SYNTHESIS OF THIAZOLO- AND OXAZOLO[3,2-*a*]PYRIDINIUM SYSTEMS (REVIEW)

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The published data on the synthesis of thiazolo- and oxazolo[3,2-a]pyridinium systems are systematized.

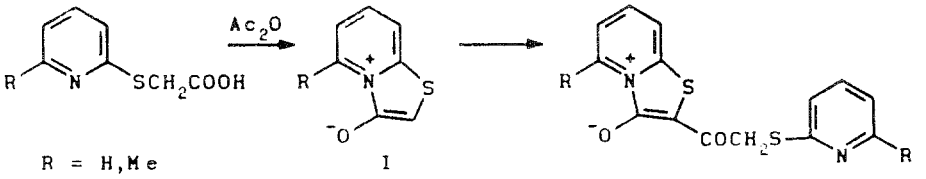
Thiazolo- and oxazolo[3,2-*a*]pyridinium derivatives are analgesics [1, 2], display anti-inflammatory [3] and hypoglycemic [4] activity, and are used as surface-active substances (surfactants) and antistatic agents [5]. Dyes can be obtained from them [6-8].

A review [9], which was published in 1981 and basically correlated the review author's research results, was devoted to the chemistry of thiazolo[3,2-*a*]pyridinium compounds. No reviews on the synthesis and properties of oxazolo[3,2-*a*]pyridinium compounds are available. In our review we correlate the methods used to obtain thiazolo- and oxazolo[3,2-*a*]pyridinium systems.

1. CYCLIZATION OF ACIDS AND THEIR DERIVATIVES

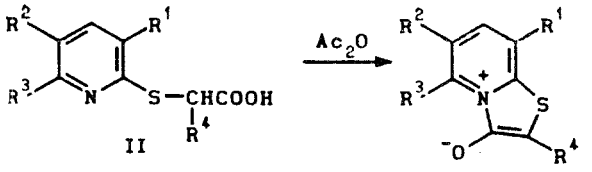
The first information regarding the synthesis of thiazolo[3,2-*a*]pyridinium systems was published in 1951 [10]. The authors of this publication reported that thiazolo[3,2-*a*]pyridinium 3-oxide I is formed when (2-pyridylthio)acetic acid is heated in acetic anhydride to 140°C. It was later established [11, 12] that, under the indicated conditions, the reaction does not stop at this step but continues with acetylation in the 2 position.

Compound I is formed by brief heating in acetic anhydride at 40-50°C or in the case of maintenance in acetonitrile in the presence of dicyclohexylcarbodiimide at 0-10°C and cannot be isolated in the individual state from the solutions.



The cyclization of (2-pyridylthio)acetic acids with simultaneous acylation of the thiazole ring proceeds under the influence of trifluoroacetic anhydride, acetyl chloride, chloroacetyl chloride, ethoxalyl chloride, cinnamic and benzoic acid chlorides, and phosgene [13].

In the case of (2-pyridylthio)acetic acids that contain alkyl or aryl groups in the α position, the subsequent acylation of the thiazole ring does not occur. Thus 2-(2-pyridylthio)-2-alkyl(aryl)acetic acids II are readily cyclized by the action of acetic acid in the presence of pyridine [14, 15].



R^1=H, OH, NO_2, OAc; R^2=H, NO_2; R^3=H, Me; R^4=Me, Ph, *p*-$NO_2C_6H_4$

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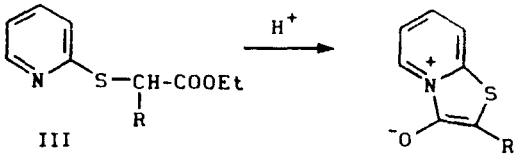
3-(2-Pyridylthio)alkanoic acids do not undergo cyclization under the influence of acetic anhydride [16].

Similarly, (2-pyridylthio)acetic acid amides [17] and esters [18] III undergo cyclization under the influence of acids to form thiazolo[3,2-*a*]pyridinium compounds:

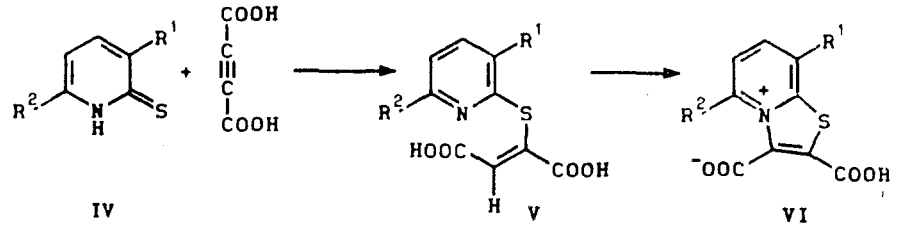


III

R = Ph

Thiazolo[3,2-*a*]pyridinium systems have been obtained without prior isolation of the (pyridylthio)acetic acids by the reaction of pyridine-2-thiones with α-halo acids in toluene by prolonged refluxing or with their acid halides in the presence of acetic anhydride [19].

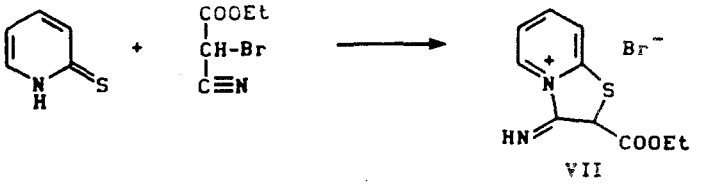
Pyridine-2-thiones IV react with acetylenedicarboxylic acid in anhydrous ethyl acetate to give trans-2-carboxydihydrothiazolo[3,2-*a*]pyridinium 3-carboxylates VI [20] through a step involving the formation of (2-pyridylthio)fumaric acid V:



IV V VI

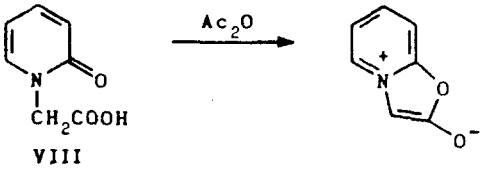
IV - VI R^1 = H,OH,OEt; R^2 = H,Me

The reaction of pyridine-2-thione with thyl bromocyanoacetate leads exclusively to cyclization product VII [21].



VII

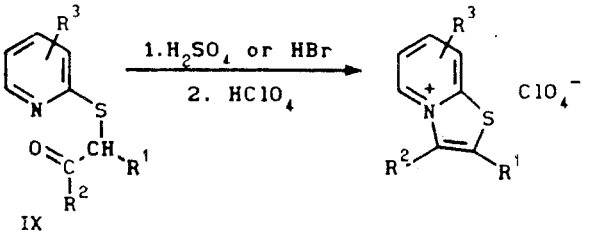
Cyclodehydration under the influence of acetic anhydride in order to synthesize oxazolo[3,2-*a*]pyridinium salts has been realized only in the case of (2-oxo-1-pyridyl)acetic acid (VIII) [22].



VIII

2. CYCLIZATION OF CARBONYL COMPOUNDS

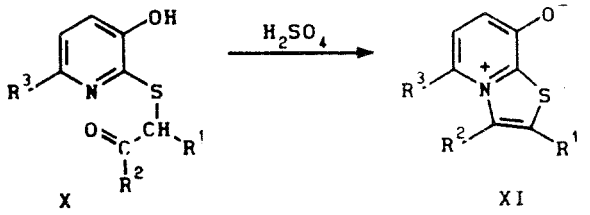
In 1964 two groups of researchers [23, 24] virtually simultaneously demonstrated that 2-pyridyl sulfides with a carbonyl group in the β position relative to the sulfur atom, under the influence of sulfuric or hydrobromic acid, undergo cyclodehydration to give thiazolo[3,2-*a*]pyridinium salts. The cyclodehydration of (2-pyridylthio) acetones IX or their hydrohalides under the influence of 48% hydrobromic acid [23, 25] proceeds with prolonged heating, whereas the reaction takes place in the cold under the influence of sulfuric acid [24-27] (see scheme, top of next page).



IX

$R^1 = R^3 = H, Alk;\ R^2 = Alk$

Inner thiazolo[3,2-*a*]pyridinium salts XI are formed in the action of sulfuric acid on (pyridylthio) carbonyl compounds X, which contain a hydroxy group in the 3 position of the pyridine ring [28].



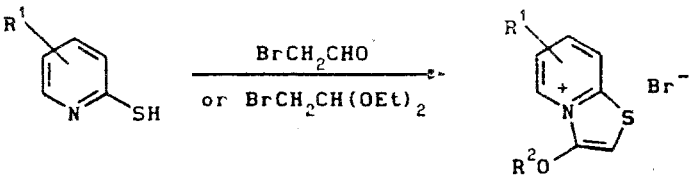
X XI

$R^1 = R^3 = H, Alk;\ R^2 = Alk$

(2-Pyridylthio)acetaldehyde acetals obtained by the reaction of pyridine-2-thione with α-halo acetals also may undergo cyclization [24, 26]. The acetals were initially subjected to hydrolysis with hydrochloric acid and then to cyclization under the influence of sulfuric acid. Bradsher and Lohr assumed that the hydrolysis gives a (2-pyridylthio)acetaldehyde, which also undergoes cyclization.

In [28] it is asserted that the reaction of pyridine-2-thione with α-halo acetals in DMF in the presence of K_2CO_3 with heating (15 h) leads to the immediate formation of (2-pyridylthio)acetaldehyde, which then cyclizes under the influence of sulfuric acid.

In later research [29] spectral methods were used to establish that pyridine-2-thiones XII react with α-bromoacetaldehyde and its diethylacetal in the absence of a base to give dihydrothiazolo[3,2-*a*]pyridinium salts XIII.



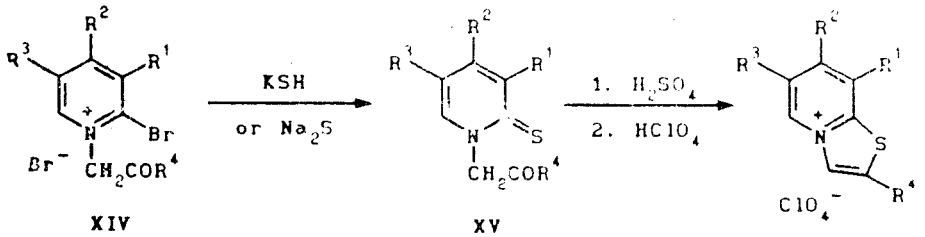
XII XIII

$R^1 = H, Me;\ R^2 = H, Et$

It is assumed [30] that the reaction of 2-mercapto-3-(5-nitro-2-pyridylamino)pyridine with the diethylacetal gives the corresponding (2-pyridylthio)acetaldehyde diethylacetal, which, under the influence of hydrochloric acid (5°C), undergoes cyclization to a dihydrothiazolo[3,2-*a*]pyridinium derivative.

It has been established [4] that thiazolo[3,2-*a*]pyridinium 8-oxide is formed in the reaction of 3-hydroxypyridine-2-thione with bromoacetaldehyde dimethylacetal.

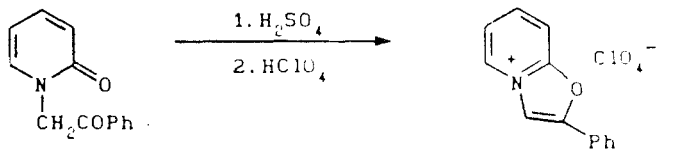
1-Acylalkylpyridine-2-thiones XV, obtained from 2-bromo-1-acylalkylpyridinium halides XIV and KSH or Na_2S, also undergo cyclodehydration under the influence of strong acids [4, 27, 31].



XIV XV

$R^1 = R^2 = R^3 = H, Me;\ R^4 = Ph, p\text{-}BrC_6H_4,\ t\text{-}Bu$

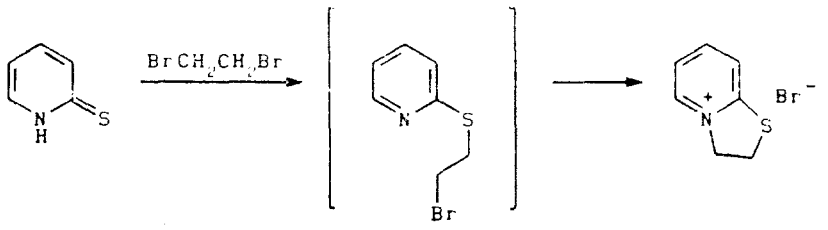
2-Phenyloxazolo[3,2-*a*]pyridinium salts were obtained by cyclization of 1-phenacyl-2-pyridone (XVI) by means of sulfuric acid [32].



XVI

3. CYCLIZATION THROUGH INTERMEDIATE B-HALO SULFIDES

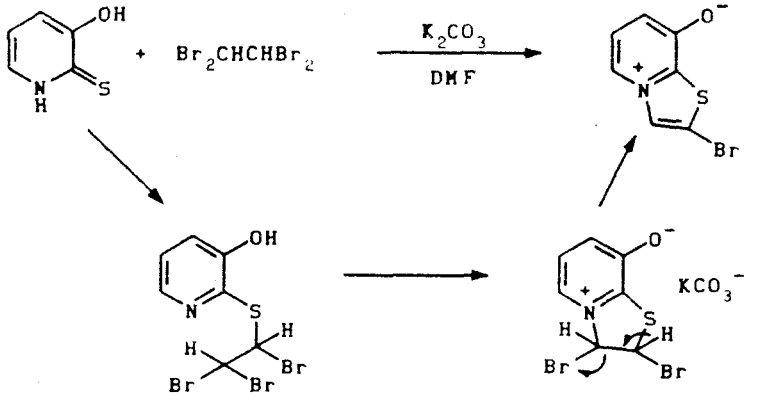
As a rule, the reaction of pyridine-2-thione with 1,2-dihaloalkanes does not stop at the step involving the formation of 2-(2-haloethyl) pyridyl sulfide XVII but proceeds with subsequent cyclization to give dihydrothiazolo[3,2-*a*]pyridinium salts [33-35].



XVII

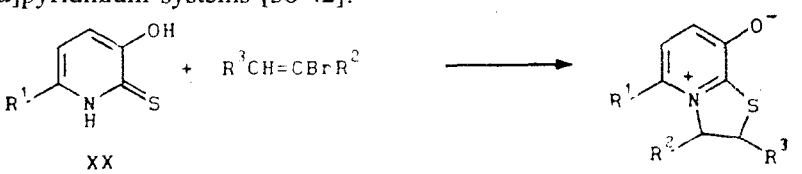
Similarly, dihydrothiazolo[3,2-*a*]pyridinium halides are formed in the reaction of 3,6-disubstituted pyridine-2-thiones with 1,2-dibromoethane and with methyl 2,3-dibromopropionate in methanol in the presence of sodium methoxide upon prolonged (20 h) stirring [36].

1,1,2,2-Tetrabromoethane reacts with 3-hydroxypyridine-2-thione in the presence of K_2CO_3 in DMF (20°C, 20 days) to give 2-bromothiazolo[3,2-*a*]pyridinium 8-oxide in 17% yield [37]. The yield of the final product decreases when the temperature is raised.



XVIII XIX

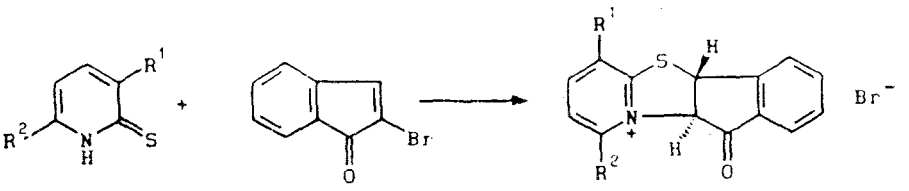
In the reaction of 6-substituted 3-hydroxypyridine-2-thiones XX with α,β-unsaturated α-bromo acids and their nitriles and amides one observes trans addition to the double bond and subsequent cyclization of the β-halo sulfide to give dihydrothiazolo[3,2-*a*]pyridinium systems [38-42].



XX

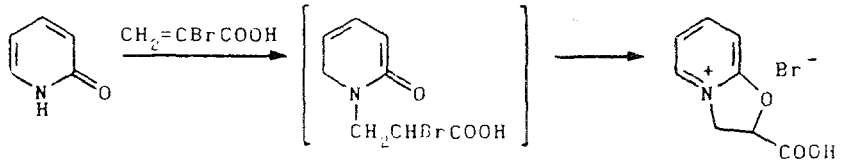
R^1=H, Me; R^2=COOH, CN, $CONH_2$; R^3= H, Me, Ph, COOH

The addition of a 3,6-disubstituted pyridine-2-thione to 2-bromoindenone XXI (a 2-bromo-2-cyclohexenone) leads to dihydrothiazolo[3,2-*a*]pyridinium salt XXII, which has a cis configuration [43].



XXI XXII

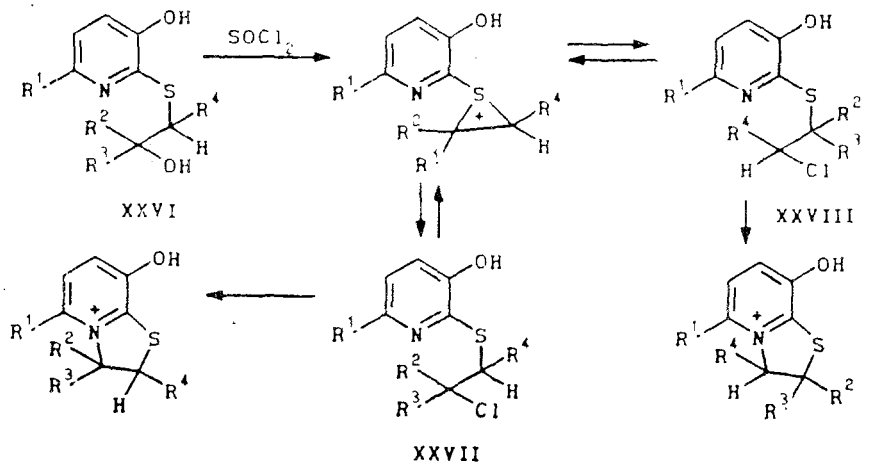
2-pyridone XXIII reacts with α-bromoacrylic acid to give 2-carboxy-2,3-dihydrooxazolo[3,2-*a*]pyridinium bromide XXV; no intermediate XXIV is isolated [33].



XXIII XXIV XXV

2-(2-Hydroxyethylthio)pyridines XXVI react with thionyl chloride at room temperature (12-14 h) to give two isomeric β-chloroalkylthiopyridines XXVII and XXVIII, which undergo cyclization to the corresponding dihydrothiazolo[3,2-*a*]pyridinium systems [44, 45]. Only one isomer (XXVII) is formed in the successive action of acetic and hydrochloric acids on sulfide XXVI [44].

The diazotization of (R)-2-amino-3-(3-hydroxy-6-methyl-2-pyridylthio)propionic acid leads to (R)-2-bromo-3-(3-hydroxy-6-methyl-2-pyridylthio)propionic acid, which, upon neutralization, undergoes cyclization to give a mixture of (S) and (R) isomers of 2-hydroxy-5-methyldihydrothiazolo[3,2-*a*]pyridinium 2-carboxylate hydrobromide [46].

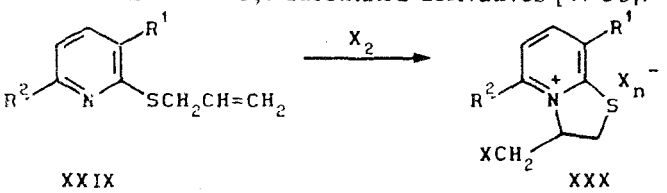


XXVI XXVIII XXVII

R^1, R^3 = H, Me; R^2 = Me, Ph; R^4 = H

4. ELECTROPHILIC HETEROCYCLIZATION OF UNSATURATED COMPOUNDS

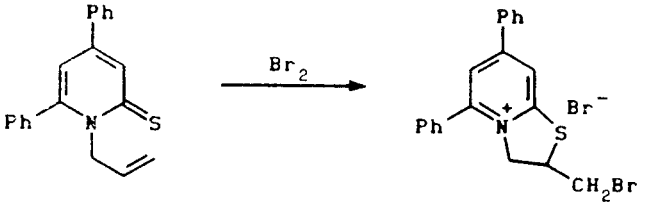
A large number of 3-halomethyl-2,3-dihydrothiazolo[3,2-*a*]pyridinium halides XXX were synthesized by cyclization of 2-(allylthio)pyridine and its 3- and 3,6-substituted derivatives [47-56].



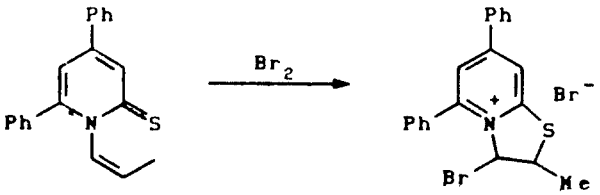
XXIX XXX

R^1 = H, OH, CN, COOH; R^2 = H, Me, Ar; X = Br, I; n = 1, 3

Rodinovskaya and coworkers [48] note the high regioselectivity of reactions involving the halo cyclization of 2-allylthiopyridines, which is due to the simultaneous action of acceptor (the halogen molecule) and donor (the pyridine nitrogen atom) electrons on the double bond of the allyl fragment.



XXXI

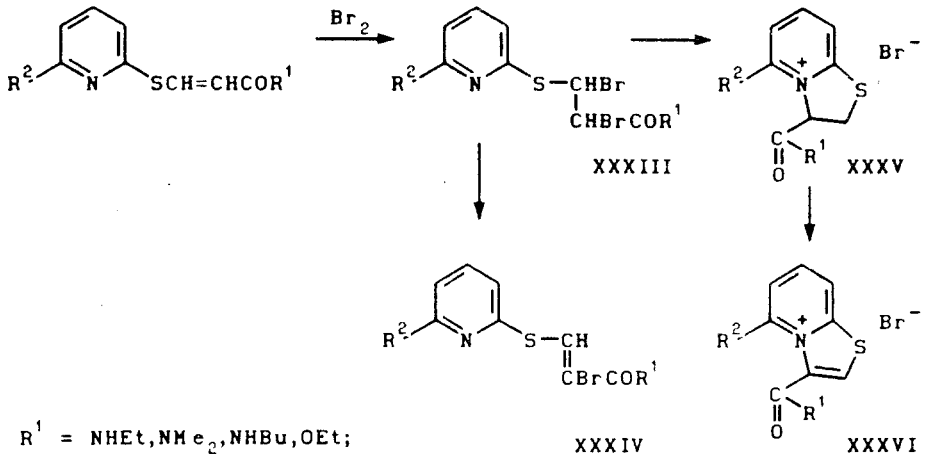


XXXII

The dihydrothiazolo[3,2-*a*]pyridinium system was also obtained in the cyclization of 1-allyl-4,6-diphenylpyridine-2-thione (XXXI) and 1-(1-propenyl)-4,6-diphenylpyridine-2-thione (XXXII) [57].

The halo cyclization of 2-allyloxypyridine [58, 59] and its 3,6-disubstituted derivatives [56] leads to 3-halomethyl-2,3-dihydrooxazolo[3,2-*a*]pyridiniumhalides.2-Halomethyl-2,3-dihydrooxazolo[3,2-*a*]pyridiniumhalides are obtained by halo cyclization of 1-allyl-2-pyridone [60-62].

Depending on the nature of the solvent and the substituents, the bromination of substituted 2-(vinylthio)pyridines leads to acyclic XXXIII and XXXIV and cyclic reaction products XXXV and XXXVI [63].



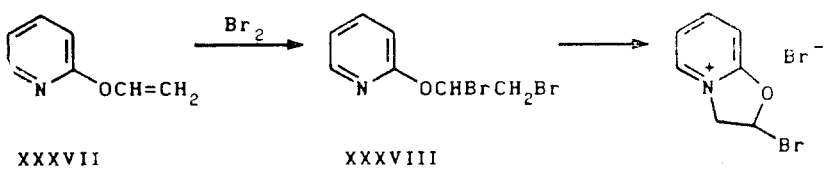
XXXIII XXXV XXXIV XXXVI

R^1 = NHEt, NMe_2, NHBu, OEt;

R^2 = H, Me

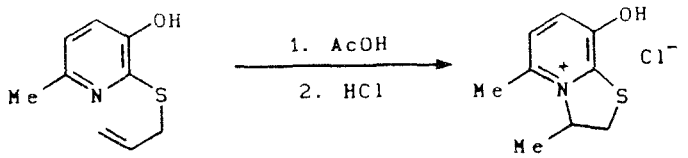
Unsubstituted 2-(vinylthio)pyridine reacts immediately with bromine to give thiazolo[3,2-*a*]pyridinium bromide [64].

In contrast to 2-(vinylthio)pyridine, 2-vinyloxypyridine (XXXVII) reacts with bromine to give 2-bromo-2,3-dihydrooxazolo[3,2-*a*]pyridinium bromide [65, 66] through the intermediate 2-(1,2-dibromoethoxy)pyridine (XXXVIII):

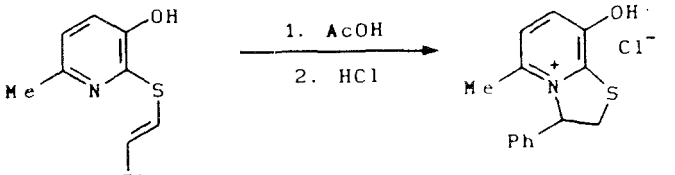


XXXVII XXXVIII

The electrophilic heterocyclization of 2-allylthio- (XXXIX) and 2-styrylthio-3-hydroxy-6-methylpyridine (XL) is realized by heating (145-150°C) in acetic acid in a sealed tube [44].



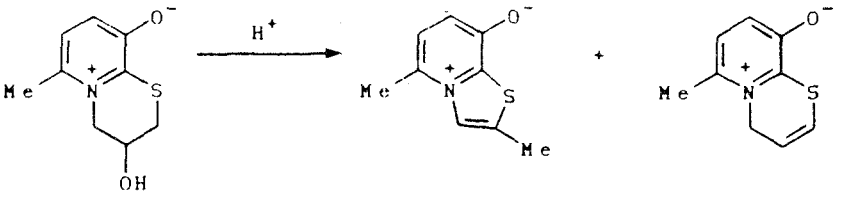
XXXIX



XL

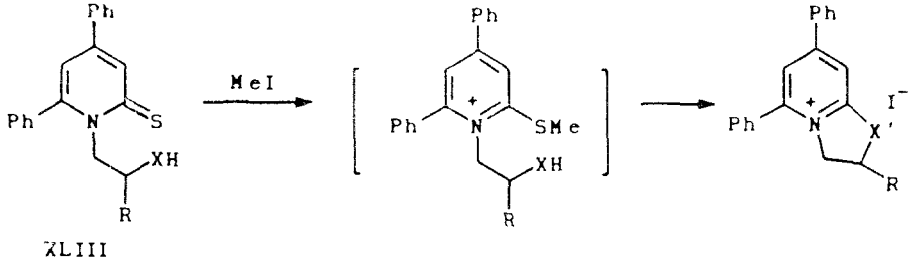
5. OTHER METHODS OF SYNTHESIS

Upon treatment with acids, 2,3-dihydro-3-hydroxy-4H-[1,3]thiazino[3,2-*a*]pyridinium 9-oxide XLI undergoes rearrangement to thiazolo[3,2-*a*]pyridinium 8-oxide XLII [47].



XLI XLII (36%)

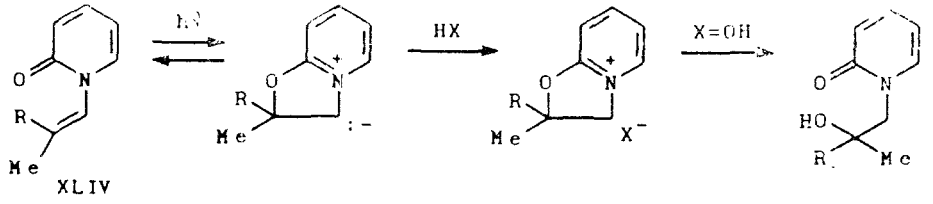
The reaction of 1-(2-hydroxyethyl)-4,6-diphenylpyridine-2-thione XLIII with CH_3I gives dihydrooxazolo[3,2-*a*]pyridinium systems [67], while dihydrothiazolo[3,2-*a*]pyridinium salts are formed by replacing the hydroxy group with a mercapto group.



XLIII

X = O,S; R = H,Me

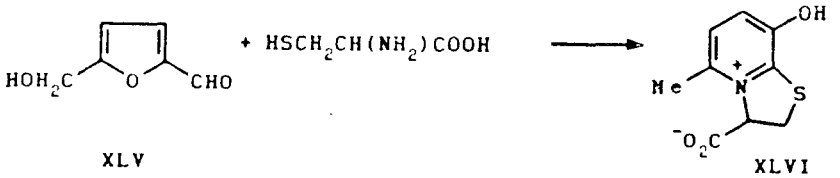
Dihydrooxazolo[3,2-*a*]pyridinium systems are also obtained by the photocyclization of 1-propenyl-2-pyridones XLIV in an acidic medium [68].



XLIV

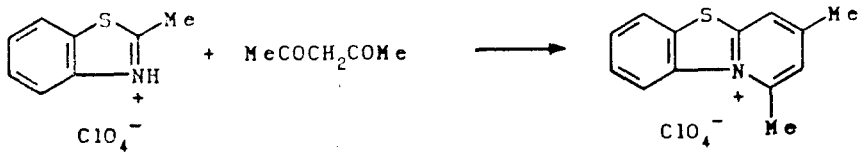
R = H,CH_3

5-(Hydroxymethyl)furfural (XLV) reacts with cysteine to give 2,3-dihydro-8-hydroxy-3-carboxy-5-methylthiazolo[3,2-*a*]pyridinium salt XLVI [9, 34].



XLV XLVI

Benzothiazolo[3,2-*a*]pyridinium salt derivatives XLVII were obtained [69] by condensation of β-diketones with 2-methylbenzothiazolium perchlorate at 140-150°C for 6-20 h.



XLVII

Thiazolo[3,2-*a*]pyridinium bromide can be obtained by a three-step synthesis from 2-cyanothiazole [70].

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