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STRUCTURE AND REACTIVITY OF β-ENAMINONES

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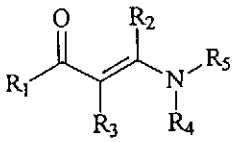
The structure of β-enaminones is discussed from three points of view: distribution of electron density and related reactivity towards electrophiles, geometrical isomerism and tautomerism. Geometrical isomerism and tautomerism are discussed from various aspects.

Introduction

β-Enaminones are important organic intermediates [1]. They have wide application in synthetic organic chemistry as precursors for preparation of the heterocyclic compounds [2], drugs [3] and are considered to be biologically active compounds [4].

These compounds can be expressed by general formula (I)



(I)

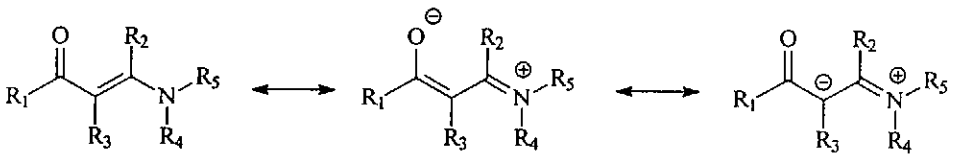
By substitution on amino group, compounds I can be classified as primary, secondary and tertiary enaminones. If R_1=OR or NRR', they are called enaminoesters or enaminoamides. Important derivatives of enaminones are 2,2-diacylenamines (R_3 = acyl) which are also used as precursors in synthetic organic chemistry.

The structure of the enaminones can be discussed from several points of view:

- Distribution of the electron density and the related reactivity.
- Geometrical isomerism.
- Tautomerism.

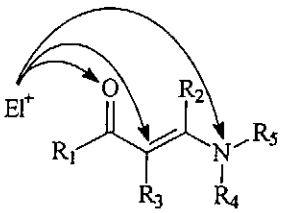
The Electronic Structure of the Enaminones and their Reactions with Electrophiles.

Molecules of the enaminones contain five-atom π-electron system which can be described by three resonance structures (II–IV)



(II) (III) (IV)

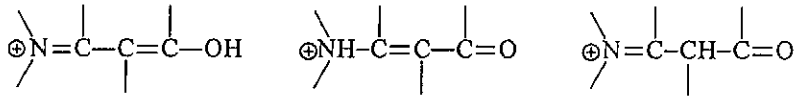
From these structures it is evident that enaminones can be attacked by electrophiles on oxygen, on carbon or on nitrogen as illustrated by Scheme 1.



Scheme 1

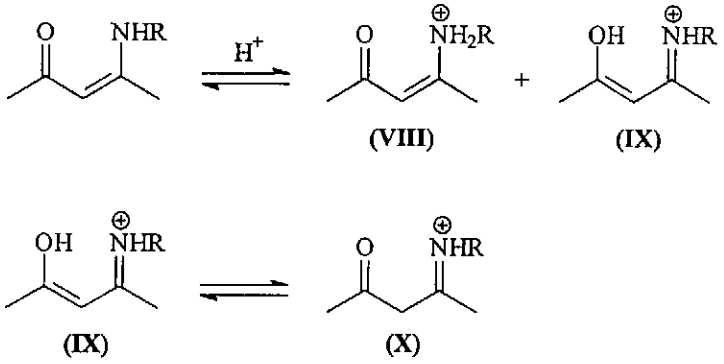
Protonation

Enaminones can be protonated on oxygen, nitrogen and carbon (V–VII) [5]



(V) (VI) (VII)

Enaminoketones form stable perchlorates, chlorides, bromides and iodides and these salts have been found to be protonated on oxygen [6–10]. These *O*-protonated enaminones are the most stable in slightly polar media because delocalized charge does not need such effective solvation. In polar media the proton is moved to carbon [10,11]. However, later detailed kinetic studies proved that this process is more complex than a mere *O*-protonation [11]. Oxygen and nitrogen of the enaminone are, according to HSAB theory [12], hard reaction centres and carbon is a soft reaction centre. Hence, the proton as a hard acid attacks enaminones preferably on oxygen and on nitrogen and species VIII and IX are formed. *O*-Protonated form IX strongly predominates. After that, a slower conversion of the form IX to C-protonated form X takes place (Eq. 1).

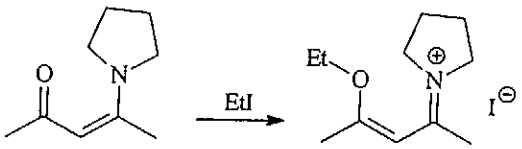


(VIII) (IX) (1)

(IX) (X)

Alkylation

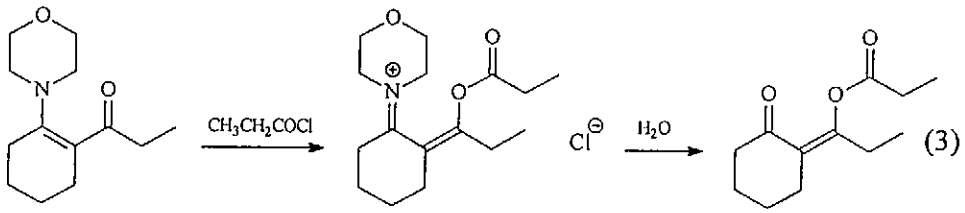
Alkylation of enaminones proceeds on oxygen [7,8,13,14]. For example, the reaction of 4-(*N*-pyrrolidino)pent-3-en-2-one (XI) with ethyl iodide gives the corresponding *O*-ethylpyrrolidinium iodide XII [7] (Eq. 2).



(XI) (XII) (2)

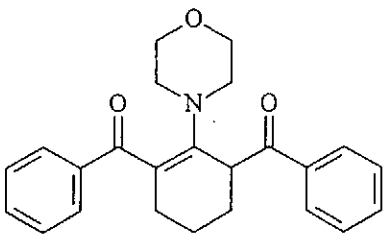
Acylation

Acylation can proceed either on oxygen or on carbon. The first variant is more frequent. The first reaction product is first iminium salt, which can undergo subsequent reactions [15–18]. The case first described was the reaction of enaminone XIII with propionylchloride [15]. The iminium salt XIV formed undergoes hydrolysis to the enolester XV under mild conditions



(XIII) (XIV) (XV) (3)

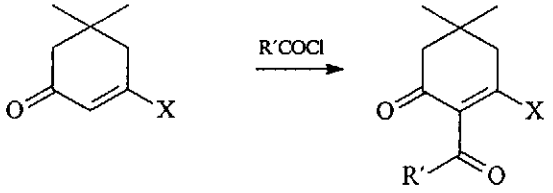
Reactions with other aliphatic acid chlorides proceed in similar way. *O*-Acylation has been observed also in the case of acylation of compound XIII with benzoyl chloride [17]. 2,6-Diacylenamine XVI was formed as minor by-product



(XVI)

From the facts mentioned above it could appear that the acylation of the enaminones occurs on oxygen only. However, the cases are described when the acylation proceeds on carbon. This acylation has been observed in the case of acylation of enaminones derived from dimedone and pyrrolidine XVIIa and

morpholine XVIIb by acid chlorides having no hydrogen on their α-carbon (benzoyl chloride, pivaloyl chloride). The product of *C*-acylation XVIII is then formed [19]



(XVIIa,b) **(XVIII)** (4)

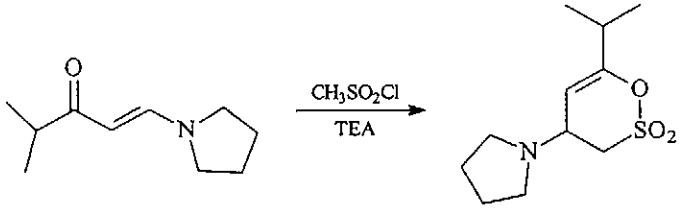
a X = —N

b X = —N O

The corresponding C-acetylated product is also formed from enaminone XVIIa by its reaction with acetyl chloride [19]. Enaminone XVIIb only gives hydrochloride under these conditions [19]. These differences in reactivity are explained by differences in basicity between secondary amines.

Reactions with Sulphonyl Halogenides

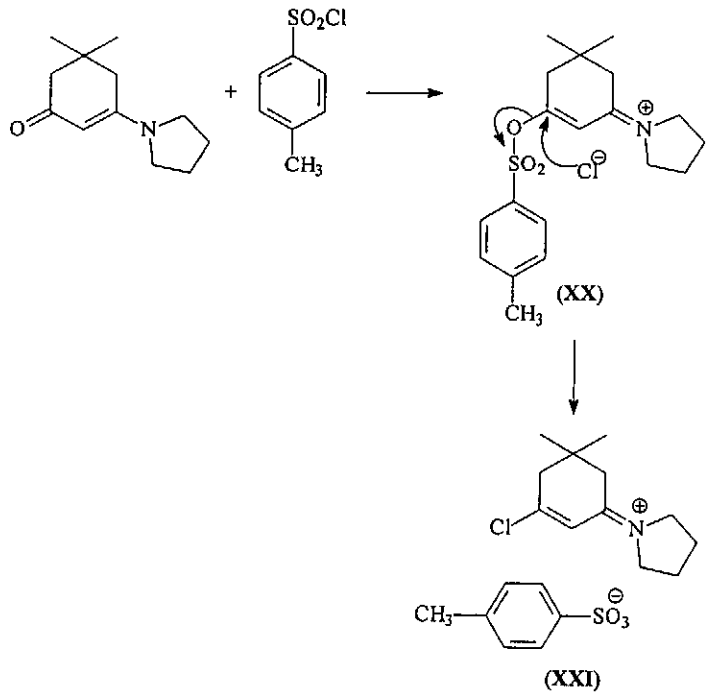
Methanesulphonyl chloride reacts with the enaminones to give the enolsulphones XIX in good yields [20]. From this fact it is obvious that sulphonyl chloride attacks the molecule of the enaminone at oxygen atom



(XIX) (5)

However, only the sulphonyl halogenides having α-hydrogen are able to give enolsulphones. Sulphonyl halogenides without α-hydrogen, e.g. aromatic sulphonyl halogenides, react in a different way. At first, tosyliminium salt XX is formed by attack of oxygen. The subsequent attack by chloride anion leads to

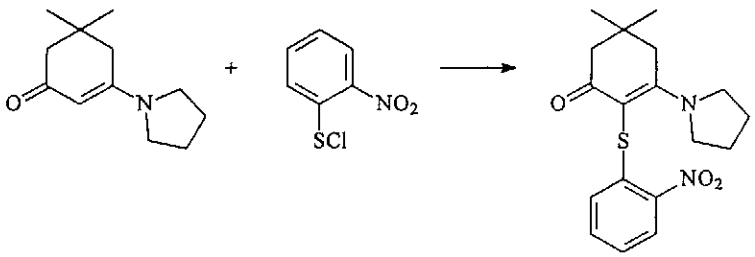
elimination of tosylate as a good leaving group and to formation of the chloroiminium cation XXI [21] (Scheme 2). Similar behaviour has been observed during acylation of the enaminones by trichloroacetyl chloride [18]



Scheme 2

Reactions with Sulfenyl Chlorides

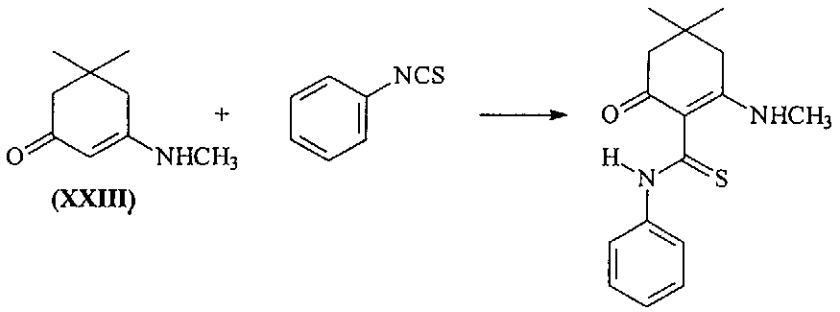
Enaminones react with 2-nitrobenzenesulfenyl chloride at carbon atom C-2 to form compound XXII [19]



(XXII) (6)

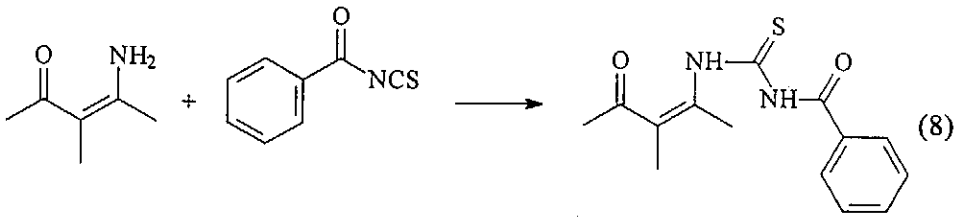
Reactions with Isocyanates and Isothiocyanates

Reactions of enaminones with substituted phenyl isocyanates proceed on nitrogen and on carbon so that mixture of products is formed. These products differ in the position of attack by electrophile — either on nitrogen or on carbon [22]. Isothiocyanates, which are softer electrophiles, attack enaminones on carbon atom only [22,25]. For example, the reaction of enaminone XXIII with phenyl isothiocyanate gives the corresponding *N*-phenylthioamide XXIV



(XXIII) (XXIV) (7)

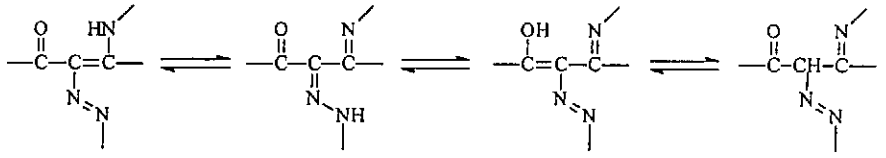
Even benzoyl isothiocyanate, which is more reactive but softer electrophile than substituted phenyl isocyanates, reacts with 4-aminopent-3-en-2-one exclusively on its β-carbon atom [23]. Only when β-carbon does not carry any hydrogen atom (e. g. in the case of 4-amino-3-methylpent-3-en-2-one), benzoyl isothiocyanate attacks nitrogen reaction centre to form substituted thioureas as for example XXV [24]



(XXV) (8)

Reactions with Aromatic Diazonium Salts

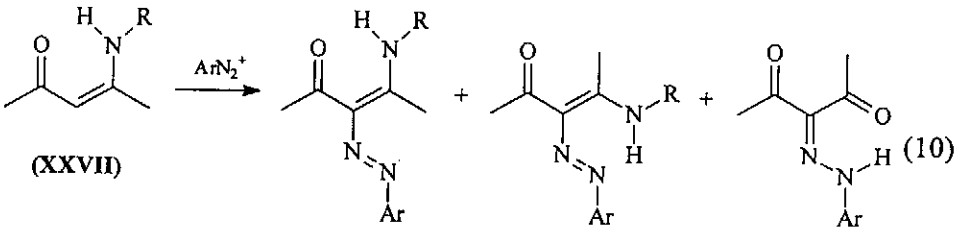
Azo coupling reactions of the aromatic diazonium salts with enaminones are very little explored. The products of these reactions can theoretically exist in several tautomeric forms XXVIa–d



(9)

(XXVIa) keto-azo-enamino | (XXVIb) keto-hydrazo-imino | (XXVIc) enol-azo-imino | (XXVId) keto-azo-imino

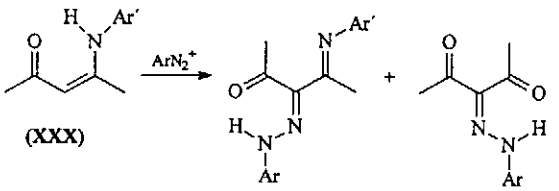
There is practically only one work dealing systematically with these problems [25]. During the reaction of 4-aminopent-3-en-2-one and its *N*-substituted derivatives the molecule of the agent attacks carbon C-3 of the enaminone skeleton. The structure of the product depends on type of substitution on the amino group. When the enaminone contains primary amino group or *N*-alkylamino group XXVII the reaction product is the azo compound XXVIIIa,b. In addition, this compound occurs in the form of two geometrical isomers (a,b) differing in the arrangement of the intramolecular hydrogen bonding. The by-product is 3-arylhydrazonopentane-2,4-dione (XXIX) which is the product of hydrolysis. The isomer (XXVIIIa) is major (about 80%) and the isomer XXVIIIb is minor (about 20%) [25]



(10)

(XXVII) | (XXVIIIa) | (XXVIIIb) | (XXIX)

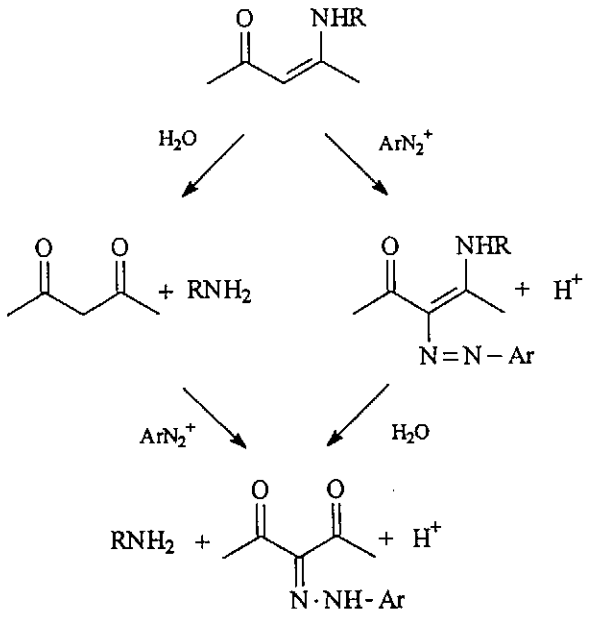
If the enaminone is substituted on amino group by aryl group (XXX), the product of the azo coupling is hydrazo compound XXXI. This compound occurs, in contrast to previous case, as a single form only. The by-product is hydrazo compound XXIX again [25]



(11)

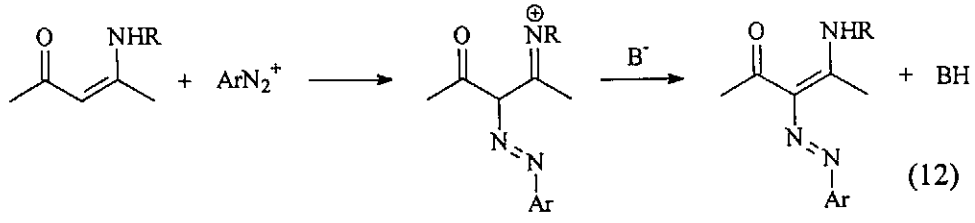
(XXX) | (XXXI) | (XXIX)

Compound XXIX could be formed by two ways [25]. The first consists in the hydrolysis of the enaminone to the starting diketone, which subsequently undergoes the reaction with arenediazonium salt. The second consists in azo coupling to form the azo coupled enaminone, which then hydrolyses (Scheme 3).



Scheme 3

The authors [25] have also studied kinetics and mechanism of the azo coupling to enaminones. The azo coupling reaction could be described by the following mechanism [25]



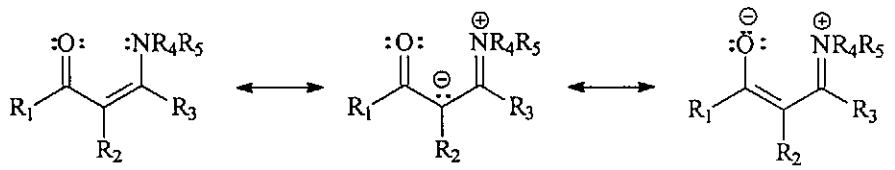
(12)

From the results presented in work [25] it is obvious that if the passive component (enaminone) is unsubstituted on amino group or if the amino group is substituted by alkyl group, then the position of the tautomeric equilibrium is shifted to the keto-azo-enamino form XXVIa. On the contrary, if there is aryl group on the amino group, the position of the tautomeric equilibrium is shifted to

the keto-hydrazo-imino form XXVIb. All the conclusions about the structure of the azo coupling products from arenediazonium salts and enaminones have been made on the basis of the proton NMR spectra only [25].

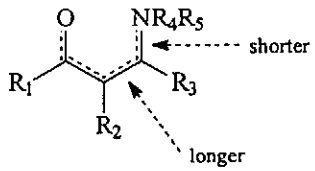
Geometrical Isomerism

β-Enaminones are systems having electronwithdrawing as well as electrondonating group on their double bond. Free electron pair of the amino group is in conjugation with the C=C-C=O system, and this leads to extended delocalization which can be expressed by the resonance structures XXXIIa-c



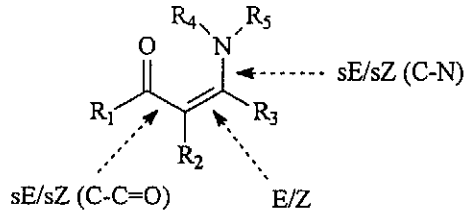
(XXXIIa) **(XXXIIb)** **(XXXIIc)**

This delocalization has been proved by X-ray measurements. By comparing the bond lengths of enaminones and enamines it has been found that the bond C=C is longer and the bond C–N is shorter in the enaminone molecules [26–29]. This fact is depicted in Scheme 4. It is possible to say that the β-enaminones are mesomeric systems, being planar or almost planar



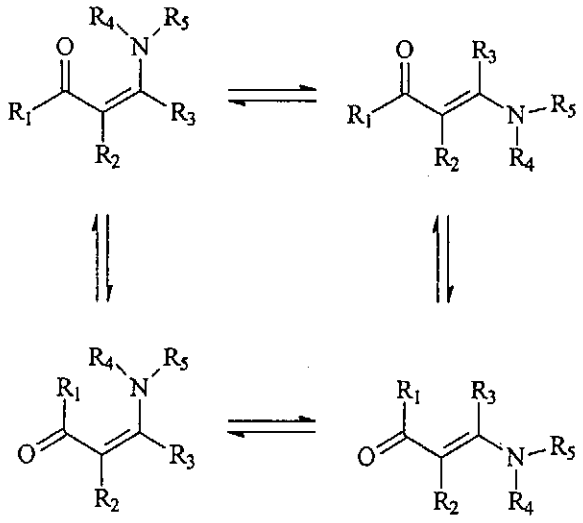
Scheme 4

A consequence of the delocalisation is a decrease in bond order of C=C double bond and increase in bond order of C–N bond. Thanks to these facts, hindered rotations of substituents around these bonds are possible. Hence the molecules of the β-enaminones can show various kinds of the geometrical isomerism. The possibilities are shown in Scheme 5



Scheme 5

All the processes including the hindered rotation are dynamic and the individual conformers are interchanging. Mutual interconversion is shown in Scheme 6 (the interconversions caused by the rotation around the C–N bond are not shown).



Scheme 6

Predominance of particular structure is affected especially by these three factors:

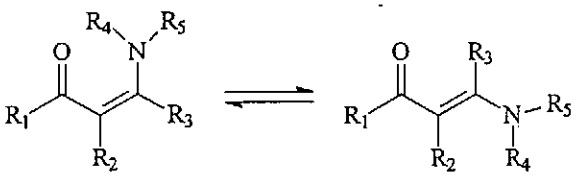
- Substitution on amino group
- Nature of substituents R
- Solvent

Isomerism on C=C Double Bond

The double bond in β-enaminones differs in its character from the double bond in e.g. alkenes. The double bond in alkenes is rigid, the energy of the rotation around the bond is $260 - 270$ kJ mol^{-1}. Due to the presence of electron-acceptor as well

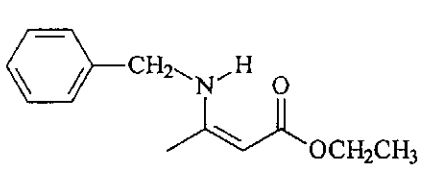
as electron-donor groups, the character of the double bond of β-enaminones is *polarised.* As mentioned above, the bond order of the bond is decreased and so the energy of rotation around the bond is decreased too ($\Delta G^{\ddagger} \sim 50-70$ kJ mol^{-1}) [30]. This barrier decreases with increased polarity of the solvent [31–33].

Isomerism *E/Z* around the C=C bond in β-enaminones can be depicted by equation 13

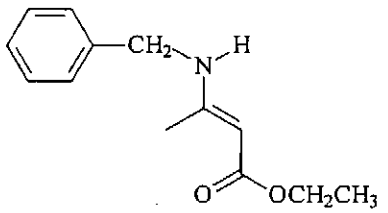


(13)

The enaminones having primary amino group (R_4 4 and R_5 = H) exist predominantly in their *Z* configuration with the intramolecular hydrogen bonding –N–H···O=C– (Refs [31,34–36]). Introduction of an N-substituent leads to increased content of the *E* form (Ref. [37]) as a consequence of the increased steric hindrance of the form *Z*. This steric disadvantage can finally be large enough to overbalance the advantages of the arrangement with the intramolecular hydrogen bonding. The increase in the steric hindrance already leads to disturbance of the molecular planarity and to decrease in conjugation. This can be demonstrated by the example of 3-benzylaminocrotonates XXXIIIa,b whose *E* and *Z* isomers can be obtained separately as crystalline substances [38]



(XXXIIIa)



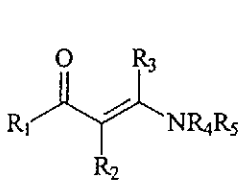
(XXXIIIb)

3-Aminocrotonates bearing electron-acceptor group on the nitrogen have much more stabile *Z* form (Refs [39–41]). This is probably caused by strong intramolecular hydrogen bond. This hydrogen bond is so strong that this arrangement overbalances the steric hindrance of the molecule.

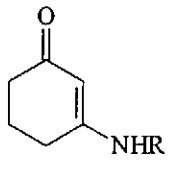
The proportion of the *Z* form increases with increasing size of the substituent R_1 (Refs [42–50]). The same effect show the substituents R_2 and R_3 (Refs [50–52]). An exception is phenyl group because the enaminones having 1-phenyl group exist predominantly in form *E*. If the phenyl group is at 2- position, the isomer *Z* predominates.

The enaminones with tertiary amino group XXXIV occur predominantly in form E [6,30,53,54].

Cyclic type enaminones XXXV have fixed *E* configuration at their double bond (Ref. [50]).



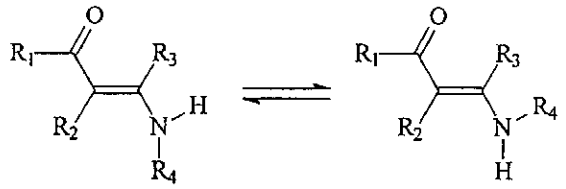
(XXXIV)



(XXXV)

Isomerism on C–N Bond

As can be seen from structures XXXIIa–c, C–N bonding in the enaminones has less or more extended bond order. This has its consequence in increased rotational barrier of C–N bond which develops the hindered rotation (Eq. 14). A similar phenomenon is seen in amides. The hindered rotation is the most developed with *E*-isomers [55] and enaminones having a tertiary amino group [34,35,37]. We can observe broadened signals in NMR spectra of these compounds. The rotation around the C–N bond takes place at a medium rate on the NMR time scale [37]. The *sZ* conformer predominates with the enaminones having no substituent at the C–2 carbon, whereas the *sE* conformer is more preferred at C–2 alkyled substrates because these arrangement partially decreases the steric hindrance caused by interaction between the substituents R_2 and R_4 (Ref. [37]).



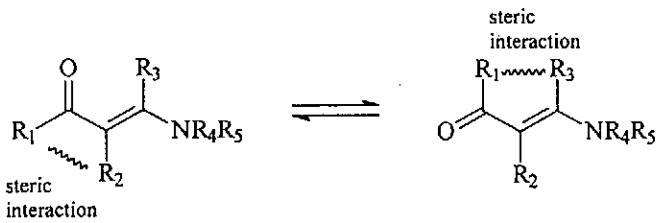
sZ sE (14)

Isomerism of C–C=O Bond

The *sZ/sE* isomerism is also possible on C–C=O bond (Ref. [37]). Because of increased bond order of the bonding there also exists a possibility of hindered rotation. This isomerism is depicted by equation 15

(15)

Position of this equilibrium depends on steric interactions. The *sZ* conformation XXXVI predominates in the cases when there is a bulky substituent bound to carbonyl. When this substituent is *tert.*butyl, then this conformation even dominates [37]. For the *sE-E* conformations (the first sign indicates situation on C–C=O bonding and the second one on C=C bonding) a nonplanar character has been described [56]. The steric interactions in structure XXXVI are smaller.

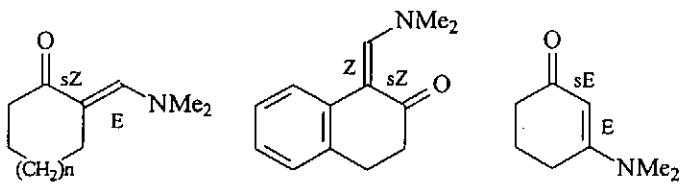


(XXXVI) (XXXVII)

(16)

Thanks to these interactions the carbonyl or NR_4R_5 grouping are distorted out of the molecular plane which leads to the increased extent of delocalization [26]. In the case of the enaminones it can be stated that the torsion effects have greater influence on planarity and hence on extent of delocalization as compared with the electronic effects [26].

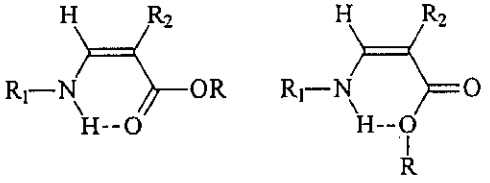
In the case of cyclic enaminones the situation depends upon the fact whether the carbon bearing amino group forms a part of ring or not [26]. The enaminones exist in the *sZ* form when their molecule contains the exocyclic double bond (XXXVIII and XXXIX). If the carbon bearing the amino group is a part of ring, the enaminones exist as the *sE* isomer XL.



(XXXVIII) (XXXIX) (XL)

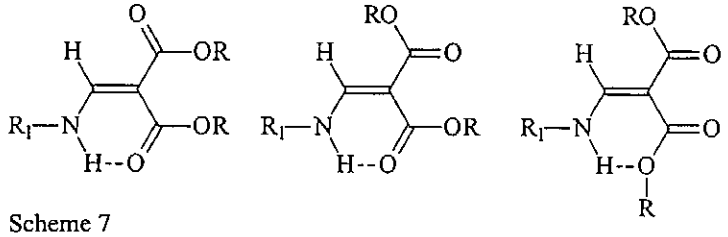
An unusual case of the rotational isomerism exists in the case of enaminoesters (R_1 = OR). Thanks to the presence of two different oxygen atoms

we can draw two different *Z* isomers with intramolecular hydrogen bond (XLI and XLII).



(XLI) **(XLII)**

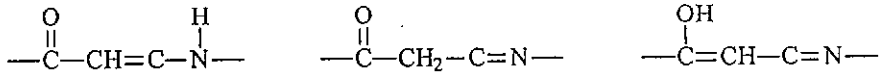
In the following Scheme 7, the possibilities are shown for the case of dialkyl 2-aminomethylenpropanedioates [26]. The first two structures predominate in nonpolar medium and the third join them in polar medium.



Scheme 7

Tautomerism

Three tautomeric structures can be presumed (XLIIIa–c)



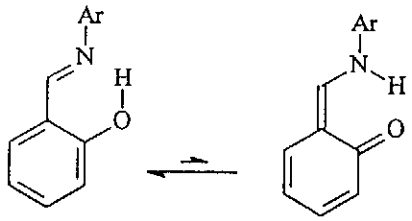
keto-enamino keto-imino enol-imino

(XLIIIa) **(XLIIIb)** **(XLIIIc)**

In the case of acyclic and alicyclic enaminones it is well proved that the ketoform predominates. From pK_a values of series 3-aminocyclohex-2-en-1-ones and their *O*-methyl and *N*-methyl derivatives it has been proved that the carbonyl group is preferred against the enolform by the factor 10^8 (Ref. [58]).

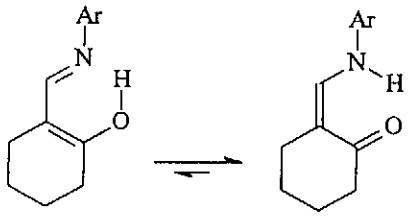
Various NMR [50,59,60] and crystallographic [61] studies have proved that the enaminones being able to form intramolecular hydrogen bond exist in the keto-enamino form XLIIIa.

On the other hand, *N*-salicylanilides (i.e. the Schiff bases of salicylaldehyde) were proved to exist in the enol-imino form [62,63] XLIVa. It was found that electron-donating groups on the amine moiety of the Schiff base shift the equilibrium to the ketoform [64]. This effect was explained by increased basicity of nitrogen in the Schiff base owing to electron-donating activity of the substituent [64].



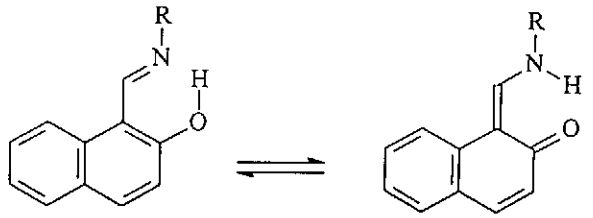
(XLIVa) (XLIVb) (17)

In the case of the Schiff bases from salicylaldehyde, the stability of the aromatic system probably affects the position of the tautomeric equilibrium. Similar Schiff bases XLVa, which are not aromatic, have their equilibrium shifted quite to the keto form [62] (XLVb).



(XLVa) (XLVb) (18)

These two mentioned cases are examples of the "border" situations when the position of tautomeric equilibrium is shifted to one or the other side. However, thehe are systems where the position of the tautomeric equilibrium is between the two extremes. These cases involve the Schiff bases derived from 2-hydroxynaphtalene-1-carbaldehyde. These compounds exist as the equilibrium mixtures of tautomers [62,63] (XLVIa,b).



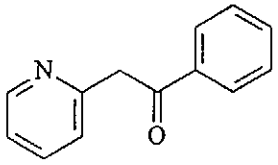
(XLVIa) (XLVIb) (19)

The position of the equilibrium has been found to depend upon several factors [62]:

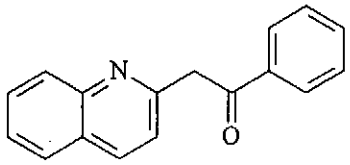
- Type of R
- Temperature
- Solvent

Alkyl group at nitrogen shifts the equilibrium to the keto-amino form, the same effect being also exerted by an enhancement of the solvent polarity. Temperature has an only small effect. The content of the ketoform in this system has been generally found to lie in the interval of 20 – 60% (Ref. [62]).

Similar effect of the annellation of benzene ring has been observed in the study of the tautomerism of 2-phenacylpyridines XLVII and 2-phenacylquinolines XLVIII [65]

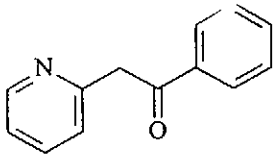


(XLVII)



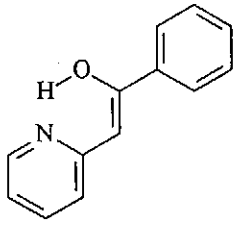
(XLVIII)

Both these compounds can exist in several tautomeric forms. In the case of 2-phenacylpyridine, the most stable form in aqueous medium is the keto-imino form XLIXa. In contrast to this, in nonpolar media the enolform XLIXb dominates [65]



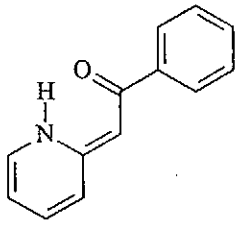
keto-imino

(XLIXa)



enol-imino

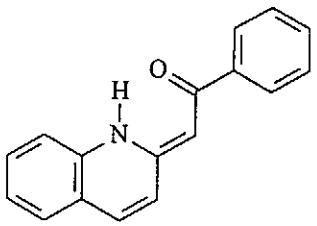
(XLIXb)



keto-enamino

(XLIXc)

By an annellation of benzene ring, i.e. by moving to 2-phenacylquinolines, the keto-enamino form (L) was found to become predominant [65]



(L)

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