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SYNTHESIS, STRUCTURE, AND PROPERTIES OF N-, O-, AND S-VINYL DERIVATIVES OF AZINES (REVIEW)

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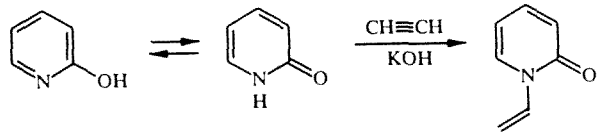
The published data on the synthesis, structure, and properties of N-, O-, and S-vinyl derivatives of azines are reviewed.

The literature contains reviews [1-7] on the synthesis and properties of N-vinylpyrroles, N-vinylindoles, and N-vinyllactams. Data on the synthesis and polymerization of certain N-vinyl compounds of the azine series were given in [8]. In the present review we have summarized for the first time data on the synthesis, structure, and chemical properties of the N-, O-, and S-vinyl derivatives of azines. These compounds and their derivatives include substances that have bacteriostatic [9], antistaphyllococcal [10], tuberculostatic [11], cancerostatic [12], radioprotective [13], and ichthyotoxic [14, 15] characteristics and are antiaging agents for light resins [16], sensitizers [17-19], and stabilizers for polyurethane compositions [20].

SYNTHESES OF N-VINYL COMPOUNDS

A large number of investigations have been devoted to the synthesis of the N-vinyl derivatives of 2- and 4-pyridones and quinolones. 1-Vinyl-2-pyridone and its 3- and 5-halogeno derivatives were first obtained by the direct vinylation of 2-hydroxypyridine(2-pyridone) with acetylene under pressure in the presence of alkali [21-23].

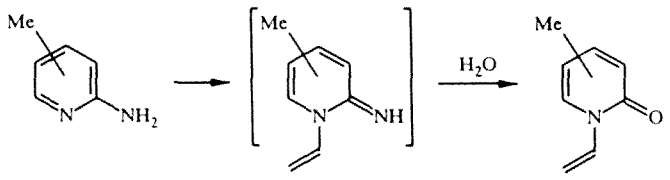


Acridone and its derivatives react with ethyl propiolate in the presence of triethylamine and a palladium catalyst in a nitrogen atmosphere also with the formation of N-alkenyl derivatives [31].

1-Vinyl-2-pyridones and 1-vinyl-4-pyridones were obtained by the transvinylation of 2- and 4-trimethylsilyloxypyridines with vinyl acetate in the presence of mercuric acetate and sulfuric acid in a nitrogen atmosphere [32]. Transvinylation of 2-hydroxypyridine itself gives a low yield.

Phenylacetylene [28], hexafluorobutyne [29], dimethyl acetylenedicarboxylate, and ethoxyacetylene [30] react with 2-hydroxypyridine with the formation of N-aikenyl derivatives.

1-Vinyl-2-pyridone [33, 34], its 3-, 4-, 5-, and 6-methyl and 5-chloro derivatives [35], 1-vinyl-4-quinolone, and 2-vinyl-1-isoquinolone [27, 34, 36] were obtained by the reaction of the respective aminoheterocycles with acetylene in the presence of cadmium acetate [33, 34].



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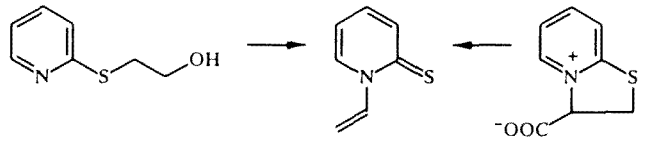
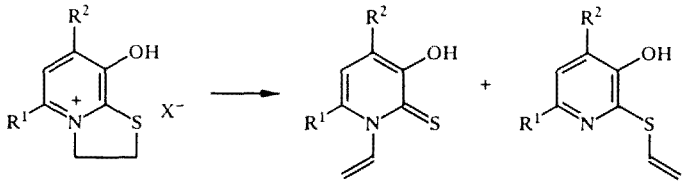
A mixture of N-*endo*- and N-*exo*-alkenyl derivatives is formed during the reaction of 2-aminopyridine with ethyl propiolate and dibenzoylacetylene [37, 38]. The syntheses of 1-vinyl-4-pyridone, 1-vinyl-4-quinolone, and 1-vinyl-4-methyl-2-quinolone by the direct vinylation of 4-pyridone and 2- and 4-quinolones were carried out similarly [24-27]. In the presence of alkali 2-aminopyridine reacts with acetylene to form 2,3-dimethylimidazo[1,2-*a*]pyridine [39]. Imidazo[1,2-*a*]pyridines are also formed during the reaction of 2-aminopyridine with dimethyl acetylenedicarboxylate and ethyl propiolate [40, 41]. 2-Aminopyridine reacts with acetylenic ketones with the formation of pyrido[1,2-*a*]pyrimidines [42].

1-Vinyl-2-pyridone was synthesized from 1-(2-hydroxyethyl)- and 1-(2-acetoxyethyl)-2-pyridones [43, 44], and 1-vinyl-6,7-methylenedioxy-4-quinolone-3-carboxylic acid was synthesized from 1-bromoethyl-6,7-methylenedioxy-4-quinolone-3-carboxylic acid [45] by elimination reactions.

1-Vinyl-2-pyridinethione was obtained by the reactions of 2-(2-ethoxyethylthio)pyridine with sodium hydride and p-toluenesulfonyl chloride [43] and by decarboxylation of 3-carboxydihydrothiazolo[3,2-*a*]pyridinium systems with ring opening [46].



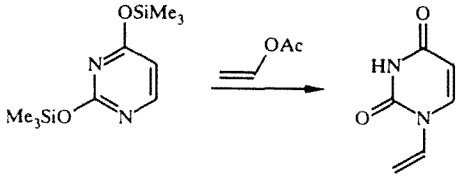
A mixture of substituted 1-vinyl-2-pyridinethione and 2-vinylthiopyridine is formed in the reaction of dihydrothiazolo[3,2-*a*]pyridinium systems with potassium *tert*-butoxide during pyrolysis under vacuum in the presence of potassium carbonate [47-49].



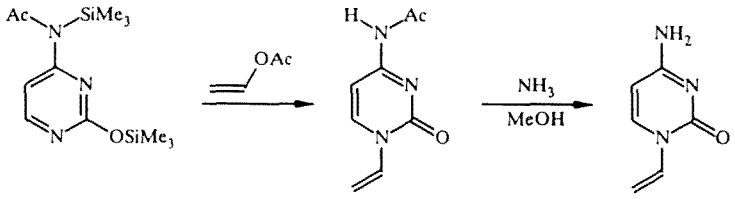
R^1 = Me, Pr, Cl; R^2 = H, Cl

1-Vinyl-3-hydroxy-2-quinolinethione is formed during the reaction of 10-hydroxydihydrothiazolo[3,2-*a*]quinolinium salts with potassium *tert*-butoxide [50].

A series of papers were devoted to the synthesis of N-vinyldiazines. Thus, 1-vinyluracil was obtained by the transvinylation of 2,4-bis(trimethylsilyloxy)pyrimidine in the presence of mercuric acetate and sulfuric acid, by the dehydrohalogenation of 1-(2-chloroethyl)uracil, and by the cyclization of N-β-ethoxyacryloyl-N-vinylurea [32, 51].



The reaction of 2,4-bis(trimethylsilyl)-N-acetylcytosine with vinyl acetate gave N-acetyl-1-vinylcytosine, which was then converted into 1-vinylcytosine and then into 1-vinyluracil [32, 51].



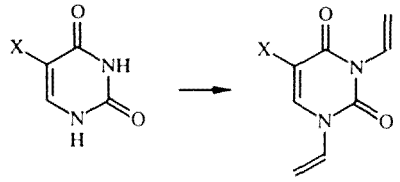
Transvinylation of uracil itself gives a low yield of 1-vinyluracil [52]. In [53] it was mentioned that transvinylation of uracil, 3-benzoyluracil, and cytosine does not take place with vinyl acetate.

1-Vinyluracil and 1,3-divinyluracil were obtained by the direct vinylation of uracils with acetylene under pressure in the presence of cadmium, copper, and zinc salts [54, 55].

6-Methyl-1-vinyluracil, 6-methyl-1,3-divinyluracil, and 1,3-divinylazauracil were obtained in a similar way [56].

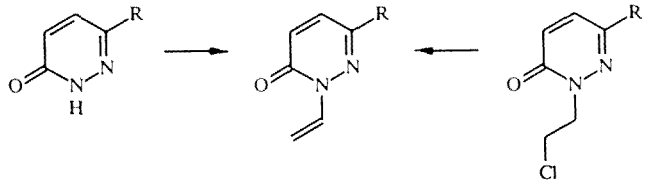
Barbituric acid does not form N-vinyl derivatives under the conditions of direct vinylation [52].

In the direct vinylation of 5-chloro- and 5-fluorouracils in the presence of cadmium acetate at 220-225°C in dioxane and in mono- and diglyme the divinyl derivatives are formed [57].



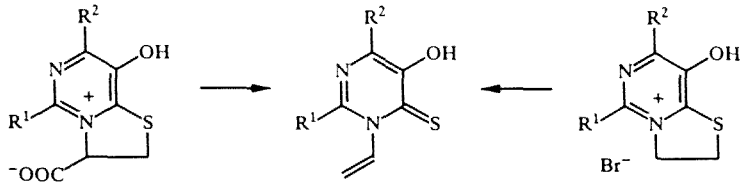
X = Cl, F

2-Vinyl-3-pyridazone and its derivatives were obtained by the direct vinylation of 3-pyridazones in the presence of potassium hydroxide, cadmium oxide and acetate, and zinc oxide, by transvinylation with vinyl acetate in the presence of mercuric acetate, and by dehydrochlorination of the corresponding 2-(2-chloroethyl)-3-pyridazones [8, 58-61].



R = H, Me, Et, COOMe, COOEt, COOPr, COOPr-*i*, COOBu

5-Hydroxy-3-vinyl-4(3H)-pyrimidinethiones were obtained by heating 8-hydroxythiazolo[3,2-*a*]pyrimidinium-3-carboxylates with quartz sand under vacuum and by the action of potassium *tert*-butoxide in DMFA on 8-hydroxy-dihydrothiazolo[3,2-*c*]pyrimidinium bromides [62].



R^1 = H, Me, Ph; R^2 = H, Br

1-Vinylperimidine was obtained by the vinylation of pyrimidine with vinyl acetate in the presence of mercuric acetate and sulfuric acid [63].

10-Vinylphenothiazine and 10-vinylnaphthphenothiazine were obtained by the direct vinylation of phenothiazines with a mixture of acetylene and nitrogen in a rotating autoclave in the presence of sodium amide [1].

More recently [64, 65] 10-vinylphenothiazine and 10-vinyl-2-chlorophenothiazine were obtained by the vinylation of phenothiazines with acetylene under pressure at 463-468 K in the presence of potassium. Phenylacetylene reacts with phenothiazine with the formation of the *cis* and *trans* isomers of 10-styrylphenothiazine [66].

SYNTHESIS OF O-VINYL DERIVATIVES

As mentioned above, 2- and 4-hydroxypyridines and 2- and 4-hydroxyquinolines react with acetylene in the presence of alkali-metal hydroxides with the formation of N-vinyl derivatives. In the presence of cadmium acetate the vinylation of 2- and 4-hydroxypyridines as a rule takes place with the formation of a mixture of the O and N derivatives [24, 67-72]. At the present time 2- and 4-vinyloxypyridines, 2,6-dimethyl-3,5-dichloro-4-vinyloxypyridine, 2-vinyloxyquinoline, 4-methyl-2-

vinyloxyquinoline, 4-vinyloxyquinoline, 2-methyl-4-vinyloxyquinoline, and 2,4-divinyloxyquinoline have been obtained by this method [24, 57-74].

In [75, 76] it was shown that a mixture of the O- and N-vinyl derivatives of 2-hydroxypyridine is formed during vinylation in the presence of copper, zinc, and mercury acetates, oxides, and hydroxides. Isomerization of the O- and N-vinyl derivatives was not observed under the vinylation conditions. A mixture of the O- and N-vinyl derivatives is also formed in the reaction of ethoxyacetylene with 2- and 4-hydroxypyridines without a catalyst [31].

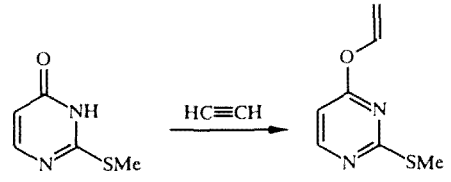
3-Hydroxypyridine and 3-, 6-, and 8-hydroxypyridines belong to the compounds incapable of prototropic tautomerism and react with acetylene in the presence both of metal hydroxides and of copper acetate with the formation of only the O-vinyl derivatives (3-vinyloxypyridine, 3-vinyloxy-2-methyl-4-methoxy-5-hydroxymethylpyridine, and 3-, 6-, and 8-vinyloxyquinolines) [67, 68, 73, 77-80].

The 2-, 3-, and 4-vinyloxymethylpyridines were obtained by the vinylation of 2-, 3-, and 4-hydroxymethylpyridines with acetylene in the presence of cadmium acetate and alkali [68, 81].

2-Vinylpyridine is formed in the reaction of 2-(2-hydroxyethyl)pyridine with acetylene in the presence of potassium hydroxide, while 2-(2-vinyloxyethyl)pyridine is formed in the presence of cadmium acetate [67].

The vinyl and divinyl esters of pyridine- and quinolinecarboxylic acids were obtained by the direct vinylation of the respective acids with acetylene in the presence of copper chloride and cadmium oxide and acetate [82, 83] and by the reaction of the hydrochlorides and chlorides of the acids with mercuriobisacetaldehyde [84, 85].

The vinylation of 2-methylthio-4(3H)-pyrimidine gave 2-methylthio-4-vinyloxypyrimidine [86].

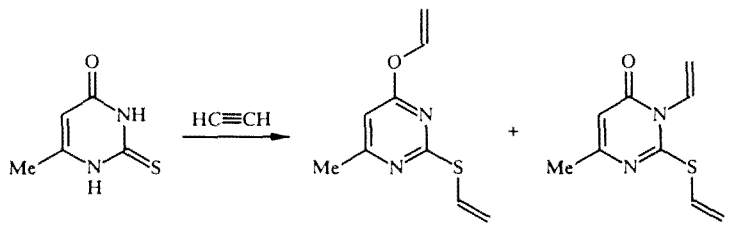


Phenylacetylene reacts with 8-hydroxyquinoline in the presence of alkali with the formation of 8-styryloxyquinoline [87] and with 2-hydroxyquinoline and 2-hydroxypyridine, as mentioned above, with the formation of the N-styryl derivatives [28].

SYNTHESIS OF S-VINYL DERIVATIVES

Unlike the 2-hydroxyazines, the 2-mercaptoazines react with acetylene regioselectively irrespective of the nature of the catalyst (metal hydroxides, cadmium acetate, copper chloride) with the formation of only the S-vinyl derivatives. 2-Vinylthiopyridine, 2- and 4-vinylthioquinolines [12. 88-92], and 2-vinylthiopyrimidine [93] were obtained in this way.

6-Methyl-2-thiouracil reacts with acetylene with the formation of a mixture of the S,O- and S,N-divinyl derivatives [86].



The direct vinylation of the respective mercaptoquinolines with acetylene in an alkaline medium gave 5- and 8-vinylthioquinolines and 2- and 4-methyl-8-vinylthioquinolines [88, 89, 95, 96].

3-Bromo-5-vinylthiopyridine was obtained from 3,5-dibromopyridine and sodium ethenethiolate, generated from divinyl sulfide [94].

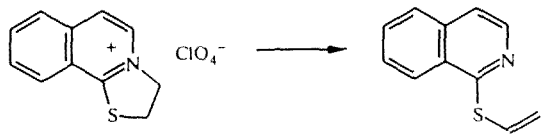
Phenylacetylene reacts with 2-mercaptopyridine [28, 91], 2-mercaptoquinoline [89, 90], and 2-mercaptopyrimidine [93] in an alkaline medium in dioxane at 170-180°C with the formation of the *cis* isomers of the S-styryl derivatives.

In a superbasic medium [97, 98] the reactions of 2- and 8-mercaptoquinolines, 6-methyl-2-thiouracil, 2-thiouracil, 4,6-dimethyl-2-mercaptopyrimidine, and 4,5,6-triamino-2-mercaptopyrimidine with phenylacetylene take place at 100°C with the formation of the S-styryl derivatives.

2-Mercaptopyridine and its derivatives react with propiolic and phenylpropiolic acids with the formation of a mixture of the *cis* and *trans* isomers of the S-alkenyl derivatives and with acetylenedicarboxylic with the formation of thiazolo[3,2-*a*]pyridinium systems [99].

3-Hydroxy-2-vinylthiopyridines and 3-hydroxy-2-vinylthioquinolines were obtained in mixtures with the N-vinyl derivatives by reaction of the dihydrothiazolo[3,2-*a*]pyridinium and quinolinium systems with potassium *tert*-butoxide [47, 50].

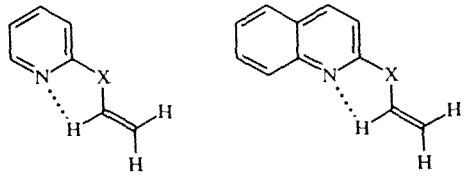
1-Vinylthioisoquinoline was obtained by the decomposition of dihydrothiazolo[2,3-*a*]isoquinolinium perchlorate with potassium carbonate at 150-180°C [100].



2,3,5,6-Tetrachloro-4-pyridyl vinyl sulfone and 2-methyl-3,5,6-trichloro-4-pyridyl vinyl sulfone were obtained by the dehydrochlorination of the respective 4-pyridyl chloroethyl sulfones by the action of triethylamine [101, 102].

STRUCTURE

According to data from the ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR spectra and quantum-chemical calculations, vinyloxy-(thio)pyridines and vinyloxy(thio)quinolines exist in the planar S-*trans* conformation [69, 88, 89]. In 2-vinyloxy(thio)pyridines, 2-vinyloxy(thio)quinolines, and 2-vinylthiopyrimidines the signal of the α-proton of the vinyl group in the PMR spectra is shifted anomalously downfield. This is one piece of evidence for the existence of an intramolecular hydrogen bond C—H···N between the α-proton of the vinyl group and the endocyclic nitrogen atom [74, 88, 103, 104].



X = O, S

There are no signs of the formation of an intramolecular C—H···N hydrogen bond in 8-vinyloxy(thio)quinolines [103].

In contrast to the unsubstituted 2-, 3-, and 4-vinyloxypyridines the 2,4-dimethyl-3,5-dichloro-4-vinyloxypyridine and 2-methyl-3-vinyloxy-4-methoxymethyl-5-hydroxymethylpyridine exist predominantly in the sterically strained *S-cis* conformation with the heteroaryl ring deflected from the plane of the vinyloxy group by an angle in the order of 60° [73].

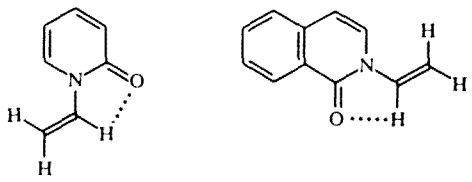
5-Vinylthioquinoline is characterized by an equilibrium between the *S-cis* and *S-trans* forms with an essentially nonplanar arrangement of the vinylthio group of the heterocycle [88].

In vinyl ethers of the pyridine and quinoline series [69, 74] the p—π conjugation with the vinyl group and the heterocycle is concurrent in nature, as also in aryl vinyl ethers [105].

In 2- and 8-vinylthioquinolines the vinylthio group exhibits π-donating characteristics, while in 5-vinylthioquinoline it exhibits π-accepting characteristics [69].

It was shown by quantum-chemical methods that the two unshared electron pairs of the sulfur atom in vinyl sulfides of the azine series are essentially nonequivalent [92].

According to the ^{1}H and ^{13}C NMR spectra, the vinyl group and the heterocycle in 1-vinyl-2-pyridone, 1-vinyl-4-pyridone, 1-vinyl-4-quinolone, and 3-, 4-, and 5-methyl- and 5-chloro-1-vinyl-2-pyridone are coplanar, and the vinyl group has the *trans* orientation in relation to the carbonyl group [26, 35, 44]. In 1-vinyl-2-pyridone and 2-vinyl-1-isoquinoline there is specific intramolecular interaction between the α-proton of the vinyl group and the oxygen atom [27].



In 6-methyl-1-vinyl-2-pyridone the vinyl group is withdrawn substantially from the plane of the heterocycle on account of steric hindrances [35].

In the molecules of 1-vinyl-2-quinolone and 1-vinyl-2-methyl-4-quinolone the vinyl group is also withdrawn from the plane of the ring on account of steric interaction with the benzene ring and with the substituents at the *ortho* position [26].

In vinyl 2-pyridinecarboxylate the carbonyl group exists predominantly in the *S-trans*-(N) conformation, while in vinyl 3-pyridinecarboxylate it exists both in the *S-trans*-(N) and in the *S-cis*-(N) conformation with the *syn* orientation of the vinyl and carbonyl groups, stabilized by a C—H··· hydrogen bond involving the α-proton of the vinyl group [106].

REACTIONS

Compared with alkyl and aryl vinyl ethers [1, 105, 107, 108], alkyl vinyl sulfides [1, 109], N-vinylpyrroles [4, 6, 110], and N-vinyllactams [5], the properties of the N-, O-, and S-vinyl derivatives of aromatic azines have been considerably less studied. Vinyl compounds of the azine series have several reaction centers, and the reaction can therefore take place both at one of them and at several reaction centers simultaneously.

Metal chlorides react with 8-vinyloxy(thio)quinolines [79, 111-113], with 2-vinylthiopyridine [114], and with vinyl carboxylic esters [83] with the formation of complex compounds. It was shown by IR spectroscopy, NMR spectroscopy, and quantum-chemical methods [115] that the main donor center is the nitrogen atom [114].

Iodomethane reacts with vinyl nicotinate [83] and 2-vinylthiopyridine [91] with the formation of quaternary salts.

Hydrogen chloride in organic solvents reacts with 2-vinyloxypyridine [75, 116], 1-vinyl-2-pyridine [75, 116], 2-vinylthiopyridine [91, 114], 8-vinylthioquinoline [13, 15], 3-, 4-, 6-, and 8-vinyloxyquinoline [107, 116], 1-vinyl-4-methyl-2-quinolone [116], and vinyl pyridinecarboxylates [84] with the formation of the hydrochlorides.

The vinyl derivatives of azines are hydrolyzed by the action of aqueous solutions of acids [66, 75, 117, 118]. The kinetics of the hydrolysis of 10-vinylphenothiazines and 10-vinylacridone were studied in [66, 81, 84, 117, 118].

Polymerization was investigated for some vinyl derivatives of azines. Data on the polymerization of vinylpyridazones were reported in [8]. 10-Vinylphenothiazine polymerizes both by a radical mechanism by an ionic mechanism [65, 119-121].

2-Vinylthiopyridine [91], 8-vinylthioquinoline [95], 2-vinylpyridazones [8, 60, 122-124], and 1-vinyl-2-pyridone [75, 114] polymerize by a radical mechanism. 2-Vinylthioquinoline and 2-vinyloxy-4-methylquinoline enter into copolymerization with diethyl maleate under the conditions of free-radical initiation [12].

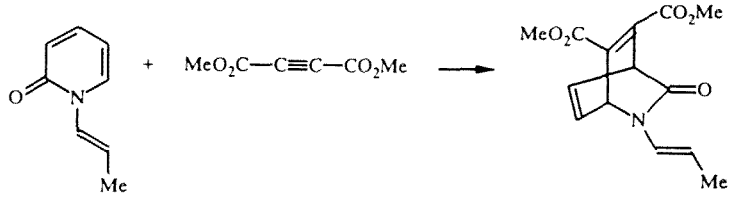
Under the influence of sulfur dioxide and boron trifluoride 8-vinyloxyquinoline polymerizes by an ionic mechanism [77].

Thiols add to 2- and 3-vinyloxymethylpyridines [125], 2-vinyloxy(thio)pyridines [75, 114], 1-vinyl-2-pyridones [75], 8-vinyloxy(thio)quinolines [95, 126], and vinyl nicotinates [83] by a radical mechanism with the formation of β-addition products.

Phenol, thiophenol, aromatic amines, and alcohols add to tetrachloro-4-pyridyl vinyl sulfone at the double bond in the presence of triethylamine [102]. In the reaction with primary aromatic amines and thiols the vinylsulfonyl group is displaced with the formation of 4-alkylamino- or 4-alkylthiotetrachloropyridines [102, 127].

The 6- and 8-vinyloxyquinolines, 8-vinylthioquinolines, and 2-, 3-, and 4-vinylmethylpyridines enter into diene condensation with acrolein to form dihydropyrans [78, 128].

1-(1-Propenyl)-2-pyridone enters into the Diels—Alder reaction with dimethyl acetylenedicarboxylate at 105°C [129].

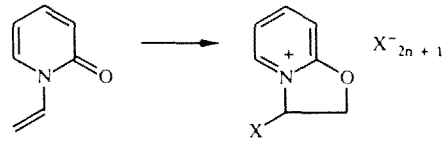


1-Vinyl-2-pyridone does not enter into diene synthesis under these conditions, and the reaction leads to the formation of tetramethyl 1,2,4,5-benzenetetracarboxylate [129].

In [130] it was shown that 1-vinyl-2-pyridone dimerizes under the influence of light with the participation of the carbon atoms at positions 3 and 6. The irradiation of 1-(1-propenyl)-2-pyridone leads to cyclization with the formation of an oxazole ring [131].

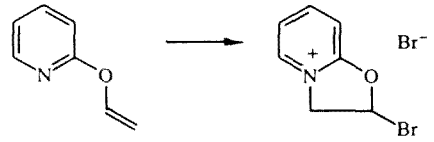
10-Vinylphenothiazine reacts with tetracyanoethylene in benzene with the formation of 10-(2,2,3,3-tetracyano-1-cyclobutyl)phenothiazine [132]. The reaction of 10-vinylphenothiazine with chloroaniline does not stop at the cycloaddition stage but leads further to the elimination of hydrogen chloride and the formation of 2-[2-(10-phenothiazenyl)vinyl]-3,5,6-trichlorobenzoquinone [133].

Chlorine and bromine react with 1-vinyl-2-pyridone in carbon tetrachloride with the formation of 1,2-dihalogenoethyl derivatives [21, 116, 134, 135]. Bromine and iodine react in alcohols with the formation of the 3-halogeno-2,3-dihydro-oxazolo[3,2-*a*]pyridinium halide [132].



Bromine and iodine react similarly with 1-vinyl-4-methyl-2-quinolone by a halogenocyclization scheme [135].

The chlorination of 2-vinyloxypyridine leads to the formation of 2-(1,2-dichloroethoxy)pyridine. Bromination leads to the formation of 2-bromo-2,3-dihydrooxazolo[3,2-*a*]pyridine [136, 137].



Unlike 2-vinyloxypyridine, 2-vinylthiopyridine reacts with bromine with the formation of thiazolo[3,2-*a*]pyridinium bromide [138].

2-Vinylthiopyridines containing carbonyl, alkoxycarbonyl, or acetyl substituents at the β-carbon atom of the vinyl group react with bromine to form dihydrothiazolo- and thiazolo[3,2-*a*]pyridinium systems and the products from the addition of the bromine at the double bond [139].

2-Vinyloxy(thio)quinolines react with bromine with the formation of dihydrooxazolo(thiazolo)[3,2-*a*]quinolinium bromides [140, 141, 142]. 8-Vinyloxy(thio)quinolines react with bromine and iodine to form 2H-oxazolo(thiazolo)[5,4,3-*ij*]quinolinium halides [142, 143, 144].

The reaction of 2-vinyloxymethylpyridine with bromine and iodine gave the 3-halogenomethyl-1,3-dihydrooxazolo[3,4-*a*]pyridinium halides [137], while the reaction of 2-(2-vinyloxyethyl)pyridine with bromine gave 4-bromomethyl-1,2-dihydro-1,4-oxazino[3,2-*a*]pyridinium bromide [137].

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