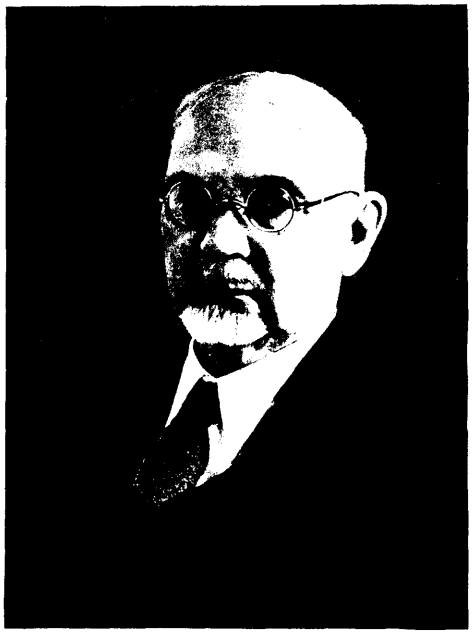
RUSSIAN CHEMICAL REVIEWS
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A. E. ARBUZOV

The Editorial Board of the journal Uspekhi Khimii warmly congratulate Aleksandr Erminingel'dovich Arbuzov on celebrating his 85th birthday and completing 60 years of scientific work and wish him good health and progress in his beloved scientific profession.

# CHEMISTRY OF VINYLETHYNYLCARBINOLS

S. A. Vartanyan

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## INTRODUCTION

Owing to the high activity of the hydroxyl group and the ability of the triple bond to take part in various addition, polymerisation, and condensation reactions, vinylacetylenic

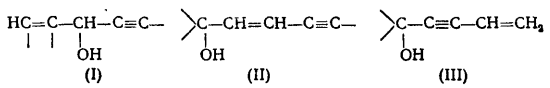
alcohols are important starting materials in the synthesis of a great many compounds. Some of these compounds have emerged from laboratory practice and become important industrial products or intermediates [1,2].

Nazarov's review [1] of the chemistry of vinylacetylenic alcohols covers all the data published prior to 1945. Nevertheless, since this aspect of the chemistry of acetylene is being continually and intensively developed, the need has arisen to collate recently published data. In the present review an effort has been made to gather, and where possible, systematise the extensive information which has accumulated on this subject.

## 1. SYNTHESIS OF VINYLACETYLENIC ALCOHOLS

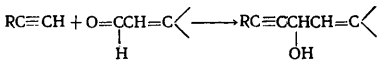
The condensation of acetylene and its monosubstituted derivatives with carbonyl compounds in the presence of alkali, first carried out by Favorskii [3], has been the subject of many investigations in the last few decades [4]. The Favorskii reaction is at present one of the simplest and most accessible methods for the synthesis of a great many acetylenic alcohols.

A further step in the development of this reaction was the preparation of acetylenic alcohols containing a double bond. Three types of such compounds are known:

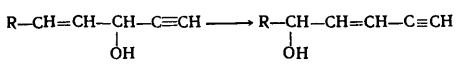


(I) (II) (III)

Carbinols of type (I) are obtained by condensing monosubstituted acetylenic hydrocarbons with $\alpha\beta$-unsaturated aldehydes and ketones [5-19]; condensation by means of sodium in liquid ammonia [20,21] gives satisfactory yields.



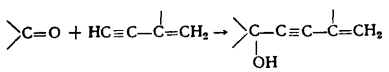
Carbinols of type (II) are obtained by anionotropic isomerisation of carbinols (I) under the influence of acids [5,18]:



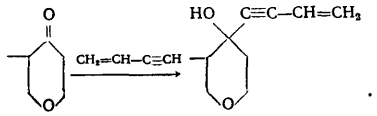
The ease of isomerisation depends on the nature of the carbinol. In many cases the rearrangement goes to completion in the cold during the decomposition of the Iotsich complex with a dilute acid [22,23]. The first member of these carbinols, $CH_2:CH\cdot CHOH\cdot C\vdots CH$, however, does not undergo isomerisation even in the presence of 25% sulphuric acid.

Finally, carbinols of type (III) are obtained by the condensation of vinylacetylene or its homologues with aldehydes or ketones.

In 1938 Nazarov [24] showed that vinylacetylene is also capable of condensation with ketones according to the Favorskii method, forming vinylethynylcarbinols in good yields. The reaction proceeds more rapidly than in the case of acetylene itself. This method was used for the condensation of vinyl- and isopropenyl-acetylene with a series of aliphatic and alicyclic ketones [24,26]:

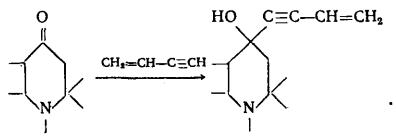


Vinylacetylene reacts with tetrahydro-4-pyrones yielding the expected vinylethynyltetrahydropyran-4-ols [27-29]:

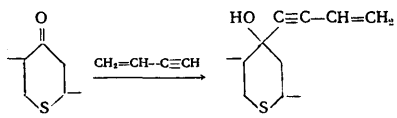


The yield of tetrahydropyranols is small. They are obtained in large yields by the reaction of vinylethynylmagnesium bromide with the corresponding tetrahydropyrones [30].

Nazarov and Raigorodskaya showed, however, that 4-piperidones behave quite differently in these reactions [31-33]. In fact, in this particular case the opposite results are obtained: vinylacetylene reacts with 4-piperidones forming high yields of vinylacetylenic piperidinols, according to the Favorskii reaction. The yields in the condensation of vinylethynylmagnesium bromide with 4-piperidones are small:

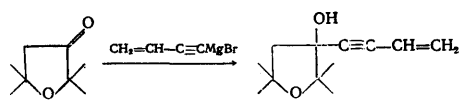


The synthesis of vinylacetylenic tetrahydrothiopyranols was carried out by Nazarov *et al.* [34], who showed that under the conditions of the Favorskii reaction vinylacetylene is capable of undergoing condensation with tetrahydro-4-thiopyrones:

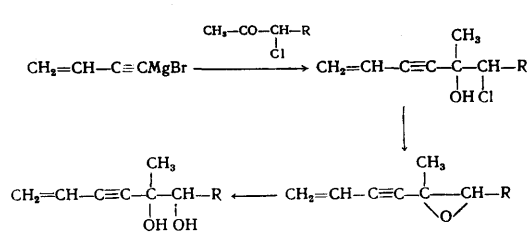


Attempts to condense vinylacetylene with tetrahydro-3--furanones in the presence of powdered potassium hydroxide were unsuccessful, apparently owing to the formation of an alkoxide from the enol form of the furanone, which inhibits further reaction. Certain furanones are known to react with the Grignard reagent only in the enol form, while in the presence of potassium hydroxide they form enolates [35].

3-Vinylethynyltetrahydrofuran-3-ol was obtained in 90% yield by reacting vinylethynylmagnesium bromide with tetrahydro-3-furanones [36]:

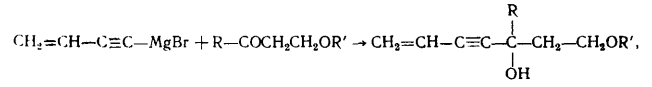


By condensing vinylacetylene with $\alpha$-chloro-ketones, Perveev and Kudryashova [37,38] obtained the corresponding vinylethynylcarbinols, which, after elimination of hydrogen chloride by means of potassium hydroxide, gave vinylacetylenic epoxides. The condensation of the resulting epoxides with alcohols in the presence of sulphuric and oxalic acids gave $\alpha$-alkoxy-$\beta$-hydroxyvinylacetylenic alcohols:

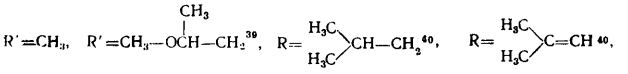


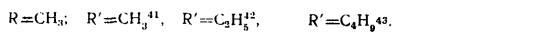
It is interesting that β-alkoxy-ketones completely fail to condense with vinylacetylene in the presence of powdered potassium hydroxide in anhydrous ether, forming instead high-molecular-weight products which cannot be distilled and are insoluble in organic solvents. Moreover, an almost theoretical amount of the alcohol corresponding to the alkoxy-group can be isolated from the ether solution, thus providing evidence that the alkoxy-group is split off during the condensation of β-alkoxy-ketones.

Synthesis of β-alkoxyvinylacetylenic alcohols was effected by reacting vinylethynylmagnesium bromide with the appropriate β-alkoxy-ketones:

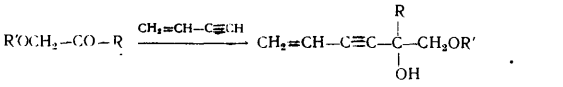


where

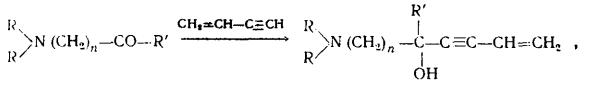




Good yields of vinylethynylcarbinols containing alkoxy--groups were thereby obtained, and their chemical reactions were studied. In contrast to β-alkoxy-ketones, α-alkoxy--ketones are readily condensed with vinylacetylene in the presence of powdered potassium hydroxide in anhydrous ether, forming α-alkoxyvinylethynylcarbinols[44,45]:

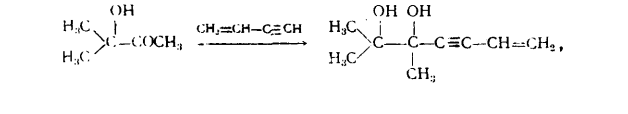


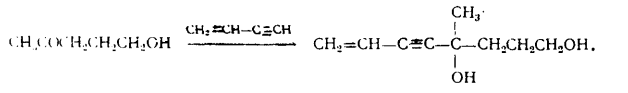
It is interesting that, under the conditions of the Favorskii reaction, amino-ketones condense with vinylacetylene, forming good yields of amino-alcohols of the vinylacetylenic series[46-48]:



where R = $CH_3$, $C_2H_5$; $n$ = 1 or 2.

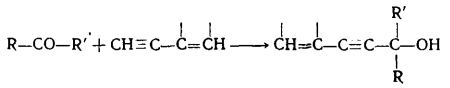
Keto-alcohols can also be condensed with vinylacetylene, forming vinylacetylenic glycols[28]:





As shown above, the synthesis of vinylacetylenic alcohols with unsubstituted vinyl groups was studied in great detail by the Nazarov school, but the synthesis of these alcohols with substituted vinyl groups has so far received little attention.

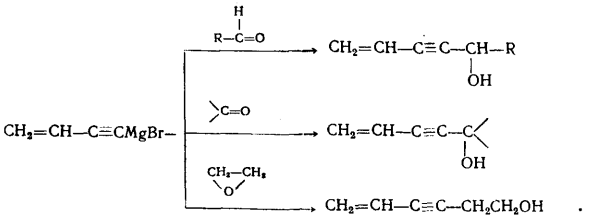
Vinylacetylenic hydrocarbons containing two substituents in the vinyl group require 48 h to condense with ketones, according to the Favorskii–Nazarov reaction, at 30°–35°. At 60°, in anhydrous benzene solution, and in the presence of powdered KOH this reaction lasts 6 h, whereas other acetylenic and vinylacetylenic hydrocarbons undergo condensation at temperatures below zero in the course of a few hours. It was also shown that these hydrocarbons are capable of reacting with ketones in the presence of powdered KOH and without a solvent. A series of vinylacetylenic alcohols with two substituents in the vinyl group were obtained in this way[49]:



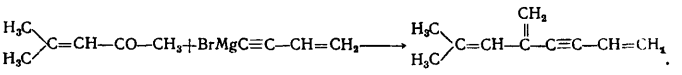
Under the conditions indicated vinylacetylene itself can be condensed with ketones to form the corresponding carbinols[49]. It is worthy of note that despite some data in the literature to the contrary[24,50], vinylacetylene undergoes condensation with ketones even in the presence of powdered NaOH without a solvent, but the reaction is slower[51].

At low temperatures and in the presence of powdered KOH aldehydes can be condensed with vinylacetylenic hydrocarbons to form secondary vinylacetylenic alcohols[49].

Before this method became available, the synthesis of primary and secondary vinylacetylenic alcohols was effected by reacting vinylethynylmagnesium bromide with the appropriate aldehydes and ketones[20,50-60]:



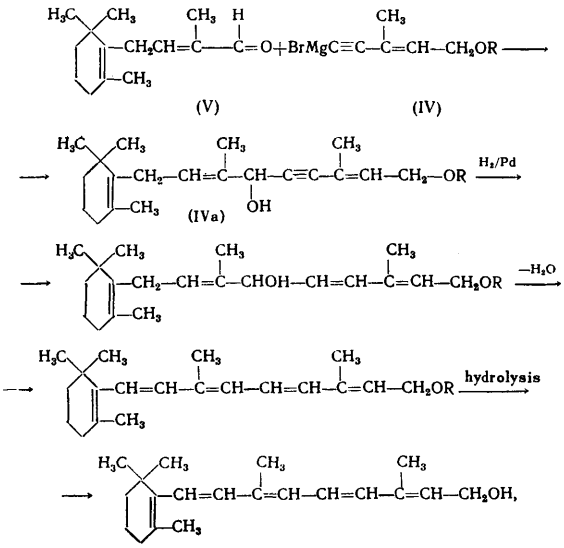
These alcohols could not, however, always be isolated, especially in the case of αβ-unsaturated ketones, since dehydration tended to proceed concomitantly with the decomposition of the Grignard complex. Nazarov and Elizarova[56] showed, for instance, that, unexpectedly, vinylethynylmagnesium bromide reacts with mesityl oxide (4-methyl-3-penten-2-one) forming the corresponding trienyne hydrocarbon:



Of great interest is the condensation of isopropenylacetylene with β-ionone leading to carotenoid compounds[53,54]. Satisfactory results were also obtained by using sodium in liquid ammonia[55], and, even better, by using tertiary potassium alkoxides; this made possible the preparation of acetylenic alcohols from unsaturated ketones, which are very sensitive to alkali.

The Grignard reagents from the vinylacetylenic alcohol (IV, R = H) or from the methyl ether derived from it (IV, R = $CH_3$) react with aldehyde (V)[61,62] forming the corresponding glycol and glycol monoether, respectively (IVa, R = H, $CH_3$). By subsequent selective hydrogenation and dehydration, accompanied by an allyl rearrangement, vitamin A methyl ether was obtained, whose hydrolysis

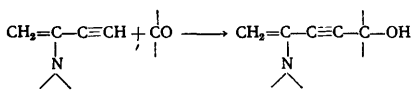
gave the alcohol identical with natural vitamin A [17,18] (in the case of the glycol the primary hydroxy-group should be converted to an ether prior to dehydration):



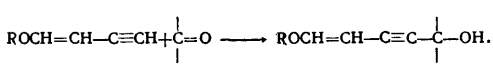
where R = H, $CH_3$.

It may be noted that all the above methods of preparation of acetylenic carbinols require stoichiometric ratio of the reactants, and at least an equimolar quantity of an alkali metal or one of its active compounds, with the complete exclusion of moisture. The condensation of acetylene and its monosubstituted derivatives with acetone in the presence of aqueous alkali under pressure [63] as catalyst may indeed be considered a major achievement.

Aminovinylacetylenes also condense with ketones under the above conditions, forming aminovinylacetylenic alcohols [64]:



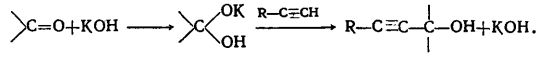
Condensation of alcohols with diacetylene leads to alkoxyvinylacetylenes [65] which, like vinylacetylene, in the presence of alkali can be condensed with ketones to form alkoxyvinylethynylcarbinols [65]:



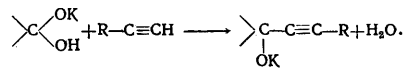
Another, basically new, method for the synthesis of acetylenic alcohols was developed by Reppe. He showed that copper and some other metal acetylides are good catalysts for the condensation of acetylene with formaldehyde in aqueous solution [66]. The reaction rate decreases with the rising molecular weight of the aldehyde. In fact, formaldehyde is the only aldehyde which reacts at a satisfactory rate. The same reaction with ketones has no special merits, since it is very slow and the greater part of the ketone remains unchanged [67].

## 2. MECHANISM OF THE FAVORSKII REACTION

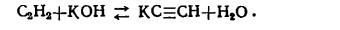
The following mechanism was put forward by Favorskii for the condensation of acetylenic hydrocarbons with ketones: potassium hydroxide unites with the ketone to form the corresponding hydroxyalkoxide; this undergoes condensation with the acetylenic hydrocarbon to form an acetylenic alcohol [68], and liberates potassium hydroxide:



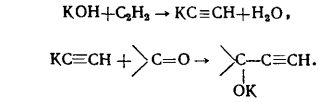
Acetylenic alcohols or glycols formed in this reaction do not pass into the ether solution. It was concluded on the strength of this that the condensation does not yield the alcohol itself, but rather the corresponding alkoxide. Consequently water, not potassium hydroxide, separates in the reaction [69].



It has recently been shown [50,70] that the solubility of acetylene in ether greatly increases on addition of powdered potassium hydroxide. The authors are right in considering that this phenomenon is connected with the formation of potassium acetylide. They carried out the condensation under an acetylene pressure of 5–10 atm in order to shift the equilibrium towards the formation of potassium acetylide:

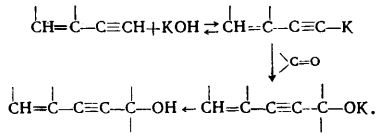


This method gave good yields of a series of secondary and tertiary acetylenic alcohols. Using kinetic methods, Korotkov and Parfenova [50] showed that the condensation of acetylene with carbonyl compounds proceeds *via* the formation of organometallic compounds. Gvertsiteli and Mikadze [71] established that acetylene passed through dry powdered potassium hydroxide is completely absorbed. They also think that potassium acetylide is thereby formed, quoting as evidence the formation from ketones of an acetylenic alcohol by the action of potassium hydroxide through which acetylene had previously been passed at a low temperature:



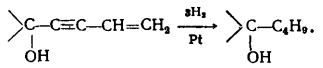
Petrov *et al.* [72] have recently shown that the Favorskii reaction can only be carried out with impure potassium hydroxide, containing traces of iron. On the strength of this, they suggested a chain mechanism for the above reaction.

On mixing 1 mole of $\alpha$-ethynylcyclohexene with 2–3 moles of potassium hydroxide, the resulting reaction in a few hours yields a solid mass. Only a small amount of the added hydrocarbon can be extracted with ether, but the addition of a ketone leads to the corresponding carbinol in high yield. Apparently in this case also potassium acetylide is formed, which reacts with the carbonyl compound like a Grignard reagent [49]:

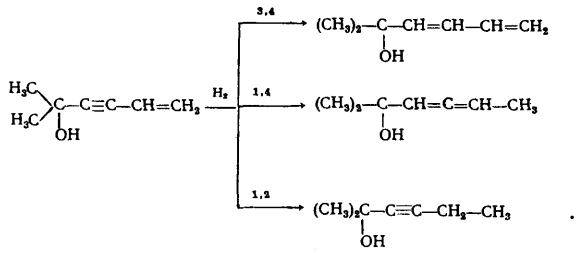


## 3. HYDROGENATION OF VINYLETHYNYLCARBINOLS

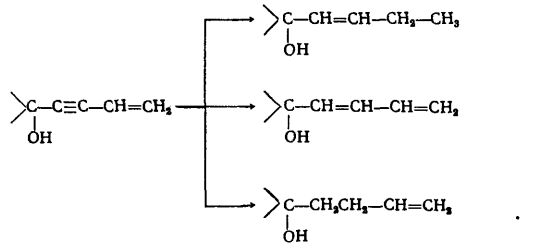
In the presence of platinum vinylethynylcarbinols are readily hydrogenated, forming the corresponding saturated alcohols[73]:



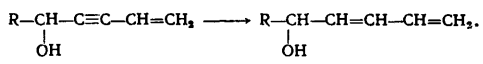
Golovchanskaya[74,75] studied the electrochemical hydrogenation of vinylacetylenic alcohols. The addition of hydrogen occurs in 1,3-, 1,4-, and 3,4-positions. This is the only case reported in the literature of the addition of hydrogen to the vinylethynyl radical in the 3,4-position:



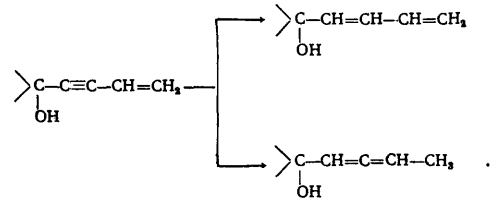
Unlike acetylenic alcohols, vinylethynylcarbinols proved incapable of selective hydrogenation in the presence of either palladium or nickel. For this reason, the addition of one molecule of hydrogen to vinylethynylcarbinols in the presence of these catalysts does not result entirely in 1,3-dienic alcohols, but in a mixture of the initial vinylethynylcarbinol with dienic and olefinic alcohols[76]:



Nazarov worked out a method for the selective hydrogenation of the triple bond to a double bond in vinylacetylenic alcohols. The hydrogenation of vinylethynylcarbinols was carried out by shaking them with a water suspension of zinc powder. This method was used for preparing 1,3-dienic alcohols. During hydrogenation with powdered zinc–copper couple increase in the radical size, R, of secondary vinylethynylcarbinols does not significantly affect the rate or the course of the reaction, which is not the case with tertiary vinylethynylcarbinols[77]:

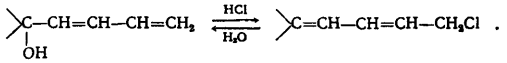


No side-products are formed during hydrogenation of vinylethynylcarbinol, but the hydrogenation rate of methylethyl-, methylpropyl-, and diethyl-vinylethynylcarbinols is slowed down considerably, and hydrogen is added to the vinylethynyl group in the 1,4-position to form the corresponding allenic alcohols[78].

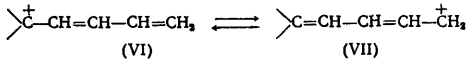


Boroda[79] showed recently that diethylvinylethynylcarbinol undergoes hydrogenation in the presence of colloidal palladium, yielding 95% of diethylbutadienylcarbinol.

1,3-Dienic alcohols are capable of undergoing a reversible anionotropic isomerisation, namely a migration of the hydroxy-group to the opposite end of the diene chain with a simultaneous shift of double bonds, resulting in the formation of a new 1,3-dienic alcohol[80,81]:



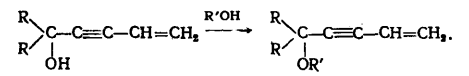
The equilibrium was found to be shifted strongly towards the formation of tertiary alcohols, whereas the opposite was the case with ethers, esters, and halogen derivatives[82-84]. This seems to be connected with the difference in the positive charge on the tertiary ion and on the isomeric primary ion.



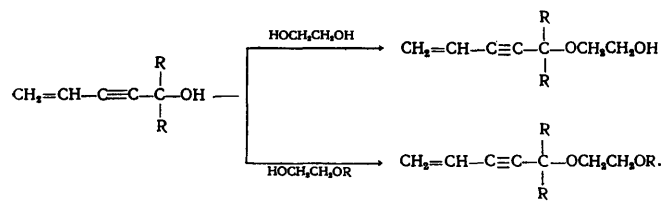
The hydroxide anion unites mainly with the carbonium ion having the tertiary structure (VI), forming tertiary alcohols, while the chloride anion, on the contrary, reacts primarily with the carbonium ion having the primary structure (VII), forming primary chlorides.

## 4. ETHERS AND ESTERS DERIVED FROM VINYLETHYNYLCARBINOLS

Unlike saturated carbinols, which form ethers only with difficulty, tertiary vinylethynylcarbinols readily form ethers with alcohols in the presence of mineral acids. In the presence of small amounts of sulphuric acid the reaction proceeds even in the cold, and on heating on a water-bath it is complete in a few hours[85].



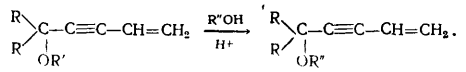
Glycols and ethylene glycol monoalkyl ethers also react with vinylethynylcarbinols in the presence of sulphuric acid to form the corresponding ethers[80-88]:



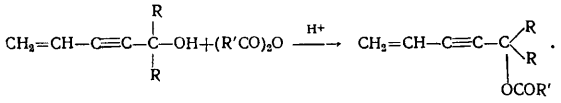
Ethers derived from primary vinylethynylcarbinols are easily obtained by the reaction of vinylethynylmagnesium bromide with $\alpha$-chloromethyl ethers[89]:

$$CH_2=CH-C\equiv C-MgBr+Cl-CH_2OR \longrightarrow CH_2=CH-C\equiv C-CH_2OR.$$

On heating the resulting ethers with alcohols in the presence of sulphuric acid, a reversible alcoholysis occurs. If the alcohol radical is smaller than the radical of the ether group, alcoholysis proceeds to completion[90]:



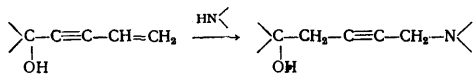
Vinylethynylcarbinols react with acid anhydrides in the presence of trace amounts of sulphuric acid[91], forming up to 80% of the corresponding esters. This reaction proceeds even without a catalyst, but is then considerably slower:



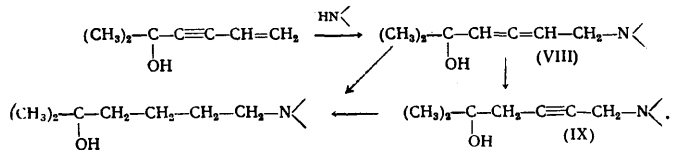
Acylation proceeds readily in the presence of zinc chloride[92]. Polymerisation studies on vinylethynylcarbinols established an interesting correlation between the structure of the starting compound and its polymerisation rate. If the hydroxy-group is esterified, the rate of polymerisation is considerably slower. For instance, esters undergo polymerisation 4–5 times more slowly than the corresponding vinylethynylcarbinols[1].

## 5. ADDITION OF AMINES AND SILANES TO VINYLETHYNYLCARBINOLS

In 1956 Vartanyan and Badanyan showed that vinylacetylenic alcohols react readily with aqueous solutions of appropriate amines on heating in sealed tubes and form good yields of aminoacetylenic alcohols[93-95]:

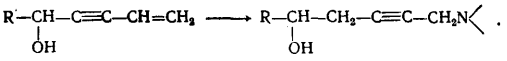


Amines combine with the vinylethynyl group in the 1,4-position; the addition proceeds through the intermediate formation of an allenic amino-alcohol (VIII), which under the effect of the excess of the amine present in the reaction mixture isomerises to the corresponding acetylenic amino-alcohol (IX):

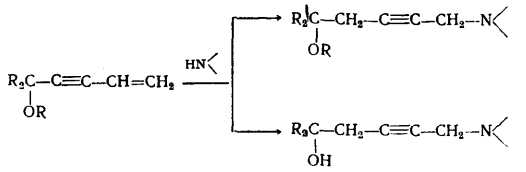


On reducing the reacting time two unsaturated amino-alcohols are obtained, which on hydrogenation yield identical amino-alcohols. Continued heating of the allenic amino--alcohol (VIII) with the aqueous amine solution leads to isomerisation and the formation of $\beta$-acetylenic amino--alcohol (IX). The structure of the amino-alcohol (IX) has been established by hydrogenation and oxidation.

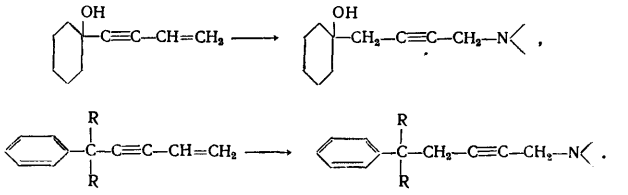
Addition of amines to secondary vinylacetylenic alcohols proceeds similarly:



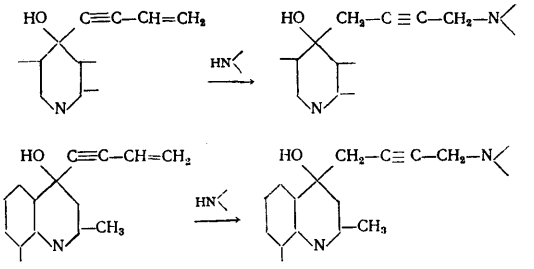
Amines react with vinylacetylenic ethers to form aminoacetylenic ethers[96]. In the case of ethers derived from tertiary vinylacetylenic alcohols, small amounts of the corresponding aminoacetylenic alcohols are obtained in addition to the main reaction product:



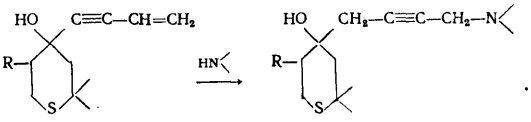
These alcohols are formed by the reaction of amines with the vinylacetylenic alcohol produced by hydrolysis of the vinylacetylenic ethers under the reaction conditions employed. Amines also add readily to secondary and tertiary vinylacetylenic alcohols, containing aliphatic, alicyclic, and aromatic radicals[93-95]:



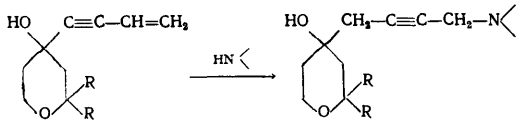
Amines can also combine with vinylacetylenic alcohols containing piperidine, tetrahydrothiopyran, and tetrahydropyran rings. For instance, the reaction of vinylacetylenic piperidin-4-ols with amines results in large yields of the corresponding acetylenic aminopiperidinols[97]:



Addition of amines to vinylacetylenic tetrahydrothiopyran-4-ols proceeds similarly and yields aminoacetylenic tetrahydrothiopyranols[98]:

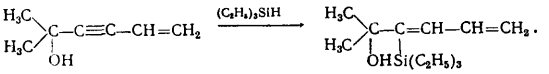


Addition of amines to 4-vinylethynyltetrahydropyran-4-ols yields the aminoacetylenic tetrahydropyranols[29].

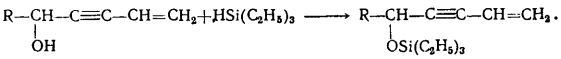


Hydrogenation of aminoacetylenic piperidinols, tetrahydrothiopyranols, and tetrahydropyranols in ethanol in the presence of a platinum catalyst gave the corresponding saturated aminopiperidinols, tetrahydropyranols, and tetrahydrothiopyranols.

It has recently been shown that triethylsilane adds to vinylethynylcarbinols in the presence of platinum and forms the corresponding dienic alcohols[98,99]:

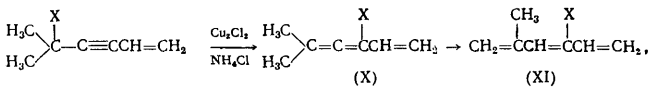


In the presence of $H_2PtCl_6.6H_2O$ this reaction takes 2 h at room temperature, and the yield of dienic alcohols is 55–63%. It proceeds differently with secondary vinylethynylcarbinols, leading to ethers instead:



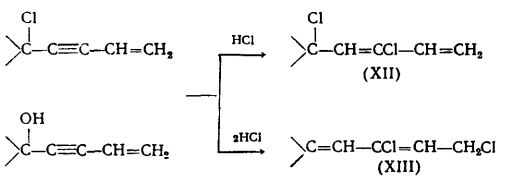
## 6. HYDROHALOGENATION OF VINYLETHYNYLCARBINOLS

Nazarov and Yanbikov showed that tertiary vinylethynylcarbinols can easily exchange their hydroxy-groups for halogens when acted upon by hydrogen halides[24,100]. On shaking dimethylvinylethynylchloromethane with 1% cuprous chloride and ammonium chloride at room temperature, the acetylene–allene rearrangement occurs resulting in two isomeric chlorine-containing trienes (X, XI):

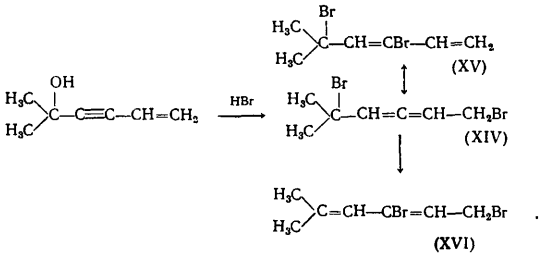


where X = Cl, Br.

Further studies showed that the addition of hydrogen chloride to the conjugated system of a double and a triple bond in tertiary vinylethynylcarbinols does not occur until the substitution of the hydroxy-group has been completed. Thus, by the action of hydrogen chloride on dimethylvinylethynylchloromethane, or by the simultaneous action of two molecules of hydrogen chloride on dimethylvinylethynylcarbinol, two isomeric dichlorides are formed, (XII) and (XIII):

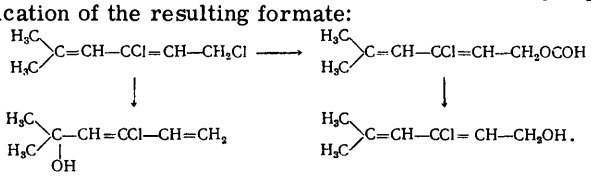


Hydrogen chloride, therefore, as in the case of vinylacetylene[101–103], is added in the 1,4-position of the vinylethynyl group in dimethylvinylethynylcarbinol. The resulting allene dichloride, which contains two mobile chlorine atoms, spontaneously undergoes isomerisation to yield a mixture of diene dichlorides (XII) and (XIII), containing only one mobile chlorine atom. The reaction of four molecules of hydrobromic acid with one molecule of dimethylvinylethynylcarbinol yields a mixture of two diene dibromides (XV) and (XVI),[104] whose structure has been established by oxidation and ozonisation:



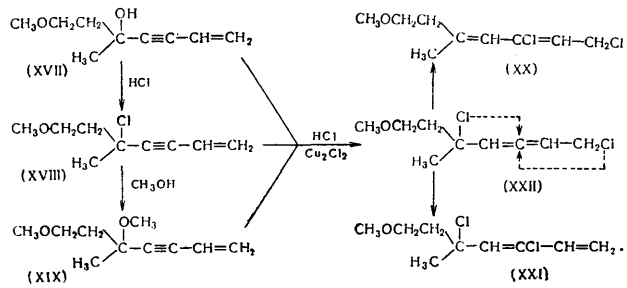
The formation of two isomeric dibromides is interpreted in the following manner: the hydroxyl is substituted by bromine by the action of an excess of hydrogen bromide; simultaneously hydrogen bromide reacts with the vinylethynyl radical in the 1,4-position forming the allene dibromide (XIV), which, since it contains two mobile bromide atoms, undergoes isomerisation to dibromides with conjugated double bonds.

Later work by Nazarov and his coworkers showed[105] that in the reaction of hydrogen chloride with dimethylvinylethynylcarbinol a dichloride containing a primary chlorine atom is formed (XIII), which on hydrolysis in an alkaline solution undergoes a complete diene rearrangement forming a tertiary chlorodiene alcohol. A primary chlorodiene alcohol can be obtained from a primary diene dichloride by treating the latter with formic acid salts followed by saponification of the resulting formate:



This proved that hydrochlorination of dimethylvinylethynylcarbinol yields only one diene dichloride with a primary chlorine atom.

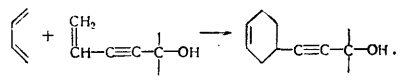
Nonetheless, by shaking methyl-β-methoxyethylvinylethynylcarbinol (XVII), and the monochloride (XVIII) and methyl ether (XIX) derived from it, with concentrated hydrochloric acid in the presence of a catalyst for 1–1.5 h, two isomeric dichlorides are obtained: 1,3-dichloro-5--methyl-7-methoxyhepta-2,4-diene (XX) and 3,5-dichloro--5-methyl-7-methoxyhepta-1,3-diene (XXI).[106] On being heated with concentrated hydrochloric acid in the presence of cuprous chloride, (XXI) is completely isomerised to the primary dichloride (XX). Under similar conditions the carbinol (XVII) undergoes hydrochlorination, forming mainly the dichloride (XX).



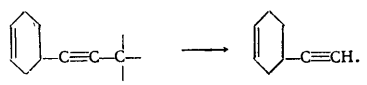
Clearly, the methyl ether derived from the carbinol (XIX) is split by hydrogen chloride to form methanol and the chloride (XVIII). The formation of two isomeric dichlorides (XX) and (XXI) may be accounted for by the addition of another molecule of hydrogen chloride in the 1,4-position of the chloride (XVIII), similar to the addition of hydrogen chloride to vinylacetylene. The resulting allyl dichloride (XXII) contains two mobile chlorine atoms and is immediately isomerised into a mixture of dichlorides (XX) and (XXI). Mainly the tertiary chlorine atom migrates, and the mixture chiefly contains the dichloride (XX).

## 7. VINYLETHYNYLCARBINOLS IN THE DIENE SYNTHESIS

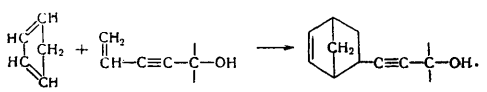
Nazarov and Nagibina[107] showed that vinylethynylcarbinols react with 1,3-dienes at 130° – 160° according to the general mechanism of the diene synthesis, forming $\Delta^3$-cyclohexenylethynylcarbinols of various structures. Only the vinyl group participates in this reaction, the triple bond and the hydroxy-group remain intact:



On being heated with powdered potassium hydroxide, $\Delta^3$-cyclohexenylethynylcarbinols are quantitatively decomposed into the corresponding ketones and $\Delta^3$-cyclohexenylacetylenes:

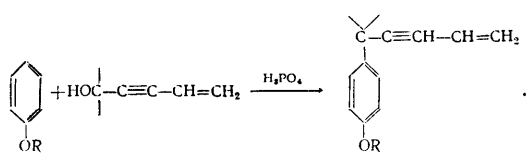


The diene reaction between cyclopentadiene and vinylacetylenic alcohols yields *endo*-methylene-$\Delta^3$-cyclohexenylcarbinols:

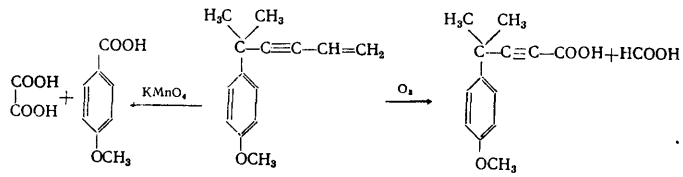


## 8. ALKYLATION WITH VINYLETHYNYLCARBINOLS

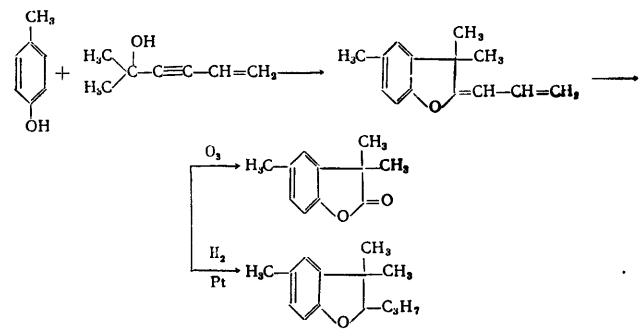
Vinylacetylenic intermediates, particularly the substituted phenols of the vinylacetylenic series, have not so far been studied much, owing to difficulties involved in their synthesis. The development of a suitable method for their preparation would be of practical as well as of theoretical interest, since by the hydrogenation of vinylacetylenic phenols a series of new substituted phenols might be obtained, with possible practical applications. Nazarov and Kuznetsova[108] were the first to show that condensation of phenol with vinylethynylcarbinols in the presence of phosphoric acid yields *p*-substituted phenols:



Condensation of anisole with dimethylvinylethynylcarbinol gave *p*-substituted anisole. The structure of these *p*-substituted phenols was established by oxidation. For instance, heating *p*-substituted anisole with an aqueous potassium permanganate solution gave anisic and oxalic acids, while its ozonisation gave *p*-methoxyphenyldimethyltetrolic acid:

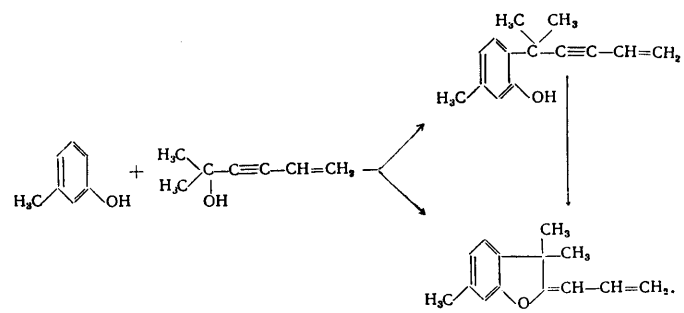


Alkylation of *p*-cresol with dimethylvinylethynylcarbinol under the same conditions proceeds much less readily, yielding instead of the expected *o*-substituted *p*-cresol, its cyclisation product 3,3,5-trimethyl-2-allylidenecoumaran[109]:



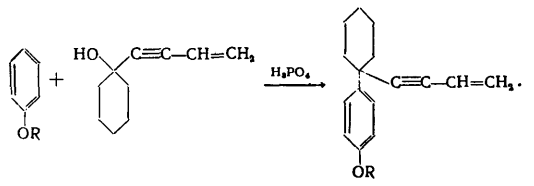
On ozonisation, this cyclic product gave 3-methyl-6-hydroxyphenyldimethylacetic acid lactone, and on hydrogenation 3,3,5-trimethyl-2-propylcoumaran was obtained. Condensation, under above conditions, of *o*-cresol and dimethylvinylethynylcarbinol yields the corresponding *p*-substituted *o*-cresol.

Condensation of dimethylvinylethynylcarbinol with *m*-cresol proceeds vigorously with the evolution of heat, yielding almost equal amounts of the *p*-substituted *m*-cresol, and its cyclisation product, 3,3,6-trimethyl-2-allylidenecoumaran[110]:

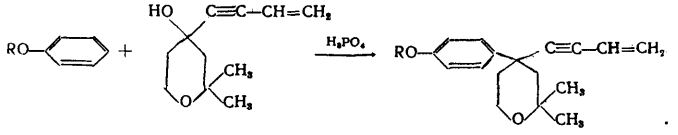


It was shown later that similar reactions occur with alicyclic vinylacetylenic alcohols. Thus, condensation of

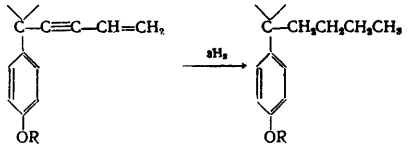
vinylethynylcyclohexanol with phenol and anisole gives high yields of the corresponding phenol derivative [111]:



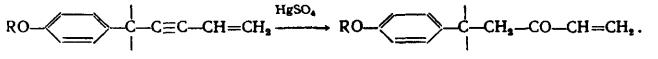
Alkylation by means of 4-vinylethynyltetrahydropyran-4-ol also proceeds according to the above mechanism, yielding the expected *p*-substituted phenol [111]:



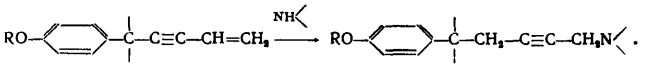
In the presence of a platinum catalyst vinylacetylenic phenols are hydrogenated to saturated *p*-alkylphenols [108,112]:



Vinylacetylenic phenols can be hydrated in an aqueous solution of methanol in the presence of small amounts of mercuric sulphate and sulphuric acid, to form the corresponding vinyl ketones in good yields [113]:

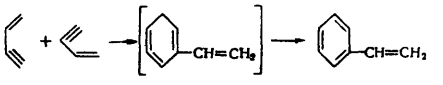


On being heated with vinylacetylenic phenols, secondary amines in aqueous solutions combine with the vinylethynyl group in the 1,4-position, forming acetylenic aminophenols [114]:



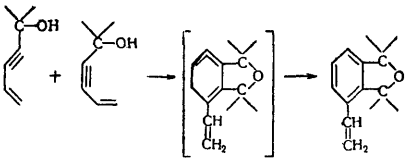
## 9. CONDENSATION REACTIONS OF VINYLETHYNYLCARBINOLS

Dykstra showed that, on being heated in the presence of acidic reagents (acetic, chloroacetic, malonic, and hydrochloric acids), vinylacetylene undergoes dimerisation to styrene [115]. One molecule of vinylacetylene adds in the 1,4-position to the acetylenic bond of another molecule, and the resulting allene compound isomerises under the experimental conditions to styrene:

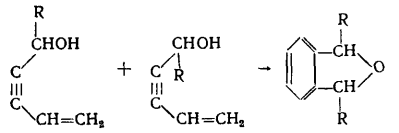


Favorskii and Zakharov showed that vinylacetylene derivatives undergo similar cyclisation on being heated in methanol solution in the presence of glacial acetic acid [116-118]. When heated in benzene in the presence of acidic reagents, or better, ferrous chloride, vinylethynylcarbinols yield a cyclic derivative, isocoumaran [119,120]. This reaction is a unique example of cyclisation by way of the dimerisation of two molecules of vinylethynylcarbinol with the elimination of water and the formation of vinylisocoumarans. This reaction is also of interest because all three functional groups of vinylethynylcarbinol participate in it.

It appears that the formation of the six-membered ring occurs first, and that it is subsequently followed by the isomerisation of the allene compound and the elimination of water:

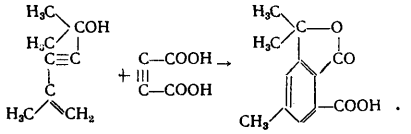


The structure of isocoumarans was established by oxidation and ozonisation. Although tertiary vinylethynylcarbinols undergo ring-closure much more rapidly than secondary ones, the latter can also be condensed to form the corresponding isocoumarans [121]:

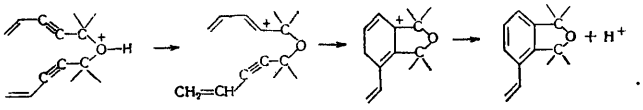


Vinylisocoumarans are colourless liquids which, on heating with benzoyl peroxide, polymerise to a transparent vitreous mass.

Johnson showed that 2,5-dimethylhex-5-en-3-yn-2-ol reacts readily with acetylenedicarboxylic acid in benzene solution and forms 3,3,5-trimethylphthalide-7-carboxylic acid [122].



Torgov and Verkholetova suggested a mechanism for this reaction [123] whereby, in the presence of $FeCl_3$, a hydroxyl is split off from the tertiary carbinol, to a carbonium ion. The carbonium ion reacts with another molecule of carbinol forming an 'onium complex. This in turn undergoes an intramolecular diene condensation and a concomitant migration, to yield an aromatic system.



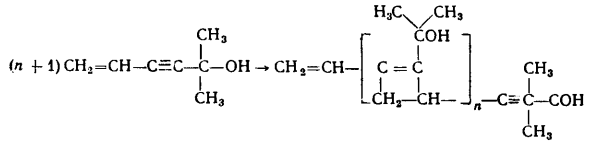
The reaction course is determined by the mobility of the hydroxyl. Vinylethynylcarbinol, where the hydroxyl is the least mobile, is incapable of undergoing ring-closure.

## 10. POLYMERISATION OF VINYLETHYNYLCARBINOLS

Non-stabilised vinylethynylcarbinols polymerise rapidly, and are gradually converted into a solid vitreous mass [124]. Oxygen, ozone, and peroxides catalyse the polymerisation of vinylacetylenic alcohols, the most efficient catalyst being nitric acid.

Good stabilisers of vinylethynylcarbinols are pyrogallol, hydroquinone, catechol, ammonia, $\alpha$- and $\beta$-naphthylamines, diphenylamine, and agerite†. In the presence of 0.01% of any of these stabilisers vinylethynylcarbinols can be kept up to one year, and in the presence of 0.1% of stabiliser they remain unchanged for years. Tertiary vinylethynylcarbinols polymerise more rapidly than secondary ones, and the corresponding esters, as already mentioned, do so more slowly than the corresponding carbinols. Consequently, the hydroxyl displays a greater activating activity with respect to the enyne system than the alkoxy- or acetoxy-groups.

Vinylethynylcarbinols can also be copolymerised with vinyl and 1,3-diene compounds. Dimethylvinylethynylcarbinol[125] polymerises like vinylacetylene, *i.e.* by the reaction of the triple bond of one molecule and the double bond of another molecule of carbinol, to form cyclobutene rings:

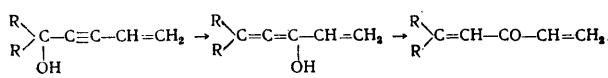


The product of partial polymerisation of dimethylvinylethynylcarbinol, well known as the "carbinol adhesive", is widely used in industry (electrical engineering, aviation, instruments) as adhesive for metals, glass, marble, china, plastics, etc. A mixture of 20–30% chloroprene and the carbinol can be used as adhesive for cementing rubber to metals and other materials mentioned above[1].

Partially polymerised dimethylvinylethynylcarbinol has a high adhesive capacity. It is obtained as a syrup by heating freshly distilled dimethylvinylethynylcarbinol for 20–25 h on a water-bath. In the presence of 0.05–0.1% of benzoyl peroxide the polymerisation time can be reduced to 5–10 h. The carbinol adhesive can be stabilised by 0.25% of agerite, which is added to the 10% solution of the monomer. The stabilised carbinol adhesive can be kept in a cool, dark place for six months. The syrup can be prepared from stabilised carbinol by heating it for 6–10 h in the presence of 0.2–0.3% of benzoyl peroxide.

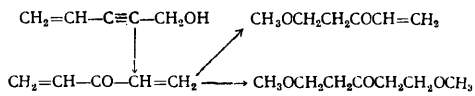
## 11. ISOMERISATION OF VINYLETHYNYLCARBINOLS

Nazarov first showed that, in the presence of mercuric sulphate in acetone solution, vinylethynylcarbinols isomerise to divinyl ketones[26,127]:

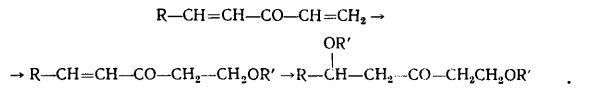


This isomerisation, however, can be readily carried out with the formation of up to 40% of the expected ketone, only in the case of dimethylvinylethynylcarbinol (R = $CH_3$). Other acetylenic alcohols (R = $C_2H_5$, $C_3H_7$, etc.) can only be isomerised with difficulty, and, owing to side-reactions, particularly dehydration of the carbinol, the yields are below 5%.

Further studies showed that vinylethynylcarbinols are very readily isomerised in solutions of alcohols which are capable of addition to divinyl ketones[90,117,128]. The ease of isomerisation in alcoholic media (especially methanol) is explained by the fact that alcohol adds to the resulting divinyl ketones to form alkoxy-ketones which are removed from the reaction sphere. Detailed investigations of the addition of alcohols to divinyl ketones showed that alcohols can unite with the unsubstituted vinyl group even in the absence of a catalyst[128]. Isomerisation of the primary vinylethynylcarbinol under these conditions yields 1-methoxypent-4--en-3-one and 1,5-dimethoxypentan-3-one[129]:

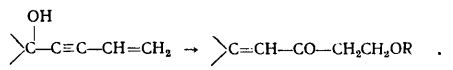


In the presence of mercury salts secondary vinylethynylcarbinols also undergo isomerisation to divinyl ketones, which readily add one molecule of alcohol to the unsubstituted vinyl group and form unsaturated alkoxy-ketones[130]:

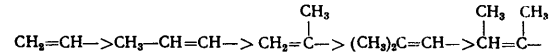


Under the influence of mercury salts (or other catalysts) the $\beta$-alkylvinyl group can combine with another molecule of alcohol, to form saturated $\beta\beta$-dialkoxy-ketones.

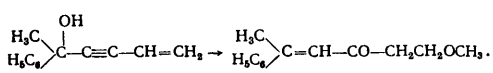
The selectivity observed in the addition of alcohols to $\beta\beta$-dialkyldivinyl ketones is even greater. Here, even in the presence of a catalyst, one molecule of alcohol usually combines with the unsubstituted vinyl group, so that isomerisation of tertiary vinylacetylenic alcohols yields the corresponding unsaturated $\beta$-alkoxy-ketones[131]:



According to the rate of addition of alcohols (as well as amines and other compounds) to $\alpha\beta$-unsaturated ketones, vinyl radicals can be arranged in the following series[131–136]:

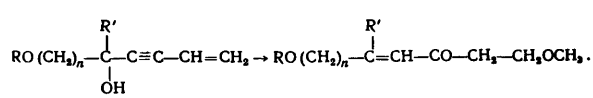


Vinylacetylenic alcohols containing aromatic radicals behave like their aliphatic or alicyclic analogues. For example, methylphenylvinylethynylcarbinol is converted into 1-methoxy-5-phenylhex-4-en-3-one[137]:



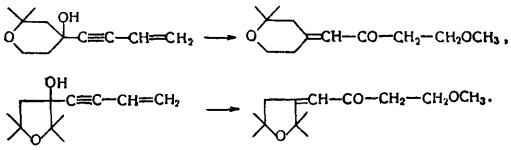
Thus isomerisation of vinylethynylcarbinols in alcohol solutions in the presence of mercury salts is a very simple and convenient method of preparation of $\beta$-alkoxy-ketones.

It has been shown that vinylacetylenic alcohols containing one or two alkoxy-groups in the $\alpha$- or $\beta$-positions are also capable of being isomerised to corresponding alkoxy--ketones[39–45]:



† Agerite is *p*-hydroxyphenylbenzyl ether (Ed. of Translation)..

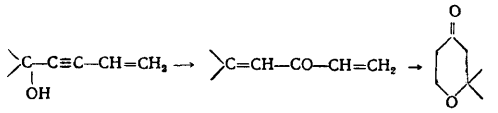
It has recently been shown that isomerisation of vinylethynylcarbinols also occurs in the case of 4-vinylethynyltetrahydropyran-4-ols[27], 3-vinylethynyltetrahydrofuran-3-ols[36], etc.



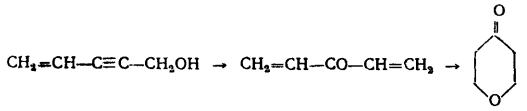
Since they are relatively simple to obtain, it was possible to study their various reactions[138]. Of special interest is the synthesis of vinyl ketones, carried out by the splitting off of the alcohol from β-alkoxy-ketones. A series of very reactive vinyl ketones were thus prepared in satisfactory yields[139,140].

## 12. HYDRATION OF VINYLETHYNYLCARBINOLS AND THEIR ETHERS AND ESTERS

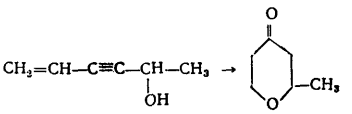
In 1943 Nazarov and his coworkers established that, on heating with dilute sulphuric acid in the presence of mercuric sulphate, vinyl ketones undergo ring-closure, forming tetrahydropyrones[127,141]. It was further shown that under the above conditions vinylethynylcarbinols are isomerised to divinyl ketones. Tetrahydro-4-pyrones can be obtained in one stage by combining the isomerisation of vinylethynylcarbinols to divinyl ketones with their hydration[142]:



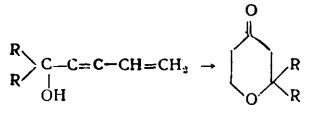
Heating the first member of this series, vinylethynylcarbinol, with dilute sulphuric acid in the presence of mercuric sulphate gave 70% of tetrahydro-4-pyrone. Isomerisation of this carbinol in anhydrous methanol yields 1,5-dimethoxypentan-3-one, which on hydrolysis forms tetrahydro-4-pyrone:



Under similar conditions methylvinylethynylcarbinol also easily undergoes isomerisation and cyclohydration[141], as do other secondary vinylethynylcarbinols or β-alkyldivinyl ketones:

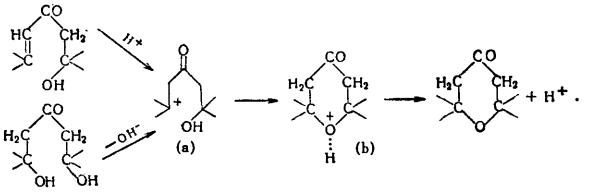


This reaction also proceeds readily with tertiary vinylethynylcarbinols, which form 2,2-dialkyltetrahydro-4-pyrones in good yields[142]:



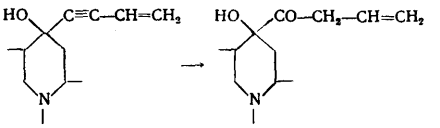
Experiments on the hydration of β-methyl-β-ethyldivinyl ketone in aqueous acetone solution have shown that the first product of hydration of divinyl ketone is an unsaturated β-keto-alcohol, formed by the addition of water to the unsubstituted vinyl group. Under the action of dilute acids the resulting unsaturated β-keto-alcohol undergoes cyclisation to 2-methyl-2-ethyltetrahydro-4-pyrone[143].

Cyclisation of αβ-unsaturated and β-hydroxy-compounds is usually induced by hydrogen ions. In neutral or alkaline media these compounds are either completely stable, or tend to undergo isomerisation in other ways. Nazarov suggested the following mechanism for the formation of tetrahydro-4-pyrones[144]:

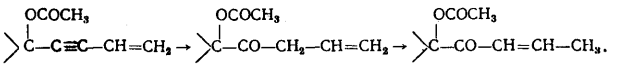


The first stage of the reaction consists of the addition of a hydrogen ion to unsaturated keto-alcohols or the scission of a hydroxide ion from the corresponding ββ-keto-glycols. This leads to the formation of a carbonium ion (a), which cyclises to an oxonium ion (b), which becomes stabilised by splitting off a proton and undergoing conversion into the corresponding tetrahydro-4-pyrone[144].

It is interesting that, in contrast to other vinylacetylenic alcohols, the vinylacetylenic alcohols containing piperidine rings do not isomerise during hydration. Instead, direct hydration of the triple bond occurs, resulting in unsaturated α-keto-alcohols[145]:



All attempts to avoid isomerisation during hydration of vinylethynylcarbinols in order to obtain α-hydroxy-ketones were unsuccessful[92,146-148]. Nevertheless, hydration of vinylethynylmethyl acetates in 75–90% acetic acid in the presence of mercuric acetate at 60°–80° results in the formation of unsaturated α-acetoxy-ketones. The keto-group assumes the α-position exclusively with respect to the acetoxy-group. The resulting dialkyl(vinylacetyl)methyl acetates undergo isomerisation to dialkylcrotonylmethyl acetates[92,146-148]:



At higher temperatures (105°) this reaction yields only the dialkylcrotonylmethyl acetates, whereas at 35°–45° the principal reaction products are dialkyl(vinylacetyl)methyl acetates. On heating (50°–60°) with a solution of *p*-toluenesulphonic acid, sulphuric acid, or with mercury or sodium acetates, the latter compounds isomerise to form dialkylcrotonylmethyl acetates.

The course of hydration of ethers derived from vinylethynylcarbinols is completely different[39]. In contrast to the reaction with esters, water reacts with the triple bond of vinylacetylenic alcohols forming β-keto-derivatives.

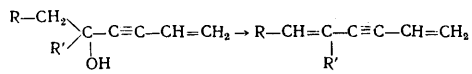
Under the conditions of the Kucherov reaction the resulting divinyl ketones undergo ring-closure, forming tetrahydro--4-pyrones[89]. In methanol solution and in the presence of mercuric sulphate the latter compounds react again, first with water and then with methanol, yielding β-methoxy--ketones[149].

In the presence of sulphuric acid the rate of hydration of ethers derived from vinylethynylcarbinols is considerably enhanced. This is interpreted using the fact that in acid media ethers are capable of forming oxonium compounds, which, on the one hand, increase the polarisability of the triple bond, and, on the other hand, hinder the binding of the catalyst (mercuric sulphate) to the ether. Consequently, methyl ethers of vinylethynylcarbinol cannot be hydrated in dioxane solution owing to the tendency of this solvent to bind acids and acid salts into oxonium compounds.

The course of hydration of the triple bond in esters, which are unable to form oxonium ions, is determined by the vinyl group, which has quite the reverse effect.

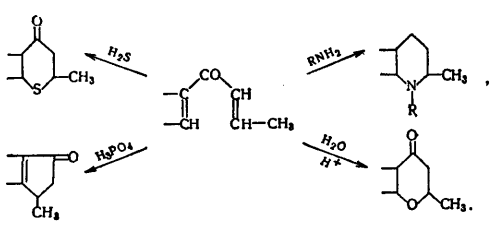
## 13. DEHYDRATION OF VINYLETHYNYLCARBINOLS

Vinylethynylcarbinols can be readily dehydrated by the usual methods to form the corresponding hydrocarbons of the divinylacetylene series[124]:



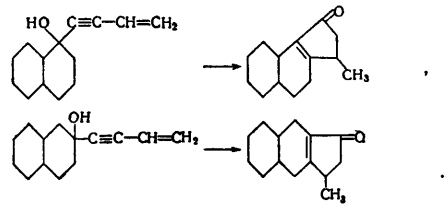
Dehydration is often carried out with 50% sulphuric acid or by distillation over powdered potassium bisulphate. The hydration of divinylacetylenic hydrocarbons in aqueous methanol solution in the presence of mercuric acetate yields divinyl ketones[141,150], which under the action of ammonia and primary amines undergo cyclisation to 4-piperidones[151,152]. These compounds are important in the synthesis of physiologically active products. One of the methylpiperidin-4-ols, called "promedol"‡, has recently found practical use as a morphine substitute[2].

Under the action of hydrogen sulphide, divinyl ketones undergo cyclisation, forming 4-thiopyrones[153-155], while their hydration in the presence of mercuric sulphate yields tetrahydro-4-pyrones[142]. On being heated with phosphoric, formic, and other acids, divinyl ketones can be converted into corresponding cyclopentenones[156]:

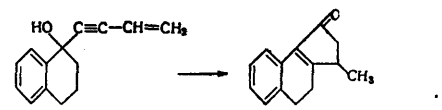


## 14. CYCLOHYDRATION OF VINYLETHYNYLCARBINOLS

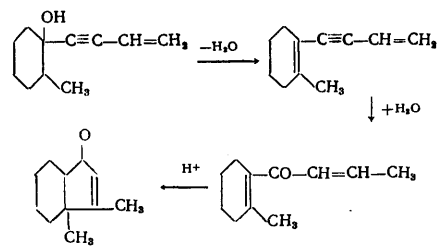
The cyclohydration of vinylethynylcarbinols in the presence of phosphoric acid, resulting in the formation of cyclopentenones, has already been mentioned. Nazarov and Burmistrova showed that, with phosphoric acid at 60°-70°, α- and β-vinylethynyldecalols undergo ring-closure, yielding the corresponding polycyclic ketones[156,157]:



1-Vinylethynyltetral-1-ols similarly gave 3-methyl-4,5--dihydro-6,7-benzoindanone[156]:



Nazarov and Pinkina showed that, on being heated with phosphoric acid, 2-methyl-1-vinylethynylcyclohexanol undergoes cyclohydration, forming 1,8-dimethyl-$\Delta^1$-hexahydro-3-indenone. The same compound was also obtained by dehydration of 2-methyl-1-vinylethynylcyclohexanol to the corresponding dienyne compound, which was subsequently hydrated to form a dienone, and cyclised[158]:



This new type of cyclohydration of vinylethynylcarbinols makes it possible to obtain readily polycyclic ketones containing angular groups, which are normally very difficult to prepare. This is important in the synthesis of steroid compounds.

It is clear from this review that vinylethynylcarbinols are being widely used in a great variety of synthetic processes, and have started a fascinating new chapter of organic chemistry. They are versatile starting materials in the synthesis of complex organic compounds and a series of invaluable products.

‡ 1,2,5-trimethyl-4-phenyl-4-propionoxypiperidine hydrochloride (Ed. of Translation).


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# THE REACTIVITY OF ACETALS AND IONIC TELOMERISATION

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## 1. INTRODUCTION

Acetals are extremely reactive compounds, and have found increasing use during recent years as starting materials in various syntheses. Among the many methods for preparing acetals, an important current technique is their formation from unsaturated ethers based on acetylene and diacetylene. Thus acetals are obtained by the addition of alcohols to unsaturated ethers[1-13]:

$$CH{\equiv}CH \xrightarrow{ROH} CH_2{=}CH{-}OR \xrightarrow{ROH} CH_3{-}CH(OR)_2,$$

$$CH{\equiv}C{-}C{\equiv}CH \xrightarrow{ROH} CH{\equiv}C{-}CH{=}CH{-}OR \xrightarrow{ROH} CH_3{-}C{\equiv}C{-}CH(OR)_2,$$

or by the addition of orthoformic esters[14-16]:

$$CH_2{=}CH{-}OR + CH(OR)_3 \rightarrow (RO)_2CH{-}CH_2{-}CH(OR)_2,$$

$$CH{\equiv}C{-}C{\equiv}CH \rightarrow BrMg{-}C{\equiv}C{-}C{\equiv}C{-}MgBr \xrightarrow{CH(OR)_3} (RO)_2CH{-}C{\equiv}C{-}C{\equiv}C{-}CH(OR)_2,$$

$$CH{\equiv}C{-}CH{=}CH{-}OR \rightarrow BrMg{-}C{\equiv}C{-}CH{=}CH{-}OR \xrightarrow{CH(OR)_3} \rightarrow (RO)_2CH{-}C{\equiv}C{-}CH{=}CH{-}OR$$

$$CH{\equiv}C{-}CH{=}CH{-}SR \rightarrow BrMg{-}C{\equiv}C{-}CH{=}CH{-}SR \xrightarrow{CH(OR)_3} \rightarrow (RO)_2CH{-}C{\equiv}C{-}CH{=}CH{-}SR.$$

In this way various acetals, alkoxyacetals, and diacetals, containing alkoxy-, alkylthio-, or arylthio-groups, and perhaps also double and triple bonds in the carbon skeleton, can be synthesised from vinyl ethers, ethynylvinyl ethers, and sulphides based on acetylene and diacetylene, and also from diacetylene itself.

A great deal of work has recently appeared in the chemical literature on the synthesis of various polyene and polyenyne compounds (for example isoprenoids). Acetals are often employed as starting materials in these syntheses. Furthermore, acetals are able to undergo ionic telomerisation with vinyl ethers and sulphides (this constitutes a new trend in the use of these compounds). Since new unsaturated compounds containing an acetal group are beginning to be employed in these interesting syntheses, it seemed to us profitable to summarise the disconnected experimental results available on this question.

The present review will deal mainly with new or little known reactions of acetals, which are from our point of view the most promising and are of interest for the chemistry of acetals in general.

Acetals can react differently, depending on their structure and the reaction conditions, the carbonyl group, substituents, or multiple bonds being involved in the reaction. Acetals are characterised by many chemical reactions, including hydrolysis, symmetrisation, hydrogenation, condensation, etc., which have been described by various workers[1,10-13,18-28].

## 2. NON-CATALYTIC AND IONIC REACTIONS OF ACETALS

Non-catalytic reactions of acetals are readily explained in terms of hydrogen bonding[29], the role of which in the formation of acetals has been discussed by Shostakovskii[1,12]. This hypothesis was later supported by optical measurements[30]. A hydrogen bond formed between the oxygen atom of the vinyl ether and the alcoholic hydrogen produces an intermediate compound[30], which can dissociate reversibly under certain temperature conditions, yielding molecules of vinyl ethers and of alcohols containing different radicals. Interaction between vinyl ether and alcohol molecules containing identical radicals results in the formation of symmetrical acetals. Thus the reaction mixture contains all possible acetals.

$$CH_2{=}CH{-}OR + R'OH \rightleftarrows CH_2{=}CH{-}OR \rightleftarrows CH_3{-}CH\begin{matrix}OR\\OR'\end{matrix},$$
$$\vdots$$
$$H{-}O{-}R'$$

$$CH_3{-}CH\begin{matrix}OR\\OR'\end{matrix} \rightleftarrows CH_2{=}CH{-}OR' \rightleftarrows CH_2{=}CH{-}OR' + ROH.$$
$$\vdots$$
$$H{-}O{-}R$$

This concept explains the mechanism of such reactions as the non-catalytic formation of acetals from vinyl ethers and alcohols on heating, and the trans-etherification of mixed into symmetrical acetals on distillation. The thermal decomposition of acetals into vinyl ethers and alcohols, which is often used for preparative purposes[1], must be regarded as a reaction of this type.

Similarly, pyrolysis of an acetaldehyde monothioacetal involves its decomposition with the elimination of an