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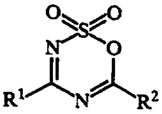
4,6-DISUBSTITUTED 1,2,3,5-OXATHIADIAZINE-2,2-DIOXIDES. SYNTHESIS, STRUCTURAL FEATURES, CHEMICAL PROPERTIES (Review)

A. A. Michurin and A. V. Shishulina

We analyze and systematize literature data on synthesis methods, structural features, and properties of 4,6-disubstituted 1,2,3,5-oxathiadiazine-2,2-dioxides.

The growing interest in 1,2,3,5-oxathiadiazine-2,2-dioxides (I) is due to their biological activity and also the accessibility of these heterocyclic compounds [1-5].



I

The 1,2,3,5-oxathiadiazine ring I is a heterocyclic system with great synthetic possibilities which can competitively react with various compounds, with formation of a broad range of cyclic and acyclic heteroatomic products with useful properties.

1. SYNTHESIS METHODS

All known methods for synthesis of 4,6-disubstituted 1,2,3,5-oxathiadiazine-2,2-dioxides I are based on reaction of the cyano group of nitriles and other cyano-containing compounds (cyanates, cyanamides) with SO_3 and its bound forms (complexes, adducts).

Dioxides I were obtained for the first time by Eitner by saturation of benzonitrile and *p*-tolunitrile with SO_3 vapors [6, 7].

I

Later it was established that the cyano group of cyanogen chloride [8], tribromo-, dichloro- [9], trichloroacetonitriles [10], α-hydrotetrafluoropropionitrile [11] reacts with SO_3 differently, with formation of another type of heterocycle: 2,6-disubstituted 1,4,3,5-oxathiadiazine-4,4-dioxides (II), isomeric to heterocycle I [8-10].

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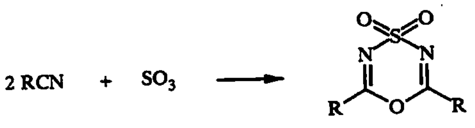
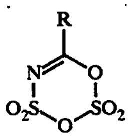


II

Investigation of the reaction of nitriles with SO_3, including early stages of the reaction [12-23], have made it possible to explain the nature of this dual behavior of the cyano group in cycloaddition with SO_3 and to develop approaches allowing us to predict the orientation of the reaction, and also to ensure its goal-oriented behavior.

In [6-14] it is shown that nitriles react with SO_3 with formation of a series of heterocyclic compounds: 1,2,3,5-oxathiadiazine-2,2-dioxides I, 1,4,3,5-oxathiadiazine-4,4-dioxides II, and 1,3,2,4,5-dioxadithiazine-2,2,4,4-tetroxides III.

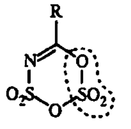


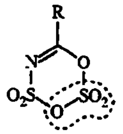
III

It has been established [9, 12, 19, 20, 23] that formation of compound III in the nitrile$-SO_3$ system is a reaction which is general and typical of nitriles. Heterocycles III are obtained from aromatic, alicyclic (including unsaturated), and also halogen-substituted nitriles [9, 17, 19, 20, 24]. The molecular structure of three typical representatives of tetroxides III (R = C_6H_5, *n*-$NO_2C_6H_4$, CCl_3) has been proven by x-ray diffraction [19].

Kinetic and spectroscopic investigations have established the presence of donor–acceptor complexes $RCN \cdot SO_3$ in the nitrile$-SO_3$ system and their participation in formation of azines III [17, 25]. It has been shown that the structure of the complexes depends on the nature of the substituent R in the nitrile [12, 17, 25].

The cyclic adducts III react easily with nitriles and other nucleophilically active compounds [14, 16, 21-23]. These reactions, depending on the electronic properties of the substituents R, occur in two directions: reactions in which the C−O bond in the ring of III is broken, and reactions with retention of the indicated bond. Ultimately, this is associated with cleavage of SO_3 during the reaction from different positions in the ring of III.





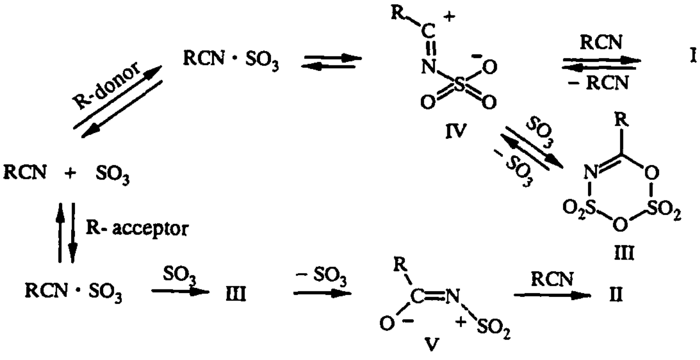
The first direction is typical for heterocycles III having donor and relatively weak acceptor substituents (R = C_6H_5, *n*-$CH_3C_6H_4$, *n*-ClC_6H_4, *n*-$NO_2C_6H_4$, CH_3, C_2H_5, etc.); the second direction is typical for tetroxides III having strong acceptor substituents (R = 3,5-$(NO_2)_2C_6H_3$, CCl_3, CBr_3, $CHCl_2$, $CHCl_2CCl_2$).

It has been shown that heterocycles III having donor substituents form 1,2,3,5-oxathiadiazine-2,2-dioxides I with the corresponding nitriles, while tetroxides III having strong acceptor substituents yield dioxides II with nitriles [16, 18, 20, 26].

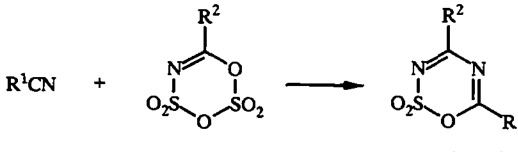
Literature data [9, 12, 17, 26] allow us to consider cyclic adducts III as a key structure in reaction of nitriles with SO_3, determining the direction of the reaction in this system.

According to the scheme presented, formation of isomeric diazines I and II is represented by processes of (4+2)-cycloaddition, occurring with participation of different types of 1,4-dipoles (IV, V) and nitriles as 1,2-dipolarophiles. Dipoles IV may be generated both from SO_3 and nitriles having donor substituents [10, 27] and from tetroxides III: Dipoles V are generated only from tetroxides III having strong acceptor groups.

Considering data on reaction of nitriles with SO_3, relatively simple synthesis methods have been developed with close to quantitative yields for a broad range of heterocyclic compounds I (R = *p*-ClC_6H_4, *m*-ClC_6H_4, *m*-$NO_2C_6H_4$, *p*-$NO_2C_6H_4$, $C(CH_3)_3$ etc.) [13, 14]. Different solvents (CH_2Cl_2, $CHCl_3$, CCl_4, SO_2) and a broad temperature range (−80 to −20°C) have been used to carry out the reaction [12].



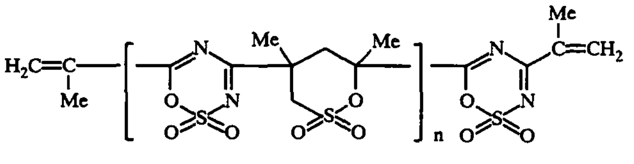
In [17, 18], methods are described for obtaining diazines I with different substituents R^1 and R^2. In this case, in the reaction with nitriles R^1CN ($R^1 = C_6H_5$, p-$CH_3C_6H_4$), tetroxides III have been used ($R^2 = p$-$NO_2C_6H_4$).



I ($R^1 \neq R^2$)

The presence of unsaturated groups ($>C{=}C<$), in the nitrile molecule which (like the cyano group) can react with SO_3 significantly complicates formation of the oxathiadiazine ring in reactions of these nitriles with SO_3.

Investigation of the reaction of SO_3 with a series of α,β-unsaturated nitriles (acrylonitrile, methacrylonitrile, crotononitrile, β,β-dimethylacrylonitrile, 1-cyclohexenecarbonitrile) made it possible to determine some characteristic patterns in the effect of the nature of the substituents on the direction of competing reactions and to develop methods for obtaining heterocycles I with unsaturated substituents ($R^1 = R^2$) [4, 27, 28]. In reaction of methacrylonitrile with SO_3 in liquid SO_2 (−20°C), we obtain dioxide I ($R^1 = R^2 = CH_2 = CCH_3$), along with which the oligomer (VI) is isolated, containing alternating oxathiadiazine and δ-sultone rings [28].



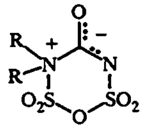
VI

n = 4-6

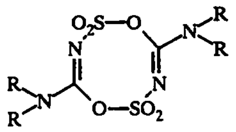
Reaction of the nitrile of cyclohexenecarboxylic acid with SO_3 proceeds similarly [27]. Under the same conditions, from acrylonitrile and SO_3 only the corresponding oligomer of type VI is obtained. Nitriles having methyl groups in the β position (crotononitrile and β,β-dimethylacrylonitrile) react with SO_3 under analogous conditions with participation of only the C=C bond [27].

As follows from literature data, oxathiadiazine systems I obtained by reaction of SO_3 and cyanides XCN ($X = R_2\ddot{N}$, $R\ddot{O}$, $R\ddot{S}$) having p-donor substituents are quite promising with a view toward synthesis and biological activity [3, 4, 29]. Since in the indicated cyanides the substituent can react with SO_3, due to which its electronic properties may change over the course of the reaction from donor to strong acceptor, $XCN-SO_3$ systems are characterized by greater potential (compared with nitriles) for chemical reactions including competing reactions (formation of isomeric heterocycles I and II) and also processes accompanied by migration of the X group [8, 24, 30, 31].

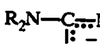
A recent study of the reaction of cyanamides (dimethyl-, diethyl-, dibutylcyanamides, N-cyanopiperidine, N-cyanopyrrolidine, N-cyanomorpholine) with SO_3 showed that in this system, along with isomeric heterocycles I and II, depending on the reaction conditions cyclic betaines (VII) and eight-membered heterocyclic systems (4,8-disubstituted 1,5,2,6,3,7-dioxadithiadiazocine-2,2,6,6-tetroxides (VIII)) are formed.

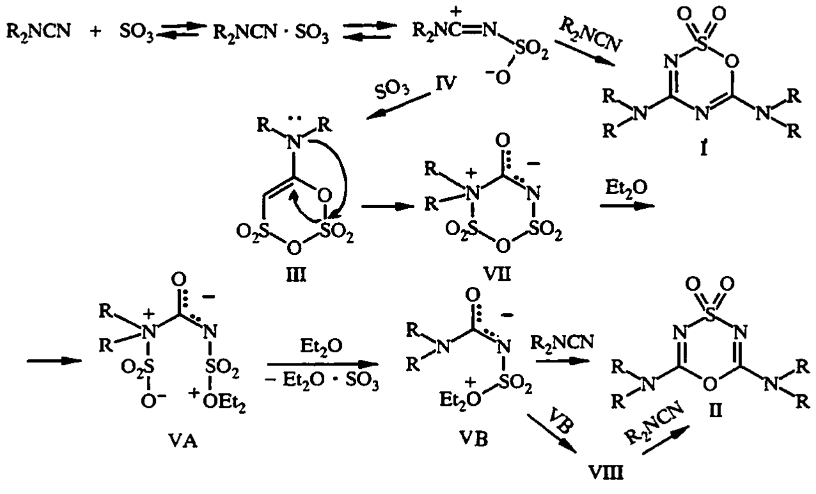


VII



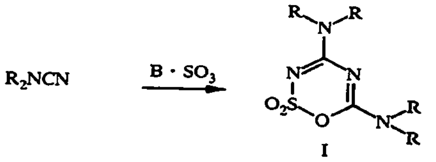
VIII

It has been established that when introducing SO_3 into an excess of cyanamide (CH_2Cl_2, −80°C), the primary orientation of the reaction is formation of S,S-dioxides I. A different orientation of the reaction of cyanamides with SO_3 occurs when the ratio between them and the order of mixing are changed. When introducing cyanamides into an excess of SO_3 under the same conditions, the starting components are bound into adducts, which are probably cyclic betaines VII. When the latter are treated with ether, they are converted to heterocycles VIII. The structure of compounds VIII has been proven by x-ray diffraction [4]; they are dimers of bipolar species of type V, sulfonylureidates  $R_2N{-}\underset{O^-}{C}{=}\overset{+}{N}SO_2$, generated from adducts VII. The reaction of cyanamides with SO_3 is represented by the scheme:

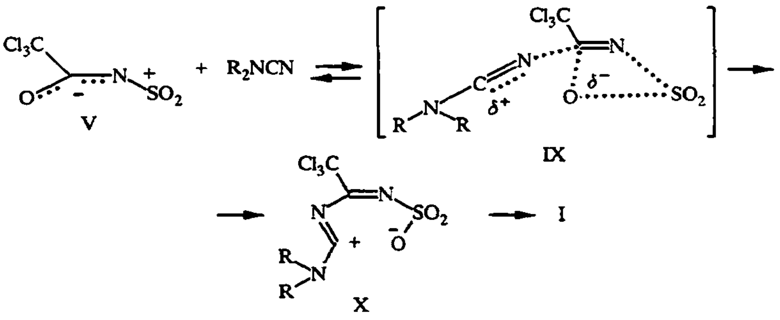


It is hypothesized that cyanamides form complexes with SO_3 with participation of the nitrogen atom of the cyano group, having the highest charge according to data in [32, 33], in coordination with SO_3. Further conversion of the zwitterion IV depends on the amount of SO_3 and cyanamide used in the reaction. With an excess of cyanamide, the reaction ends with formation of heterocycle I. With an excess of SO_3, the $R_2\ddot{N}$ of the cyanamide participates in the reaction along with the cyano group. In this case, formation of cyclic adducts VII is hypothesized, from which on treatment with ether the sulfonylureidates of type VA and VB are generated. The latter, reacted with cyanamides, yield compounds III, and on dimerization (representing a process of [4+4]-cycloaddition) form the heterocycles VIII.

Thus analysis of the reaction of cyanamides with SO_3 [3] shows that directed synthesis of diazine I is possible with exclusion of the competing orientation of the reaction of SO_3 with the $R_2\ddot{N}$ group of the cyanide. This is achieved by reducing the electrophilic reactivity of SO_3 due to its binding with bases into complexes. Thus by reaction of substituted cyanamides (N-cyanopiperidine, N-cyanomorpholine, N-cyanopyrrolidine, diethyl- and dimethylcyanamides) with complexes $B \cdot SO_3$ (B = Et_2O, Py) in methylene chloride or SO_2 (−80°C and above), the corresponding 1,2,3,5-oxathiadiazine-2,2-dioxides I are obtained in high yields [3].



Recently [2], a very simple and effective method has been developed for obtaining previously inaccessible compounds I having simultaneously strong acceptor ($R^1 = CCl_3$) and donor ($R^2 = NR_2$) groups, by reaction of cyanamides with the tetroxide III ($R = CCl_3$)−pyridine system. Since the indicated system is a source of the bipolar species V ($R = CCl_3$) [4] and reacts with cyano-containing compounds with formation of heterocycles II, it was unexpected to obtain heterocycles of another type from SO_3 and cyanamides under these conditions: 1,2,3,5-oxathiadiazines I. Probably the conversion of zwitterions V to heterocycle I includes nucleophilic attack by the cyano group on the electron-deficient carbon atom of species V with formation of intermediate X through the transition state IX.



The scheme including participation of 1,4-dipoles of type IV in this reaction [34] is unlikely.

This analysis of the reaction of nitriles and cyanamides with SO_3 allows us to more confidently interpret data available in the literature on reactions of esters of cyanic acid and other cyanides with SO_3 and to predict the directions of conversions in these and other similar systems. Contradictory data on the nature of the products of reaction of cyanates with SO_3 and specifically formation of compounds I in some papers [35] and II in others [35, 36] may be explained by the fact that in this system, as in reactions of cyanamides with SO_3, a mixture of isomeric products I and II is formed.

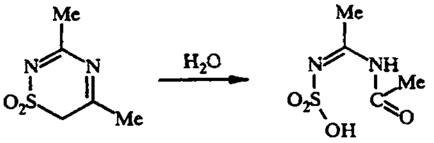
2. STRUCTURAL FEATURES

The structure of 1,2,3,5-oxathiadiazine-2,2-dioxides I has been proven by PMR and IR spectroscopy [3, 13, 14], mass spectrometry [37], and chemical conversions [6, 27, 28]. The molecular structure of one representative of this class of heterocycles I, $R^1 = CCl_3$, $R^2 = N(CH_2)_5$, has been established by x-ray diffraction [30].

In considering the structural features of diazines I, an important point is assessment of the effect of the nature of the substituents R^1 and R^2 on the change in structural and electronic characteristics and ultimately on the stability of the ring and the orientation of its reaction (rupture of specific bonds in the ring I). Special studies including the use of quantum chemical calculations and x-ray diffraction have not been done in this direction.

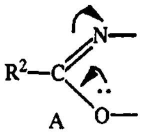
Analysis of literature data shows that the stability of the 1,2,3,5-oxathiadiazine ring I considerably depends on the nature of the substituents R^1 and R^2, to a larger degree on R^2. Using data from these investigations, we may judge the possibility or impossibility of obtaining 1,2,3,5-oxathiadiazine-2,2-dioxides, and also the most likely routes for opening of the ring I. Heterocycles I having both identical ($R^1 = R^2$) aryl (C_6H_5, p-$CH_3C_6H_4$, m-$NO_2C_6H_4$, p-$NO_2C_6H_4$, p-ClC_6H_4), unsaturated ($CH_2 = CCH_3$, 1-cyclohexenyl), p-donor (NMe_2, NEt_2, piperidino, morpholino) and different ($R^1 = p$-$NO_2C_6H_4$, $R^2 = NMe_2$, NEt_2, piperidino, morpholino) substituents are relatively stable. The stability of the ring I is preserved even when substituents R^1 and R^2 are present which have different electronic properties over a broad range from strong acceptor ($R^1 = CCl_3$) to strong donor ($R^2 = NMe_2$, NEt_2, piperidino, mopholino).

From heterocycles I having alkyl substituents, only compounds ($R^1 = R^2$) with bulky *tert*-butyl groups are obtained. The heterocycle I ($R^1 = R^2 = CH^3$) is so unstable that during isolation from the reaction mixture it is easily hydrolyzed to N-acetyl-N′-sulfacetamidine [7].



Rings I with strong acceptor substituents R^2 in general are not obtained.

The stability of ring I depends on many factors, including the state of the C–O bond, the electrophilicity of the $C_{(6)}$ atoms and their accessibility in attack by nucleophilic reagents such as water. The C–O bond may be stabilized by resonance (p, π-shift) for the condition that the moiety (A) in ring I is flat.


A

This is favored by π- and p-donor substituents R^1. The latter also promote a decrease in the electrophilic reactivity of the $C_{(6)}$ atoms. Bulky groups R^2 = $C(CH_3)_3$ block access to these centers for nucleophilic reagents, thus ensuring the stability of heterocycles I.

A change in the nature of the substituents R^1, R^2 also is responsible for a change in the orientation of the reaction of rings I. Thus when the donor substituents R^1 are replaced by strong acceptor substituents, it is not the C–O bond which breaks but rather the S–O bond of the ring [2]. This is quite consistent with x-ray diffraction data [30], from which it follows that in rings of the I type (R^1 = CCl_3, R^2 = piperidino), the S–O bond (1.632 Å) is significantly longer than the analogous bond (1.610 Å) in the cyclic trimer SO_3 [38].

3. CHEMICAL PROPERTIES, MAJOR DIRECTIONS OF THE REACTION

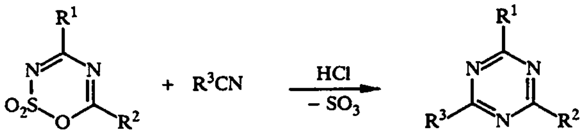
The chemical behavior of 1,2,3,5-oxathiadiazine-2,2-dioxides is determined especially by the presence of an SO_3 moiety in the ring and the presence of several electron-deficient reaction centers ($C_{(4)}$, $C_{(6)}$, S), capable of competing for reaction with nucleophilic reagents.

In this review, known reactions of heterocycles I are systematized according to the rupture of certain bonds in heterocycle I:

- reactions of substitution of the SO_3 moiety (rupture of the S–N and C–O bonds);
- reactions occurring with rupture of the C–O bond;
- reactions occurring with rupture of the S–O bond.

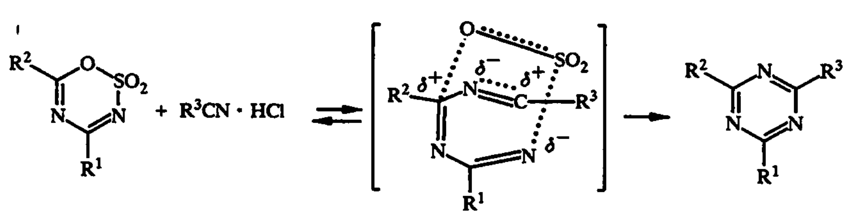
3.1. Substitution of the SO_3 Moiety in the Ring

3.1.1. Formation of 1,3,5-Triazines. An interesting and promising direction of the reaction of compounds I is their conversion to symmetric triazines. It has been shown that on heating with nitriles in the presence of HCl, heterocycles I are easily converted to triazines (XI) [3, 39].


XI

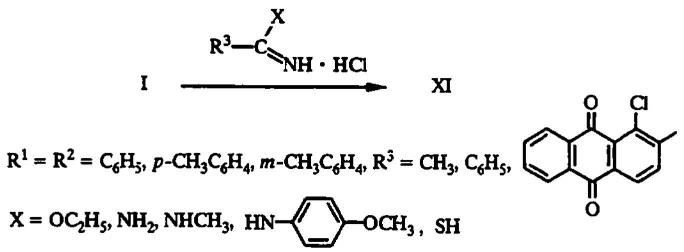
$R^1 = R^2 = C_6H_5$, p-$CH_3C_6H_4$, $R^3 = CCl_3$

Reaction of heterocycles I with nitriles and other C≡N-containing compounds is considered as a process of [4+2]-cycloaddition, in which oxathiadiazinedioxide I plays the role of the 1,4-dipole while the reagent plays the role of the 1,2-dipolarophile.



XI

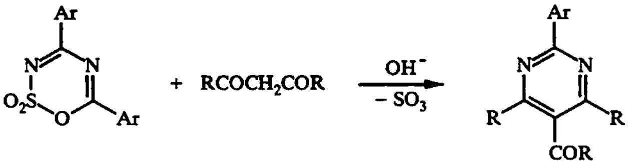
Formation of triazines XI is also observed in reaction of oxathiadiazinedioxides I with hydrochlorides of iminoesters, amidines, amides [41]. These reactions can be used to obtain triazines XI both with identical ($R^1 = R^2 = R^3$) and with different ($R^1 = R^2 \neq R^3$) substituents.



$R^1 = R^2 = C_6H_5$, p-$CH_3C_6H_4$, m-$CH_3C_6H_4$, $R^3 = CH_3$, C_6H_5,

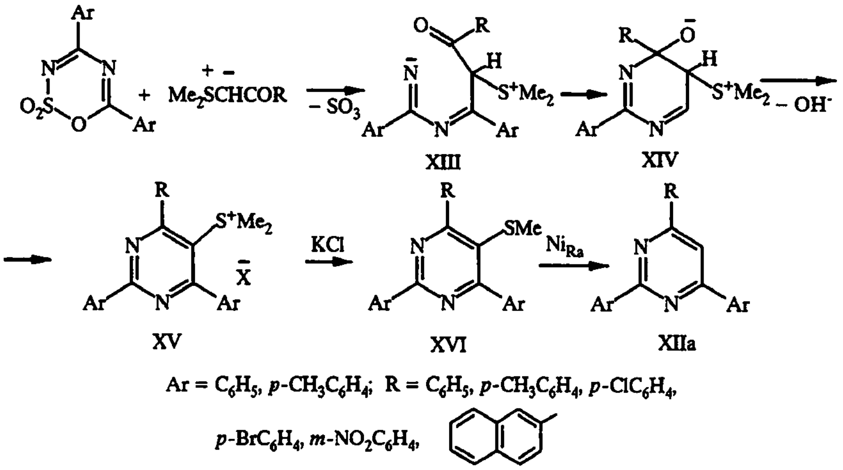
X = OC_2H_5, NH_2, $NHCH_3$, HN–C$_6$H$_4$–OCH$_3$, SH

3.1.2. Formation of Pyrimidines. A direction of the reaction of oxathiadiazine rings I which is important from a synthetic viewpoint is their conversion to pyrimidine systems (XII). It has been shown that this reaction easily occurs on reaction of heterocycle I with 1,3-dicarbonyl compounds in the presence of base [39].



XII

Sulfonium ylides stabilized by a carbonyl group have been successfully used to obtain pyrimidine systems from heterocycles I [3, 39]. It is hypothesized that the reaction proceeds according to the scheme:

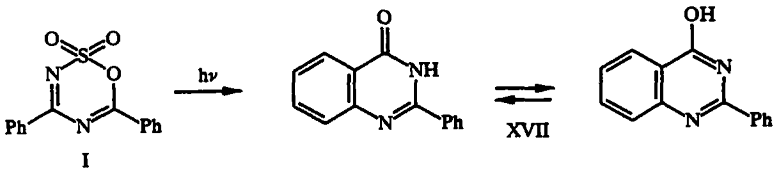


Ar = C_6H_5, p-$CH_3C_6H_4$; R = C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4,

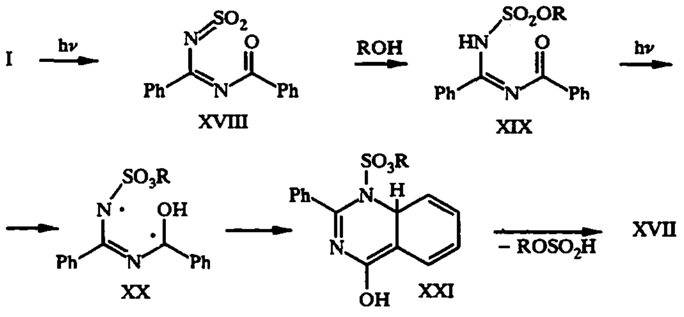
p-BrC_6H_4, m-$NO_2C_6H_4$,

The authors of [39] propose that the reaction includes nucleophilic attack by the ylide on the carbon atom $C_{(6)}$ of heterocycle I and elimination of SO_3 with formation of intermediates (XIII and XIV), which in the presence of base are easily converted to the sulfonium salt of pyrimidine (XV). The latter on heating in KCl solution yields methylthiopyrimidines (XVI). Pyrimidines XII are obtained by reductive desulfurization of sulfides XVI using Raney nickel.

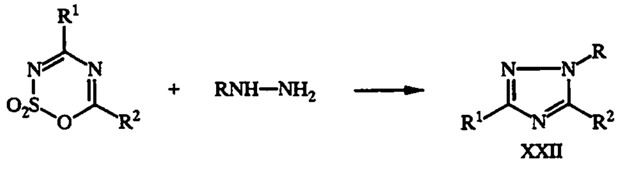
3.1.3 Formation of Quinazolines. An interesting photochemical conversion of a diphenyl-substituted compound I ($R^1 = R^2 = Ph$) to 2-phenyl-4(3H)-quinazolinone (XVII) has been accomplished by the authors of [40]. In recyclization of the 1,2,3,5-oxathiadiazine ring I to a benzopyrimidine ring, the phenyl substituent of heterocycle I participates.



The reaction occurs in the presence of alcohol. The proposed scheme includes opening of the ring I (rupture of the S–O bond) with formation of an intermediate (XVIII) and then on treatment with alcohol, formation of aminosulfonate (XIX). In the next stage, the biradical (XX) is formed, which is converted to the bicyclic system (XXI). On cleavage of the alkylsulfonate from XXI, the latter is converted to the quinazoline XVII.



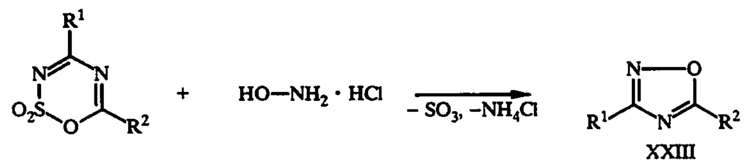
3.1.4. Formation of 1,2,4-Triazoles. Compounds I are relatively easily converted to five-membered heterocycles. Thus 1,2,4-triazoles (XXII) are obtained in high yields by reaction of heterocycles I with hydrazines [41, 42].



$R^1 = R^2 = C_6H_5$, p-$CH_3C_6H_4$, m-$CH_3C_6H_4$; $R = C_6H_5$, p-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$

Analogous products XXII with the corresponding substituents R are formed on reaction of the same heterocycles I with semicarbazide, benzhydrazide, aminoguanidine, and thiosemicarbazide [39].

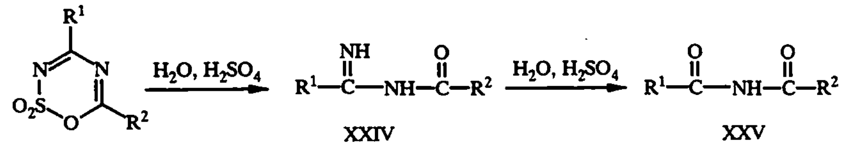
3.1.5. Formation of 1,2,4-Oxadiazoles. 1,2,3,5-Oxathiadiazine-2,2-dioxides I on heating with hydroxylamine hydrochloride are converted to 1,2,4-oxadiazoles (XXIII) [39]. This facile reaction may be used as a method for obtaining 1,2,4-oxadiazoles in high yields [39].



3.2. Reactions Occurring with Rupture of the C−O Bond

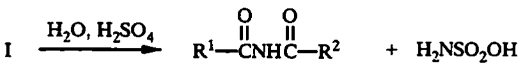
3.2.1. Hydrolysis. 1,2,3,5-Oxathiadiazine-2,2-dioxides easily react with water in acid medium with formation [depending on the nature of the substituents (R^1, R^2) in heterocycle I and the conditions] of N-acylamidines (XXIV) or acylamides (XXV).

It has been shown [6, 7] that on hydrolysis (0-20°C) of dioxides I ($R^1 = R^2 = C_6H_5$, $p\text{-}CH_3C_6H_4$), the amidines XXIV are obtained in high yields and then are converted to the corresponding amides XXV.



Under analogous conditions, amidines XXIV are not isolated from compounds I ($R^1 = R^2 = p\text{-}ClC_6H_4$, $m\text{-}NO_2C_6H_4$, $p\text{-}NO_2C_6H_4$; $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = C_6H_5$, $p\text{-}CH_3C_6H_4$), but rather amides XXV are obtained [13].

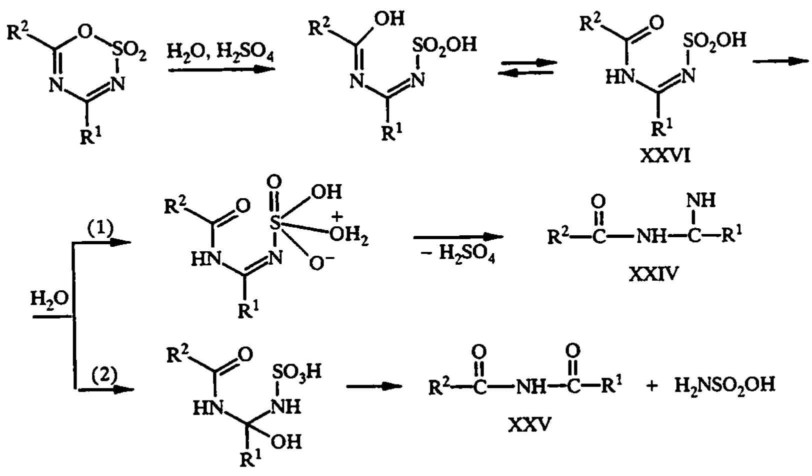
In hydrolysis of heterocycles I having unsaturated substituents ($R^1 = R^2 = CH_2{=}CCH_3$-, 1-cyclohexenyl), the corresponding acylamides XXV and sulfamic acid are isolated from the reaction mixtures [21].



$$I \xrightarrow{H_2O,\ H_2SO_4} R^1-\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}-R^2 + H_2NSO_2OH$$

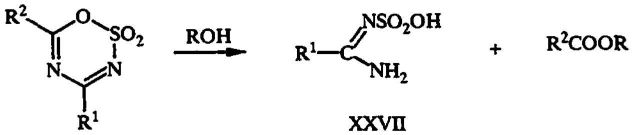
XXV

According to some data [6, 7, 17, 27], hydrolysis is a multistep process and occurs according to the following scheme:



On attack by a nucleophile (water) on the carbon atom $C_{(6)}$, the C−O bond in ring I is broken and N-acetyl-N′-sulfamidine (XXVI) is formed. Hydrolysis of the latter, depending on the nature of R^1 and R^2, can occur in two directions with participation of the $C_{(6)}$ and S atoms. In the first case (direction 1), the reaction ends with formation of amidines XXIV and sulfuric acid; in the second case (direction 2), the reaction ends with formation of amides XXV and sulfamic acid.

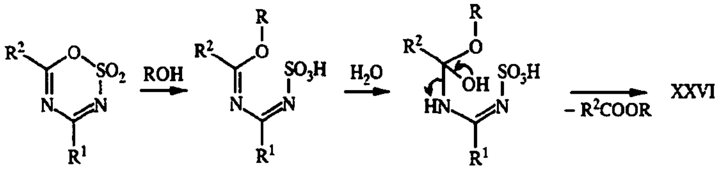
3.2.2. Alcoholysis. On reaction of dioxides I ($R^1 = R^2 = C_6H_5$, $p\text{-}CH_3C_6H_4$) with alcohol in benzene in the presence of a small amount of water, N-sulfamidines (XXVII) and esters are obtained [6, 7, 17].



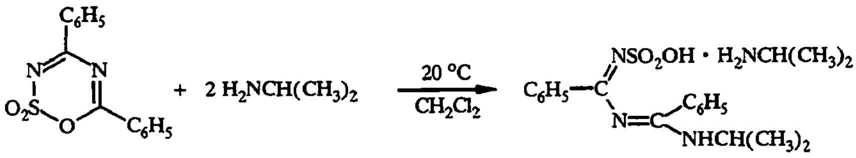
XXVII

An analogous conversion is accomplished when using dioxide I ($R^1 = R^2 = CH_2{=}CCH_3-$) and methanol. The reaction easily proceeds at room temperature with close to quantitative yields, and is a convenient method for obtaining monomers: N-sulfonylamidines of the methacryl series [28].

Alcoholysis probably proceeds according to the following scheme:

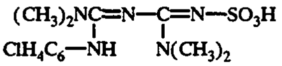


3.2.3. Aminolysis. The ring of compound I easily reacts with amines (rupture of the C–O bond). Thus when mixing heterocycle I ($R^1 = R^2 = C_6H_5$) with isopropylamine at room temperature, the corresponding salt of 1,3-diphenyl-1-isopropylamino-diimidosulfonic acid (XXVIII) is obtained in high yield [40].



XXVIII

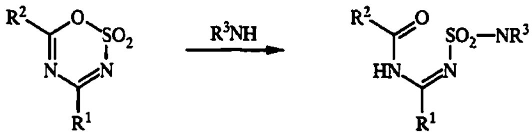
The reaction of compound I ($R^1 = R^2 = N(CH_3)_2$) with *p*-chloroaniline occurs analogously at 40°C with formation of 1,1,4,4-tetramethyl-2-(4-chlorophenyl)- biguanido-5-sulfonic acid [29].



$$(CH_3)_2N\underset{\displaystyle ClH_4C_6-NH}{C}{=}N-\underset{\displaystyle N(CH_3)_2}{C}{=}N-SO_3H$$

3.3. Reactions Occurring with Rupture of the S–O Bond

3.3.1. Reaction with Amines. Recently [3] it has been established that heterocycles I having amino groups as substituents are easily converted to sulfonylamidines (XXIX) and sulfonylguanidines (XXX) when treated with ammonia and amines (CH_2Cl_2, −60°C or higher).



XXIX, XXX

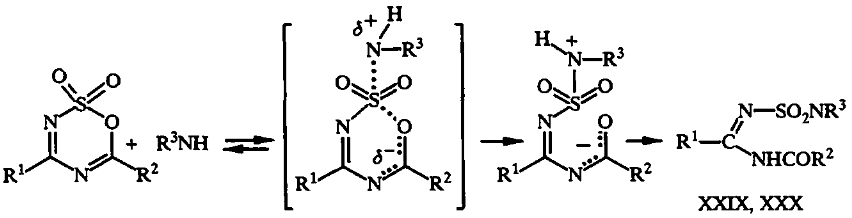
XXIX $R^1 = CCl_3$, $R^2 = (CH_2)_5N$, $R^3 = (CH_2)_5$; $R^1 = CCl_3$, $R^2 = (CH_2)_5N$, $R^3 = H_2$;

$R^1 = CCl_3$, $R^2 = (C_2H_5)_2N$, $R^3 = (CH_2)_2O(CH_2)_2$; $R^1 = CCl_3$, $R^2 = (C_2H_5)_2N$, $R^3 = (CH_3)_2$.

XXX $R^1 = R^2 = (CH_2)_5N$, $R^3 = (CH_2)_5$; $R^1 = R^2 = (CH_2)_5N$, $R^3 = (C_2H_5)_2$

The reaction of the indicated compounds I occurs with rupture of the S–O bond. The presence of several electron-deficient centers (the $C_{(6)}$ and S atoms) in the oxathiadiazine ring I is responsible for the competition for nucleophilic reagents in the reactions.

The strong donor group $R_2\ddot{N}$ significantly decreases the electrophilicity of the $C_{(6)}$ atom, and in this case reaction of the nucleophilic reagent with the sulfur atom becomes preferred. The presence of the strong electron-acceptor group CCl_3, bonded to the $C_{(4)}$ atom, favors this direction of the reaction, occurring according to the probable scheme:



XXIX, XXX

The data in this review suggest that 1,2,3,5-oxathiadiazine-2,2-dioxides are important and promising and make it possible to predict the route to take in further study of these compounds. We may assume that investigations in this direction will allow us to not only reveal the potential of 1,2,3,5-oxathia-diazine-2,2-dioxides but also to open the way to similar novel types of heterocyclic systems, which will make it possible to design methods based on them for obtaining previously inaccessible heteroatomic compounds.

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