AMINO-α,β-UNSATURATED ETHYLENIC AND ACETYLENIC CARBONYL COMPOUNDS AS SYNTHONS FOR THE ASSEMBLY OF HETEROCYCLES (REVIEW)

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The reactivity of en- and ynaminocarbonyl compounds towards two-center reactants to give five- and seven-membered heterocycles with two heteroatoms, and condensed rings, is reviewed. The behavior of these systems towards 1,3-dipolar cycloaddition is noted.

Interest has recently developed in the chemistry of conjugated en- and ynamines as starting materials for the synthesis of heterocycles.

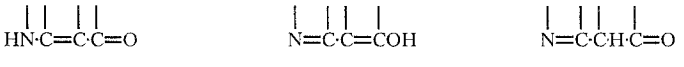
The first reports on the preparation of enaminocarbonyl compounds ((I-III)$R_2NCH{=}CHCOX$ X = H (I, IV), R^1 (II, V), OR^1 (III, VI)) appeared in the 1860's, and their chemical behavior has been examined intensively since the 1920's, being the subject of several reviews [1-4] including some recent ones [5, 6].

Acetylenic aminocarbonyl compounds $R_2NC{\equiv}CCOX$ (IV-VI) were not synthesized for a century after their ethylenic analogs [7]. This group of compounds has received much less attention, and only a few representatives have been obtained.

The present review seeks to systematize, generalize, and compare the chemistry of en- and ynaminocarbonyl compounds as synthons for the guided preparation of heterocycles.

The question of the structure of an α isomerism in enaminocarbonyl compounds has been closely studied [1, p. 52; 8-22].

Three forms are theoretically possible, namely the enaminoketone (A), ynaminoenol (B), and iminoketone (C):



A B C

Enaminoketones, aldehydes, and esters containing a tertiary amino group exist solely in the enaminoketone form (A).

N-Protonated enaminoaldehydes and enaminoketones form tautomeric mixtures A ⇄ B, the enaminoketone form usually predominating. In the case of esters of substituted aminoacrylic acids, the equilibrium is between forms A and C, although the existence of the enol structure (B) is not excluded [9].

Enaminoaldehydes and ketones containing an NH_2 group have an even greater content of form B, and this isomer may be isolated at low temperatures. The energy of activation for the conversion of form B into the tautomeric mixture is approximately 15.5 kcal/mole [17].

In discussions of the structures of enaminocarbonyl compounds, three main configuration (cis-S-cis, trans-S-cis, and trans-S-trans) are usually considered.

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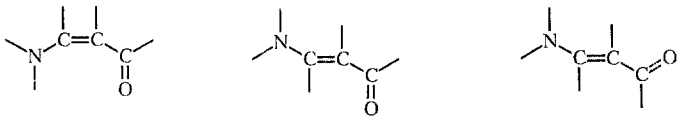


cis-S-cis trans-S-cis trans-S-trans

Acyclic N-trisubstituted enaminocarbonyl compounds exist almost exclusively in the trans-S-cis form. If, however, the nitrogen carries even a single proton, these systems exist as equilibrium mixtures of all three possible isomers and conformers. Conversion of the cis- into the trans-isomer and vice versa occurs even on vacuum distillation or brief heating of the pure isomer. The energy barrier to this conversion, according to Benary [23], is no greater than 15 kcal/mole.

With some enaminocarbonyl compounds, rotational isomerism around the C–N bond has been observed. At sufficiently low temperatures, N,N′-dimethylated enaminoketones show two signals for CH_3, which are nnequivalent as a result of restricted rotation of the amine residue. When the temperature is raised, the doublet is converted into a singlet [1, p. 62].

Similar behavior is clearly apparent in the PMR spectra of the 3-dialkylaminocaroleins (I) even at room temperature.

That N,N′-dialkylated enaminocarbonyl compounds (II) possess the trans-configuration of the ethylene moiety is indicated by the spin coupling constants for the geminal protons, which lie in the range 12.2-13.0 Hz [24, 25]. The cis-conformation in these systems is shown by the coupling constants for the aldehyde and ethylenic protons (J = 8.0...8.3 Hz) for the aminoaldehydes (I). No appreciable enolization of the acetyl moiety in the enaminoketones (II) was evident.

The N-protonic enaminoketones exist in solution mainly in the cis-S-cis form (J_{HH} = 7.2-7.6 Hz). As the size of the N-alkyl substituent is increased, the signal for the NH proton is shifted to lower field. However, the presence of the iminoenolic form is evident from both the IR and PMR spectra, with high-frequency absorption for the associated OH group at 3630-3650 cm^{-1} and an increase in the number of bands in the 'carbonyl' region. Other things being equal, the proportion of the enol tautomer decreases as the bulk of the N-alkyl substituent increases, in the sequence $CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$.

A similar, if more complex, state of affairs holds for N-protonated enaminoaldehydes (I) in solution, the iminoenol tautomer also being found [25].

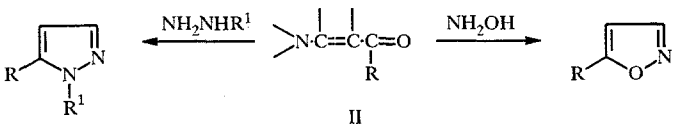
The $^{13}C-^{13}C$ coupling constants have been measured for a number of β-substituted en- and ynamines. It was found that in en(yn)aminocarbonyl compounds there is direct polar conjugation of the substituents via the multiple bonds, shown in particular by a marked decrease in the order of the double and triple bonds [26-30]. In β-substituted ynamines, there is direct polarization of the two orthogonal π-systems of the triple bond. This results in an increase in the reactivity of the triple bond in nucleophilic addition reactions. In en- and ynaminocarbonyl compounds there are two reactive electrophilic centers, namely the carbonyl carbon and the β-carbon of the multiple bond. Competition between these centers should also control the priority for nucleophilic attack. The differing nature of the multiple bonds has the consequence that carbonyl en- and ynamines differ fundamentally in their reactivity towards single-center nucleophiles [1, 7].

Conjugated ynamines containing acceptor groups should be much more reactive than simple and vinylacetylenic ynamines, which considerably enlarges their potential for the synthesis of heterocycles.

Shrot [6] developed the concept of alkynes as being 'pseudocarbonyl compounds', and formulated orientation rules. An example of the more complex behavior involved in the construction of heterocycles is provided by the chemistry of en- and ynaminocarbonyl compounds, as described below.

REACTIONS WITH HYDRAZINE, ITS DERIVATIVES, AND HYDROXYLAMINE

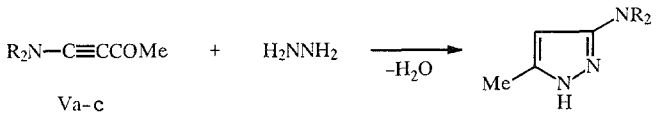
Enaminoaldehydes and enaminoketones react with hydroxylamine, hydrazine, or monosubstituted hydrazines to give five-membered isoxazoles or pyrazoles [1, p. 213; 2, 6, 31-36].



II

The structures of the products correspond to initial exchange of the amino-bases, i.e., reaction at the β-carbon of the olefinic bond. With acyclic enaminoketones, it has been possible to isolate β-ketoximes, β-ketohydrazones, and β-ketosemicarbazones [1, p. 213; 101], see for example [37].

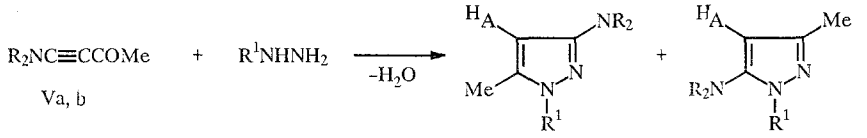
The reactions of ynaminocarbonyl compounds with hydrazine and phenylhydrazine have been reported [38]. With hydrazine itself, the reaction involves both electrophilic centers in 4-dialkylaminobut-3-yn-2-ones (Va-c) to give 3(5)-dialkylamino-5(3)-methylpyrazoles (VIIa-c).



Va-c VIIa-c

V, VII a R=Me, b R=Et, c R_2N=

The reactions of 4-dialkylaminobut-3-yn-2-ones with monosubstituted alkylhydrazines (methylhydrazine and propylhydrazine) invariably give mixtures of the isomeric products 1-alkyl-3-dialkylamino-5-methylpyrazoles (VIII, IX) and 1-alkyl-5-dialkylamino-3-methylpyrazoles (X, XI), the structures of which correspond to different orientations of the hydrazine nitrogen atoms with respect to the reactive sites in the ynaminoketones.

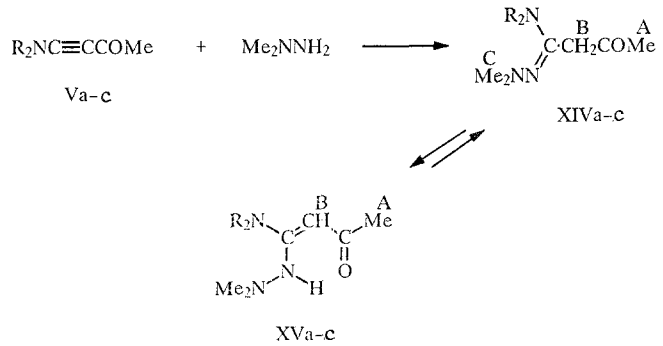


Va, b VIII,IXa,b; XIIa,c X, XI a, b; XIIIa, c

VIIIa,b, Xa,b R^1=Me; IXa,b, XIa,b R^1=C_3H_7; XIIa—c, XIIIa—c R^1=Ph

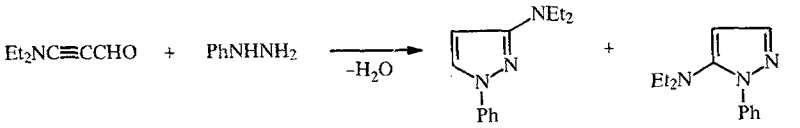
The isomer ratio (IX:X) was approximately 3:4. Reaction of the ynaminoketones (Va-c) with phenylhydrazine also afforded mixtures of the isomeric 1-phenyl-3-dialkylamino-5-methylpyrazoles (XIIa-c) and 1-phenyl-5-dialkylamino-3-methylpyrazoles (XIIIa-c) in a ratio of 3:4 [38].

In order to establish which of the electrophilic centers in ynaminoketones was the first to undergo attack by the hydrazine amino-group, the ynamines (Va-c) were reacted with asymm-dimethylhydrazine, the addition product of which could not undergo cyclization. It was found that 4-dialkylaminobut-3-yn-2-ones in this case reacted exclusively at the C≡C bond to give N,N-dimethyl-3-oxobutanehydrazonic acid dialkylamides (XIV, XV). The formation of hydrazones by reaction with the carbonyl group was not seen.



Va-c XIVa-c XVa-c

To assess the influence of the structure of iminocarbonyl compounds on the course of their reactions with hydrazine, diethylaminopropiolaldehyde (IVb) was reacted with phenylhydrazine, to give 67% of a product consisting of 1-phenyl-3-diethylamino- (XVI) and 1-phenyl-5-diethylaminopyrazole (XVII) in a ratio of 1:10 [38].



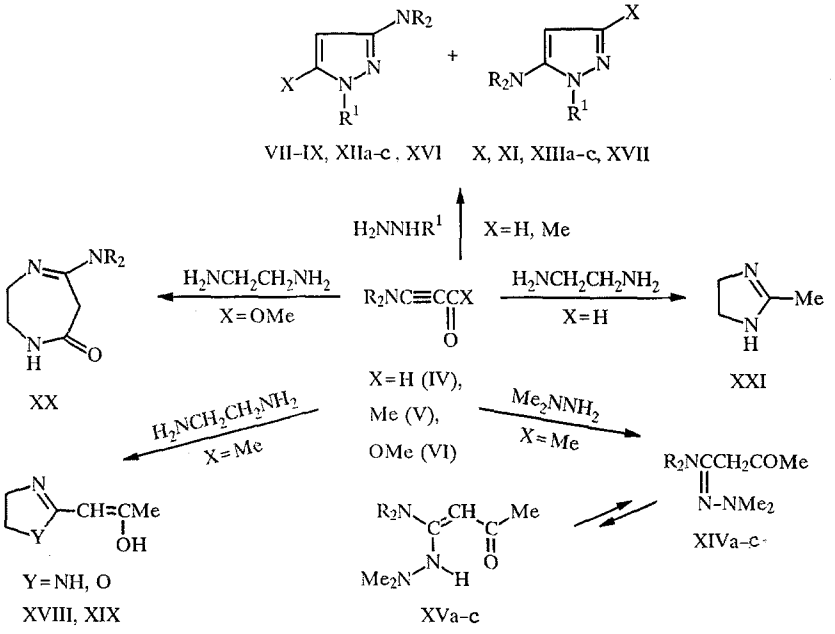
XVI XVII

Dialkylaminopropynal reacted more selectively with phenylhydrazine, at $C_{(1)}$, whereas in 4-dialkylaminobut-3-yn-2-ones both electrophilic carbons are of comparable reactivity. This is clearly due to a reduction in steric hindrance to attack on the aldehyde carbonyl group, and to its enhanced electrophilic activity.

Simple ynamines react with hydrazine and monosubstituted hydrazines in the presence of an acid catalyst, to give the products of addition at the triple bond in proportions of 1:1 or 2:1, namely hydrazines and azinic acids [39]. Acetylenic ketones react with these compounds initially at the carbonyl group to give one of the possible isomeric pyrazoles [40, 41].

In reactions with asymm-dimethylhydrazine, there is a full analogy with simple ynamines and acetylenic ketones, which add this reactant exclusively at the carbon–carbon triple bond [42, 43].

Diagram 1. Reactions of Ynaminocarbonyl Compounds with Bifunctional Aliphatic Compounds



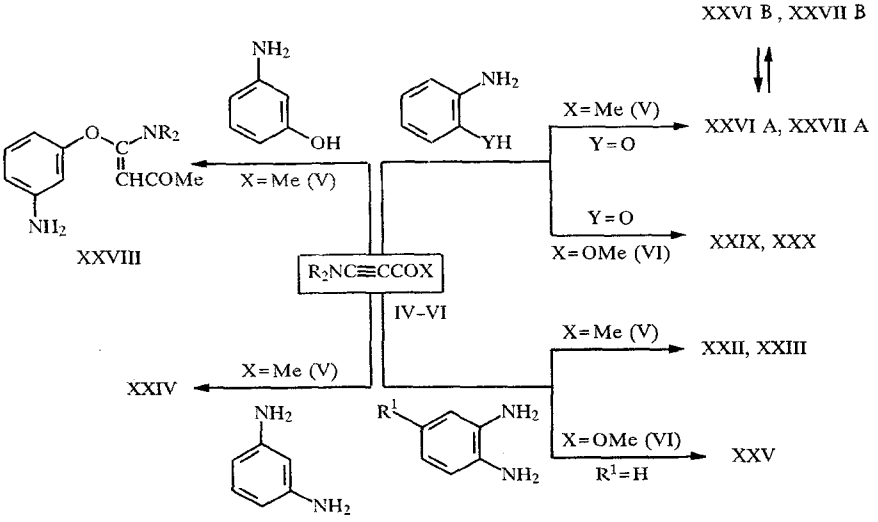
VII–IX, XIIa-c, XVI X, XI, XIIIa-c, XVII

XX XXI

X=H (IV), Me (V), OMe (VI)

XVIII, XIX XVa-c XIVa-c

Diagram 2. Reactions of Ynaminocarbonyl Compounds with Bifunctional Aromatic Compounds



XXVI B, XXVII B

XXVI A, XXVII A

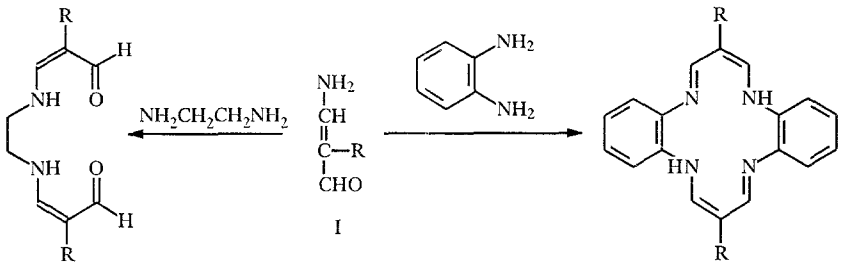
XXVIII XXIX, XXX

IV–VI XXII, XXIII

XXIV XXV

REACTIONS WITH ALIPHATIC AND AROMATIC 1,2-DINUCLEOPHILES

There have been few reports of the reactions of enaminocarbonyl compounds with binucleophiles, the reactive groups in which are separated by two carbon atoms. Specifically, it has been reported [44] that β-aminoacrolein and ethylenediamine undergo transamination to give a bis-adduct. The reaction with o-phenylenediamine gives a macrocyclic product of composition 2:2.

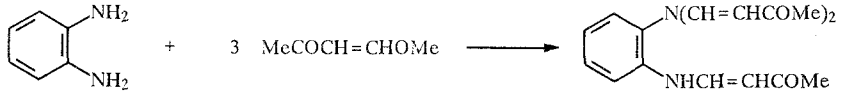


α-Nitro-β-arylaminoacrolein reacts with o-phenylenediamine to give the expected 1,3-addition product, 2-nitro-1,5-benzodiazepine [45].

Dialkylaminobutenones and ethylenediamine also react in the presence of an acid catalyst to give a diazepine. The reaction is slow, and requires heating of the reaction mixture for many hours [46].

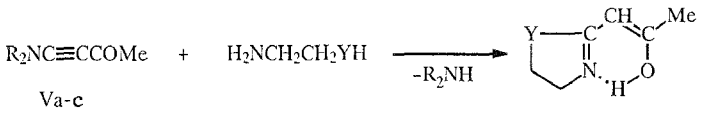
In contrast to the above nucleophiles, compounds such as guanidine react with enaminocarbonyl compounds to give pyrimidines. No acyclic reaction products have been found [6, 32, 33, 45]. It is assumed that in this case transamination of the starting material takes place first, followed by ring closure by condensation of the free amino group with the carbonyl moiety [45].

There is yet another possible mode of reaction, since in a few cases both amino groups of o-phenylenediamine participate in the reaction [49].



Reactions of acetylenic ketones with bifunctional compounds such as β-mercaptoethylamine [50], α,β-ethanedithiol [51], ethylene glycol [52], and β-mercaptoethanol [53] take place at the β-carbon of the triple bond, and require a basic catalyst (from potassium carbonate to sodium methoxide). Diethylaminopropyne reacts with ethylenediamine and ethanolamine in the presence of an acid catalyst to give 2-substituted five-membered heterocycles of the imidazoline and oxazoline type [54].

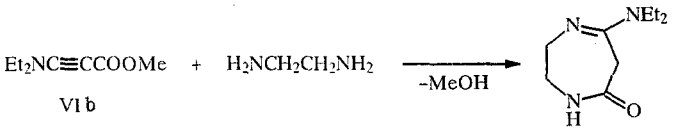
4-Dialkylaminobut-3-yn-2-ones (Va, b) react with ethylenediamine and ethanolamine in the absence of a catalyst, giving 1-(2-imidazolinyl)-prop-1-en-2-ol (XIX) in 60-70% yield [55].



The enolic tautomers of (XVIII) and (XIX) are so stable that neither changing the concentration of the solution, nor varying the solvent, resulted in the detection of the keto-form. They has been a report of imidazolines bearing a fully enolizable β-ketoalkyl grouping in the 2-position of the heterocycle [55].

Ynaminoketones therefore react with ethylendiamine and ethanolamine like simple ynamines [55], with twofold attack on $C_{(3)}$ by the electrophilic center of the substrate. Elimination of the dialkylamino-group gives 2-substituted imidazolines and oxazolines bearing fully enolized acetonyl groups.

Changing the type of carbonyl-containing grouping has an effect on cyclization. Reaction of methyl diethylaminopropiolate (VIb) with ethylenediamine yields 68% of 5-diethylamino-2,3-dihydro-1,4-diazepin-7-one (XX) [56].

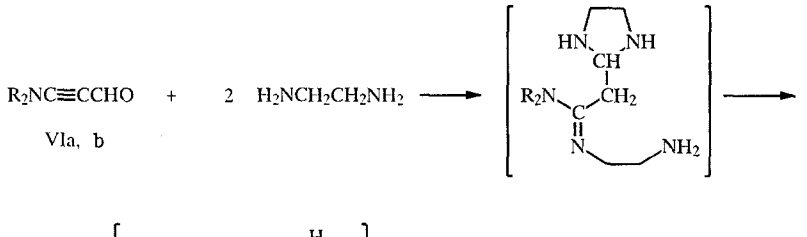


VI b XX

It is apparent that the lower electrophilicity of the reaction centers $C_{(3)}$ and $C_{(1)}$ in ynaminoesters as compared with ynaminoketones results in concerted 1,3-attack by the bifunctional nitrogenous base, and finally to the formation of a seven-membered heterocycle. This reaction course is also favored by the ease of intramolecular nucleophilic replacement of the ester methoxy group.

In ynaminoaldehydes, the activities of the reaction centers $C_{(1)}$ and $C_{(3)}$ are both enhanced, so that it is less easy to predict the course of the reaction with binucleophiles.

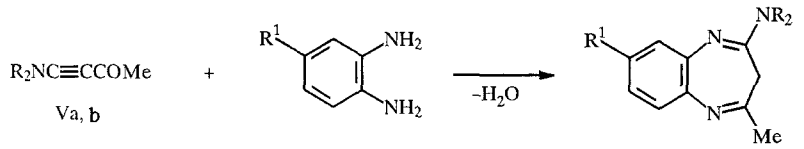
The dialkylaminopropynals (VIa, b) react with diaminoethane to give a complex, resinous mixture of products from which it was possible to isolate 2-methylimidazoline (XXI) only [56].



VIa, b XXI

Hence, the reactions with ethylenediamine display the specific behavior of all three types of aminocarbonyl compounds, the reactions following different courses. However, in their reactions with single-center nucleophiles (nitrogen bases), all three types of ynaminocarbonyl compounds react in the same way [58].

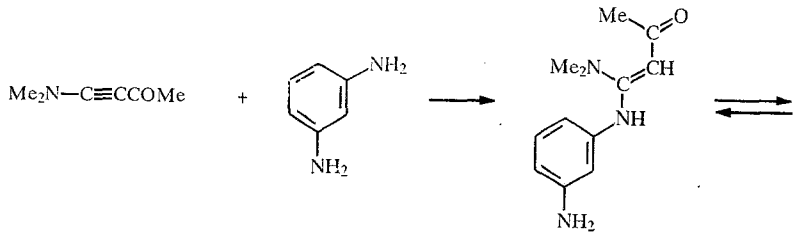
A decrease in the nucleophilicity of the reactant containing two amino groups (changing from 1,2-diaminoethane to aromatic diamines) modified the course of the reaction with ynaminocarbonyl compounds (Diagram 2). For example, o-phenylenediamine and its derivatives react with 4-dialkyl-aminobut-3-yn-2-ones (Va, b) to give seven-membered heterocycles, namely 7(8)-R^1-2-dialkylamino-4-methyl-3H-1,5-benzodiazepines (XXII, XXIII) [55, 57].



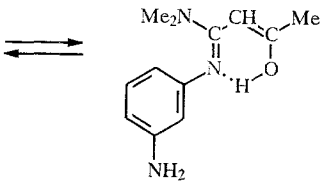
Va, b XXII, XXIII

XXII R^1 = H; XXIII R^1 = morpholino

To identify the site of primary attack of the aromatic diamine on the conjugated ynaminoketone, the reaction of 4-dimethylaminobut-3-yn-2-one (Va) with m-phenylenediamine was followed in the cell of an NMR spectrometer (the final product was not isolated preparatively). On heating in $CDCl_3$, the m-phenylenediamine added slowly to the ynaminoketone at the triple bond, the principal addition product being in the iminoenol form B.



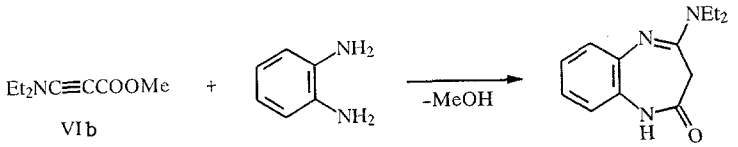
XXIV A



XXIV B

Relatively stable iminoenol forms were obtained from all the reactants with phenylenediamines only. These latter possess long conjugated chains of C=N and C=C double bonds with the aromatic ring and the hydroxyl group.

1,3-Attack by o-phenylenediamine also occurred in the case of the methyl 3-dialkylaminopropiolate (VIb), to give in this case a seven-membered condensed heterocycle, namely 4-diethylamino-1,5-benzodiazepin-2-one (XXV).

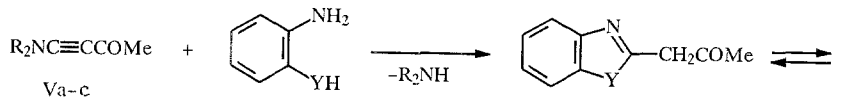


VIb

XXV

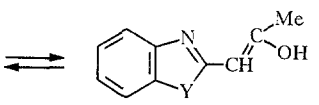
In contrast, simple ynamines and alkenylamines undergo acid-catalyzed reactions with o-phenylenediamine to give 2-substituted benzimidazoles by synchronous double attack on the triple bond [54].

o-Aminophenol and o-aminothiophenol react with 4-dialkylaminobut-3-yn-2-ones (Va-c) to give 2-substituted five-membered condensed heterocycles, 1-(2-benzoxazolyl)propan-2-one (XXVI) and 1-(2-benzothiazolyl)propan-2-one (XXVII) [55].



Va-c

XXVI A, XXVII A

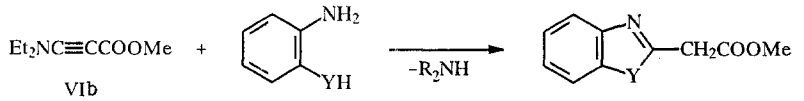


XXVI B , XXVII B

XXVI Y=O; XXVII Y=S

The benzoxazole (XXVI) and benzothiazole (XXVII) exist in solution as mixtures of the keto- (A) and enol- (B) forms.

Methyl 3-diethylaminopropiolate (VIb) reacts with o-aminophenol and o-aminothiophenol to give respectively 2-methoxycarbonylmethylbenzoxazole (XXIX) and 2-methoxycarbonylmethylbenzothiazole (XXX) [56].



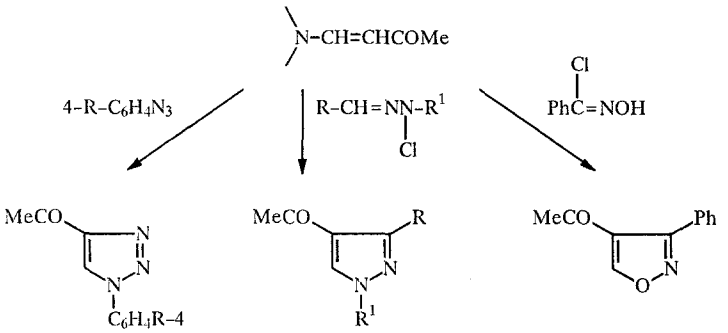
XXIX, XXX

XXIX Y=O; XXX Y=S

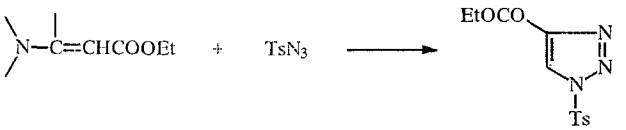
Irrespective of the acceptor strength of the carbonyl group, all three types of ynaminocarbonyl compounds react similarly with o-aminophenol and o-aminothiophenol. In this instance, the mode of attack is determined by activation of the ynamino moiety by possible autocatalysis. Like simple ynamines [54], the reaction involves double attack on the $C_{(3)}$ reaction center to give five-membered condensed benzoxazoles and benzothiazoles.

1,3-DIPOLAR CYCLOADDITION

The reactions of enaminoketones with 1,3-dipoles have been the subject of a special study [60]. It was found that phenyl azide and its derivatives, benzonitrile N′-oxide, acetyl- and ethoxycarbonyl-N-phenylnitrilimines react exclusively at the carbon−carbon double bond with elimination of the amino group to give five membered 1,2,3-triazoles, pyrazoles, and isoxazoles.

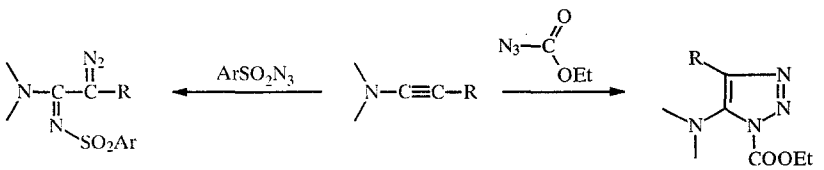


Aminoacrylate esters also react, at room temperature, with toxyl azide to give substituted triazoles, which are, however, unstable to heat [61].



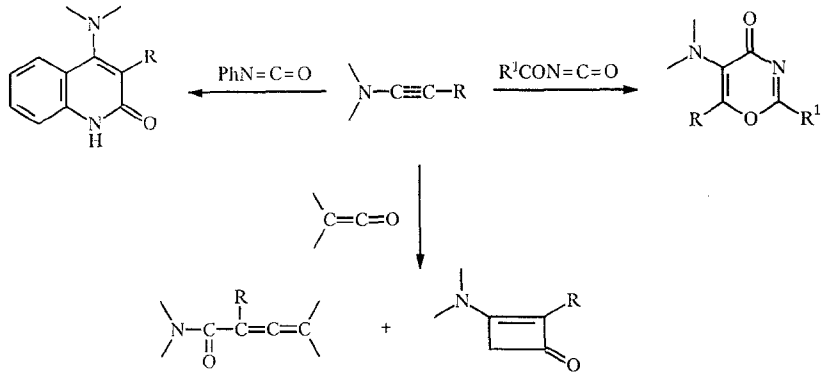
These reactions provide one-step methods of obtaining high yields of heterocycles of practical importance containing acetyl substituents, thereby opening up many possibilities for further modifications of these compounds.

Like ynamines and acetylenic carbonyl compounds, ynaminocarbonyl compounds react with 1,3-dipolar compounds [58]. For example, the reaction with ethyl azidoformate at 65°C affords high yields of substituted triazoles. Arylsulfenyl azides, however, give mainly the product of the cleavage of the triazole ring which is isomeric with the triazole, which is present in only small amounts [62].



R = CHO, COMe, COOMe

Ynaminocarbonyl compounds react differently with heterocumulenes to give [2+2]- and [2+4]-cycloaddition products [64-66].



R=CHO, COMe, COOMe

An examination of the 1,3-dipolar cycloaddition to en- and ynaminocarbonyl compounds showed that these systems, like vinylacetylenic en- and ynamines, function as dipolarophiles, reacting with 1,3-dipolar systems at the double bond in the usual way for cyclizations without incorporation of the heteroatom in the ring.

In their reactions forming ring systems, enaminocarbonyl compounds are comparable with 1,3-dicarbonyl compounds, but ynaminocarbonyl compounds behave differently. In many of their reactions, ynaminocarbonyl compounds behave in the usual way, by reaction with $C_{(1)}$ and $C_{(3)}$ of the substrate, the reactivity of the triple bond increasing in the sequence: ester < ketone < aldehyde. Some reactions, however, involve the acetylenic bond only, without the participation of the carbonyl function. This is apparently due to the large contribution of ketene-imminium resonance structures. All reactants which stabilize the formation of the latter add exclusively at the triple bond.

By varying the structures of conjugated ynamines bearing acceptor carbonyl groups, and of the bifunctional reactant, it is possible to effect the directed synthesis of five- and seven-membered nitrogen, oxygen, and sulfur heterocycles with two heteroatoms.

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