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REACTION OF ACETYLENE AND ALKYNYL COMPOUNDS WITH AMINES AND AMMONIA

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CONTENTS

1. Introduction 670
2. Reaction of acetylene with amines and ammonia 670
3. Reaction of alkyl- and aryl-alkynes with amines 672
4. Reaction of alkoxyalkynes and alkynyl sulphides with amines and ammonia 673
5. Reaction of alkynyl alcohols, their derivatives, and alkynyl oxides with amines and ammonia 674
6. Reaction of alkynyl and bisalkynyl ketones with amines and ammonia 675
7. Reaction of ethynylcarboxylic acids and their esters with amines and ammonia 675
8. Reaction of but-1-en-3-ynes and their derivatives with amines and ammonia 676
9. Reaction of buta-1,3-diyne with amines 677
10. Reaction of butenynes containing a heteroatom in the α-position to multiple bonds, with amines 678

1. INTRODUCTION

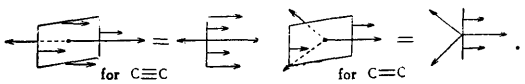
In the last few decades there has been a considerable extension of the studies in the field of the chemistry of unsaturated amines. Thanks to the presence of several reaction centres in their molecules (the amino-group, multiple bonds), unsaturated amines exhibit high reactivity and can serve as starting compounds in the synthesis of more complex nitrogen-containing substances of various classes, including high-molecular-weight materials.

Many unsaturated amines and derivatives obtained from them and based on them are of interest as physiologically active substances.

One of the main methods for obtaining unsaturated amines is by the direct action of amines and ammonia on acetylene and alkyne derivatives.

Alkynes are capable of two types of reaction with amines: addition of the amines to triple bonds and replacement of the active alkynyl hydrogen by an aminomethyl group (Mannich reaction).

The addition of amines and ammonia to alkynes can be classified as a nucleophilic addition to a triple bond. Bohlmann [1] attributed the tendency of a triple bond to participate in nucleophilic addition to the asymmetry of the electron density. During the formation of each electronic bond the centre of gravity of the electron density is displaced towards the centre of the bond. The overlap integrals are a measure of this displacement to a first approximation. If the displacement is represented by vectors leaving the plane perpendicular to the bond and passing through the nucleus of the carbon atom, an almost symmetrical picture is obtained for ethylene, but there is distinct asymmetry for acetylene:



Since this also implies asymmetry of the spherical positive field of the nucleus, the carbon atoms in alkynes already possess in their ground state an approximately electrophilic character. On passing to the polyynes the electropositive character of the terminal carbon atoms increases owing to mesomerism:

$$-\overset{\delta+}{C}\equiv C-[C\equiv C]_n- \longleftrightarrow -\overset{+}{C}=C=[C=C]_n-.$$

However, these views do not explain the influence on the reactivity of the triple bond of various substituents in alkynes.

The many experimental results on the reaction of alkynes with amines show that the reactivity of the alkynyl group and the direction of the addition to it depend essentially on the electronic structure of the substituent, on the amine reacting, and on the conditions.

A possible hypothesis is that in many instances the reaction is brought about through the formation of intermediate complexes of the alkynes with the amines, the catalyst, and the solvent.

This review is intended to survey the literature on the reactions of acetylene and alkyne derivatives with amines and ammonia and to throw light on the fundamental mechanisms of these reactions.

2. REACTION OF ACETYLENE WITH AMINES AND AMMONIA

(a) Reaction of Acetylene with Amines

The reaction of acetylene with amines proceeds in the presence of catalysts on heating and under pressure. Acetylene reacts with primary and secondary aliphatic amines in the presence of copper acetylide under pressure at 80–100° with formation of butynylamines [2–5]. It is thought that vinylamines are the intermediates in this reaction:

$$R_2NH + CH\equiv CH \rightarrow [R_2NCH=CH_2] \rightarrow R_2NCH(CH_3)-C\equiv CH.$$

The yields of butynylamines from secondary amines reach 60–80%; primary amines do not react so well with acetylene. Under these conditions hexamethylenediamine reacts at one amino-group.

Acetylene and primary amines in the presence of zinc or cadmium acetate under pressure at 120–140° form ethylideneimines [6], and not *N*-vinylamines, as Reppe and coworkers had reported [3]:

$$RNH_2 + CH\equiv CH \rightarrow [CH_2=CHNHR] \rightarrow CH_3C(=NR)H.$$

In the presence of water at 60–70° and 20 atm, acetylene also reacts with trimethylamine to form neurine [3,7] [trimethylvinylammonium hydroxide (Ed. of Translation)] in good yield:

$$(CH_3)_3N + CH\equiv CH + H_2O \rightarrow [(CH_3)_3N^+-CH=CH_2]\,OH^-.$$

Amines of structure RNHX, in which R is an alkyl, aryl, aracyl, or ester radical, and X is a chloro-, bromo-, iodo-, cyano-, nitro-, sulpho-, or nitro-aryl group, condense with acetylene in the liquid phase in the presence of a mercury catalyst — $Hg(OAc)_2$ and H_2SO_4 — to give *N*-vinyl compounds of general formula $RN(CH=CH_2)X$. [8]

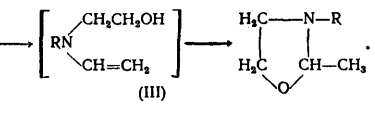
Amino-alcohols react with acetylene in the presence of alkaline catalysts (alkali, alkali metal alkoxides) under pressure at 120–160° to form the corresponding vinyl ethers [9–13]:

$$R_2NCH_2CH_2OH + CH\equiv CH \longrightarrow R_2NCH_2CH_2OCH=CH_2,$$

where R = H, alkyl, or aryl.

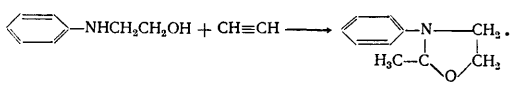
Watanabe and Conlon [14] showed that amino-alcohols with the structure $RNH(CR_2)_nOH$, where R = H or alkyl and n = 2 or 3, with acetylene under pressure, at 100–200°, in the absence of traces of water give 2-methyloxazolidine (n = 2) and perhydro-2-methyl-1,3-oxazine (n = 3), or their derivatives (when R = alkyl) with yields of 5–75%. A vinyl ether is not formed under these conditions. The authors suggest the following mechanism for the reaction:

$$RNHCH_2CH_2OH + CH\equiv CH \longrightarrow \underset{\text{(I)}}{} \left[RN^+(CH_2CH_2OH)(CH=CH^-)\right] \underset{\text{(II)}}{} \longrightarrow \left[RN(CH_2CH_2OH)(CH=CH_2)\right] \underset{\text{(III)}}{} \longrightarrow$$

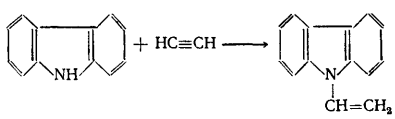


The intermediate compound (II) can be converted into the reaction product directly or through compound (III). Watanabe and Conlon did not give a convincing demonstration of the existence of (III). They represented the reaction mechanism as a special case of vinylation in which the acetylene first attacks the nitrogen of the amino-group (and not the oxygen), analogously to the reaction of aqueous tertiary amines with acetylene, as a result of which a trialkylvinylammonium hydroxide is formed. In the presence of a strongly basic catalyst at 140–150° acetylene under pressure with 2-methylaminoethanol forms a mixture of 2-methylaminoethyl vinyl ether (50%) and 2,3-dimethyloxazolidine (25%).

Aromatic amino-alcohols do not react with acetylene under these conditions. However, in the presence of cadmium acetate 2-methyl-3-phenyloxazolidine is formed from 2-anilinoethanol and acetylene [3]:



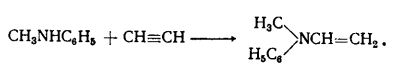
Stable *N*-vinyl compounds are obtained in the reaction of acetylene with nitrogen-containing heterocyclic compounds having a hydrogen atom on nitrogen, such as pyrrole, indole, carbazole, and imidazole [3,5]. The reaction proceeds in the presence of a strongly alkaline catalyst under pressure at 100–200° with yields up to 99%:



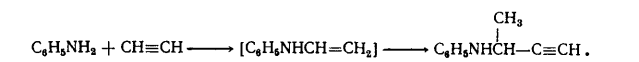
In the presence of alkaline catalysts at 100–200° diarylamines (diphenylamine, phenyl-α- and phenyl-β-naphthylamines) form relatively stable *N*-vinyl compounds [3]:

$$(C_6H_5)_2NH + CH{\equiv}CH \longrightarrow (C_6H_5)_2NCH{=}CH_2.$$

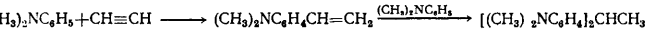
Vinyl derivatives and acetylene also form aralkylamines in the presence of potassium or zinc dust at 185°. *N*-methylaniline gives *N*-methyl-*N*-vinylaniline in 44% yield [4]:



When acetylene and aniline react in the presence of copper acetylide at 20–60° under pressure, 3-anilinobutyne is obtained in 25% yield [2]:



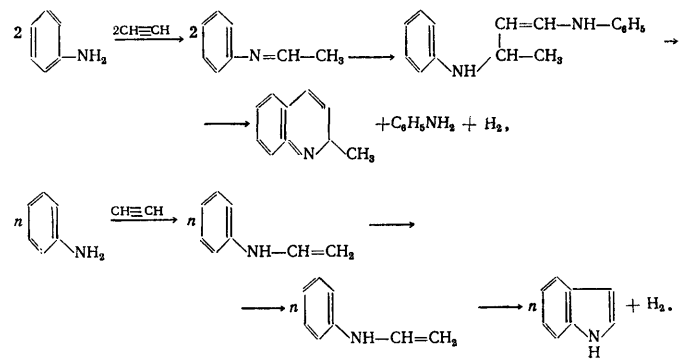
Tertiary aralkylamines are alkylated by acetylene in the aromatic nucleus in the presence of aluminium chloride [15]:



The *p*-dimethylaminostyrene which might be expected from the scheme is not observed in the reaction products.

Kozlov and coworkers [16] showed that acetylene can condense with primary aromatic amines under pressure, and without it at room temperature, or on heating, not above 30°, in the presence of various catalysts: copper(I) chloride, mercury(II) chloride, copper acetylide, or mercury salts of organic acids. Quinaldine, indole, quinoline, and their derivatives are formed.

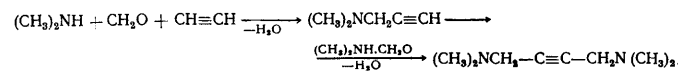
The authors suggest that the formation of quinaldine and indole in the reaction of aniline and acetylene in the presence of copper(I) chloride proceeds through an ethylidene--base and vinylaniline thus:



An analogous scheme was proposed for the reaction of acetylene and ethylaniline in the presence of mercury(II) chloride [17]. However, the authors did not provide convincing proof [16,17].

In the vapour phase at 400° in the presence of tetraethyl lead, aniline and acetylene give indole [18,19]. On an aluminosilicate catalyst at 450°, aniline and acetylene form quinoline in 50% yield [20].

Acetylene condenses with aliphatic amines and formaldehyde only under the influence of catalytic amounts of copper acetylide; with aqueous dimethylamine the products are *NN*-dimethylprop-2-ynylamine and a little *NNN'N'*-tetramethylbut-2-ynylenediamine [5,21,22]:



The reaction does not take place without a catalyst, even at elevated temperatures. Dimethylammonium chloride does not undergo this reaction [23].

(b) Reaction of Acetylene with Ammonia

The catalytic condensation of acetylene with ammonia leads to the formation of a mixture of heterocyclic bases (piperidine bases, α- and γ-picolines, pyrrole, pyridine derivatives, aniline, benzonitrile, etc.) or acetonitrile [3,24].

Among the bases we can single out 5-ethyl-2-methylpyridine, which is formed when the catalyst employed is a nickel complex or a cobalt compound [3]. Vinylamine is probably an intermediate in the reaction of acetylene and ammonia.

If the reaction is carried out in the presence of ammonium acetate at 170–200° and 20–30 atm, 5-ethyl-2-methylpyridine is obtained in up to 90% yield [24].

In the presence of cadmium catalysts, picolines can be obtained in good yield together with other pyridine bases [25,26].

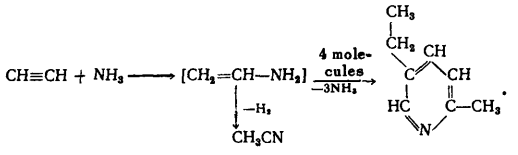
By passing mixtures of acetylene, ammonia, and hydrogen at 350° over zinc oxide and thorium oxide on

silica gel, and then over nickel on silica gel at 150°, condensates containing mainly piperidine and 2-aminoethanol are obtained. When mixtures of acetylene, hydrogen, and ammonia are heated to 650°, pyridine, pyrrole, aniline, and benzonitrile are formed as well as naphthalene and other hydrocarbons [27].

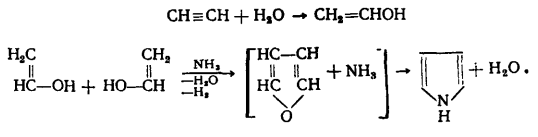
In glazed clay or quartz tubes at > 700° acetylene and ammonia form hydrogen cyanide [28].

On passing mixtures of ammonia and ethylene at 300–500° over catalysts consisting of alumina, zinc oxide, chromium(III) oxide, and 0.15% NaOH, or on using a zirconium catalyst, acetonitrile is formed in theoretical yield [29]. Other catalysts can also be used for this reaction: thorium oxide, $(ZnOH)_2CO_3$ (zinc oxide precipitated from sodium carbonate), zinc nitrate on kaolin, a mixture of sodium carbonate and alumina, carbon monoxide with hydrogen, and also molten salts ($ZnCl_2$–KCl–NaCl; $CdCl_2$–KCl–NaCl; $PbCl_2$–KCl–NaCl; $FeCl_3$–KCl–NaCl; and $SnCl_2$–KCl). [30–33] The yields of acetonitrile when these catalysts are used are 60–90%. Sometimes small quantities of MeCH=NH, pyridine bases, and hydrogen cyanide are formed.

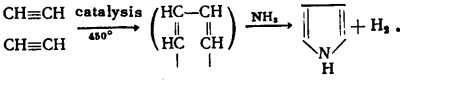
Reppe found that the reaction of acetylene and ammonia can be represented as follows [3]:



Chichibabin showed [34] that when acetylene and gaseous ammonia are passed over oxides of Al, Fe, Cr, Ti, Th, or Si on kaolin, or over aluminium phosphate at > 300°, the products are α-picoline, γ-picoline, 3-ethyl-2-methyl pyridine, pyrrole, and piperidine bases, the production of which he explained by the intermediate formation of acetaldehyde [34]. However, the formation of cyclic nitrogenous bases, for example, pyrrole, can take place in the presence of traces of moisture, as Yu'rev noted [35], by another mechanism, namely:



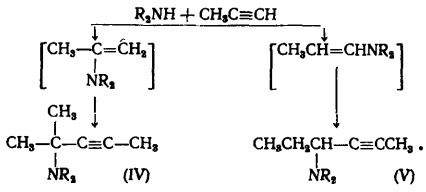
A third path of pyrrole synthesis was subsequently suggested [36]:



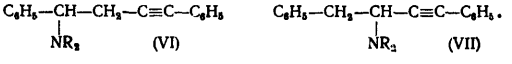
3. REACTION OF ALKYL- AND ARYL-ALKYNES WITH AMINES

Like acetylene, alkyl- and aryl-alkynes add on aliphatic amines in the presence of catalysts and on heating [37]. The direction of the reaction is determined by the nature of the substituents on the alkyne as well as by the structure of the amine being added and the conditions of the reaction. Thus, diethylamine reacts with propyne in the presence of cadmium or zinc acetate on heating to 120°, forming *NN*-diethyl-1,1-dimethylbut-2-ynylamine in 80% yield [37].

Alkylalkynes add on amines in accordance with the Markovnikov rule. Of the two possible butynylamines, (IV) and (V), only the *NN*-dialkyl-1,1-dimethylbut-2-ynylamine (IV) was isolated:

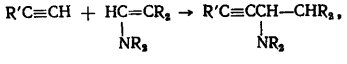


Phenylacetylene adds on secondary amines in the presence of copper(I) chloride at 100°; with morpholine, 3-morpholino-1,4-diphenylbut-1-yne and 1-morpholino-1,4-diphenylbut-3-yne are formed [38]. Compounds (VI) and (VII) were isolated from the products of the reaction between phenylacetylene and secondary alkylamines, showing that the amines add on to phenylacetylene in two ways



This suggests that, as for acetylene, when alkyl- or aryl-alkynes react with aliphatic amines, the corresponding enamines are formed as intermediates [37,38].

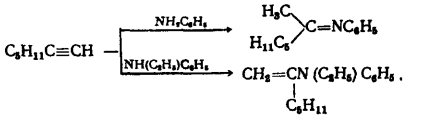
Brannock and coworkers [39] confirmed the formation of an intermediate enamine in the reactions of acetylene, alkyl-, and aryl-alkynes with amines. They continued the reaction of alkynes with enamines and obtained the expected alkynylamines:



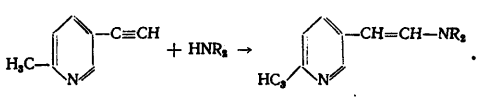
where R′ = H, C_4H_9, C_6H_5, $CH_3CO_2CH_2$, etc.

The process takes place on heating, without catalysts, but catalytic amounts of copper(I) chloride accelerate the reaction so much that it sometimes becomes explosive.

Alkyl alkynes react with aromatic amines in the presence of boron trifluoride or mercury(II) oxide [40]. Under these conditions hept-1-yne gives an anil with primary aromatic amines and a vinyl derivative with secondary aromatic amines:



Pyridylacetylenes behave similarly to the alkyl- and aryl-alkynes in reactions with amines. As Kost and coworkers showed [41], the activity of the triple bond of 5-ethynyl-2-methylpyridine in these reactions is higher than that of phenylacetylene. Actually, 5-ethynyl-2-methylpyridine adds on secondary amines on heating to 180° with up to 70% yields of β-addition products:



Bromophenylacetylene reacts with secondary amines in the cold, addition and substitution taking place simultaneously [42]:

Hexafluorobut-2-yne gives addition products with primary and secondary alkylamines at 20°.[43] Thus with cyclohexylamine it forms *N*-cyclohexyl-1,1,1,4,4,4-hexafluorobut-2-enylamine:

$$F_3CC{\equiv}CCF_3 + C_6H_{11}NH_2 \rightarrow F_3CCH{=}CCF_3NHC_6H_{11}.$$

Other halogenobutynes react analogously:

$$Cl_2CHC{\equiv}CCHF_2. \quad Cl_2CHC{\equiv}CCH_3.$$

The aminomethylation of alkyl- and aryl-alkynes at the labile alkyne hydrogen takes place comparatively readily on heating, although for alkyl alkynes it would be natural to expect retardation of the process. The explanation of this behaviour must probably be sought in Arens' work on the chemistry of alkoxyalkynes (see Section 4).

On heating to 80–100° with dialkylamines and formaldehyde, hex-1-yne forms[44,45] the corresponding alkyne derivatives in 75–81% yield:

$$C_4H_9C{\equiv}CH + R_2NH + CH_2O \rightarrow C_4H_9C{\equiv}CCH_2NR_2 + H_2O.$$

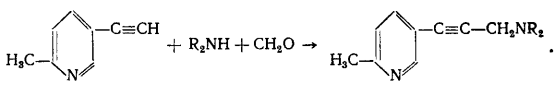
With secondary aliphatic amines and formaldehyde at 100°, phenylacetylene forms *NN*-dialkyl-3-phenylprop-2-ynylamines in yields of up to 80%:[5,46]

$$C_6H_5C{\equiv}CH + NHR_2 + CH_2O \rightarrow C_6H_5C{\equiv}CCH_2NR_2 + H_2O.$$

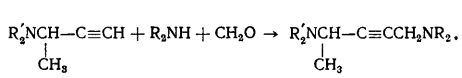
4-Phenylbut-1-yne reacts with secondary amines and paraformaldehyde in the presence of copper(II) acetate at 100° to form the corresponding compound in 76% yield[47]:

$$C_6H_5CH_2CH_2C{\equiv}CH + (CH_3)_2NH + CH_2O \xrightarrow{-H_2O} C_6H_5CH_2CH_2C{\equiv}CCH_2N(CH_3)_2.$$

The condensation of 5-ethynyl-2-methylpyridine with secondary amines and formaldehyde proceeds in the presence of potassium hydroxide on boiling in dioxan; the yields of amino-derivatives reach 92%:[41]



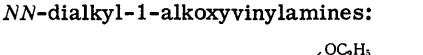
Dialkylaminoalkyl alkynes react with secondary amines and formaldehyde on heating in dioxan; alkynyldiamines are formed in 55–70% yield[48]:



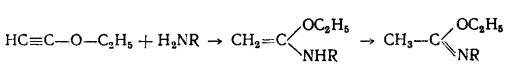
4. REACTION OF ALKOXYALKYNES AND ALKYNYL SULPHIDES WITH AMINES AND AMMONIA

Alkoxyalkynes react slowly with aliphatic amines on heating; the reaction can be accelerated by addition of water.

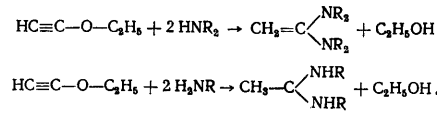
The amines add on to the α carbon atom in accordance with the polarisation of the alkoxyalkyne molecule. The structure of the final reaction product depends on the nature of the amine and the conditions of the reaction[49–51]. Thus secondary amines taken in equimolecular amount react to give *NN*-dialkyl-1-alkoxyvinylamines:



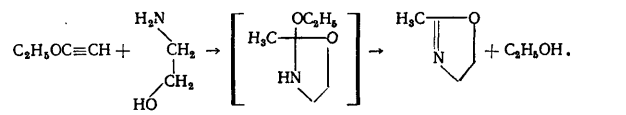
Under these conditions primary amines form the tautomeric iminoethers:



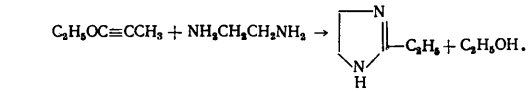
With an excess of the amine, nucleophilic replacement of the alkoxy-group proceeds as well as the addition:



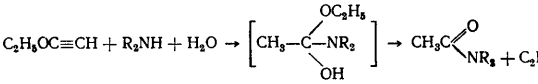
Bifunctional nucleophilic compounds, such as diamines, amino-alcohols, and amino-sulphides, give heterocyclic addition products when heated with ethoxyacetylene[49,52]:



The introduction of a methyl group into ethoxyacetylene retards the reaction with diamines and lowers the yield of addition products. The reaction is accelerated on addition of mercuric oxide. Ethylenediamine gives 2-ethyl-2-imidazoline[52,53]:



The addition of amines to alkoxyalkynes in the presence of water leads to the formation of *N*-substituted acetamides with a yield of up to 89%.[49,51,54] The authors suggest that the intermediate compound in this reaction is a derivative of orthoformic acid. When an amine of high basicity is used, the reaction is exothermic:



where R is H or alkyl.

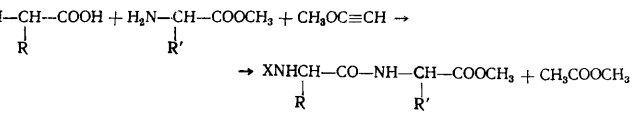
Amines of low basicity, such as aniline and diphenylamine, do not react in this way. They mainly act as catalysts for the hydration of ethoxyacetylene:

$$C_2H_5OC{\equiv}CH + H_2O \xrightarrow[\text{or } (C_6H_5)_2NH]{C_6H_5NH_2} CH_3COOC_2H_5.$$

In the presence of alkoxyalkynes, acids react smoothly (at 25–50°) with amines to form amides in quantitative yield[49,55]:

$$C_2H_5OC{\equiv}CH + RCOOH + H_2NR' \rightarrow RCONHR' + CH_3COOC_2H_5.$$

This reaction can be used for the synthesis of peptides:



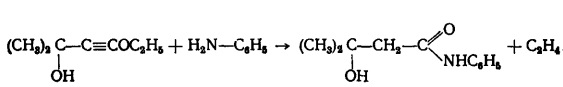
Ethoxyacetylene also reacts with tertiary amines in the presence of water to form trialkyl-(1-ethoxyvinyl)ammonium hydroxides in 55–73% yields[49,56].

The reaction with higher aliphatic amines is very slow — several months are required — but with trimethylamine and triethylamine it occurs readily even at room temperature:

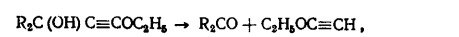
$$C_2H_5OC{\equiv}CH + N(CH_3)_3 + H_2O \rightarrow [CH_2{=}C(OC_2H_5)N(CH_3)_3]^+OH^-.$$

The compound which is formed is analogous to the vinyl derivative obtained by Reppe from acetylene, water, and a tertiary amine[3].

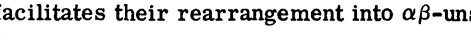
4-Ethoxy-2-methylbut-3-yn-2-ol and aniline form anilides of β-hydroxy-acids in 40% yield[49,57]:



Whereas diethylamine catalyses the decomposition of the tertiary 3-ethoxyprop-2-yn-1-ols:



nitroaniline facilitates their rearrangement into αβ-unsaturated ethers:

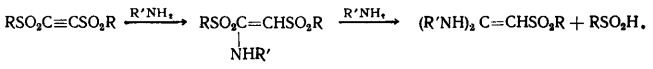


Alkynyl sulphides also react with amines on heating, to form addition products. Thus, ethyl ethynyl sulphide and diethylamine give an addition product in 65% yield[49,51].

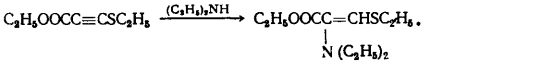
As Arens showed, the sulphide group can act as either a donor or an acceptor of electrons. A nucleophilic reagent adds on to the β carbon atom of an alkynyl sulphide in accordance with the polarisation of its multiple bond:



Alkynyl sulphones react with amines to form addition products; with an excess of the amine the sulphonyl group can be replaced by an amino-group[49,58]:

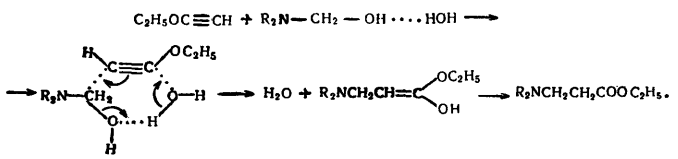


Ethyl ethylthiopropiolate adds on amines at the α carbon atom. Thus when it is heated with diethylamine an addition product is obtained in 74% yield[59]:

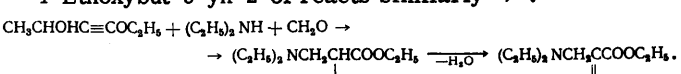


Ethylthiopropiolanilide and 1-ethylthiobut-1-yn-3-one react with amines in a similar manner[60].

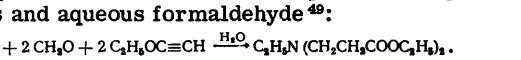
Alkoxyalkynes react readily with amines and formaldehyde. Thus, ethoxyacetylene reacts with diethylamine and aqueous formaldehyde at room temperature[49,61], when ethyl 2-diethylaminopropionate is obtained instead of a Mannich base. Arens assumes that here aminomethanols are formed, which react in a hydrated form with the ethoxyalkyne. During this the hydrogen atom of the alkyne is not replaced by an aminomethyl group, but there is electrophilic addition at the triple bond, which takes place according to this scheme:



4-Ethoxybut-3-yn-2-ol reacts similarly[49,62]:



Ethoxyalkynes form bis-addition compounds with primary amines and aqueous formaldehyde[49]:

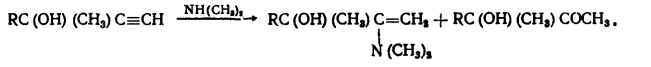


Electrophilic addition to the triple bond can probably also explain the ease of reaction of alkyl alkynes with amines and formaldehyde compared with acetylene; the decomposition of the intermediate addition product here leads to the formation of a Mannich base.

Ethylthioacetylene, unlike ethoxyacetylene, reacts with diethylamine and formaldehyde only on boiling in dioxan[63]. The product is formed by replacement of the alkynyl hydrogen by an aminomethyl group, the yield being quantitative.

5. REACTION OF ALKYNYL ALCOHOLS, THEIR DERIVATIVES, AND ALKYNYL OXIDES WITH AMINES AND AMMONIA

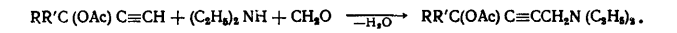
The published information on the addition of amines to the triple bond of alkynyl alcohols is restricted to the work of Vartanyan and Badanyan[64], who reported that when 2-methylbut-3-yn-2-ol or but-3-yn-2-ol are heated with aqueous dimethylamine at 100–120° vinyl amino-alcohols are formed, which are partly hydrolysed under the conditions of the experiment:



1-Ethynylcyclohexan-1-ol and 4-ethynylperhydro-2,2-dimethylpyran-4-ol react analogously.

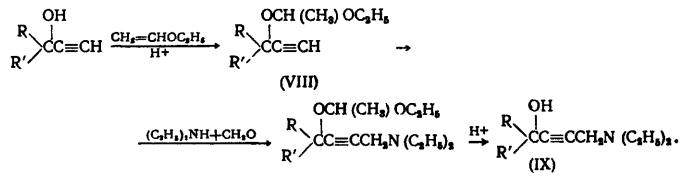
Alkynyl alcohols and their derivatives react with amines under aminomethylation conditions at the alkynyl hydrogen atom.

Whereas α-ethynylmethanols themselves react with secondary amines and formaldehyde at 80° to form the corresponding compounds in low yields, their acetates form Mannich bases in 50–90% yields[45,65]:



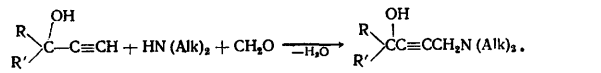
However, this method of obtaining amino-alcohols is inapplicable when R and R′ are aromatic radicals, as the corresponding alkynyl alcohols are unstable in acid and alkaline media.

Shvekhgeimer[66] used an indirect path for the synthesis of the amino-derivatives of alkynyl alcohols:

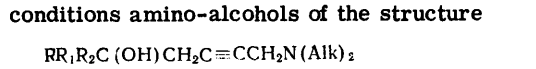


The reaction of the acetals (VIII) with paraformaldehyde and diethylamine occurs when the mixture is heated in dioxan for many hours, and leads to the formation of aminoacetals (IX) with 75–97% yield.

Libman and Kuznetsov aminomethylated tertiary ethynylmethanols in the presence of copper compounds at 80–90°. The reaction is rapid and the yield 80–95%:[67]



Under these conditions amino-alcohols of the structure



are synthesised in 83–95% yield[68].

Pent-4-yn-1-ol reacts with diethylamine and formaldehyde on heating to 40–50° in the presence of copper salts, forming 6-diethylaminohex-4-yn-1-ol in 69% yield[69,70]:

$$HOCH_2CH_2CH_2C{\equiv}CH + (C_2H_5)_2NH + CH_2O \rightarrow HOCH_2CH_2CH_2C{\equiv}CCH_2N(C_2H_5)_2.$$

The following alkoxy- and acyloxy-derivatives of alkyl alkynes also undergo aminomethylation:

$C_2H_5OCH_2C{\equiv}CH$;[71] $(C_2H_5O)_2CHC{\equiv}CH$;[72] $R_1OCR_2R_3(CH_2)_nC{\equiv}CH$;[73] $CH_3(AcO)CHC{\equiv}CH$, $C_6H_5(OAc)CHC{\equiv}CH$;[74] $AcO(CH_2)_2C{\equiv}CH$;[75] $R_1R_2C(OR_3)C{\equiv}CH$.[76]

The low reactivity of the labile hydrogen of alkynyl alcohols in reactions involving substitution by the aminomethyl group is attributed by some to the electron-donor influence of the hydroxyl[67]. Displacement of the electrons of the hydroxyl group towards the side of the alkynyl hydrogen is believed to deactivate it, hindering protonation.

The addition of amines and ammonia to oxides of alkynes and but-1-en-3-ynes does not take place at the triple bond but by opening of the oxide ring according to Krasuskii's rule[77–81].

6. REACTION OF ALKYNYL AND BISALKYNYL KETONES WITH AMINES AND AMMONIA

Alkynyl and bisalkynyl ketones, and also alkynyl diketones readily add amines at the triple bond. The amino-group enters the β position to the carbonyl group. The latter is a strong acceptor of electrons and intensifies the electrophilic nature of the triple bond, facilitating nucleophilic addition.

Alkynyl ketones add on primary and secondary amines and ammonia even at room temperature, forming 2-aminovinyl ketones in 36–97% yield[82–84]:

$$RCOC{\equiv}CR' + NHR_2'' \rightarrow RCOCH{=}CR'NR_2'',$$

where R is alkyl or aryl.

With conjugated ethynylene–vinylene ketones, the addition of the amine proceeds under analogous conditions at the triple bond[83]:

$$RCOCH{=}CH{-}C{\equiv}CH \xrightarrow{NH(C_2H_5)_2} RCOCH{=}CH{-}CH{=}CHN(C_2H_5)_2,$$

where R is alkyl.

Ketones in which the carbonyl group is between a double and triple bond also add ammonia to the triple bond[83]:

$$RCH{=}CH{-}CO{-}C{\equiv}CH \xrightarrow{NHR_2'} RCH{=}CHCOCH{=}CHNR_2'.$$

Alkynyl diketones also react readily with amines and ammonia. Dibenzoylacetylene forms the corresponding addition products with amines and ammonia[85,86]:

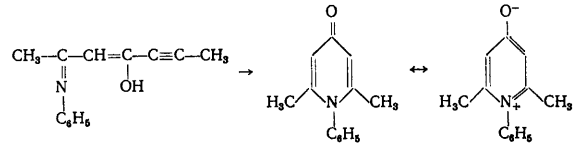
$$C_6H_5COC{\equiv}CCOC_6H_5 \xrightarrow{RNH_2} C_6H_5CO(RNH)C{=}CHCOC_6H_5$$
$$\xrightarrow{NH_3} C_6H_5CO(NH_2)C{=}CHCOC_6H_5$$

where R is alkyl or aryl.

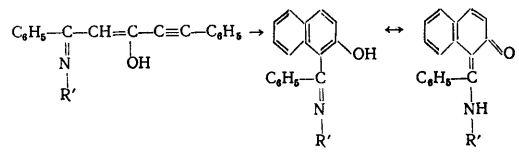
Bisalkynyl ketones readily add on ammonia and primary and secondary amines in the cold or on heating to 50°:[87–91]

$$R{-}C{\equiv}C{-}CO{-}C{\equiv}C{-}R \xrightarrow{R'NH_2} R{-}C{=}CHCOC{\equiv}C{-}R \rightleftarrows R{-}C{-}CH{=}C{-}C{\equiv}C{-}R$$
$$\xrightarrow{R_2'NH} R{-}C{=}CHCOC{\equiv}C{-}R \rightleftarrows R{-}C{=}C{=}C{-}C{\equiv}C{-}R$$

The addition products of the secondary amines are thermally stable. On heating to 150° the addition products of primary amines isomerise into a 4-pyridone, when R is an alkyl radical:



When R is an aryl radical the isomerisation proceeds in two directions; in addition to a pyridone an isomeric cyclic compound is formed[87–93]:



With aniline, the reaction starts at 150° and sometimes ends with an explosion.

The ketone $CH_3C{\equiv}CCOC{\equiv}CC_6H_5$ adds on aniline at both triple bonds, forming a mixture of two substances (XI) and (XII) with a total yield of 75%:[93]

$$CH_3C{\equiv}CCOC{\equiv}CC_6H_5 \xrightarrow{C_6H_5NH_2} \begin{cases} CH_3C(NHC_6H_5){=}CHCOC{\equiv}CC_6H_5 \ (XI) \\ CH_3C{\equiv}CCOCH{=}C(NHC_6H_5)C_6H_5 \ (XII) \end{cases}$$

Substance (XI) preponderates in the mixture; the proportion of (XII) does not exceed 2%.

7. REACTION OF ETHYNYLCARBOXYLIC ACIDS AND THEIR ESTERS WITH AMINES AND AMMONIA

Like alkynyl ketones, ethynylcarboxylic acids and their esters react readily with amines, forming unsaturated compounds with the amino-group in the β-position to the carboxy-group[94–99]:

$$R{-}\overset{\beta}{C}{\equiv}\overset{\alpha}{C}{-}C(=O)OR' + HNR_2'' \rightarrow RC(NR_2'')=CH{-}COOR'.$$

Postovskii and coworkers have shown that cyclic secondary amines add on to propiolates, tetrolates, phenylpropiolates, and ethynyldicarboxylates when cooled with ice, followed by heating to 30–60°.[98,99] Monoaddition products are formed in 16–78% yield:

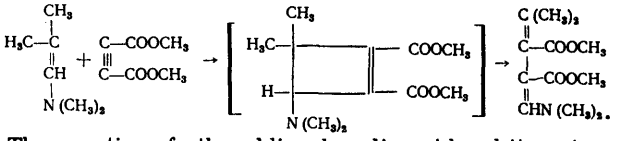
$$RC{\equiv}C{-}COOR' + HN\Big\} \rightarrow R{-}C{=}CH{-}COOR',$$
$$\qquad\qquad\qquad\qquad\qquad\quad N\Big\}$$

where $N\Big\}$ represents the residue of the cyclic amine.

Ethynyldicarboxylates also react readily with amines. Thus, diethyl ethynyldicarboxylate adds on benzylamine and aniline at room temperature, forming diethyl *N*-benzylaminofumarate and diethyl anilinofumarate, the yield being 63% in each instance[100]:

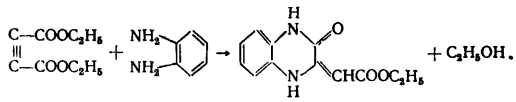
$$C(COOC_2H_5){\equiv}C(COOC_2H_5) \xrightarrow{C_6H_5CH_2NH_2} CH{-}COOC_2H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C(NHCH_2C_6H_5)COOC_2H_5$$
$$\xrightarrow{C_6H_5NH_2} CH{-}COOC_2H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C(NHC_6H_5)COOC_2H_5$$

Brannock and coworkers [101] showed that ethynyldicarboxylates react with tertiary enamines at the double bond:

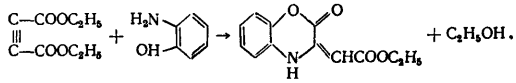


The reaction of ethynyldicarboxylic acid and its esters with bifunctional compounds, such as *o*-phenylenediamine, *o*-aminophenol, ethylenediamine, and *o*-aminobenzenethiol leads to the formation of heterocyclic compounds [102,103]. The reaction proceeds in stages: initially one amino-group reacts, forming an addition product, which then cyclises.

Diethyl ethynyldicarboxylate reacts at room temperature with *o*-phenylenediamine to form ethyl 1,2,3,4-tetrahydro-3-oxoquinoxalin-2-ylideneacetate:



Diethyl ethynyldicarboxylate and *o*-aminophenol give ethyl 3,4-dihydro-2-oxobenzo[*b*]-[1,4]-oxazin-3-ylideneacetate:



Acetylenedicarboxylic acid and *o*-phenylenediamine form 1,2,3,4-tetrahydro-3-oxoquinoxalin-2-ylideneacetic acid.

8. REACTION OF BUT-1-EN-3-YNES AND THEIR DERIVATIVES WITH AMINES AND AMMONIA

The addition of amines to but-1-en-3-yne takes place in the 1,4 position with formation of an intermediate allene derivative, which is isomerised into a diene or alkynylamine [104,105].

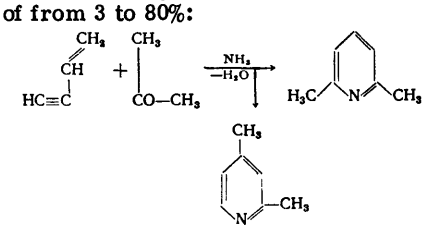
But-1-en-3-yne adds on secondary aliphatic amines on heating to 100° in aqueous solution under pressure, forming alleneamines. When the reaction occurs with an excess of the amine, then the alleneamine formed rearranges into an alkynylamine [104,105]:

$$CH_2{=}CH{-}C{\equiv}CH + R_2NH \rightarrow CH_2{=}C{=}CH{-}CH_2NR_2 \rightarrow CH_3C{\equiv}CCH_2NR_2.$$

Primary amines react analogously.

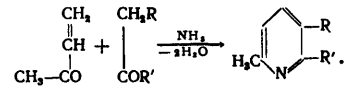
But-1-en-3-yne reacts with ammonia at 250° under the influence of a lead–cadmium catalyst deposited on aluminium oxide; aliphatic amines, picoline, and collidine are formed [105].

Vereshchagin showed [106-108] that but-1-en-3-yne condenses with ammonia and ketones at 350–400° in the presence of cadmium catalysts to form substituted pyridines in yields of from 3 to 80%:



The reaction mechanism is:

$$CH_2{=}CH{-}C{\equiv}CH + H_2O \rightarrow CH_2{=}CH{-}CO{-}CH_3$$



During the reaction of but-1-en-3-yne with piperidine, morpholine, and methylaniline in the presence of copper compounds, nitrogen-containing unsaturated bases used in rubber production are formed [105].

The reaction of but-1-en-3-yne with lithium dialkylamides can be used to obtain addition products which on treatment with water form amines with a terminal ethynyl group [105,109,110]:

$$CH{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_2N{-}Li} H{-}C{=}C{=}CH{-}CH_2NR_2 \rightarrow$$
$$\rightarrow Li{-}C{\equiv}C{-}CH_2{-}CH_2NR_2 \xrightarrow{H_2O} CH{\equiv}C{-}CH_2CH_2NR_2.$$

With alkyl substituted but-1-en-3-ynes the final product is an *NN*-dialkyl-4-alkylbuta-2,3-dien-1-amine:

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_2N{-}Li} R{-}CLi{=}C{=}CH{-}CH_2NR_2 \xrightarrow{H_2O}$$
$$\rightarrow R{-}CH{=}C{=}CH{-}CH_2NR_2.$$

The yields of these compounds reach 45–55%. But-1-en-3-yne is an exception, which mainly forms a dimer under the conditions of this reaction.

But-1-en-3-yne reacts with secondary amines and formaldehyde (in dioxan) at 100° under pressure to form the corresponding bases [111]:

$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow{R_2NH,\ CH_2O} CH_2{=}CH{-}C{\equiv}C{-}CH_2NR_2 + H_2O.$$

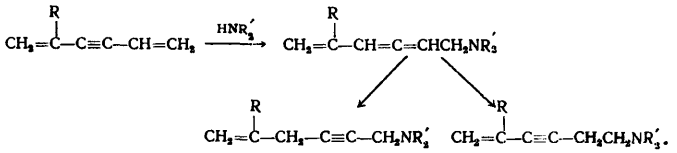
The yield varies from 9 to 91% with various amines.

Nazarov and Mistryukov showed [112] that thoroughly purified paraformaldehyde and diethylamine hardly react with but-1-en-3-ynes. It is only when catalytic quantities of iron salts [iron(III) chloride] are added to the reaction mixture that aminomethyl derivatives are formed smoothly with yields of up to 90%:

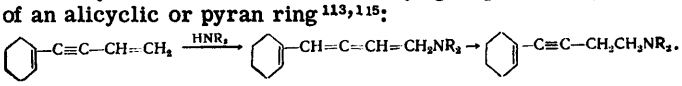
$$-C{=}C{-}C{\equiv}CH \xrightarrow[CH_2O]{(C_2H_5)_2NH} -C{=}C{-}C{\equiv}C{-}CH_2N(C_2H_5)_2 + H_2O.$$

The reaction takes place on heating in dioxan solution.

Hexa-2,5-dien-3-yne adds on secondary amines in the 1,4 position when heated in a sealed tube to 95–100°. [113,114] The triene amine formed undergoes isomerisation in two directions; as a result, hexa-5-en-2-ynyl and hexa-5-en-3-ynyl amines are obtained:

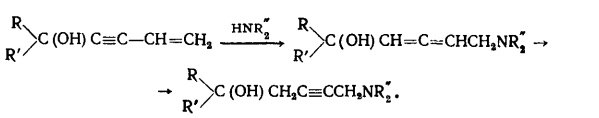


In a similar way dimethylamine adds on to hexa-1,5-dien-3-ynes in which one of the vinyl groups forms part of an alicyclic or pyran ring [113,115]:



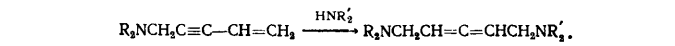
As Vartanyan and coworkers have shown, the addition of amines to but-1-en-3-ynyl alcohols [116-118] and their esters [119] takes place in the 1,4 position on heating them with an

aqueous solution of the amine, and leads to the formation of allene amino-alcohols, which isomerise into alkynyl amino-alcohols (yield > 50%):

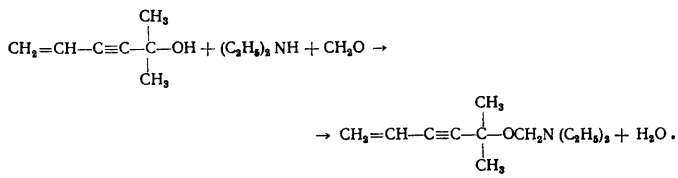


But-1-en-3-ynyl piperidols [120], tetrahydro-4-pyranols, and tetrahydro-4-thiopyranols [121], but-1-en-3-ynyl phenols and their ethers [122] behave analogously.

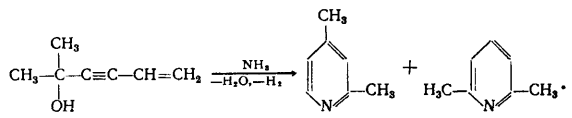
Dialkylaminomethylbut-1-en-3-ynes add on amines in the 1,4 position. The allene diamines formed do not isomerise into alkynyl diamines [123]:



But-1-en-3-ynyl alcohols undergo aminomethylation on boiling in dioxan or benzene, forming aminomethyl vinylalkynyl ethers with 43–71% yield [124]:



Tertiary but-1-en-3-ynyl alcohols undergo catalytic condensation with ammonia at 285–470°. Cadmium and chromium compounds are mainly used as catalysts. Pyridine bases are formed in low yield [106–108,125]:



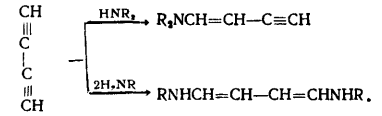
Secondary vinylethynylmethanols on condensation with ammonia on cadmium catalysts at 400° decompose into aldehydes and but-1-en-3-ynes [126]. The aldehyde formed reacts with ammonia to form pyridine bases. Vinylacetylene does not participate in this reaction.

9. REACTION OF BUTA-1,3-DIYNE WITH AMINES

The first patent communication of this reaction stated that buta-1,3-diyne reacts with diethylamine at 45° in the presence of copper or silver salts to form diethylaminobutenyne [127].

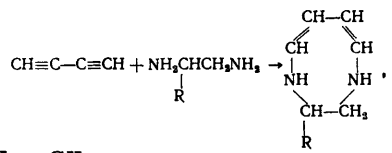
Later Petrov and his coworkers showed that the reaction of buta-1,3-diyne with secondary amines is effected in the cold without a catalyst in benzene solution to form *NN*-dialkylbut-1-en-3-ynamines [128].

The results of systematic investigation of the reaction of diacetylene with amines and amino-alcohols were given by Shostakovskii and his coworkers [129–137]. They showed that buta-1,3-diyne reacts with aliphatic amines at room temperature on passing the buta-1,3-diyne through the amine. Evidently the strongly basic amines show a catalytic action on the course of this reaction. The direction of the addition of the amines to buta-1,3-diyne depends essentially on the nature of the amine. Secondary amines add on in the 1,2 position to form *NN*-dialkylbut-1-en-3-ynamines in 60–70% yield. Primary amines react with buta-1,3-diyne under analogous conditions, adding on in the 1,2 and 3,4 positions, and forming *NN'*-dialkylbuta-1,3-diene-1,4-diamines in 80% yield [130,132,135]:



Unsaturated primary and secondary amines, such as allyl- and diallyl-amines, react similarly [137].

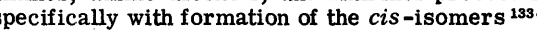
Buta-1,3-diyne reacts much more vigorously with bifunctional compounds (diamines and 2-aminoethanol) than with aliphatic amines [134]. The products of the reactions with propylenediamine and ethylenediamine are heterocyclic compounds: 1,2,3,4-tetrahydro-2-methyl-1,4-diazocine and 1,2,3,4-tetrahydro-1,4-diazocine respectively. The yields are 55–70%:



where R is H or CH_3.

Buta-1,3-diyne reacts with 2-aminoethanol at the two triple bonds, forming a linear product of addition in the 1,4 position [134].

Dialkylamino-alcohols react with buta-1,3-diyne by adding on to the triple bond in the 1,2 position [129,131]. The reaction is exothermic, without the participation of a catalyst, and leads to the formation of the corresponding ethynyl vinyl ethers with 80–90% yield:



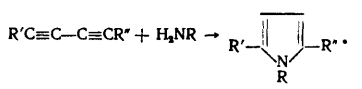
All the above-mentioned reactions of buta-1,3-diyne with amines, amino-alcohols, and diamines proceed stereospecifically with formation of the *cis*-isomers [133–135].

These reactions show the astonishing difference in the behaviour of buta-1,3-diyne and acetylene when they react with amines, amino-alcohols, and diamines. The exceptional ease of reaction of alkylamines and 2-aminoethanols with buta-1,3-diyne is apparently due, above all, to the fact that nucleophilic addition at the triple bond of buta-1,3-diyne is activated by the second ethynyl group, which behaves in relation to the first as an electron-acceptor substituent.

But here it is impossible not to consider also the role of the second component, that is, the amino-compound, which possesses basic properties. Thus, aromatic amines (aniline, methylaniline) under analogous conditions do not react, since their basic properties are diminished owing to the delocalisation of the lone pair of p electrons of the nitrogen with the π electrons of the nucleus.

The reaction of buta-1,3-diyne with aliphatic alcohols free from amino-groups takes place only at 70–100° under the influence of an alkaline catalyst [138,139].

Disubstituted buta-1,3-diyne R'C≡C–C≡CR", where R' and R" are aliphatic, aromatic, or heterocyclic radicals, reacts with primary aliphatic and aromatic amines in the presence of small quantities of copper(I) chloride to form trisubstituted pyrroles [140]:



Buta-1,3-diyne can react with a mixture of a secondary amine and paraformaldehyde in the presence of copper or silver salts [141]. It is suggested that the reaction proceeds through the intermediate formation of an aminomethanol, leading to mono- and di-substituted products:

$$CH{\equiv}C{-}C{\equiv}CH + HOCH_2NR_2 \xrightarrow[-H_2O]{} CH{\equiv}C{-}C{\equiv}CCH_2NR_2 \rightarrow$$

$$\xrightarrow[-H_2O]{HOCH_2NR_2} R_2NCH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2NR_2.$$

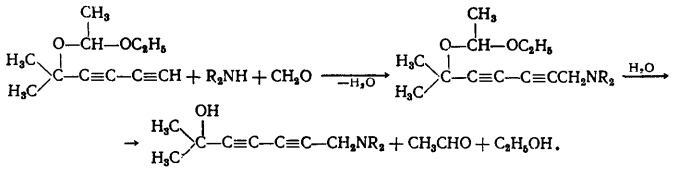
Alkadiyne compounds with isolated triple bonds react with amines and formaldehyde in dioxan solution with a copper catalyst at 80–100° and bisalkynyl ethers react at 80° to form the corresponding diamines [142–144]:

$$CH{\equiv}C{-}(CH_2)_n{-}C{\equiv}CH + 2\,R_2NH + 2\,CH_2O \rightarrow$$

$$\xrightarrow[-2H_2O]{} R_2NCH_2C{\equiv}C{-}(CH_2)_n{-}C{\equiv}CCH_2NR_2,$$

$$(CH{\equiv}CCH_2)_2O + 2\,R_2NH + 2\,CH_2O \xrightarrow[-2H_2O]{} (R_2NCH_2C{\equiv}CCH_2)_2O.$$

The acetal derivative and acetate of 2-methylhexa--3,5-diyn-2-ol react readily on heating with amines and formaldehyde at their labile hydrogen atom; diyne amino--alcohols are formed in good yield [145]:



10. REACTION OF BUTENYNES CONTAINING A HETERO-ATOM IN THE α-POSITION TO MULTIPLE BONDS, WITH AMINES

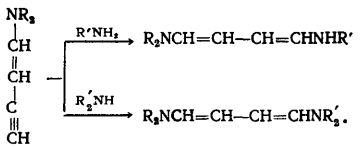
In recent years there has been an investigation of compounds of structure

$$RXCH{=}CH - C{\equiv}CH,$$

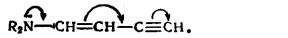
where X = O, N, or S, made in connection with the progress of work on the chemistry of buta-1,3-diyne.

The ability of these compounds to enter into nucleophilic additions is less than that of buta-1,3-diyne and approaches the reactivity of but-1-en-3-yne derivatives.

The addition of amines to butenyneamines takes place at the 3,4 position, and as a result of the reaction, 1,4-substituted dienes are formed with yields up to 80%. [132,133,135] The yield of the reaction product and the conditions of the reaction are determined by the nature of the amine being added:



The addition of amines to a triple bond of butenyneamines, despite Markovnikov's rule, does not correspond with the electron displacements in their molecules:



The displacement of the electron density in butenyne-amines, due to the delocalisation of the electron pair of the nitrogen atom over the enyne system, is confirmed by the investigation of the intensities and positions of the absorption bands of the C≡C and ≡C–H stretching vibrations in these compounds and also by the determination of the dipole moment for *NN*-diethylbut-1-en-3-yne-1-amine [146–149].

These reactions can be also regarded as electrophilic additions of an ammonium ion to the position of greatest electron density [150]:

$$\overset{+}{R}NH_3 \ldots \overset{-}{H}C{\equiv}C{-}CH{=}CHNR_2 \rightarrow H(NHR)C{=}CH{-}CH{=}CHNR_2.$$

The formation of positively-charged ions is evidently explained by transfer of a proton in consequence of the autoprotolysis of the amines, which here act as amphiprotic solvents:

$$2\,RNH_2 \rightleftarrows [RNH]^- + [RNH_3]^+.$$

The formation of ammonium ions can be made possible by the presence of traces of moisture. For example, it is well known [49] that the addition of amines to alkoxyalkyne is catalysed by water.

The addition of amines to oxygen- and sulphur-containing analogues of ethynylvinylamines under analogous conditions has not been accomplished.

Whilst this review was being considered by the editors a work was published on the addition of aqueous and dry amines to dimethyldiacetylenemethanol [151].

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THE MECHANISM OF THE ELEMENTARY ACT OF HOT REACTIONS

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CONTENTS

I. Introduction 681

II. Some physicochemical principles of hot atom chemistry 681

1. The possibility of applying the theory of absolute reaction rates to high-energy chemical processes 681

2. Reactions of excited molecules and processes of excitation energy transfer 682

3. The retardation of hot atoms (physical interpretation) 683

III. Chemical reactions of hot atoms 684

1. Mechanism of the reactions of hot tritium atoms 684

2. Reactions of hot halogen atoms 688

3. Reactions of hot carbon atoms 693