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PYRIDINE RING NUCLEOPHILIC RECYCLIZATIONS

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CONTENTS

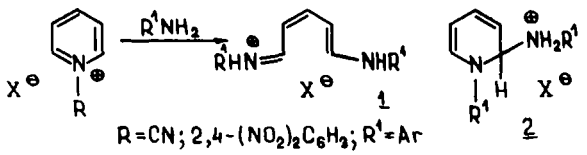
I. INTRODUCTION

The interaction of the pyridine ring with nucleophiles has been studied since the end of the XIX century.[1,2] Perhaps the best known process of this kind is the Zincke–König reaction,[3–5] or the cleavage of a quaternised pyridine ring by aromatic amines. The resulting C_5 fragment plays an important part in the synthesis of cyanine dyes[6] recently employed as optical sensitizers[7] and in the synthesis of azulenes (Hafner reaction[8,9]). Pyridine ring nucleophilic transformations have been recently receiving a great deal of attention, especially certain newly discovered rearrangements appearing to be of general significance in heterocyclic chemistry. However, no review on this topic has been published, except for brief discussions in some papers on pyridine ring fission[4,10–12] and in van der Plas's monograph.[13] The aim of the present article is to summarise important results reported before 1979. Whenever possible, the repetition of earlier reviews will be avoided. The paper will not deal with the recyclizations of hydrogenated structures or with the processes of the pyridine ring contraction or expansion which occur in photochemical conversions and in the rearrangements of pyridine carbenes (on these topics see, e.g.,[13–17]).

II. HISTORICAL INFORMATION

(a) *Zincke–König reaction as the prototype of pyridine ring nucleophilic opening*

In 1904 Zincke and König independently found that aromatic amines react with pyridinium salts to form coloured products which Zincke identified as glutaconic dialdehyde derivatives (**1**)[18,19] and König as the derivatives of 1,2-dihydropyridine (**2**)[20].



✠ Deceased.

The system of conjugated double bonds was assumed to be responsible for the intense colouring of the glutaconic dialdehyde derivatives. Later, however, coloured compounds of structure 2 were obtained as well. For instance, heating of 1 ($R = p\text{-}C_6H_4C_6H_5$) was reported to give rise to a coloured 1,2-dihydropyridine derivative 2[21]. The open-chain and the cyclic structure may sometimes exist in equilibrium.[22] To further complicate the problem, glutaconic dialdehyde dianil salts may assume two different colours, which Zincke explained by dimorphism.[19] The same effect was probably observed with cyanimines.[20,23] It is not unlikely, however, that the difference in colour is due to *cis-trans* isomerism,[23] as evidenced by the interconversion of the modifications in the presence of iodine, upon heating or upon irradiation.[19,24-27]

It is well-known that 1-phenyl- and 1-*p*-nitrophenylpyridinium salts do not react with amines[19] but their ring may be opened by alkali.[20,28,29] Moreover, even aromatic amines cause ring fission in such base-sensitive pyridine derivatives as 1-(2,4-dinitrophenyl)pyridinium cations[18,19,27,29-39] and especially N-cyano-compounds,[20,22,23,26,40-50] where the pyridine ring is even more activated.

If, therefore, the presence of strong electron acceptor groups on the nitrogen atom promotes the cleavage of pyridinium salts, there should be more examples of easy cleavage. Indeed, quite a few reactions of the N-substituted pyridine ring cleavage type were reported, for pyridinium salts with a N-containing heterocycle attached to the pyridine nitrogen.[51-60] The cleavage is, of course, largely dependent on how efficient is the transfer of the aza-substituent electron-accepting influence. Thus among the three isomeric pyridylpyridinium chlorides the 4-pyridyl salt shows the highest succeptibility to alkali.[52-54,56] However, the pyridyl radical is not a particularly efficient electron-withdrawing group, and the hydrolysis of 4-pyridylpyridinium chloride occurs less readily than that of the 1-(2,4-dinitrophenyl)pyridinium cation.

Generally speaking, an electronegative group on the pyridine nitrogen weakens the exocyclic N–C bond as well as the C–N bonds in the ring. Thus, 4-pyridylpyridinium chloride with aniline yields glutaconic dialdehyde dianil and 4-phenylaminopyridine,[61] which means that the rate of the ring cleavage is comparable to that of the N-substituent elimination. In some cases only the latter process occurs; thus potassium phenolate converts 4-pyridylpyridinium chloride into 4-phenoxypyridine[61] and 3-nitro-4-pyridylpyridinium chloride readily reacts with water to form 3-nitro-4-hydroxypyridine.[55]

The pyridine ring opening is markedly affected by the nature and position of substituents on the ring. Weak electron donors in position 3 (e.g. CH_3 or $NHCOCH_3$) decrease the yield of cleavage products as against non-substituted pyridine.[26,27,34,38,39,46,49,62,63] Aniline does not open the ring in 1-(2,4-dinitrophenyl)-3-dimethylaminopyridine, while heating leads only to elimination of the N-substituent.[27] In a similar manner aniline reacts with 1-(2,4-dinitrophenyl)-3-amino- and 3-oxypyridinium chlorides.[27,64] In the latter case the ring-stabilizing effect is undoubtfully due to the formation of a mesomeric betaine.[27,34,65]

In position 4 the effect of weak electron donor groups (e.g. Me or OMe) is greater and the yield of dianil salts in the pyridine ring nucleophilic opening is lower.[23,26,27,45-49,64,66] With acetamido- or phenylamino-groups in position 4 there are pronounced changes in the fragmentation behavior. Thus aromatic amines do not open the pyridine ring of 1-(2,4-dinitrophenyl)-4-acetamido- and 4-phenylamino-pyridinium chlorides even at high temperatures.[27,34] The amine in this case attacks primarily the exocyclic carbon attached to the pyridine nitrogen. Likewise, when passing from 3- to 4-methoxypyridine the yield of the ring fission products in reactions with cyanogen bromide and amines decreases.[23,26,47,48] The ring stabilisation in all these cases appears to arise from the efficient transfer of the γ-substituent influence.

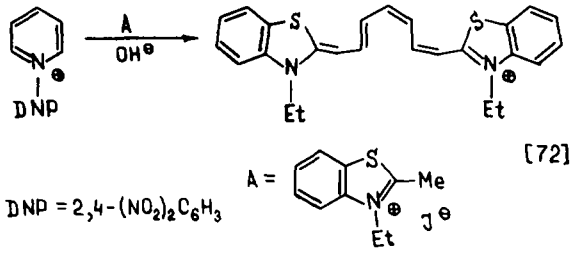
The cleavage of 2-substituted pyridines may involve steric difficulties.[26,45,46,49,67,68] Thus a methoxy- or an acetamido-group in position 2 virtually prevents the pyridine ring from opening.[26] The yield of the dianil in the reaction between 2-methylpyridine and cyanogen bromide is as low as 8%.[26]

With cyanogen bromide and amines the pyridinium bases containing electron-accepting substituents show little, if any, cleavage. For example, the attempts to open the ring of nicotinamide, 3-cyanopyridine, and 3-pyridinaldehyde, in this manner failed.[26,45,46] However, the technique proved useful in the splitting of 4-chloro-, 3-chloro- and 4-benzoylpyridine.[26,40] It seems that the high stability of most pyridine derivatives containing electron-accepting substituents is due to their low basicity which, in turn, is responsible for the fact that they are less likely to react with cyanogen bromide or 2,4-dinitrochlorobenzene. Incidentally, the introduction of a weak electron acceptor such as iodine into position 3 of the pyridine ring results in easy cleavage under the effect of aniline.[23]

It is of interest to consider the effect of amine basicity (primarily aromatic amines) on the pyridine ring opening. Under usual conditions 1-(2,4-dinitrophenyl)pyridinium chloride is known to react neither

with 2,4-dichloroaniline nor with *o*-, *m*- and *p*-nitroanilines,[19,29] while the reaction with sulfamides and aminosulfoacids is extremely slow.[31,35,69] Although N-cyanopyridinium bromide does react with aniline, no similar reaction takes place with 2,4-dinitroaniline or tribromoaniline.[20,22,29] Diamines, heterocyclic and particularly aliphatic alkyl- and dialkyl-amines were reported to cause ring fission in 1-(2,3-dinitrophenyl)pyridinium chloride.[19,31,33,37,66,70]

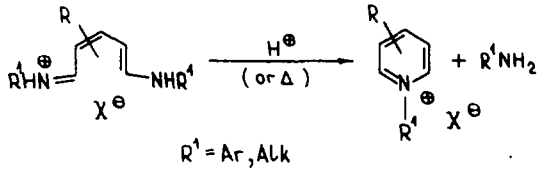
The pyridine ring fission by carbanions, i.e. by the substances containing an activated methyl or methylene group, occurs but in the presence of strong bases.[71-77] Along with the well-known direct synthesis from glutaconic dialdehyde dianils,[72] this reaction may be used to obtain cyanine dyes.[72-75] Polyhydroxybenzenes also may act as carbanions in the reaction of the pyridine ring opening.[78]



The formation of open-chain products from pyridine derivatives depends on the nature of the solvent. Indeed, in pyridine solution *o*-, *m*- and *p*-nitroanilines do cleave 1-(2,3-dinitrophenyl)pyridinium chloride.[29] 2-, 3- and 4-Methylpyridine with cyanogen bromide and aniline in water give high yields of fission products.[79]

The cleavage is largely dependent on temperature. It is likely that, in the reaction between picryl chloride and pyridine,[80] or 2,4-dinitrochlorobenzene and a pyridine base in an alcohol solution that there is an equilibrium with the pyridinium salt. At low temperatures the dissociation of the salt is low and the main effect of aromatic amines is the ring fission. As the temperature is raised and the dissociation increases, the exocyclic bond cleavage occurs.[27] In high polarity solvents, e.g. dimethyl formamide, at elevated temperatures this process readily takes place even in the case of N-methyl pyridinium cations.[81]

When treated by acids or steam or even when simply heated, glutaconic dialdehyde dianils rearrange yielding 1-arylpyridinium cations by the loss of an amine.[18-20,39,62,70,82]



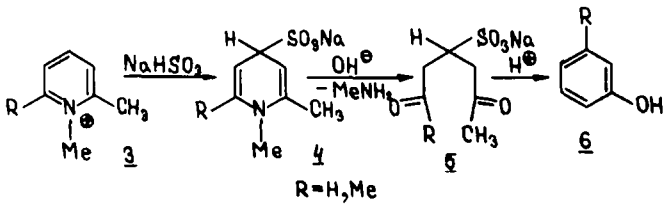
The cyclisation is essentially promoted by the presence of a donor substituent in the C_5 fragment or in the arylamine group.[32,62] The dianils whose chain terminates in alkylamine rather than arylamine groups at both ends show particularly easy cyclisation.[19,70] Later it was found that the one-stage exchange of the N-substituents is feasible by the treatment of 1-arylpyridinium salts with the excess of an amine, on addition of a stronger base or even merely in polar solvents (see, e.g.[83]).

(b) *Other reactions of ring opening*

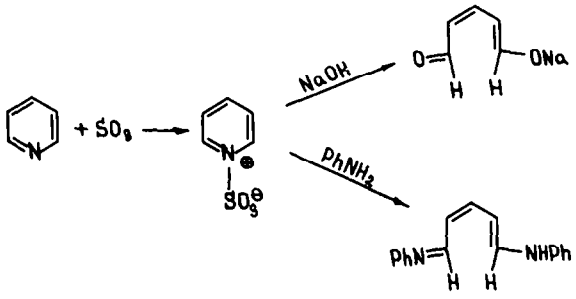
Pyridine with aqueous sodium bisulfite gives rise to an adduct containing 3 moles of the bisulfite. Alkalies decompose this product into ammonia, sodium sulfite and glutaconic dialdehyde.[84-86] Aromatic amines also open the pyridine ring with formation of the corresponding glutaconic dialdehyde anils.[85,86]

It is interesting to note that pyridinium salts may be converted into phenols by consecutive treatment with sodium bisulfite, an alkali and an acid.[87,88] Though this series of reactions may hardly be regarded as nucleophilic recyclization, some features of the process deserve special interest. The bisulfite ion HSO_3^- could be expected to add in position 2 or 4 of the pyridine nucleus of the quaternary salt **3**. However, the fact that this reaction with 3- or 4-methyl pyridines does not occur suggests addition at position 4. When treated by an alkali, the 1,4-dihydroderivative **4** undergoes ring opening by the loss of an alkylamine to yield the 1,5-dicarbonyl compound **5** which in an acidic environment cyclises

yielding the carbocyclic product **6**.

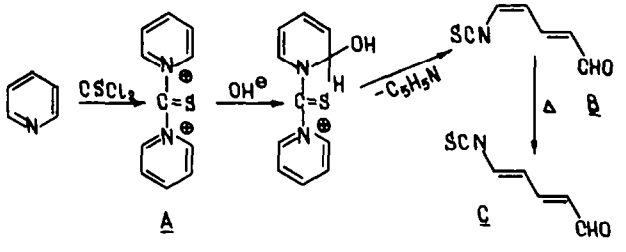


In inert solvents at low temperatures pyridine reacts with sulphur trioxide to form pyridinium δ-sulphonate.[89] The same produce results from the interaction between pyridine and chlorosulfonic acid or its ethyl ester.[90] Alkalis decompose pyridinium δ-sulphonate into glutaconic dialdehyde sodium salt and sodium sulfamate;[89,90] with aniline the ring opening results in glutaconic dialdehyde dianil.[91] Similar adducts of sulphur trioxide to 2- and 4-methylpyridine are not easy to obtain and bases bring about the resinification.[92]



Certain other reagents such as phosgene, phosphorus oxychloride, 2-chloroquinoline derivatives, benzanilide-imidochloride, dichloro- and dibromo-indenones quaternise pyridine to form salts which react with bases to give open-chain products (the two last-named reagents in the list are even more efficient than 2,4-dinitrochlorobenzene).[51,93] Under the action of bases, pyridine adducts with chlorine or bromine, as well as complex salts with zinc or mercury chloride, also form organic dyes whose structures are not yet determined.[93]

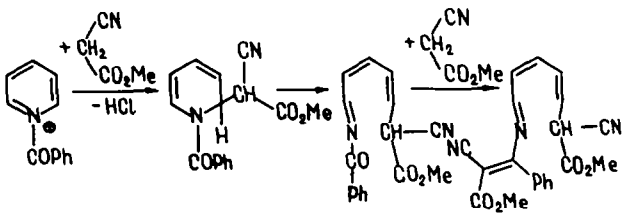
Pyridine ring opening is also promoted by thioderivatives of phosgene or phosphorous chloride type compounds. The reaction under the influence of thiophosgene and barium carbonate yields both kinetically and thermodynamically controlled products, i.e. *trans, cis*- and *trans, trans*-5-isothiocyanato-penta-2,4-dienals (*B* and *C* respectively).[94] The A and B stages of the ring cleavage may be interpreted in terms of hard and soft acids and bases. The C-2 atom, which is harder than the thiocarbonyl carbon, is attacked by the hard hydroxyl ion and the resulting anhydrobase opens to yield the *cis, trans*- and then the *trans, trans*-aldehyde.[95]



When allowed to stand, a mixture of pyridine, chloroform and caustic soda was found to form a solution of an unstable red dye.[96] After a while, sodium cyanide and sodium vinylacrylate can be isolated from the solution. Under the same conditions 2-methylpyridine affords sorbic acid, whereas both 2,4-dimethyl- and 2,4,6-trimethylpyridine do not react.[96] Bromoform, iodoform and carbon tetrachloride lead to the same products as chloroform; with methylene chloride and methylene iodide the yields are somewhat lower. In the presence of bases the pyridine ring opens also under the effect of diphenyldichloromethane and phenyltrichloromethane.[97,98]

Though acyl chlorides were once believed to be incapable of causing the pyridine ring cleavage,[51,19] a reaction between diphenylcarbamoyl chloride and pyridine in an alkaline medium does take place.[99] Moreover, benzoyl chloride and benzoic anhydride in alkaline media were also reported to react with pyridine in the same manner[100,101] (the yields of these processes were not specified). The formation of coloured glutaconic dialdehyde derivatives seems to account for the intense purple colouring of aqueous and water-alcohol solutions of pyridine and its derivatives on addition of an alkali and arylsulfonyl chlorides. The reaction is a sensitive assay for pyridine derivatives.[102-109]

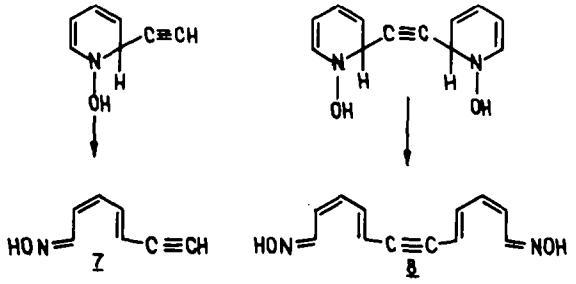
The splitting of 1-acylpyridine salts is promoted by compounds containing active methyl or methylene groups. Thus in the presence of cyanoacetic acid methyl ester, oxindole or coumarone-2, pyridine readily reacts with acyl chlorides.[75,76] Consecutive treatment of 2-methylpyridine by ethyl-



chloroformate and a dilute acid gives rise to an adduct of composition 2:1. The ring in the pyridinium salts conceivably opens under the action of a second 2-methylpyridine molecule which under these conditions acts as a methylene component.[110]

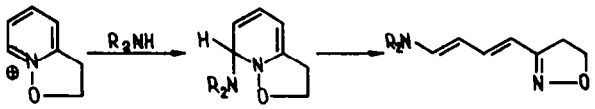
The base-induced cleavage of pyridines with conjugated substituents also occurs and acyclic products are readily formed under the effect of alkalis, primary and secondary amines,[111-115] and with compounds containing activated methyl or methylene groups.[116,117]

It is well-known that N-oxides of heteroaromatic compounds are highly reactive with respect to nucleophiles and electrophiles alike.[118,119] It has been observed, for instance, that phenylmagnesium bromide brings about electrocyclic opening of the ring in pyridine N-oxide.[120-122] When treated by acid anhydrides or even simply heated, the acyclic products show easy recyclization into pyridine bases or their N-oxides.[120,121] In contrast to earlier evidence,[123] the reaction between pyridine N-oxide and sodium acetylide does not lead to 2-ethynylpyridine N-oxide, since the reaction products as identified by PMR are those of the ring opening (7,8).[124]



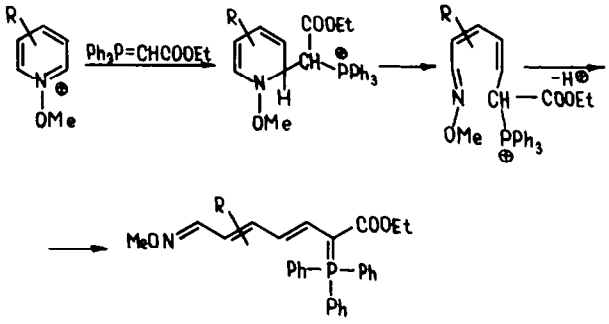
The formation of 1-alkozy- or 1-acyloxypyridinium salts by quaternization of pyridine N-oxide increases still further the propensity of the pyridine ring for nucleophilic opening. For example, the intermediary formation of 1-acetoxypyridinium salts is apparently involved in the interaction of pyridine N-oxide with mercaptans in the presence of acetic anhydrode and triethylamine. Apart from the ring cleavage products, this reaction was found to result in substituted Δ^2- and Δ^3-tetrahydropyridines.[125]

On additional activation by such electron acceptors such as CN or $CONH_2$, 1-methoxypyridinium salts readily react with secondary amines to form mono-O-methyloximes of glutaconic dialdehyde.[126,127] On the contrary, unsubstituted 1-methoxypyridinium salts or those with an electron donor on the pyridine ring react with aqueous secondary amines to give rise primarily to pyridine N-oxides by the O–C bond fission.[128-131] The pyridinium salts in this case act as methylating agents.[129] Under certain conditions, however, hydroxyl ions were observed to cause ring cleavage of such salts, as evidenced first by UV-spectroscopy and then by the isolation of crystalline enamines in the reaction between bicyclic isoxazoline [2,3-a] pyridinium ions and secondary amines.[131-133]

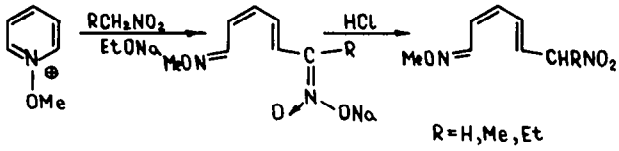


Such open-chain structures usually lend themselves to isolation, provided the reaction was carried out in an aprotic solvent containing no water.[134] PMR data suggest a *trans*-structure for the conjugated bonds; however, *cis–trans* intermediates corresponding to the kinetic control may also be observed sometimes.[126,127,134–136]

Pyrylium salts have long been used for the synthesis of benzene and azulene derivatives.[137,138] As for 1-methoxypyridinium salts, they react with phosphoranes only to undergo ring opening leading to stable vinylogues of phosphoranes. The double bonds of the latter were also found to have a *trans*-configuration.[139]



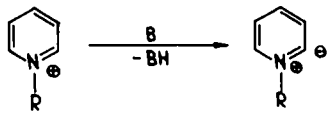
Similarly, upon treatment by an equivalent amount of a nitroalkane and sodium ethoxide, 1-methoxypyridinium iodide is converted into the corresponding nitropolyenes.[140,141] The yield is the highest with nitromethane and the lowest with 1-nitropropane because of steric difficulties.[141]



III. MECHANISM OF PYRIDINE RING NUCLEOPHILIC OPENING

The two mechanisms suggested for nucleophilic substitution in the pyridine ring were "addition–elimination" (AE) and "elimination–addition" (EA or the hetaryne mechanism).[142,143] The formation of anionic σ-complexes in the AE reactions was for a long time merely postulated until such adducts were reported for reaction with butyl lithium, lithium aluminium hydride, sodium methoxide and hydroxide anions.[144–146] The EA mechanism put forward to account for the amination of pyridine halogen derivatives and involving intermediate formation of hetarynes was studied in detail as well.[142] Though more appropriate for pyrimidine compounds, the so-called ANRORC mechanism recently advanced by van der Plas also sheds some light on the behaviour of pyridine halogen derivatives.[147]

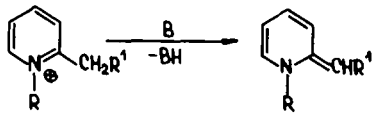
PMR deuterium exchange investigations point out that strong nucleophiles may deprotonate the 2-position of 1-alkylpyridinium salts to form ylides.[148–150]



The Me-group in 1-methylpyridinium salts shows virtually no deuterium exchange; the 1-allyl-pyridinium salt in the presence of pyrrolidine, however, exchanges four hydrogens for tritium *via* an intermediate ylide.[151,152]

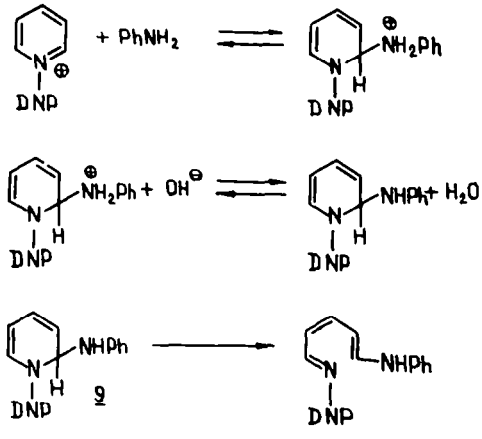
2-Alkylpyridinium salts feature rather easy side chain deprotonisation leading to an

anhydrobase.[153-156] The C–H acidity of the side chain of non-quaternised 2-alkylpyridines is relatively low.[157-160]

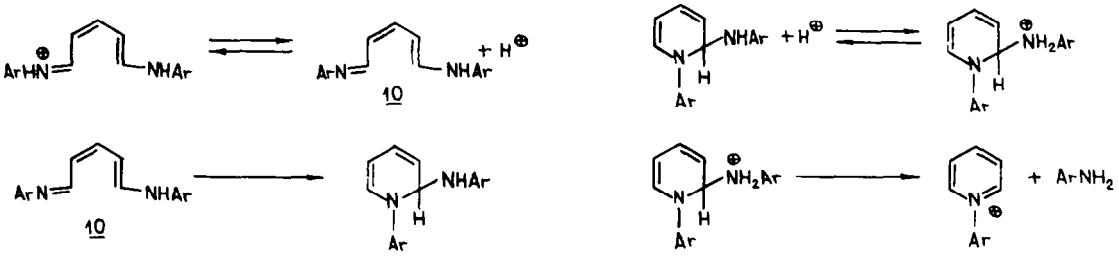


There is competition for this deprotonation either by attack on the carbon attached to the pyridine nitrogen, dealkylation of the quaternary salt, [81,131,161,162] or the nucleophilic addition to the ring. For non-quaternised pyridines the latter process occurs only under severe conditions. For example, Chichibabin's amination is generally assumed to involve addition of the NH_2^- anion in the 2 position of the pyridine ring.[163] An alternative attack on the position 4 evidently takes place only with 2,6-substituted derivatives as observed, for example, with the reaction between the NH_2^- ion and 2,6-dimethylpyridine.[164] Such addition of a hard anion is somewhat more likely if the pyridine ring bears a strong electron acceptor[146] or if it is annelated, that is, the pyridine ring is a fragment of a condensed structure more capable of nucleophilic reactions.[165,166]

As in pyridine bases, the N atom in pyridinium salts polarizes primarily the adjacent carbon with respect to hard nucleophiles.[167] Thus ammonia adds to pyridinium salts to form dihydropyridines. Whether the 2- or the 6-amino compound will be the main product depends on the substituent in the pyridine nucleus. Conversely, soft nucleophiles whose behaviour is controlled by frontier orbitals tend to attack the 4 position.[167] This holds in the case of carbanions.[170-173] Cyanide ion also adds to position 4, though the reaction is reversible.[174] Nitromethide and ethanethiolate anions attack both position 2 and position 4.[173] In 1957 Belgian researchers found that the interaction between 1-(2,4-dinitrophenyl) pyridine and aniline in 50% aqueous ethanol is a first-order reaction in both components and hydroxide anion.[175] They suggested that the limiting stage of the process was the electrocyclic opening of the covalent amination product **9**[175-177] The pyridine ring opening by amines, hydroxyl ion and C-nucleophiles was studied also by a number of other workers.[181-187]

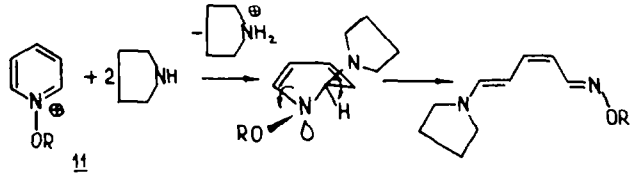


The rate of conversion of glutaconic dialdehyde dianil salts into the salts of 1-arylpyridinium is not just a function of the substrate concentration in methanol.[182-183] In fact, the addition of triethylamine or methoxide anions first gives rise to 5-anilineo-N-aryl-2,4-pentadienyl dimine (**10**) which is converted into the 1-arylpyridinium cation and the arylamine in a first-order reaction. The electrocyclic ring closure of the imine **10** was therefore assumed to be the rate limiting step of the reaction.



An attempt to correlate the results by means of Hammett's equation using σ^+ or σ-constants of the substituents failed, though the correlation was better ($r = 0.93$) when σ-constants were employed. The value of $\rho = 0.35$ indicates that the reaction is not very sensitive to the polarity of *para*-substituents, which is not unexpected if the redistribution of bonds is concerted and the transition state is not dipolar.[184]

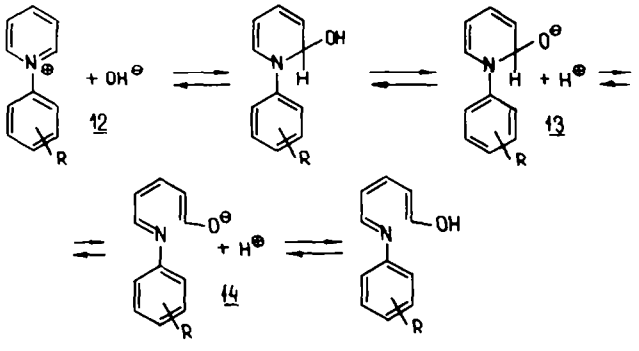
It has been proved that the diene fragment of isolated products of the pyridine ring opening has the *trans*, *trans*-configuration (see, e.g.[127,133]). This geometry contradicts the concept of electrocyclic opening of the covalent amination products. However, the initial *syn-cis-trans* configuration compounds were successfully detected by PMR in the kinetically controlled opening of the 1-alkoxypyridinium salt **11**. The process apparently involves stereoselective opening of the intermediate 1,2-dihydrocompound and occurs as a disrotatory thermal reaction permitted by Woodward–Hoffmann rules for electrocyclic transformations.[35]



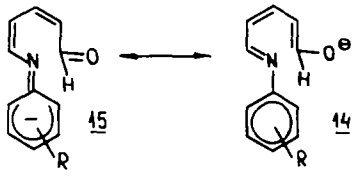
11

R = CMe_2COOEt

Though Hantzsch and Kalb[155] observed that pyridinium salts as compared with, for instance, quinolinium ions are far less likely to form covalent pseudobases, ultimately attempts to isolate stable carbinol bases of pyridine derivatives were successful.[185,186,28,35] Moreover, amines of high basicity in aqueous media give rise not only to covalent amination products but also to pseudobases which sometimes are even major components of the reaction mixture.[187,188] This makes it necessary to allow for possible recyclization under the effect of hydroxide anions. The ring opening of 1-methoxy- and 1-acylpyridinium salts by hydroxide anions is a first-order reaction with respect to the salt and a second-order reaction with respect to the OH^- ion.[132,179,189,190] It was found that in very alkaline media the predominant reaction for 1-arylpyridinium salts **12** is the hydroxide anion addition to the ring. At lower concentrations of the hydroxide anion, the predominant reaction is electrocyclic cleavage of the anion **13**. The greatest order in OH^- is equal to 2 and this decreases as the OH^- concentration grows. The logarithms of the equilibrium and the rate constants correlate well with Hammett's σ-constants.[191]



It appears that at the first stage of the conversion of **13** into **14**, the energetically favourable withdrawal of electrons by the benzene ring and the substituent R, promotes the C–N bond cleavage. If the electron shift were continuing up to the end of the reaction, the product would have been a Meisenheimer complex structure **15**. This intermediate, however, provides for less stabilisation than the structure **14**. Accordingly, after a certain point in the reaction coordinate (probably near the activated complex) the opposite electron shift, i.e. to the carbonyl group oxygen, becomes more favourable.

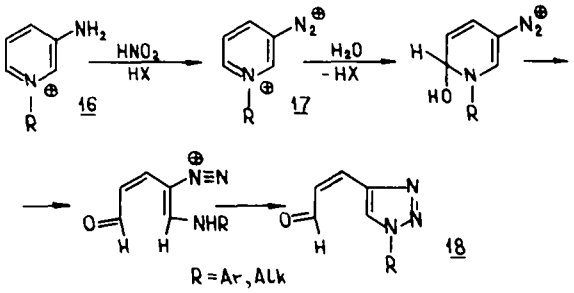


The above reactions may be regarded as possible stages of pyridinium salts recyclization via the exchange of the N-substituent. A recent stopped-flow investigation of the N-substituent exchange kinetics in the recyclization of 1-(2,4-dinitrophenyl)-3-carbamoylpyridinium chloride with aqueous amines and amino acids[192] has directly shown that in this case, as in the preceding ones, the ring opening takes place under the action of the hydroxide anion rather than the amine.

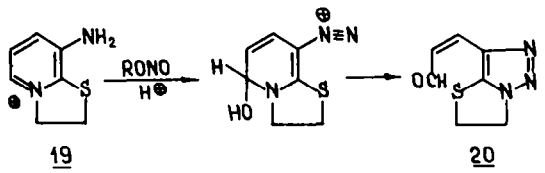
IV. PYRIDINE RING RECYCLIZATIONS TO HETEROCYCLES

(a) *Formation of 5-membered heterocycles*

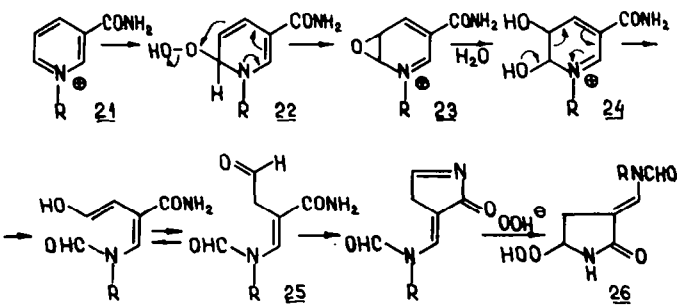
The acyclic products of the nucleophilic transformations of pyridinium salts may subsequently show cyclization with ring contraction. Thus 1-phenyl-3-aminopyridinium bromide (**16**, R = Ph) with nitrous acid gives rise to an intensely coloured solution which after a while yields a colourless crystalline precipitate of 3-(1-phenyl-1,2,3-triazolyl-4)-acrolein (**18**, R = Ph).[62] The reaction conceivably involves intermediate formation of an unstable diazonium salt **17**. The highly electronegative diazo-group makes the C-6 atom of the pyridine ring more susceptible to nucleophilic attack resulting in the ring opening. The similar fission of 1-alkylpyridinium salts occurs only in the acetate buffer.[193] At the next stage the diazo-group attacks the amino group to cause cyclization in the same manner as with the formation of triazenes in the benzene series.



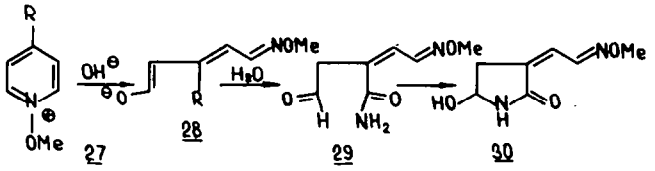
The same type of mechanism may be proposed for the diazotisation of 8-aminodihydrothiazolo-[3,2-a]-pyridinium acetate (**19**) which leads to 3-(4-dihydrothiazolo-[3,2-c]-1,2,3-triazolyl)acrolein (**20**).[194]



When treated by alkaline hydrogen peroxide, 1-methyl- or (1-benzyl)-3-carbamoylpyridinium chloride (**21**) gave rise to 7–8% pyrrolidone hydroperoxide **26** rather than to the expected hydroperoxide **22**.[195] The likely mechanism of this reaction involves the intermediary formation of the oxide **23** from the hydroperoxide **22**, followed by solvolysis of the epoxide into the diol **24** and the ring opening into the dialdehyde **25** whose cyclization and subsequent oxidation result in the formation of the lactam **26**.

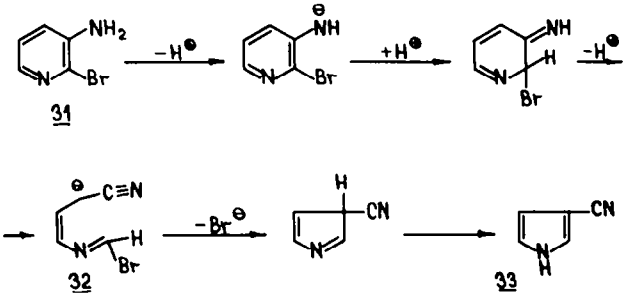


An example of the pyridine ring recyclization involving the participation of a γ-substituent is the rearrangement of 1-methoxy-4-carbamoyl (cyano) pyridinium salts in alkaline media. In the case of the cyanide the open-chain structure **28** after solvolysis gives rise to the intermediate **29** which is identical for both starting substances. At the next stage the amide nitrogen attacks the carbonyl group to cause cyclization into the 5-oxypyrrolidone-2 (**30**).[196]

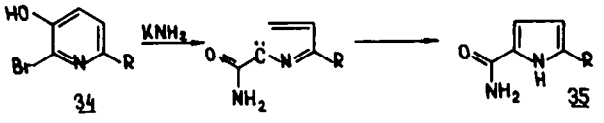


R = CN, $CONH_2$

In nucleophilic reactions pyridine derivatives are essentially more reactive than benzenoid derivatives whose ring opening occurs but very rarely.[197,198] The capacity of pyridine and its derivatives for being attacked by nucleophilic agents has been studied primarily in terms of Chichibabin's amination.[163] This reaction, however, causes no ring transformations. Pyridine halogen derivatives react with alkali amides in a different way. For example, 3-amino-2-bromopyridine (**31**) and potassium amide in liquid ammonia afford 3-cyanopyrrole (**33**) in the 80% yield. The process apparently involves intermediary formation of 3-cyanopropenyliso-cyanide (**32**).[199]

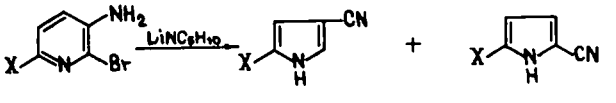


Under the same conditions 3-amino-2-chloropyridine gives no more than 1% cyanopyrrole. The treatment by lithium piperidide in liquid piperidine, however, causes recyclisation into the nitrile **33** in a good yield.[13,200] An excess of potassium amide in liquid ammonia breaks the C_3–C_4 bond in 3-hydroxy-2-bromopyridine (**34**, R = H) and 3-oxy-2,6-dibromopyridine (**34**, R = Br) to give rise to 2-carboxamidopyrrole (**35**).

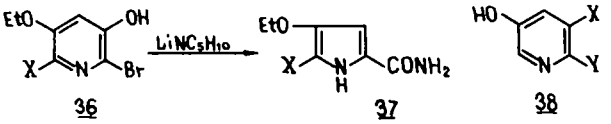


It is not easy to explain the rearrangement of bromopyridine (**34**, R = H) under the effect of lithium piperidide in piperidine, since the product is a 3-substituted pyrrole (3-carbopiperididopyrrole) rather than a 2-substituted derivative.[13]

In some cases the reaction products are not predictable and clearly the reaction pathway is dependent on the nature and position of substituents.[13]



The recyclization of 3-hydroxypyridines (**36**) leads only to the product identified as 2-carboxamidopyrrole (**37**).[13].

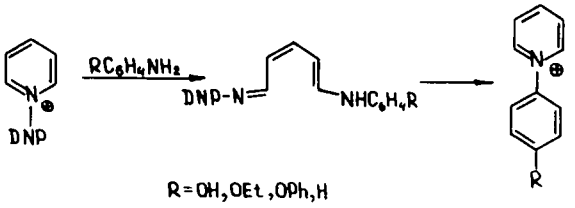


36 **37** **38**

The recyclizations of the type under discussion were also carried out with the use of model compounds **38** where X is H, Y is Br; X is OEt, Y is H; X is OEt and Y is Br.[202] These reactions, too, appear to involve the isocyanide mechanism (32→33) or the carbene mechanism (34→35).

(b) *Formation of 6-membered heterocycles*

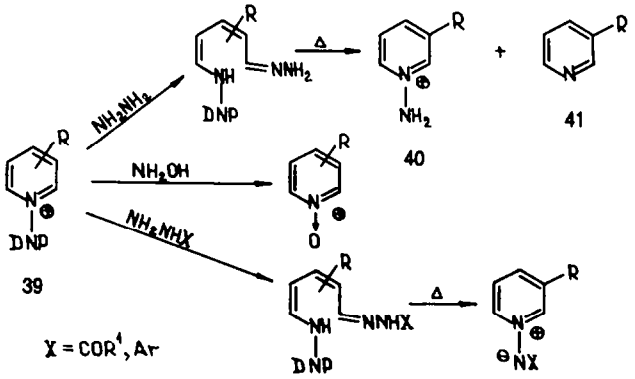
(1) *Recyclizations to N-substituted pyridines.* As shown by Zincke,[19,70] 1-(2,4-dinitrophenyl)pyridinium chloride with aqueous methylamine readily produces 1-methylpyridinium chloride. The reaction proved an efficient means of obtaining such 1-arylpyridinium salts which cannot be synthesized directly from pyridine.[43,29] Thus anilines containing electron donor groups easily substitute for the N-aryl group of 1-(2,4-dinitrophenyl)pyridinium chloride in the 80–90% yield.[29] The reaction requires that the medium be alkaline or contain an excess of the amine; sometimes, however, it is enough to use a polar solvent such as alcohol.[29] The same conditions may be used to achieve the corresponding reaction with heterocyclic amines.[33]



R = OH, OEt, OPh, H

The exchange recyclization may also be accomplished with more complex amines including tryptamine, desacetylcolchicine, 4-homosulphanilamide and 7-aminocholesterol.[83] The reaction of N-(2,4-dinitrophenyl)-3-carbamoylpyridinium chloride with amines and amino acids whose mechanism has been studied in detail,[192] is of interest as a preparative technique. It was also used to obtain certain new polyelectrolytes catalyzing the hydrolysis of esters from poly-[N(2,4-dinitrophenyl)-4-vinylpyridinium chloride].[203]

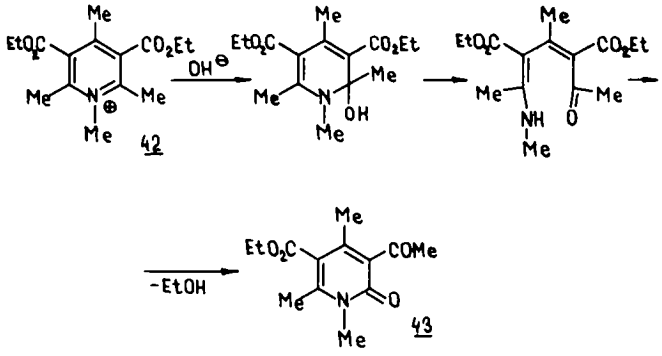
Owing to the strong electron acceptor effect of the dinitrophenyl group on the nitrogen atom, the C–N bond exhibits easy cleavage under the effect of other nucleophiles as well. Thus heating of pyridinium salts **39** with hydrazine hydrate, acylhydrazines or arylhydrazines brings about high yields of 1-aminopyridinium salts **40** containing Me, NHAc, I, $CONH_2$ or $CONEt_2$ in the 3-position.[204–209] An Et, CH_2OH or OH group in position 3 prevents the reaction or yields a mixture of the dearylation product **41** and a minor amount of the 1-aminopyridinium salt **40**. The reaction is also extremely sensitive to 4-substituents. While the synthesis of 1-amino-4-methylpyridinium was reported, no attempt to obtain the salts of 1-amino-4-acetamido- and 4-methoxypyridinium has been successful. On the other hand, hydroxylamine in aqueous dioxan does convert 1-(2,4-dinitrophenyl)-pyridinium derivatives into pyridine N-oxides.[205,206]



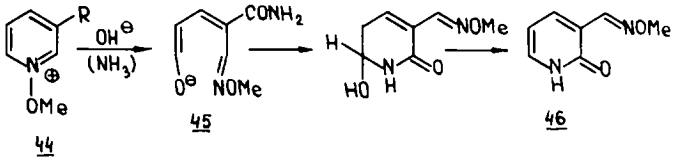
39 **40** **41**

X = COR^1, Ar

The pyridinium salts recyclizations with the exchange of the N-substituent can lead to the inclusion of the nucleophilic agent in the ring. Hantsch, whose results were later supported by Mumm and Hingst,[210,211] showed that in alkaline media 1,2,4,6-tetramethyl-3,5-diethoxycarbonylpyridinium iodide (**42**) undergoes a conversion which apparently involves the pyridine ring hydrolytic fission and subsequent ring closure yielding 1,4,6-trimethyl-3-acetyl-5-ethoxycarbonyl-2-pyridone (**43**) as the final product. Phenylhydrazine brings about the same conversion.[210,211]

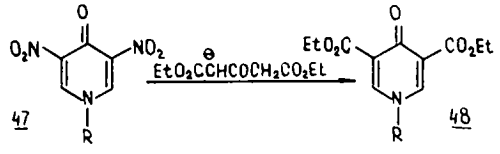


Ammonia with 3-substituted 1-methoxypyridinium salts (**44**, R = COOH, COOMe), or alkali with **44** (R = $CONH_2$) in an aqueous solution, give 3-methoxyiminomethylpyridone 2 (**46**).[196] During this rearrangement the ammonolysis of the carboxyl and the methoxycarbonyl group takes place at the open-chain stage, so that the following recyclization of **45** involves the amino group of the β-substituent.



R = $CONH_2$, CO_2Me, CO_2H

When treated with β-ketoester sodium salts, 1-substituted 3,5-dinitropyridines (**47**) recyclise yielding the corresponding 1-substituted 3,5-diethoxycarbonyl-4-pyridones (**48**). The initial stage is the addition of the carbanion in the position 2 or 6 and the formation of Meisenheimer complex; the position 6 or 2 is then attacked by the other nucleophilic centre. The resulting bicyclic intermediate undergoes splitting of the C_2–C_3 and C_5–C_6 bonds to yield the pyridone **48**.[212]

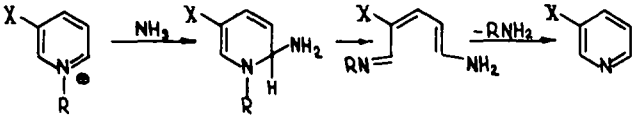


R = Me, 2-C_5H_4N, H, 4-C_5H_4N, 2-C_5H_3(6-Me)N

Finally, in degenerate recyclisations both the N-substituent and the pyridine ring are retained. The reversible ring opening probably accounts for certain aspects of the behaviour of diphosphopyridine nucleotide in alkaline media. The open-chain form of NAD is likely to be crucial to the accumulation of the enzyme in live organisms.[189]

(2) *Recyclization of pyridinium salts to pyridine bases.* When a pyridine ring contains a strong electron acceptor group, quaternization by alkyl or aryl halides suffices to provide for the nucleophilic ring opening. Thus the 3-substituted pyridinium salts (**49**) adds liquid ammonia at position-6. As the temperature is raised and ammonia evaporates, the adducts decompose into 3-substituted pyridine and

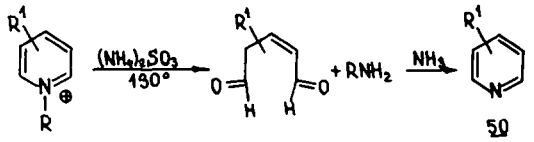
alkyl- or arylamine. Nitropyridinium salts are particularly active in this process.[168,169]



X = NO_2, $MeSO_2$, COMe, $CONH_2$, COOMe, CF_3, CN.

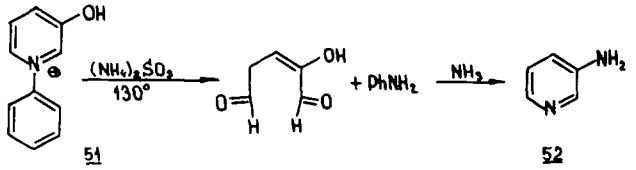
R = Me, CH_2Ph, $CH_2C_6H_4NO_2$-p

Our experiments have shown that 2-methyl-3(5)-nitropyridinium salts eliminate the N-substituent by ring opening of the intermediate even in aqueous ammonia, to yield 70% of the corresponding pyridine base.[213] It is interesting to note that the 1-methylpyridinium cation in liquid ammonia forms no covalent adducts in amounts detectable by PMR,[168] but ammonium sulphite, in contrast with ammonia, makes it possible to open the pyridine ring even when no activating electron acceptor substituent is present. The best results were achieved with 1,2-dimethyl- and 1,2,6-trimethylpyridinium salts, though the formation of pyridine bases and alkyl amines in modest yields was also observed in the case of 1,3-dimethyl-, 1,4-dimethyl- and 1,2,4,6-tetramethylpyridinium salts.[214] The reaction apparently involves the formation of a corresponding glutaconic dialdehyde derivative whose interaction with ammonia or ammonium sulphite yields substituted pyridines **50**. On heating 1,2,6-trimethylpyridinium bromide with ammonia, in the absence of sulphite ion, this process does not take place.



50

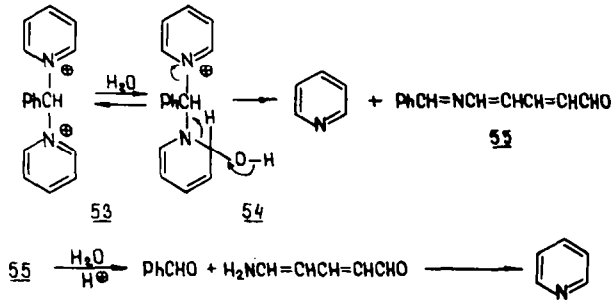
This reaction is also largely dependent on the N-substituent. For example, the phenyl group is a strong enough acceptor to provide for dearylation of 1-phenyl-3-oxypyridinium chloride **51** in which the pyridine ring is essentially deactivated by the donor group. It is true that the product is 3-aminopyridine (**52**) rather than the 3-hydroxypyridine expected. However, it does not result from Bucherer's reaction involving 3-hydroxypyridine, because the amino-group enters the molecule at the stage of oxyglutaconic aldehyde or its bisulphite derivative.



51 **52**

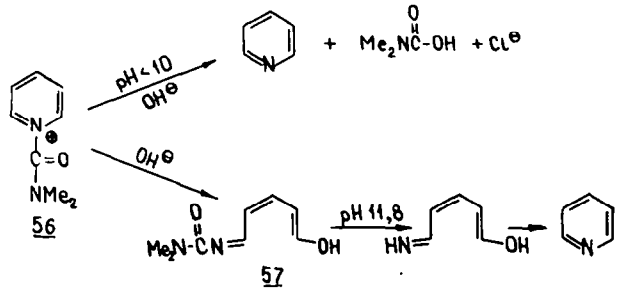
Certain other models also show the N-substituent elimination, ring opening and subsequent cyclization. Specifically, the pyridine nitrogen of the starting substance in such conversions is transferred into the final product without intermediate exchange at the open-chain stage.

When heated with water, the dication **53** gives rise to benzaldehyde and two equivalents of pyridine.[215] In the presence of alkali, the solution yields a precipitate of the intermediate **55** (which evidently forms from the pseudobase **54**) and one equivalent of pyridine. The precipitate then dissolves slowly to yield benzaldehyde and a second equivalent of pyridine. The latter reaction is also promoted by acids.

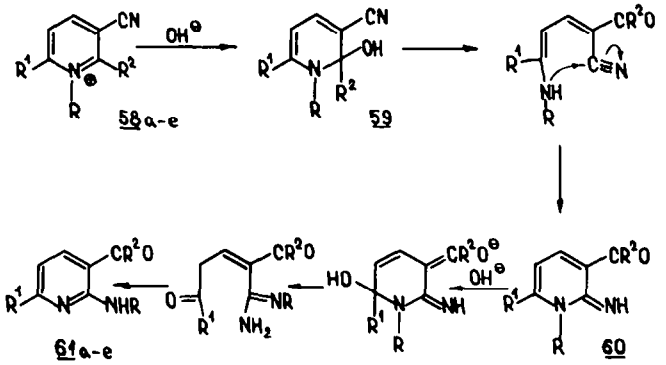


53 **54** **55**

A similar mechanism was advanced to account for alkali-induced deacylation of 1-(N,N-dimethylcarbamoyl)pyridinium (**56**).[189,216] This is a first-order reaction with respect to both the starting salt **56** and the hydroxide anion. At pH 10 the unstable intermediate **57** is formed. Its further decomposition gives glutaconic dialdehyde and 1,1-dimethylurea at low and high pH or pyridine and dimethylamine at medium pH. The maximum rate of the latter reaction being observed at pH 11.8.



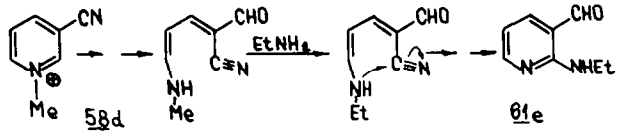
The authors have studied an intriguing nucleophilic recyclization of the cyanopyridinium salts (**58a–e**) with the incorporation of the nitrile group into the ring. The likely mechanism involves the C–N bond fission of the initially formed 1,2-dihydropyridine followed by cyclisation on to the electron-deficient carbon of the nitrile group to form the 1,2-dihydropyridine **60**. Such structures then undergo another rearrangement of the amidine type to yield the 2-alkylamino-3-formyl(acetyl)pyridines (**61a–e**).



58 a–e a $R^1=R=Me, R=H$; b $R^2=R=Me, R^1=H$; c $R^2=Me, R=Et, R^1=H$;

d $R^1=R^2=H, R=Me$; e $R^1=R^2=H, R=Et$

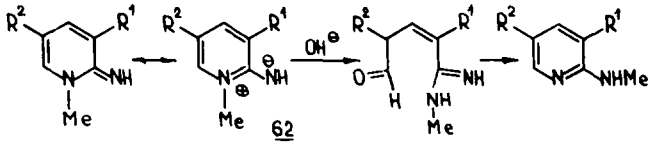
A methyl group at position-2 does not prevent nucleophilic addition in this position and no steric difficulties were observed even with 1-ethyl-2-methyl-3-cyanopyridinium (**58c**). The recyclization also occurs in the absence of lateral alkyl groups (**58d**).[219] With this substance we have also observed the methylamine group replacement under the action of aqueous ethylamine.



Accordingly, with 3-cyanopyridine ethiodide (**58e**) as a starting substance aqueous methylamine causes recyclization, by elimination of the ethylamine group and the formation of 2-methylamino-3-formylpyridine (**61d**).

(3) *Amidine rearrangement.* The amidine or Dimroth rearrangement[220,221] deserves special attention among the processes leading to pyridine bases. In this process the exocyclic atom is the nitrogen of the amidine fragment present in the initial molecule or appearing during the reaction. In other words, after the C–N bond opens, the pyridine ring forms again with a newly formed C–N bond. The rearrangement may therefore be regarded as an isomerisation.

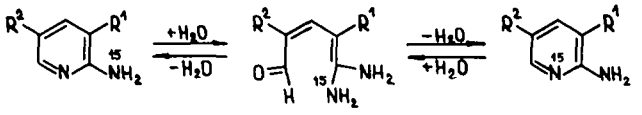
Dimroth recyclization begins with an imide-type compound in which the donor group (see structure **62**) substantially de-activates the susceptibility of the pyridine ring to nucleophilic attack. The reaction therefore takes place only if there is a nitrogroup in the position 3 or 5.[222-224] Neither 1 - methyl - 2 - imino - 2,2 - dihydropyridine[225] nor its 5 - chloro -, 3,5 - dichloro - and 5 - cyanoderivatives[224] are capable of recyclization yielding the corresponding 2 - methylaminopyridines. In contrast, the nitro-compounds react very easily and provide high yields (τ = 11 sec at 20° at pH 11.5[224]).



62

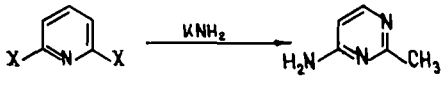
$R^1, R^2 = H, NO_2$

As for 2-amino-^{15}N-pyridine itself, its rearrangement under the influence of aqueous alkali was carried out but at 200° the yield was as low as 4%. The main process in this reaction is the rapid hydrolysis of the amino-group and the formation of 2-pyridone.[266,227] A 3- or 5-nitro-group accelerates the recyclization. At 100° in diluted alkali the half-conversion period for ^{15}N-labelled amino compounds is about one minute, which still much slower than is the rearrangement of 3- or 5-nitro-1-methyl-1,2-dihydropyridines.[228]



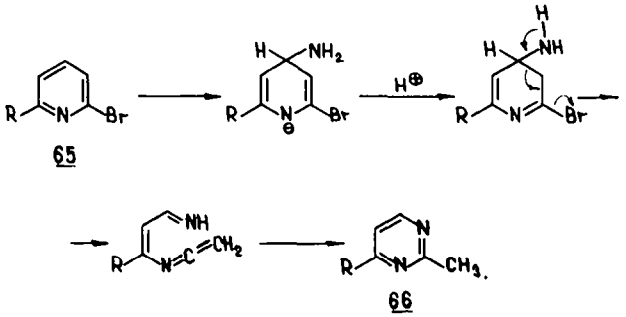
$R^1, R^2 = H, NO_2$

(4) *Formation of diazines and condensed azines.* Halogen derivatives of pyridines react with alkali amides to form pyrimidines. Thus with potassium amide in liquid ammonia (see, for instance,[229]) 2,6-dibromopyridine (**63**, X = Br) gives rise to 6-amino-2-methylpyrimidine (**64**).[230,199] Though less rapidly, 2,6-dichloropyridine (**63**, X = Cl) reacts as well, while 2,6-difluoropyridine gives a high yield of 2-amino-6-fluoropyridine instead of undergoing recyclization.



63 **64**

Among the 6-bromopyridines (**65**, R = 2-NH_2, 2-NHPh, 2-$CONH_2$, 2-MeC_6H_4, 2-Me, 2-Ph, 2-OEt, 2-OPh, 2-p-$EtOC_6H_4$, 2-m-$EtOC_6H_4$, 2-p-FC_6H_4 and 2-NO_2) only 2-phenoxy- and 2-substituted phenoxy-6-bromopyridines afford the corresponding pyrimidine derivatives in the 40–50% yield.[231,232]

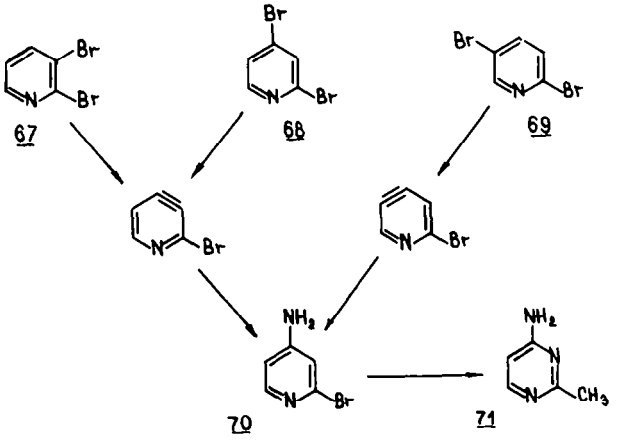


65

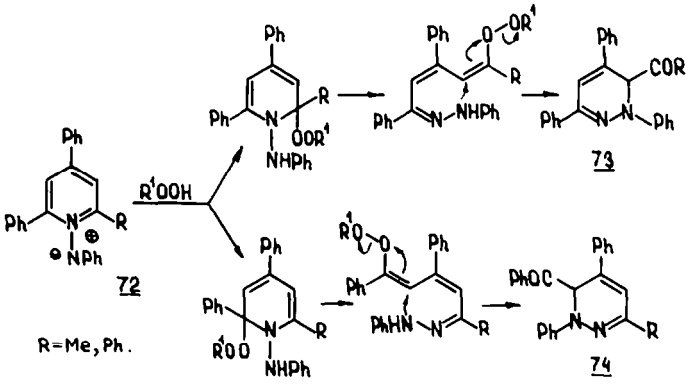
66

The pyridine-into-pyrimidine recyclization of these compounds occurs, therefore, by the C_3–C_4 bond cleavage (65 → 66). This bond fission was also observed by British authors with other models containing a pyrimidinium nitrogen atom.[233]

A detailed study of these conversions is complicated because of accompanying reactions such as addition-elimination, cine- and tele-substitution. Thus potassium amide converts 2,3-dibromo- (**67**), 2,4-dibromo- (**68**) and 2,5-dibromo-pyridine (**69**) into one and the same 2-methyl-4-aminopyrimidine (**71**). This observation is conceivably due to the intermediate formation of 2,4-bromo-4-aminopyridine (**70**) by the dehydroarene mechanism.[234]

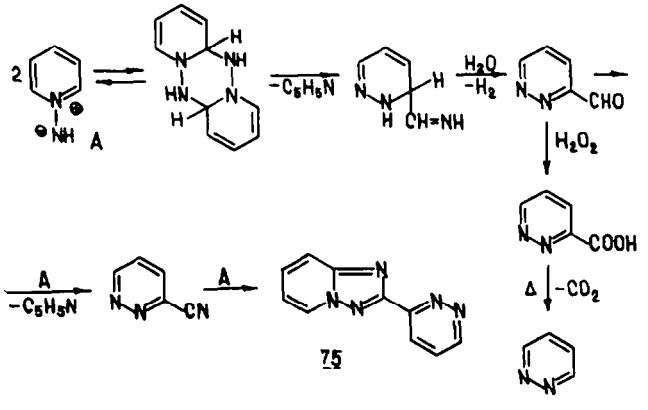


Interesting information was reported for recyclizations involving the N-substituent of the precursor. Thus the 1-iminoderivative **72** with tertbutyl hydroperoxide yields a mixture of the 1,6-dihydropyridazones **73** and **74**.[235] If R is Ph, then **74** is the only product.

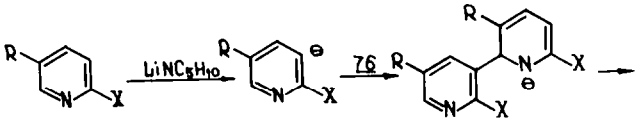


Pyridine N-imine undergoes an interesting transformation in warm methanol during a few days yielding the adduct **75** containing a triazolopyridine and a pyridazine ring. The N-imines of 2- and 4-methylpyridine exhibit the same behaviour. The following mechanism advanced for this reaction was confirmed by studies in the presence of hydrogen peroxide.[236]

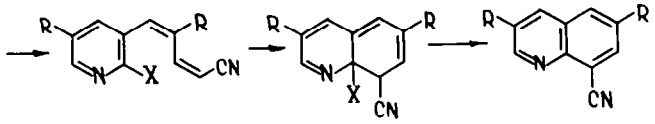
In the presence of H_2O_2 the compound **75** is not formed, since the intermediary 3-formylpyridazine is oxidized to the corresponding acid whose decarboxylation gives pyridazine.



In an unusual recyclization two molecules of 2-halogeno pyridine **76** give rise to a quinoline nucleus.[237] On the dimerisation of **76** and the pyridine ring opening under the action of lithium piperidide the benzene ring closes.

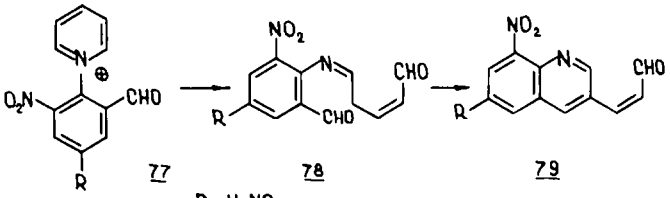


76



R=Me, EtO

The formation of quinolines may also be illustrated by the reaction between an alkali and the pyridinium salt **77**, in which the pyridine ring opens to form the anil **78**. This compound then undergoes intramolecular condensation leading to the substituted 3-quinolylacroleins **79**.[238]



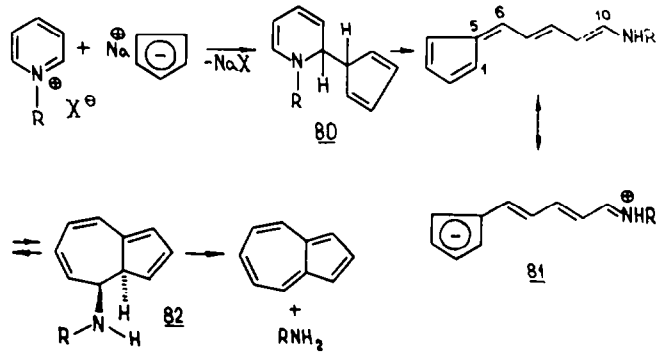
77 **78** **79**

R=H, NO_2

V. PYRIDINE RING RECYCLIZATIONS INTO CARBOCYCLES

(a) *Synthesis of azulenes*

There is only one example of the recyclization of pyridinium salts under the effect of carbanions, namely the Ziegler–Hafner synthesis of azulenes in the variant using pyridinium salts and sodium cyclopentadienide.[8,9,239,240] Just as 1-alkylquinolinium salts with Grignard reagents give rise to 1,2-dihydroquinolines,[241] so 1-alkylpyridinium salts react with sodium cyclopentadienide to form rather unstable 1-alkyl-2-cyclopentadienyl-1,2-dihydropyridine (**80**) whose heating to 200° in benzidine yields azulene. The process involves the pyridine ring opening in **80** and the formation of the fulvene **81** which again closes the ring by elimination of alkylamine.

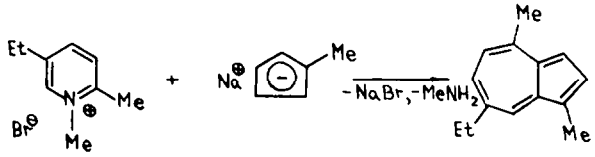


80 **81** **82**

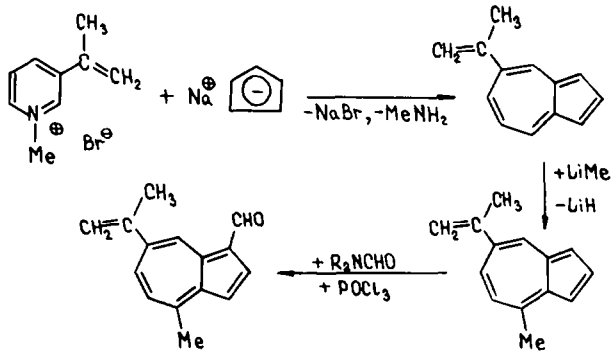
According to Woodward[242,243] this thermal process involves electrocyclic ring closure ($\pi 10s$). It may also seem likely that the hypothetic intermediate **82** results from the electrophilic attack of the atom 10 in the electron-excessive position 1 of **81**. In fact, however, the two reaction pathways are not very

different in terms of mechanisms. Indeed, during cyclization the σ-bond arises from the shift of two π-electrons of the structure **81**, so that a certain amount of resonance energy is lost. If cyclization is reversible, the reaction may be thought to obey the disrotatory mechanism which provides for smooth but irreversible elimination of the alkylamine from **82** and the immediate formation of azulene. It appears that the cyclization stage is associated with the higher activation energy and is the rate determining step.

Azulenes synthesized according to the Ziegler–Hafner reaction may be substituted in the 7- as well as 5- membered ring. For example, the procedure was used to obtain 1,4-dimethyl-7-ethylazulene (chamuzulene) from 1,2-dimethyl-5-ethylpyridinium bromide and sodium methylcyclopentadienide.[9]

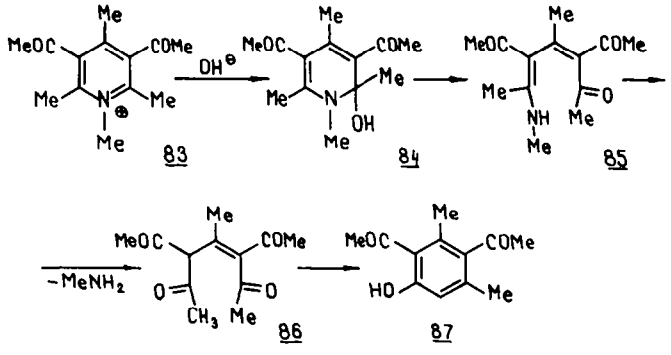


Likewise, in the complete synthesis of 4-methyl-7-isopropenylazulenaldehyde-1 (lactaroviolin) the first stage was the reaction between sodium cyclopentadienide and 1-methyl-3-isopropenylpyridinium bromide.[244,245]



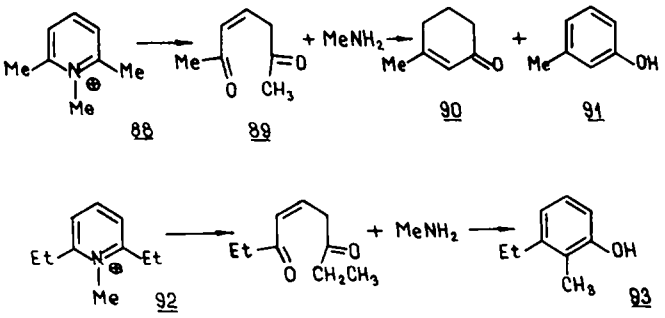
(b) *Pyridine ring recyclizations to benzene rings*

(1) *Recyclization of pyridinium salts to phenols.* Mumm *et al.* demonstrated[246] that alkalis react with 1,2,4,6 - tetramethyl - 3,5 - diacetylpyridinium (**83**) to open the pyridine ring by intermediate formation of the pseudobase **84** and the simultaneous solvolysis of the acyclic intermediate **85**. The subsequent intramolecular cyclization of the 1,5-dicarbonyl compound **86** results in a low yield of the substituted phenol **87**.



The presence of acceptor substituents in position 3 is not obligatory and the reaction may still be achieved by more drastic experimental conditions. Thus 1,2,6-trimethylpyridinium (**88**) and 1-methyl-2,6-diethylpyridinium ((**92**) iodides, when heated to 200° with an alkali, yield the phenols **91** and **93** in the 70–80% yield.[247,248] When carried out in a silver autoclave, the reaction yields the cresol **91**, and 1-methylclcyclohexen-1-en-3-one (**90**), which apparently results from partial reduction of the intermediate

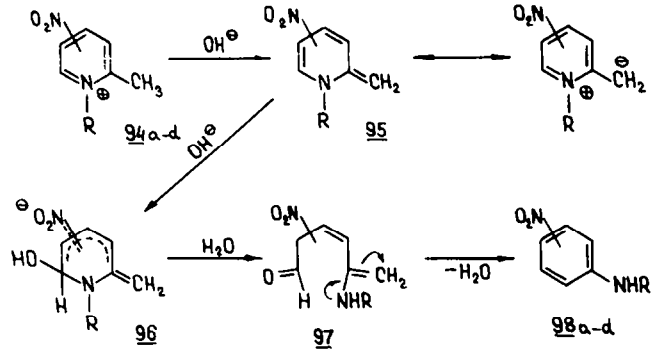
89. Similar reactions have been reported for related compounds.[249]



Similar properties of pyrylium salts were used for a synthesis of polysubstituted phenols by means of hydrolytic ring opening followed by recyclization involving the 2-methyl group.[250] However, the few recyclizations of pyridinium salts into phenols which have been considered are not isomerisation processes, because the open-chain intermediate is solvolysed to eliminate the alkylamino-group.

(2) *Enamine rearrangement.* The recyclization of pyridinium salts into anilines discovered by the authors[251,252] appears to be a fundamental type of pyridine-into-benzene ring transformation. In this reaction, as well as in the related processes discussed below, the exocyclic atom which becomes incorporated into the ring is the β-carbon of the enamine fragment either present in the starting material or appearing during the reaction. In other words, the pyridine C–N bond fission results in an open-chain intermediate whose recyclization brings about a new C–C bond. The consequence of these reactions may therefore be defined as a enamine rearrangement in which the reagent is not included in the product of isomerisation (except for the reactions involving the amino-group exchange).

Thus aqueous-alcoholic alkali was reported to convert 1,2-dimethyl-3-nitropyridinium iodide (**94a**) into N-methyl-2-nitroaniline (**98a**). The yield was rather poor because of hydrolysis and resinification, however, in aqueous methylamine the yield of the corresponding *o*- and *p*-methylnitroanilines was as high as 30–50%.[218,253]



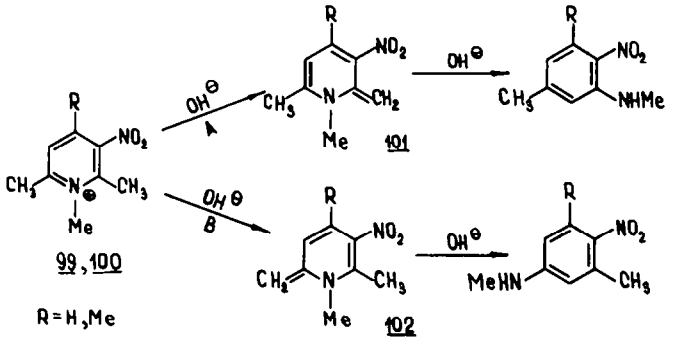
94 a R=Me,3-NO_2; b R=Me,5-NO_2; c R=Et,3-NO_2; d R=Et,5-NO_2.
98 a R=Me,2-NO_2; b R=Me,4-NO_2; c R=Et,2-NO_2; d R=Et,4-NO_2

The initially formed anhydrobase **95** adds an hydroxide anion in the α-position with respect to the nitrogen and gives rise to the anionic σ-complex **96**. After ring opening the recyclization into a benzene ring takes place.

It is of interest that 1,2 - dimethyl - 3 - nitropyridinium iodide (**94a**) gives rise to N - methyl - 2 - nitroaniline (**98a**) in a higher yield (50%) than the isomeric 1,2 - dimethyl - 5 - nitropyridinium iodide (**94b**) (25%). This means that deprotonisation involves preferential attack of the hydroxide anion in the para- rather than ortho-position with respect to the nitro-group.

The same holds true with 1,2,6 - trimethyl - 3 - nitropyridinium (**99**) and 1,2,4,6 - tetramethyl - 3 - nitropyridinium iodides (**100**). The compounds containing an *ortho*-nitro-group with respect to the 2-methyl-group give products in a substantially higher yield than the *para*-isomers. The Me group in

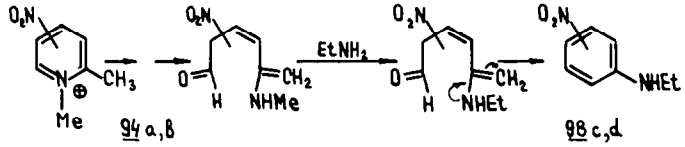
position 4 is largely irrelevant to this correlation.



The predominant formation of *ortho*-anilines was explained in terms of the π-electron approximation of the LCAO MO approach (the localised version of the perturbation theory).[254] The reaction presumably occurs *via* the different anhydrobases **101** and **102** whose ratio depends on the C–H acidity of methyl groups in the pyridinium salts **99** and **100**. Calculations indicate that the residual π-electron charge on the methylene-group in **102** is by 0.0523 higher than in **101**. This suggests the *ortho*-Me group is more acidic with respect to the nitro-group than the *para*-Me group. Therefore the path A is more likely for the recyclization of 1,2,6 - trimethyl - 3 - nitro - pyridinium (**99**) and 1,2,4,6 - tetramethyl - 3 - nitropyridinium (**100**) iodides.

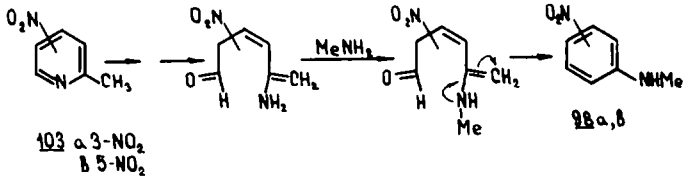
The electrophilicity of the α-positions in the nitropyridinium cations **94c** and **100** was directly estimated by means of X-ray structural analysis.[255] The iodine anion proved to have closer contact with the C_2 atoms of the pyridine ring. It appears therefore that the inductive effect of the nitro-group gives rise to a higher positive charge on the C_2 than on the C_6 atoms, so that the base-induced deprotonisation of the C_2 atom must occur more readily. Again, this is in accord with the preferential formation of *ortho*-anilines.

The open-chain intermediate involved in pyridinium salts recyclization into anilines may undergo competing hydrolysis or, if amines are used as bases, form a ring by complete or partial amine exchange. Thus 1-ethyl-2-methyl-3-nitropyridinium (**94a**) or 2-ethyl-2-methyl-5-nitropyridinium (**94b**) iodide in aqueous ethylamine give rise to the corresponding *ortho*- or *para*-isomers of N-ethylnitroaniline (**98c,d**).[213,256]



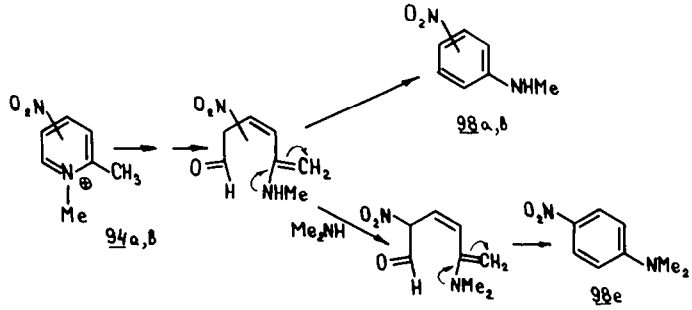
The re-amination of enamines could be reversible, so the formation of N-methylnitroanilines also could be expected. This, however, was prevented by the great excess of ethylamine. With 1-ethyl-2-methyl-3-nitropyridinium (**94c**) iodide as a starting substance the reaction with aqueous methyamine leads to recylisation, expulsion of the ethylamine group and formation of N-methyl-2-nitroaniline (**98a**).

In aqueous methylamine the non-quaternised pyridine bases **103a,b** open their ring by the substitution of methylamino group for the amine fragment. The products (whose yield is not high) result from recyclization of the acyclic enamine and are identified as N-methylnitroanilines (**98**).

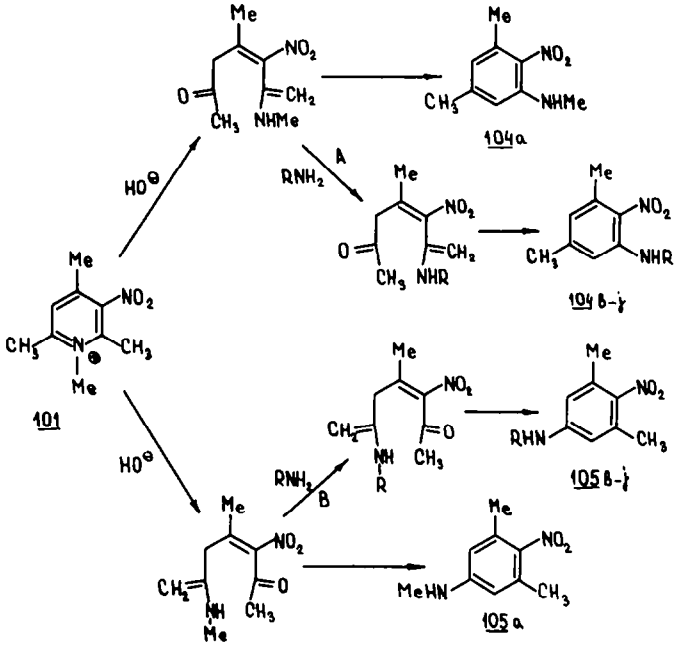


Secondary amines are much less capable of recyclization and products usually contain no dialkylamine fragment. For example, 1,2-dimethyl-3-nitropyridinium iodide (**94a**) with dimethylamine yields

N-methyl-2-nitroaniline (**98a**); the isomer **94b**, on the other hand, gives a mixture of the nitroanilines **98b** and **98e** (mostly the former component). That is, secondary amines, like aqueous alkalis, result mainly in recyclization in which the alkylamine fragment of the initial quaternary salt is retained.[218,256]



If two Me groups are present in the α-positions of the pyridine nucleus and reamination is involved, recyclisation may be expected to afford two pairs of the isomeric nitroanilines **104** and **105**. 1,2,4,6-Tetramethyl-3-nitropyridinium iodide (**101**) proved a convenient model for the investigation of steric effects in reamination: its reaction with aqueous methylamine results in high yield of the nitroanilines (90%), while the ratio between the *o*- and the *p*-isomers (2:1) seems to be independent of the steric difficulties arising from the part played by the methylamino group during cyclization. The dominant influence appears to be that the hydroxide anion prefers to attack the *para*-position with respect to the nitro-group. In aqueous ethyl-, n-propyl- and n-butyl-amines the *o*-and the *p*-isomers are formed in equal amounts, which suggests the predominance of the B pathway. The ratio is virtually independent of the medium (Table 1). However, in an aqueous alcoholic solution of pentadecylamine, the yield of the *ortho*-isomer suddenly increases to 60%. This fact may result from the surface activity of the reagent.



The reaction in aqueous β-carbon-branched isobutylamine proved to result in equal yields of the *o*- and the *p*-nitroaniline. With isopropylamine and sec-butylamine the overall yield of the reamination products decreases considerably, though the yield of *p*-nitroanilines is still about 40%. Thus the formation of the *ortho*-isomers is suppressed. Finally, tert-butylamine fails to cause reamination. Like aqueous alkali, it brings about the recyclization in which the initial quaternary salt alkylamino-group is retained.

Table 1. Interaction of 1,2,4,6-tetramethyl-3-nitropyridinium iodide (**101**) with amines

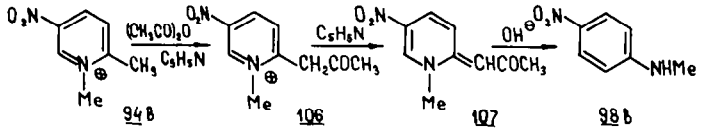
Amine	Yields, %			
	104a	104b-j	105b-j	105a
$MeNH_2$	63	---	---	31
$EtNH_2$	--	b 40	b 36	---
$n\text{-}PrNH_2$	2	c 38	c 41	1
$n\text{-}BuNH_2$	2	d 42	d 37	1
$n\text{-}BuNH_2$*	2	d 46	d 38	2
$n\text{-}C_{15}H_{31}NH_2$	2	e 63	e 24	1
$i\text{-}BuNH_2$	2	f 41	f 40	5
$i\text{-}PrNH_2$	5	g 11	g 41	3
$sec\text{-}BuNH_2$	2	h 12	h 38	5
$t\text{-}BuNH_2$	32	---	---	21
Me_2NH	3	i 6	i 63	7
$(CH_2)_5NH$ *	3	j 3	j 33	13

* In 50% aqueous ethanol.

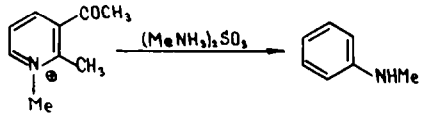
The 1,2,4,6-tetramethyl-3-nitropyridinium iodide (**101**) with primary amines (except for t-butylamine) affords, apart from the re-amination products **104b–j** and **105b–j**, a minor amount of N - methyl - 3,5 - dimethyl - 4 - nitroaniline (**104a**) and N - methyl - 3,5 - dimethyl - 2 - nitroaniline (**105a**). Aqueous dimethylamine and piperidine cause the same rearrangement. The direction of re-amination in this case is also largely dependent on the steric effects of the dialkylamino-group.[256]

To sum up, the re-amination during recyclization is a process depending on the number of alkyl groups attached to the amine nitrogen and the extent of their branching, particularly at the α- and, somewhat less significantly, at the β-carbon atoms. Steric effects decrease the yield of *ortho*- and increase that of *para*-nitroanilines as reamination products. These data provide further support for the above mechanism of recyclization of pyridinium salts.

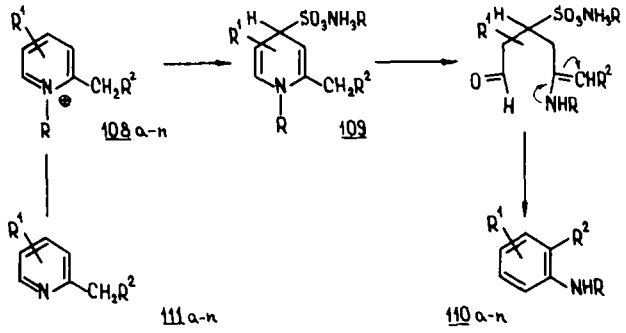
It was our belief that the activation of the α-Me group by an acceptor substituent would increase its C–H acidity, thus promoting the benzene ring formation from the open-chain intermediate. To check this assumption we have treated 1,2-dimethyl-5-nitropyridinium iodide (**94b**) with acetic anhydride in pyridine. The product obtained in the 45% yield was the anhydrobase (**107**) apparently formed *via* the 2-acetonyl-5-nitropyridinium salt **106**. In aqueous methylamine the anhydro-base shows recyclisation by the elimination of the acyl fragment and gives N-methyl-4-nitroaniline (**98b**) in the 35% yield.[257] The acetyl-group elimination appears to arise from the solvolytic instability of the 1,3-dicarbonyl fragment in the open-chain intermediate.



It is important to note that under these conditions the 1,2-dialkylpyridinium salts which bear no activating nitro-group on the nucleus do not show any recyclization. 1,2-Dialkyl-3-cyanopyridinium salts exhibit a sophisticated double rearrangement leading to 2-aminopyridine derivatives containing no cyano-group (see above). The substitution of an acetyl group for the nitro-group in compounds of type (**94**) makes recyclization possible but under the action of methylammonium sulphite the process involves elimination of the acetyl group.[257]



In a series of experiments in our laboratory it was expected that the sulfite ion would add to 1,2-dialkylpyridinium salts to cause their recyclization into anilines even for the compounds containing no electron acceptor-group. Indeed, the heating of 1,2-dialkylpyridinium iodides (**108a–n**) with methylammonium sulphite resulted in N-alkylanilines **110a–n** in 40–80% yield (Table 2).[258-260] A parallel process was dealkylation by virtue of direct attack in the C atom of the quaternising radical R and the formation of pyridine bases **111a–n**.



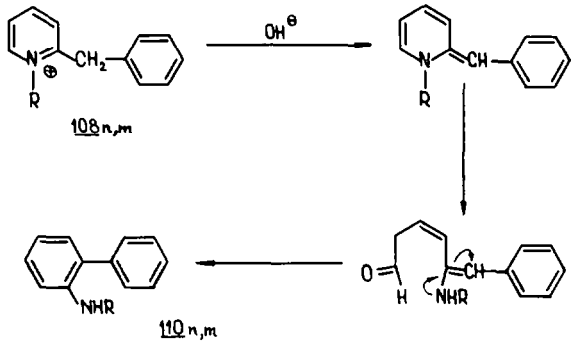
Alkyl groups (R') reduce the electron deficiency of the ring and give rise to steric difficulties for the sulphite ion addition. Accordingly, the yield of R'-substituted recyclization products decreases, parti-

Table 2. Recyclization of 1,2-dialkylpyridinium iodides **108a–n** into N-alkylanilines **110a–n** under the effect of methylammonium sulfite

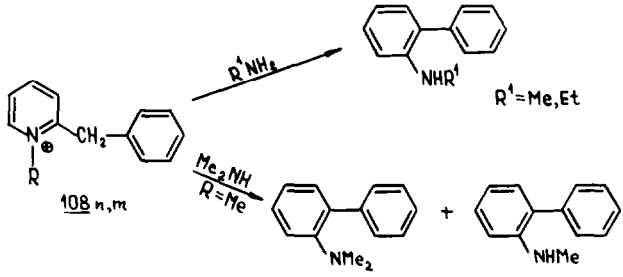
Initial compound	Product		Yields, %	
108	110	111	110	111
a-h R = Me	a-h R = Me	a-h R = Me		
a-k R^2 = H	a-k R^2 = H	a-k R^2 = H		
a R^1=4-Me	a R^1=3-Me	a R^1= 4-Me	44	36
b R^1=6-Me	a R^1=3-Me	b R^1= 6-Me	71	17
c R^1=3-Me	c R^1=2-Me	c R^1= 3-Me	59	22
d R^1=4,6-Me	d R^1=3,5-Me	d R^1=4,6-Me	24	49
e R^1=5-Et	e R^1=4-Et	d R^1=5-Et	19	70
f R^1=5-Me	f R^1=4-Me	f R^1=5-Me	48	35
j R^1=6-Me	j R^1=3-Me	j R^1=6-Me	96	--
R = $C_{16}H_{33}$	R=$C_{16}H_{33}$	R=$C_{16}H_{33}$		
h-n R^1= H	h-n R^1=H	h-n R^1=H		
h R = Me	R = Me	R = Me	80	--
i R = Et*	i R=Et	------	40	--
j R=$C_{12}H_{25}$	j R=$C_{12}H_{25}$	------	31	--
k R=$C_{16}H_{33}$	k R=$C_{16}H_{33}$	------	82	--
l R=Me	l R=Me	l R=Me	67	13
R^2=Pr	R^2=Pr	R^2=Pr		
m-n R^2=Ph	m,n R^2=Ph	m,n R^2=Ph		
m R=Me	n R=Me	n R=Me	73	8
n R=Et*	n R=Et	n R=Et	68	10

*) Recyclization was accomplished under the effect of ethylammonium sulfite.

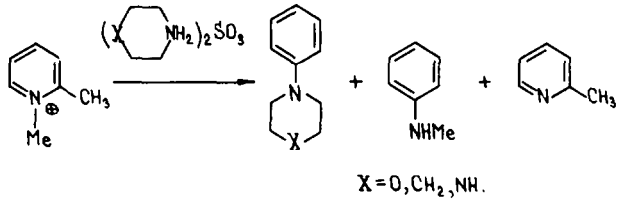
cularly with γ-2-methylpyridines. 3-Methylpyridines and especially 2-methylpyridines are less susceptible to this effect. This suggests predominant addition of the sulfite ion to the C-4 atom, so that the initial products are the 1,4-dihydropyridines **109** which recyclise into aromatic compounds by eliminating the reagent. By this process, good yields of 2-(N-alkylamino)biphenyls (**110m–n**) were obtained by heating N-alkyl-2-benzylpyridinium iodides (**108n–m**) with methyl- or ethylammonium sulfite.[261]



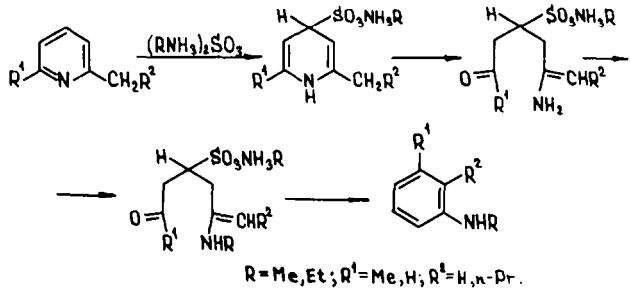
In the same manner 1-alkyl-2-benzylpyridinium salts with alkylammonium sulfite exhibit easy recyclization involving the N-substituent exchange. Secondary amines show largely similar behaviour, though the yields are lower and the products contain no dialkylamine fragment.



Sulfites of heterocyclic amines (morpholine, piperidine and piperazine) may also bring about the recyclization of pyridinium salts into anilines, provided the amine is of sufficient basicity. As in the previous case, the recyclization may be accompanied or not accompanied by the alkylamino-group exchange. Another process observed is N-dealkylation.[262]

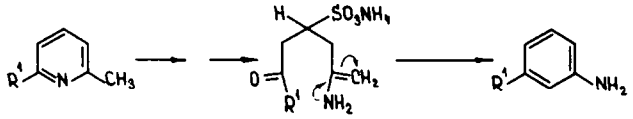


The method permits recyclization of non-quaternised compounds as well. Namely, 60–70 hr heating of 2-methyl-, 2,6-dimethyl- and 2-butylpyridine with aqueous methylammonium sulfite resulted in satisfactory yields of N-methyl-, N,3-dimethyl- and N-methyl-2-propylaniline respectively. The reaction between ethylammonium sulfite and 2-methylpyridine in the presence of $ZnCl_2$ gave rise to 6% yield of N-ethylaniline.[258]

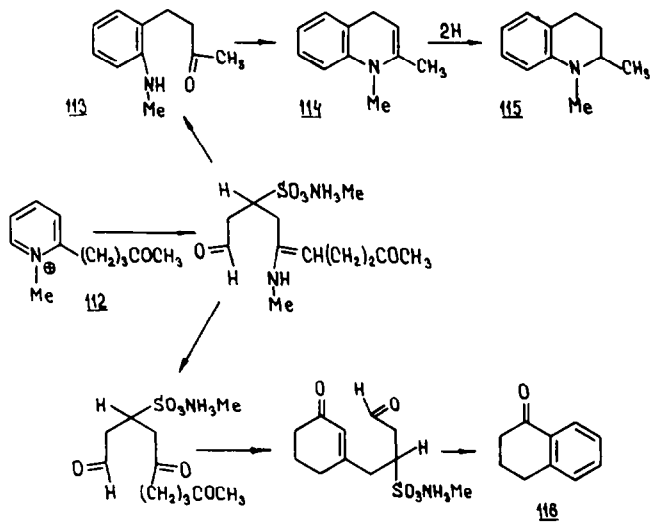


On addition of zinc chloride the yield of N-methylaniline from 2-methylpyridine was as high as 40%. The effect of zinc salts is not yet completely understood. However, it may be assumed that this activation depends on the equilibrium involving the pyridine base complex which undergoes further conversion. It is interesting to note that in this case, as with pyridinium salts, the 3- and 4-Me groups impede the reaction.

Dialkylamines cause no recyclisation of 2-methylpyridines. The goal can be attained, however, by heating with a mixture of aqueous ammonia, ammonium sulfite and zinc chloride. In this manner aniline and 3-methylaniline were obtained in about 10% yield. In principle, therefore, recyclization into primary arylamines is possible.[258]



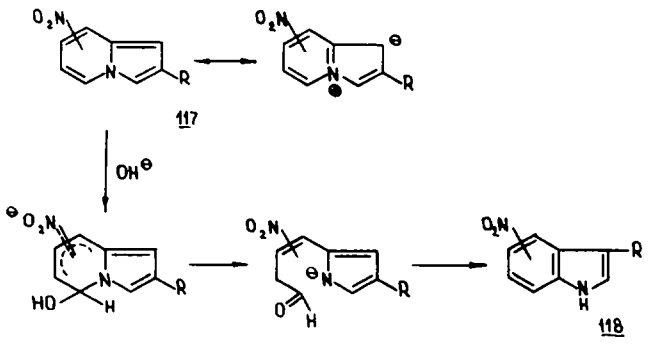
If a functional group is present in a substituent, then the recyclization of pyridinium salts may give rise to a new heterocycle. Thus 1-methyl-2-(pentanon-2-yl)pyridinium iodide (**112**) when heated with methylammonium sulfite forms 1,2-dimethyl-1,2,3,4-tetrahydroquinoline (**115**, 48% yield), tetralone-1 (**116**, yield 24%) and 1,2-dimethyl-1,4-dihydroquinoline (**114**).[263]



The recyclization of the pyridinium salt **112** in the presence of the sulfite ion, therefore, leads to 1,4-dihydroquinoline **114** rather than the aniline derivative **113**. Subsequently **114** is reduced to the tetrahydroquinoline **115** by the excess of the sulfite ion.

In terms of structure the pyridine ring is evidently the simplest heteroaromatic system capable of enamine rearrangement. In other words, its recyclization into anilines is of general significance in the chemistry of heteroaromatic compounds including condensed systems containing a pyridine ring. In these terms the simplest heteroaromatic structure conceivably capable of recyclization are indolizines.

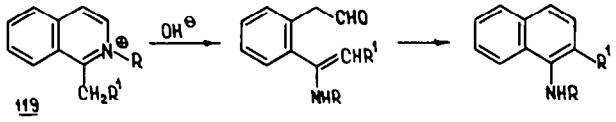
In accord with expectation, the nitroindolizines **117** when heated in water–alcohol alkali rearranged yielding the corresponding nitroindoles **118** in 40–90% yield.[264,265]



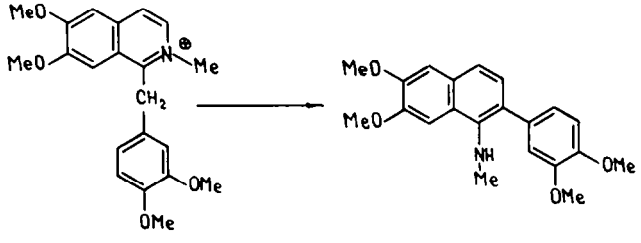
This reaction, too, begins with the nucleophilic attack by the hydroxide anion directed at the carbon atom by the aromatic nitrogen. The next stage is the ring opening (probably according to the electrocyclic mechanism) by C–N bond fission. It is then followed by ring closure and the C–C bond formation.

An intriguing fact is that the isomerisation is caused solely by the hydroxide anion. In anhydrous media with alkoxide anions or amines as nucleophilic agents, the pyridine ring did not open, though PMR data suggested the formation of stable σ-complexes. In the presence of atmospheric oxygen the σ-complexes with aliphatic amines were rapidly oxidised leading to 5-aminonitroindolizines.[265,266]

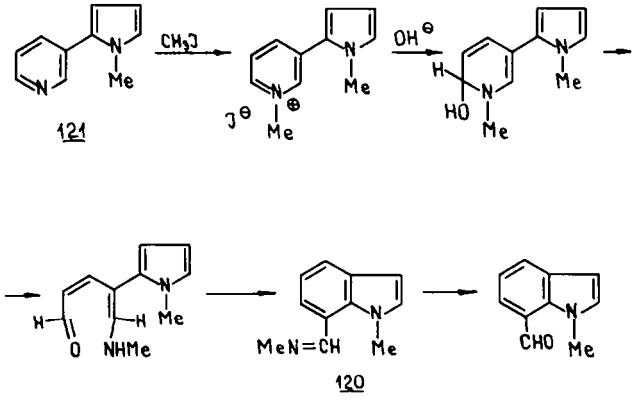
The electron excessive substances such as indolizines required additional activation by electron acceptor substituents.[267] In contrast, heating of the 1,2-dialkylisoquinolinium salts **119** in aqueous or alcoholic alkylamine caused their recyclization into α-naphthylamines in 70–90% yield.[268]



Similarly 3-substituted isoquinolinium salts yield β-naphthylamines.[269] With 1,3-dialkyl derivatives two competing processes are observed; they result in both the α- and the β-naphthylamines, the fission occurring primarily at the C_3–N bond. Like pyridinium salts, isoquinolinium salts may recyclise into naphthylamines by exchange of the N-substituent. Papaverine methiodide with methylammonium acetate also recyclises into the corresponding naphthalene derivative.

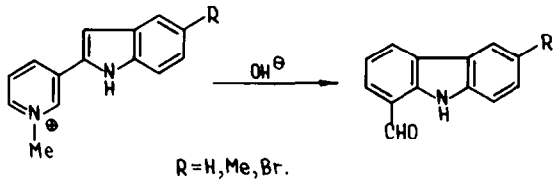


The above-discussed pyridine ring recyclizations include the reactions involving the α-carbon attached to the 2-position of the pyridine ring, or, in other words, the enamine fragment of the corresponding anhydropyridine. A formal structural approach, however, suggests that the recyclization could involve more remote but reactive substituents. In fact, recently it has been shown that β-nicotyrine methiodide under the effect of an alkali undergoes recyclization leading to an indole nucleus.[270,271]



In this reaction the substituent which becomes involved is attached to the position 3 of the pyridine ring. The necessary nucleophilicity is provided by the general electron availability from the pyrrole ring. In a rearrangement with methylammonium sulfite, it is possible to isolate the corresponding aldimine **120**. Both processes are accompanied by nicotyrine N-demethylation yielding β-nicotyrine **121**.

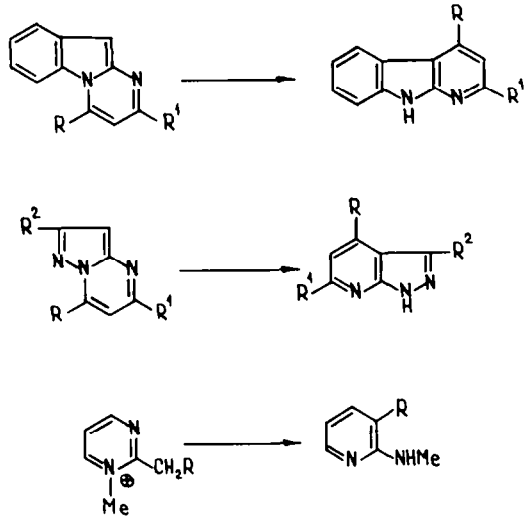
A similar rearrangement into 1-formylcarbazoles was observed with 1-methyl-3-(2-indolyl)pyridinium iodides.[272]



R=H,Me,Br.

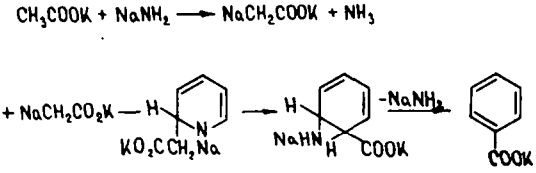
These examples show new ways of synthesizing the indole and the carbazole nuclei. They also indicate the direction of research to expand the opportunities of the rearrangement under consideration.

The new type of recyclization described in this chapter is not characteristic of pyridine only. We have also observed base-induced recyclizations of monocyclic and polycyclic structures containing a pyrimidine ring. For instance, 1,2-dialkylpyrimidinium salts may be converted into 2-alkylamino-pyridines. In a similar manner the pyrimidinium ring gives rise to a pyridine structure in reactions between bases and pyrazolo[1,2-a]pyrimidines[275] or pyrimido[1,2-a]indoles.[276]



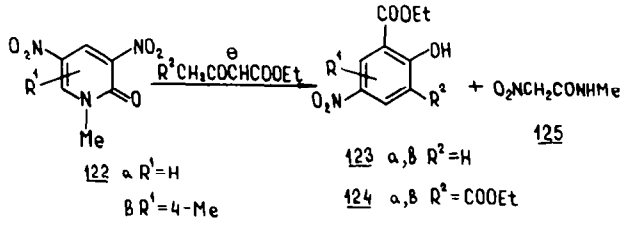
Further investigations of the enamine rearrangement is promising. The general approach developed by the authors[277] recognises the requirements in the initial structure and in the reagent. Thus it becomes possible to predict and carry out new types of chemical transformations.

(3) *More examples of benzene ring formation.* The reaction of pyridine with a mixture of potassium acetate and sodium amide at 200° under 50 atm was found to afford potassium benzoate. Sodium amide may be replaced by sodium, sodium hydride, potassium or butyllithium. The yield of benzoic acid in these reactions varied from 0.5 to 6%, with only a minor part of pyridine reacting.[278]



Another reaction leading to benzene ring formation is the transformation of pyridine bases into isonitrile benzenes under the effect of chloroform and alkali.[279] Thus 2- and 4-methylpyridines give rise to phenylisonitriles; the recyclisation was also observed with all the dimethylpyridines except for the 3,5-compound. Though the mechanism of this reaction is unknown, it must be essentially dependent on the formation of dichlorocarbene.

When treated with sodio-derivatives of β-keto-esters ($R^2CH_2COCH_2COOEt$, R^2 is H or COOEt), the derivatives of the 3,5-dinitropyridones **122a,b** undergo recyclization into the corresponding ethyl esters of 2-hydroxy-5-nitrobenzoic acid (**123** $R^2 = H$ and $R^2 = COOEt$) and nitroacetamide **125**. At first the carbanion apparently adds in the position 6 or 4 to form a Meisenheimer complex; the position 4 or 6 is then attacked by another nucleophilic centre to yield a bicyclic intermediate. The latter affords the final products **123**, **124** and the nitroacetamide **125** after the C_1–C_6 and the C_3–C_4 bond cleavage.



VI. CONCLUSION

The evidence on the pyridine ring recyclizations available at present concerns primarily the formation of hetero- and carbo-cycles involving the alkyl(aryl)amino-group exchange, which is quite natural considering the high solvolysability of the N=CH bond in pyridinium salts. Some of these reactions are significant as preparative methods. On the other hand, in certain recyclizations the substituent takes part in the formation of a new ring. This type of conversion is of both theoretical and practical interest, particularly as an efficient preparative means. The enamine rearrangement of pyridinium salts into anilines described by the authors is a new type of recyclization. The information on the structural factors and reaction conditions obtained so far promises to provide new exciting results. Our concept suggested in[251,252] makes it possible to predict certain new conversions of heteroaromatic compounds. Moreover, the unusual recyclisations involving substituents and leading to heteroaromatic structures or to benzene rings offer excellent prospects concerning the adjacent fields of heterocyclic chemistry.

The recyclizations of pyridine derivatives not activated by quaternization are relatively scarce. Due to the insufficient polarisation of the aromatic ring in this case the nucleophilic attack is non-selective and the C–C as well as C–N bond cleavage takes place.

REFERENCES

[1]A. Deninger, *J. Prakt. Chem.*[2], **50**, 479 (1894).
[2]E. Vongerichten, *Ber. Dtsch. Chem. Ges.* **32**, 2571 (1899).
[3]S. Greyf and L. Roosens, *Ind. Chim. Belge* **23**, 855 (1958).
[4]M. Ferles and J. Jizba, *Chemie Pyridinu*, Praha (1957).
[5]G. Mosher, Heterocyclic Compounds (Edited by R. Elderfield), IL, Vol. 1, p. 327, in Russian. Moscow (1953).
[6]F. Hamer, *Cyanine Dyes and Related Compounds*. Interscience, New York (1964).
[7]B. I. Stepanov, *Vvedenie v Khimiyu i Tekhnologiyu Organicheskikh Krasiteley*, p. 99. Khimiya, Moscow (1977).
[8]K. Hafner, *Liebigs Ann.* **606**, 79 (1957).
[9]K. Hafner, *Angew. Chem.* **70**, 419 (1958).
[10]E. N. Shaw, *The Chemistry of Heterocyclic Compounds*, Vol. 14, Part II: *Pyridine and its Derivatives* (Edited by E. Klinsberg), p. 58. Interscience, New York (1961).
[11]A. N. Kost, S. I. Suminov and A. K. Sheinkman, *Immonium Salts in Organic Chemistry* (Edited by H. Böhme and H. G. Viehe), Part 2. Wiley, New York (1978).
[12]Yu. I. Chumakov, *Piridinovye Osnovaniya, Teknika*, Kiev (1965).
[13]H. C. van der Plas, *Ring Transformations of Heterocycles*, Vol. 2. Academic Press, New York (1973).
[14]F. Bellamy, J. Streith, *Heterocycles* **4**, 1391 (1976).
[15]T. Kametani and H. Nemoto, *Ibid.* **10**, 349 (1978).
[16]C. Wentrup, *Topics in Current Chemistry* **62**, 173 (1976).
[17]M. Tišler and B. Stanovnik, *Heterocycles* **4**, 1115 (1976).
[18]Th. Zincke, *Ann. Chim.* **330**, 361 (1903).
[19]Th. Zincke, G. Heuser and W. Möller, *Ibid.* **333**, 296 (1904).
[20]W. König, *J. Prakt. Chem.*[2], **69**, 105 (1904).
[21]N. E. Grigor'yeva and I. K. Gintse, *Zh. Ob. Khim.* **24**, 169 (1954).
[22]W. König, *J. Prakt. Chem.*[2], **70**, 19 (1940).
[23]A. F. Vompe and N. F. Turitsyna, *Dokl. Akad. Nauk. SSSR* **114**, 1017 (1957).
[24]F. Dorn, J. Kotschy and H. Kausen, *Ber. Buns. Phys. Chem.* **69**, 11 (1965).
[25]R. Kuhn and E. Teller, *Liebigs Ann.* **715**, 106 (1968).
[26]A. F. Vompe, I. I. Levkoev, N. F. Turitsyna, V. V. Durmashkina and L. V. Ivanova, *Zh. Ob. Khim.* **34**, 1758 (1964).

[27]A. F. Vompe and N. F. Turitsyna, *Ibid.* **28**, 2864 (1958).
[28]N. E. Grigor'yeva and M. D. Yavlinsky, *Ukr. Khim. Zh.* **18**, 82 (1952).
[29]N. E. Grigor'yeva, I. K. Gintse and M. I. Rosenberg, *Sbornik Statey po Obschey Khimii* (Papers on General Chemistry), Vol. 2, p. 1446. AN SSSR, Moscow (1953).
[30]Th. Zincke and W. Würker, *Ann. Chim.* **338**, 107 (1905).
[31]F. Reitzenstein and J. Rothschild, *J. Prakt. Chem.*[2], **73**, 257 (1906).
[32]P. Karrer, G. Schwarzenbach and G. E. Utzinger, *Helv. Chim. Acta* **20**, 72 (1937).
[33]I. L. Knunants and T. Ya. Kefeli, *Zh. Ob. Khim.* **15**, 628 (1945).
[34]A. F. Vompe and N. F. Turitsyna, *Dokl. Akad. Nauk SSSR* **64**, 341 (1949).
[35]N. E. Grigor'yeva and I. K. Gintse, *Ukr. Khim. Zh.* **18**, 89 (1952).
[36]N. E. Grigor'yeva and R. M. Zueva, *Zh. Ob. Khim.* **26**, 107 (1956).
[37]N. E. Grigor'yeva and N. K. Gintse, *Ibid.* **26**, 232 (1956).
[38]N. E. Grigor'yeva, N. K. Gintse and N. G. Karpyuk, *Ibid.* **26**, 3455 (1956).
[39]R. Lukeš and J. Jizba, *Chem. Listy* **51**, 2334 (1957).
[40]W. Dieckmann, *Ber. Dtsch. Chem. Ges.* **38**, 1650 (1905).
[41]W. König, *J. Prakt. Chem.*[2], **83**, 406 (1911).
[42]W. König and G. A. Becker, *Ibid.*[2], **85**, 353 (1912).
[43]W. König, G. Ebert and K. Centher, *Chem. Ber.* **56**, 758 (1923).
[44]G. Schwarzenbach and R. Weber, *Helv. Chim. Acta* **25**, 1628 (1942).
[45]M. Strell, W. B. Braunbruck, W. F. Fuhler and O. Huber, *Liebigs Ann.* **587**, 177 (1954).
[46]M. Strell and K. Rost, *Chem. Ber.* **90**, 1905 (1957).
[47]A. F. Vompe, N. V. Monich, N. F. Turitsyna and L. V. Ivanova, *Dokl. Akad. Nauk SSSR* **114**, 1235 (1957).
[48]A. F. Vompe, N. V. Monich, N. F. Turitsyna and L. V. Ivanova, *Tetrahedron* **2**, 361 (1958).
[49]K. Hafner and K. D. Asmus, *Liebigs Ann.* **671**, 31 (1964).
[50]A. F. Vompe, N. V. Monich, N. F. Turitsyna and L. V. Ivanova, *Zh. Org. Khim.* **7**, 2590 (1971).
[51]W. König and R. Bayer, *J. Prakt. Chem.*[2], **83**, 325 (1911).
[52]E. Koenigs and H. Greiner, *Ber. Dtsch. Chem. Ges.* **64**, 1049 (1931).
[53]E. Koenigs and H. Greiner, *U.S. Pat.* 1879324 (24/9/1933); *Chem. Abstr.* **27**, 313 (1933).
[54]P. Baumgarten and E. Damman, *Ber. Dtsch. Chem. Ges.* **66**, 1633 (1933).
[55]E. Koenigs and G. Jung, *J. Prakt. Chem.*[2], **137**, 157 (1933).
[56]P. Baumgarten, *Ber. Dtsch. Chem. Ges.* **69**, 1938 (1936).
[57]G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* 3988 (1959).
[58]E. P. Lira, *J. Heterocyclic Chem.* **9**, 713 (1972).
[59]P. Wild and F. Kröhnke, *Liebigs Ann.* 849 (1975).
[60]R. D. Chambers, W. K. R. Musgrave and P. G. Urben, *Chem. Ind.* **89**, (1975).
[61]E. Koenigs and H. Greiner, *Ber. Dtsch. Chem. Ges.* **64**, 1053 (1931).
[62]W. König, M. Coenen, W. Lorenz, F. Bahr and A. Bassl, *J. Prakt. Chem.*[4], **30**, 96 (1965).
[63]H. Auferhoff and A. Weinmann, *Arch. Pharm.* **307**, 332 (1974).
[64]A. F. Vompe and N. F. Turitsyna, *Dokl. Akad. Nauk SSSR* **74**, 509 (1950).
[65]A. F. Vompe and N. F. Turitsyna, *Zh. Ob. Khim.* **27**, 3282 (1957).
[66]G. Köbrich, *Liebigs Ann.* **648**, 114 (1961).
[67]N. E. Grigor'yeva and V. I. Kovalenko, *Uch. Zap. Kharkovskogo Gos. Universiteta* **30**, 7 (1950).
[68]K. J. Laidler, *J. Chem. Soc.* 1786 (1938).
[69]S. I. Lur'ye and M. M. Shemyakin, *Zh. Ob. Khim.* **17**, 1356 (1947).
[70]Th. Zincke and W. Würker, *Ann. Chim.* **341**, 365 (1905).
[71]F. Reitzenstein and J. Rothschild, *J. Prakt. Chem.*[2], **73**, 192 (1906).
[72]N. J. Fischer and F. M. Hamer, *J. Chem. Soc.* 189 (1933).
[73]Gevaert-Photo-Producten N.Y., *Photo Produits Gevaert S. A. Fr. Pat.* 796789 (26/10/1935); *Dhem. Zentr.* II, 419 (1936).
[74]Gevaert-Photo-Producten N. Y., A. E. van Dormael and T. H. Ghys, *Br. Pat.* 628837 (6/911949); *Chem. Abstr.* **44**, 7066 (1950).
[75]P. Pfeiffer and E. Enders, *Chem. Ber.* **84**, 313 (1951).
[76]H. von Dobeneck and W. Goltsche, *Ibid.* **95**, 1484 (1962).
[77]Y. Tamura, K. Sumoto, M. Mano and T. Masui, *Yakaguchi Zasshi* **92**, 371 (1972); *Chem. Abstr.* **77**, 34261r (1972).
[78]N. E. Podkletov, *Zh. Ob. Khim.* **34**, 3362 (1964).
[79]F. M. Hamer and R. J. Rathbone, *J. Chem. Soc.* 960 (1947).
[80]F. W. Hodges, *Ibid.* 2417 (1926).
[81]D. Aumann and L. W. Deady, *J. Chem. Soc. Chem. Comm.* 32 (1973).
[82]V. A. Izamilsky, *Zh. Rus. Fiz. Khim. Ob.* **50**, 190 (1918).
[83]H. Lettré, W. Haede and E. Ruhbaum, *Liebigs Ann.* **579**, 123 (1953).
[84]H. Th. Bucherer and J. Schenkel, *Ber. Dtsch. Chem. Ges.* **41**, 1346 (1908).
[85]J. Schenkel, *Ibid.* **43**, 2597 (1910).
[86]F. Reitzenstein and W. Breuning, *Ibid.* **43**, 2939 (1910).
[87]R. Lukeš and J. Jizba, *Chem. Listy* **52**, 1126 (1958).
[88]R. Lukeš and J. Jizba, *Coll. Czech. Chem. Comm.* **24**, 1868 (1959).
[89]P. Baumgarten, *Ber. Dtsch. Chem. Ges.* **59**, 1166 (1926).
[90]P. Baumgarten, *Ibid.* **57**, 1622 (1924).
[91]P. Baumgarten, *Ibid.* **64**, 1502 (1931).
[92]F. Klages and H. Träger, *Chem. Ber.* **86**, 1327 (1953).
[93]F. Reitzenstein and W. Breuning, *J. Prakt. Chem.*[2], **83**, 97 (1911).
[94]R. Hull, *J. Chem. Soc.* (C), 1777 (1968).
[95]E. T. Boyle and R. Hull, *Ibid.* Perkin I 1541 (1974).
[96]A. Treibs, *Liebigs Ann.* **497**, 297 (1932).
[97]J. Bartos, *Ann. Pharm. Fr.* **29**, 221 (1971).
[98]R. J. Molyneux and R. Y. Wong, *Tetrahedron* **33**, 1931 (1977).
[99]J. Herzog, *Ber. Dtsch. Chem. Ges.* **40**, 1831 (1907).

[100]H. Freytag, *Ibid.* **67**, 1995 (1934).
[101]A. Deninger, *J. Prakt. Chem.*[2], **50**, 479 (1894).
[102]S. Zawadzki, *Pr. Cent. Inst. Ochr. Pr.* **21**, 127 (1971); *Chem. Abstr.* **76**, 89683q (1972).
[103]E. Gebauer-Fülnegg and F. Riesenfeld, *Monatsh.* **47**, 185 (1926).
[104]P. Dounzon and A. Le Clore, *Anal. Chim. Acta* **12**, 239 (1955).
[105]W. Ciusa and G. Barbiroli, *Ann. Chimica* **53**, 1248 (1963); *Rzh. Khim.* **17**, G177 (1964).
[106]J. Fuentes-Duchemin and E. Casassas, *Anal. Chim. Acta* **44**, 462 (1969).
[107]K. Gierschner and G. Baumann, *Z. Lebnsm.-Unters.-Forsch.* **139**, 132 (1969), *Chem. Abstr.* **70**, 95514c (1969).
[108]J. Bartos, *Ann. Pharm. Fr.* **29**, 71 (1971).
[109]M. I. Bukovsky and S. A. Psaltyra, *Issled. v. Obl. Tekhn. Bezopasn.* 107 (1973); *R. Zh. Khim.* **121**, 600 (1974).
[110]S. F. Arens and D. A. Van Dorp, *Rec. Trav. Chim. Pays-Bas* **65**, 722 (1946).
[111]G. Schwarzenbach, *Helv. Chim. Acta* **26**, 418 (1943).
[112]F. Kröhnke, *Angew. Chem.* **65**, 605 (1953).
[113]F. Kröhnke and J. Vogt, *Liebigs Ann.* **589**, 26 (1954).
[114]F. Kröhnke and J. Vogt, *Ibid.* **589**, 45 (1954).
[115]G. W. Fischer, *Chem. Ber.* **103**, 3489 (1970).
[116]F. Kröhnke, M. Meyer-Delins and I. Vogt, *Liebigs Ann.* **597**, 87 (1955).
[117]Y. Tamura, N. Tsyjimoto and Y. Hirano, *Yakaguchi Zasshi* **92**, 546 (1972); *Chem. Abstr.* **77**, 88236e (1972).
[118]E. Ochiai, *Aromatic Amine Oxides*. Elsevier, Amsterdam (1967).
[119]I. F. Belk'sy, G. N. Dorofeenko, N. S. Prostakov, V. P. Sherstyuk and Yu. I. Chumakov, *Geterotsikly v Organicheskom Sinteze* (*Heterocycles in Organic Synthesis*). Tekhnika, Kiev (1970).
[120]T. Kato, H. Yamanaka, T. Adachi and H. Hiraunma, *J. Org. Chem.* **32**, 3788 (1967).
[121]T. J. van Bergen and R. M. Kellogg, *Ibid.* **36**, 1705 (1971).
[122]P. Schiess and P. Ringele, *Tetrahedron Letters* 311 (1972).
[123]J. H. Blumenthal and N. J. Plainfield, *U.S. Pat.* 2874162 (17/2/1959); *Chem. Abstr.* **53**, 12311 (1959).
[124]V. Fritzsche and S. Hünig, *Liebigs Ann.* 1407 (1974).
[125]J. M. Kokosa, L. Bauer and R. S. Egan, *J. Heterocycl. Chem.* **13**, 321 (1976).
[126]J. Schnekenburger and D. Heber, *Chem. Ber.* **107**, 3408 (1974).
[127]J. Schenkenburger and D. Heber, *Arch. Pharm.* **308**, 594 (1975).
[128]V. Bockelheide and W. Feedly, *J. Am. Chem. Soc.* **80**, 2217 (1958).
[129]N. A. Coats and A. R. Katritzky, *J. Org. Chem.* **24**, 1836 (1959).
[130]V. Boekelheide and R. Scharrer, *Ibid.* **26**, 3802 (1961).
[131]A. R. Katritzky and E. Lunt, *Tetrahedron* **25**, 4291 (1969).
[132]R. Eisenthal and A. R. Katritzky, *Ibid.* **21**, 2205 (1965).
[133]R. Eisenthal, A. R. Katritzky and E. Lunt, *Ibid.* **23**, 2775 (1967).
[134]J. Schnekenburger and D. Heber, *Arch. Pharm.* **309**, 592 (1976).
[135]H. Sliwa and A. Tartar, *Tetrahedron Letters* 4717 (1976).
[136]H. Sliwa and A. Tartar, *Ibid.* 311 (1977).
[137]K. Dimroth, *Aromatische Verbindungen aus Pyryliumsalzen, in Neuere Methoden der Präparativen organischen Chemie*, B. III. Verlag Chemie, Veinheim/Bergstr. (1961).
[138]A. Kirby and S. Warren, *Organicheskaya Khimiya Fosfora* (*Organic Chemistry of Phosphorus*), p. 214. Mir, Moscow (1971).
[139]J. Schnekenburger, D. Heber and E. Herber-Brunschveiger, *Tetrahedron* **33**, 457 (1977).
[140]T. Okamoto in E. Ochiai, *Aromatic Amine Oxides*, p. 307. Elsevier, Amsterdam (1967).
[141]H. Takayama and T. Okamoto, *Chem. Pharm. Bull. Japan* **26**, 2422 (1978).
[142]T. Kauffmann and R. Wirthwein, *Angew. Chem. Int. Ed.* **10**, 20 (1971).
[143]J. A. Zoltewicz, *Topics in Current Chemistry* **59**, 33 (1975).
[144]P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.* **85**, 2236 (1963).
[145]G. Fraenkel and J. C. Cooper, *Tetrahedron Letters* 1825 (1968).
[146]M. J. Strauss, *Chem. Rev.* **70**, 667 (1970).
[147]H. C. van der Plas, *Acc. Chem. Res.* **11**, 462 (1978).
[148]J. A. Zoltewicz, G. M. Kauffmann and C. L. Smith, *J. Am. Chem. Soc.* **90**, 5939 (1968).
[149]J. A. Zoltewicz and L. S. Helmick, *Ibid.* **92**, 7547 (1970).
[150]J. A. Zoltewicz and R. E. Cross, *J. Chem. Soc.* Perkin II 1363 (1974).
[151]D. N. Kursanov, V. N. Setkina and E. V. Bukova, *Dokl. Akad. Nauk SSSR* **97**, 835 (1954).
[152]I. L. Duling and C. C. Price, *J. Am. Chem. Soc.* **84**, 578 (1962).
[153]H. Decker, *Ber. Dtsch. Chem. Ges.* **38**, 2493 (1905).
[154]W. Schneider, K. Gaertner and A. Jordan, *Ibid.* **57**, 522 (1924).
[155]A. Hantzsch and M. Kalb, *Ibid.* **32**, 3109 (1899).
[156]J. G. Aston and P. A. Lasselle, *J. Am. Chem. Soc.* **56**, 426 (1934).
[157]A. I. Shatenshtein, *Dokl. Akad. Nauk SSSR* **60**, 1029 (1950).
[158]T. I. Abramovich, I. P. Gragerov and V. V. Perkalin, *Zh. Ob. Khim.* **31**, 1962 (1961).
[159]N. N. Zatsepina, I. F. Turitsyna and L. S. Efros, *Ibid.* **33**, 2705 (1963).
[160]N. N. Zatsepina, I. F. Turitsyna and L. S. Efros, *Dokl. Akad. Nauk SSSR* **154**, 148 (1964).
[161]D. I. Kursanov and O. M. Shemyakina, *Ibid.* **62**, 341 (1948).
[162]U. Berg, R. Gallo and J. Metzger, *J. Org. Chem.* **41**, 2621 (1976).
[163]A. F. Pozharsky, A. M. Simonov and V. N. Doron'kin, *Usp. Khim.* **47**, 1933 (1978).
[164]A. E. Chichibabin, *Zh. Rus. Fiz. Khim. Ob.* **47**, 835 (1917).
[165]F. W. Bergstrom, *J. Org. Chem.* **2**, 411 (1937).
[166]J. A. Zoltewicz, L. S. Helmick, T. M. Oestreich. R. W. King and P. E. Kandetzki, *Ibid.* **38**, 1947 (1973).
[167]G. Klopman, *Reaktsionnaya Sposobnost' i Puty Reaktsiy* (*Reactivity and Reaction Pathways*) (Edited by G. Klopman), p. 83. Mir, Moscow (1977).
[168]J. A. Zoltewicz, T. M. Oestreich, J. K. O'Halloran and L. S. Helmick, *J. Org. Chem.* **38**, 1949 (1973).
[169]J. A. Zoltewicz, L. S. Helmick and J. K. O'Halloran, *Ibid.* **41**, 1303 (1976).
[170]T. Severin, H. Lerche and O. Bätz, *Chem. Ber.* **102**, 2163 (1969).

[171]A. A. Onishchenko, T. V. Ternikova, O. A. Luk'yanov and V. A. Tartakovsky, *Izv. AN SSSR, ser. Khim.* 2530 (1976).
[172]J. Kaválek, A. Lyčka, V. Macháček and V. Štěrba, *Coll. Czech. Chem. Comm.* **41**, 67 (1976).
[173]J. A. Zoltewicz, L. S. Helmick and J. K. O'Halloran, *J. Org. Chem.* **41**, 1308 (1976).
[174]J. Vanbroeckhoven, J. Lepoivre and F. Alderweireldt, *Heterocycles* **9**, 603 (1978).
[175]E. van der Dungen, J. Nasielski and P. van Laer, *Bull. Soc. Chim. Belg.* **66**, 661 (1957).
[176]J. Kaválek and V. Štěrba, *Coll. Czech. Chem. Comm.* **38**, 3506 (1973).
[177]J. Kaválek, A. Barteček and V. Štěrba, *Ibid.* **39**, 1717 (1974).
[178]R. Oda and S. Mita, *Bull. Chem. Soc. Japan* **36**, 103 (1963).
[179]S. L. Johnson and K. A. Rumon, *Tetrahedron Letters* 1721 (1966).
[180]J. Kaválek, A. Lyčka, V. Macháček and V. Štěrba, *Coll. Czech. Chem. Comm.* **41**, 1926 (1976).
[181]H. Sliwa and A. Tartar, *J. Heterocycl. Chem.* **14**, 631 (1977)
[182]E. N. Marvell, G. Caple and I. Shahidi, *Tetrahedron Letters* 277 (1967).
[183]E. N. Marvell, G. Caple and I. Shahidi, *J. Am. Chem. Soc.* **92**, 5641 (1970).
[184]E. N. Marvell and I. Shahidi, *Ibdi.* **92**, 5646 (1970).
[185]D. Beke, *Advances in Heterocyclic Chemistry* **1**, 167 (1963).
[186]V. Simanek and V. Preininger, *Heterocycles* **6**, 475 (1977).
[187]J. Kaválek, A. Lyčka, V. Macháček and V. Štěrba, *Coll. Czech. Chem. Comm.* **39**, 2056 (1974).
[188]V. Beránek, J. Kaválek, A. Lyčka and V. Štěrba, *Ibid.* **39**, 2047 (1974).
[189]S. L. Johnson and K. A. Rumon, *Biochem.* **9**, 847 (1970).
[190]S. L. Johnson and D. L. Morrison, *Ibid.* **9**, 1460 (1970).
[191]J. Kaválek, J. Polanský and V. Štěrba, *Coll. Czech. Chem. Comm.* **39**, 1049 (1974).
[192]S. Kunugi, T. Okubo and N. Ise, *J. Am. Chem. Soc.* **98**, 2282 (1976).
[193]W. König, M. Coenen, F. Bahr, B. May and A. Bassl, *J. Prakt. Chem.*[4], **33**, 54 (1966).
[194]S. Hagen, G. A. Ulsaker and K. Undheim, *Acta Chem. Scand.* **B28**, 523 (1974).
[195]D. W. Bristol and D. C. Dittmer, *J. Org. Chem.* **35**, 2487 (1970).
[196]J. Schnekenburger and D. Heber, *Tetrahedron* **30**, 4055 (1974).
[197]R. Foster and T. J. Thompson, *Trans. Faraday Soc.* **58**, 860 (1962).
[198]R. Foster and C. A. Fyfe, *Tetrahedron* **22**, 1831 (1966).
[199]H. J. den Hertog, R. J. Martens, H. C. van der Plas and J. Bon, *Tetrahedron Letters* 4325 (1966).
[200]H. N. M. van der Lans, H. J. der Hertog and A. van Veldhuizen, *Ibid.* 1875 (1971).
[201]W. A. Roelfsema and H. J. van der Hertog, *Ibid.* 5089 (1967).
[202]W. A. Roelfsema, *Meded. Landouwhogesch. Wageningen* 72, 56 (1972); *Chem. Abstr.* **77**, 19492 (1972).
[203]N. Ise, T. Okubo, H. Kitano and S. Kunugi, *J. Am. Chem. Soc.* **97**, 2882 (1975).
[204]H. Beyer and E. Thieme, *J. Prakt. Chem.*[4], **31**, 293 (1966).
[205]Y. Tamura and N. Tsujimoto, *Chem. Ind.* 926 (1970).
[206]Y. Tamura, N. Tsujimoto and M. Ma-no, *Chem. Pharm. Bull. Japan* **19**, 130 (1971); *Chem. Abstr.* **74**, 125362d (1971).
[207]Y. Tamura, N. Tsujimoto and M. Uchimura, *Yakaguchi Zasshi* **91**, 72 (1971); *Chem. Abstr.* **74**, 99804c (1971).
[208]Y. Tamura, Y. Miki, T. Honda and M. Ikeda, *J. Heterocyclic Chem.* **9**, 865 (1972).
[209]N. Tsujimoto, M. Mano and Y. Tamura, *Jap. Pat.* 7304785 (28/10/1968); *Chem. Abstr.* **78**, 147813m (1973).
[210]O. Mumm and G. Hingst, *Ber. Dtsch. Chem. Ges.* **56**, 2301 (1923).
[211]O. Mumm and G. Hingst, *Ann. Chim.* **443**, 273 (1925).
[212]E. Matsumura, M. Ariga and Y. Touda, *Heterocycles* **9**, 108 (1978).
[213]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Khim. Geterots. Soed.* 98 (1979).
[214]R. Lukeš and J. Jizba, *Chem. Listy* **52**, 1131 (1958).
[215]R. A. Olofson and D. M. Zimmerman, *J. Am. Chem. Soc.* **89**, 5047 (1967).
[216]S. L. Johnson and K. A. Rumon, *Tetrahedron Letters* 1721 (1966).
[217]S. P. Gromov, A. N. Kost and R. S. Sagitullin, *Zh. Org. Khim.* **14**, 1316 (1978).
[218]R. S. Sagitullin, S. P. Gromov and A. N. Kost, *Dkol. Akad. Nauk SSSR* **236**, 634 (1977).
[219]J. H. Blauch and K. Fretheim, *J. Chem. Soc.*(C), 1892 (1971).
[220]D. J. Brown, *Mechanisms of Molecular Migrations*, Vol. 1, p. 209. Wiley, New York (1968).
[221]M. Wahren, *Z. Chem.* **7**, 241 (1969).
[222]A. E. Tschitschibabin and A. W. Kirssanow, *Ber. Dtsch. Chem. Ges.* **61**, 1223 (1928).
[223]J. Goerdeler and W. Roth, *Chem. Ber.* **96**, 534 (1963).
[224]D. J. Brown and J. S. Harper, *J. Chem. Soc.* 5542 (1965).
[225]A. E. Tschitschibabin, R. A. Konowalowa and A. A. Konowalowa, *Ber. Dtsch. Chem. Ges.* **54**, 814 (1921).
[226]M. Wahren, *Z. Chem.* **6**, 181 (1966).
[227]M. Wahren, *Tetrahedron* **24**, 441 (1968).
[228]M. Wahren, *Ibid.* **24**, 451 (1968).
[229]H. den Hertog and H. van der Plas, *Advances in the Chemistry of Acetylenes* (Edited by G. G. Wiye), Vol. 2. Khimiya, Moscow (1973).
[230]H. J. den Hertog, H. C. van der Plas, M. J. Pieterse and J. W. Streef, *Rec. Trav. Chim. Pays-Bas* **84**, 1569 (1965).
[231]J. W. Streef and H. J. den Hertog, *Tetrahedron Letters* 5945 (1968).
[232]J. W. Streef and H. J. den Hertog, *Rec. Trav. Chim. Pays-Bas* **88**, 1391 (1969).
[233]G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* 3988 (1959).
[234]J. W. Streff and H. J. den Hertog, *Rec. Trav. Chim. Pays-Bas* **85**, 803 (1966).
[235]V. Snieckus and G. Kan, *Tetrahedron Letters* 2267 (1970).
[236]T. Okamoto and M. Hirobe, *J. Synth. Organ. Chem.* **26**, 746 (1968).
[237]H. N. M. van der Lans and H. J. den Hertog, *Tetrahedron Letters* 1887 (1973).
[238]D. Allan and J. D. London, *J. Chem. Soc.* 821 (1949).
[239]W. König and H. Rösler, *Naturwissenschaften* **42**, 211 (1955).
[240]K. Haffner and K. Ziegler, *Angew. Chem.* **67**, 301 (1955).
[241]M. Freund and L. Richard, *Ber. Dtsch. Chem. Ges.* **42**, 1101 (1909).
[242]R. B. Woodward and R. Hoffmann, *Angew. Chem.* **81**, 797 (1969).
[243]R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **10**, 761 (1971).

[244]E. Heilbronner and R. W. Schmid, *Helv. chim. Acta* **37**, 2018 (1954).
[245]F. Šorm, V. Benešová, J. Krupička, V. Šheberk, L. Dolejs, V. Herout and J. Sicher, *Chem. Ind.* 1511 (1954).
[246]O. Mumm and R. Petzold, *Ann. Chim.* **536**, 1 (1938).
[247]R. Lukeš and M. Pergal, *Chem. Listy* **52**, 68 (1958).
[248]R. Lukeš and J. Jizba, *Coll. Czech. Chem. Comm.* **24**, 36 (1959).
[249]R. Lukeš and J. Jizba, *Chem. Listy* **46**, 622 (1952).
[250]G. N. Dorofeenko, E. I. Sadekova and E. V. Kuznetsov, *Preparativnaya Khimiya Pirilievykh Soley* (*Preparative Chemistry of Pyrylium Salts*). RGU, Rostov-on-Don (1972).
[251]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Khim. Geterots. Soed.* 1141 (1978).
[252]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Discovery* No. 205.
[253]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *U.S.S.R. Pat.* 597669 (12/11/1976).
[254]Yu. B. Vystosky, B. P. Zemsky, T. V. Stupnikova, R. S. Sagitullin, A. N. Kost and O. P. Shvaika, *Khim. Geterots. Soed.* 1496 (1979).
[255]V. A. Tafeenko, L. A. Aslanov, A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Dokl. Akad. Nauk SSSR* **252**, 126 (1980).
[256]R. S. Sagitullin, S. P. Gromov and A. N. Kost, *Tetrahedron* **34**, 2213 (1978).
[257]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Khim. Geterots. Soed.* 417 (1978).
[258]R. S. Sagitullin, S. P. Gromov and A. N. Kost, *Dokl. Akad. Nauk SSSR* **243**, 937 (1978).
[259]A. N. Kost, R. S. Sagitullin, S. P. Gromov, V. P. Marshtupa, T. V. Stupnikova and V. N. Kalafat, *U.S.S.R. Pat.* 709619 (1/3/1978).
[260]T. V. Stupnikova, V. N. Kalafat, V. P. Marshtupa, R. S. Sagitullin and A. N. Kost, *Dokl. Akad. Nauk Ukr. SSR*, ser. B 58 (1980).
[261]S. P. Gromov, R. S. Sagitullin, A. N. Kost and A. Fadda, *Reaktsionnaya Sposobnost' Azinov* (*Reactivity of Azines*), p. 7. SO AN SSSR, Novosibirsk (1979).
[262]V. N. Kalafat, V. P. Marshtupa, T. V. Stupnikova, B. P. Zemsky, Yu. B. Vysotsky and L. A. Rybenko, *Ibid.* 45 (1979).
[263]P. B. Terent'yev, Le Ty Chin and A. N. Kost, *Khim. Geterots. Soed.* 564 (1980).
[264]R. S. Sagitullin, S. P. Gromov and A. N. Kost, *U.S.S.R. Pat.* 514822 (8/1/1975).
[265]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Dokl. Akad. Nauk SSSR* **230**, 1106 (1976).
[266]A. N. Kost, R. S. Sagitullin and S. P. Gromov, *Heterocycles* **7**, Special Issue No. 2, 997 (1977).
[267]N. S. Prostakov and O. B. Baktibaev, *Usp. Khim.* **44**, 1649 (1975).
[268]A. N. Kost, L. G. Yudin, R. S. Sagitullin, V. I. Terenin and A. A. Ivkina, *Khim. Heterots. Soed.* 1386 (1979).
[269]L. G. Yudin, V. I. Terenin and A. A. Ivkina, *Novoe v Khimii Azotsoderzhashchikh Geterotsiklov* (*News in Chemistry of Nitrogen-Containing Heterocycles*). Vol. 1, p. 134. Zinatne, Riga (1979).
[270]A. N. Kost, L. G. Yudin, R. S. Sagitullin and A. Muminov, *Khim. Geterots. Soed.* 1566 (1978).
[271]L. G. Yudin, A. N. Kost, A. Muminov, R. S. Sagitullin, P. B. Terent'yev and O. A. Solov'yev, *Ibid.* 338 (1979).
[272]A. N. Kost, T. V. Stupnikova, R. S. Sagitullin, B. P. Zemsky and A. K. Sheinkman, *Dokl. Akad. Nauk SSSR* **244**, 103 (1979).
[273]A. N. Kost, R. S. Sagitullin and G. G. Danagulyan, *Khim. Geterots. Soed.* 1400 (1978).
[274]R. S. Sagitullin, A. N. Kost and G. G. Danagulyan, *Tetrahedron Letters* 4135 (1978).
[275]A. N. Kost, R. S. Sagitullin and G. G. Danagulyan, *Khim. Geterots. Soed.* 558 (1977).
[276]R. S. Sagitullin, T. V. Mel'nikova and A. N. Kost, *Ibid.* 1436 (1974).
[277]R. S. Sagitullin and A. N. Kost, *Zh. Org. Khim.* **16**, 658 (1980).
[278]L. Schmerling and W. G. Toekelt, *J. Am. Chem. Soc.* **86**, 1259 (1964).
[279]J. Ploquin, *Bull. Soc. Chim. Fr.* 901 (1947).