ANHYDRO BASES OF THE PYRIDINE SERIES (REVIEW)

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Methods for the preparation of anhydro bases of the pyridine series by deprotonation of the corresponding quaternary salts under the influence of bases, as well as by the direct reaction of quaternary pyridinium or halopyridinium salts with CH acids in the presence of bases, are examined. The reactions of anhydro bases with various reagents (alkyl cations, acylium cations, the proton, aldehydes, isothiocyanates, carbon disulfide, the hydroxide ion, etc.), which constitute evidence for their high reactivities, are examined. The participation of anhydro bases as intermediates in many reactions intended for the preparation of new heterocyclic systems is demonstrated.

Compounds of the anhydro base class, which are generated from heterocyclic cations that have hydrogen-containing substituents, have long been of interest to researchers owing to the diversity of their chemical and physical properties. Inasmuch as they have high reactivities, they are starting models in the construction of various heterocyclic systems: indolizines [1-4], pyridazines [5, 6], substituted pyridines [7], etc. The interest in these compounds is also due to the fact that many natural alkaloids – sempervirine [8, 9], flavopereirine [10, 12], flavocorpine [13], alstoniline [14], serpentine [15], alstonine [16-19], and a number of others – have anhydro base structures. Preparations with hypotensive [20], antiphlogistic, and analgesic action [21] and anticoagulants [22] have been found among anhydro bases in recent years. Despite the rather long acquaintanceship that researchers have had with this interesting class of organic compounds, much of their chemistry remains unclear. Thus in the pyridine series only methylene anhydro bases and their variants or anhydro bases formed from structures with a condensed pyridine ring such as the anhydro bases of isomeric carbolines, information regarding which has been correlated in a monograph [23], are thus far known. Anhydro bases that can be generated from quaternary pyridinium salts that contain a heterocyclic substituent with a labile hydrogen atom (indole, for example) have remained unknown up until most recently, although a study of their formation would make it possible to obtain new data on the criteria for the stability of the compounds, which constitute a completely uninvestigated part of the chemistry of anhydro bases. In addition, anhydro bases with a structure of this type open up new preparative possibilities for the production of difficult-to-obtain bisheterocyclic systems. The problem of the effect of substitution in the pyridine ring on the formation and reactivity of the corresponding anhydro bases remains completely unexplored. Very little study has been devoted to the reactivity and preparative possibilities of this class of compounds. Except for one source [23], in which data on anhydro bases of isomeric carbolines are correlated, there are no reviews in which data on anhydro bases of the pyridine series have been systematized. The large amount of disparate data on anhydro bases of the pyridine series and the importance of this class of compounds in the chemistry of heterocycles from both a theoretical and practical point of view have made it necessary to write the present review.

Electronic Structure and Spectral Characteristics of Anhydro Bases

Anhydro bases of the pyridine series are unstable compounds, and it is therefore a rather complex problem to determine their structures with sufficient accuracy. Let us note that even the structure of α-picoline was not established prior to 1949 and that two formulas – pyridine formula I and 2-methylene-1,2-dihydropyridine formula II – were used for it [24]. Chichibabin postulated that α-picoline exists as a tautomeric mixture of both forms [25]:

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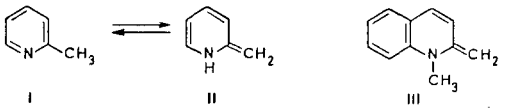
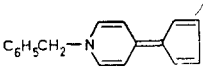


I II III

A structure of the II type, in which the hydrogen attached to the nitrogen atom is replaced by an alkyl or alkoxy substituent, has been proposed for anhydro bases. A similar structure (III) has been proposed to explain the role of piperidine as a catalyst in the condensation of a quaternary salt of quinaldine with aromatic aldehydes [26, 27]. The structure of III is confirmed by the PMR spectrum, which is similar to the spectra of enamines. Thus the protons of the methylene group of the compound give a signal at 3.5-3.8 ppm, and the position of the signal depends only slightly on the solvent. When one hydrogen atom of the methylene group is replaced by a methyl group, this signal is shifted to the weak-field side and is observed at 4.05-4.08 ppm. The absorption of the protons of the methylene group is shifted to the weaker-field side than the corresponding methyl groups in the starting quaternary salt [28].

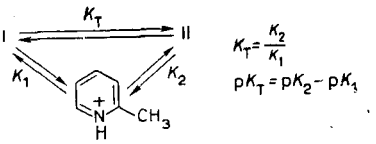
It is apparent from formulas II and III that the structure of the anhydro bases should be similar to the pyridone structure; this was demonstrated by means of IR spectroscopy. The absorption at 1637-1651, 1530-1583, 1511-1550, and 1438-1449 cm^{-1} and the intensities of these bands for anhydro bases of the II type are virtually the same as the absorption and intensities for pyridones and pyridinethiones [29, 30].

The structure of an anhydro base has been established most accurately in the case of 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (IV) [31, 32], the oxidation of which leads to pyridine-4-carboxylic acid, while reduction leads to 1-benzyl-4-cyclopentylpiperidine; the UV spectrum of IV differs markedly from the spectrum of the isomeric γ-benzyl pyridinium N-cyclopentadienylid.



IV

Since anhydro bases are fixed structures of the II type, they are widely used to study the tautomerism of alkylpyridines. From the fact that the UV spectra of the anhydro bases differ markedly from the UV spectra of the corresponding pyridine bases [33, 34], it may be concluded that the I $\rightleftarrows$ II equilibrium is shifted markedly to the left. The tautomeric equilibrium constants have been determined quantitatively by the pK_a method:

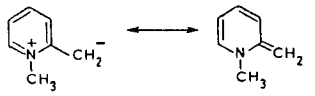


$K_T = \frac{K_2}{K_1}$

$pK_T = pK_2 - pK_1$

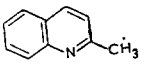
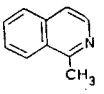
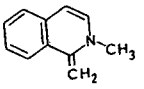
The pK_a values of various anhydro bases are presented in Table 1. It follows from Table 1 that anhydro bases have high basicities ($pK_a > 14$); this is associated with the loss of the aromatic character of the pyridine ring, as evidenced also by their NMR spectra [28, 38, 39].

All of the chemical properties of anhydro bases can be explained by means of two limiting structures:



Quantum-chemical calculations [39, 40-43] show that there is significant separation of the charges between the nitrogen atom and the exocyclic methylene group, as well as pronounced alternation of the bonds, in the anhydro base molecule. The latter fact evidently explains the relatively low stability of anhydro bases. It should be noted that all of the calculations are in good agreement with one another. Significant negative charge is localized on the exocyclic methylene group in anhydro base II, and this indicates the great local π-surplus character of this carbon atom. Consequently, electrophilic attack will be directed primarily to the methylene group, in agreement with a large number of experimental data. The results of a calculation of the electrophilic localization energy [43] also constitute evidence in favor of this. The pyridine ring in anhydro bases has π-deficient character, since the positive charge of a zwitter-ion structure, which is distributed between the C_2, C_4, C_6, and nitrogen atoms, is localized primarily in it. The presence of two centers with different natures (a π-surplus exocyclic group and a π-deficient pyridine ring) in the anhydro bases determined the possibility of the participation of the anhydro bases in reactions with both electrophilic and nucleophilic agents (see below for information regarding this). Annelation of the anhydro base at both the 5,6 and 3,4 bonds decreases the negative charge on the exocyclic methylene group somewhat [39, 40, 42]. The π-electron charges [42] on the exocyclic methylene groups in 1-R-2-methylene-1,2-dihydropyridine (II), 1-R-2-methylene-1,2-dihydroquinoline

TABLE 1. Basicities and Tautomeric Equilibrium Constants of Methylpyridines and Their Anhydro Bases

Compound	pK_a	Compound	pK_a	pK_T	ΔG^0, kcal/mole
I	5,97	II	19,8	13,83	12,0
	5,80	III	15,0	9,21	13,1
	—		15,6	—	—

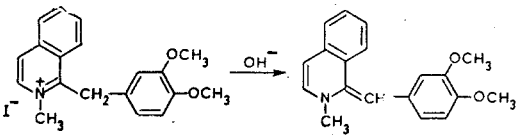
(III), and 2-R-1-methylene-1,2-dihydroisoquinoline (V) change symbatically with respect to the experimentally found basicities [44] of these anhydro bases: −0.240022 (19.8), −0.18758 (15.6), and −0.18254 (15.0) for II, V, and III, respectively.

The energies of the $\pi-\pi^*$ transitions were calculated on the basis of calculations of the ground states of the anhydro bases [37, 38, 40, 45]. It was shown that the transitions in the UV spectra of the anhydro bases are similar to the transitions in pyridines [39]. The calculated UV spectra are in good agreement with the experimental UV spectra. In a comparison of the calculated spectra of anhydro bases with the calculated spectra of the corresponding quaternary salts [46] it was found that the spectra of the anhydro bases have a longer-wave absorption band than the spectra of the quaternary salts. This pattern in the UV spectra of the anhydro bases and quaternary salts was also observed experimentally [24, 47]; the UV spectra of the anhydro bases and quaternary salts are characterized by the presence of an isobestic point [48, 49], which indicates the establishment of an equilibrium between the quaternary salt and the anhydro base in solution and makes it possible to determine the basicities of anhydro bases [36, 37].

Preparation of Anhydro Bases

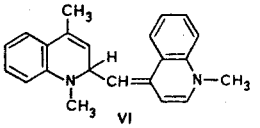
All of the reactions that lead to the formation of anhydro bases reduce basically to the reaction of the quaternary salts of the corresponding base with an alkaline agent. However, these reactions can be subdivided into principle types: 1) reaction of quaternary pyridinium salts that have hydrogen-containing substituents in the 2 or 4 positions with bases; 2) reaction of unsubstituted quaternary pyridinium salts with CH acids in the presence of bases; 3) replacement of a halogen atom in the pyridinium salt by CH acids.

Reaction of Quaternary Pyridinium Salts with Bases. An anhydro base of the pyridine series were first obtained by treatment of papaverine methiodide with alkali [50]:



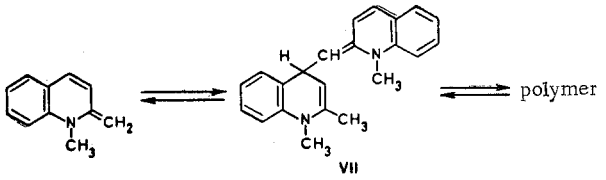
A systematic study of the reactions of quaternary pyridinium salts that contain a substituent with a labile hydrogen atom in the 2 or 4 position with alkali showed that extremely unstable anhydro bases that decompose when they are distilled in vacuo [24, 51] can be isolated in relatively pure form by their extraction either from strongly alkaline solutions of pyridinium salts or from a dry mixture of the pyridinium salt and potassium carbonate [52].

Annelation of the pyridine ring makes the resulting anhydro bases somewhat more stable. Thus an anhydro base that was stable in the dimeric form, which, judging from the NMR spectral data, has structure VI, was obtained in the reaction of lepidine methiodide with alkali [53]:



VI

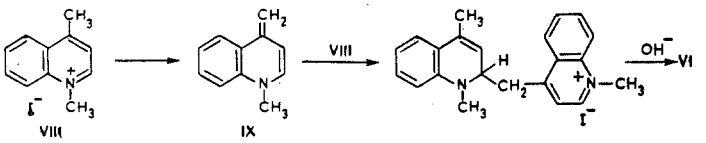
The anhydro base obtained from quinaldine methiodide is quite stable (it can be recrystallized from benzene–petroleum ether); however, it also forms dimers and a polymer in solutions. Depending on the concentration solvent, and temperature, the following equilibrium is established [47, 52]:



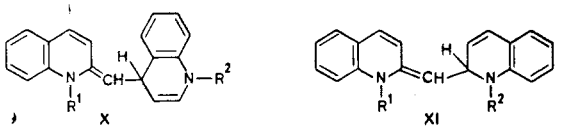
VII

Anhydro bases of the VI and VII type, which are formed by dimerization of identical rings, are called symmetrical anhydro bases. However, if different heterorings are included in the composition of the molecule, such anhydro bases are called mixed [53].

The mechanism of the formation of anhydro bases VI and VII evidently consists in the fact that the anhydro base of the IX type that is initially formed by the action of alkali on quaternary salt VIII reacts rapidly with a second molecule of the salt to give anhydro bases VI and VII:



This assumption is confirmed by the fact that mixed anhydro bases X and XI were isolated when a mixture of quaternary quinaldinium and quinolinium salts was treated with alkali [53]:

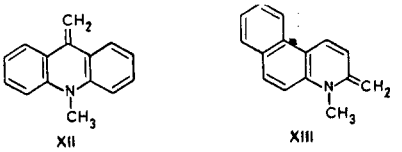


X

XI

X $R^1=R^2=C_2H_5$; $R^1=C_2H_5$, $R^2=CH_3$; XI $R^1=C_2H_5$, $R^2=CH_3$

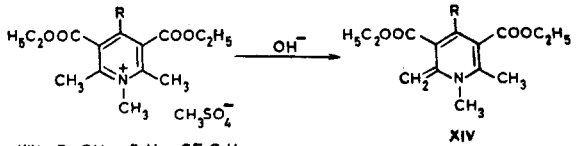
Two benzene rings annelated to a pyridine ring make the corresponding anhydro bases so stable that it becomes possible to isolate them in the form of monomers, as, for example, anhydro bases XII and XIII, which were obtained from quaternary acridinium and benzo[f]quinolinium salts [51, 54, 55]:



XII

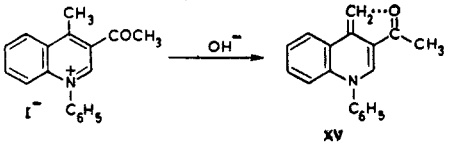
XIII

An increase in the stability of the anhydro bases is promoted not only by annelation of the pyridine ring but also by the introduction of electron-acceptor substituents in it. Anhydro bases of the XIV type, which were obtained from quaternary salts of diethyl esters of 2,4,6-trisubstituted pyridinecarboxylic acids, constitute a classic example of stable pyridine anhydro bases with an unsubstituted methylene group [21, 56-58]:

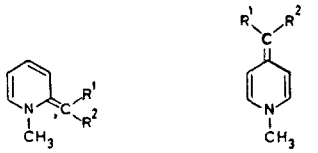


XIV R = CH_3, C_6H_5, $CF_3C_6H_4$

The presence of an electron-acceptor acetyl group in the 3 position of lepidine also stabilizes resulting anhydro base XV even more through intramolecular hydrogen bonding and makes it possible to isolate it in the monomeric form [59]:

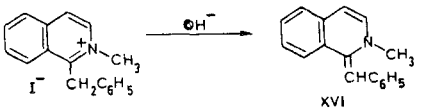


Numerous investigations of the synthesis of anhydro bases from quaternary pyridinium salts that have various hydrogen-containing substituents in the 2 or 4 position have made it possible to formulate yet another criterion of the stability of anhydro bases: If one or two hydrogen atoms of the methylene group of the anhydro bases are replaced by electron-acceptor groupings, these anhydro bases are stable [33, 40, 57, 58, 60-63]:



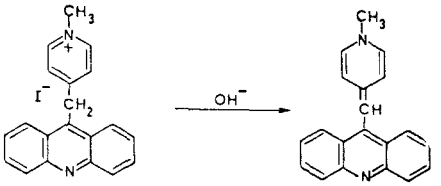
$R^1, R^2 = CN, CO_2C_2H_5, CONH_2, C_6H_5;$
$p\text{-}NO_2C_6H_4, COC_6H_5, SO_2C_6H_5$, etc.

The anhydro base of 2-benzylpyridine cannot be isolated from this series because of its rapid dealkylation to give 2-benzylpyridine [61, 64]. However, the concerted effect of a phenyl group in the side chain and an annelated benzene ring makes it possible to obtain stable anhydro base XVI from 1-benzylisoquinolinium methiodide [65]:



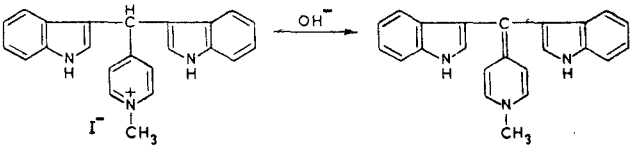
XVI

There is yet another variant of the formation of stable anhydro bases, viz., their synthesis from quaternary salts of pyridylhetarylmethanes. For example, anhydro base XVII is formed from 4-(9-acridinyl)methylpyridine by reaction with alkali [66]:



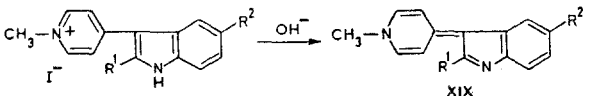
XVII

Quaternary salts of di(3-indolyl)(4-pyridyl)methane also form stable anhydro bases [67]:



XVIII

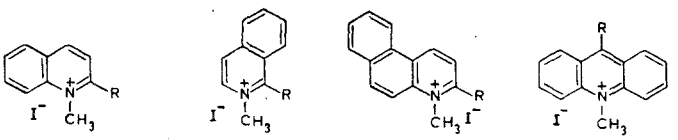
If the quaternary pyridinium salt contains an indole ring with an unsubstituted NH group, the corresponding anhydro base proves to be extremely stable, since the indole fragment in it is conjugated with the heterocyclic ring, as has been postulated also for other similar systems [68]. Thus 1-methyl-4-(3-indolenylidene)-1,4-dihydropyridines XIX are formed in good yields by the action of an aqueous or aqueous alcohol solution of alkali on 3-(4-pyridyl)indole methiodides [69, 70]:



XIX

R=H; R^1=H, C_6H_5; R^2=H, CH_3, Br

Anhydro bases are also similarly formed from quaternary salts of 3-benzopyridylindoles, viz., 3-(2-quinolyl)- (XX), 3-(1-isoquinolyl)- (XXI), 3-(benzo[f]-2-quinolyl)- (XXII), and 3-(9-acridinyl)indoles (XXIII) [71]. However, the process in these cases is complicated by competitive N-dealkylation of the salt, the contribution of which increases from XX to XXIII. Annelation of the benzene ring in this case has a significant effect not only on the stability of the corresponding anhydro bases but also on the direction of the reaction of quaternary benzopyridinium salts with alkali. This sort of effect of annelation in the synthesis of anhydro bases was previously unknown:



XX
R = 3-indolyl

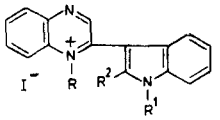
XXI

XXII

XXIII

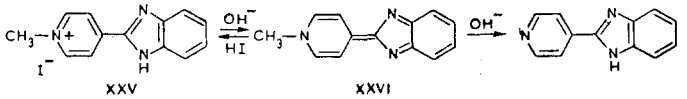
In the latter case dealkylation becomes the principal process, and the anhydro base is formed in low yield under comparable conditions. The results of quantum-chemical calculations made it possible to interpret the ratio of these two competitive processes, which depends on the difference in the residual positive π-electron charges on the nitrogen atoms of the pyridine and indole rings in cations XX-XXIII. Since the π-electron charge on the nitrogen atom in the indole ring determines the tendency for the detachment of a proton, while the charge on the nitrogen atom in the pyridine ring determines the tendency to undergo dealkylation, the difference in the charges on these atoms changes symbatically with respect to the ratio of the yields of the competitive deprotonation and dealkylation processes, i.e., the difference in the charges on the nitrogen atoms in the indole and pyridine rings decreases in the order XX > XXI > XXII, and the contribution of dealkylation increases in the same order.

The addition of another nitrogen atom to the pyridine ring of the quinolylindole cation, i.e., the transition to benzopyrazinium salt XXIV, directs the reaction with alkali exclusively along the path involving dealkylation of the pyridine nitrogen atom – a base is formed as a result of the reaction, and the corresponding anhydro base cannot be isolated in even trace amounts [73]:



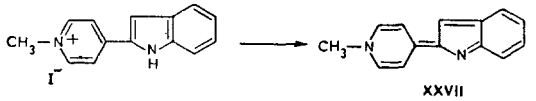
$R = CH_3, C_2H_5$; $R^1, R^2 = H, CH_3$

However, aza substitution in the pyrrole ring of indole, i.e., the transition to pyridylbenzimidazolium salt XXV, promotes deprotonation to give corresponding anhydro base XXVI [74], which subsequently is readily dealkylated with the liberation of the corresponding base [75]:



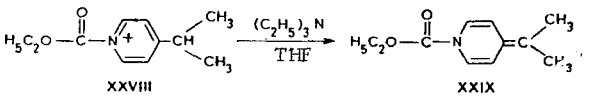
XXV XXVI

In contrast to the cases described above, anhydro bases are obtained from quaternary salts of 2-(4-pyridyl)indole only in an anhydrous medium and are less stable [76]. For a long time the prevailing opinion was that it is impossible to obtain them at all because of their low stability due to complete disruption of the aromatic character of the indole ring [77]:



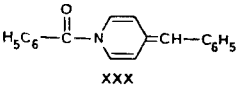
XXVII

All of the previously examined cases have pertained to the preparation of anhydro bases from quaternary salts that contain an alkyl or (less frequently) aryl group as the N-substituent. Up until recently anhydro bases that contain an acyl or alkoxycarbonyl residue as the N-substituent in the pyridine ring were unknown, evidently in view of the low stability of the corresponding N-acyl or N-alkoxycarbonyl salts and their high tendency to undergo hydrolysis even under the influence of the traces of moisture that are found in air [78]. However, a number of methods that make it possible to isolate anhydro bases of this type in pure form have been developed in recent years. Thus, for example, hydrolysis processes are suppressed in the case of the action of triethylamine on 1-ethoxycarbonyl-4-isopropylpyridinium chloride (XXVIII) in dry tetrahydrofuran, and deprotonation takes place to give anhydro base XXIX in good yield:



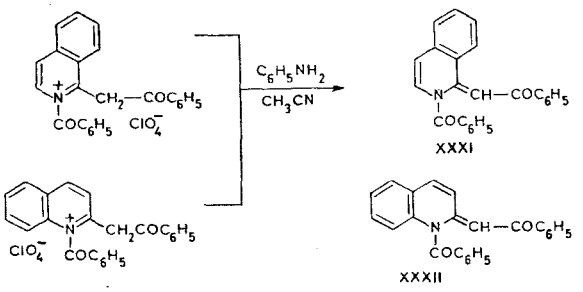
XXVIII XXIX

A communication regarding the synthesis of a 4-benzylpyridine anhydro base (XXX) that contains an acyl fragment as the N-substituent was recently published [79]:



XXX

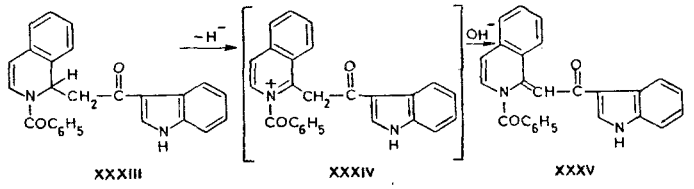
The concerted effect of an electron-acceptor benzoyl group and an annelated benzene ring in N-acyl 1-phenacylisoquinolinium and 2-phenacylquinolinium salts makes it possible to obtain very stable N-acyl anhydro bases XXXI and XXXII, which are hydrolyzed only when they are refluxed in an aqueous alcohol solution of alkali [80]:



XXXI

XXXII

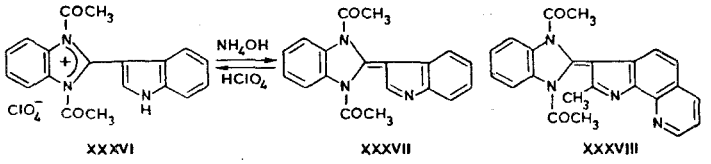
Yet another example of a stable N-acyl anhydro base is XXXV, which is obtained in the process of splitting out a hydride ion from corresponding dihydro derivative XXXIII:



XXXIII XXXIV XXXV

It is formed, in all likelihood, through intermediate N-acyl salt XXXIV, which, without isolation from the reaction mixture, splits out a proton [80].

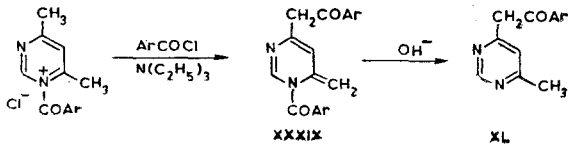
Stable anhydro bases with an N-acyl residue are known not only in the pyridine series but also among other heterocyclic systems. Thus rapid treatment of N,N'-diacetyl-2-(3-indolyl)benzimidazolium perchlorate (XXXVI) with concentrated ammonium hydroxide in the cold gives a colored compound (XXXVII), which is converted to the starting salt when it is treated with perchloric acid [81]:



XXXVI XXXVII XXXVIII

Compound XXXVIII is also similarly formed.

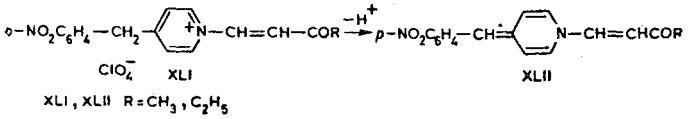
A rather stable methylene anhydro base (XXXIX) that contains an N-acyl residue is known among pyrimidine derivatives [83]:



XXXIX XL

Compound XXXIX is hydrolyzed to corresponding base XL when it is refluxed in butyl alcohol.

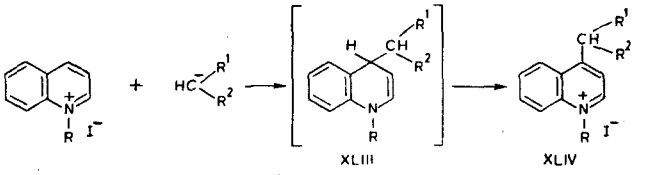
In the pyridine series one can also cite vinylogs of N-acyl anhydro bases (XLII), which are completely stable and are formed from corresponding salts XLI even by the action of solvents that have basic properties [84]:



XLI, XLII R = CH_3, C_2H_5

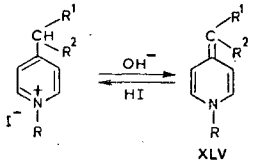
It should be noted that the formation of anhydro bases is characteristic not only for pyridinium salts but also for salts of other nitrogen heterocycles [48, 51, 85, 86].

Reaction of Quaternary Pyridinium Salts with CH Acids. Pyridinium and benzopyridinium salts react with methyl ketones and β-dicarbonyl compounds in the presence of strong bases to give 4-substituted pyridinium and quinolinium cations of the XLIV type [87-90]:

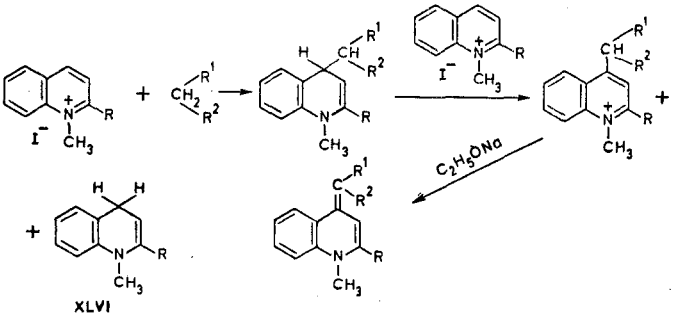


R = Alk ; R^1 = H, $COOCH_3$, CN ; R^2 = NO_2, $COOCH_3$, COC_6H_5

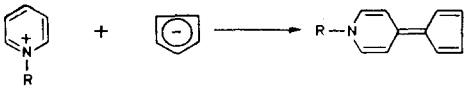
Under these conditions isoquinolinium salts form 1-substituted isoquinolinium cations [87, 91]. The intermediates are dehydro derivatives of the XLIII type, which are readily oxidized by air oxygen [92]. Dihydro structures of the XLIII type sometimes require oxidation with lead tetraacetate, potassium permanganate, chloranil, and other oxidizing agents [93]. Colored dihydro compounds of the quinoid type, i.e., anhydro bases XLV, which are again aromatized by the action of acids, are formed in the case of oxidation in the presence of alkalis [87]:



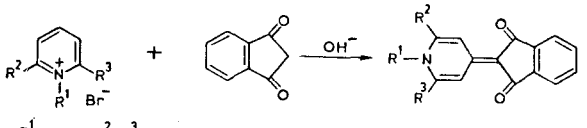
Thus in this case also anhydro base XLV is formed from the quaternary salt by reaction with alkali; however, the salt is obtained here as an intermediate in the process of the reaction. In some cases oxidation of dihydro compounds is realized by the starting quaternary salt (evidently due to hydride transfer) [94]:



The formation of dihydropyridine structure XLVI in the course of the reaction is a confirmation of this mechanism. The cyclopentadienyl anion reacts similarly with pyridinium salts [31, 32, 95, 96]; the resulting anhydro bases are nitrogen analogs of sesquifulvalene:

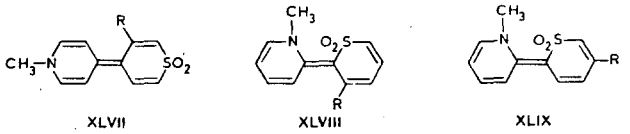


Similar structures, i.e., pyrophthalones, are also obtained in the condensation of indandione with 2-R^1-6-R^2-pyridine alkylbromides in the case of oxidation with oxygen in an alkaline medium [21, 22]:



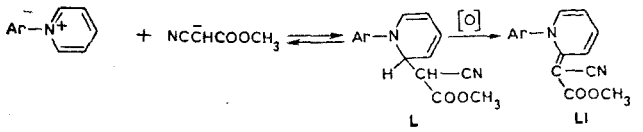
R^1 = Alk ; R^2, R^3 = H, Alk

Compounds XLVII-XLIX were also similarly obtained [97]:



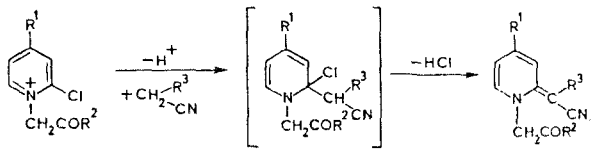
R = H, CH_3

Anhydro bases LI were recently synthesized by oxidation of the dihydro derivatives (L) that are formed as a result of the reaction of N-arylpyridinium salts with the anions of the methyl esters of acetoacetic, cyanoacetic, and malonic acids:



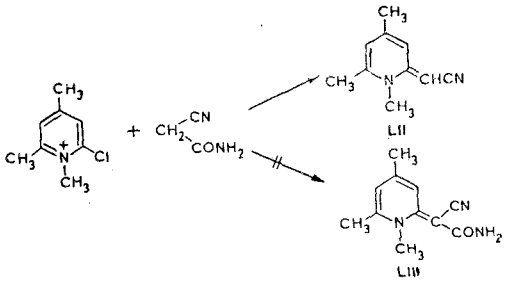
The mechanism and kinetics of the reaction have been investigated [98].

Replacement of a Halogen Atom in the Pyridinium Salt by CH Acids. Anhydro bases are also readily formed in the condensation of 2- or 4-halo-substituted pyridinium salts with CH acids in the presence of bases [95, 99, 100]:

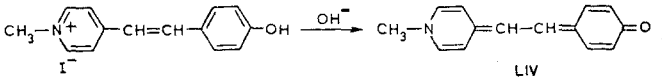


$R^1 = CH_3$; $R^2 = C_6H_5$; p-$CH_3C_6H_4$; p-BrC_6H_4 ; $R^3 = CN, CO_2C_2H_5$

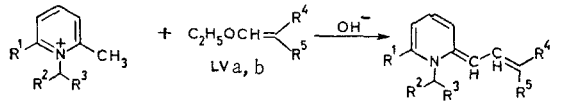
It has been noted that under similar conditions the condensation of 2-chloro-1,4,6-trimethylpyridinium perchlorate with cyanoacetamide gives LII in high yield [63]:



Other Syntheses. The so-called merocyanine dyes, which are obtained by treatment of o- and p-hydroxystyrylpyridinium and quinolinium cations of the LIV type with alkali, constitute a large group of anhydro bases [101-112]:



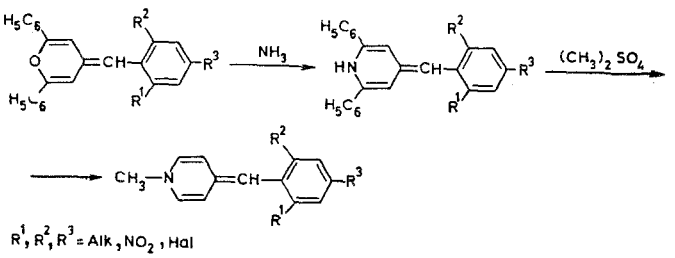
Extremely similar to them in structure are 2-allylidene-1,2-dihydropyridines LVI, which are readily obtained from various α-picolinium salts by reaction with ethyl ethoxymethylenecyanoacetate (LVa) or 3-ethoxymethylenepentane-2,4-dione (LVb) in the presence of alkalis [1-4, 113, 114]:



LV a $R^4 = CO_2C_2H_5$, $R^5 = CN$; b $R^4 = Ac$, $R^5 = Ac$

LVI a $R^1 = R^2 = H$, $R^3 = R^4 = CO_2C_2H_5$, $R^5 = CN$; b $R^1 = CH_3$, $R^2 = H$, $R^3 = R^4 = CO_2C_2H_5$, $R^5 = CN$;
c $R^1 = CH_3$, $R^2 = H$, $R^3 = CO_2C_2H_5$, $R^4 = R^5 = Ac$; d $R^1 = H$, $R^2 = CH_3$, $R^3 = R^4 = CO_2C_2H_5$, $R^5 = CN$;
e $R^1 = H$, $R^2 = CN$, $R^3 = CO_2C_2H_5$, $R^4 = R^5 = Ac$; f $R^1 = R^2 = R^3 = H$, $R^4 = CO_2C_2H_5$, $R^5 = CN$;
g $R^1 = R^2 = H$, $R^3 = C_6H_5$, $R^4 = CO_2C_2H_5$, $R^5 = CN$

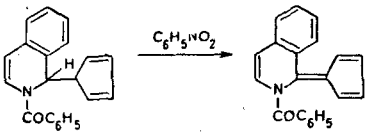
The preparation of anhydro bases of the pyridine series by the reaction of similarly constructed pyran structures with ammonia has been described [115]:



$R^1, R^2, R^3 = Alk, NO_2, Hal$

Recyclization of the pyran ring with replacement of the heteroatom occurs during the reaction in this case.

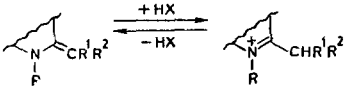
There is, perhaps, only one reference in the literature to the synthesis of stable N-acyl anhydro bases by oxidation of 1-benzoyl-2-cyclopentadienyl-1,2-dihydroisoquinolines with nitrobenzene [116]:



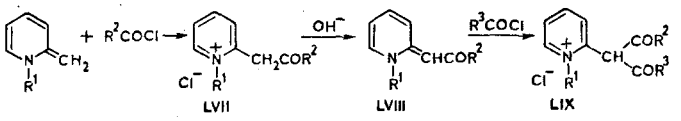
Similar N-acyl anhydro bases have also been obtained by the direct reaction of N-acylpyridinium cations with cyclopentadienylsodium [116].

Reactivities of Anhydro Bases

The reactivities of anhydro bases of the pyridine series are determined by their electronic structures, which were examined above. They are strong bases [36, 37] (Table 1) and therefore react readily with various electrophilic agents. At the very beginning of the investigation of anhydro bases it was noted that the color of their solutions changes from red to yellow or colorless when water is added [64]. This was ascribed to protonation of the anhydro bases and the formation of hydroxides. It was later shown [33, 34, 63] that the UV spectrum of the anhydro base in aqueous solution or in a solution of mineral acid is identical to the spectrum of the corresponding quaternary salt, which indicates protonation of the anhydro bases at the methylene group. Even a weak acid such as methanol may act as a proton donor [47], since the UV spectrum of 1-methyl-2-methylene-1,2-dihydroquinoline in methanol solution has two absorption bands that are characteristic for the anhydro base and the quinaldinium ion. These two forms exist in equilibrium, since the addition of acid or alkali increases the intensity of one absorption band and decreases the intensity of the other. The position of the equilibrium depends on the substituents in the pyridine ring and in the methylene group. Thus 1,4,6-trimethyl-2-cyanomethylene-1,2-dihydropyridine in dilute aqueous solutions exists only in the form of a quaternary ammonium base hydroxide, since its UV spectrum is identical to the spectrum of a dilute solution of the base in sulfuric acid, whereas 1-methyl-4-dicarbethoxymethylene-1,4-dihydropyridine is only partially hydrated in water [63]:



Anhydro bases react just as readily with acylating agents; acylation takes place at the methylene group to give salt LVII, which under alkaline conditions is again converted to anhydro base LVIII [117]:

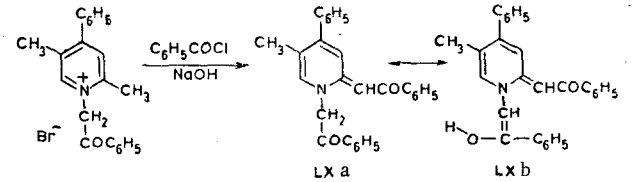


LVII LVIII LIX

R^1 = Alk; R^2 = C_6H_5, p-$NO_2C_6H_4$; R^3 = C_6H_5, p-$NO_2C_6H_4$

This anhydro base can be acylated further at the methylene carbon atom to give diketones [117].

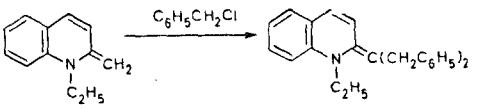
The acylation of an anhydro base without its isolation has been described. Thus an anhydro base to which structure LXb was assigned was obtained by treatment of a mixture of 1-phenacyl-2,5-dimethyl-4-phenylpyridinium bromide with benzoyl chloride in methylene chloride–water with alkali [118]:



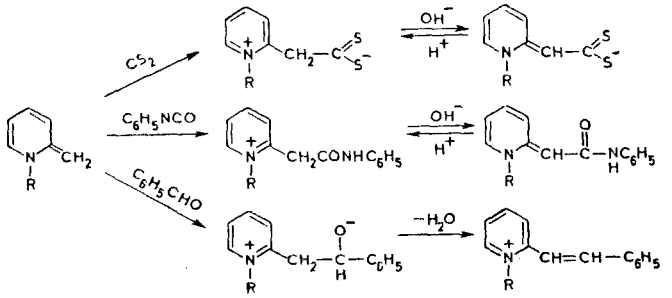
LX a LX b

In this case also 1-phenacyl-2-methylene-4-phenyl-5-methyl-1,2-dihydropyridine, which is acylated to give a quaternary salt, is evidently formed by the action of alkali. The quaternary salt under alkaline conditions gives anhydro base LX.

It has been noted that the alkylation of anhydro bases, like acylation, takes place at the methylene carbon atom. The benzylation of 1-ethyl-2-methylene-1,2-dihydroquinoline is an interesting process; a dibenzylated anhydro base is formed immediately when it is treated with benzyl chloride in benzene [119]:

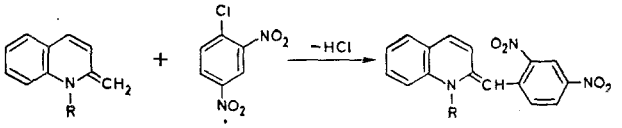


Isocyanates [117], isothiocyanates [120], carbon disulfide [121], aromatic aldehydes [122, 123], and other electrophilic agents add to the methylene group of anhydro bases in inert solvents:

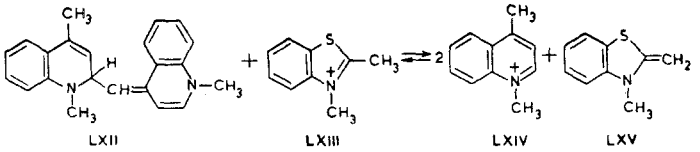


Inasmuch as they are strong nucleophilic agents, anhydro bases react with electrophiles of moderate strength such as quaternary salts of pyridine bases to give the so-called mixed anhydro bases [47, 53] (see above); this reaction is the only example of hetarylation by quaternary salts of pyridine bases, which do not react with less nucleophilic compounds such as π-surplus heterocycles – indole, pyrrole, etc.

Anhydro bases nucleophilically replace the chlorine atom in 2,4-dinitrochlorobenzene [124]:

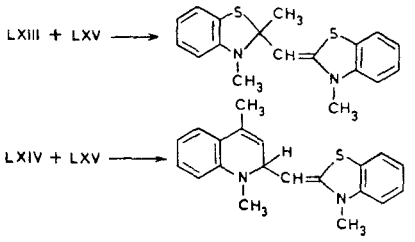


Anhydro bases of the LXII type are also strong bases and react with quaternary salts at the methylene group; if the quaternary salt contains a substituent with a labile hydrogen atom, the anhydro bases deprotonate it to give a new anhydro base and a new quaternary salt [47, 48, 53, 85]:

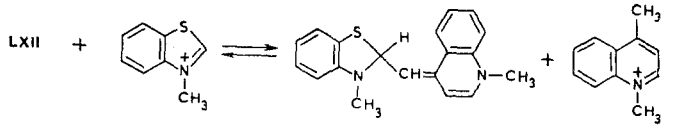


LXII LXIII LXIV LXV

Anhydro base LXV can subsequently react with both salt LXIII and salt LXIV:

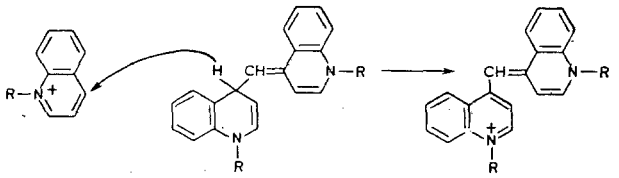


If the quaternary salt does not have a methyl group, anhydro base LXII reacts with it to give a new salt and a new mixed anhydro base [47, 48, 53, 85]:



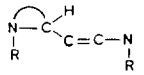
This reaction is similar to the transhetarylation that occurs in the case of N-acyl salts [125].

Anhydro bases play an important role in the synthesis of cyanine dyes. Thus anhydro bases of the LXVI type have a labile hydrogen atom that is capable of being split out in the form of a hydride ion. Quaternary salts, Malachite Green, Methylene Blue, quinones, thioacetamides, carbon tetrachloride, and betaines can serve as hydride-ion acceptors [28, 47, 53]:

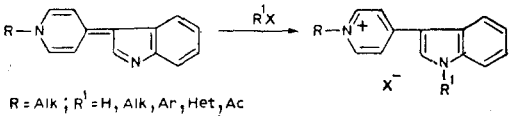


LXVI

The detachment of a hydride ion is a common property of anhydro bases of the type

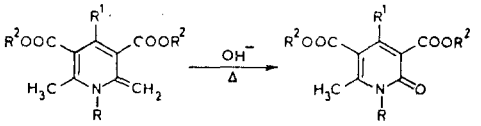


In the reaction of anhydro bases of pyridylindoles with electrophilic agents the latter, as a consequence of an increase in the conjugation chain, do not attack the methylene link but rather the nitrogen atom of the azomethine fragment in the pyrrole ring to give quaternary salts of pyridylindoles that are substituted at the indole NH group [69, 71, 74, 75]:

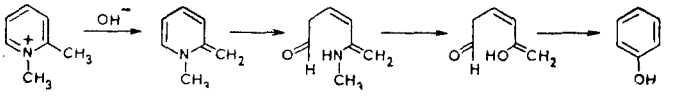


R = Alk; R' = H, Alk, Ar, Het, Ac

Of the reactions of anhydro bases with nucleophiles, up until recently several examples were known; when they were heated with alkali, they formed pyridones [57]:

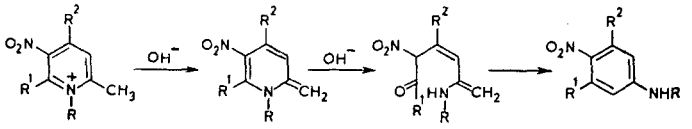


In addition, it has been found that phenols are formed in the reaction of quaternary pyridinium salts that contain a methyl group in the α position with sodium bisulfite [126, 127]. The reaction evidently proceeds through a step involving the formation of anhydro bases, which under hydrolytic conditions undergo ring opening with the subsequent formation of a benzene ring; the amine fragment is lost in the process because of the severe reaction conditions:

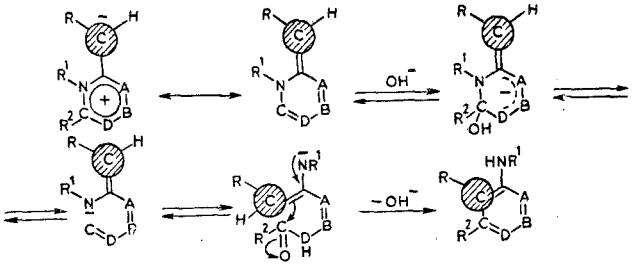


However, the possibility that the reaction also takes place as a result of direct attack by the hydroxide ion on the pyridinium cation is not excluded.

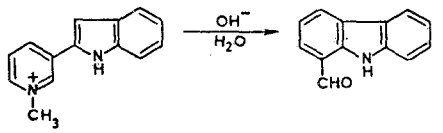
A new reaction involving recyclization of quaternary 2-alkylpyridinium salts to give anilines under the influence of alkaline agents was recently discovered [128-130]. The recyclization evidently also proceeds through a step involving anhydro bases but without the loss of an amine fragment:



The recyclization takes place not only in aqueous alcoholic alkali but also in aqueous and alcohol solutions of primary and secondary amines. An increase in the yield of recyclization product was noted when the reaction was carried out in the presence of primary and secondary amines; this is evidently associated with the suppression of side processes involving exchange of the amine fragment [130]. The reaction may be of practical interest, since it makes it possible to produce difficult-to-obtain anilines on the basis of cheap coal-tar-chemical raw material, as well as theoretical interest, since it is a direct route from a heterocyclic system to a carbocyclic system. This previously unknown rearrangement with recyclization of the pyridine (and pyrimidine) ring has been developed extensively in a number of models (see [131-142]). The overall scheme of these transformations can be formalized in the following way [135]:

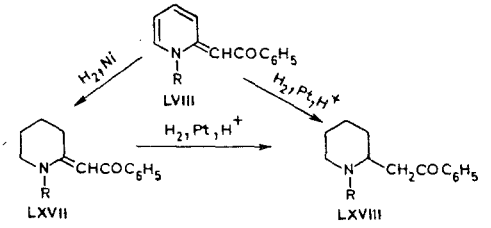


The electron-surplus exocyclic group that is the object of attack during recyclization may not be directly bonded to the ring that is undergoing opening. The recyclization of 3-(2-indolyl)pyridine to 1-formylcarbazole may serve as an example [138]:

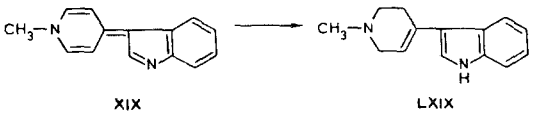


The recyclization of nicotyrine methiodide to 1-methyl-7-formylindole proceeds similarly [139].

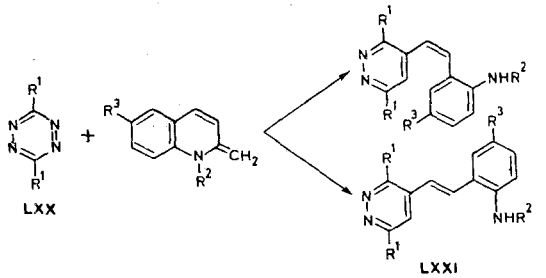
In the reduction of anhydro bases of the LVIII type in the presence of a platinum catalyst 3 moles of hydrogen are absorbed, and 1-R-2-phenacylpiperidine LXVIII is formed, whereas in the case of reduction with a Raney nickel catalyst 2 moles of hydrogen are absorbed with the formation of piperidylene ketone LXVII, with a UV spectrum that is typical for the N−C=C−C=O system. Subsequent reduction of LXVII in dilute acid in the presence of platinum gives LXVIII [117]:



The reduction of anhydro bases of the XIX type with sodium borohydride in an alkaline medium leads to tetrahydropyridine LXIX [143]:



A new reaction of methylene anhydro bases of six-membered nitrogen heterocycles, viz., cycloaddition to symmetrical tetrazines, was recently observed [5, 6]. Thus the reaction of 3,6-di(2-pyridyl)-sym-tetrazine LXX with quinaldine methiodide in the presence of triethylamine as the base proceeds with opening of the intermediately formed anhydro base and with the production of the cis and trans isomers of LXXI:



Pyrazole derivatives, various spiro compounds, and azomethines have also been obtained by means of this reaction with various anhydro bases.

Thus it is apparent from this review that anhydro bases of the pyridine series are highly reactive compounds that are intermediates in the synthesis of various heterocyclic and carbocyclic systems – indolizines, pyridazines, pyridines, anilines, pyrazoles, spiro compounds, etc. They play an important role in organic synthesis as the basis for the preparation of physiologically active compounds, cyanine dyes, anticoagulants, etc.

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