketones and further into 2,5-disubstituted furans[183].

Gorn and Gorin investigated the hydration of diacetylene over a cadmium phosphate–calcium phosphate catalyst in the gas phase[184]. The liquid-phase hydration of diacetylene in an acid medium in the presence of mercury salts is known to result in the formation of diacetyl. German investigators[185] concluded that, together with diacetyl, another product is ethynyl methyl ketone (XXXV), which becomes wholly polymerised under the conditions of this reaction:

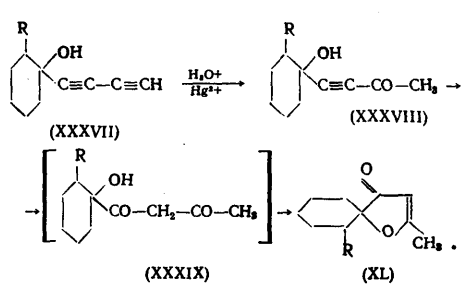
$$HC{\equiv}C{-}C{\equiv}CH \rightarrow [HC{\equiv}C{-}CO{-}CH_3] \rightarrow H_3C{-}CO{-}CO{-}CH_3 .$$
(XXXV)

The vapour-phase hydration of diacetylene yields the same results. The authors propose a hydration mechanism similar to that described above. They infer indirectly the intermediate formation of ethynyl methyl ketone from an appreciable amount of a polymeric deposit on the catalyst.

Acid-catalysed hydration may be used to synthesise ethynyl ketones with a monosubstituted triple bond. Sokolov and Petrov[186] obtained propionyl- and butyryl-acetylenes from penta-1,3-diyne and hex-1,3-diyne respectively. Water then adds to the triple bond adjacent to the alkyl substituent. On the other hand, the reaction of 5-methylhexa-1,3-diyn-5-ol with methanol in the presence of mercury salts results in the formation of the dimethylketal of 5-hydroxy-5-methylhex-3-yn-2-one (XXXVI):[187]


(XXXVI)

Volkov et al.[188] and Gusev et al.[189] studied the hydration of tertiary diacetylenic alcohols (XXXVII) in alkaline and acid media and the choice of conditions for the selective involvement of the triple bond of the alcohols (XXXVII) under the conditions of this reaction:

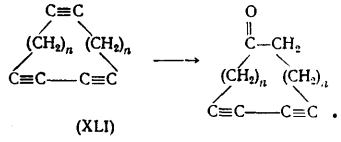

(XXXVII) (XXXVIII) (XXXIX) (XL)

Gusev et al.[189] found that the sole reaction products in an acid medium are the dihydrofuranones (XL) formed via the cyclisation of the intermediate β-diketones (XXXIX).

After a thorough study of the hydration of diacetylenic alcohols in an acid medium[188], it was concluded that the reaction takes place in stages. It is believed that the

principal primary products are ethynyl ketones (XXXVIII), which were isolated in good yields.

Under the conditions of Kucherov's reaction, macrocyclic triacetylenes (XLI) very readily combine with water at the isolated triple bond[190]; the hydration of the conjugated triple bonds requires more severe conditions:



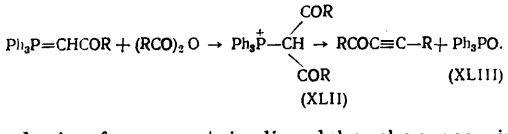
(XLI)

The hydration of acetylenes for preparative purposes is not particularly complicated and, if one remembers that at the present time there exist many methods for the synthesis of diacetylenic systems, one may hope that the above reaction will occupy an important place among the methods of synthesis of ethynyl ketones.

## VII. OTHER SYNTHETIC METHODS

Apart from the general methods discussed in this review, there exist also many specific methods for the preparation of ethynyl ketones which are of value only in specific cases and have not found wide practical application.

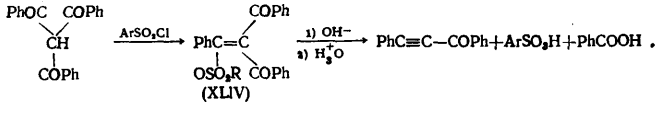
In recent years the intramolecular Wittig reaction has been widely used for the synthesis of various unsaturated compounds. Chopard et al.[191] used this method to prepare ethynyl ketones: on heating with acid anhydrides, stable phosphoranes with acyl substituents are acylated at the carbon atom adjacent to the phosphorus atom, forming diacylphosphoranes (XLII), the pyrolysis of which results in their conversion into ketones (XLIII) in high yields:



(XLII) (XLIII)

The pyrolysis of asymmetric diacylphosphoranes gives a mixture of ethynyl ketones. The yields of the desired products are 70–90%.

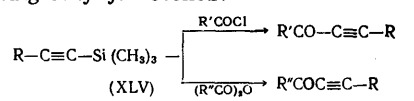
A novel method for the synthesis of ethynyl ketones was recently described by Brown and Harley-Mason[192]; under the action of an arenesulphonyl chloride, tribenzoylmethane is converted into the enolic ether (XLIV), which is converted by treatment with alkali in a dioxan–water mixture into phenylbenzoylacetylene and benzoic and arenesulphonic acids:



(XLIV)

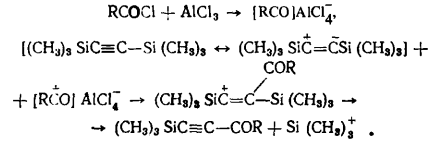
Bromobenzenesulphonyl and toluenesulphonyl chlorides may be used as the sulphonyl component.

We believe that the organosilicon synthesis of $\alpha$-ethynylcarbonyl compounds by the method of Birkoffer[193] is promising. Bistrimethylsilylacetylene is known to be stable towards boiling water and alkali. Trimethylsilyl derivatives of hept-1-yne and hex-1-yne are also insensitive even to the action of inorganic acids. However, in the presence of aluminium chloride silylacetylenes (XLV) react with the chlorides and anhydrides of carboxylic acids, forming the corresponding ethynyl ketones:

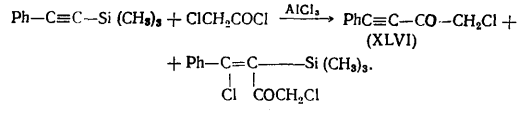


(XLV)

It is believed that the reaction has the following mechanism

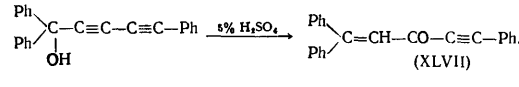


The synthesis is carried out at temperatures below 10°C in carbon disulphide or nitrobenzene. With the disilyl derivative of acetylene, only one trimethylsilyl group is replaced by an acyl residue. Usually the reaction takes place easily, ketones being formed in a yield of 40–90%. Only when chloroacetyl chloride is employed is the yield of the ketone (XLVI) reduced due to a side reaction involving its addition to the triple bond:



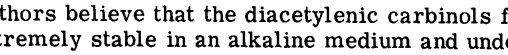
(XLVI)

Certain rearrangements of acetylenic carbinols leading to the formation of ketones undoubtedly merit attention. Thus, under the conditions of the Meyer–Schuster rearrangement, Cadiot and coworkers[194] obtained the ethynyl vinyl ketone (XLVII) from 1,1,5-triphenylpenta-1,3-diyn-5-ol:



(XLVII)

In the alkaline hydrolysis of the acetates of secondary diacetylenic carbinols (XLVIII), ethynyl vinyl ketones (XLIX) are formed instead of the respective alcohols[195]:

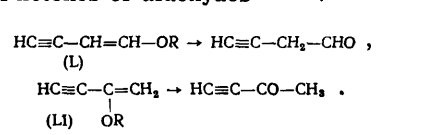


(XLVIII) (XLIX)

The authors believe that the diacetylenic carbinols formed are extremely stable in an alkaline medium and undergo a prototropic rearrangement. This hypothesis was confirmed by Kucherov[196]. On heating with a 3% alcoholic solution of potassium hydroxide, 6-phenylhexa-1,3-diyn-5-ol is readily converted into 6-phenylhex-3-en-1-yn-5-one:

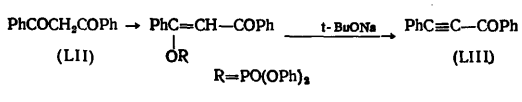


The acid hydrolysis of alkoxyvinylacetylenes (L, LI) yields ethynyl ketones or aldehydes[197-200]:



(L) (LI)

Readily enolisable $\beta$-diketones (LII) can react smoothly with alcohols to form the corresponding enolic ethers[201], which are converted by alkaline hydrolysis into ethynyl ketones (LIII):[202]



(LII) (LIII)

Dibromotriphenylphosphorane is sometimes used as the esterifying agent[203] and the reaction is carried out in triethylamine:

$$PhCOCH_2COPh + Ph_3PBr_2 \rightarrow [PhC(OPPh_3)=CH-COPh]Br \rightarrow PhC\equiv C-COPh + Ph_3PO .$$

The interaction of diphenylketen with phenylethynylmagnesium bromide leads to the formation of ethynyl ketone (LIV):[204]

$$Ph_2C=C=O + PhC\equiv CMgBr \rightarrow Ph_2CH-CO-C\equiv C-Ph .$$

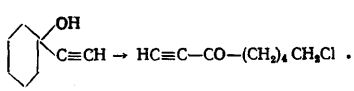
(LIV)

However, the reaction of diphenylketen with ethynylenedimagnesium dibromide led to a substance without the properties of ketones or the corresponding dienols[205].

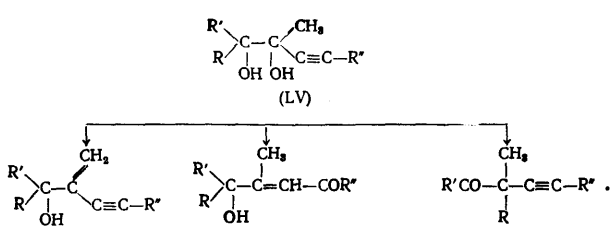
The method of synthesis of ethynyl ketones by the treatment of the sodium salt of acetylacetone with the chlorides of propiolic acids is noteworthy[206]:

$$PhC\equiv C-COCl + NaCH(COCH_3)_2 \rightarrow PhC\equiv C-CO-CH(COCH_3)_2 .$$

Good yields of monosubstituted ketones are quoted in a patent[207] where a method is proposed for the rupture of the cycloalkane ring in ethynyl alcohols with hypochlorous acid according to the following mechanism:

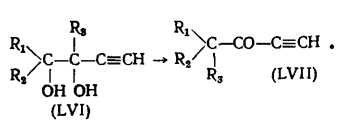


Recently a fairly detailed study was made of the isomerisation of various dihydroxyacetylenes to β-ethynyl ketones[208-215]. Numerous studies by Venus-Danilova and coworkers have been devoted to the elucidation of the reactions of acetylenic ditertiary α-glycols (LV) catalysed by sulphuric acid[210-214]. On heating with 20–40% sulphuric acid, these glycols are converted into compounds with the following structures:



(LV)

Usually the isomerisation takes place simultaneously via all three pathways. One of the reaction products is a β-ethynyl ketone. On the other hand, it has been stated that similar α-glycols (LVI) yield α-ethynyl ketones (LVII) after being passed over a dehydrating catalyst at 200–400°C:[215]



(LVI) (LVII)

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