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To the memory of Professor A. A. Petrov

Specific Features of Alkenynamines Chemistry

I. A. Maretina and M. V. Kormer

St. Petersburg Technological Institute, St. Petersburg, 198013 Russia

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Abstract—The reactivity of alkenynamines is considered. Main publications are reviewed concerning reactions of these unsaturated amines with unicentric and multicentric reagents, their participation in cycloadditions affording new classes of polyfunctional compounds and furnishing new approach to building up heterocyclic systems. This research treats a kind of fine organic synthesis promising for industrial applications.

I. INTRODUCTION

New trends appeared recently in the alkyne chemistry, and a special place belonged here to the study of hetero-substituted acetylenes [1–26]. Among the latter a prominent group includes (*N*,*N*-dialkyl)-alk-3-en-1-yn-1-amines (**I**) and (*N*,*N*-dialkyl)alk-1-en-3-yn-1-amines (**II**) differing in reactivity both from conjugated hydrocarbons and tertiary amines [6–12]. Investigation of reactions between alkenynamines **I** and amines, alcohols, and sulfides resulted in development of new synthetic methods for preparation of previously unknown polyfunctional derivatives, for instance, 3-alkenoic acids and (*N*,*N*-dialkyl)-1-heteroalkylalka-1,3-dien-1-amines. The most valuable result of the study is the possibility to prepare heterocyclic compounds.

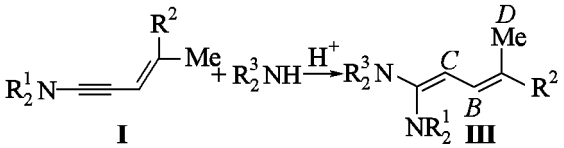
It is also feasible that amines **I, II** may be prepared from the products provided by industrial syntheses: from diacetylene [27–41], vinylacetylene, and propargyl alcohol [42–49]. In the operating chemical factories the diacetylene is recovered exclusively with the use of nucleophilic reagents. Therefore the (*N*,*N*-dialkyl)alk-1-en-3-yn-1-amines [11, 12] are the most interesting safe in handling diacetylene synthons for preparative chemistry of heterocycles.

A lot of recently published studies concerned the effect on the reaction direction of the conjugated tertiary amino group located either at the triple or double bong of the vinylacetylene system; some of the reactions provided heterocyclic compounds. This research was not yet systematized and summarized, and the goal of the present review is to fill in this gap.

II. REACTIONS OF ALKENYNAMINES WITH UNICENTRIC ELECTROPHILIC AND NUCLEOPHILIC REAGENTS

Nitrogen-containing nucleophiles. The study of electronic structure of alkenynamines **I** revealed a deficiency of electron density on C[1] and demonstrated that just this carbon atom of the conjugated system was the object of the nucleophile attack. The CNDO/2 calculation of the electronic structure of alkenynamines and also the data of electron absorption spectroscopy demonstrated that the electron density shift from the triple to double bond was insignificant [50].

Addition to (*N*,*N*-dialkyl)(4-methyl)pent-3-en-1-yn-1-amines (**I**) of secondary allyl and propargyl type amines (H^+, 30–35°C, 3 h, 68%) and also aliphatic-aromatic and heterocyclic amines (H^+, 70–80°C, 3 h, 65–72%) occurred regioselectively and *cis*-stereospecifically across acetylene bond furnishing con-



I **III**

R^1 = Et, Pr; R^2 = H, Me; R^3 = Alk, Ar, Het.

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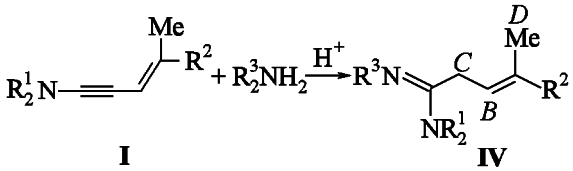
jugated *N*,*N*-dialkylaminals of ketenes, (*N*,*N*,*N*',*N*'-tetraalkyl)(4-methyl)penta-1,3-diene-1,1-diamines (**III**) [51, 52].

The integral intensity of proton signals in the ^{1}H NMR spectra shows that the addition proceeded strictly in 1:1 ratio. Even with excess amine no transamination or addition of the second molecule of a heterocyclic amine was observed. In the ^{1}H NMR spectra of compounds **III** (R^2 = Me) [51, 52] the proton signals of the methyl groups (H_D) are observed in 1.7 ppm region as doublets, $J_{B,D}$ 1.25 Hz. Signals from protons H_B and H_C appear as *AB*-parts of two ABX_3Y_3-systems indicating the presence of two geometrical isomers at the $C^1=C^2$ bond. Two doublets at 4.41 and 4.26 ppm, $J_{B,C}$ 10.2 Hz correspond to H_C proton, and two multiplets at 5.88 and 5.78 ppm, $J_{B,C}$ 10.2 Hz, $J_{B,D}$ 1.25 Hz belong to H_B proton.

At heating of primary aliphatic, cycloaliphatic, and aromatic amines in the presence of catalytic amounts of sulfuric acid occurred addition to compounds **I** affording in 72-84% yield *N*,*N*,*N*'-substituted amidines of 5-pentenoic and 4-methyl-3-pentenoic acids (**IV**) [53].



I **IV**

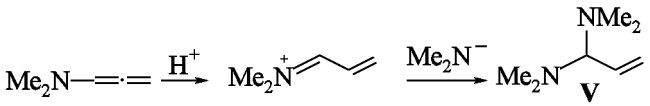
R^1 = Et, Pr; R^2 = H, Me; R^3 = Bu, C_6H_{11}, All, Ph.

This direction of reaction results from addition of primary amine to C^1 atom followed by prototropic isomerization involving the second labile hydrogen of the primary amino group. Nonconjugated character of the double bond in compounds **IV** is confirmed by the splitting into doublet of proton H_C signal from the methylene group (2.87 ppm) due to coupling with the H_B proton. The resonance of H_D protons of methyl group appears as a doublet at 1.64 ppm, $J_{B,D}$ 1.25 Hz [50].

Evaluating the reactivity data on behavior of primary and secondary amines of various basicity in acid-catalyzed reactions with (*N*,*N*-dialkyl)alk-1-yn-1-amines H. G. Viehe concluded that amines of low basicity frequently were more reactive than those of high basicity since the latter blocked the catalyst [54]. The data of [50] on reactivity of alkenynamines in reactions with amines of various basicity confirm in general this conclusion. Actually, primary aliphatic amines (butylamine, pK_B 3.2; cyclohexylamine, pK_B 3.34) under conditions of catalysis with protons react with compounds **I** much more difficultly than less basic allylamine and aniline [50]. Secondary heterocyclic amines (piperidine, pK_B 2.88) react less readily than aliphatic-aromatic ones (*N*-methylaniline, pK_B 9.15) although the steric hindrances in the latter case are more pronounced.

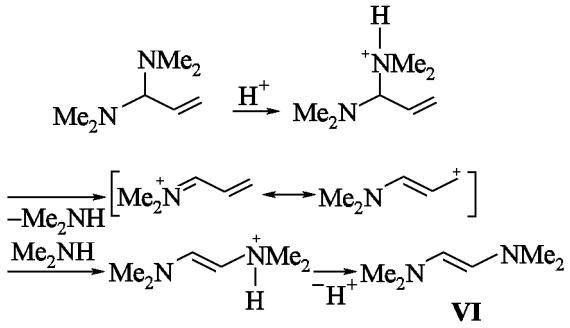
However this dependence of amine reactivity on their basicity in reactions with alkenynamines is valid only within certain limits of the basicity scale. At further decrease in basicity the reactivity is governed by the capability of amine to attack the activated substrate complex. For instance, aniline (pK_B 9.37) reacts with alkenynamines **I** with heat evolution whereas the *p*-nitroaniline (pK_B 12.98) does not react at all due to low basicity [50].

The reaction of allenyl(dimethyl)amine with dimethylamine occurs without catalyst (Et_2O, 0°C, 30 min, 78%) affording (*N*,*N*,*N*,*N*-tetramethyl)-2-propene-1,1-diamine (**V**) [55].



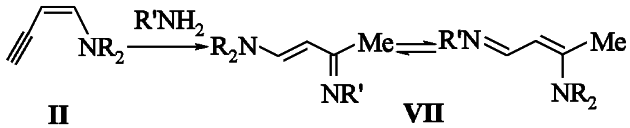
V

The reaction decelerates and does not go to completion in the presence of bases (KOH, *t*-BuOK). H^+ (H_2O, NH_4Cl) causes rearrangement of compound **V** into (*N*,*N*,*N*,*N*-tetramethyl)-(*E*)-prop-1-ene-1,3-diamine (**VI**) (yield 78%, 100% of trans-isomer) [55].



VI

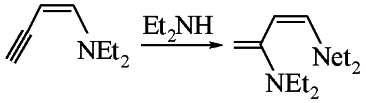
Amines with another position of the multiple bonds, (*N*,*N*-dialkyl)alk-1-en-3-yn-1-amines (**II**) possessing primary alkyl groups, in reaction with primary amines undergo amino groups exchange to form tautomeric aminocrotonaldimines **VII** [11].



II **VII**

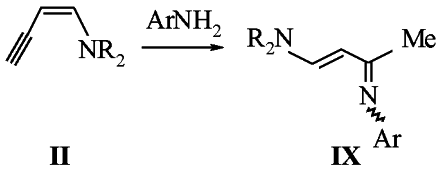
R = Me, Et, Pr, Bu.

Secondary amines with enamine **II** in diluted solutions in aqueous acetonitrile or THF form diadduct, (*N*,*N*,*N*,*N*-tetraethyl)-1,3-butadiene-1,3-diamine (**VIII**) [56].



II **VII**

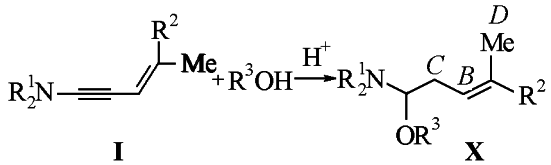
During the reaction between diethylamine and enamine **II** in the UV spectrum of the reaction mixture arises an absorption band in 325 nm region that grows in intensity in the course of reaction, and simultaneously decreases the intensity of the absorption band at 275 nm belonging to the initial amine **II**. On completion of the reaction only the first band remains corresponding to the product of double addition having a diene structure. In the IR spectrum appears an absorption band at 1580 cm^{-1} that grows in intensity; therewith the band of the initial enyne **II** shifts to lower frequencies revealing the formation of product **VIII** with *Z*-configuration [56]. Arylamines add to alkenynamines **II** furnishing *N*-(aryl)azomethine **IX** [57].



II **IX**

R = Me, Et, Pr, Bu.

Oxygen-containing nucleophiles. Alcohols and phenoles. Whereas the alcohols addition to acetylene amines was relatively well studied [54, 57], the reactions with phenols were not considered. It was demonstrated further that reaction of alkenynamines **I** with primary alcohols (H^+, EtOH, 60–70°C, 5 h, 56%) and phenols (Et_2O, 20 min, 70–90%) resulted in *N*,*O*-ketenacetals, (*N*,*N*-dialkyl)-1-alkoxy(aryloxy)-(4-methyl)-1,3-pentadien-1-amines (**X**) [54, 58, 59].



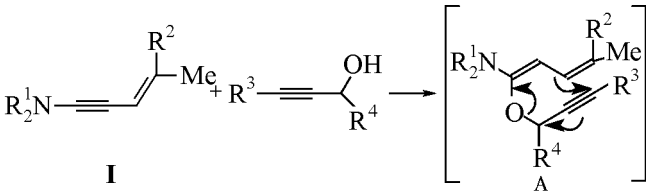
I **X**

R^1 = Et, Pr; R^2 = H, Me; R^3 = Et, Pr, $CH_2CF_2CHF_2$, Ph, *p*-ClPh.

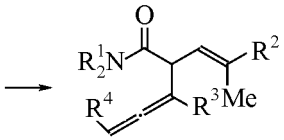
The reaction with the primary aliphatic alcohols proceeds only when catalyzed with sulfuric acid or boron trifluoride etherate. 2,2,3,3-Tetrafluoropropan-1-ol without acid added across the acetylene bond of alkenynamines **I** with heat evolution. Phenols readily add to compounds **I** with no catalyst at room temperature [53, 59].

The double bond $C^1=C^2$ in the (*N*,*N*-diethyl)-1-phenoxy-4-methyl-1,3-pentadien-1-amine has a *Z*-configuration. The trans-location of H_C proton and phenoxy group is confirmed by ^1H NMR spectrum recorded in the presence of lanthanide shift reagents [53]. Thus the catalysts are required only in reactions with primary alcohols. The hydroxy-containing compounds of $pK_a < 16$, among them acetylene alcohols [6], react with enynamines without catalyst.

Compounds **I** readily reacted with β-acetylene alcohols (2-propyn-1-ol and 2-butyn-1-ol) furnishing dialkylamides of (3-methyl)-2-[(2-methyl)-1-propenyl]-3,4-pentadienoic acid (**XI**) [60].



I A



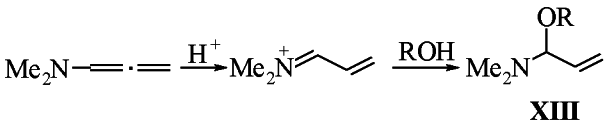
XI, XII

R^1 = Et, Pr; R^2 = H, Me: R^3 = H, Me; R^4 = H (**XI**); R^3 = R^4 = Me (**XII**).

The reaction of primary acetylene alcohols with alkenynamine **I** affords nonisolated product A undergoing Claisen rearrangement into dialkylamides of α-substituted β-allene carboxylic acids **XI** [60]. The secondary β-acetylene alcohol, 3-butyn-2-ol, reacted with alkenynamine **I** only at heating with catalytic amounts of sulfuric acid and boron trifluoride etherate [50, 60]. The change in reactivity in going from primary to secondary β-acetylene alcohols is caused presumably by growing sterical hindrances. The homogeneity of adducts **XI, XII** was proved by GLC, and their structure was confirmed by ^1H NMR spectra [50, 60]. The studies of reactions with β-acetylene alcohols showed the possibility of preparation of highly unsaturated branched carboxamides from akenynamines **I**.

Allenyl(dimethyl)amine took up anhydrous ethanol and *tert*-butanol (Et_2O, 0°C and 40°C, 1 h, 88%) to

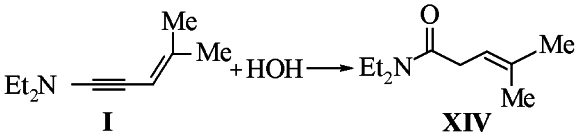
form N,O-acetals **XIII** [55]. In contrast to reaction of allenyl(dimethyl)amine with amines and thiols the rearrangement into (*N*,*N*-dimethyl)-3-alkoxy-2-propen-1-amine is hampered and is observed only with methanol (120°C) [55].



XIII

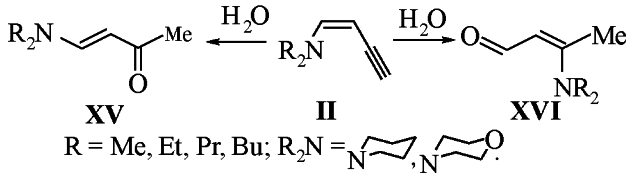
R = Me, *t*-Bu.

Hydration. Water added across the triple bond of alkenynamine **I** giving 3-butenoic acid diethylamide (**XIV**) [42, 61]. (*N*,*N*-dialkyl)-4-methylpent-3-enoic acid amides (**XIV**) were prepared from compound **I** [62].



I **XIV**

The reaction takes several days without catalyst and several minutes in the presence of traces of mineral acids. The hydration proper of alkenynamines **I** is interesting as synthetic procedure for hard-to-obtain derivatives of 3-alkenoic acids with nonconjugated C=C bond. Besides the dehydrating activity of alkenynamines **I**, even stronger than that of dicyclohexylcarbodiimide, can be utilized in synthesis of functional derivatives of acids, halogenated derivatives [62], and peptides [54]. The hydration of amines **II** furnishes depending on the conditions either 4-(dialkylamino)-3-buten-2-ones (**XV**) [2, 11, 63, 64] or 3-(dialkylamino)-2-butenals (**XVI**) [10, 11, 33, 64].

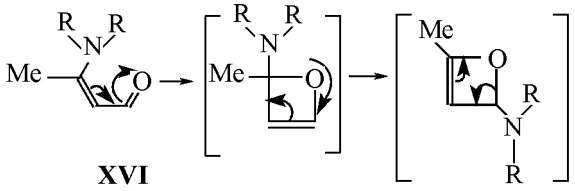


XV **II** **XVI**

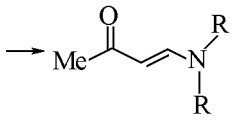
R = Me, Et, Pr, Bu; R_2N =

From the water-alcoholic solutions of primary and secondary amines and diacetylene with subsequent hydration of enamines **II** were obtained enaminoketones **XV**. It was noted however that the constants of hydration products **XV** were not the same as those of compounds synthesized by transamination of alkoxyketones [65]. This discrepancy was attributed to formation alongside the enaminoketones **XV** also of enaminals **XVI** [11, 33]. The aldehyde content in the mixture depends on the size of alkyl substituents at the nitrogen and on concentration of the aqueous alkali (3–5%), and it can exceed 40%. Thus although 3-(dimethylamino)-2-butenal arises only in trace amount, the yields of 3-(diethylamino)-2-butenal and 3-(dibutylamino)-2-butenal are 35 and 43% respectively [11, 33].

Enaminoketones **XV** may form from diacetylene and water solutions of secondary amines also through aldehydes **XVI** [27] that further rearrange into ketones. At higher temperature the ratio ketone-aldehyde shifts to enaminoketone **XV** formation. The thermal isomerization occurs quantitatively, probably via oxetene ring. Aldehyde **XVI** at 150°C completely isomerized into ketone **XV** within 4 h [64].

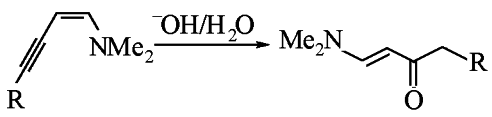


XVI



XV

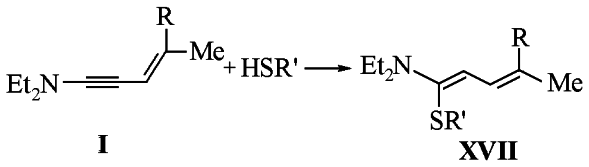
To homologs of amines **II** water adds readily in the presence of catalytic amount of alkali exclusively into position *3* giving rise to 1-(dimethylamino)-1-alken-3-ones [66].



R = Me, Et.

Sulfur-containing nucleophiles. Thiols and thiophenols. Thiol group is considerably more acidic than hydroxy group of analogous compounds, therefore the reaction with RSH should have occurred more readily than with water and alcohols. Reactions were described of propenethiol with dialkyl(ethynyl)amine [67] and (*N*,*N*-dialkylamino)propynonitrile [68] accompanied by a thio-Claisen rearrangement and resulting in thioamides.

Thiols and thiophenols add to alkenynamines **I** (Et_2O, phenyl-β-naphthylamine, 30 min, 60–69%) across the triple bond affording nitrogen analogs of



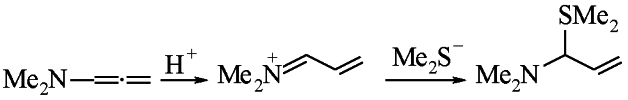
I **XVII**

R = H, Me; R' = Et, Ph, Het.

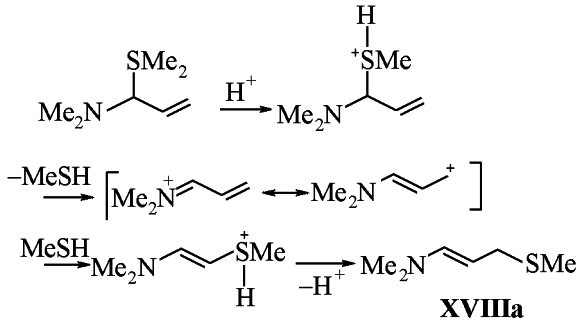
diene N,S-ketenethioacetals, (*N*,*N*-diethyl)-1-[alkyl-(aryl)sulfanyl]-1,3-pentadien-1-amines (**XVII**) [69, 70].

The IR and ^{1}H NMR spectra showed that alkylthio group added to C^{u1} atom similarly to behavior of oxygen- and nitrogen-containing nucleophiles under conditions of acid catalysis [9, 69, 70]. However unlike reactions of alkenynamines with phenols resulting in stereospecific cis-addition, the processes with thiols and thiophenols furnish mixture of geometrical isomers with respect to the $C^1=C^2$ bond. The isomers ratio varies from 60 to 80% and is irreproducible in repeated runs. This fact is in agreement with the published data on easily occurring isomerization of sulfur-containing compounds [71].

Allenyl(dimethyl)amine took up methanethiol (Et_2O, −10°C, 30 min) to furnish (*N*,*N*-dimethyl)-1-(methylsulfanyl)-2-propen-1-amine [55].

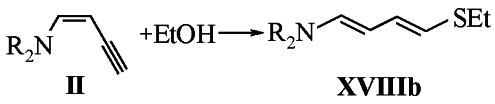


The attempt to eliminate the residual solvent resulted in the rearrangement of the latter compound into (N,N-dimethyl)-3-(methylsulfanyl)-1-propen-1-amine (79%) (**XVIIIa**). The reaction proceeds via desulfurization and subsequent sufurization of the arising conjugated imminium ion [55].



XVIIIa

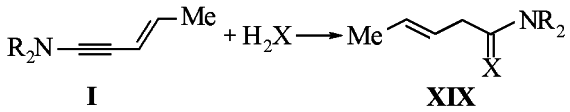
It was reported that enamines **II** added ethanethiol under conditions of radical reaction via attack on the C^4 atom of the conjugated bond system providing compound **XVIIIb** [2, 72, 73].



II **XVIIIb**

R = Me, Et, Bu.

Hydrogen sulfide and hydrogen selenide. The addition of dry hydrogen sulfide or selenide to alkenynamines **I** occurs easier than hydration. 1-Dialkylamino-3-pentene-1-thiones(selenones) (**XIX**) form with heat evolution [74, 75]. The process affords products of high purity and in high yield and therefore can be recommended as preparative procedure for the corresponding aminothiones and selenones [74, 75].

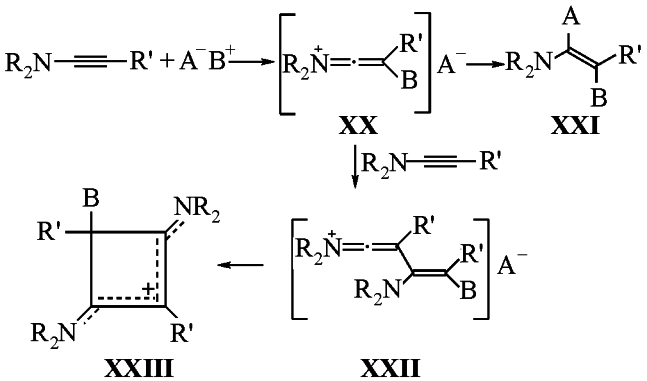


I **XIX**

R = Et, Pr, X = S, Se.

Syntheses of ynamines from N,S-ketenacetals [76] and 1-dialkylamino-1-thiones [54], i.e., reaction reversed with regard to the above mentioned, have been reported.

Electrophilic reagents with a strongly nucleophilic anion. According to data published by Viehe [76, 54] the reaction of ynamines with a polar $A^{\delta-}B^{\delta+}$ molecule occurs at C^2 atom giving rise to ketene immonium salt **XX**. The mechanism involving addition of B^+ to nitrogen atom is quite presumable, and then the character of the reaction would resemble that of enamines [77, 78]; however this type salts have not been obtained.

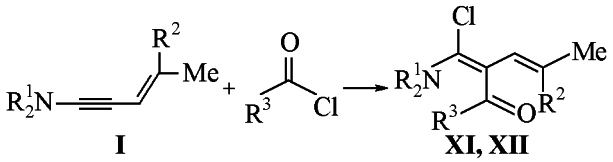


XX **XXI** **XXIII** **XXII**

The acid-catalyzed hydration of ynamines was studied with the use of UV spectroscopy by the stopped-flow procedure. The data obtained confirmed the features of proton transitions in the reaction complex that had been suggested from kinetic

measurements [79]. The hydration rate constant of ynamines is 2000 times larger than that of enamines. This fact originates from concerted transfer of a proton from the nitrogen atom to the β-carbon of ynamine (elimination and addition of proton occurs simultaneously) [79]. The reactivity of alkenynamines **I** is considerably lower than that of simple alkynamines; therefore the latter with phenols form adducts **XXIII** whereas compounds **I** undergo regio- and stereospecific addition of phenols to furnish diene N,O-ketenacetals **X** [59].

In reaction with electrophilic reagents containing strongly nucleophilic anion ketene immonium salt **XX** takes up the anionoid part (A^-) giving adduct **XXI**. For instance, compounds **I** with acetyl or benzoyl chloride provide adducts in nearly quantitative yield; these 1-dialkylamino-1-chloro-2-cetyl(benzoyl)-1,3-pentadienes (**XXIII**) are well distillable substances [80].

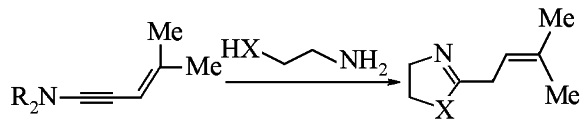


I **XI, XII**

R^1 = Et, Pr; R^2 = H, Me; R^3 = Me, Ph.

III. HETEROCYCLIZATION INVOLVING BIFUNCTIONAL REAGENTS

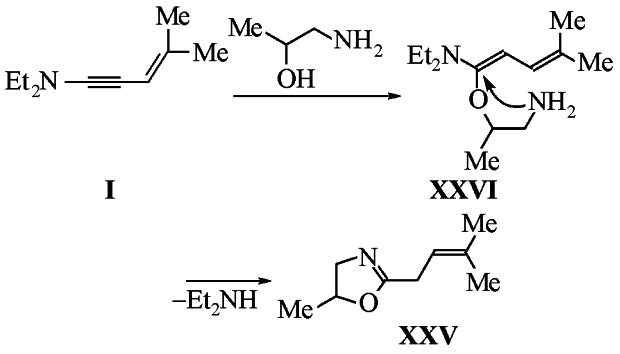
Reactions with diamines, aminophenols, aminothiols, and dithiols. Alkenynamines possess electrophilic qualities, and their reactions with bifunctional reagents giving rise to cyclic compounds are unlike those with simple alkynamines [54, 81] and enamines [10, 11]. For instance, the reaction of alkenynamines **I** with anhydrous ethylenediamine or aminoethanol in dioxane at 100°C in the presence of traces of sulfuric acid gave rise to 2-(3-methyl-2-buten-1-yl)imidazolines (**XXIV**) and 2-(3-methyl-2-buten-1-yl)oxazolines (**XXV**) in 75 and 68% yield respectively [82].



I **XXIV, XXV**

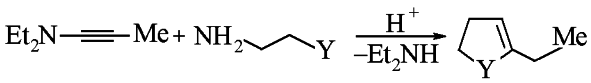
R = Et, Pr, X = NH (**XXIV**), O (**XXV**).

The reaction of alkenynamines **I** with aminoethanol is concerted, but with 1-amino-2-propanol it is a stepwise process. The ^{1}H NMR spectroscopy revealed that in the reaction products of 1-amino-2-propanol and (*N*,*N*-diethyl)-3-penten-1-yn-1-amine alongside cyclization product was present N,O-ketenacetal of diene structure **XXVI** which at heating eliminated diethylamine giving rise to oxazoline [10, 82]. The formation of the open-chain product **XXVI** was presumably caused by steric hampering of the concerted process.



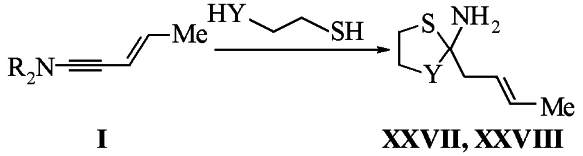
I **XXVI** **XXV**

In reaction of (*N*,*N*-diethyl)-1-propyn-1-amine with ethylenediamine and aminoethanol in the presence of traces of sulfuric acid occurs elimination of diethylamino group giving rise respectively to 2-ethylimidazoline and 2-ethyloxazoline in 43 and 45% yield [81].



Y = N, O.

The same direction of enynamines **I** reaction was observed with bifunctional sulfur-containing compounds, but cyclization occurred without elimination of dialkylamino group. With 2-mercaptoethanol and 1,2-ethanedithiol were obtained within 0.5 h with no catalyst 2-dialkylamino-2-(2-buten-1-yl)-1,3-oxathiolanes (**XXVII**) and 2-dialkylamino-2-(2-buten-1-yl)-1,3-dithiolanes (**XXVIII**) in 43 and 45% yield respectively [82].



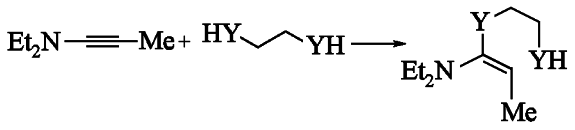
I **XXVII, XXVIII**

R = Et, Pr; Y = O (**XXVII**), S (**XXVIII**).

The reactivity in reaction with alkenynamines **I** grows with increasing acidity of nitrogen-, oxygen-, and sulfur-containing reagents due to electrophilic catalysis of addition. The reagents possessing acid functions (1,2-ethanedithiol, 2-mercaptoethanol) enter into the reaction with alkenynamines **I** without

catalyst, whereas the process with ethylenediamine and 2-aminoethanol requires the presence of catalytic amounts of acid in agreement with the previously stated rule [10].

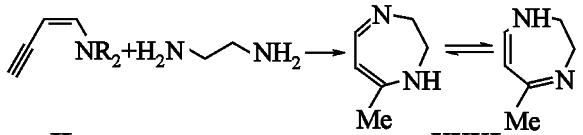
The (*N*,*N*-diethyl)-1-propyn-1-amine takes up ethylene glycol (H^+, dioxane, 60°C, 4 h, 20%) and 1,2-ethanedithiol (0.5 h, 40%) furnishing mono-adducts at the more acid function: *N*,*O*-ketenacetal [2-(1-diethylamino-1-propenyloxy)-1-ethanol (**XXIX**)] and N,S-ketenacetal [2-(1-diethylamino-1-propenyl-mercapto)ethyl hydrosulfide (**XXX**)] [81].



XXIX, XXX

Y = O (**XXIX**), S (**XXX**).

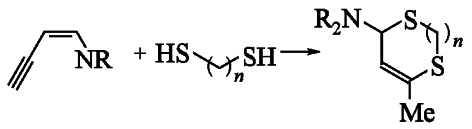
Enynamines **II** with ethylenediamine (80°C, H^+, benzene, 2 h) give rise to a mixture of tautomers of 5-methyl-2,3-dihydro-1,4-diazepine (**XXXI**) (on the scheme are given the most stable tautomers) [83, 84]. The cyclization occurs under acid catalysis (2 drops of 2% sulfuric acid in anhydrous dioxane) to afford reaction products in 76% yield.



II **XXXI**

R = Me, Et.

Reaction of (*N*,*N*-dialkyl)alk-1-en-3-yn-1-amines (**II**) with 1,2- and 1,3-alkanedithiols also yields 1,3-adducts [85, 86], but unlike the reaction with ethylenediamine the dialkylamino group of the initial enamine is conserved. With 1,2-ethanedithiol alkenynamines **II** easily (0°C, 30 min) on mixing reagents afford (*N*,*N*-dialkyl)-7-methyl-2,3-dihydro-5H-1,4-dithiepin-5-amines (**XXXII**) in 91–96% yield.

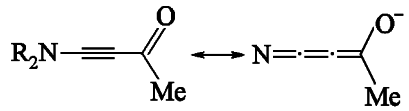


II **XXXII, XXXIII**

R = Me, Et; R_2N = $O(CH_2)_2N$; *n* = 2 (**XXXII**), 3 (**XXXIII**).

Under similar conditions with 1,3-propanedithiol were obtained in 52–67% yield (*N*,*N*-dialkyl)-8-methyl-3,4-dihydro-8*H*-6,7-dihydro-2*H*,6*H*-1,5-dithiocin-6-amines (**XXXIII**) [85].

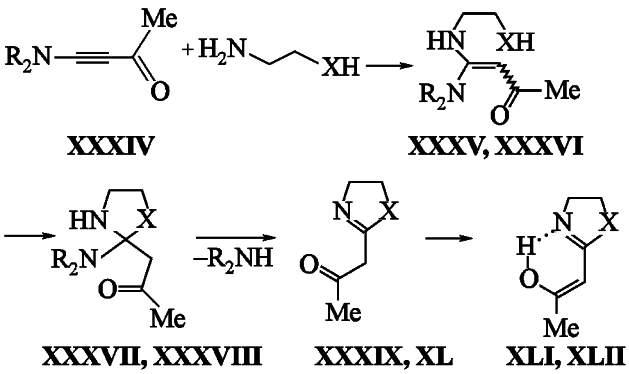
Reactions of dialkylaminoalkynones. It is known [87] that in enamino and ynamino carbonyl compounds the measured coupling values $^{13}C–^{13}C$ are significantly smaller than those calculated by an additive procedure due to levelling of the bonds multiplicity caused by direct polar conjugation through the multiple carbon-carbon bond of the unshared electron pair of the amine nitrogen and the π-system of the carbonyl fragment [87]. This feature essentially distinguishes the class of compounds **XXXIV** from simple ynamines [81]. The contribution of a bipolar resonance form is around 30% for enamino carbonyl compounds, whereas for their acetylene analogs it exceeds 50% [87].



XXXIV

The comparison of the chemical shifts in the ^{13}C NMR spectrum of carbons belonging to the triple bond in the substituted ynamines with those of carbons at the double bond in the analogous compounds of the ethylene series suggested that in the ynamines with acceptor groups existed back polarization of the orthogonal π-system of the triple bonds. This effect is revealed in the abnormally low contribution to shielding by dialkylamino group of the carbon atom in the triple bond closest to the nitrogen [87]. Therefore the alkylaminobutynones have specific features unlike those of ynamines [10, 81] or acetylene ketones [88].

Dialkylaminobutynones **XXXIV** contain a push-pull system with a strongly electron-withdrawing carbonyl group, and thus they possess an electrophilicity. The cyclization reactions therewith are not



XXXIV **XXXV, XXXVI**

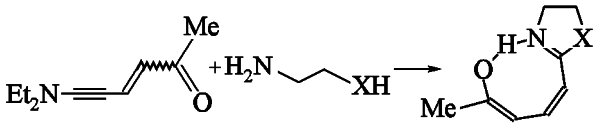
XXXVII, XXXVIII **XXXIX, XL** **XLI, XLII**

R = Me, Et, Pr, X = NH (**XXXV, XXXVII, XXXIX, XLI**); O (**XXXVI, XXXVIII, XL, XLII**).

like those with ynamines [10, 81] or acetylene ketones [88]. For instance, 4-dialkylamino-3-butyn-2-ones react with ethylenediamine or 2-aminoethanol in THF at 65–70°C without catalyst yielding within 2 h respectively 2-(acetylmethyl)-1,3-imidazolines (**XLI**) (yield 70%) and 2-(acetylmethyl)-1,3-oxazolines (**XLII**) (yield 61%) [89, 90].

Apparently the cyclization proceeds through open-chain intermediates **XXXV, XXXVI** that undergo closure into imidazolidine **XXXVII** and oxazolidine **XXXVIII**; the latter compounds lose a secondary amine yielding imidazoline **XXXIX** and oxazoline **XL** which exist in solution exclusively in enol forms **XLI, XLII** stabilized by conjugation and internal hydrogen bonds [91].

The reactions of enynaminoketone **XLIII** [49] with ethylenediamine and 2-aminoethanol occur with a double nucleophilic attack on the triple bond and elimination of a dialkylamino group resulting respectively in imidazoline **XLIV** and oxazoline **XLV** containing totally enolized vinylacetyl groups [92, 93].

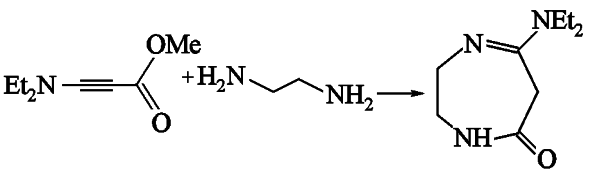


XLIII **XLIV, XLV**

X = NH (**XLIV**); O (**XLV**).

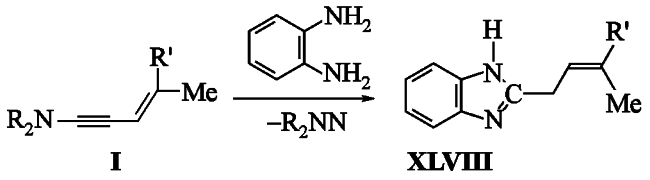
The reaction was carried out by heating in THF to 65–70°C for 3 h. The structure of the heterocycles obtained was established from the ^{1}H NMR and IR spectral data.

The change in the character of the carbonyl fragment affects the direction of cyclization. The reduced acceptor properties of the ethoxycarbonyl group in methyl 3-diethylamino-2-propynolate [94] resulted in 1,3-orientation of the bifunctional reagents. Methyl ester **XLIV** with ethylenediamine in ethanol within 3 h at 70–75°C afforded in 68% yield 5-diethylamino-2,3,6,7-tetrahydro-1*H*-1,4-diazepin-7-one (**XLVII**) [94].



XLIII **XLIV, XLV**

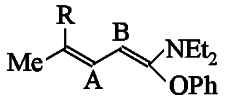
Reactions of alkenynamines with phenylenediamines, aminophenols, pyrocatechol, aminothiols, and dithiophenols. The reactions of enynamines **I** with α,β-bifunctional reagents from aromatic and naphthalene series also occur regioselectively and stereospecifically at the triple bond. Compounds **I** with *o*-phenylenediamine (pK_B 9.6) as with the other aromatic amines [53] react in the presence of two drops of 5% sulfuric acid with heat evolution giving in 69–72% yield 2-[(3-methyl)-2-buten-1-yl)benzimidazoles (**XLVIII**) [95, 96].



I **XLVIII**

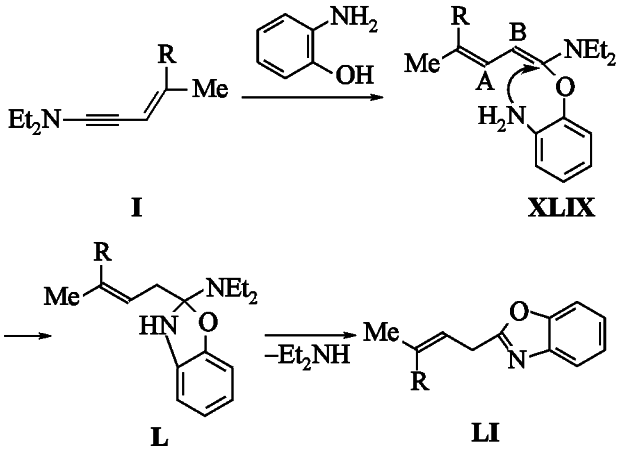
R = Et, Pr, R' = H, Me.

Ynamines **I** on mixing with an equimolar amount of *o*-aminophenol (pK_a 9.66) in ether solution provide in 73% yield 2-[(3-methyl)-2-buten-1-yl)benzoxazoles (**LI**) [96, 97]. Apparently the reaction starts by an attack of oxy group on enynamine **I** for phenols react faster than amines [10]. This assumption was confirmed by the ^{1}H NMR spectrum taken in the course of reaction: The appearance in the spectrum of proton signals (δ, ppm) from H_B at 4.78 (d, 1H) and H_A at 5.85 (d, 1H) in keeping with published data [94] indicated the presence in the reaction mixture of adduct **XLIX**.



XLIX

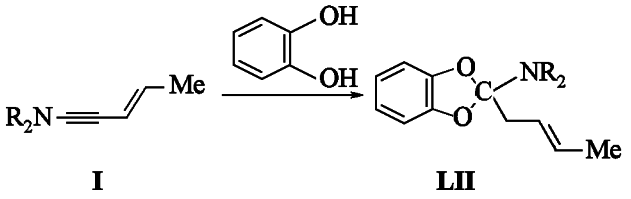
After removing the solvent (ether) these signals completely disappeared; however the isolation of adducts **XLIX** and **L** in pure state did not succeed. During vacuum distillation the secondary amine was eliminated, and benzoxazole **LI** was obtained.



I **XLIX** **L** **LI**

R = H, Me.

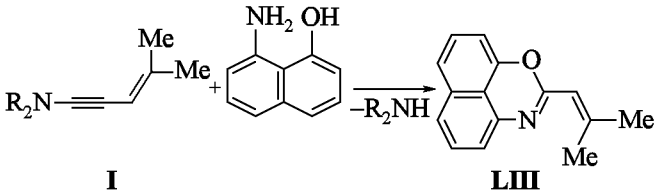
Alkenynamine **I** reacts at cooling with pyrocatechol (pK_a 9.44) affording in 70% yield 2-dialkylamino-2-[(3-methyl)-2-buten-1-yl]-1,3-benzodioxoles (**LII**) [96, 98] that suffer fast decomposition in air.



I **LII**

R = Me, Et.

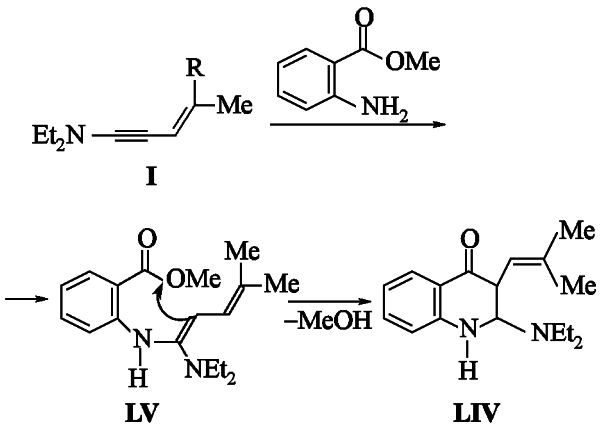
Alkenynamines readily condense with compounds of naphthalene series [99, 100]. Derivatives of naphtho[1,8-e][1,3]oxazines (**LIII**) were obtained in reaction with 8-amino-1-naphthol [99].



I **LIII**

R = Me, Et.

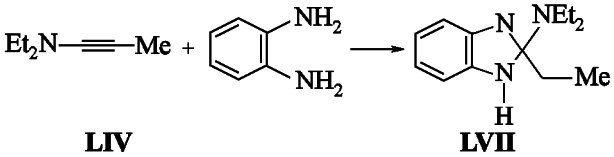
When the bifunctional reagent contains groups of different character (e.g., methyl anthranilate), the reaction with compounds **I** under acid catalysis provides 2-diethylamino-3-(2-methyl-1-propenyl)-3-quionolones (**LIV**) [101]. The reaction proceeds in two stages, and the intermediate amidine **LV** have been isolated and by heating without elimination of diethylamino group has been transformed into quinolone **LIV**.



I **LV** **LIV**

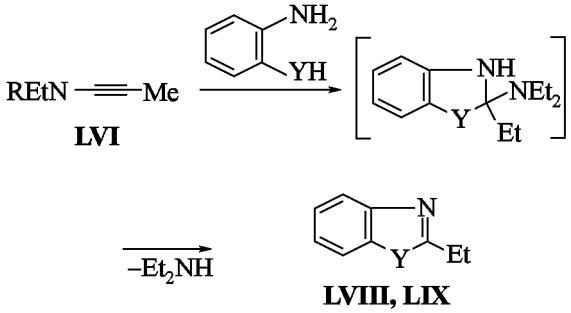
R = H, Me.

In the above reactions the alkenynamines play role of certain acylating agents that provide a possibility to synthesize cycles with two heteroatoms fused to a benzene ring and containing a substituent with nonconjugated alkenyl fragment. Comparison of reactions between alkenynamines **I** and *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol permits a qualitative conclusion, that in the absence of acid catalyst the ease of reagent addition to the substrate is in agreement with growing acidity of the functional groups in the series NH_2 < OH < SH presumably suggesting the autocatalysis of the nucleophilic addition [10]. However (*N*,*N*-diethyl)-1-propyn-1-amine (**LVI**) with *o*-phenylenediamine in benzene in the presence of traces of sulfuric acid afforded in 48–52% yield a single (according to TLC) product with conservation of diethylamino group: 2-diethylamino-2-ethylbenzimidazoline (**LVII**) [81].



LIV **LVII**

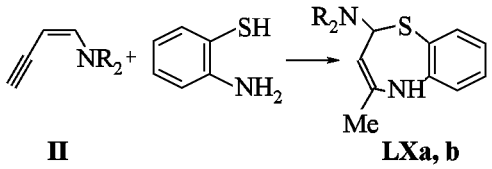
Ynamine **LVI** with *o*-aminophenol and *o*-aminothiophenol in benzene at room temperature gave rise in 70–80% yield to 2-ethylbenzoxazole (**LVIII**) and 2-ethylbenzothiazole (**LIX**) respectively [81].



LVI **LVIII, LIX**

R = Et, Ph; Y = O (**LVIII**), S (**LIX**).

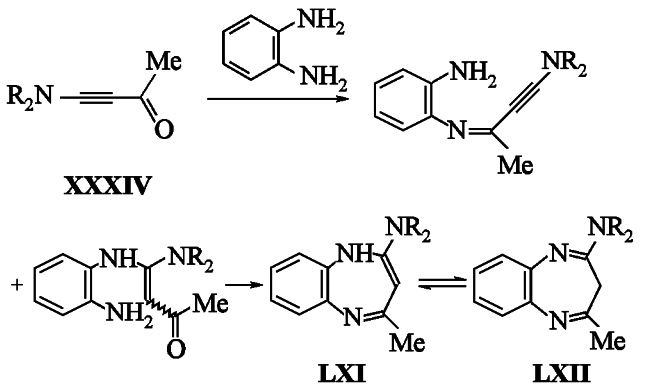
With (*N*,*N*-dialkyl)alk-1-en-3-yn-1-amines (**II**) and *o*-aminothiophenol occurs 1,3-addition (0°C, Et_2O, 20 min) to furnish 2-dialkylamino-4-methyl-5*H*-1,5-benzothiazepines (**LXa, b**) in 87 and 91% yield respectively [101–103].



II **LXa, b**

R = Me (**a**), Et (**b**).

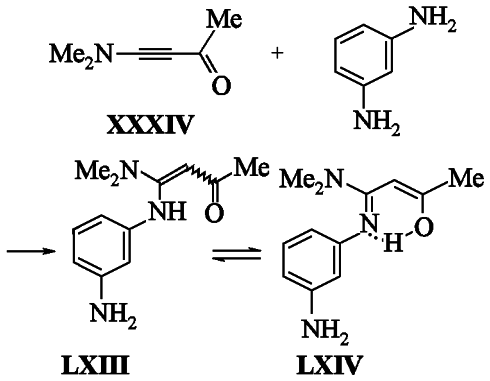
Alkynaminoketones **XXXIV** react with aromatic binucleophiles quite unlike alkenynamines. The decrease in nucleophilicity of a reagent with vicinal amino groups in going from ethylenediamine to *o*-phenylenediamine results in altered character of the reaction: Instead of imidazolines the reaction (60–70°C, THF, 3–7 h) provides in 55–75% yield seven-membered heterocycles, 7(8)-R-2-dialkylamino-4-methyl-3*H*-1,5-benzodiazepines (**LXI, LXII**) [104, 105]. Apparently primarily occurs amino groups addition both to the carbonyl and the triple bond, and the arising intermediate cyclizes into azepine **LXI** that turns into bisimine tautomer **LXII**.



XXXIV **LXI** **LXII**

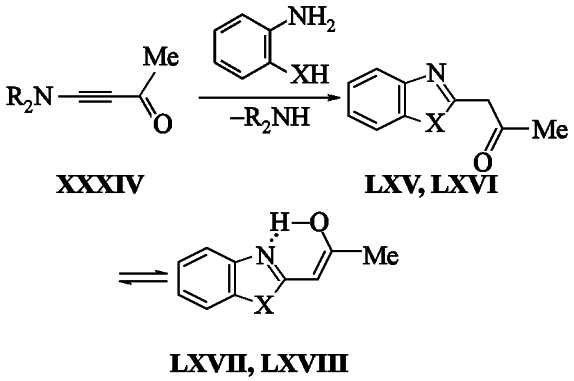
R = Me, Et; R_2N = $O(CH_2)_2N$.

The ^1H NMR spectra indicate that diazepines exist in bisimine form that is considered to be the most favorable for these systems [106]. The place of the primary attack of aromatic diamine was revealed by monitoring the reaction of compound **XXXIV** with *m*-phenylenediamine by NMR spectroscopy [10]. It turned out that in $CDCl_3$ at 60°C *m*-phenylenediamine slowly added to the triple bond giving iminoenol tautomers **LXIII** and **LXIV** with the latter prevailing [9, 10]. The intensity of signals corresponding to the olefin proton (–CH=) and hydroxy group are approximately equal. Thus the enaminoketone tautomer **LXIII** is present in small amount.



XXXIV **LXIII** **LXIV**

The reaction of acetylene ketones with *o*-phenylenediamine takes a similar route, but requires acid catalysis [88]. At the same time alkynamines and alkenynamines with *o*-phenylenediamine afford substituted benzimidazoles as a result of double attack on the C^1 acetylene carbon [81, 82]. Compounds **XXXIV** react with *o*-aminophenol and *o*-aminothiophenol a lot easier (65–70°C), 20–40 min) than with *o*-phenylenediamine furnishing respectively 2-acetylmethyl-1,3-benzoxazoles (**LXV, LXVII**) and 2-acetylmethyl-1,3-benzothiazoles (**LXVI, LXVIII**) [104, 107].

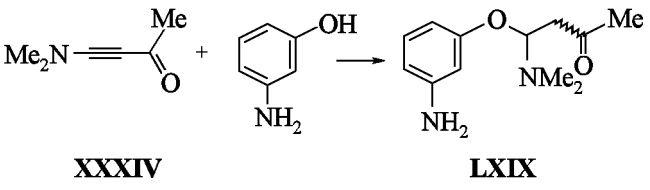


XXXIV **LXV, LXVI** **LXVII, LXVIII**

R = Me, Et; X = O (**LXV, LXVII**); S (**LXVI, LXVIII**).

Unlike the condensation products of ethylenediamine and 2-aminoethanol with aminobutynones (**XXXIV**) which exist nearly exclusively as enols, benzoxazoles **LXV, LXVII** and benzothiazoles **LVI, LXVIII** in solutions are present in both tautomer forms, ketone (**LXV, LXVI**) and enol (**LXVII, LXVIII**). Apparently it originates from the reduced basicity of the imine nitrogen due to the proximity of oxygen or sulfur.

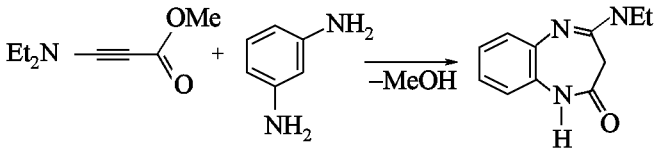
Mass spectrum of thiazole derivatives **LXVI, LXVIII** contains strong peaks of molecular $[M]^+$ and fragment $[M–Me]^+$, $[M–Ac]^+$ ions. The fragment peak $[M–RCN]^+$ (9%) corresponds to benzothiazole ring rupture at carbon–nitrogen and carbon–sulfur bonds with charge localization on the sulfur-containing fragment [104]. To reveal the place of the primary attack a reaction of 4-dimethylamino-3-butyn-2-one with *m*-aminophenol was carried out



XXXIV **LXIX**

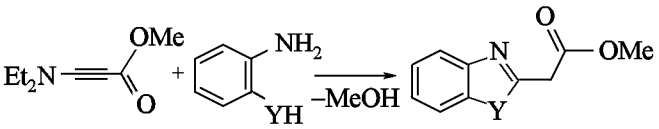
(65–70°C, THF, 20 min). It turned out that reacted only the hydroxy group to yield N,O-ketenacetal, 4-dimethylamino-4-(*m*-aminophenoxy)-3-buten-2-one (**LXIX**) [9, 10].

As a result of *o*-phenylenediamine 1,3-addition to methyl 3-diethylaminopropynolate (**XLVI**) (EtOH, 70°C, 2 h, 58%) formed 4-diethylamino-1,5-benzodiazepin-2-one (**LXX**) [9, 10, 107].



XLVI **LXX**

However reactions of compound **XLVI** with *o*-aminophenol and *o*-aminothiophenol (MeOH, 30°C, 40 min, yield 60%) gave rise to a product of 1,1-attack on the acetylene atom C^1, 2-(methoxycarbonylmethyl)benzoxazole (**LXXI**) and 2-(methoxycarbonylmethyl)benzothiazole (**LXXII**) [9, 10, 107].

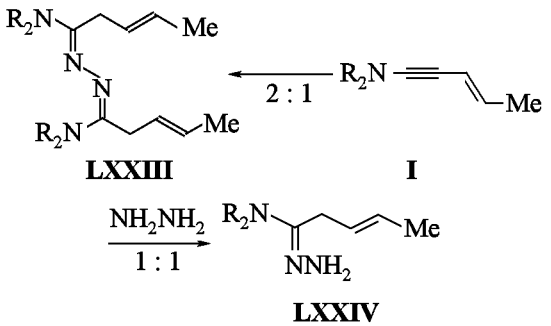


XLVI **LXXI, LXXII**

Y = O (**LXXI**), S (**LXXII**).

Thus *p*,π-unsaturated amines with various bifunctional reagents permit preparation of desired five-membered and seven-membered heterocycles with two heteroatoms containing nitrogen, oxygen, and sulfur.

Reaction with hydrazine. Reactions of alkenynamines **I** with hydrazine occur only when catalyzed with acid, involve the electrophilic center C^1, and furnish open-chain adducts, bis(1-dialkylaminopent-3-en-1-ylidene)diazane (**LXXII**) [108], similarly to the direction of hydrazine addition to (*N*,*N*-diethyl)-phenylethynylamine [54].



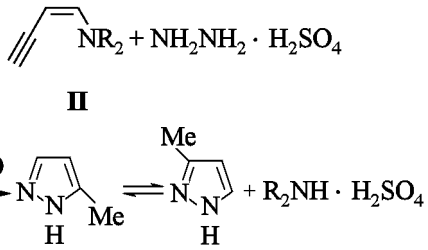
LXXIII **I**

LXXIV

R = Et, Pr.

At stoichiometric amounts of the reagents a monoadduct, (1-dialkylaminopent-3-en-1-one)hydrazone (**LXXIV**) [108] was isolated.

The treatment of alkenynamines **II** with hydrazine constitutes the main synthetic path to pyrazoles. This is described in a monograph [109] on pyrazole and also in a review concerning hydrazones [110]. The preparation of 3(5)-methylpyrazole (**LXXV**) from enamines **II** and hydrazine sulfate was described (80°C, H^+, EtOH/H_2O, 2 h, yield 72%) [111].

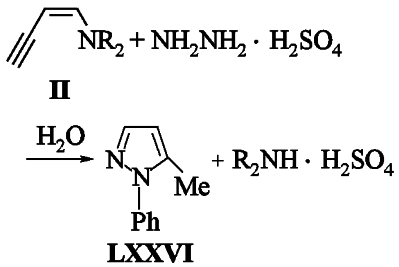


II

LXXV

R = Me, Et.

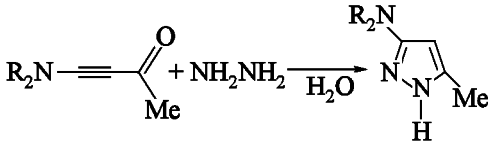
The information on the cyclization direction was obtained from reaction with phenylhydrazine: In this case positions *3* and *5* in the arising pyrazole are not equivalent [111]. The only product obtained (80°C, H^+, EtOH/H_2O, 3 h, yield 65%) was 5-methyl-1-phenylpyrazole (**LXXVI**).



II

LXXVI

A series of investigations [112–114] treated cyclization of alkynaminoketones **XXXIV** with hydrazine, its alkyl and phenyl derivatives, and also with unsymmetrical dialkylhydrazines. With unsubstituted hydrazine in anhydrous THF and dichloromethane (50°C, 3 h) formed (*N*,*N*-dialkyl)-5(3)-methyl-1*H*-pyrazol-3(5)amines (**LXXVII**) in 56–63% yield [112].

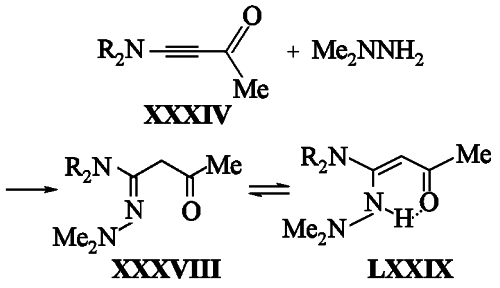


XXXIV **LXXVII**

R = Me, Et; R_2N = $O(CH_2)_2N$.

In the mass spectra of compounds **LXXVII** are observed molecular ion peaks $[M]^+$ of intensity 52–100% with respect to the maximal peak. A characteristic fragment ion in the spectra of all pyrazoles has the mass of [*M*–15] corresponding to cleavage dialkylamino group from the molecular ion of methyl group; another fragment ion arises from rupture, $[M–NR_2]^+$ [115]. Further occurs cleavage of the pyrazole ring at the N–N bond, in agreement with the published data [116].

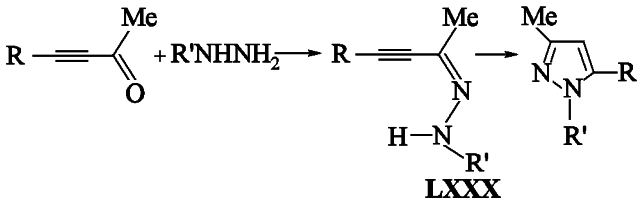
The reaction with unsymmetrical dimethylhydrazine [108] (70–75°C, THF, CH_2Cl_2, 3 h, yield 50%) occurs exclusively at the triple bond. The isolated 4-(dialkylamino)-4-(dimethylhydrazono)-butan-2-one exists in solution as tautomer mixture of hydrazone **LXXVIII** and enhydrazine **LXXIX** forms [9, 112]. No hydrazones were obtained from reaction at carbonyl function.



XXXIV **XXXVIII** **LXXIX**

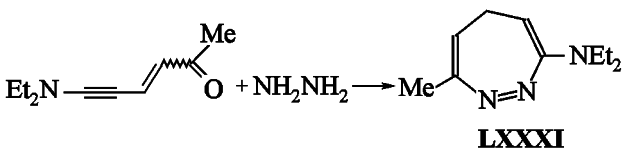
R = Me, Et; R_2N = $O(CH_2)_2N$.

In contrast to alkynaminoketones the α-acetylene ketones react with hydrazine primarily by the carbonyl group affording only one of the possible pyrazoles **LXXX** [88].



LXXX

In reaction of hydrazine with 6-diethylaminohex-3-en-5-yn-2-one, a vinylog of alkynaminoketones, 3-methyl-7-(diethylamino)-3*H*-1,2-diazepine (**LXXXI**) was obtained [11, 117].



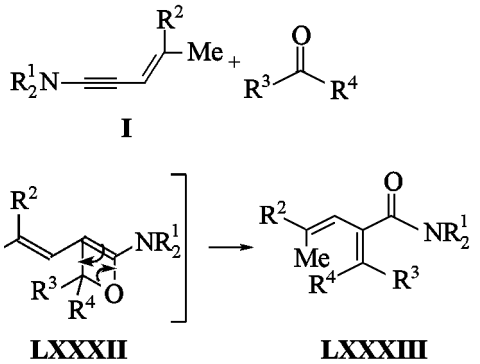
LXXXI

Preparative procedures were developed for 1*H*-, 3*H*-, and 4*H*-isomers of 1,2-diazepines [118, 119]. Among the four possible tautomeric diazepines 1*H*- and 4*H*-tautomers containing only C=C and C=N bonds are more stable; the isomers 3*H* and 5*H* possessing N=N fragment are less stable. In contrast to the conjugated aminoenyne carbonyl compounds (e.g., 6-diethylaminohex-3-en-5-yn-2-one), systems N–C≡C–C=C without carbonyl do not form 3*H*-1,2-diazepines in reaction with hydrazines [108].

IV. CYCLOADDITION AND 1,3-DIPOLAR CYCLOADDITION

The alkenynamines **I** react with carbonyl compounds (aldehydes, ketones, and esters) to provide intermediate cycloaddition products.

Cycloaddition of weak aprotic nucleophilic reagents. The published data on the chemistry of alkenynamines [9] suggest that their reactivity is essentially affected by conjugation of the double and triple bonds reducing the activity in reactions with nucleophiles under acid catalysis. Therefore special conditions activating the reagent are required for addition of so weak nucleophiles as carbonyl compounds [9]. The reaction of alkenynamines **I** with aldehydes both of aliphatic and aromatic series (BF_3, $MgBr_2$, Et_2O, PhMe, 120°C, 2–5 h, yield 60–65%) afforded (N,N-dialkyl)amides of substituted alkenoic acids **LXXXIII** [120].



I **LXXXII** **LXXXIII**

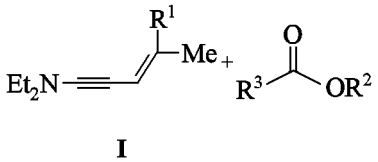
R^1 = Et, Pr; R^2 = H, Me; R^3 = H, Pr, Ph, *o*-C_6H_4Cl, *p*-C_6H_4OMe; R^4 = H, Me, Ph.

Without catalyst adducts **LXXXIII** were obtained in low yield: 40% with formaldehyde and propionaldehyde, and no more than 20% with benzaldehyde and its derivatives [120]. The addition of catalytic quantity of boron trifluoride etherate reduces the reaction time to some hours and increases the yield to 61–83%. The use as catalyst of stoichiometric

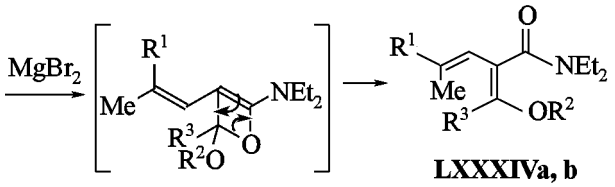
amount of magnesium bromide etherate resulted in 90–92% yield within 15–20 min [120]. As showed the ^{1}H NMR spectrum, a single isomer was obtained. This fact testifies to intermediate formation in the course of the reaction of a four-membered oxetane ring **LXXXII** that further rearranges into the alkenoic acids dialkylamides **LXXXVIII** [120].

Acetone and acetophenone react with alkenynamines **I** ($MgBr_2$, Et_2O, 32°C, 30 min, yield 84–90%) providing similar amides **LXXXVIII** [120]. The esters of aliphatic and aromatic acids strongly differ in reactivity.

The magnesium bromide etherate catalyzed addition of ethyl acetate (MeCN, 3 h, yield 57–60%) to furnish 2-[1-(ethoxyethylidene]-(4-methyl)-3-pentenoic acid (*N*,*N*-diethyl)amide (**LXXXIVa**) [121]. To bring methyl benzoate into this reaction catalysis by boron trifluoride etherate was required resulting in 70% yield of 2-[1-(methoxy-1-phenylmethylidene]-(4-methyl)-3-pentenoic acid (*N*,*N*-diethyl)amide (**LXXXIVb**) [121].



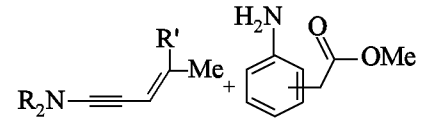
I



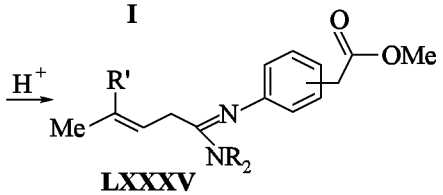
LXXXIVa, b

R^1 = H, Me: R^2 = Et, R^3 = Me (**a**); R^2 = Me, R^3 = Ph (**b**).

The addition proceeds chemoselectively exclusively to the triple bond of the ynamine along the mechanism of [2+2] cycloaddition. The oxetene intermediate was not detected, immediately arose diethylamides of the unsaturated acids [121].



I

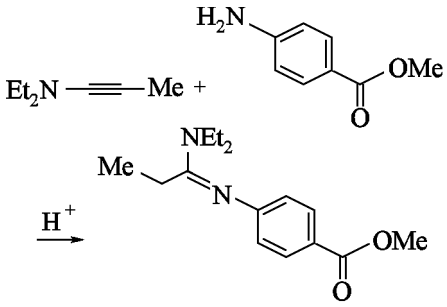


LXXXV

R = Et, Pr; R' = H, Me.

Introduction of an amino group into the ring of methyl benzoate results in a changed direction of addition. Alkenynamines **I** with methyl *o*- or *p*-aminobenzoates in the presence of catalytic amounts of mineral acid or stoichiometric amounts of magnesium bromide (H^+, Et_2O, 8 h, yield 92%) react as with primary amines [53] providing methyl 2(4)(1-dialkylamino-4-methylpent-3-enylidenamino)benzoates (**LXXXV**) [121].

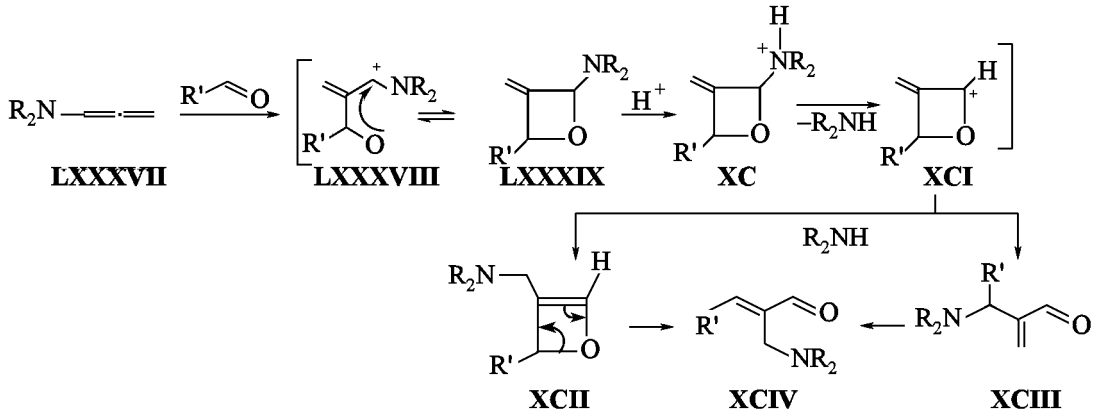
The reaction of (*N*,*N*-diethyl)-1-propyn-1-amine with methyl benzoate catalyzed by boron trifluoride etherate occurred at the carbonyl group [122], whereas with methyl *p*-aminobenzoate methyl 4-(1-diethylaminopropylidenamino)benzoate (**LXXXVI**) was obtained [121].



LXXXVI

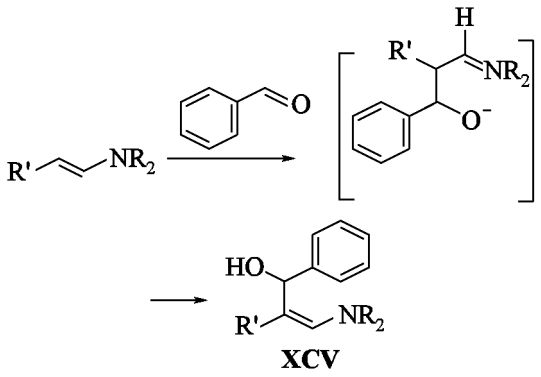
The reaction of alkenynamines **I** with aldehydes, ketones, and esters apparently follows the route of [2+2]cycloaddition. The oxetene intermediate formation is in accordance with the structure of the final products identified by IR and ^{1}H NMR spectroscopy. From the allene amines [allenyl(dimethyl) amine, *N*-allenylmorpholine] with aromatic and heterocyclic aldehydes were obtained (THF, 20°C, 15 min, yield 69–71%) heteroaromatic aldehydes **XCIV** [123, 124] see the Scheme.

The allenyl(dimethyl) amine takes up benzaldehyde in the temperature range from –20 to 30°C in THF, ethyl ether, or acetonitrile in the presence of LiBr giving rise exclusively to adduct **XCIV** in 75% yield [123]. The structure of the product was proved by ^{1}H and ^{13}C NMR and mass spectra. The direction of reaction is due to zwitter-ion **LXXXVIII** formation that is present in equilibrium with a cyclic structure **LXXXIX**. A protonation followed by elimination of amino group results in a carbocation **XCI** that via oxetene derivative **XCII** or aldehyde **XCIII** transforms into the main product **XCIV**. The presence in the reaction products of compound **XCIII** was not found by NMR spectroscopy.

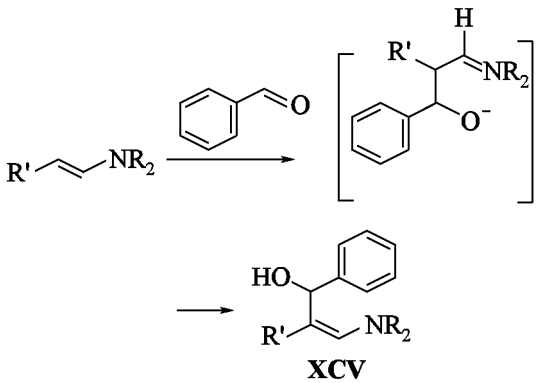


R = Me_2N, $O(CH_2)_2N$; R' = Ph, 2-thienyl, 2-furyl, cyclohexyl.

The benzaldehyde attacks the β-carbon of the double bond in the enamines, and the subsequent intramolecular proton transfer to the oxygen affords compounds **XCV** [125].

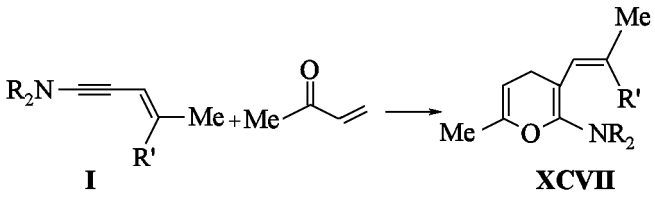


The reaction of α,β-unsaturated aldehydes and ketones with alkenynamines **I** takes two routes [126]. The α,β-unsaturated aldehydes (cinnamic and phenylpropiolic) react (hexane, 2 h, yield 84%) along [2+2]cycloaddition path through an intermediate with an oxetene ring which undergoes electrocyclic opening by the way of the least sterical hindrances. Therewith from cinnamic aldehyde was obtained 2-[(2-methyl)prop-1-en-1-yl]-5-phenyl-2,4-pentadienoic acid amide (**XCVI**), and from phenylpropiolic aldehyde formed 2-[(2-methyl)prop-1-en-1-yl]pent-2-en-4-ynoic acid amides [126].



R = Et, Pr; R' = H, Me.

The homogeneity of the adducts was proved by TLC on Silufol plates, eluent pentane–ethyl ether–methanol, and the structure was confirmed by IR and ^{1}H NMR spectra [126]. Reaction of alkenynamines **I** with methyl vinyl ketone proceeded as [2+4]cycloaddition (Et_2O, 2 h, yield 62%) furnishing 2-diethylamino-3-[(2-methyl)prop-1-en-1-yl]-6-methyl-4H-pyran (**XCVII**) [126].

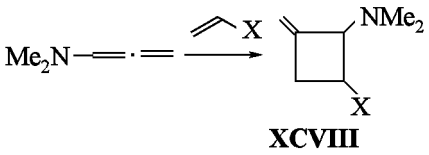


R^1 = Et, Pr; R^2 = H, Me.

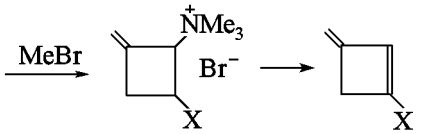
Compounds **XCVII** are well distillable liquids unstable at storage (no more than 24 h). Published information on this class compounds is scanty, but they are interesting for the synthesis of pyrylium salts and unsaturated 1,5-diketones [127].

Allene amines enter into [2+2]cycloaddition with methyl acrylate and acrylonitrile (–20°C, 30 min, 93%) [123]. Substituted cyclobutanes **XCVIII** are transformed into quaternary salts **XCIX** and after elimination along Hofmann reaction yield 3-alkylidenecyclobutenes (**C**).

The addition of acrolein and methyl vinyl ketone to allenyl(dimethyl)amine takes several minutes (MeCN, –10°C, yield 90%) and occurs as [2+4]cycloaddition providing pyrylium salts (**CI**) [123].

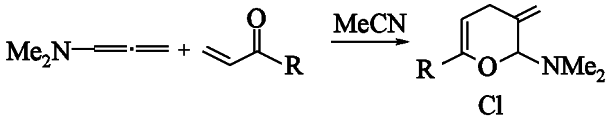


XCVIII



XCIX **C**

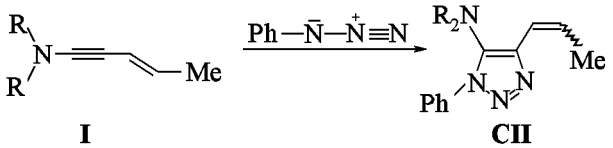
X = COOMe, C≡N.



Cl

R = H, Me.

Reactions of 1,3-dipolar additions. In reactions of 1,3-dipolar addition the substituted vinylacetylene systems are involved by their double bond [128]. The behavior of alkenynamines **I** in these reactions is different [9]. With aromatic azides they form 1-aryl-4-vinyl-5-dialkylamino-1,2,3-triazoles (**CII**) [129].

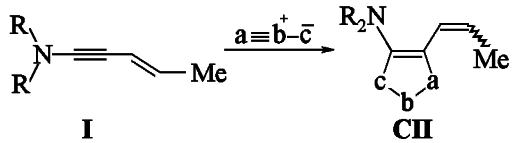


I **CII**

R = Me, Et.

The dipole attack is directed to the disubstituted triple bond. The aryl azide addition to alkenynamines occurs regiospecifically and provides a single isomer as proved by TLC and ^{1}H NMR spectra. These data are in agreement with the published data on 1,3-dipolar cycloaddition of aryl azides to compounds with strongly polarized multiple bond [9].

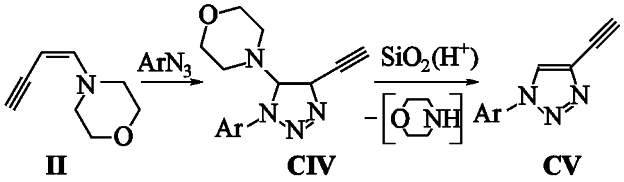
The studies carried out with the other octet-stabilized 1,3-dipoles (benzonitrile N-oxide, *p*-R-phenylnitrile-C-imine) showed that the reaction was general enough and occurred regioselectively at the triple bond independent of the structure of the ethylene fragment [9].



I **CII**

R = Me, Et.

However 1-heteroalk-1-en-3-ynes behave differently in these reactions. The orientation essentially depends on the character of the heteroatom. From 1-(but-1-en-3-yn-1-yl)morpholine and aromatic azides 1-aryl-4-ethynyl-5-morpholino-Δ^2-triazolines (**CIV**) were obtained which readily eliminated morpholine affording 1-aryl-4-ethynyltriazole (CV) in the course of chromatographic purification [12, 130].

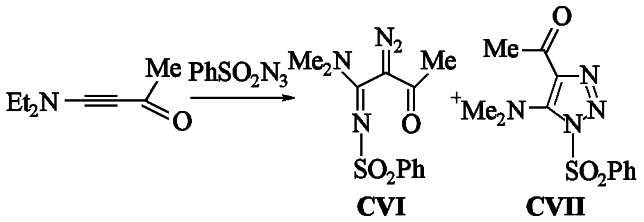


II **CIV** **CV**

Ar = Ph, *p*-$C_6H_4NO_2$.

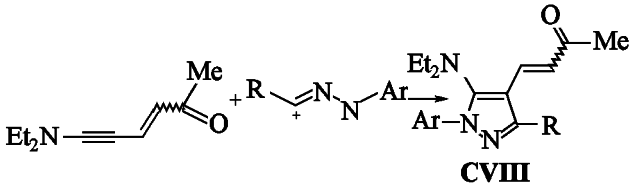
Ynaminocarbonyl compounds like alkynamines and carbonyl-containing acetylenes react with 1,3-dipolar substances [12, 131, 132].

Reaction of 4-dimethylamino-3-butyn-2-one with diphenylketene proceeds as [2+2]cycloaddition (30°C, THF, 1 h) furnishing in 75% yield 2-acetyl-3-dimethylamino-4,4-diphenylcyclobut-2-en-1-one. With ethyl azidoformate (30°C, THF, 3 h) triazole was obtained in 82% yield, with phenyl isocyanate along [2+4]cycloaddition formed quinolone in 70% yield [132]. The compounds obtained were characterized by UV, ^{1}H, and mass spectra (M^+) [132]. However aryl sulfenylazide in this reaction gave rise mainly to products of triazole ring opening **CVI** isomeric to triazole **CVII** present as a minor component [133].



CVI **CVII**

Vinylogs of ynaminoketones react with 1,3-dipolar compounds (C,N-disubstituted nitrilimines, benzonitrile N-oxide) regio and stereospecifically at the triple bond [134–136]. For instance, 6-diethylamino-3-hexen-5-yn-2-one with C,N-disubstituted nitril-

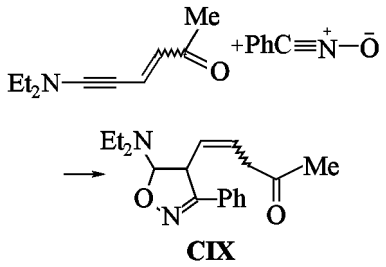


CVIII

R = MeC(O), Ar = Ph; R = Ph, Ar = *p*-BrC_6H_4.

imines (40°C, Et_2O, 18–30 h) gives rise to substituted pyrazoles in 33–48% yields [134–136].

The structure of pyrazoles **CVIII** obtained was proved by X-ray diffraction analysis carried out on a single crystal of 3-acetyl-4-(3-oxobut-1-en-1-yl)-1-phenyl-5-diethylaminopyrazole [135]. The cyclization of enynaminoketone with benzonitrile N-oxide (40°C, Et_2O, 24 h) occurred similarly and afforded in 27% yield 4-(3-oxobut-1-en-1-yl)-3-phenyl-5-diethylamino-isoxazole (**CIX**) [132–134].



CIX

Thus the amino group conjugated with the triple bond of the 1,3-enyne system considerably activates this bond with respect to 1,3-dipoles. The ynamino-ketones react with 1,3-dipoles only at the triple bond; therewith the negatively charged atom of the 1,3-dipole adds to the carbon atom attached to nitrogen. The heterocycle formation is not accompanied by elimination of the dialkylamino group.

CONCLUSION

p,π-Unsaturated amines are relatively new compounds in organic chemistry. Their extensive investigation is due not only to theoretical but also to practical interest in heterocycles prepared therefrom [137, 138]. Another important point is the availability of these compounds basing on industrial raw materials.

We hope that the present review will attract attention of researchers working in the fields of heterocycles and purposeful synthesis of biologically active compounds.

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