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THE CHEMISTRY OF N-SUBSTITUTED PYRIDINIUM SALTS

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Abstract - Syntheses, physicochemical and biological properties of N-substituted pyridinium salts, as well as their applications are described.

I. INTRODUCTION

The present paper, a continuation of our research concerning cycloaddition reactions of benzo[h]naphthyridines[1-7] deals with N-substituted pyridinium salts and their analogues; N-aminopyridiniums, precursors of N-iminoylides, used in cycloaddition reactions are not described here[8-13].

Pyridinium salts, **interesting for their reactivity, biological properties and applications, are compounds of great importance.**

Among reactions of pyridinium salts one ought to mention their nucleophilic substitution with amines; numerous publications deal with kinetic measurements and mechanism elucidation of these reactions, along with the study of pyridine ring-substituents' influence on its effectiveness as the leaving group[14-16]. Pyridinium salts are synthons of pyridinium N-methylides used in dipolar cycloaddition reactions[17-19]. As the material concerning the reactivity of pyridinium salts is very large[20-35], this topic is not included here.

In the present work the syntheses of pyridinium salts and their physicochemical properties, along with their applications are presented.

II. SYNTHESES

Synthetic approaches for pyridinium salts, described in recent publications can be divided into:

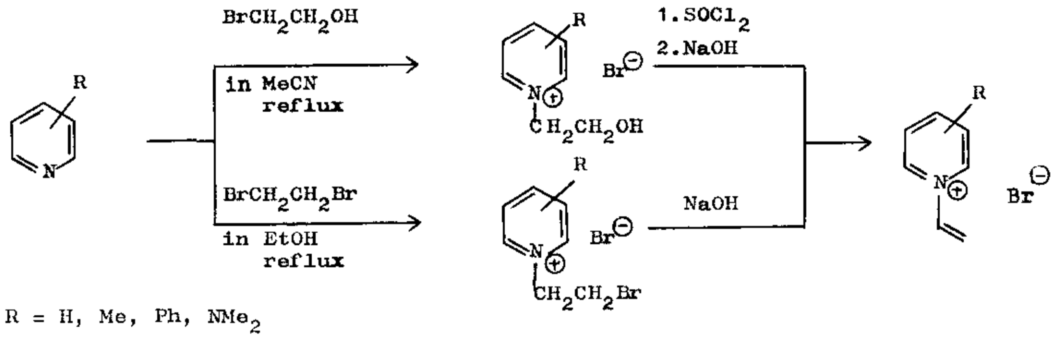
A. Quaternization reactions of pyridines with organic halides, and related reactions.

B. Reactions of pyrylium salts with primary amines.

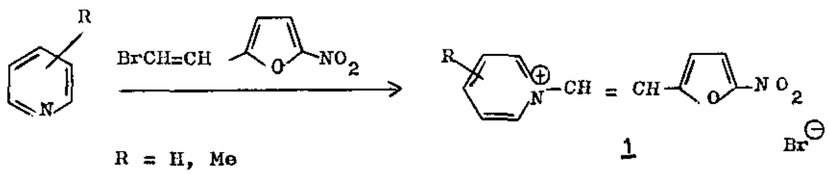
C. Other syntheses.

A. QUATERNIZATION REACTIONS OF PYRIDINES WITH ORGANIC HALIDES, AND RELATED REACTIONS

N-Vinylpyridinium salts, interesting as polymer components can be obtained by two procedures.[36,37]

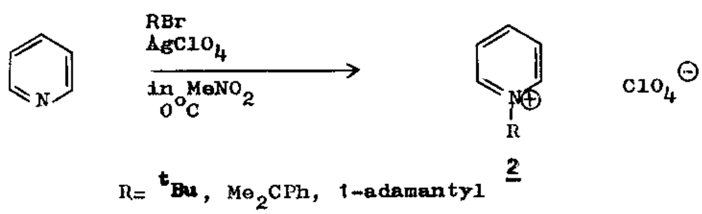


In the study of vinylpyridinium salts, their derivatives 1 have been prepared in the reaction proceeding via an addition-elimination mechanism[38]:



1

So far, few N-t-alkylpyridinium salts are known; examples of them are 2, obtained from pyridine and corresponding alkyl bromide in the presence of silver perchlorate[39].



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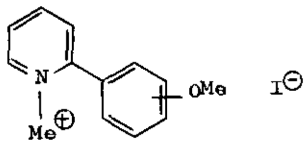
By quaternization of appropriately substituted pyridines, 3 and 4 have been synthesized[40].



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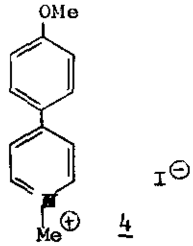
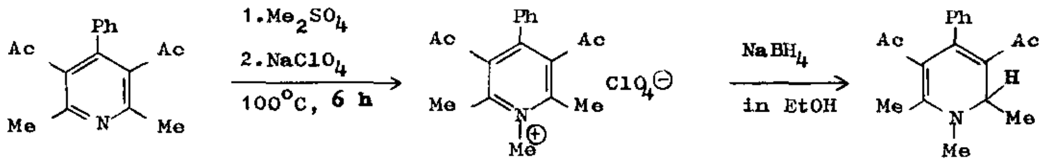


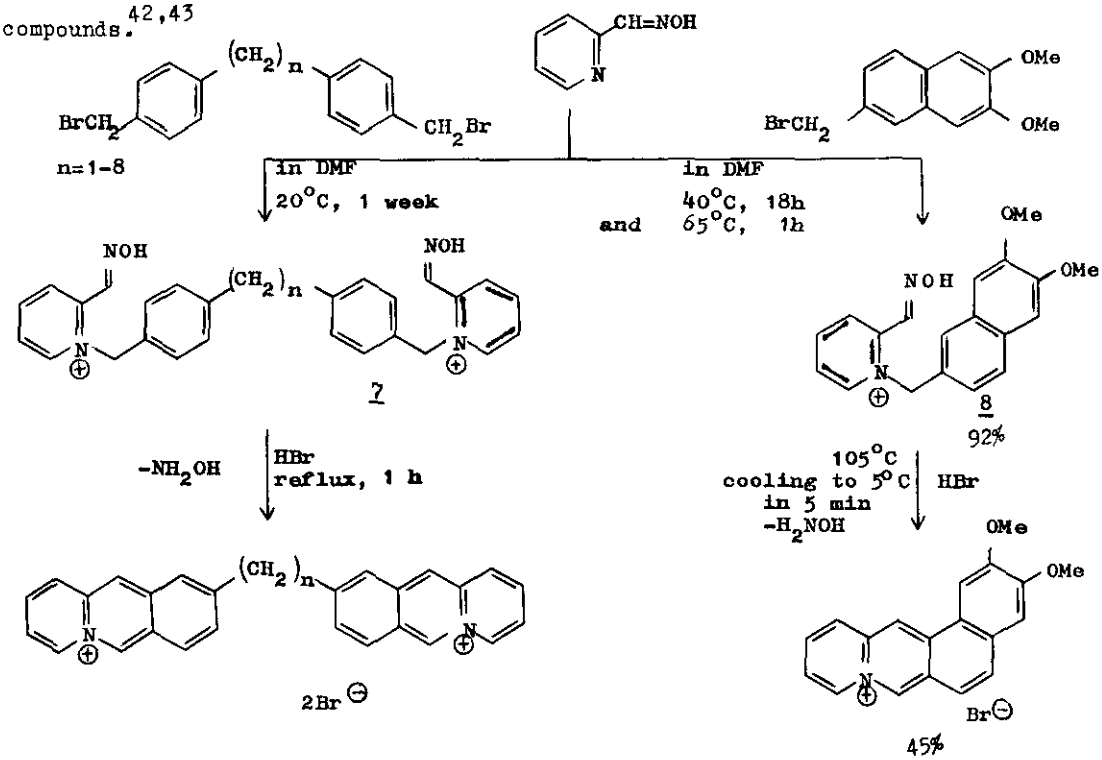
4

The following reaction leads to pyridinium salt 5, which was reduced to give so far unknown 1,2-dihydropyridine 6 [41].

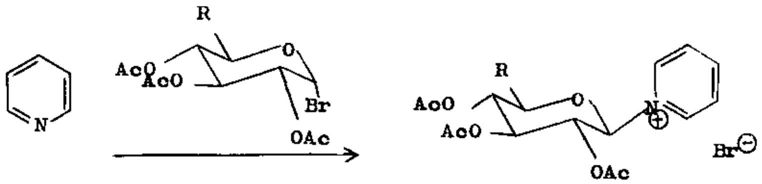


5 6

Quaternization reactions of pyridinium-2-aldoxime with bromomethylated aromatics yield pyridinium salts 7 and 8 which undergo Friedel - Crafts cyclization to azonia compounds.[42,43]

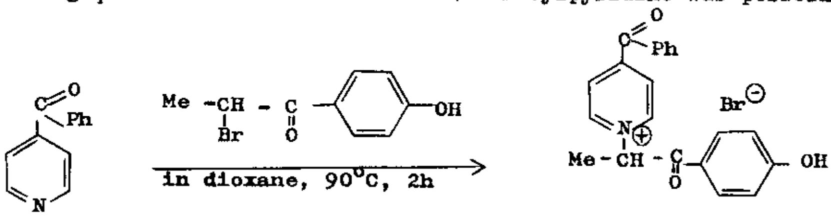


Pyridinium salts 9 containing α-D-xylopyranose and α-D-glucopyranose systems were obtained and their hydrolysis mechanism has been discussed[44].



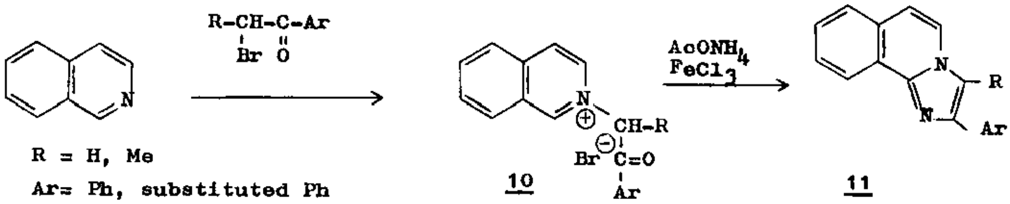
9 R=H; D-xylo
R=CH_2OAc; D-gluco

The following quaternization reaction of 4-benzoylpyridine was performed[45].



99,5%

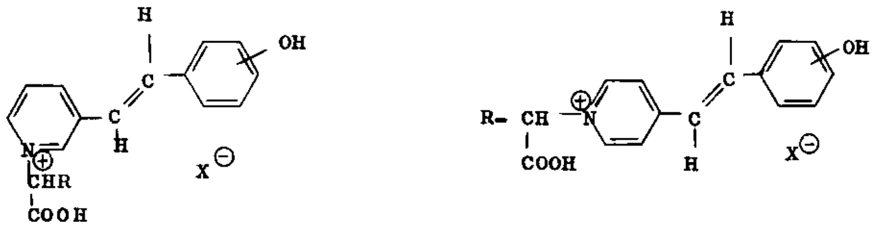
Similar reaction carried out with isoquinoline leads to 10, which undergoes cyclization with ammonium acetate in the presence of Fe(III) chloride to give biologically active 11[46].



R = H, Me
Ar= Ph, substituted Ph

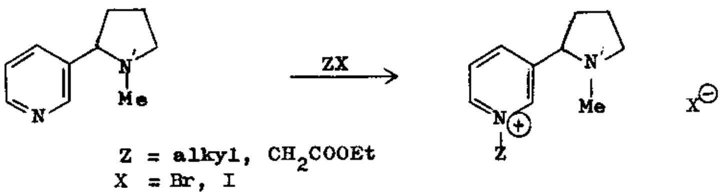
10 11

Quaternization of (E)-hydroxystilbazoles with halocarboxylic acids results in (E)-N-carboxyalkylated hydroxystilbazolium halides[47]:



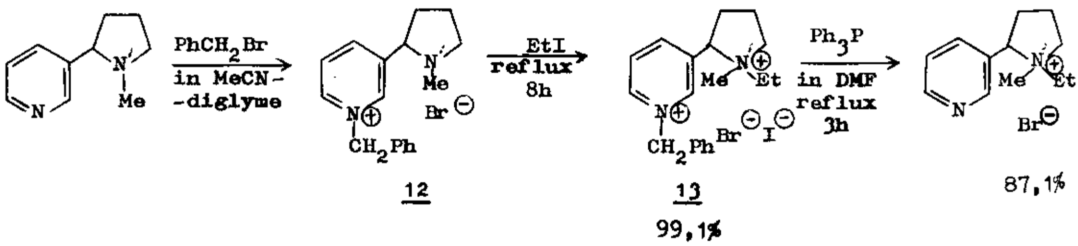
R = H, Me
X = Cl, Br

An attention has been paid to quaternization of nicotine. In the following reaction of nicotine only the pyridine N atom undergoes quaternization.[48,49]

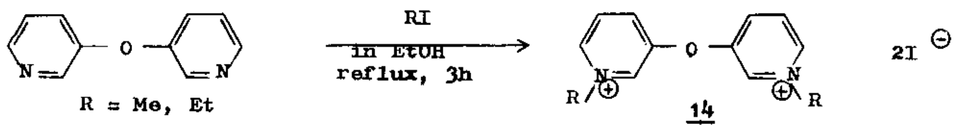


Salts quaternized at the pyrrolidine N′ atom are accessible by dealkylation of N,N′-dialkylnicotinium compounds.

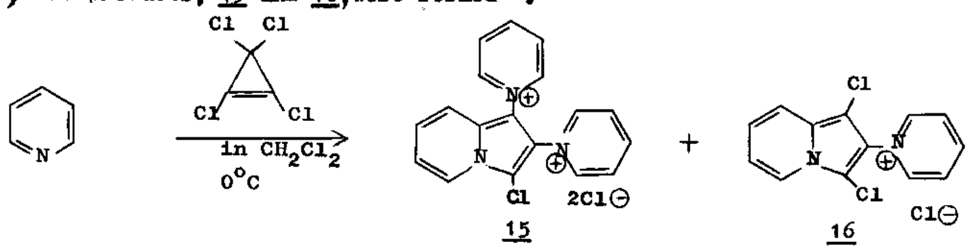
For instance, the reaction of 12 with ethyl iodide gives rise to 13, which is dealkylated by treatment with triphenylphosphine to the desired N′-alkylated product[50].



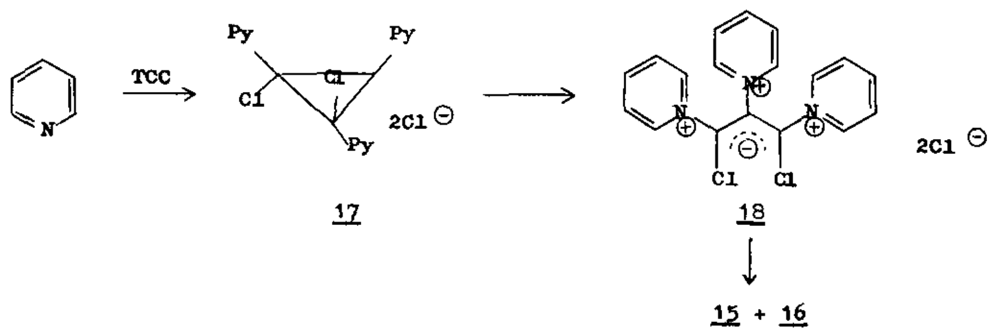
Quaternization of 3,3′-oxybispyridine, obtained in one-step procedure by treatment of 3-bromopyridine with 3-hydroxypyridine, yields 14[51]:



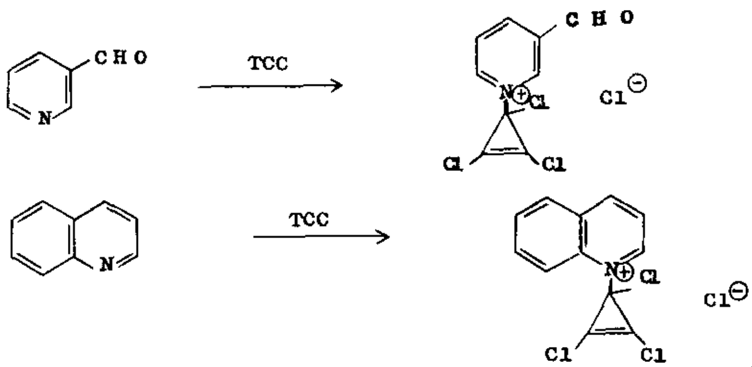
Reaction of pyridine with tetrachlorocyclopropene (TCC) offers a new, rather unexpected approach to indolizines. When pyridine was treated with TCC in methylene chloride, two products, 15 and 16, were formed[52].



The mechanism of this reaction involves a sequential addition of pyridine to TCC to form tris pyridinium cyclopropyl anion 17, undergoing electrocyclic ring opening leading to pyridinium N-allylide 18; the subsequent electrocyclic ring closure of 18 yields indolizines 15 and 16.

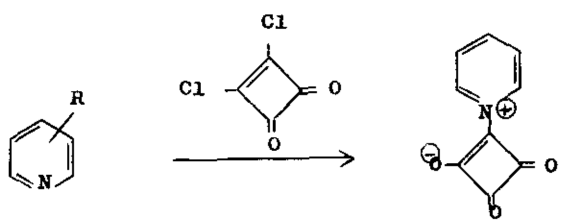


However, pyridines with electron-withdrawing groups, as well as azaaromatics with electron-deficient nitrogen atoms do not form indolizines, instead of only the corresponding quaternary salts could be obtained[52].



Similar reaction leading to indolizine system was carried out on 4-(dimethylamino)-pyridine[53].

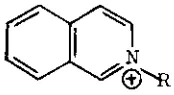
The squaric acid derivatives can be synthesized in the following procedure[54].



R = Me, CN, NMe_2, $CONH_2$

Analogous reactions were performed using dimethylpyridines or quinoline and isoquinonoline as starting materials.

Quaternization reactions are used for isolation of isoquinoline, contained in tar base. For example, isoquinolinium salts 19 were prepared by treatment of tar base containing isoquinoline, quinoline, 2-methylquinoline etc. with appropriate alkyl salts at 100 - 200°C [55].

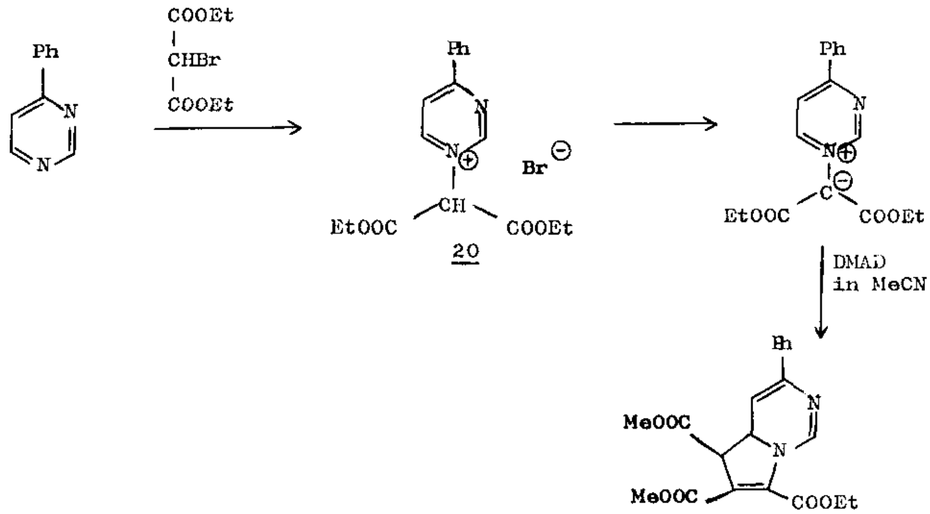


19

$X^{\ominus}$

R= C_{1-20} alkyl
X= halo, sulfate, arylsulfonate

Among pyridinium salts one ought to mention 20 obtained by quaternization of 4-phenylpyrimidine. Compounds 20 are precursors of ylides, undergoing cycloaddition reactions, e. g. with DMAD[56].

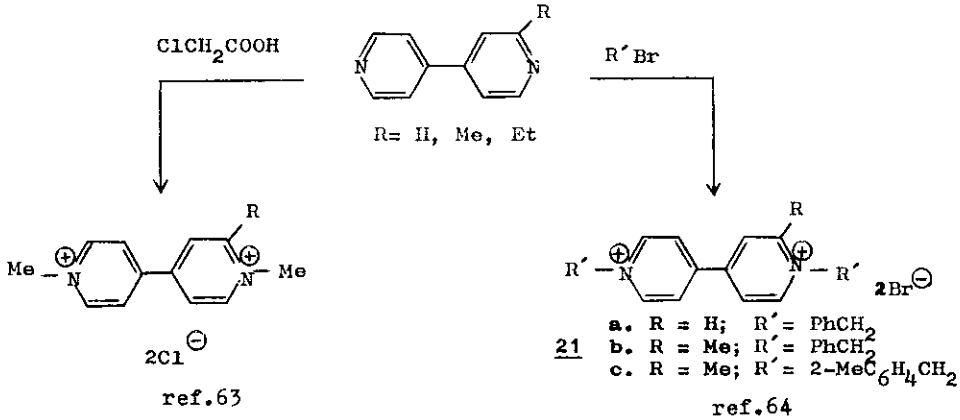


Similar quaternization reactions were performed on substituted quinazolines[57].

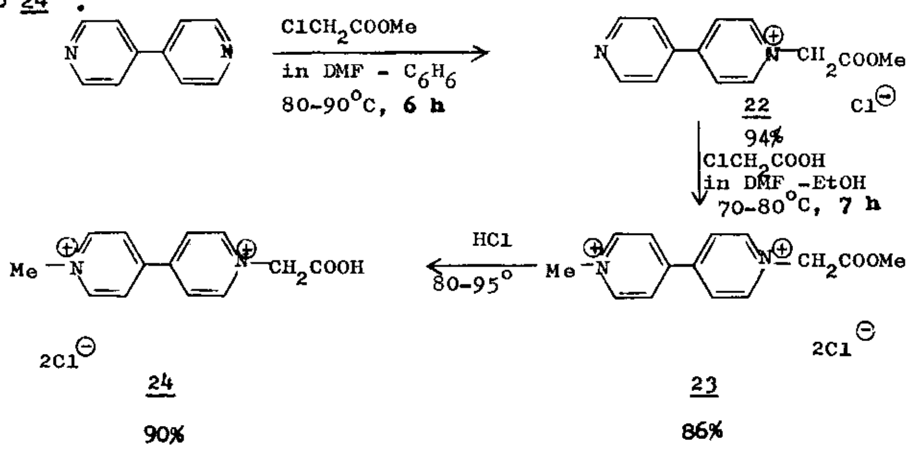
A special interest deserve 4,4-bipyridinium salts (viologens) having in view their electrochromism and development of a new electronic display technology. Viologens are investigated in the field of synthetic organic metals[58], as well as electron mediators for solar energy conversion systems[59-61]; compounds of this type are used also as herbicides, an example is paraquat.[62]

Many publications deal with the syntheses of viologen derivatives.

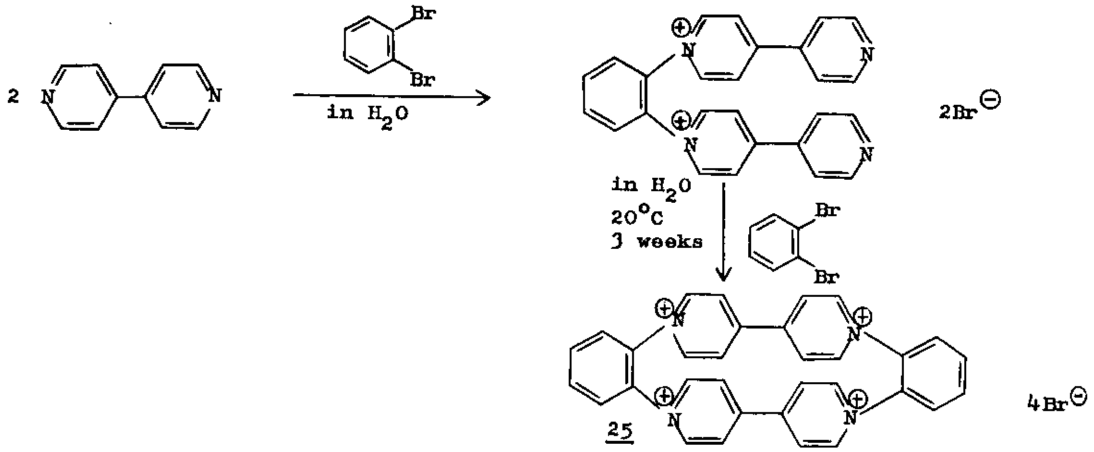
N,N′-Disubstituted salts were prepared in the following procedures.



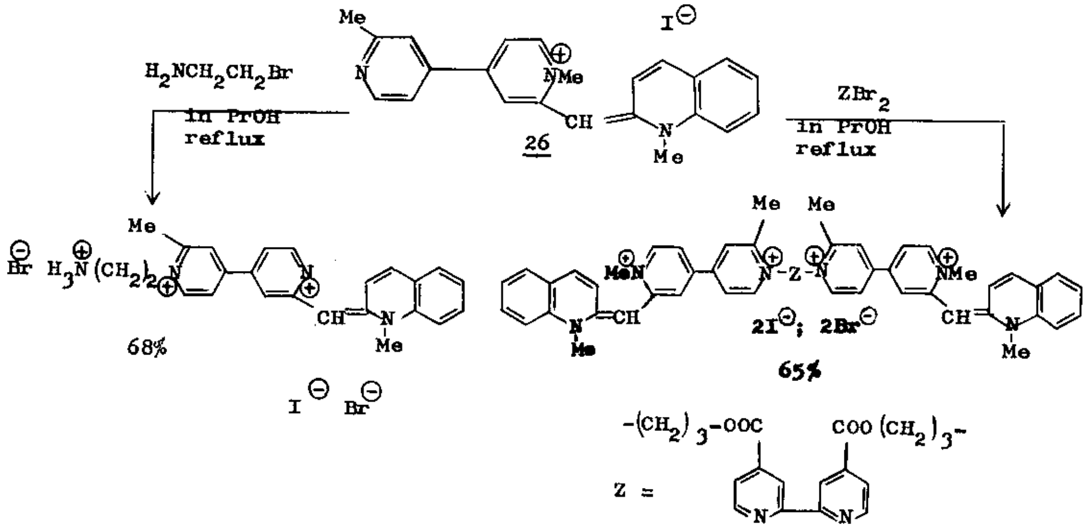
An example of the synthesis of diquaternary salt bearing different N-substituents is the reaction of 4,4-bipyridine with methyl chloroacetate, giving rise to 22. The subsequent treatment of 22 with chloroacetic acid yields 23, which hydrolyzed to 24[65].



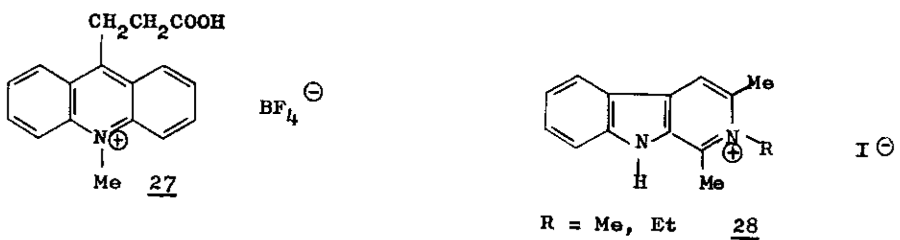
Compounds containing two 4,4′-bipyridinium moieties linked via ortho- or meta-xylene bridges can be easily prepared in the following way (for o-xylene bridged system)[66]:



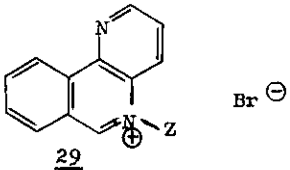
Studying viologen derivatives, two quaternization reactions of 26 were examined[67]:



In investigations of quaternization reactions, also those of polycyclic azaaromatics were performed, e. g. 27[68] and 28[69] have been obtained in this way.



Examples of 1,5- and 1,6- benzo[h]naphthyridinium salts are <u>29</u> and <u>30</u> [70].



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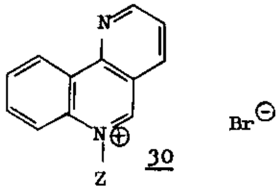
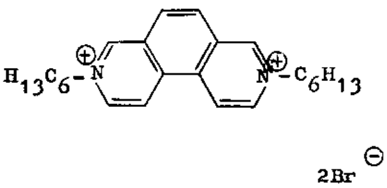


<u>30</u>

Z = $CH_2C(=O)-Ph$, CH_2COOEt

In these reactions **the N1 atoms in both isomeric compounds do not undergo quaternization, this fact being due to steric hindrance.**

Also the viologen analogues <u>31</u>[64] and <u>32</u>[71] were prepared by quaternization reactions.



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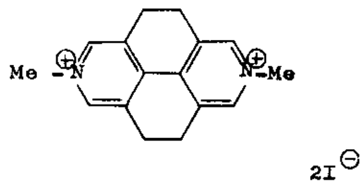
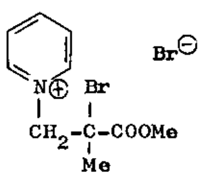


<u>32</u>

Among reactions related to simple quaternization, the following ones will be described.

Pyridine - bromine complex treated with methyl methacrylate yields <u>33</u> and <u>34</u>, while with acrylonitrile <u>35</u> and <u>36</u> are formed[72].



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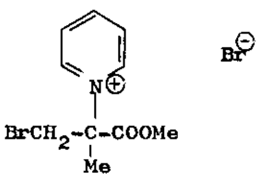

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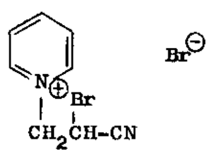
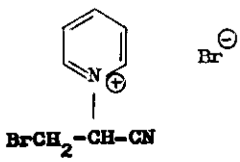
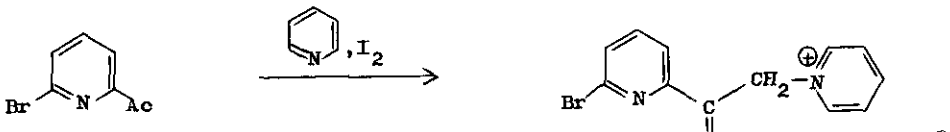


<u>35</u>



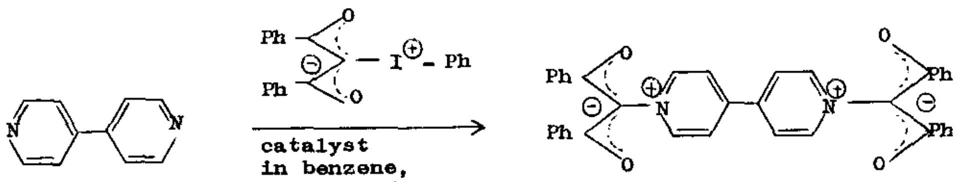
<u>36</u>

Pyridinium iodide 37 could be synthesized in the Ortoleva - King reaction of 2-acetyl-6-bromopyridine[73].



37

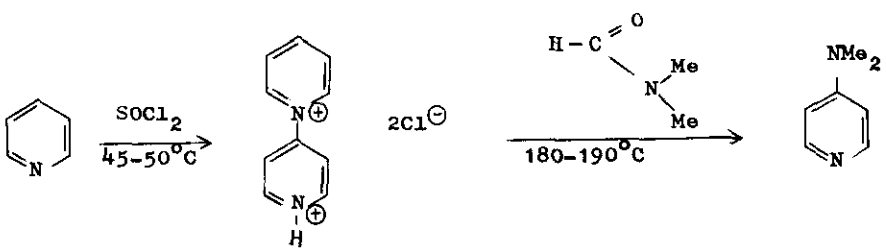
Viologen di-ylides 38 have been prepared by catalytic cleavage of phenyliodonium compounds of 1,3-diketones in the presence of 4,4′-dipyridyl, using cupric acetylacetonate as a catalyst[74].



38

32%

Treatment of pyridine with thionyl chloride gives 39, which in the substitution reaction with DMF yields 4-dimethylaminopyridine, an efficient acetylation catalyst[75].

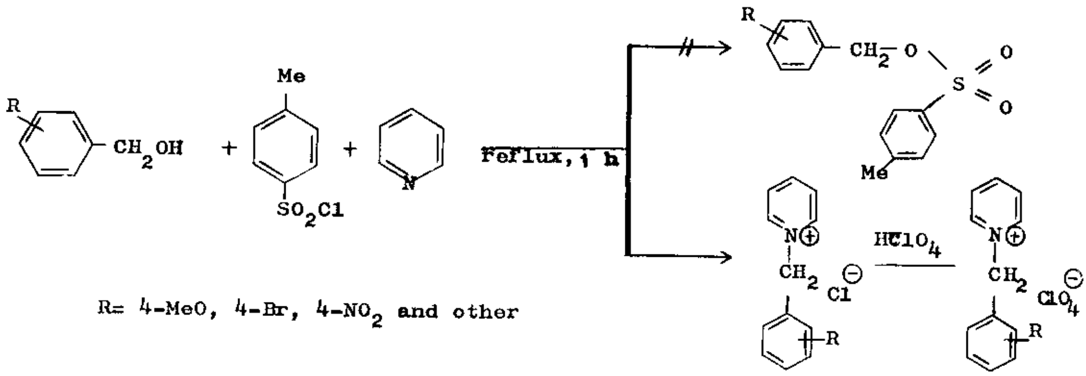


39

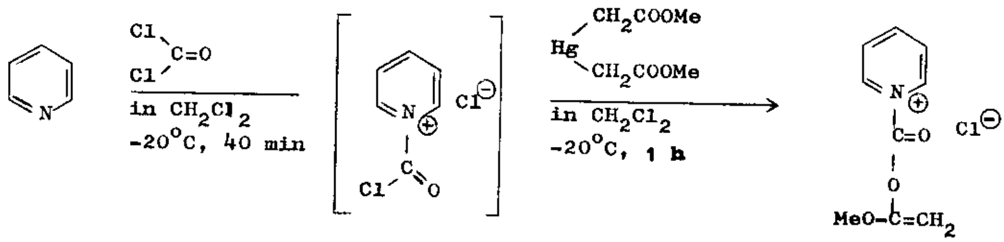
50%

N-Cetylpyridinium chloride can be synthesized reacting cetyl alcohol with thionyl chloride in pyridine[76].

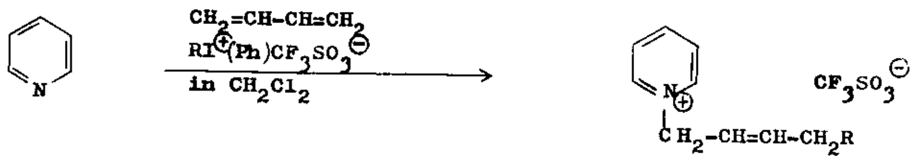
The reaction of benzyl alcohols with toluenesulfonyl chloride carried out in pyridine gave, instead of the expected tosylates, N-benzylpyridinium salts[77]:



Another example of the synthesis of pyridinium salts is as follows[78]:



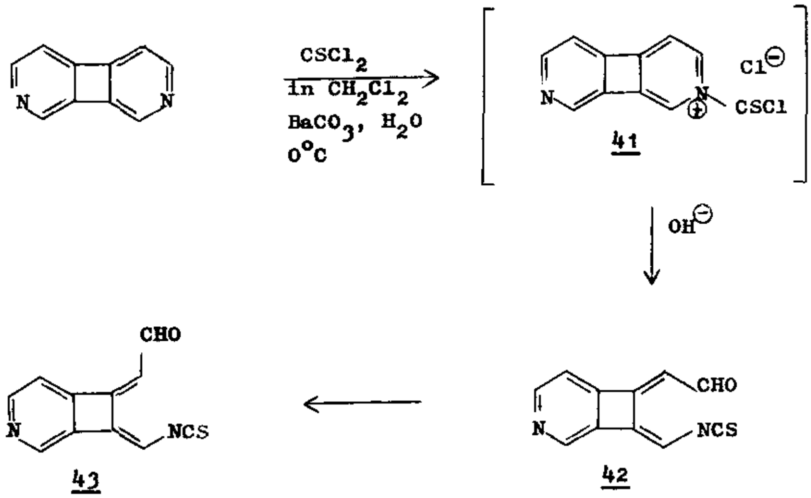
Perfluoroalkylpyridinium salts of the type 40 can be obtained in the following procedure[79].



40

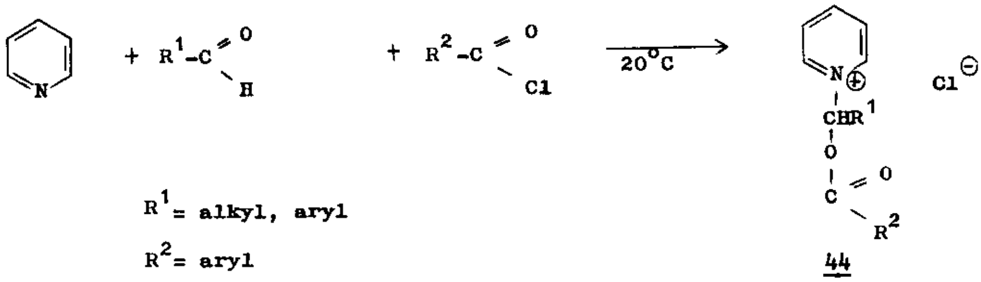
An example of pyridine ring opening of 2,7-diazabisphenylene is its reaction with thiophosgene and barium carbonate in a two-phase water-dichloromethane system.[80] The initially formed quaternary salt 41 undergoes a nucleophilic attack of hydroxide ion to give 42, isomerizing to 43.

The reaction is interesting, because nucleophilic attack of hydroxide ion on diazabisphenylenes usually opens the cyclobutane ring to form pyridyl-pyridones[81].



60%

Aldehydes treated with acyl chlorides in pyridine yield pyridinium salts 44 [82].



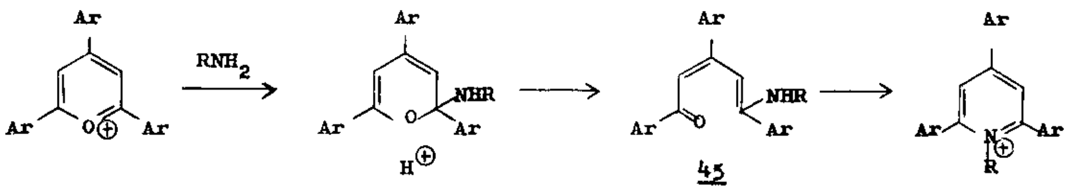
75-90%

B. REACTIONS OF PYRYLIUM SALTS WITH PRIMARY AMINES

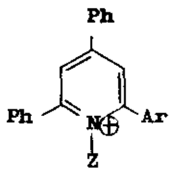
Pyrylium salts are very important synthons of pyridiniums and a considerable number of these compounds has been obtained on this route.

Reaction of a pyrylium ion with an amine initially forms a 2*H*- pyran, whose ring spontaneously opens to give divinylogous amide 45; however, in the case of sterically crowded pyryliums, the 2*H*-pyrans could be detected by ^{13}C NMR spectroscopy.

The kinetic studies of pyridinium ion formation in organic solvents confirm the following reaction mechanism[83]:

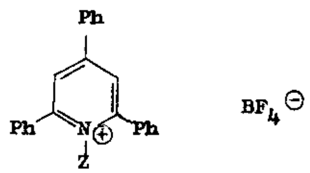


Examples of pyridiniums obtained from pyrylium salts are:



Ar = ^{i}Pr, ^{n}Bu, $PhCH_2$, 2,5-$Me_2C_6H_4$, 4-$NO_2C_6H_4$, 1-naphthyl, 2-naphthyl

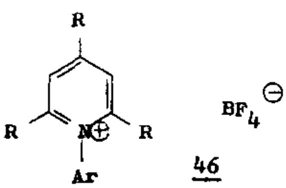
ref.84



Z = ^{i}Pr, ^{s}Bu, cycloalkyl C_{3-6}

ref.85

Compounds 46 were prepared using pyrylium salts, however the synthesis of ring unsubstituted pyridinium salts 47 was accomplished via Zincke - König procedure, from N-(2,4-dinitrophenyl)pyridinium chlorides as starting materials, having in view the dangerous handling of pyrylium perchlorates[86,87].



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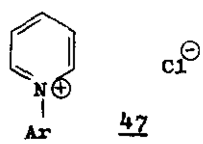
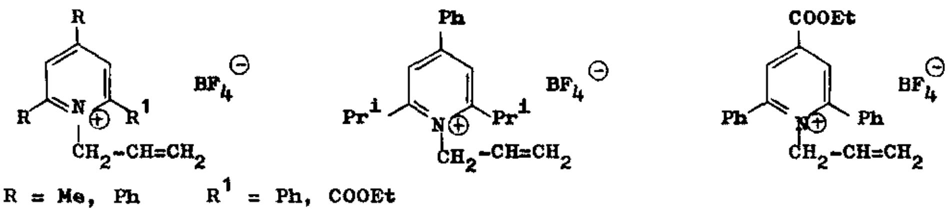


47

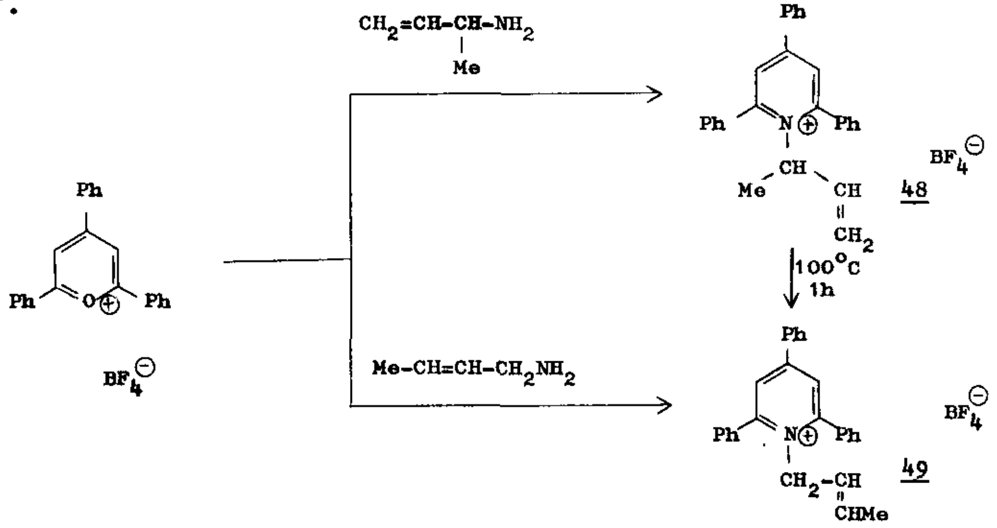
R = Me, Ph

Ar= Ph, 3-F C_6H_4, 4-F C_6H_4, 4-$NH_2C_6H_4$

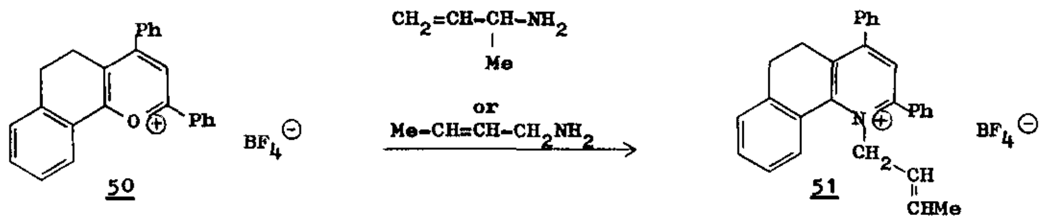
The following N-allylpyridinium salts can be prepared from appropriate pyryliums[88]:



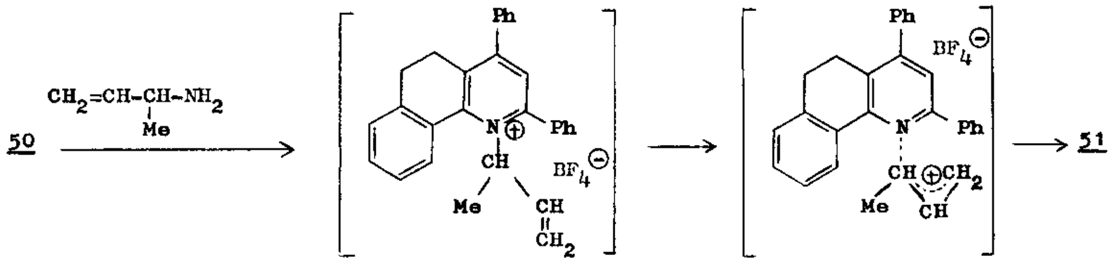
When 2,4,6-triphenylpyrylium undergoes reaction with α- or γ-methylallylamine, corresponding 48 and 49 are formed; the thermal rearrangement of these products was observed[89].



On the contrary, tricyclopyrylium 50 gives with both methylallylamines 51 .

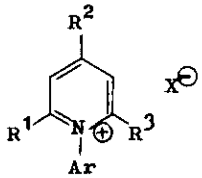


This observation can be explained by the fact that triphenylpyridine is a poorer leaving group than its tricyclic analogue and the spontaneous change of 52 into 51 involves an intermediate 53 leading to 51 by a process analogous to ion return[89].



52 53

In order to synthesize pyridiniums N-substituted by heterocyclic system, pyrylium salts have been treated with appropriate primary heterocyclic amines; on this way the following compounds were prepared[90,91]:

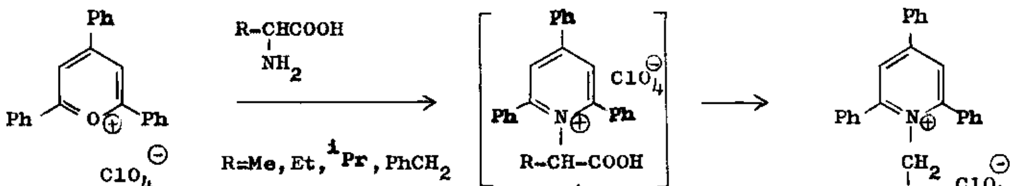


R^1, R^2, R^3 = Me, Ph

X = ClO_4 , CF_3SO_3

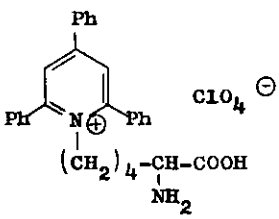
Ar = 2-thiazolyl
5-Me-3-isoxazolyl
2-benzothiazolyl
2-benzimidazolyl
2-pyridyl and other

Reaction of pyrylium salts with α-aminoacids gives rise to alkyl-substituted N-methylpyridiniums via the spontaneous decarboxylation of initial products 54.[92,93]

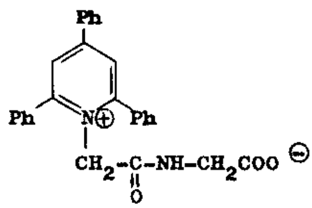


54

On the other hand, analogous reactions with lysine and glycylglycine occur without decomposition, and the formed 55 and 56 can serve as models for amino-residues in proteins and polypeptides[92,93].

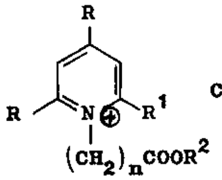


55

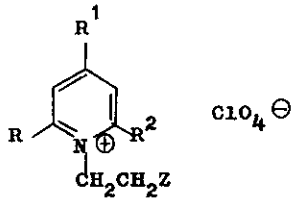


56

On this way also the following compounds have been synthesized[94].

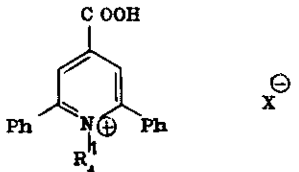


R,R^1 = Me, Et, Ph
R^2 = H, Et
n = 1,2,3,5



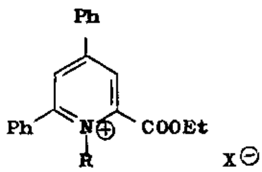
R,R^1,R^2 = Me, Ph
Z = NEt_2, Ac, CF_3CO,
$4\text{-}MeC_6H_4SO_2$ and other

Among pyridinium salts carboxy- or carboethyxy-ring substituted one ought to mention 57 and 58[14,95-98].



R^1 = Me, ^{i}Pr, Bu, Ph, $PhCH_2$
X = ClO_4, BF_4

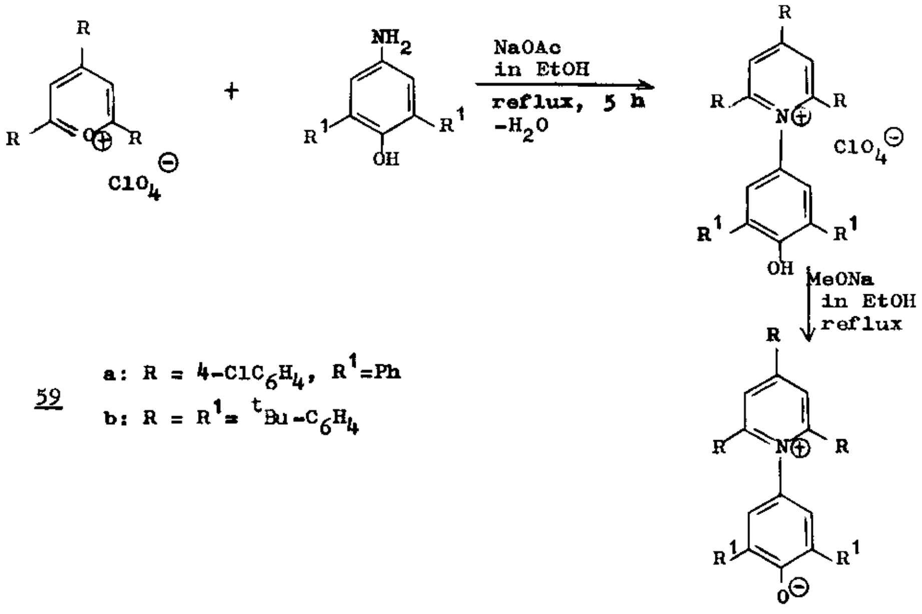
57



R=Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$
$4\text{-}MeOC_6H_4$, $4\text{-}NO_2C_6H_4$
2-pyridyl
4-Me-pyridyl

58

Pyridinium N-phenoxide betaines 59 have been formed in the reaction of pyrylium salts and aminophenols, followed by deprotonation with bases[99,100].



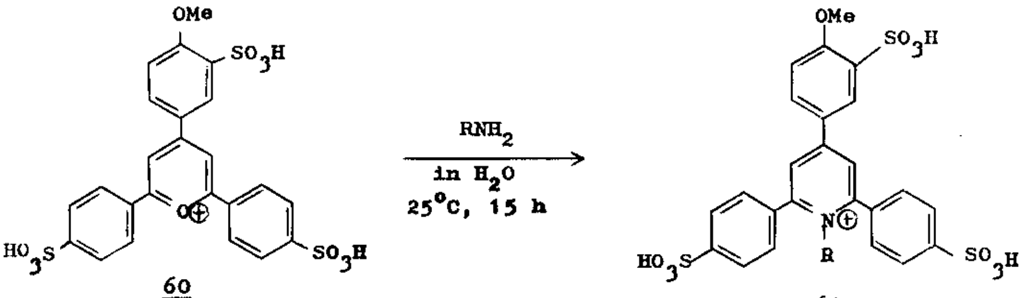
59 a: R = $4\text{-}ClC_6H_4$, R^1=Ph
b: R = R^1= $^tBu\text{-}C_6H_4$

In a series of papers, the influence of pyrylium ion structure on the rate of pyridinium ion formation is studied. The aim of these investigations is to develop a method for the selective transformation of primary amino groups present in water-soluble natural products such as polypeptides.

As a model of natural products containing primary amino groups, lysine, reacting with its ω-amino group is chosen[83].

Reactions were performed in aqueous solutions, using the water-soluble pyrylium ion 60, which was converted into pyridiniums 61 by an addition of acidic solutions of 60 to amine buffers.

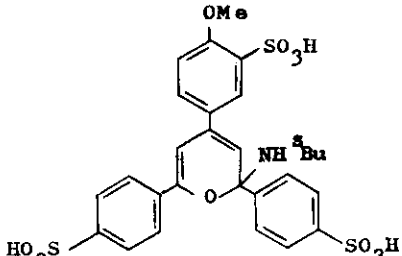
Kinetic rate constants are described for reactions with lysine and compared with those for reactions with other primary amines such as n-butylamine, benzylamine or aniline.



60 61

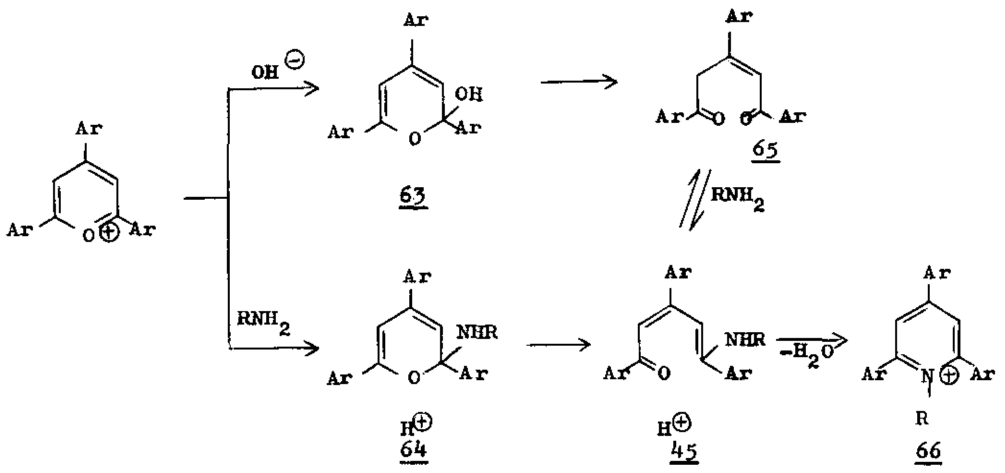
R: a $(CH_2)_4CH(NH_2)COOH$ c $PhCH_2$
b ^nBu d Ph

In contrast to the above primary amines, sec-butylamine reacts to give the 2*H*-pyran 62.



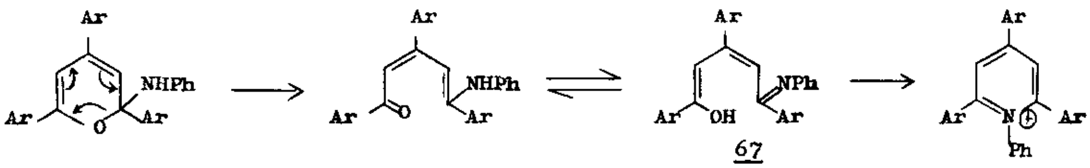
62

The mechanism of these reactions, performed in aqueous solution is shown as follows:



Pyrylium forms with hydroxide ion as well as with primary amines 2*H*-pyrans 63 and 64, undergoing a spontaneous ring opening to yield a pseudobase 65 or a divinylogous amide 45, respectively. Cyclization of 45, formed also in the reaction of 65 with amine, leads to 66.

Unexpectedly, less nucleophilic aniline reacts faster than aliphatic amines with pyrylium ions; the pyridinium salt was formed rapidly and no divinylogous amide could be detected. This observation can be explained by the fact, that the conjugation of the aromatic ring with the open chain should favour a higher concentration of the imino-enol tautomer 67, which rapidly undergoes electrocyclization[83].

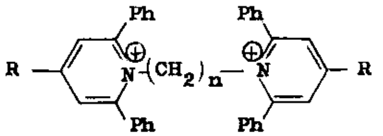


In the study of these reactions, also other water soluble pyrylium salts were used, leading to the following pyridinium betaines[101]:

R= ${}^{n}Bu$, $PhCH_2$, $(CH_2)_4$-$CH(NH_2)COOH$

Similar kinetic investigations were performed, using gelatin and chymotrypsin, proteins containing 30 and 14 residues of lysine, as well as aminoglycoside antibiotics, kanamycin and neomycin.[102]

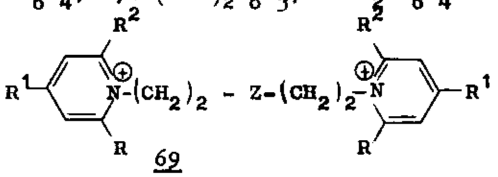
By reaction of pyrylium salts with amines, bispyridinium compounds 68, 69 and 70, as well as trispyridinium 71 have been prepared.



$2ClO_4^{\ominus}$ ref.103

68

R= 2-$MeOC_6H_4$, 2,4-$(MeO)_2C_6H_3$, 4-$Me_2NC_6H_4$

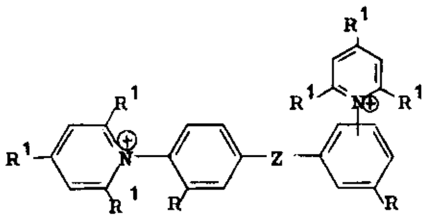


69

$2X^{\ominus}$

R, R^1, R^2= Me, Ph
Z= NH, $NH(CH_2)_2NH$
X= ClO_4, HO_3S-CH_2-CO_2, $FeCl_4$, BF_4, $AlCl_4$

ref.104

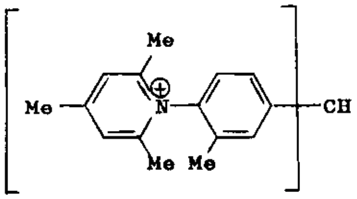


70

$2X^{\ominus}$

R^1=Me, Ph
Z=bond, $(CH_2)_2$, CHPh, NH
R=H, OMe

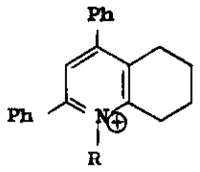
ref.105



71

$3X^{\ominus}$ ref.105

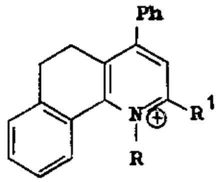
In the same procedure the following polycyclic pyridinium salts have been synthesized:



$CF_3SO_3^{\ominus}$

R = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-ClC_6H_4 and other

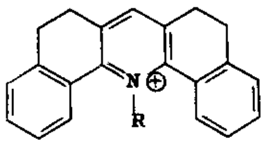
ref.106



$X^{\ominus}$

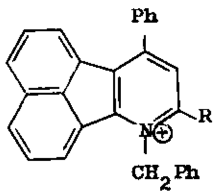
R^1 = ^{t}Bu, Ph
R = ^{n}Bu, CH_2CMe_3, $PhCH_2$
X = Cl, Br, ClO_4, BF_4, CF_3SO_3 etc.

refs.107-109



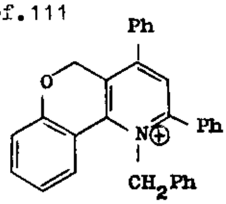
$CF_3SO_3^{\ominus}$ R= Ph, $PhCH_2$, C_{6-8} alkyl

refs.109,110



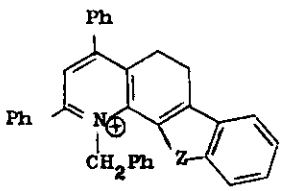
$CF_3SO_3^{\ominus}$ R= ^{t}Bu, Ph

ref.111



$ClO_4^{\ominus}$

ref.111

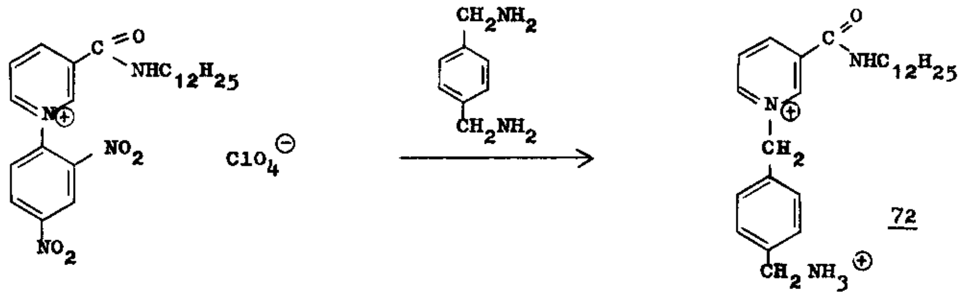


$CF_3SO_3^{\ominus}$ Z = NH, S

ref.112

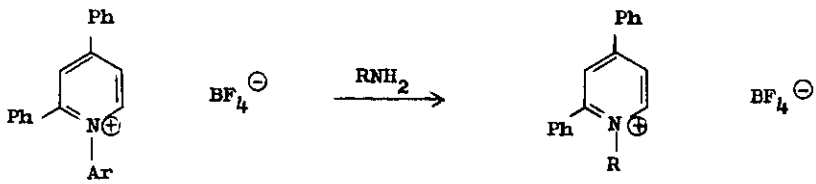
C. OTHER SYNTHESES

Among other synthetic approaches to pyridinium salts one ought to describe the Zincke-König procedure, i. e. nucleophilic displacement of N-substituent in N-(2,4-dinitrophenyl)pyridinium salts. On this way 47[86] and 72[113] have been obtained.



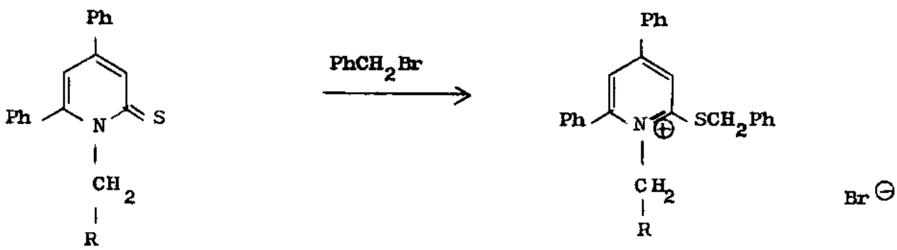
72

Similar to the above reactions is the following one:

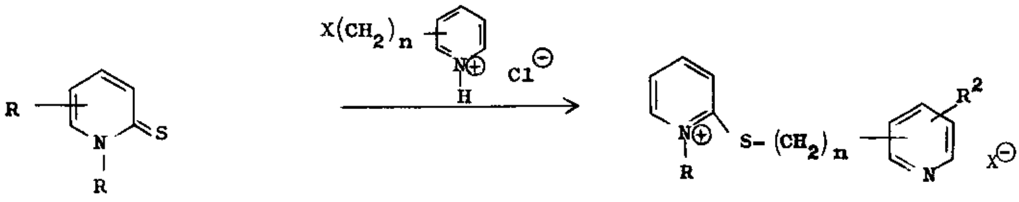


This procedure is useful, having in view the fact that the conversion of pyrylium salts into pyridiniums usually requires the presence of 2,6-substituents, what is here not the case[114,115].

For the synthesis of 2-alkylthio-substituted pyrydinium salts can serve the S-alkylation of pyridine-2-thiones[116-118]



R= H, Ph, 4-MeC_6H_4



R = alkyl, Ph, $PhCH_2$ 73

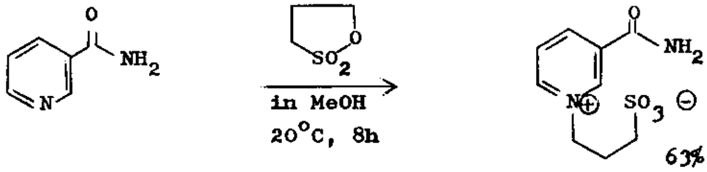
R^1,R^2= H,OH, halo, alkyl, hydroxyalkyl and other

n=1-6

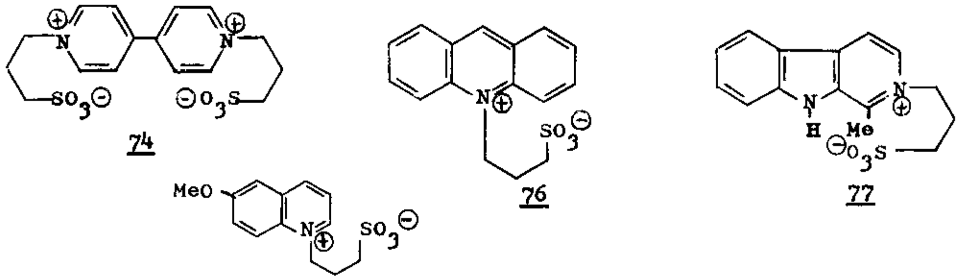
X = a pharmaceutically acceptable anion

ref.119

Reaction of azaaromatics with 1,3-propanesultone affords in a simple procedure pyridinium zwitterionic compounds, e. g.[60]:

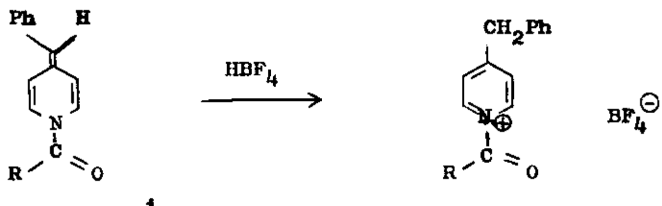


In a similar manner there were prepared 74 - 77 [60,120].



74 75 76 77

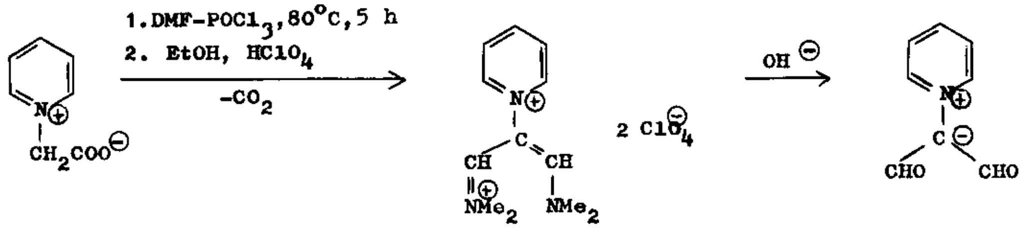
Treating 1,4-dihydropyridines 78 with tetrafluoroboric acid one can easily obtain 1-acylpyridinium salts 79, useful acylating agents of carbonyl compounds[121].



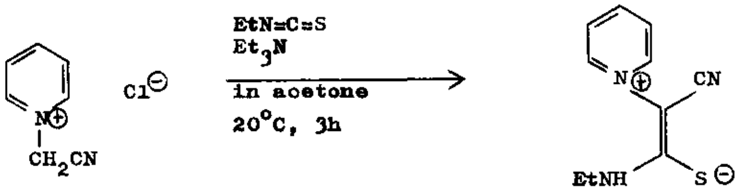
R= Me, ^{i}Pr

78 79

Very little known pyridinium ylides bearing two formyl groups at the ylide carbon atom were synthesized in the following way[122].

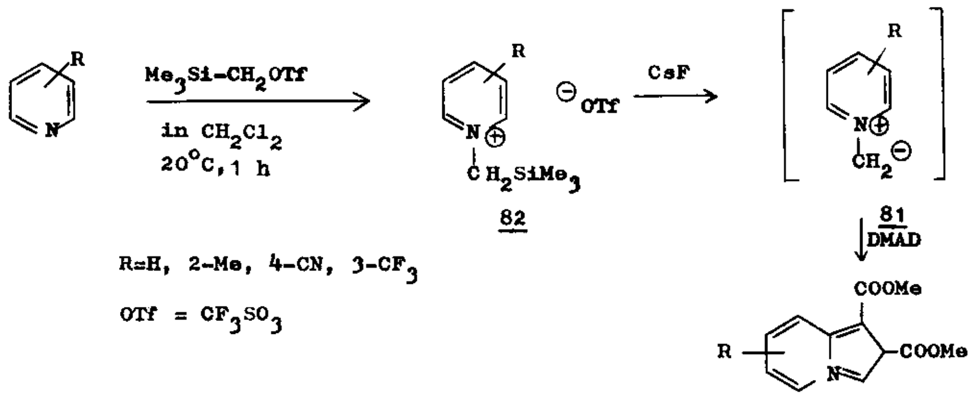


Reaction of 1-cyanomethylpyridinium salts with isocyanates yields pyridinium betaines 80[123].



80

Studying nonstabilized pyridinium methylides 81, their precursors, i.e. pyridinium triflates 82 have been synthesized. Heating 82 with cesium fluoride liberated 81, trapped in the cycloaddition reaction with DMAD.[124,125]



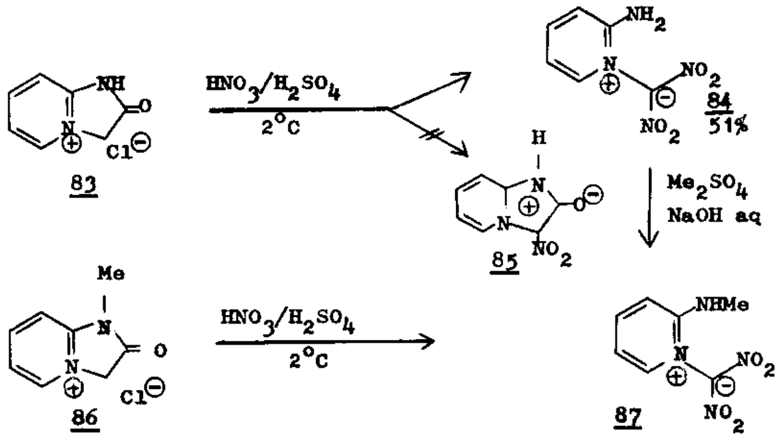
82

R=H, 2-Me, 4-CN, 3-CF$_3$

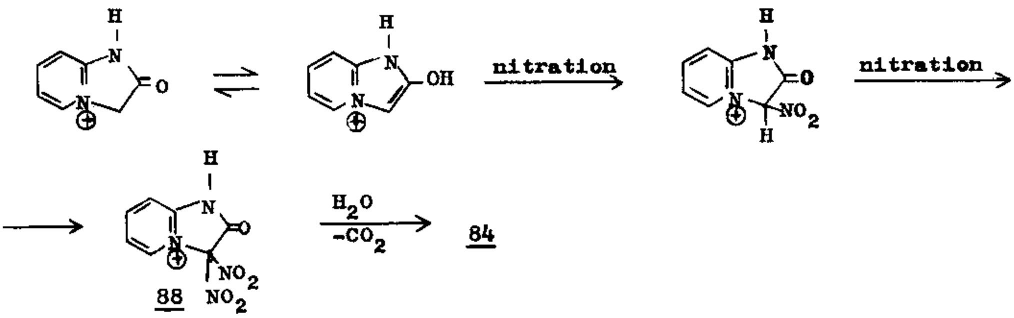
OTf = CF_3SO_3

Quinoline and isoquinoline reacted in a similar manner.

2-Aminopyridinium dinitromethylides can be prepared in a simple procedure, involving ring cleavage of the readily available imidazo[1,2-a] pyridines upon nitration. Nitration of 83 gives rise to 84 instead of the expected 85. Analogous reaction of 86 leads to 87, formed also by methylation of 84.

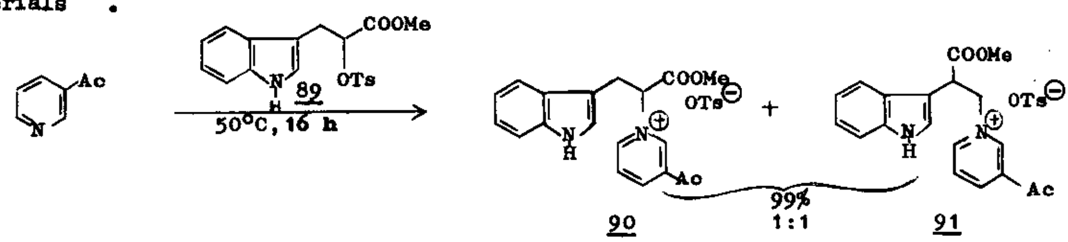


The proposed mechanism involves mono- and ipso-nitration of 83 followed by the opening of the five-membered ring of 88 and decarboxylation.[126,127]

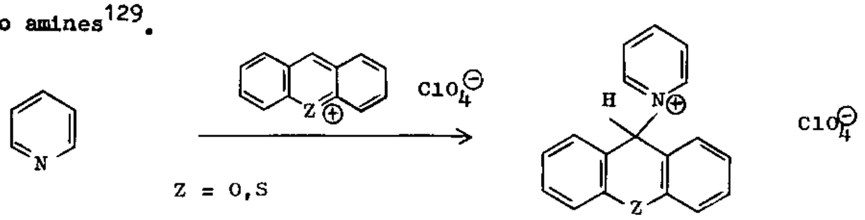


Reaction of 3-acetylpyridine with indole derivative 89 leads to the pyridinium salt 90, along with its rearrangement product 91.

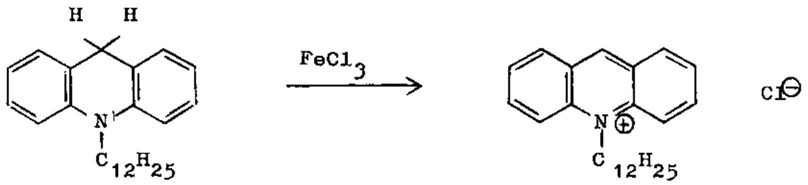
Analogous reactions were performed using 3-methyl- and 3-ethylpyridines as starting materials[128].



Pyridine and quinoline react smoothly with xanthyl or thioxanthyl perchlorates to give quaternary salts, useful for the introduction of these heterocyclic groups into amines[129].

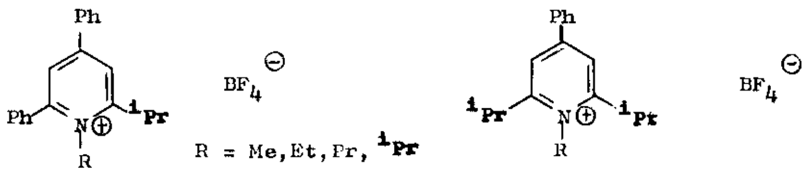


N-Dodecylacridinium chloride, applicable as $NAD^{\oplus}$ model, can be obtained by oxidation of N-dodecylacridan[130].



III. PHYSICOCHEMICAL PROPERTIES

Temperature - variable ^{1}H NMR spectra of the following pyridinium salts were interpreted in terms of restricted rotation[131].



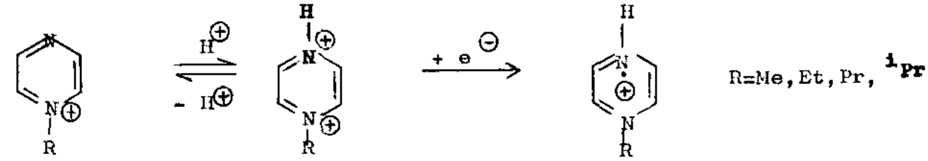
The conformational analysis of 9 was performed, using ^{1}H NMR spectra[44].

The study of ^{1}H NMR spectra of 59b in aqueous solutions of surfactants affords information on the orientation of these molecules in the interface region micelle/solution[99].

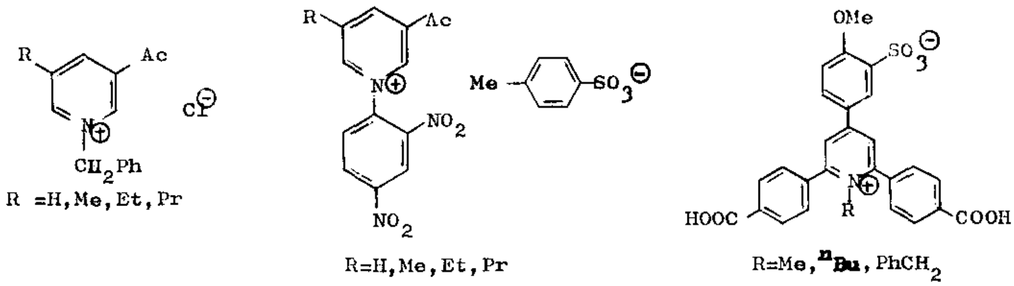
^{1}H NMR spectroscopy and FAB mass-spectrometry were used in the determination of the structure of phanes 25[66].

The ^{1}H, ^{13}C and ^{19}F NMR spectra of 46 and 47 have been discussed, along with the determination of Hammett and Taft σ values for pyridinium, 2,4,6-trimethyl- and 2,4,6-triphenylpyridinium substituents[86].

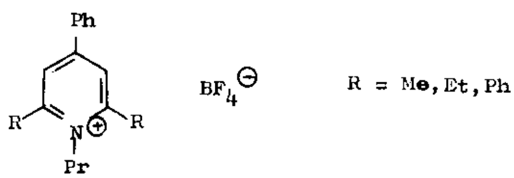
^{15}N NMR spectrum of $[(^{15}NO_2)_2]$-84, obtained with the use of ^{15}N-enriched nitric acid was described and conformation of such pyridinium ylides discussed.[126]
Studying flavosemiquinone model systems, there was performed reduction of 1-alkylpyrazinium iodides in acidic medium, leading to 4-hydro-1-alkylpyrazinium radical cations, which were identified by high resolution esr spectra.[132]



The esr and ENDOR spectra of radical cations derived from 4,4'-dimethyl- and 4,4'-diphenylbipyridinium chlorides have been discussed.[133]
Among ^{13}C NMR spectroscopy studies of pyridiniums one ought to mention those of the following compounds[101,134]:

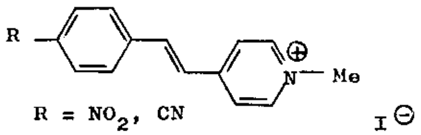


In the investigations of electrochemical reduction of pyridinium salts, there was found that 92 form π-radicals, which are stable in DMF on the time scale of cyclic voltammetry, while the corresponding 1-benzyl and allyl derivatives undergo C - N bond cleavage at the rates dependent on the size of 2,6-substituents[135].

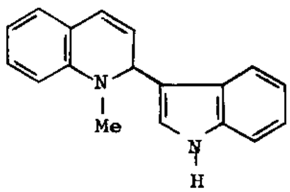


92

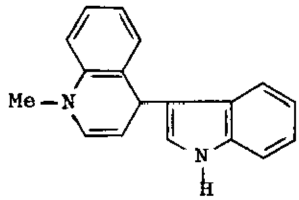
Studying N-decylpyridinium compounds, complexes of 3-hydroxy-N-decylpyridinium chloride with Cu(I)ions were formed and investigated by potentiometric methods[136]. The application of pyridinium N-phenoxide betaines of the type 59b for the characterization of solvent polarities is discussed[100].
Quantum yield measurements were performed for the trans - cis photoisomerization of the following azastilbene quaternary salts[137].



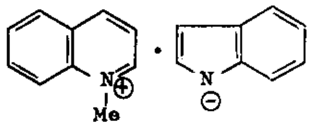
Structures of a series of alkyl-substituted N-methylpyridinium cations were calculated using MINDO / 3 self-consistent-field procedures, and the effects of alkyl substituents on aromatic ring bond angles and bond lenghts have been discussed[138].
Electronic spectra of viologen derivatives 32[71] and 38[74] have been described.
In the investigation of equilibrium between 93, its isomer 94, and the ionic form 95, the ir spectroscopy has been applicated[139].



93

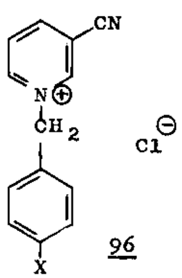


94



95

The polarographic reduction of 14[51] and of 96[140] was studied, and in the latter case solvent and substituent effects on the polarographic characteristics have been discussed.



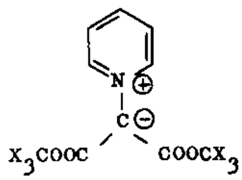
96

X = H,F,Cl,Me,OMe,CN,NO_2 and other

A special attention deserve pyridinium - TCNQ salts; there was observed a high conductivity of $(4,4'\text{-bipyridinium})^{2\oplus}(\text{TCNQ})_2^{2\ominus}$; also there was found that the complex salt $[1,2\text{-bis-}(1\text{-ethyl-4-pyridinium})\text{ethane}]^{2\oplus}(\text{TCNQ})_4^{2\ominus}(H_2O)$, i.e. (DEPA)(TCNQ)$_4$(H$_2$O) exhibits the low temperature metallic properties.[58]

Having in view their interesting conductivity properties, the crystal structures of $[1,1'\text{-bis-}(p\text{-cyanophenyl})\text{-}4,4'\text{-bipyridinium}]^{2\oplus}(\text{TCNQ})_4^{2\ominus}$ and of $[N\text{-}(n\text{-butyl})\text{-quinolinium}]^{\oplus}(\text{TCNQ})_2^{\ominus}$ were investigated.[58,141]

Among crystal structure determinations one ought to mention also those of 80[123] and of 97[142].

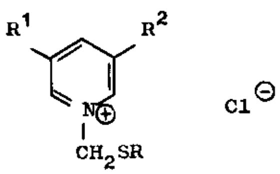


X = F, Cl

97

IV. BIOLOGICAL ACTIVITY

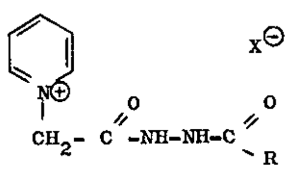
Numerous pyridinium salts possess biological activities, e. g. 98, 99 and 100 have antibacterial, antiviral and fungicidal properties, and 101 are used in treating skin disorders.



R = Me(CH$_2$)$_n$
n = 3,7,9,11,13
R^1,R^2 = H,Cl,Br,Me

98

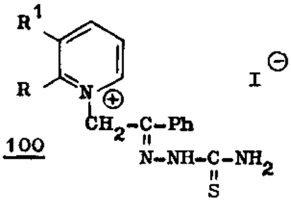
refs.143,144



R = C$_9$-C$_{19}$ alkyl, C$_{13}$-C$_{19}$ alkenyl, Ph and other
X = halide

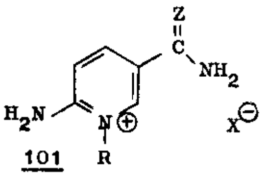
99

ref.145



100 ref.146

R= H,Me
R^1= H, PhCO-NHCH$_2$NHCO and other

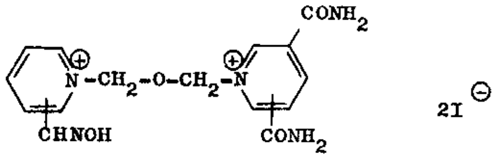


101 ref.147

Z = O, S
R = alkyl, Ph, phenylalkyl, carbamoylalkyl
X = inorganic or carboxylic acid anion

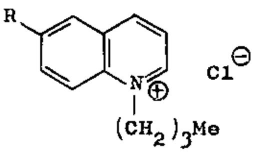
Compounds 1[38], 68[103,148] and 69[104] show antibacterial, fungicidal or antiphage properties, and 73[119] has an antisecretory activity.

Bipyridinium salt 23 exhibits herbicidal activity comparable with that of paraquat, although its toxicity is much lower[65], and 102 were found to be reactivators of phosphorylated and phosphonylated acetylcholinesterases[149].



102

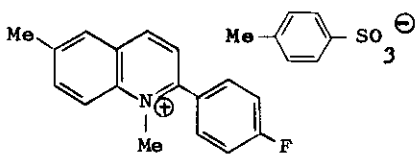
Among quinolinium salts one ought to mention 103 and 104 showing bactericidal, fungicidal and antiviral activities, as well as 105, possessing antileukemic properties.



103

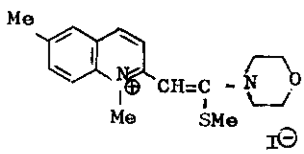
R= H,Me
n= 3,4,5,7,11

ref.150



104

ref.151

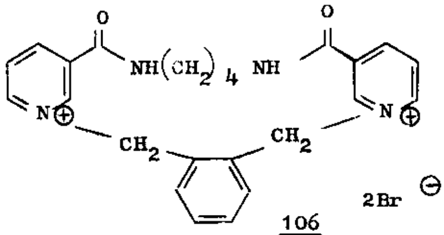


105

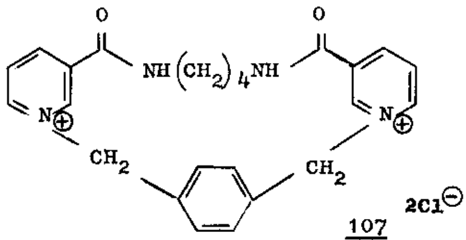
ref.152

Also benzo[h]naphthyridinium salts 29 and 30 possess antibacterial activities[70]. Many pyridinium salts can be applicated as biological model systems. In the study of pyridinium salts structurally related to NAD⊕, there was shown, that they can serve as enolate transferring agents[153].

As a convenient NAD⊕ model N-dodecylacridinium chloride[130] and 72[113] can be used. Studying biological redox systems, as well as oxidation reactions with NAD⊕ models much attention has been paid to the development of catalysts promoting multi-electron transfer reactions; as such multicenter organic redox systems can serve bisnicotinamides 106 and 107 [154].

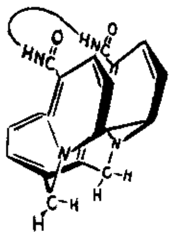


106



107

Compound 106 is easily reduced with hydroxide ion to give intramolecular 6,6'-coupling product 108, while 107 does not react in this manner. This observation is due to the fact, that in 106 the pyridine rings have the face to face geometry, enhancing the reduction.

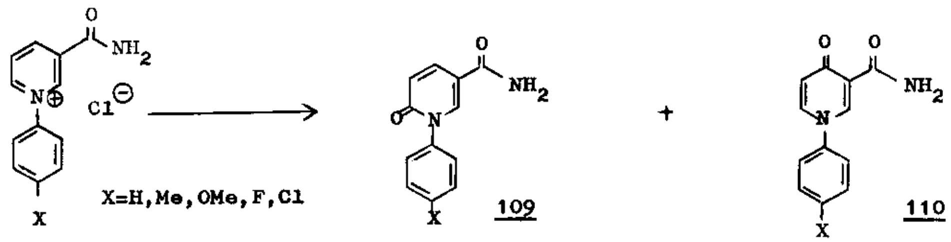


108

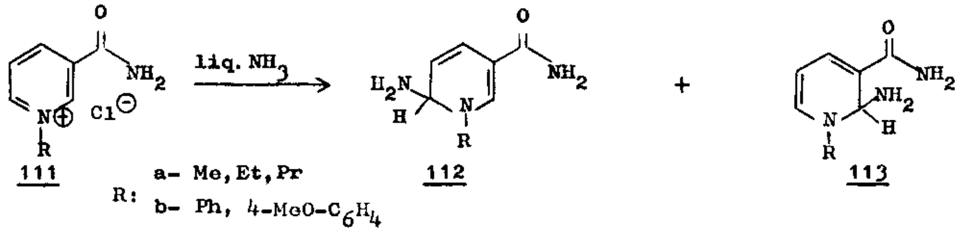
In investigations of the selective alkylation of nicotine, the application of this reaction to the synthesis of artificial antigen of nicotine is discussed[48].

Studying the use of immobilized enzymes in organic synthesis, 1-aryl-3-carbamoylpyridinium chlorides were oxidized by rabbit liver aldehyde oxidase and bovine milk xanthineoxidase.

In these reactions two isomeric pyridones, 109 and 110 were obtained, 109 in the first case being the main product, and in the second - the minor[155].



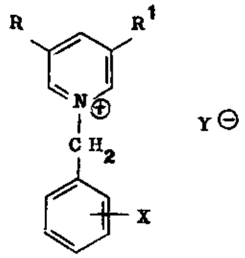
Amination products of the reaction of 111 with liquid ammonia are considered as in vitro models for covalent σ -adducts formed between 111 and aldehyde oxidase.
The site of amination is dependent on the kind of N-substituent: N-alkylated pyridinium salts 111a yield exclusively 112, while their N-aryl analogues 111b give two isomeric σ -adducts 112 and 113[156].



V. APPLICATIONS

Among applications of pyridinium salts, the following ones will be described.
Quaternary salts 75, 76 and 77 are highly fluorescent cationic indicators. Their fluorescence intensity is practically pH -independent in the neutral pH -range, what can be of use in physiological studies for fluorescence measurements in intra- and extracellular liquids[120].
Pyridinium salts 27, 75 and 76 can be used as indicators in the fluorometric method of halides' determination, this process involving quenching of fluorescence of these indicators by halides[68, 157].
In the study of spectroscopic determination of germanium there was observed that the reaction of Ge(IV) with 2,3,7-trihydroxyfluorones carried out in the presence of 1-cetylpyridinium chloride allows to increase the sensibility of the method[158].
3-Hydroxy-N-decylpyridinium chloride was found to be the inhibitor of acid corrosion of metals[136] and 114 are used in zinc electroplating baths to give a shiny

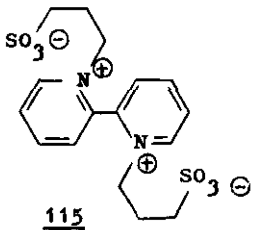
metal deposit[159].



R = H, C_{1-4} alkyl
R^1 = COOR, $CONH_2$, $COO^{\ominus}$
X,Y = Cl, Br

114

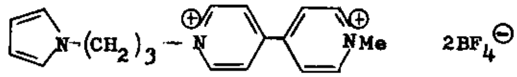
The evolution of hydrogen and oxygen by photosensitized decomposition of water is of great interest in the storage and conversion of solar energy. Photoreduction of water to hydrogen has been performed using viologens as electron acceptors and colloidal platinum[59]. Having in view, that the use of viologens is limited to acidic and neutral solutions, for the formation of hydrogen from basic silica gel colloids, 115 was used[59].



115

The hydrogen generation in the photosensitized reduction of water with use of the model system consisting of methylviologen, $Ru(bpy)_3Cl_2$, EDTA and platinum catalyst was studied, and the catalyticel activity of platinum sols has been discussed[61]. In the study of storage and conversion of solar energy, for efficient storage of the energy the stabilization of photoproducts is required; for this purpose some interfacial systems, such as micelles or charged colloidal silica gel particles can be used.[60] As viologens do not change their electrical properties during the electron - transfer process, and therefore their use in interfacial systems is limited, the application of zwitterionic electron acceptors and donors was examined. There were accomplished photosensitized electron transfer reactions using 74 as electron acceptor[60].

In electrochemical investigations, there was found, that electrodes coated by a poly (pyrrole) film containing the viologen system 116 are useful in electrocatalysis of redox reactions and in electrochromism[160].



116

Examining new viologen - based materials, 21c was shown to have interesting electrochromic properties, suitable for electronic display applications[64].

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