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REARRANGEMENT OF ACETYLENIC COMPOUNDS WITH PARTICIPATION OF THE π-ELECTRONS OF THE TRIPLE BOND

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INTRODUCTION

After the discovery of the isomerisation of acetylenic hydrocarbons, the rearrangement of acetylenic compounds containing the most diverse functional groups became the subject of many investigations. It was found that acetylenic, vinylacetylenic, and diacetylenic compounds which contain a hydroxyl group, halogens, sulphur, nitrogen, phosphorus, etc. smoothly undergo various rearrangements with the formation of isomeric compounds. Most of these rearrangements are unique, and often the only method of making previously inaccessible new classes of unsaturated alcohols, aldehydes, ketones, and other compounds.

A review of rearrangements of acetylenic compounds has not appeared in the literature, with the exception of Jasiobedzki's article [1] dealing only with the acetylene–allene rearrangement.

In the present article we have tried to collect, and as far as possible, systematise the very interesting and abundant material relating to this subject which has now accumulated.

I. PROTOTROPIC REARRANGEMENT OF ACETYLENIC HYDROCARBONS

During the synthesis of acetylenic hydrocarbons from dihalogenoalkyls Favorskii [2] found that instead of the expected monosubstituted acetylenes disubstituted compounds are obtained. He concluded that under the conditions of the experiment isomerisation of the triple bond along the chain occurred. Subsequently he and his coworkers [3-8] found that various alk-1-ynes isomerise into the

corresponding alk-2-ynes when heated with alcoholic potassium hydroxide solution to 170°C:

$$R{-}CH_2C{\equiv}CH \rightarrow R{-}C{\equiv}C{-}CH_3.$$

On heating disubstituted acetylenes with metallic sodium the reverse process takes place, that is, they are converted into monosubstituted acetylenes[9-15]:

$$R{-}C{\equiv}C{-}CH_3 \rightarrow R{-}CH_2C{\equiv}CH.$$

Hence Favorskii discovered the very interesting reversible isomerisation of acetylenic hydrocarbons [alkynes]. Detailed study of the mechanism of this reaction led the authors to conclude that it proceeds through allenic compounds according to the scheme:

$$R{-}CH_2C{\equiv}CH \rightarrow R{-}CH{=}C{=}CH_2 \rightarrow R{-}C{\equiv}C{-}CH_3.$$

Direct confirmation of this is provided by the fact that under analogous conditions[2,10,16-19] allenic hydrocarbons are isomerised into acetylenes.

Subsequently an analogous rearrangement was observed also in the dehydrohalogenation of polyhalogeno-compounds by sodium amide[20-23].

Isomeric conversions of acetylenic hydrocarbons were widely studied[24-47]. Various examples showed that the triple bond can migrate to either the middle[24-42] or the end[42-47] of the chain.

It must be noted that in dehydrohalogenation by solid or molten alkali without a solvent the specified isomerisation proceeds very weakly or is generally not observed[16].

It has been found that in several instances dehydrohalogenation of polyhalogeno-compounds often leads, not to the expected non-conjugated alkadiynes, but to conjugated alkadiynes[16,48-52]:

$$CH_2BrCHBrCH_2CH_2CHBrCH_2Br \rightarrow \begin{cases} HC{\equiv}C{-}CH_2CH_2C{\equiv}CH \\ H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \end{cases}.$$

Recently a series of authors[53] have also studied the isomeric conversions of various alkadiynes.

Thus it has been shown that when non-conjugated diacetylenes are heated with alkaline agents (potassium hydroxide, sodium amide, etc.) they are isomerised into conjugated diacetylenes[53-55]. When the reaction is carried out in the presence of potassium t-butoxide, both vinylacetylenic and diacetylenic hydrocarbons are converted into conjugated polyenes and polyenynes respectively[56,57]:

$$\begin{array}{ll} RC{\equiv}CCH_2CH_2C{\equiv}C{-}R' & R{-}C{\equiv}CCH_2CH_2C{\equiv}C{-}R' \\ \downarrow & \downarrow \\ R{-}CH{=}CHCH_2C{\equiv}C{-}R' & R{-}CH{=}C{=}CHCH_2C{\equiv}C{-}R' \\ \downarrow & \downarrow \\ R{-}(CH{=}CH)_3R' & R{-}(CH{=}CH)_2C{\equiv}C{-}R' \end{array}.$$

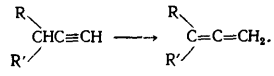
In the presence of potassium t-butoxide various cyclic polyacetylenes are converted into conjugated enynes[58-62] or dienes[63].

As well as the catalysts mentioned, metal oxides, fluorides, and other catalysts have been used for the rearrangement of acetylenic hydrocarbons[64-80]. The isomerisation of acetylenic[7,8,81,82] or vinylacetylenic[83] hydrocarbons was also observed during their alkylation by methyl iodide in the presence of metallic sodium.

Usually the isomerisation of acetylenic hydrocarbons takes place at 160–250°C. Isomerisation does not occur at lower temperatures[34,84,85]. It has been shown experimentally[86] that isomerisation proceeds readily when in monosubstituted acetylenic compounds there is a primary radical at the acetylenic carbon atom:

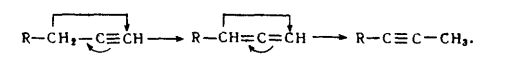
$$R{-}CH_2C{\equiv}CH \rightarrow R{-}C{\equiv}C{-}CH_3.$$

With a secondary substituent at the carbon atom the isomerisation proceeds only to the allene compound:

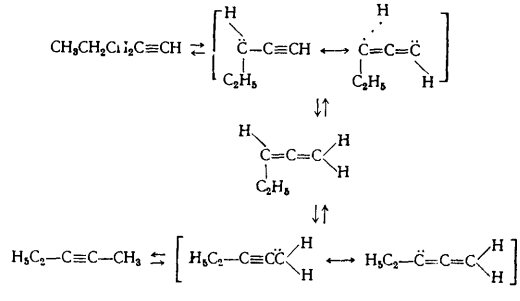


When the substituent in these compounds is a tertiary radical, isomerisation generally does not occur.

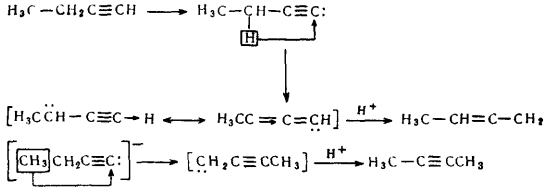
After detailed study of the reaction of mutual conversions of acetylenic compounds, Favorskii[86] concluded that the isomerisation of acetylenes in alcoholic solutions takes place not by addition and loss of the alcohol, as he thought earlier[2], but simply by jumping over of the β hydrogen atom with simultaneous migration of a multiple bond:



In the opinion of Jacobs and coworkers[75] and of other authors[87,88] under the action of alkali deprotonation of one of the labile α hydrogen atoms of the acetylenic or allenic compound takes place. Subsequently the intermediate carbonium ion which is formed rearranges according to the scheme:



Müller[89] suggests that in the isomerisation of acetylenic compounds the proton is detached not from the methylene but from the methine [presumably methylidyne (Ed. of Translation)] group; the anion formed undergoes cationotropic or prototropic rearrangement according to the scheme:

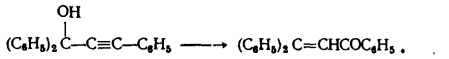


II. ANIONOTROPIC REARRANGEMENT OF ACETYLENIC ALCOHOLS

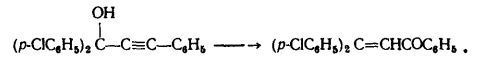
1. Rearrangement of Acetylenic Alcohols into $\alpha\beta$-Unsaturated Ketones. The Meyer–Schuster Rearrangement

In studying the reaction of acetyl chloride with phenylethynyldiphenylcarbinol [1,1,3-triphenylprop-2-yn-1-ol],

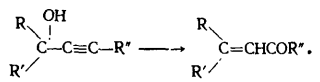
Meyer and Schuster[90] isolated phenylbenzalacetophenone [β-phenylchalcone]:



The authors found that this ketone was the only product when acetyl chloride was replaced by thionyl chloride, hydrogen chloride, acetic anhydride, or sulphuric acid. They showed, by the example of phenylethynyldi-(*p*-chlorophenyl)carbinol [1,1-di-(*p*-chlorophenyl)-3-phenylprop-2-yn-1-ol] that in the above rearrangement it is the hydroxyl group, not the aromatic radical, that migrates:

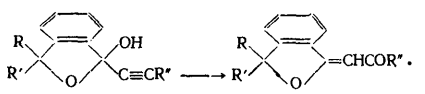


Subsequently various acetylenic alcohols with aliphatic, alicyclic, and aromatic substituents were subjected to rearrangements of this type in the presence of various acid agents[91-106]:

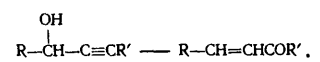


To obtain the best yield it was necessary to carry out the reaction in solvents; often dioxan, acetone, alcohols, and esters of organic acids were used. Acids (sulphuric, formic, sulphonic, etc.) were used as catalysts.

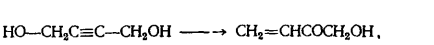
Recently Venus-Danilova and her coworkers have shown that ethynyl derivatives of hydroxyphthaleins undergo the Meyer–Schuster reaction[107,108]:



It has been shown that the rearrangement of secondary acetylenic alcohols proceeds analogously[104]:



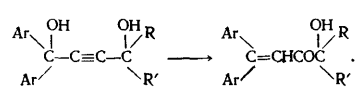
With acetylenic 1,4-glycols the rearrangement leads to the production of α-hydroxy-αβ-unsaturated ketones[109-111]:



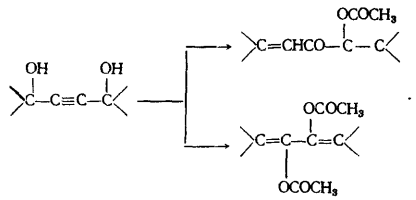
When the reaction is carried out in alcoholic solutions β-alkoxy-α-hydroxyketones or furanidones are formed[110-117].

In the rearrangement of primary-tertiary acetylenic glycols[118,119] under Meyer–Schuster conditions the hydroxyl group which migrates is that connected with the tertiary carbon atom.

In acetylenic glycols with aromatic and aliphatic substituents, on rearrangement it is the hydroxyl group at the carbon connected with the aromatic substituent that migrates[118-122]:

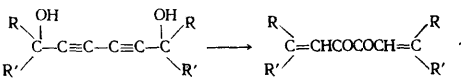


With alicyclic and aromatic symmetrical glycols both hydroxyls migrate, with the formation of acetates of keto-alcohols or diacetates of enols[118,123,124]:

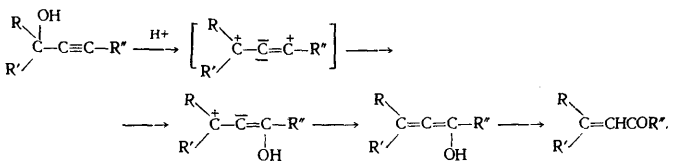


In all instances when the reaction proceeds in the presence of acetyl chloride acetoxy-derivatives of the keto-alcohols produced are obtained.

It was shown recently that on heating diacetylenic glycols in methanol solution in the presence of mercury sulphate they undergo rearrangement with the formation of unsaturated α-diketones[125]:



Dornow and Ische[126] suggest that the Meyer–Schuster rearrangement proceeds by a carbonium ion mechanism with formation of an intermediate vinyl alcohol and its subsequent isomerisation into a vinyl ketone:

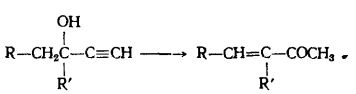


2. Rearrangement of Acetylenic Alcohols into αβ-Unsaturated Aldehydes and Ketones

The rearrangement of acetylenic alcohols with an active acetylenic hydrogen was first studied by Rupe and coworkers. They showed that when acetylenic alcohols react with formic acid they are rearranged into αβ-unsaturated aldehydes[127-135]:



Subsequent studies[136-138] did not confirm the results of Rupe and coworkers. The authors cited reported that αβ-unsaturated ketones, not aldehydes, are obtained in the rearrangement of acetylenic alcohols with active acetylenic hydrogen:

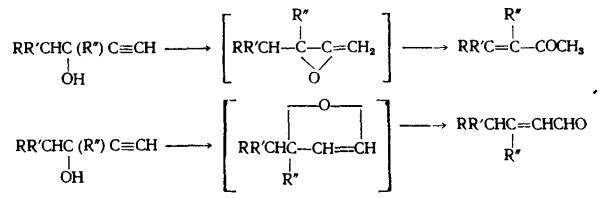


It must be noted that in the work there are no convincing data on the absence of the isomeric aldehydes.

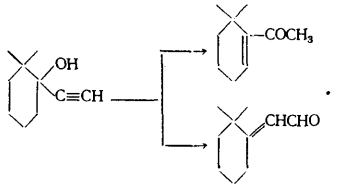
In later communications Rupe and coworkers also mention that ketones are also formed as well as aldehydes[131,134,139].

To explain the chemistry of the formation of aldehydes and ketones, the authors propose a mechanism for the

rearrangement with the intermediate formation of oxidic compounds[134]:

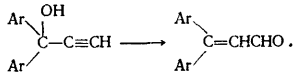


Chanley[140] showed convincingly that in the rearrangement of 1-ethynylcyclohexan-1-ol and its derivatives, in addition to ketones the corresponding $\alpha\beta$-unsaturated aldehydes are formed, in particular 1-ethynylcyclohexan-1-ol gives 50% of the expected ketone and 0.8% aldehyde, and 1-ethynyl-2,2-dimethylcyclohexan-1-ol gives 56% of the ketone and 6% of the aldehyde:



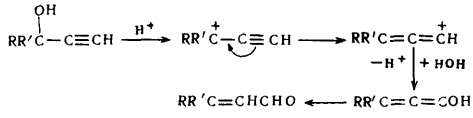
Despite this, in several papers the authors state that in the rearrangement of acetylenic alcohols with aliphatic[141-146], alicyclic[103,141,147-152], and aromatic[153] substituents only the $\alpha\beta$-unsaturated ketones are obtained. Other papers give results showing that in the isomerisation of a series of aliphatic[154-157] and alicyclic[158,159] acetylenic alcohols in addition to the ketones the corresponding $\alpha\beta$-unsaturated aldehydes are isolated.

In contrast to the above results the rearrangement of aromatic acetylenic alcohols with an active acetylenic hydrogen leads to the formation mainly of the expected aldehydes[104,160-169]:

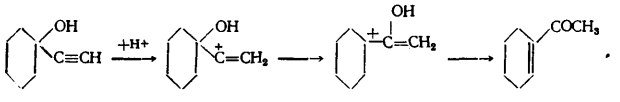


According to Bergmann[154], in the catalytic isomerisation of ethynyldimethylmethanol [2-methylbut-3-yn-2-ol] in the vapour phase β-methylcrotonaldehyde is formed in 30% yield. Other results have been published about the rearrangement of various acetylenic alcohols into aldehydes or ketones in the presence of various catalytic agents[170-176].

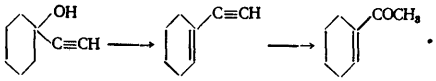
Hennion and coworkers[144] represent the mechanism of the rearrangement of ethynylcarbinols as an allyl rearrangement:



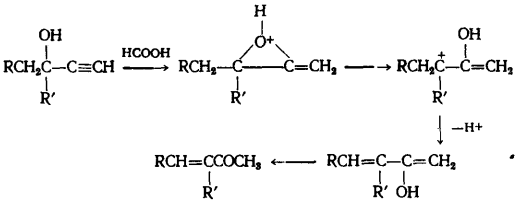
Newman[146,155] suggests that the rearrangement of ethynylcarbinols into $\alpha\beta$-unsaturated ketones proceeds by a carbocation mechanism:



Others think[138,144,177] that under the reaction conditions acetylenic alcohols are dehydrated into enynes and their subsequent hydration leads to the formation of ketones:



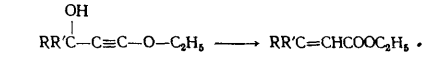
Cram and Hammond[178] explain the formation of $\alpha\beta$-unsaturated ketones by the following scheme:



It is evident that the mechanism of the formation of aldehydes and ketones from acetylenic alcohols has not been established and additional studies are needed.

3. Rearrangement of Alkoxyacetylenic Alcohols into the Esters of $\alpha\beta$-Unsaturated Acids

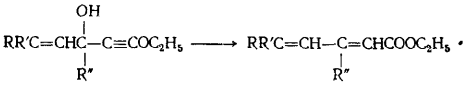
In the presence of sulphuric or hydrochloric acids alkoxyacetylenic alcohols undergo anionotropic rearrangement with the formation of the esters of $\alpha\beta$-unsaturated acids[179-182]:



Arens and coworkers[183] showed that alkoxyacetylenic alcohols are also rearranged in the presence of weakly basic amines, particularly in the presence of nitroaniline.

Heterocyclic[184], aldehydo-[185], and keto-[186] alkoxyacetylenic alcohols undergo this reaction.

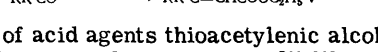
Esters of dienic acids are obtained in the rearrangement of vinyl(alkoxy)acetylenic alcohols[179,180,187]:



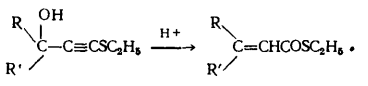
Alcohols in which the double bond is in the $\beta\gamma$-position or further removed undergo rearrangement in an analogous manner[187,189].

This reaction has been used for the preparation of perfumes[180,190], steroids[191-196], and terpenes[197]. Other studies of the rearrangement of various alkoxyacetylenic alcohols have appeared[198,199].

It has been shown that in the reaction of carbonyl-containing compounds with ethoxyacetylene in the presence of BF_3, esters of $\alpha\beta$-unsaturated acids are formed[200]:

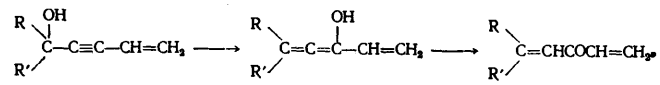


In the presence of acid agents thioacetylenic alcohols are also rearranged in an analogous manner[201,202]:



4. Rearrangement of Vinylacetylenic and Divinylacetylenic Alcohols

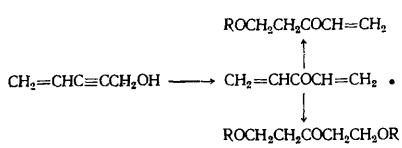
Nazarov and coworkers have shown that in acetone solution in the presence of mercury sulphate vinylacetylenic alcohols are isomerised into divinylketones by the following scheme[203,204]:



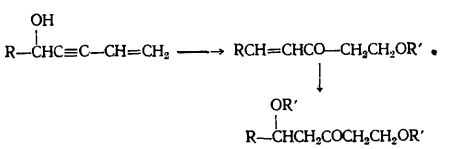
This reaction was carried out with a yield of ketone up to 40% for dimethyl(vinylethynyl)methanol [2-methylhex-5-en-3-yn-2-ol] alone. On increasing the molecular weight of the tertiary alcohol the reaction proceeds with difficulty and the yields of the divinyl ketones do not exceed 5% owing to side-reactions, particularly the dehydration and cyclodehydration of the alcohol.

It was found later that the isomerisation of vinylacetylenic alcohols takes place exceptionally readily in a solution of alcohols capable of adding to divinyl ketones. BF_3.HgO and mercury sulphate are catalysts for isomerisation[204,205]. The ease of isomerisation under these conditions (especially in methanol) is explained by the fact that the divinyl ketones formed are converted by addition of the alcohols into β-alkoxyketones and leave the sphere of reaction.

The isomerisation of the primary vinylethynylmethanol under these conditions leads to the formation of a divinyl ketone. Under the conditions of the experiment one or two methanol molecules add to the latter to form 1-methoxypent-4-en-3-one and 1,5-dimethoxypentan-3-one[206]:

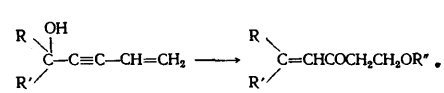


In solution in alcohols in the presence of mercury salts secondary vinylethynylmethanols are isomerised into divinyl ketones, which readily add one molecule of the alcohol at the unsubstituted vinyl group to form unsaturated alkoxy-ketones[207]:

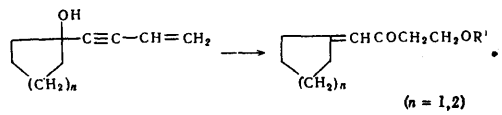


Under the influence of mercury salts a second alcohol molecule can be added to a β-alkoxyvinyl ketone to form dialkoxy-ketones.

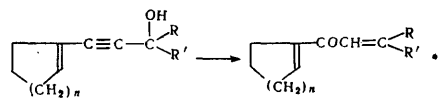
A still greater number of stages is observed in the addition of alcohols to ββ-dialkyldivinyl ketones [bis-(2-alkylvinyl)ketones]. Thus in the isomerisation of tertiary vinylacetylenic alcohols usually only one molecule of alcohol can be added to the divinyl ketones formed at the unsubstituted vinyl group and during this the corresponding unsaturated β-alkoxy-ketones are mainly formed[204,205,208,209]:



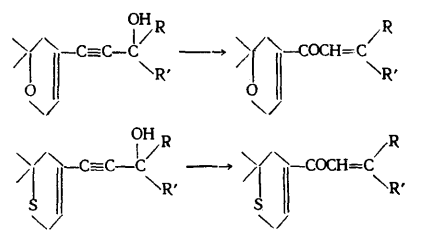
It has been shown that alicyclic vinylacetylenic alcohols are also rearranged with the formation of a mixture of the corresponding divinyl and β-alkoxy-ketones[210,211]:



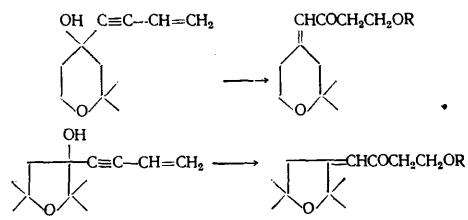
The isomerisation of Δ′-cyclohexenylethynylmethanols[212] and also of Δ′-cyclopentenylethynylmethanols[213] leads to the formation of divinyl ketones:



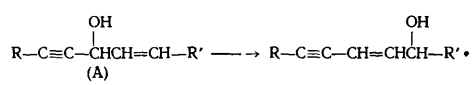
The isomerisation of vinylacetylenic alcohols which contain a vinyl group in the heterocyclic ring undergo isomerisation in an analogous manner[214-216]:



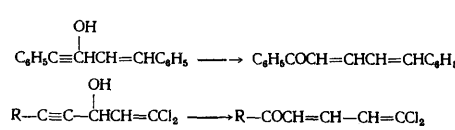
Many results on the rearrangement of vinylacetylenic alcohols containing various substituents have been published[217-226]. It has been found that 4-(vinylethynyl)tetrahydropyran-4-ols[226,227] and also vinylacetylenic furanols[228] undergo isomerisation with the formation of the expected ketones:



It is interesting to note that vinylacetylenic alcohols (A), depending on the nature of the substituent, undergo either allyl or prop-2-ynyl rearrangement. Thus the carbinols (A) undergo the allyl rearrangement[229-248]:

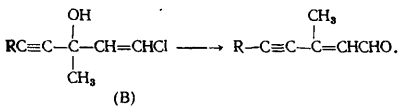


When R and R′ are electron-acceptor atoms or groups, particularly chlorine[102] or phenyl radicals[249], these alcohols undergo prop-2-ynyl rearrangement to form divinyl ketones:



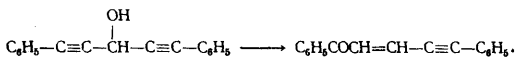
The prop-2-ynyl rearrangement is also observed when in the alcohols (A) R = C_6H_5 and R′ is a methyl[249] group or

hydrogen[169]. It is curious that the monochlorovinylacetylenic alcohols (B) undergo an allyl rearrangement under analogous conditions[250]:



(B)

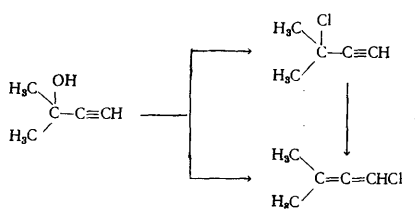
It has been found that diacetylenic methanols also rearrange in a similar manner[104]:



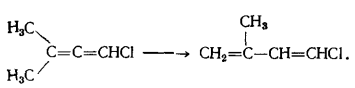
III. ACETYLENE–ALLENE REARRANGEMENT

1. Rearrangement of α-Halogenoacetylenes

Favorskii and Favorskaya found that reaction of dimethylethynylmethanol with hydrogen chloride in the presence of copper(I) chloride and ammonium chloride gives, in addition to the expected chloroalkyne, a derivative of allyl chloride[251]:



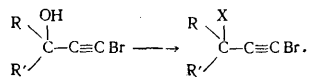
It was shown later that under the specified conditions chloroacetylene is actually rearranged into chloroallene[252]. On prolonged standing over ammonium chloride and copper(I) chloride, the latter is subjected to allene–diene rearrangement with the formation of the diene chloride[252]:



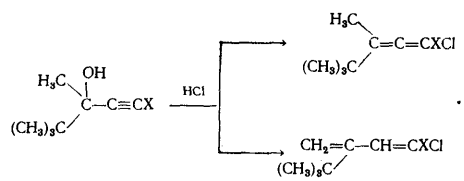
In studying the reaction of hydrogen chloride with dimethylethynylmethanol Hennion and coworkers[253] showed that when the reaction is carried out in the presence of calcium chloride, chloroacetylene is obtained in good yield. However, when the reaction is carried out in the presence of copper(I) chloride and ammonium chloride the main reaction product is allenyl chloride. An analogous picture is also observed with other acetylenic alcohols[143,254,255]. According to the results of Favorskaya[256–258] and others[143,259–261] this reaction proceeds similarly with hydrogen bromide. Campbell and coworkers[262] showed that in the reaction of hydrogen chloride with ethylethynylmethylmethanol the expected isomeric chloro-compounds are obtained. Favorskaya[263] showed that when this reaction is carried out in the presence of copper(I) chloride and ammonium chloride the chloroalkyne which is formed slowly rearranges into both the allenyl chloride [chloroalka-1,2-diene] and the diene chloride. When the reaction is carried out without catalysts[143] a chloroalkyne is mainly obtained.

Isomerisation of 3-chloro-3-ethylpent-1-yne proceeds even more slowly; a chloroalka-αβ-diene is still obtained but does not rearrange into the diene [chloride][264].

In the hydrochlorination of t-butylethynylmethylmethanol [3,4,4-trimethylpent-1-yn-3-ol] the sole product of the reaction is a chloroalka-1,2-dien[265]. Dialkyl(bromoethynyl)methanols react with hydrogen halides to form the corresponding halogenoalkynes[266]:



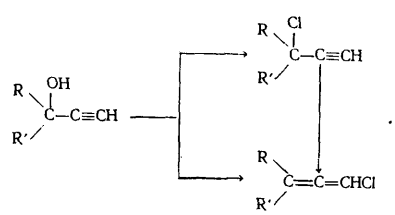
It was found also that t-butyl(halogenoethynyl)methylmethanols react with hydrogen chloride to give chloroalka-1,2-dienes[267] but the corresponding bromo-alcohols give mainly the bromoalka-1,3-dienes:



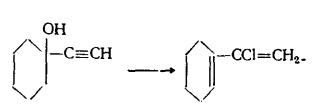
Dialkylethynylcarbinols react with hydrogen chloride[268,269] or phosphorus(III) chloride[270] to form chloroacetylene; however, according to the results of other authors[92], the action of hydrogen bromide on this alcohol gives, in addition to bromoalkynes, halogen derivatives of allene.

All attempts to carry out this reaction with other dialkylethynylcarbinols were unsuccessful[271,272]. The acetylene–allene rearrangement was also observed in the reaction of secondary acetylenic alcohols with hydrogen halides[255,273].

The reaction of aliphatic ethynylcarbinols with thionyl chloride[273,274] or phosphorus(V) chloride[275] in ethereal solution leads to the formation of two isomeric chlorides:

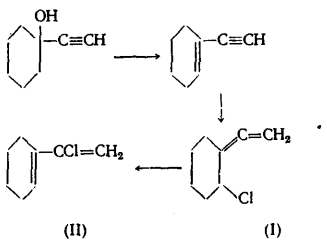


It should be noted that when a bromoallene derivative is formed in the reaction of tertiary acetylenic alcohols with $[(C_6H_5O)_3PBr_2]$, secondary and primary acetylenic alcohols form only bromoalkynes[261]. Jones and coworkers[276] found that thionyl chloride reacts with ethynylcyclohexanol in the presence of pyridine to give 1-chlorovinylhexene:



We think that a diene chloride could be obtained by the dehydration of an acetylenic alcohol followed by the addition of hydrogen chloride to the enyne formed in the 1,4 position to give an allenic chloride (I). The latter isomerises

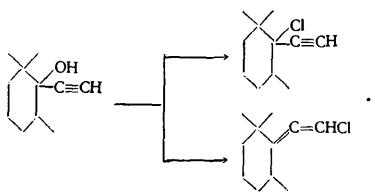
under the conditions of the experiment into the diene chloride (II):



(II) (I)

The formation of chlorides in the work of Bergmann and others[275] can be explained similarly.

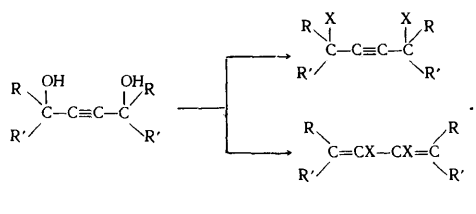
In the reaction of ethynylcyclohexanol and other alicyclic ethynylcarbinols with thionyl chloride in the presence of pyridine in various solvents both acetylenic and allenic chlorides are formed[255,272]:



Acetylene–allene rearrangement was also observed in the reaction of thionyl chloride with aromatic acetylenic alcohols[278]. It was shown that when prop-2-ynyl halides are heated in the presence of copper salts they are rearranged into halogenoalka-$\alpha\beta$-dienes[279]; during this, partial isomerisation of the halogenoalka-$\alpha\beta$-dienes was also noted.

Other information on the rearrangement of halogenoacetylenes into halogenoalka-$\alpha\beta$-dienes is available[280-285].

The reaction of acetylenic glycols with hydrogen halides leads to the formation of dichlorodienes (III)[286-302] by the scheme:



(III)

It was found that in the action of hydrogen halides on acetylenic 1,4-glycols hydroxyl is replaced by halogen and acetylenic dihalogeno-derivatives are obtained. Under the reaction conditions the latter undergo isomerisation into dihalogeno-derivatives of dienes.

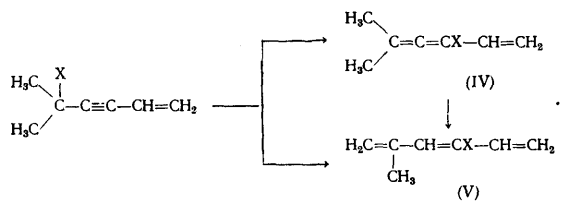
According to Johnson[109] 1,4-dibromo- or 1,4-di-iodobut-2-ynes are converted on standing into 2,3-dihalogenobutadienes:

$$XCH_2C{\equiv}CCH_2X \longrightarrow CH_2{=}CX{-}CX{=}CH_2.$$

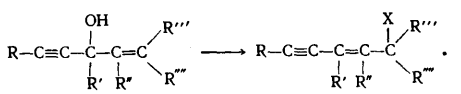
1,4-Dichlorobutynes rearrange similarly in the presence of copper(I) chloride and ammonium chloride[303].

Nazarov and coworkers[304] showed that on shaking chlorodimethyl(vinylethynyl)methane with copper(I) chloride and ammonium chloride at room temperature it undergoes rearrangement with the formation of allenic (IV) and trienic (V) chlorides.

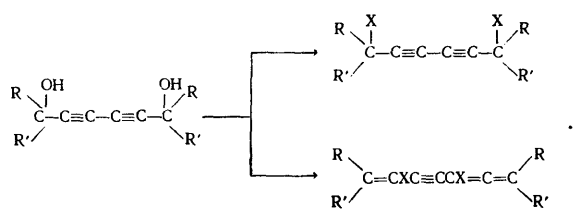
It is interesting to note that in the production of vinylacetylenic bromides only allenic (IV) and trienic (V) bromides are obtained[305]:



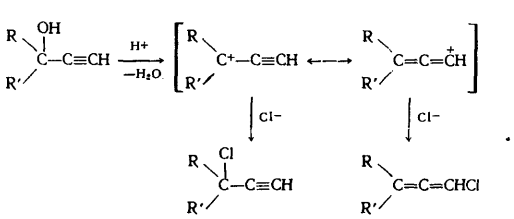
In contrast with this, in the reaction of the vinylacetylenic carbinols mentioned below with hydrogen chloride, thionyl chloride, or phosphorus(III) bromide the reaction passes through an allyl rearrangement[236,249,306-310]:



Diacetylenic glycols react with hydrogen chloride to form diacetylenic and diallenic chlorides[311]:

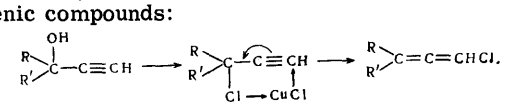


It is interesting that the reaction of hydrogen halides with diethynylquinols also proceeds through a rearrangement[312,313]. Hennion and coworkers[253,314-317] represent the mechanism of the reaction as follows. Under the influence of a proton initially hydroxyl is detached from the alcohol to form a carbonium ion; addition of a chloride anion to the latter leads to the formation of acetylenic and allenic chlorides:

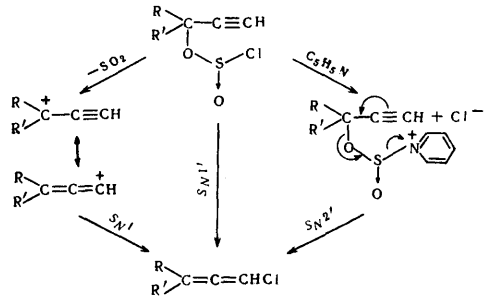


Other authors[302,318,319] regard the isomerisation of chloroalkynes analogously.

The isomerisation of chloroalkynes under the influence of catalysts is improbable, according to Hennion and coworkers[253,315], taking into account the linear structure of acetylenic compounds:

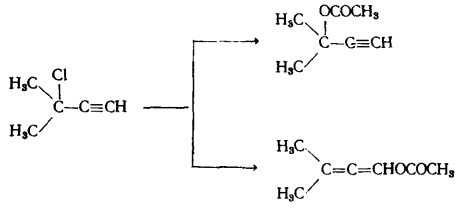


Other authors[259,320] suggest that a chloroalka-1,2-diene can be formed both by an S_N1 and by an S_N2' mechanism:

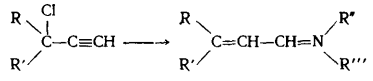


2. Rearrangement on Replacement of the Halogen in α-Halogenoacetylenes

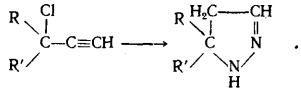
In the nucleophilic replacement of chlorine in α-chloroacetylenes the final product of the reaction is often the corresponding allene compound. Thus in the reaction of sodium acetate with chloroethynyldimethylmethane [3-chloro-3-methylbut-1-yne], in addition to an acetate derivative of acetylene the acetate of allenic alcohol [3-methylbut-1,2-dienyl acetate] is obtained[321]:



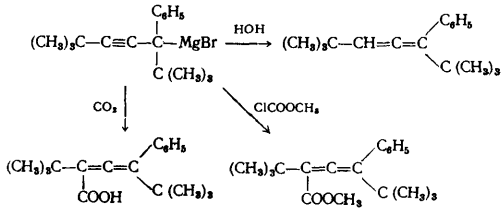
It was found recently that acetylenic chlorides react with substituted hydrazines to form the hydrazones of the isomeric aldehydes[322]:



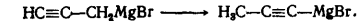
With unsubstituted hydrazine instead of the acetylenic hydrazines 5,5-dialkyl-Δ^2-pyrazolines are obtained[323]:



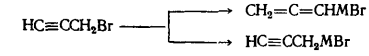
Marvel and coworkers[92] found that during the hydrolysis of an Iotsich complex obtained from an acetylenic chloride instead of the acetylenic hydrocarbon the corresponding allenic hydrocarbon was obtained. The acetylene–allene rearrangement is observed also in the reaction of an Iotsich complex with carbon dioxide or with methyl chloroformate[92]:



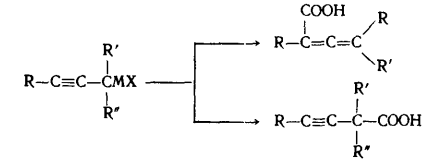
Isomerisation is not observed in the formation of magnesium or sodium derivatives from prop-2-ynyl bromides, but on standing the prop-2-ynylmagnesium complex is isomerised into the prop-1-ynyl complex[324]:



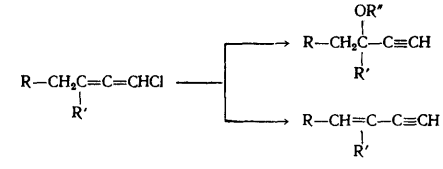
However, in making prop-2-ynylzinc bromide a mixture of acetylenic and allenic derivatives is formed, but with aluminium only a derivative of allene structure is obtained[324,325]:



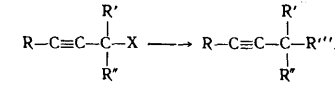
When the prop-2-ynyl Grignard complex reacts with carbon dioxide, a mixture of acetylenic and allenic acids is obtained[324,326-331]:



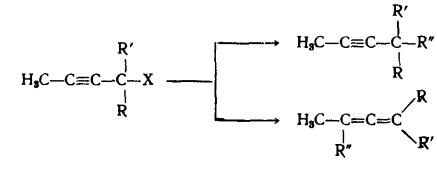
In halogenoalkynes with a halogen atom in β or other positions isomerisation was not observed[332]. It must be noted that an acetylene–allene rearrangement does not occur in the preparation of ethers from the corresponding alkyne chlorides and alcohols in the presence of alkali[314,333] and also in the replacement of halogen in various prop-2-ynyl halides by a variety of agents (amines, alkoxides, salts of acids, sodioacetoacetic ester and sodiomalonic ester[324]). In contrast to this in the replacement of allenic chlorides by a hydroxyl[252,255,333] or alkoxyl[314] group the reaction proceeds with rearrangement:



It was shown that when acetylenic chlorides react with Grignard complexes normal substitution products are obtained[334-336]:

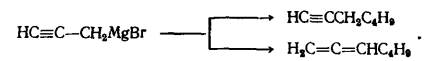


However, in a more detailed study of this reaction, Zakharova noted that in addition to the normal substitution product rearrangement products are obtained—allenic hydrocarbons[337-339]:



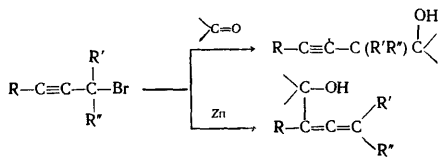
Subsequently the above results were confirmed by other authors[324,340-345] by various examples with primary, secondary, and tertiary acetylenic chlorides. Here allenic hydrocarbons are sometimes the main products of the reaction[346].

The rearrangement also takes place during the reaction of prop-2-ynylmagnesium bromide with dibutyl sulphate[347]:



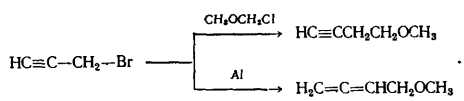
Lithium or sodium acetylides react with benzyl chloride to form allenic compounds[348].

In the presence of zinc acetylenic halides are condensed with aldehydes and ketones with the formation of β-hydroxyacetylenes or -allenes[325,349-351]:

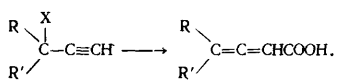


The above halides react similarly with esters[352] and with amides[349] of acids in the presence of metallic magnesium.

It is interesting to note that allenic Grignard complexes under these conditions form mainly acetylenic alcohols[325, 349,353,354]. The complex of prop-2-ynyl bromide with aluminium reacts with chlorodimethyl ether with the formation of a mixture of acetylenic and allenic esters[325]:

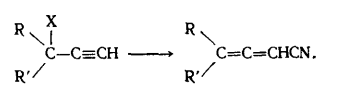


In the reaction of α-halogenoalkynes with tetracarbonylnickel in ethanol or water solution an acetylene–allene rearrangement takes place with the formation of the corresponding allenic acids or their esters[355,356]:

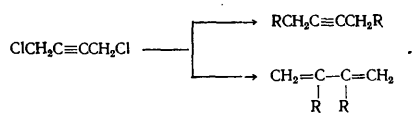


It has been shown that under the same conditions chloroallenes do not react[355], consequently the preliminary rearrangement of chloroacetylenes into chloroallenes and the subsequent course of the reaction is ruled out.

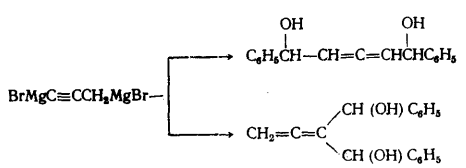
According to patent claims[357] α-halogenoalkynes react with sodium cyanide so that allenic nitriles are obtained:



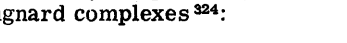
Levina and coworkers[358-360] showed that in the reaction of 1,4-dichlorobutyne with alkylmagnesium bromides a mixture of acetylenic and 1,3-dienic hydrocarbons is obtained:



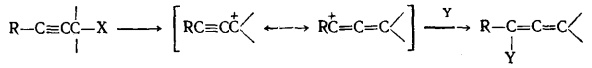
It was also found that the dimagnesium derivative of prop-2-ynyl bromide reacts with benzaldehyde to form an allenic alcohol[324]:



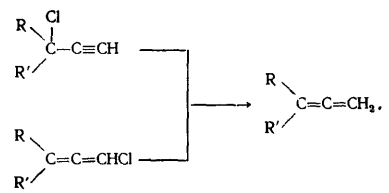
Gaudemar explains the formation of allenic alcohols from acetylenic halides by the prototropic isomerisation of intermediate Grignard complexes[324]:



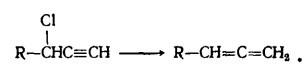
However, in the opinion of many authors the above rearrangements take place through a carbonium ion mechanism according to the scheme[302,324,361]:



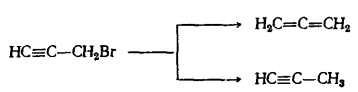
Ginzburg[362,363] showed that in the reduction of α-halogenoacetylenes by zinc instead of the expected acetylenic hydrocarbons allenic ones are obtained. The latter are also obtained in the reduction of allenic chlorides:



Reactions proceed similarly with secondary acetylenic chlorides[364,365]:



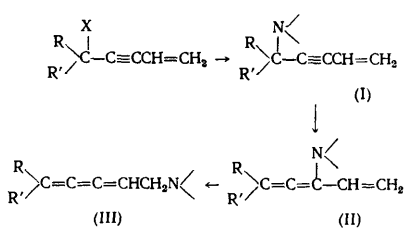
Under these conditions prop-2-ynyl bromide is reduced to a mixture of allene and methylacetylene[273,366,367]:



An analogous reaction is observed in the reduction of chloroacetylenes by metallic zinc, magnesium amalgam and silver, and also by lithium tetrahydroaluminate[75,273, 361,367-369]. Vinylacetylene and diacetylene halides are reduced similarly[370]. Several authors[361,364] have discussed the mechanism of reduction of chloroacetylenes by the above reagents.

IV. ACETYLENE–ALLENE–CUMULENE REARRANGEMENT

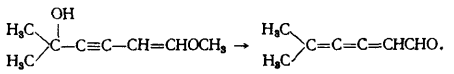
It has recently been found that various vinylacetylenic chlorides smoothly react with amines at room temperature both in the presence of water and also in various solvents: a mixture of vinylacetylenic (I), allenic (II), and cumulenic (III) amines is obtained[371-374]:



It has been found that in the presence of equimolecular amounts of amines the amount of cumulenic amine in the reaction products is increased[372]. The reaction proceeds smoothly at 20–25°C over a few days. It was shown that

under the conditions of the reaction vinylacetylenic and allenic amines undergo rearrangement with the formation of allenic and cumulenic amines.

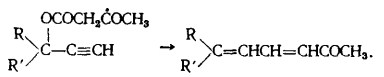
It was found recently that during the slow distillation of a (methoxyvinylethynyl)dimethylcarbinol in the presence of potassium hydrogen sulphate a cumulenic aldehyde is obtained[375,376]:



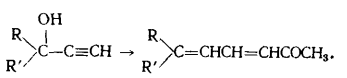
The production of cumulenes from acetylenic and diacetylenic glycols and dihalogen derivatives is another type of rearrangement with participation of the π electrons of the triple bond. There is a review article about this problem[377] so we shall not discuss it.

V. REARRANGEMENT OF ACETOACETATES AND OF ACETATES OF ACETYLENIC ALCOHOLS

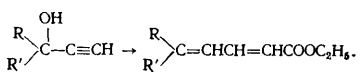
It has been shown that the acetoacetates of acetylenic alcohols are decarboxylated on heating to 160–200°C with the formation of dienic ketones[378,379]:



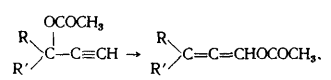
It was found later that this reaction also occurs on the gradual heating of tertiary acetylenic alcohols with acetoacetic ester[380,381]:



Preobrazhenskii and coworkers[382] showed that malonic ester also reacts with acetylenic alcohols, esters of dienic acids being formed as a result:

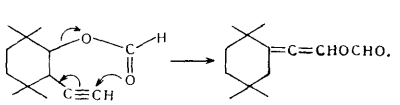


It was also shown that in the pyrolysis of acetates or formates[383–386] of ethynylcarbinols in a steam of nitrogen, acetates of allenic carbinols are obtained as a result of a rearrangement:



The mechanism of the above reaction has been discussed in several papers. Some authors think that it proceeds without the formation of intermediate vinyl esters, others[387–398] explain the formation of the final products through a Claisen rearrangement of the vinyl esters.

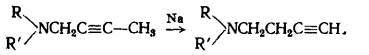
The mechanism of the rearrangement of acetates of acetylenic alcohols has been presented by Landor and Landor[150] as a cyclic process:



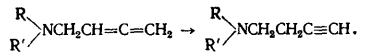
This problem is discussed in greater detail elsewhere[389,390].

VI. REARRANGEMENT OF ACETYLENIC COMPOUNDS CONTAINING OTHER FUNCTIONAL GROUPS

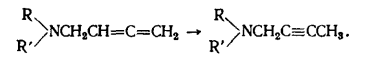
Babayan and coworkers found that 1-dialkylaminobut-2-yne is readily isomerised into 1-dialkylaminobut-3-yne in ethereal solution in the presence of metallic sodium at room temperature[391,392]:



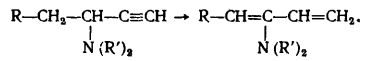
Under these conditions allenic amines also isomerise to form acetylenic amines[393]:



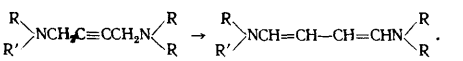
On heating allenic amines in the presence of bases isomerisation proceeds in the reverse direction[394]:



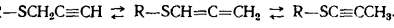
When 3-dialkylaminobut-1-ynes are heated in the presence of aluminium oxide and 1% $Fe(OH)_3$ they are rearranged into the corresponding dienic amines[144,395]:



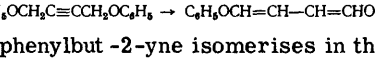
On passing 1,4-bisdialkylaminobut-2-ynes over Cr_2O_3 catalyst[396] at 320–330°C and also in the presence of metallic sodium[397] they are isomerised with formation of the dienic amines:



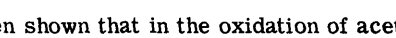
It has been shown that acetylenic thioesters also undergo isomerisation[398] in the presence of bases:



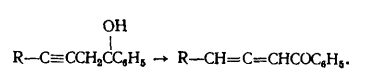
1,4-diphenoxybut-2-ynes are rearranged similarly on heating with potassium t-butoxide[399]:



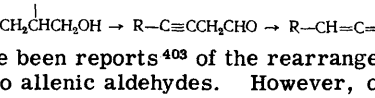
1,1,4,4-Tetraphenylbut-2-yne isomerises in the presence of sodium ethoxide into 1,1,4,4-tetraphenylbuta-2,3-diene[400]:



It has been shown that in the oxidation of acetylenic carbinols or keto-carbinols, instead of the expected acetylenic ketones allenic ketones are obtained[349,401]:

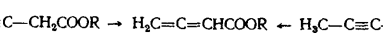


Winter[402] observed similar behaviour in the oxidation of acetylenic glycols with sodium [periodate. (Ed. of Translation)]:



There have been reports[403] of the rearrangement of acetylenic into allenic aldehydes. However, other results[404,405] contradict this.

Johnson and coworkers studied the prototropic conversions of acetylenic acids by many examples. It was shown that prop-2-ynylcarboxylic acid or its esters and also prop-1-ynylcarboxylic acid in the presence of potassium hydroxide is rearranged into an allenecarboxylic acid or its esters[406]:



However, it was found that but-2-yncarboxylic or buta-2,3-diencarboxylic acids are isomerised into but-3-yncarboxylic acid[407]:

$$\left.\begin{matrix} H_3C{-}CH_2C{\equiv}CCOOH \\ H_3C{-}CH{=}C{=}CHCOOH \end{matrix}\right] \rightarrow H_3C{-}C{\equiv}C{-}CH_2COOH.$$

In the presence of amines acetylenic hydroxy-acids are also rearranged into allenic[408]:

$$C_6H_5CHC{\equiv}CCO_2Me \rightarrow \left[C_6H_5\overset{OH}{\overset{|}{C}}{=}C{=}CHCO_2Me\right] \rightarrow C_6H_5COCH{=}CHCO_2Me.$$

It is curious that in the presence of potassium hydroxide acetylenic alcohols with aromatic substituents are converted into $\alpha\beta$-unsaturated ketones by prototropic rearrangement[409]:

$$(C_6H_5)_2CHC{\equiv}CC_6H_5 \rightarrow \left[C_6H_5\overset{OH}{\overset{|}{C}}{=}C{=}CHC_6H_5\right]$$
$$\downarrow$$
$$C_6H_5COCH_3 + C_6H_5CHO \leftarrow C_6H_5COCH{=}CHC_6H_5$$

It was found that acetylenic acids in which the triple bond is further removed from the carboxyl group undergo rearrangement with formation of the corresponding allenic and dienic acids[407]:

$$R{-}C{\equiv}C{-}CH_2CH_2COOH \rightarrow RCH{=}C{=}CHCH_2COOH \rightarrow RCH{=}CHCH{=}CHCOOH$$

[R = CH_3 (Ed. of Translation)].

In the oxidation of acetylenic glycols with the aid of Cr_2O_3 Jones and coworkers[410] isolated isomeric allenic acids:

$$HOCH_2(CH_2)_nC{\equiv}CCH_2(CH_2)_nCH_2OH \rightarrow HOOC(CH_2)_nCH{=}C{=}CH(CH_2)_nCOOH.$$
$$\uparrow\downarrow$$
$$HOOCCH_2(CH_2)_nC{\equiv}C(CH_2)_nCOOH$$

In the presence of bases vinylacetylenic[350] and diacetylenic[411] acids are converted by a prototropic rearrangement into the corresponding allenic and dienic acids:

$$RC{\equiv}CCH{=}CHCH_2COOH \rightarrow RCH{=}C{=}CHCH{=}CHCOOH$$
$$\left.\begin{matrix} HOOCCH_2C{\equiv}CC{\equiv}CCH_2COOH \\ HOOCC{\equiv}C(CH_2)_2C{\equiv}CCOOH \end{matrix}\right] \rightarrow HOOCCH{=}CHCH{=}CHC{\equiv}CCOOH.$$

The isomerisation of conjugated diacetylenic acids leads to the production of polyenic acids[411]:

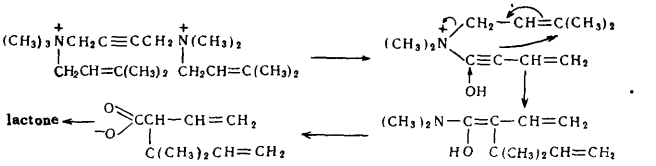
$$HOOC(CH_2)_2(C{\equiv}C)_2(CH_2)_2COOH \rightarrow HOOC(CH{=}CH)_4COOH.$$

It was shown recently that prop-2-ynyl vinyl ethers undergo a Claisen rearrangement as follows[412]:

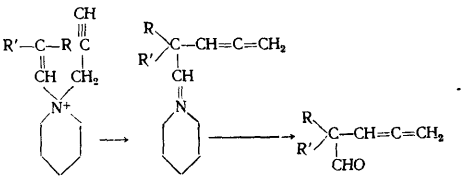
$$CH_2{=}CHOCH_2C{\equiv}CH \xrightarrow[CO_2]{C_2H_5MgBr} HOOCC{\equiv}CCH_2OCH{=}CH_2$$
$$\downarrow$$
$$HOOC{-}\overset{CH{-}CHO}{\overset{\|}{C}}{-}CH{=}CH_2 \leftarrow HOOC{-}\overset{CH_2CHO}{\overset{|}{C}}{=}C{=}CH_2$$
$$\downarrow\uparrow$$
$$CH{-}CH{-}OH$$
$$\|\quad\diagdown O$$
$$H_2C{=}CHC{-}\overset{|}{C}{=}O$$

According to some investigators[412,413], other prop-2-ynyl vinyl ethers undergo this reaction, particularly the prop-2-ynyl acetal of isobutyraldehyde. It was also shown that the 1,4-bisdiphenyl esters of but-2-yn-1,4-diol undergo a Claisen rearrangement when heated in diethylaniline[414].

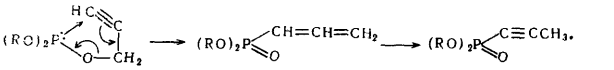
Babayan and coworkers[415] showed that quaternary ammonium bases which contain $\beta\gamma$-acetylenic and allyl radicals form acids or the corresponding lactones under the influence of aqueous alkalis, by the scheme:



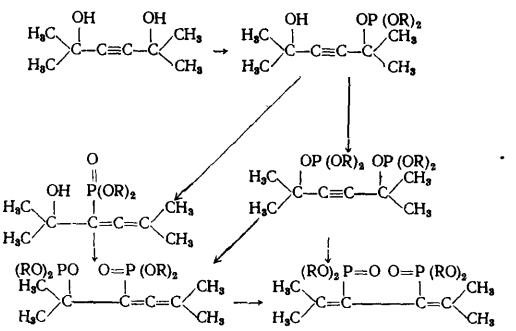
According to the result of Opitz[416], prop-2-ynyl vinyl bases undergo a Claisen rearrangement with the formation of intermediate enamines which are hydrolysed into allenic aldehydes:



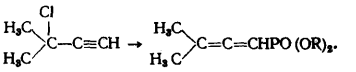
Pudovik and coworkers[417] showed that dialkyl-$\beta\gamma$-propynyl phosphites isomerise on standing into the dialkyl esters of $\alpha\beta$-propynylphosphinic acids:



It has been shown that phosphoric esters of butyndiols[418,419] also undergo the rearrangement described above:



Analogous results were obtained in the reaction of chloroethynyldimethylmethane [3-chloro-3-methylbut-1-yne] with a trialkyl phosphite[420]:



An acetylene–allene rearrangement was observed in the reaction of acetylenic carbinols with R_1R_2PCl, R_1PCl_2, PCl_3.[421] Allenic and acetylenic esters of phosphonic acids readily undergo prototropic isomerisation on heating in the presence of a catalytic amount of sodium ethoxide[422]:

$$RCH{=}C{=}CHPO(OR)_2 \rightarrow RCH_2C{\equiv}CPO(OR)_2,$$
$$CH{=}CH{-}C{\equiv}CCH_2PO(OC_2H_5)_2 \rightarrow CH_3CH{=}CHC{\equiv}CPO(OR)_2.$$

The authors state that these rearrangements proceed more smoothly than the rearrangement of the corresponding ethylene esters of phosphoric acid[423].

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C-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

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I. INTRODUCTION

From the time it was established that cellulose is a high-molecular-weight polysaccharide, the elementary unit of which contains alcoholic hydroxyls, investigations in the field of cellulose chemistry were directed mainly towards the study of the reactions involving replacement of the hydrogen atoms of the hydroxyl groups by acyl and alkyl radicals, that is, reactions of *O*-acylation and *O*-alkylation. The interest in obtaining cellulose ethers and esters is due to their widespread use in various products. Existing reviews and monographs mainly survey the progress in the field of the preparation and investigation of the properties of *O*-derivatives of cellulose. Even in the reviews which have appeared recently, in addition to such problems of cellulose chemistry as the dependence of the reactivity of cellulose on its physical structure and the comparative reactivity of the hydroxyl groups in alkylation and acylation, only problems arising in connection with the preparation of cross-linked cellulose macromolecules and graft copolymers of cellulose are considered[1,2].

The present review considers the development of the chemistry by the *C*-derivatives of cellulose, in which the hydroxyl groups are replaced by other functional groups. After the publication of the last monographs on cellulose chemistry[3,4] a number of new syntheses of aminodeoxy- and halogenodeoxy-celluloses have been effected. Hydrazino-, thiocyanato-, nitro-, mercapto-, and other new *C*-derivatives of cellulose have now been obtained.

The chemistry of the *C*-derivatives of cellulose is of great theoretical interest for the further study of the structure of cellulose. It allows a large number of reactions to be used for studying the glucopyranose unit. The investigation of the properties of *C*-derivatives of cellulose with a specified position of a substituent in the elementary unit allows information to be obtained about the carbon atom at which a given substituent is located. This will evidently facilitate an understanding of the complex problems of the mutual influence of groups in carbohydrates and the induction effects acting in them.

The practical interest in the chemistry of *C*-derivatives of cellulose consists both in the modification of cellulose materials with the aim of discovering new possibilities for their use, and also in the search for new ways of using cellulose as an organic raw material.

II. AMINO-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

Attempts to replace the hydroxyl groups in cellulose and starch by amino-groups were made about 75 years ago[5], but the interest in this problem has never waned since then. Amination was carried out with the aim of increasing the dyeability of cellulose fibres[6,7], and for the production of