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SYNTHESIS AND REARRANGEMENT OF CHLOROALKOXY-, CHLOROALKYLTHIO-, AND CHLOROALKYLAMINO-*sym*-TRIAZINES (REVIEW)

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*Results from the synthesis of chloroalkoxy-, chloroalkylthio-, and chloroalkylamino-*sym*-triazines and study of their rearrangement are summarized.*

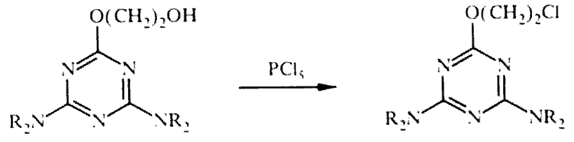
In contrast to their simple alkoxy, alkylthio, and alkylamino analogs, chloroalkoxy-, chloroalkylthio-, and chloroalkylamino-*sym*-triazines have proved unstable to some degree or other. This is due primarily to intramolecular interaction between the chloroalkyl group and the nucleophilic nitrogen center of the triazine ring. For this reason to produce these compounds successfully it is necessary to use special reagents and to create specific conditions that exclude destruction of the required chlorides. On account of the clearly defined susceptibility to intramolecular interactions during heating at moderate temperature (100-120°C) and also spontaneously at room temperature and even at lower temperature they either rearrange through the hetero-*sym*-triazinium chlorides to the N-chloroalkyl-*sym*-triazinones or form imidazo(*asym*-triazino)-, oxazolo-(oxazino)-, and thiazolo(thiazino)-*sym*-triazinones, after undergoing dehydrochlorination or dechloroalkylation. The direction of these transformations and the nature of the obtained compounds are due to a considerable degree to the nature of the substituent in the triazine ring. Particularly significant here is the directing effect of the alkyl and alkylamino groups. It was found that intramolecular quaternization of the chloroalkoxy-, chloroalkylthio-, and chloroamino-*sym*-triazines, the formation of the N-chloroalkyl derivatives, and addition of the new ring to the existing triazine ring take place at the cyclic nitrogen atom, situated at the *para* position to the indicated groups.

Apart from purely chemical interest, the regioselective and effective conversion of chloroalkoxy-, chloroalkylthio-, and chloroalkylamino-*sym*-triazines into hetero-*sym*-triazinones may occupy a special position among the methods described in the literature [1-7] for the synthesis of the given series of condensed heterocycles in view of the high almost quantitative yields and the exceptional purity of the reaction products.

Owing to their obvious structural similarity to familiar drugs and pesticides [4, 6, 8] the synthesis of the compounds described in the present review is also of interest in connection with the search for new physiologically active substances.

1. METHODS OF SYNTHESIS

During the chlorination of 2-hydroxyethoxy-*sym*-triazines (I) with thionyl chloride at the temperature of boiling benzene, as found subsequently, the products from their more deep-seated degradation are formed instead of the expected chloroethoxy derivatives (II). The chlorination of the alcohols (I) at low temperature (−5°C) in ether gave the normal chlorination products [9]:



I

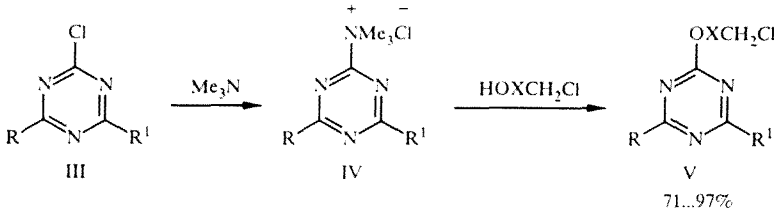
II

68...87%

R = Alk

Armenian Agricultural Academy, Erevan. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 435-448, April, 1996. Original article submitted April 3, 1996.

The most universal and convenient reagents for the given purpose were trimethyl-*sym*-triazinylammonium chlorides (IV), which are easy to obtain by the action of trimethylamine on the chlorotriazines (III) in aprotic solvents [10-12]. On account of their enhanced electrophilicity compared with the chlorine derivatives (III) the salts (IV) react readily with the derivatives of alcohols and other polyfunctional nucleophiles at low temperature, and this predetermines both successful protection of the functional groups of the reactants sensitive to bases and the stability of the chloroalkoxy-*sym*-triazines (V) formed here [9, 13-24, 29]:



III

IV

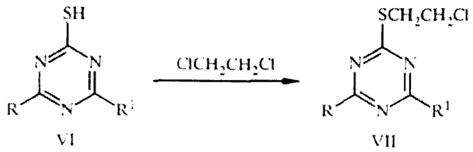
V

71...97%

X = CH_2, $CHCH_2Cl$

R = alkyl(dialkyl)amino groups, R^1 = amino, alkyl(dialkyl)amino, arylamino, cyanoamino, methoxyamino, hydrazino, alkoxy, and alkylthio groups

The chloroalkylthio-*sym*-triazines (VII) were obtained by the chloroalkylation of the sodiomercaptides of *sym*-triazines (VI) at 50-60°C. Dichloroethane and partly α-chloroacrylonitrile were mainly used as chloroalkylating agents [25-27]:

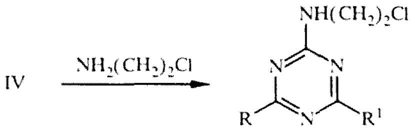


VI

VII

79...93%

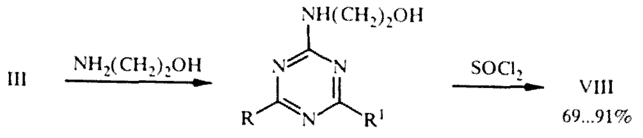
The above-mentioned salts (IV) were also used successfully for the synthesis of chloroethylamino-*sym*-triazines (VIII) by reacting them with chloroethylamine at room temperature [28, 29]:



VIII

65...90%

Compounds (VIII) were also synthesized by the chlorination of 2-hydroxyethylamino-*sym*-triazines (IX), obtained by the action of aminoethanol on compound (III) [28]:



IX

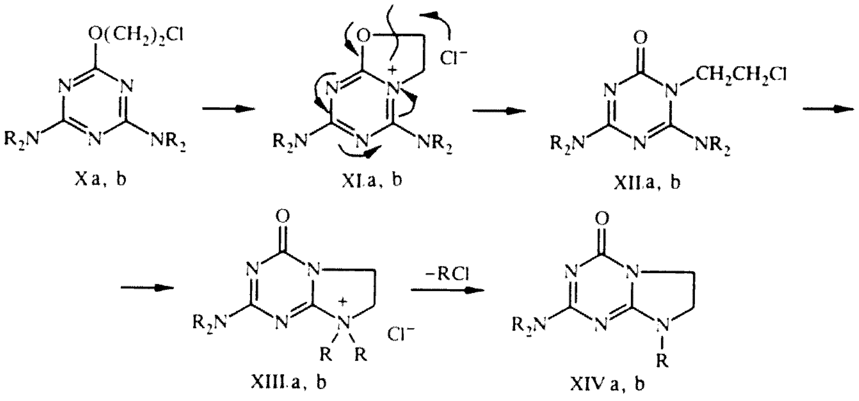
69...91%

2. REARRANGEMENTS OF CHLOROALKOXY-, CHLOROALKYLTHIO-, AND CHLOROALKYLAMINO-*sym*-TRIAZINES

The rearrangements of chloroalkoxy-, chloroalkylthio-, and chloroalkylamino-*sym*-triazines were studied for the case of the model compounds (V, VI, VIII), which were broken down into the groups indicated below, according to the nature of the heteroatom in their chloroalkylhetero side chain and the substituent R^1.

2.1. 2-CHLOROALKOXY-4,6-BISAMINO-SUBSTITUTED *sym*-TRIAZINES

The rearrangement of this series of compounds usually leads to the formation of substituted imidazo-*sym*-triazines, as was first discovered during the thermolysis of 2-(2-chloroethoxy)-4,6-bisdialkylamino-*sym*-triazines (Xa,b). Brief heating in xylene at 120-130°C led to the vigorous release of alkyl chlorides and to the production of imidazo-*sym*-triazinones (XIIa, b) with high yields (90% or more) [9, 13]:

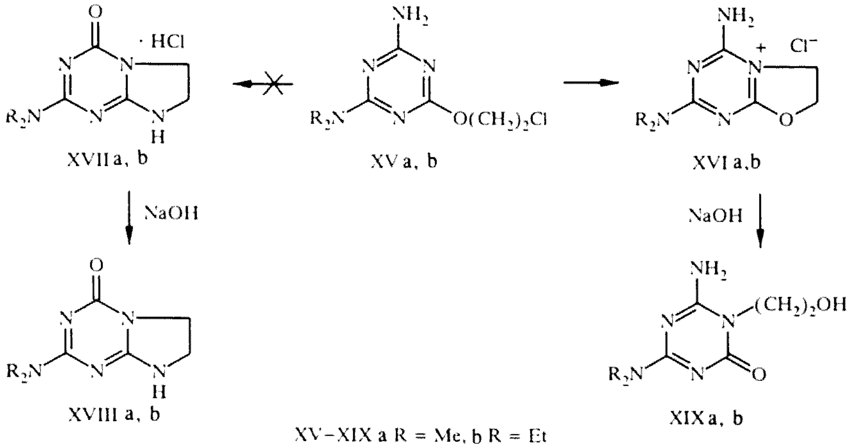


X–XIV a R = Me, b R = Et

The motivating force of this rearrangement is intramolecular quaternization of the compounds (Xa,b) with the formation of oxazolo-*sym*-triazinium chlorides (XIa,b). The latter are transformed through the 3-N-chloroethyl derivatives (XIIa, b) into imidazo-*sym*-triazinium chlorides (XIIIa,b), which eliminate the alkyl chlorides and are converted into compounds (XIVa,b).

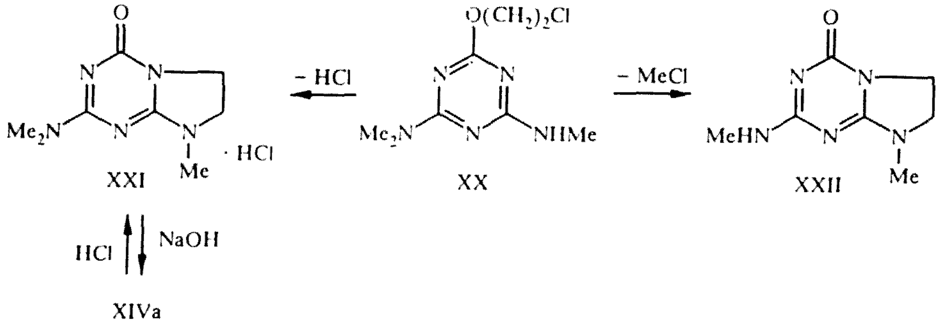
The presented scheme of consecutive reactions proved common to the rearrangement of all the compounds of the (V, VII, VIII) type and was confirmed by the isolation of the indicated intermediates, which in a number of cases were also the final products of the rearrangement. Thus, during the thermolysis of compound (Xa) under milder conditions at the temperature of boiling benzene with a reaction time of 1.5 h it was possible to obtain the intermediate (XIa) with a 22% yield.

After 3 h at the temperature of boiling toluene the 2-amino-4-dialkylamino-6-(2-chloroethoxy)-*sym*-triazines (XVa,b) change quantitatively into the stable oxazolo-*sym*-triazinium chlorides (XVIa,b), which are not changed even under more drastic thermolysis conditions. The alternative formation of the hydrochlorides of imidazo-*sym*-triazinones (XVIIa,b) evidently does not arise, since treatment with alkali gave 2-amino-4-oxo-3-N-2-hydroxyethyl-*sym*-triazines (XIXa,b) instead of the bases (XVIIIa, b), and this favors the formation of a quaternary salt [29]:



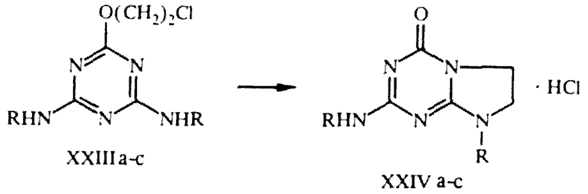
XV–XIX a R = Me, b R = Et

During the thermolysis of 2-(2-chloroethoxy)-4-methylamino-6-dimethylamino-*sym*-triazine (XX) it was possible to expect the formation of two different rearrangement products as a result of initial quaternization of the nitrogen atoms situated at the *para* position to the dimethylamino or methylamino groups:



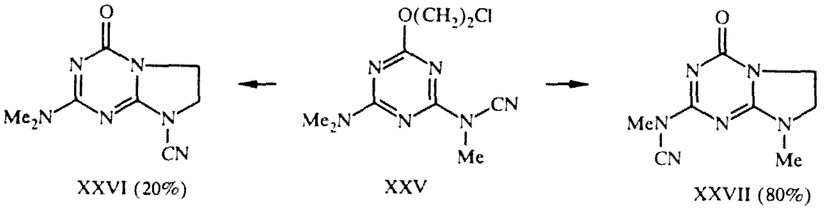
Investigations showed that at the temperature of boiling xylene and with thermolysis for 5 h only the first path was realized. As a result the hydrochloride of imidazo-*sym*-triazinone (XXI), identical with the hydrochloride of compound (XIVa), was formed with a quantitative yield (98%) [9].

As expected, the 2-(2-chloroethoxy)-4,6-bisalkylamino-*sym*-triazines (XXIIIa-c) rearrange with the release of hydrogen chloride and form the hydrochlorides of imidazo-*sym*-triazinones (XXIVa-c) [9]:

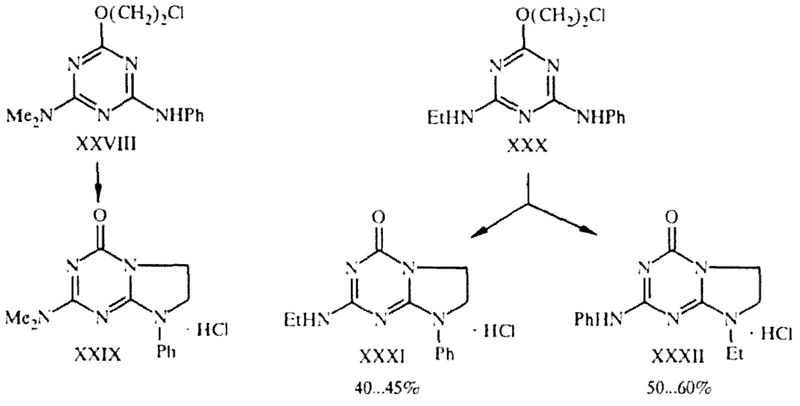


XXIII, XXIV a R = Me, b R = Et, c R = *i*-Pr

Under analogous conditions 2-(2-chloroethoxy)-4-dimethylamino-6-N-methyl-N-cyanoamino-*sym*-triazine (XXV) forms a mixture of two imidazo-*sym*-triazinones (XXVI, XXVII) [18]:

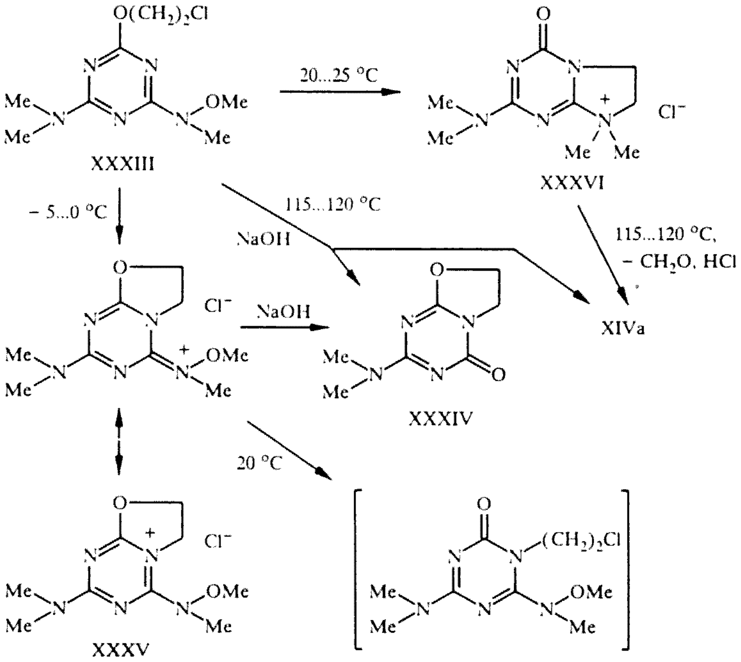


The behavior of chloroethoxy-*sym*-triazines containing an arylamino substituent under the rearrangement conditions does not differ from that of the aliphatic analogs. Thus, 2-chloroethoxy-4-dimethylamino-6-phenylamino-*sym*-triazine (XXVIII) rearranges with the participation of the hydrogen atom of the phenylamino group. At the same time 2-chloroethoxy-4-ethylamino-6-phenylamino-*sym*-triazine (XXX) forms a mixture of the hydrochlorides of two imidazo-*sym*-triazinones (XXXI) and (XXXII) [24]:

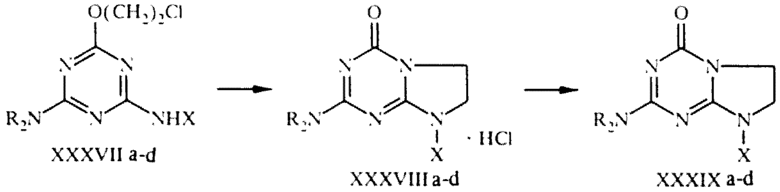


For 3 h in toluene at 115-120°C 2-(2-chloroethoxy)-4-dimethylamino-6-N-methyl-N-methoxy-*sym*-triazine (XXXIII) undergoes deep-seated degradation. After treatment with alkali the obtained compound changes into a mixture of imidazo(oxazolo)-*sym*-triazinones (XIVa, XXXIV).

If compound (XXXIII) is allowed to stand at −5-0°C for three months, oxazolo-*sym*-triazinium chloride (XXXV) is obtained with a 60% yield, while after 20-25 days at room temperature imidazo-*sym*-triazinium chloride (XXXVI) is obtained with a 35% yield. The salt (XXXV) is converted by the action of alkali into oxazolo-*sym*-triazinone (XXXIV), while the salt (XXXVI) decomposes at 115-120°C with the formation of imidazo-*sym*-triazinone (XIVa). It was also established that the chloride (XXXV) changes into the chloride (XXXVI), and this probably takes place through the N-2-chloroethyl derivative [23]:

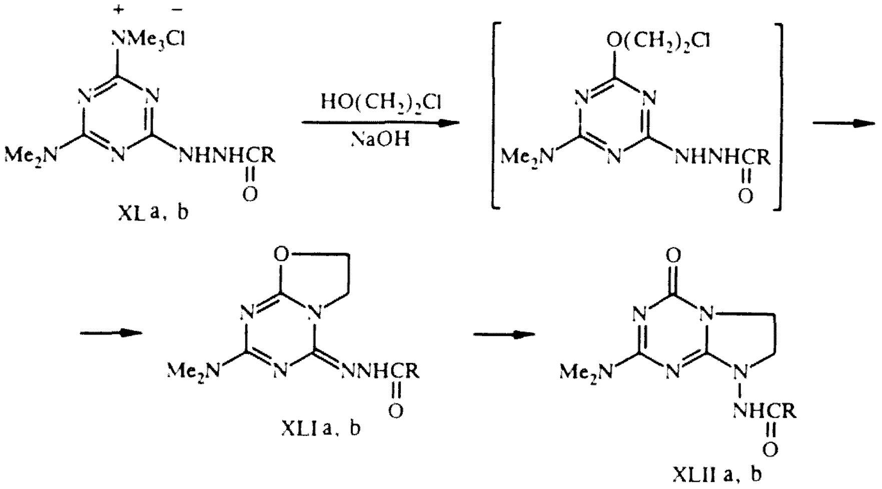


Even when held for a short time at room temperature or for 1 h at 120°C, the chloroethoxy-*sym*-triazines (XXXVIIa-d), which are NH acids on account of the nitrile and methoxyl substituents at the amino group, are transformed into the hydrochlorides of imidazo-*sym*-triazinones (XXXVIIIa-d). The action of alkali on the latter gives the free bases (XXXIXa-d) [19, 20]:



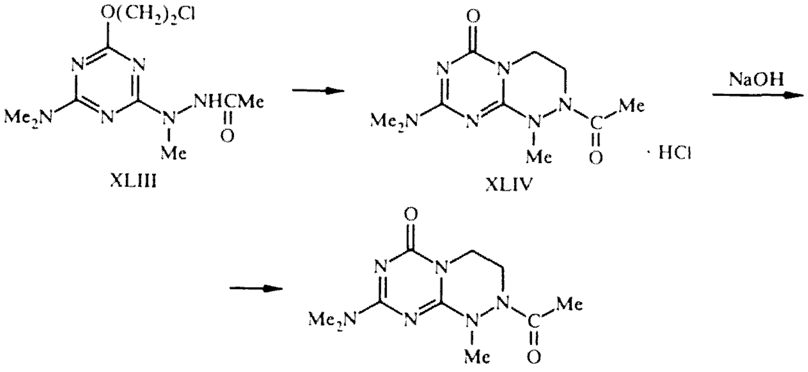
XXXVII–XXXIX a R = Me, X = C≡N; b R = Et, X = C≡N;
c R = Me, X = MeO; d R = Et, X = MeO

The products from the reaction of acylhydrazino-*sym*-triazines with ethylene chlorohydrin in the presence of alkali at low temperature undergo rearrangement even during their preparation. Thus, the salt (XLa) is transformed into oxazolo-*sym*-triazinone (XLIa), which is fully transformed into imidazo-*sym*-triazinone (XLIIa) on heating (200°C). Under the same conditions the salt (XLb) gives a mixture of oxazolo(imidazo)-*sym*-triazinones (XLIb) and (XLIIb) in a ratio of 4:3. When this mixture is heated in xylene, compound (XLIb) changes completely into the more stable compound (XLIIb) [22].


XLa, b; XLIa, b; XLIIa, b

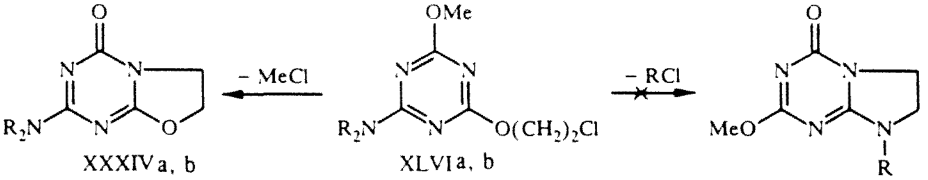
XL–XLII a R = Ph, b R = Me

If the hydrogen atom at the N_2 atom of the acetylhydrazine fragment of compound (XLb) is substituted by a methyl radical the comparatively stable chloroethoxy derivative (XLIII) is formed. During thermolysis the latter rearranges into the hydrochloride of *asym*-triazino-*sym*-triazinone (XLIV), which forms the respective base (XLV) when treated with alkali [21]:


XLIII; XLIV; XLV

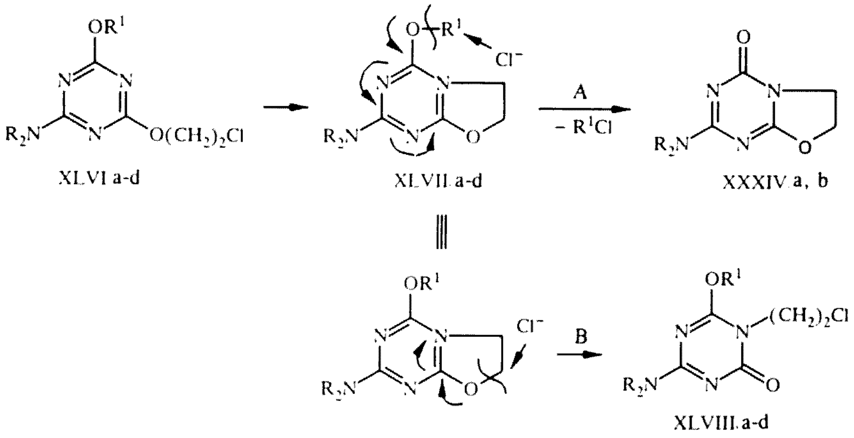
2.2. 2-ALKOXY-4-DIMETHYLAMINO-6-CHLOROALKOXY-*sym*-TRIAZINES

A special feature of the thermolysis of 2-methoxy-4-dialkylamino-6-(2-chloroethoxy)-*sym*-triazines is the elimination of methyl chloride and not the alkyl chlorides, leading to the formation of the oxazolo-*sym*-triazinones (XXXIVa,b) [14]:


XXXIVa, b; XLVIa, b

XXXIV a R = Me, b R = Et

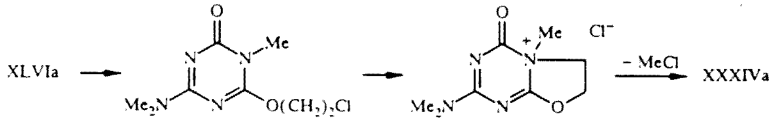
This result can be interpreted satisfactorily in terms of the quaternization of the initial compounds (XLVIa,b) and the direct removal of methyl chloride from the salts (XLVIIa,b) (path A). The formation of compounds (XXXIVa,b) can also arise through the usual intermediates for the given rearrangement, i.e., the N-2-chloroethyl derivatives (XLVIIIa,b) (path B):



XLVI–XLVIII a R = R^1 = Me; b R = Et, R^1 = Me; c R = Me, R^1 = Et; d R = Me, R^1 = Pr

When this transformation was realized in the case of compound (XLVIa) containing a CH_3O^{18} group, compound (XXXIVa) with the labelled oxygen in the carbonyl group and not in the oxazolidine ring was obtained, indicating rearrangement according to scheme A. In the transition from compounds (XLVIa, b) to their ethoxy and propoxy analogs (XLVIc,d) the reaction path changes. On account of steric hindrances the alkoxy group and not the oxazolidine ring undergoes nucleophilic attack by the chloride ion in the salt (XLVII), and this leads to cleavage of its $-O-C$ bond with the formation of the intermediate (XLVIII), which then changes into compound (XXXIV) (path B).

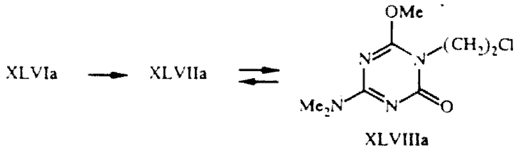
In [14] an alternative rearrangement mechanism, based on possible isomerization of (XLVI) to the N-methyl derivative according to the following scheme, was also discussed:



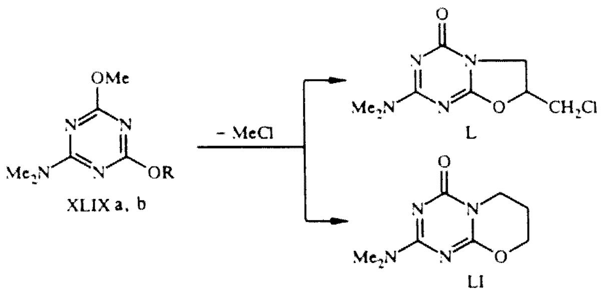
It was found that the methoxy-*sym*-triazines do not change at all at the optimum temperature for the rearrangement. According to published data, the O–N isomerization indicated in the scheme is only possible at 170-195°C [30].

At the same time at the temperature of boiling n-heptane or toluene with brief heating and also with prolonged holding at room temperature compounds (XLVIa, b) rearrange quantitatively to (XXXIVa, b) [14].

When an aqueous suspension of compound (XLVIa) is heated, the salt (XLVIIa) stable in water is formed. The stabilization of such salts in water is probably explained by the solvation factor. If the water is evaporated, the salt (XLVIIa) is converted completely into compound (XLVIIIa), which changes back into the salt when dissolved in water [16]:



It was shown that chloromethyloxazolo- and oxazino-*sym*-triazinones (L, LIa,b) are formed with quantitative yields during the thermolysis of 2-methoxy-4-dimethylamino-6-(1,3-dichloropropoxy)- and 2-methoxy-4-dimethylamino-6-(3-chloropropoxy)-*sym*-triazines (XLIXa,b) [17]:

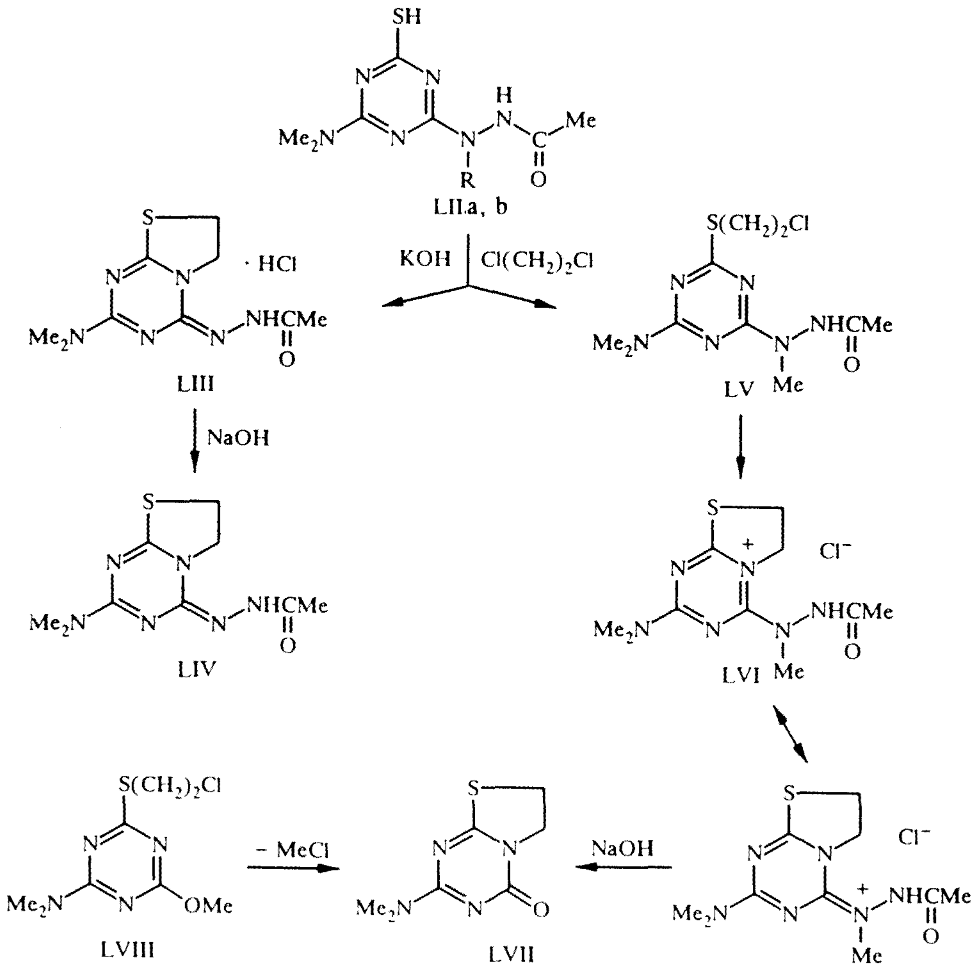


XLIX a R = $CH(CH_2Cl)_2$, b R = $(CH_2)_3Cl$

The presence of the two chloromethyl groups in compound (XLIXa) increases the probability of intramolecular interactions, and it therefore rearranges more readily than the related compound (XLVIa) (40 min and 2 h 30 min respectively at 120°C). Compound (XLIXb) changes into the oxazino-*sym*-triazinone (LI) under more drastic conditions (120°C, 6 h), and this is due to steric hindrance during the formation of the six-membered ring instead of the five-membered ring.

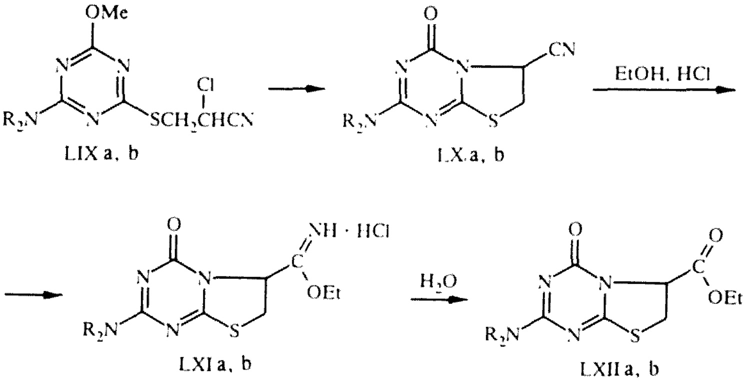
2.3. CHOROALKYLTHIO-*sym*-TRIAZINES

The reaction of 2-mercapto-4-dimethylamino-6-(2-acetyl-1-methyl-2-acetylhydrazino)-*sym*-triazines (LIIa,b) with dichloroethane in the presence of potassium hydroxide was described in [26]. Here, instead of the expected chloroethylamino derivative, compound (LIIa) is converted into its intramolecular heterocyclization product (LIIIa), which forms the free base LIV, stable in water, under the influence of alkali. Under the same conditions compound (LIIb) forms 2-chloroethylthio-4-dimethylamino-6-(1-methylamino-2-acetylhydrazino)-*sym*-triazine (LV), the thermolysis of which in xylene leads to the production of thiazolo-*sym*-triazinium chloride (LVI). By reacting in the form of the exocyclic onium cation, under the influence of alkali compound (LVI) forms the thiazolo-*sym*-triazinone (LVII), identical with the product from the thermolysis of 2-methoxy-4-dimethylamino-6-(2-chloroethyl)-*sym*-triazine (LVIII) [25]:



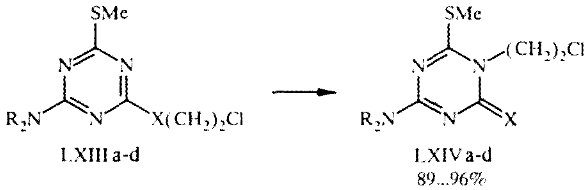
a R = H, b R = Me

The fundamental possibility of producing functionally substituted thiazolo-*sym*-triazinones (LXa,b-LXIIa,b) during the thermolysis of 2-methoxy-4-dialkylamino-6-(2-chloro-2-cyanoethyl)-*sym*-triazines (LIXa,b) was demonstrated in [27]:



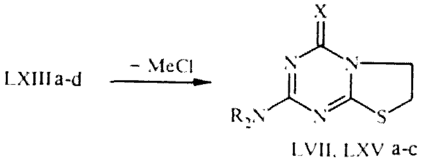
LIX–LXII a R = Me, b R = Et

It can be concluded on the basis of the presented data that the rearrangement of chloroalkylthio-*sym*-triazines containing amino, hydrazino, and methoxy groups does not differ fundamentally in direction from the rearrangement of the corresponding chloroalkoxy derivatives. In the mean time the presence of the methylthio group in place of the methoxy group has a substantial effect on the depth of the rearrangement transformations of chloroalkoxy- and chloroalkylthio-*sym*-triazines. As a result of the replacement of the polar C – O bond by the less polar C – S bond the removal of the methyl chloride at the position of the CH_3S group is significantly hindered, and this leads to an increase in the stability of its intermediates. This is clearly illustrated in the case of the thermolysis of 2-methylthio-4-dialkylamino-6-[2-chloroethoxy(ethylthio)]-*sym*-triazines (LXIIIa-d). Under the optimum condition conditions for complete rearrangement of 2-methoxy-4-dialkylamino-6-[2-chloroethoxy(ethylthio)]-*sym*-triazines (XLVIa,b, LVIII) to oxazolo(thiazolo)-*sym*-triazinones (LVIII) compounds (LXIIIa-d) are converted into 2-methylthio-3-N-chloroethyl-4-oxo(thioxo)-6-dialkylamino-*sym*-triazines (LXIVa-d) [15]:



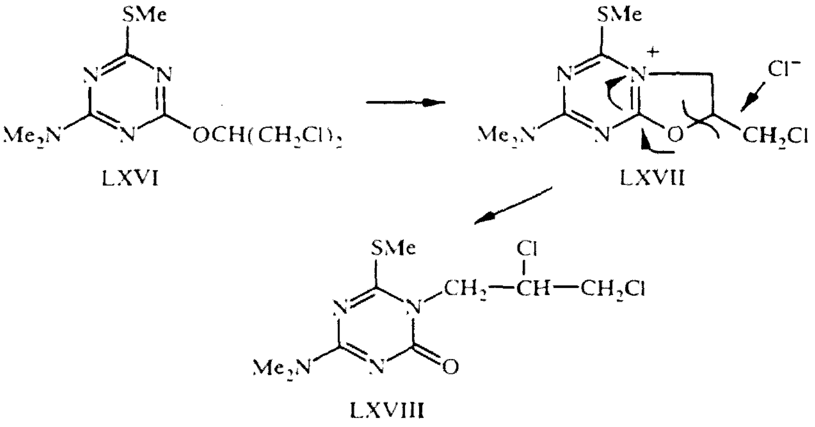
LXIII, LXIV a X = O, R = Me; b X = O, R = Et; c X = S, R = Me; d X = S, R = Et

When heated at high temperature (180-190°C) for 3 h the N-2-chloroethyl derivatives (LXIVa,b) obtained in this way eliminate methyl chloride and form thiazolo-*sym*-triazinones (LVII, LXVa). The latter are also formed with good yields (82-89%) directly from compounds (LXIIIa-d) during their thermolysis under harsher conditions [15]:



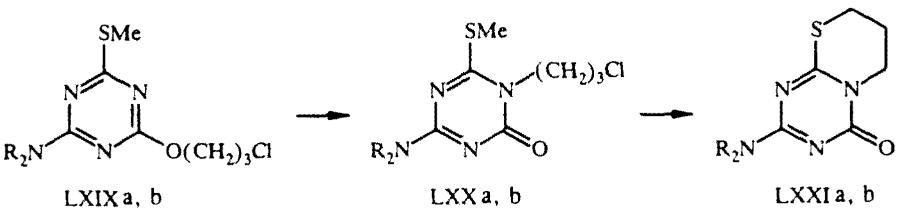
LXV a X = O, R = Et; b X = S, R = Me; c X = S, R = Et

During the thermolysis of 2-methylthio-4-dimethylamino-6-(1,3-dichloropropoxy)-*sym*-triazine (LXVI) a compound with a migrated chlorine atom, i.e., 2-methylthio-3-N-(2,3-dichloropropyl)-6-oxo-*sym*-triazine (LXVIII), was obtained [17]. The migration of the chlorine atom at the C – C bond can be explained in terms of the O – N isomerization of the chloroalkoxy(alkylthio)-*sym*-triazines (LXVIIa-d) to the N-chloroalkyl derivatives (LXIVa-d) through the quaternary salts (LXVII) [15]:



LXVI LXVII LXVIII

According to data in [17], under the conditions for the rearrangement of the methoxyl analogs [14, 17] 2-methylthio-4-dialkylamino-6-(3-chloropropoxy)-*sym*-triazines (LXIXa,b) do not undergo any changes, but after prolonged heating (20 h, 125°C) they rearrange to 2-methylthio-3-N-3-chloropropyl-4-dimethylamino-6-oxo-*sym*-triazines (LXXa,b). The latter only form the thiazino-*sym*-triazinones (LXXIa, b) after 6.5 h at 180-185°C:

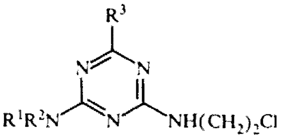


LXIXa, b LXXa, b LXXIa, b

LXIX–LXXI a R = Me, b R = Et

2.4. CHLOROETHYLAMINO-*sym*-TRIAZINES

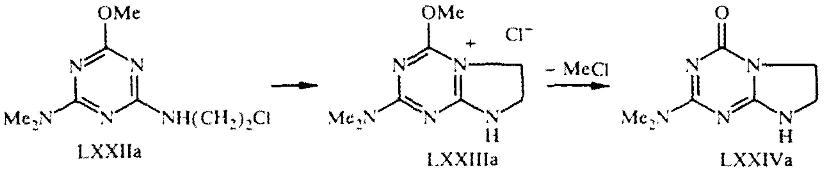
The rearrangement of chloroethylamino-*sym*-triazines was investigated for the case of their derivatives (LXXIIa-d):



LXXII a-d

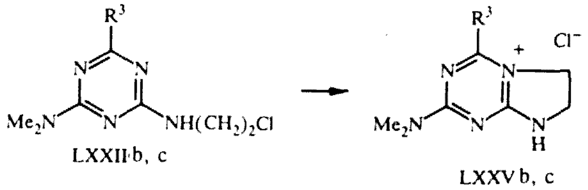
LXXII a $R^1 = R^2 = CH_3$, $R^3 = CH_3O$; b $R^1 = R^2 = CH_3$, $R^3 = SCH_3$; c $R^1 = R^2 = CH_3$, $R^3 = (CH_3)_2N$; d $R^1 = H$, $R^2 = C_2H_5$, $R^3 = C_2H_5NH$

Under relatively mild thermolysis conditions compounds (LXXIIa-d) are transformed with high yields (80-97%) into substituted imidazo-*sym*-triazinones. Compound (LXXIIa) forms compound (LXXIV) through the quaternary salt (LXXIIIa) by eliminating methyl chloride [29]:

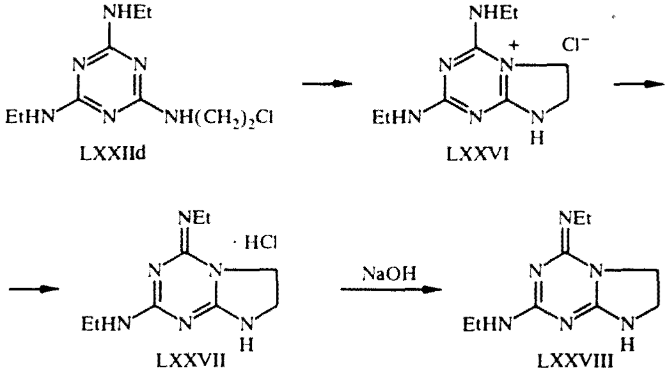


LXXIIa LXXIIIa LXXIVa

Although the imidazo-*sym*-triazinium chloride indicated in the scheme was not isolated, the probability that it is formed is obvious. This is demonstrated not only by the data on the rearrangement of the corresponding chlorooalkoxy-*sym*-triazines but also by the result obtained during the thermolysis of compounds (LXXIIb,c). Under the standard thermolysis conditions the latter are transformed almost quantitatively into the quaternary salts (LXXVb,c) [29]:



The salts (LXXVb) obtained in this way do not change even under harsh thermolysis conditions. The high thermal stability of these compounds must be explained by the presence of the imidazole fragment and the substituents Me_2N and MeS, which unlike the oxazolidine ring and the comparatively labile MeO group are not subject to nucleophilic attack by the chloride ion. At the initial stage of the rearrangement compound (LXXIId) probably also forms the quaternary salt (LXXVI), which is then transformed into the hydrochloride of imidazo-*sym*-triazinone imine (LXXVII); the latter is transformed by the action of alkali into the free base (LXXVIII) [29]:



The data from the IR, UV, PMR, and mass spectra of the initial, intermediate, and final rearrangement products that strictly confirm the structure of the compounds are given in the cited papers. In addition, many of the compounds described in the present review have become the subject of special mass-spectrometric investigations, the results of which are given in [31-33].

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