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# N-SUBSTITUTED PYRIDINIUM SALTS

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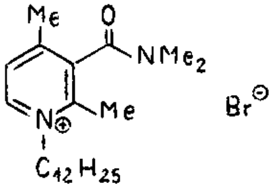
Abstract - N-Substituted pyridinium salts are presented in view of their syntheses, reactivity and physicochemical properties, along with their biological activities and applications.

## I. INTRODUCTION

In a continuation of our reviews on pyridinium salts [1-5], connected with our research concerning benzo[h]naphthyridinium salts [6-14] and metal complexes [15-17], we present here syntheses, reactivity and physicochemical properties of N-substituted pyridinium salts, along with their biological activities and applications. These compounds deserve a considerable attention in view of their reactivity [18-21], as well as in the aspect of their applications as model substances in biochemical processes, and for their biological properties[22].
As viologens, interesting for their usefullness in the conversion and storage of solar energy, cover a large amount of publications [23,24], this topic is not included here.

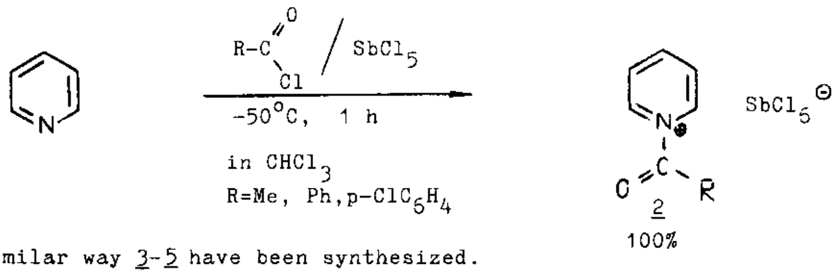
## II. SYNTHESES

Optically active 1 has been obtained in quaternization reaction; the chirality of its carbamoylpyridinium moiety is due to the out-of-plane orientation of the carboxamide group by the two adjacent methyl groups[25].

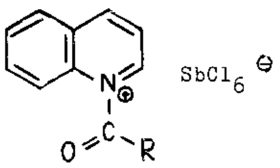


1

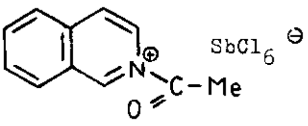
Stable 1-acylpyridinium salts 2 are formed in the following reactions [26].



In a similar way 3-5 have been synthesized.


R=Me,Ph,p-ClC$_6$H$_4$

3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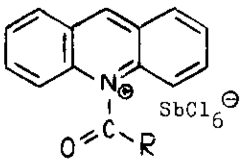
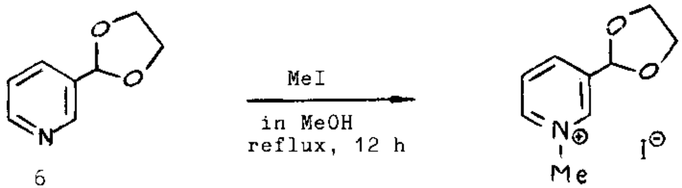

R=Me,Ph

5

Another example of quaternization is the reaction of nicotinaldehyde acetal 6 with methyl iodide[27].



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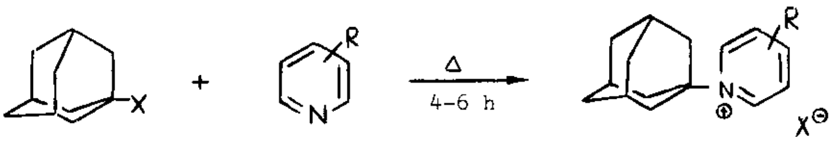
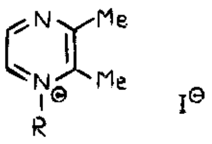
Quaternization of 3- and 4-substituted pyridines with 1-bromo and 1-iodoadamantanes was carried out in the presence of a small amount of water; in the absence of water the higher reaction temperature was needed, and the yield decreased [28].



X=Br,I

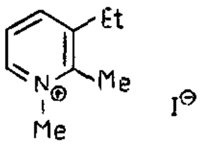
R=H, 3-Me,
4-Me, 3-CONEt$_2$,
4-(4′-pyridyl)

Pyrazinium iodides 7-9 have been synthesized by quaternization of appropriate pyrazines [29,30] .



R=Me,Et,$^{i}$Pr

7



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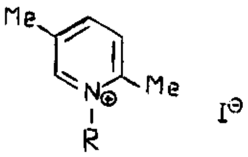
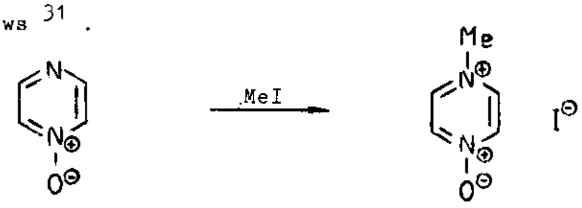
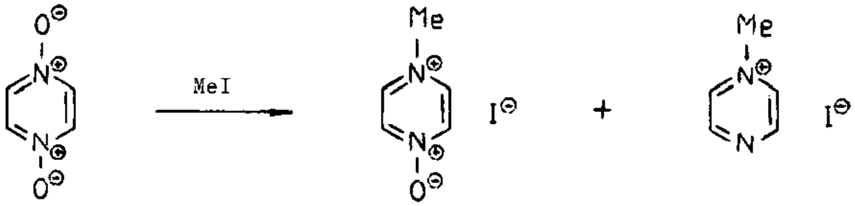


R=Me,Et

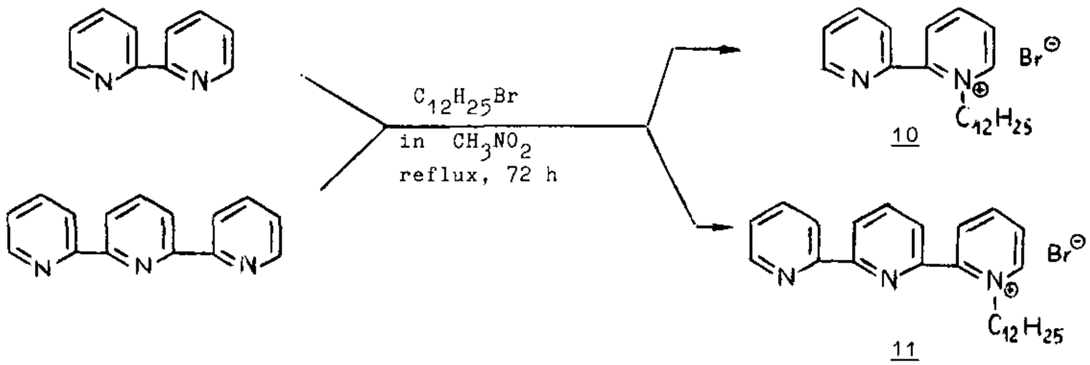
9

The same reaction carried out on pyrazine-1-oxide and pyrazine-1,4-dioxide proceeds as follows [31] .



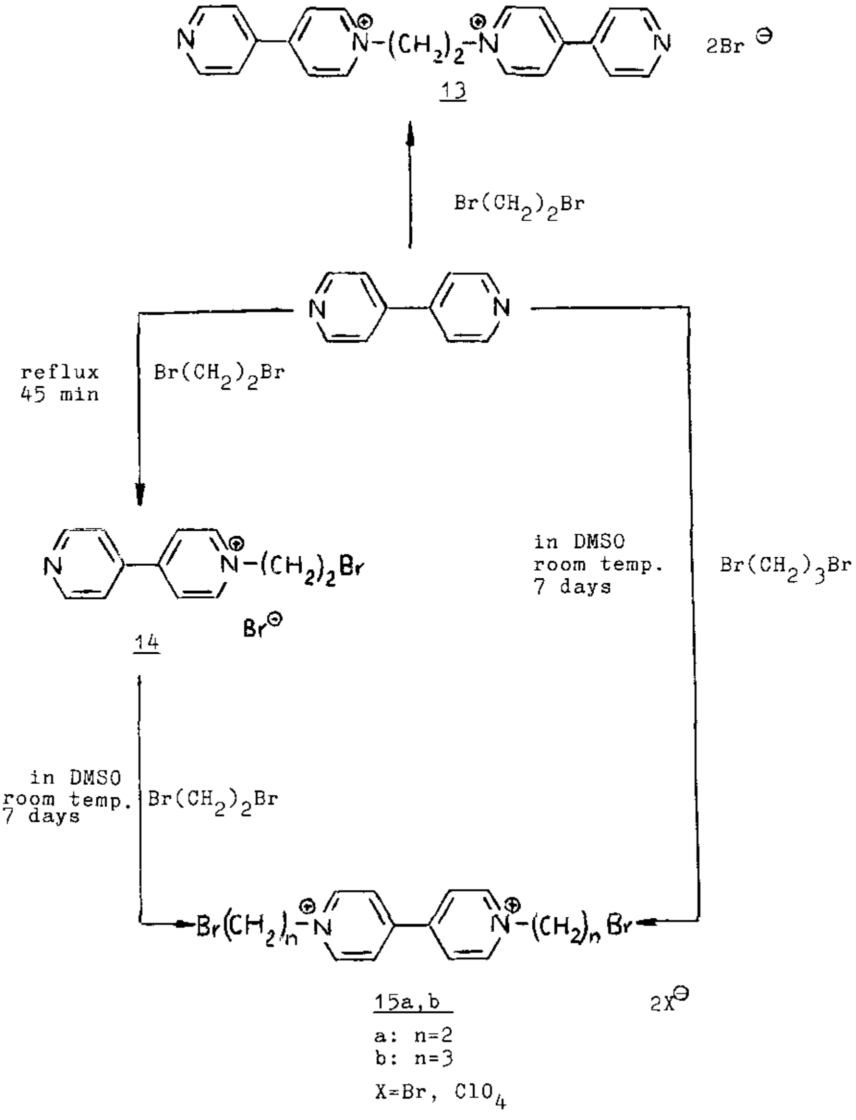


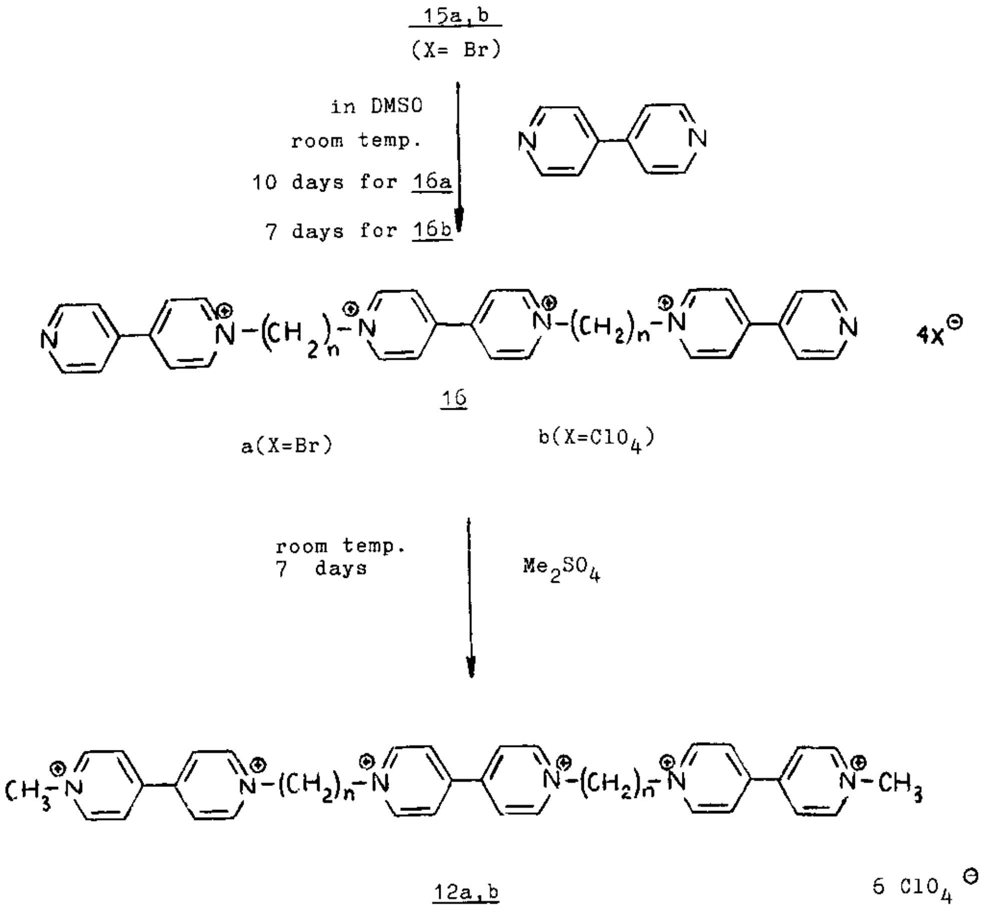
In the study of cation - exchange membranes, quaternization reactions leading to 10 and 11 have been performed [32].



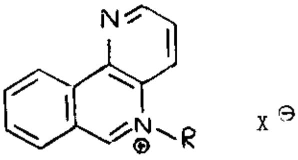
Hexaquaternary salts 12a,b derived from 4,4′-bipyridine have been synthesized in the following manner. Treatment of 4,4′- bipyridine with 1,2-dibromoethane yields 13 or 14 depending on conditions [33-35]; here the latter procedure was used.

Compound 14 reacted with 1,2-dibromoethane to give 15a (X = Br), while 15b (X = Br) formed from 4,4′ bipyridine and 1,3-dibromopropane. The reaction of 15a,b (X = Br) with 4,4′ bipyridine afforded 16a (X=Br) and 16b (X=$ClO_4$) which were quaternized by dimethyl sulfate to yield 12a,b . The bromides obtained were converted into the perchlorates by treatment with lithium perchlorate[36].





On studying the reactivity of 1,5- and 1,6-benzo[h] naphthyridines, their quaternization reactions giving rise to allyl, benzyl and 2,4-dinitrophenyl salts 17 and 18 have been performed [10].



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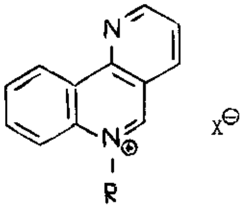
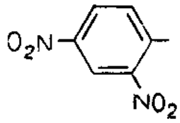
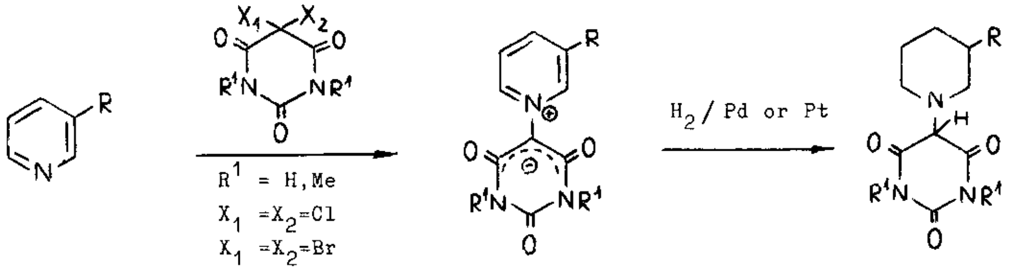


18

|  | R | X |
|---|---|---|
| a | $CH_2=CH-CH_2-$ | I |
| b | $PhCH_2$ | Cl |
| c |  | Cl |

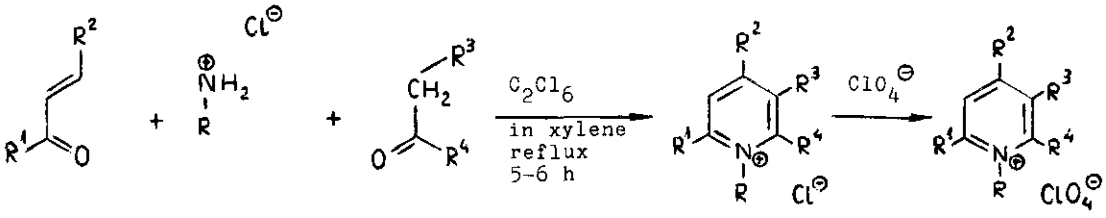
Pyridine or nicotinic acid derivatives, when treated with 5-chloro-, 5,5-dichloro- or 5,5-dibromobarbituric acids, give pyridinium ylides of barbituric acids which submitted to catalytic hydrogenation over Pd or Pt to afford piperidylbarbituric acids 19 [37].



R=H, COOEt, $CONH_2$

19

An example of the synthesis of quaternary pyridinium salts, without quaternization is the reaction of α, β -unsaturated ketones with primary amines and compounds with active hydrogen atoms; the used hexachloroethane serves for oxidation of dihydropyridine intermediates similar to those of the Hantsch synthesis [38].



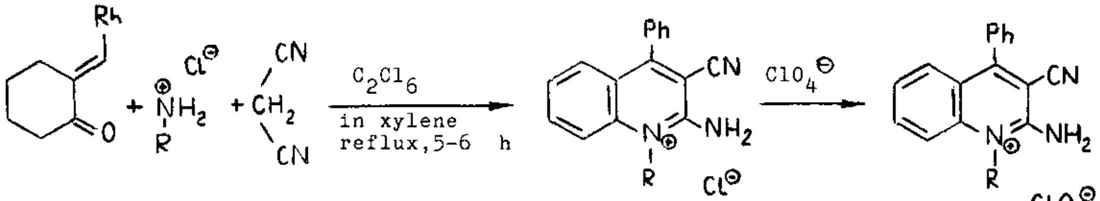
R=Ph, β- naphthyl

$R^1$=Ph, $^tBu$

$R^2$=Ph, $C_6H_4OH$-p

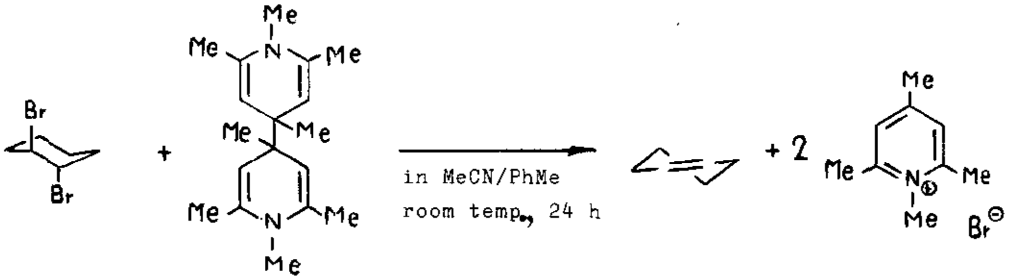
$R^3$ = H, Ph

$R^4$ = Et,$C_6H_4NO_2$-p



R=Ph, $C_6H_4OMe$-p

Among the reactions involving formation of pyridinium ions, noteworthy is a reduction carried out by means of dimeric dihydropyridines, for instance reduction of trans-1,2-dibromocyclohexane by $P_2$.

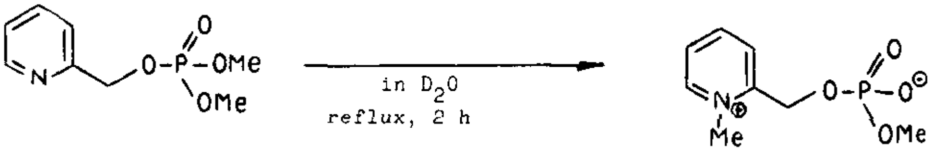


In this reaction a simultaneous transfer of two electrons to the substrate, combined *with the dissociation of* $P_2$ *into two pyridinium ions* $P^{\oplus}$, *takes place.* The reduction of heterocyclic cations $Q^{\oplus}$ (e.g. 1-ethylquinolinium or 1,2-dimethylquinolinium) leads to dimers $Q_2$, along with $P^{\oplus}$ ions.

$$2\,Q^{\oplus} + P_2 \longrightarrow Q_2 + 2\,P^{\oplus}$$

Reactions performed in acetonitrile/toluene were followed by electrochemical and kinetic methods [39].

In the research concerning the alkylating properties of trialkyl phosphates [40], interesting in the aspect of the synthesis of oligonucleotides, there was investigated the transfer of the methyl group from oxygen to nitrogen atom resulting in the isomerization to the corresponding zwitterionic product 20; as an example of phosphate ester dimethyl 2-pyridylmethylphosphate was chosen[41].



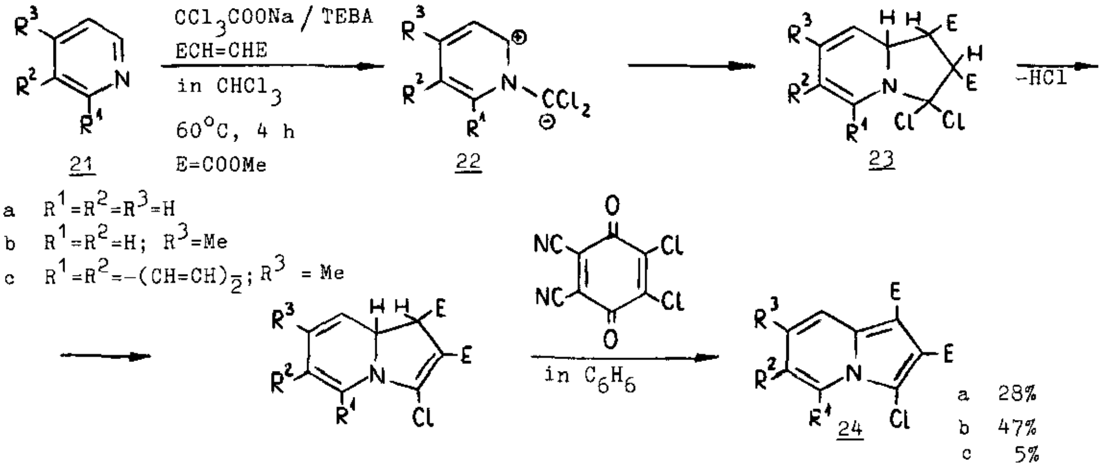
20

## III CHEMICAL REACTIVITY

Reactivity of substituted pyridinium salts will be presented with cyclization reactions proceeding via cycloaddition or cyclocondensation mechanisms, followed by their reduction, and finally other types of reactions.

### 1.CYCLIZATION REACTIONS

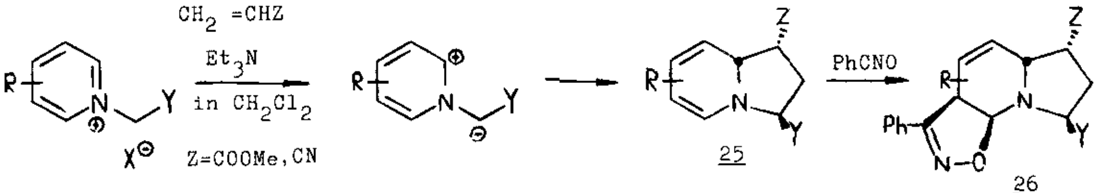
Among cycloadditions one ought to mention the reaction of substituted pyridine 21 with dichlorocarbene, formed by thermal decomposition of sodium trichloroacetate in chloroform in the presence of benzyltriethylammonium chloride (TEBA),giving the ylide 22; this in the 1,3- dipolar cycloaddition with dimethyl maleate or fumarate yields the primary cycloadduct 23 which undergoes dehydrohalogenation and subsequent oxidation with 2,3- dichloro- 5,6 - dicyanoquinone to give 24 [42].



a $R^1=R^2=R^3=H$
b $R^1=R^2=H$; $R^3=Me$
c $R^1=R^2=-(CH=CH)_2$; $R^3$ = Me

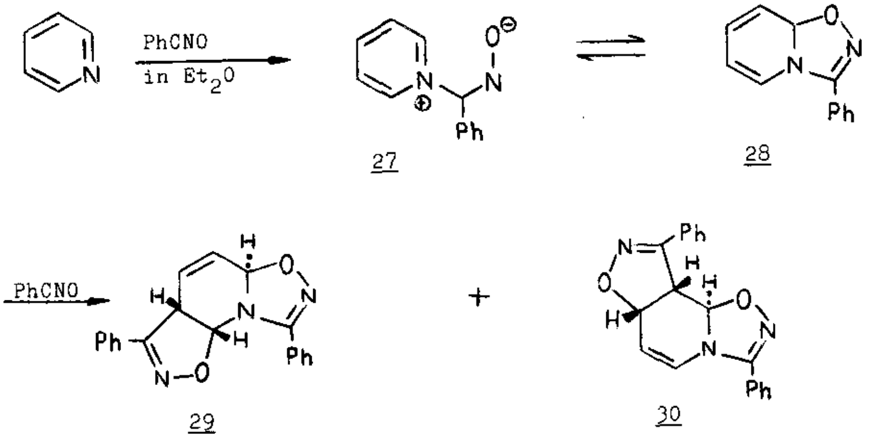
a 28%
b 47%
c 5%

Pyridinium and isoquinolinium methylides generated from the corresponding quaternary salts and triethylamine react with olefinic dipolarophiles to give unstable tetrahydroindolizines 25 which are treated in situ with nitrile oxides to yield, in highly stereo- and regioselective fashions, stable isoxazole-fused cycloadducts 26 [43].

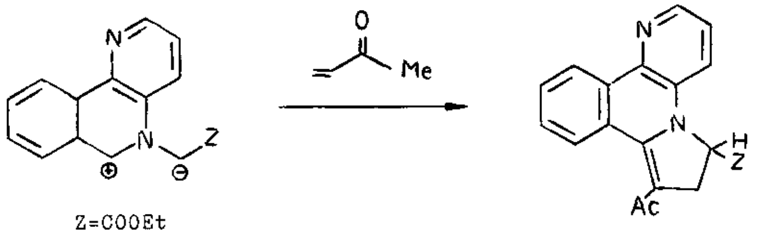


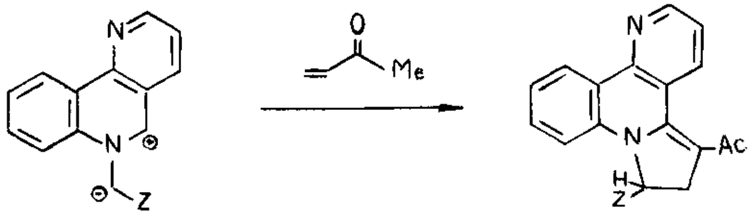
R=H,2-Me,4-Me
Y=COPh,COOMe,CN
X=Cl,Br

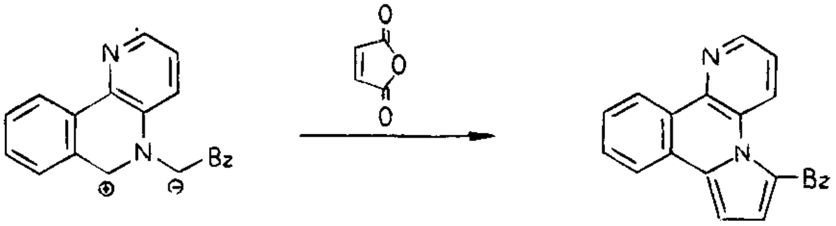
In the course of the reaction of pyridine with benzonitrile oxide carried out in nonpolar solvents, there was observed the formation of the zwitterion 27 which further undergoes an eletrocyclic ring closure into 28;the latter reacts with another molecule of benzonitrile oxide to give two bisadducts 29 and 30[44].

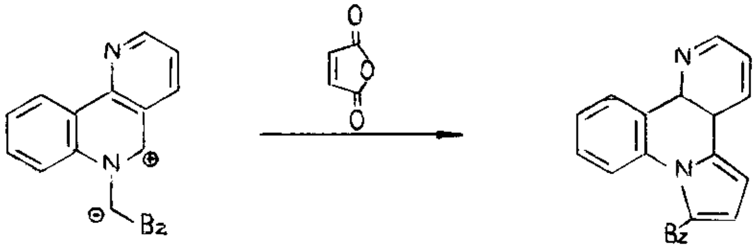


In investigation of 1,5- and 1,6-benzo[h]naphthyridines 1,3-dipolar cycloaddition reactions of N-ylides (generated in situ from the corresponding quaternary bromides by means of triethylamine) with DMAD, methyl acrylate, diethyl maleate, methyl vinyl ketone and maleic anhydride have been performed [6,9,12]; the examples are:

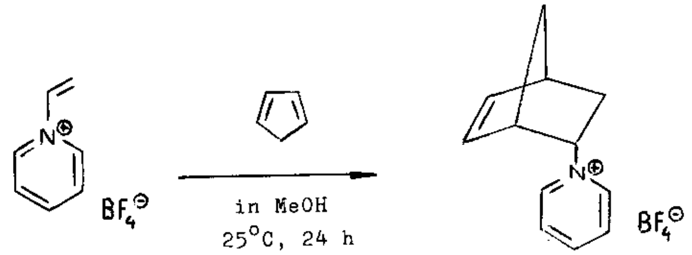








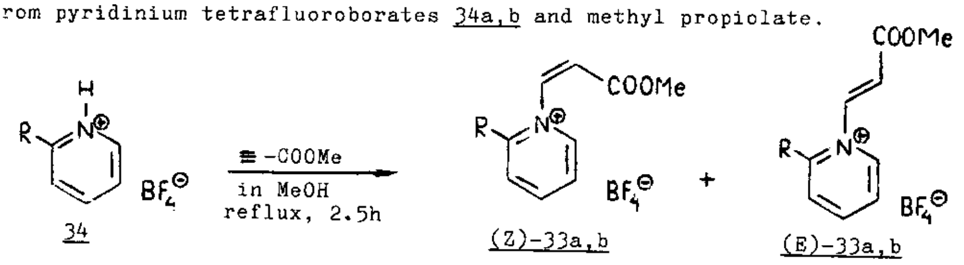
N-Alkenylpyridinium salts can also be used as dienophiles, for instance ethylene is converted into a very reactive dienophile by the presence of activating N-pyridinium group [45] .An example is the Diels-Alder cycloaddition of cyclopentadiene with <u>31</u> , prepared from pyridine and 1,2-dibromoethane [46]; this reaction carried out at 25° C yields exclusively the endo adduct <u>32</u>.



31

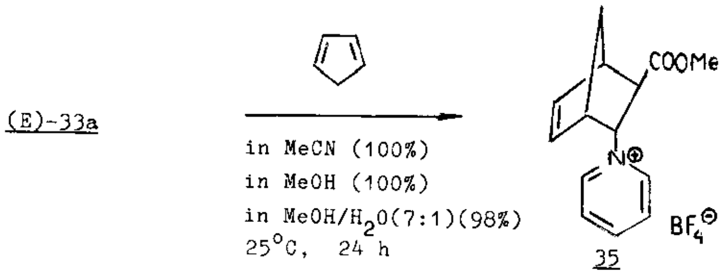
32

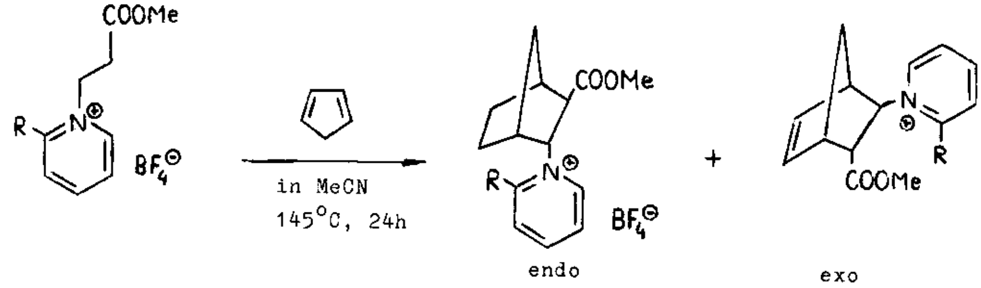
Other dienophiles (E)-33a,b are available as a mixture with isomeric (Z)-33a,b from pyridinium tetrafluoroborates 34a,b and methyl propiolate.



a:R=H
b:R=Me

(E)-33a reacts with cyclopentadiene at room temperature to give 35 as the sole product, while at 145°C the 1:1 mixture of stereoisomeric 35 and 36 is formed. So presumably at lower temperatures the more sterically hindered transition state with the exo pyridinium group is disfavoured. The suggestion that the endo selectivity is due to the steric bulk of the pyridinium salt is confirmed by the similar reaction of (E)-33b,resulting in 37 and 38 in the ratio 9:1 [45] .

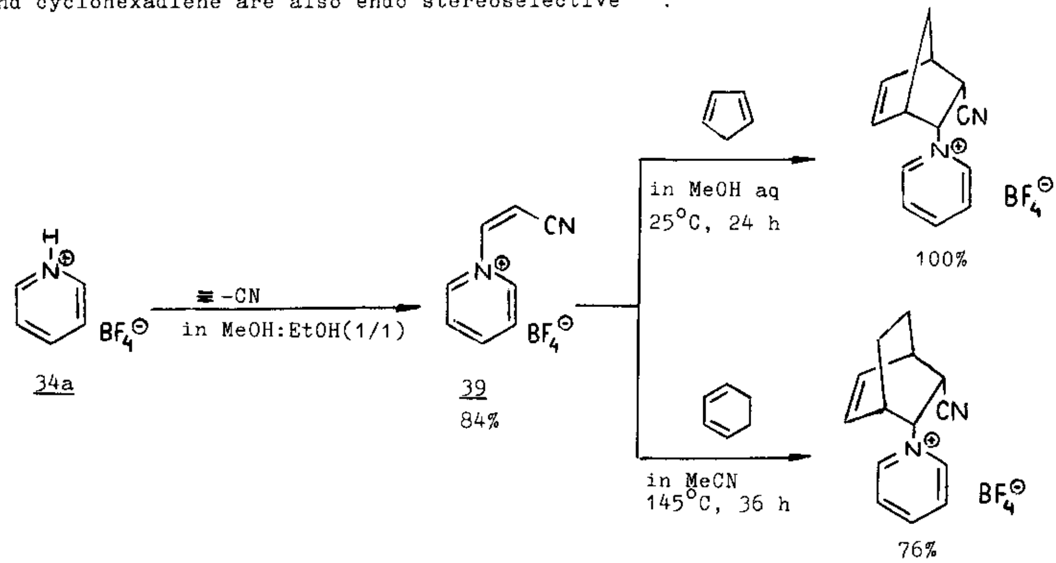




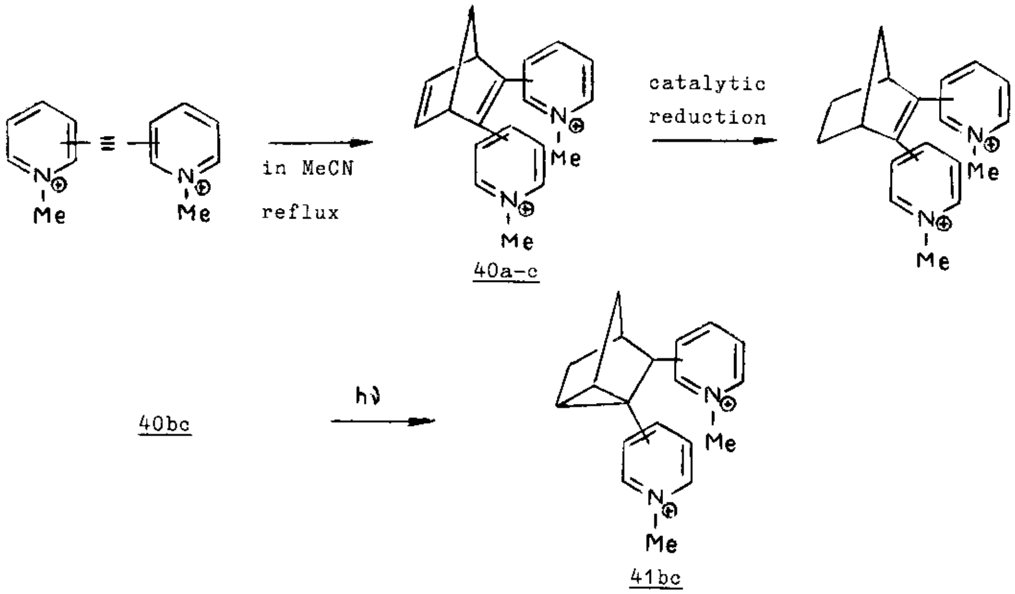
(E)-33a (R=H) 35 1:1 36

(E)-33b (R=Me) 37 9:1 38

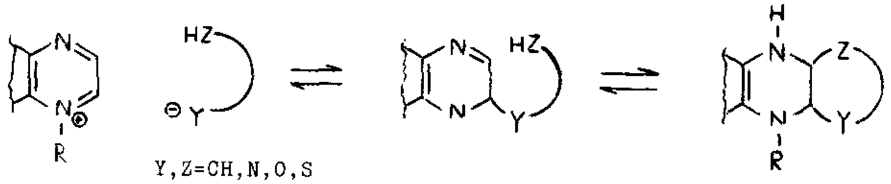
The reactions of 39 (prepared from 34a and propynenitrile ) with cyclopentadiene and cyclohexadiene are also endo stereoselective [45].

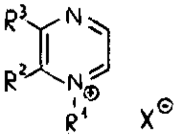


In the study of bispyridylacetylenes, there was shown that their reactivity as dienophiles was increased when they are quaternized. These electron-withdrawing substituents lower the LUMO level of the acetylene moiety.The following Diels-Alder reaction leads to bispyridylnorbornadienes 40a-c; among them 40a,b undergo photocyclization to quadricyclanes 41 [47].



Another example of cyclization is the reaction of N-alkyl-1,4-diazinium ions with bifunctional nucleophiles [48-50]:



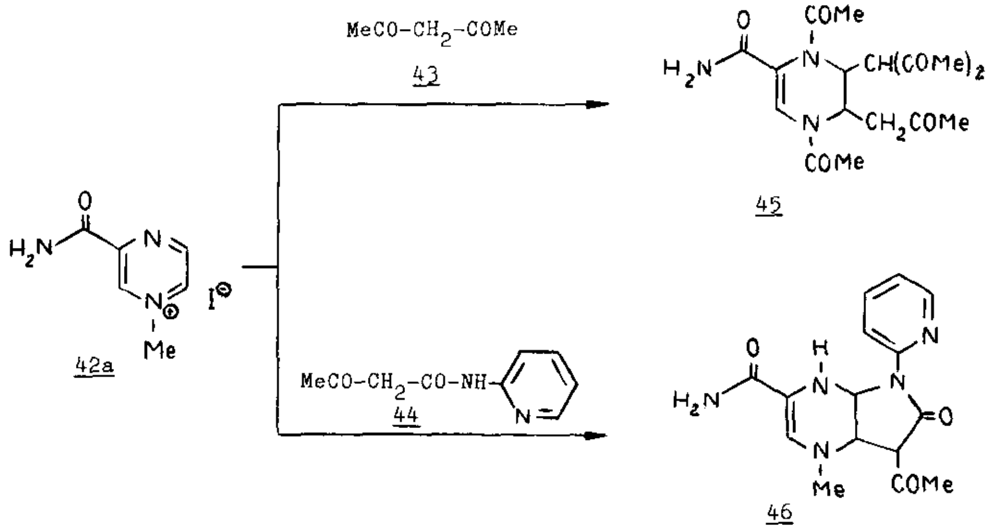


42

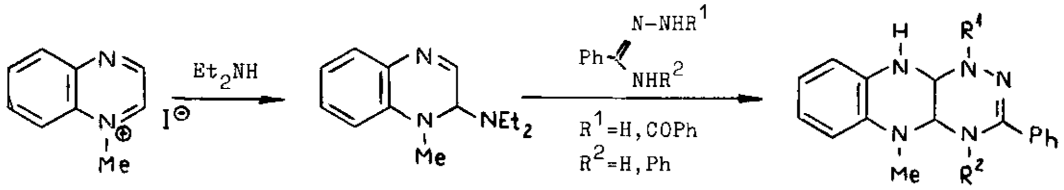
| | $R^1$ | $R^2$ | $R^3$ | X |
|---|---|---|---|---|
| 42a | Me | H | $CONH_2$ | I |
| | Et | COOMe | COOMe | $BF_4$ |
| | | benzo<br>pyrido [2,3- | | $ClO_4$ |

In order to find the dependence of electrophilic properties of 42 on their structure, the polarographic reduction of a series of variously substituted species was performed and their half-wave potentials $E_0$ were determined. It was observed that cyclizations could occur for 42 with $E_0 \geqslant -0.5V$.

Thus, in the case of unsubstituted 42 ($E_0$ = -0.67 V) cyclizations do not take place, while 42a bearing an electron-releasing substituent ( $E_0$= -0.5V) undergoes cyclization albeit limited scope of nucleophiles. An example is the reaction of 42a with 43 and 44; with 43, instead of the expected cyclization only the addition leading to 45 occurs, whereas with 44 the cyclized product 46 is formed [48].



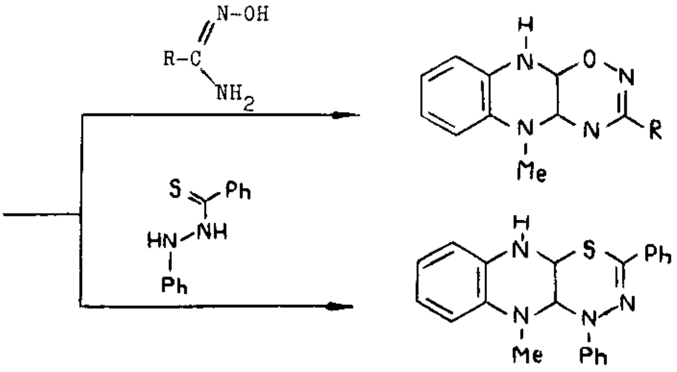
The reaction of quinoxalinium salt 47 with amidrazones gives rise to a new heterocyclic system, 1,2,4-triazino [5,6-b] quinoxaline [51]; to avoid formation of tetrazines which is expected if 47 reacts with amidrazone, 47 is treated primarily with diethylamine to yield 48 [52].



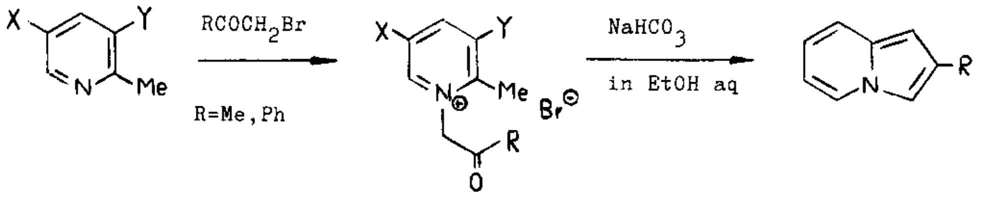
47 48

Analogous reactions occur with amidoximes [51] and thiobenzhydrazides [53].

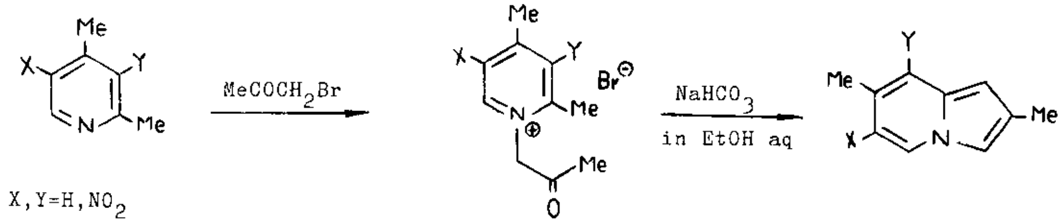
47

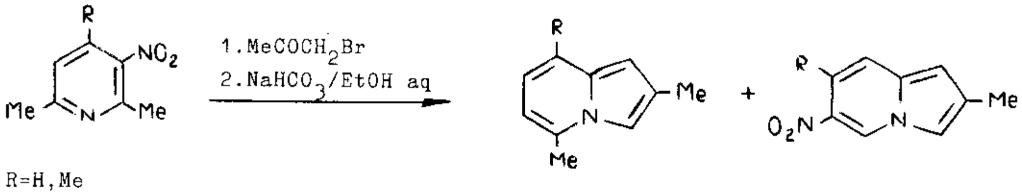


Among cyclocondensation reactions the following ones were reported [54,55].

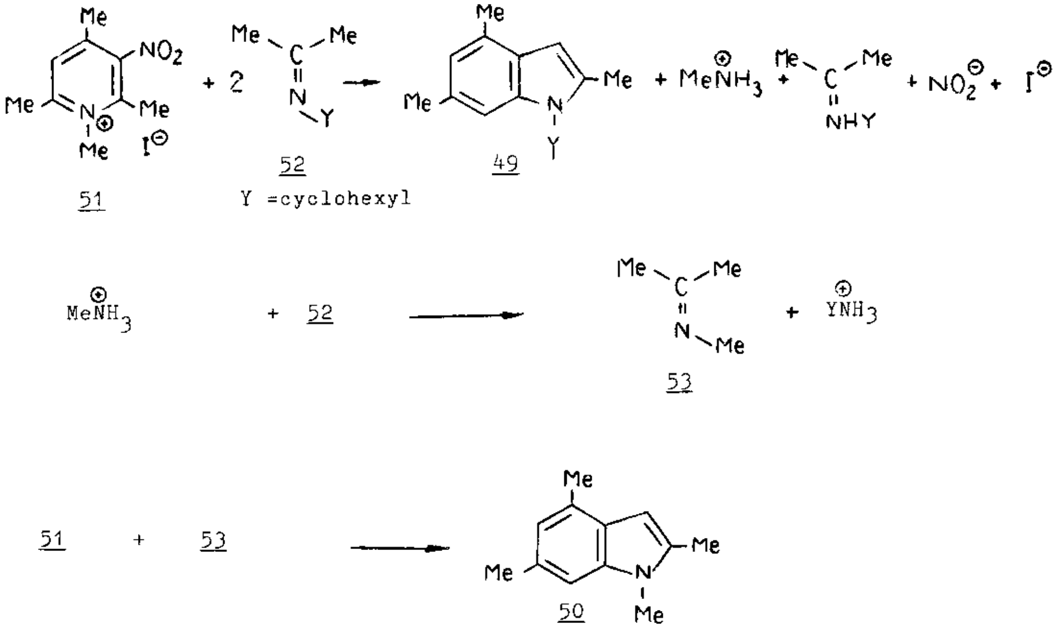


X,Y=H,Ac,CN

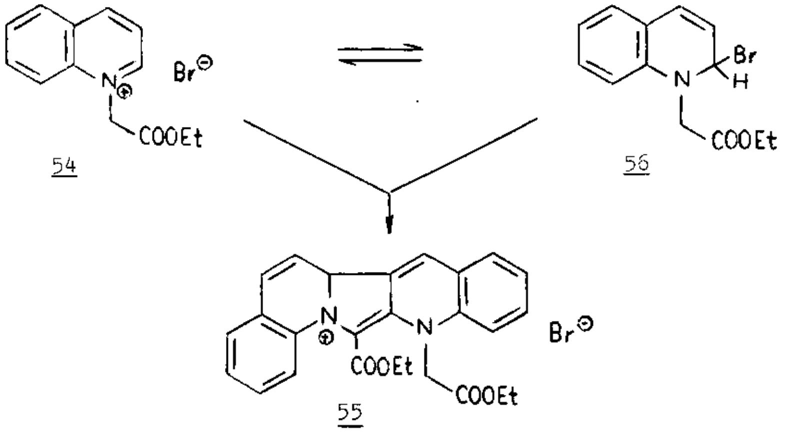




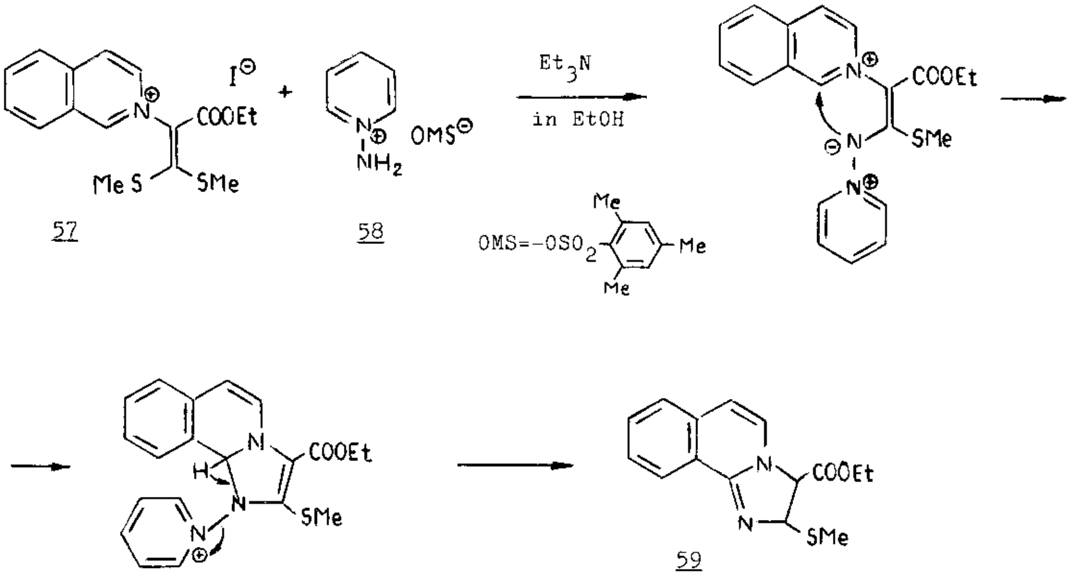
Indoles 49 and 50 can be synthesized from pyridinium salt 51 and ketimine 52. The mechanism involves the primary formation of indole 49 along with the elimination of methylammonium ion, which in a transamination with 52 yields ketimine 53. The reaction of 51 with 53, analogous to that with ketimine 52, gives rise to the indole 50 [56].



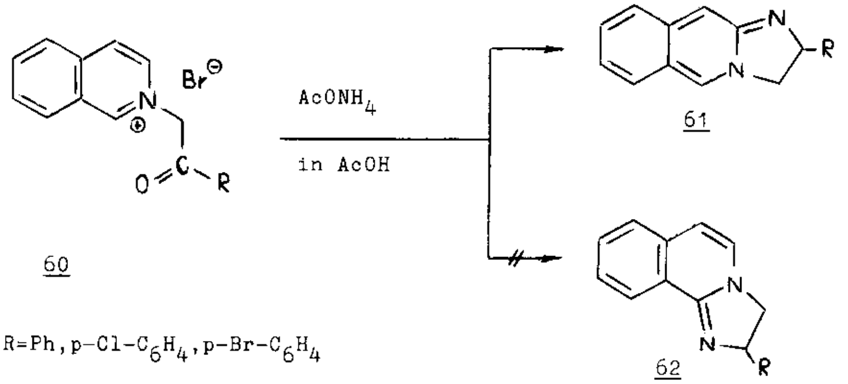
The treatment of quinoline with ethyl bromoacetate leads to pyrrolodiquinolinium salt 55 besides the quaternized product 54 which is converted into 55 by reacting with quinoline [57]. The proposed mechanism involves an equilibrium between 54 and dihydro compound 56:



The reaction of 57 with 1-aminopyridinium mesitylenesulfonate 58 in ethanol in the presence of triethylamine results in 59; the process occurs via the initial displacement of a methylthio group of 57 with the amino group of 58, followed by intramolecular cyclization and subsequent liberation of the pyridinium moiety [58].



Nucleophilic substitution of isoquinolines and their quaternary salts usually proceeds preferably in the position 1 and not 3, however the treatment of 60 with ammonium acetate in glacial acetic acid gave rise to 61 instead of the expected 62 [59].



60

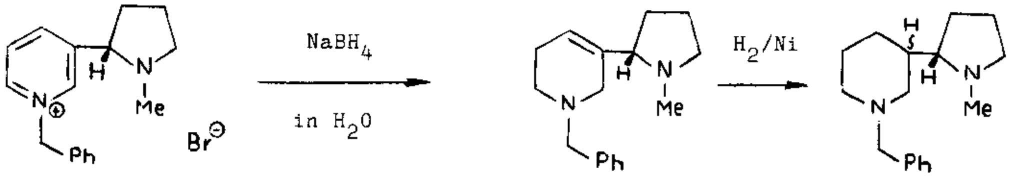
61

62

R=Ph, p-Cl-$C_6H_4$, p-Br-$C_6H_4$

## 2. REDUCTION REACTIONS

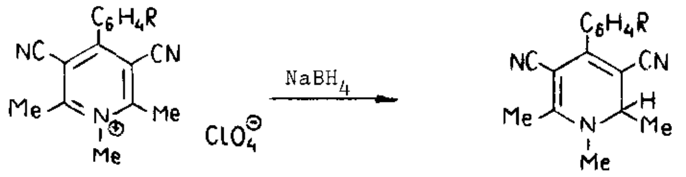
The reduction of 1-benzylnicotinium bromide with sodium borohydride leads to tetrahydronicotine 63, which upon catalytic reduction gives 1-benzylhexahydronicotine as a mixture of two diastereomers [60].



63
80%

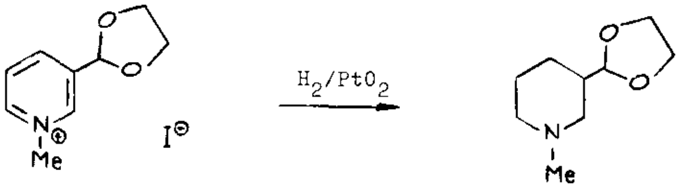
72% and 23%

Other examples of reduction of quaternary pyridinium salts are :



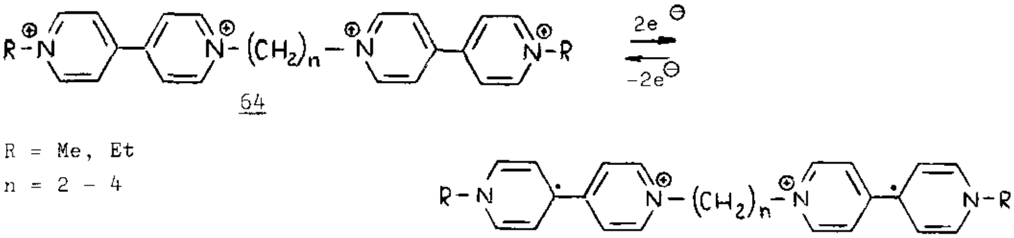
ref.61

R=H,4-OMe, 2-$NO_2$, 4-$NO_2$



ref.27

Tetraquaternary cations 64 can be reversibly reduced to diradical dications 65 by the uptake of two electrons [33].



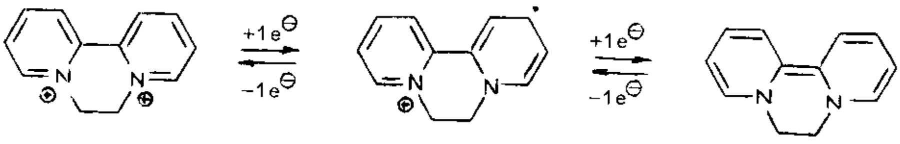
64

R = Me, Et
n = 2 - 4

65

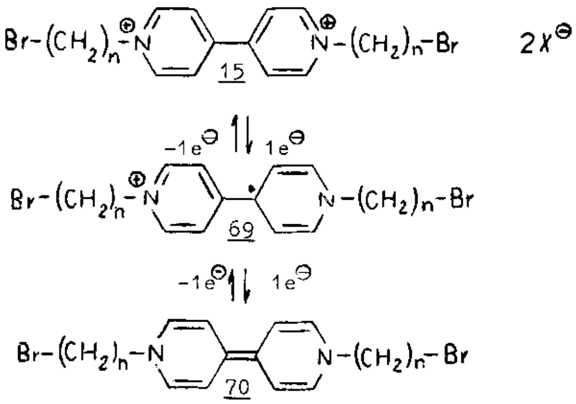
The results of the direct current polarography at the dropping mercury electrode of 15ab (X=$ClO_4$), 16a(X=Br), 16b (X=$ClO_4$) and 12a,b are reported. In this process carried out in aqueous solutions with diquat dibromide 66 as the reference, the dependence of reduction potential on pH was investigated [36].

Compound 66 is reduced by two distinct one electron reduction steps to give firstly the radical cation 67, and then the neutral species 68.

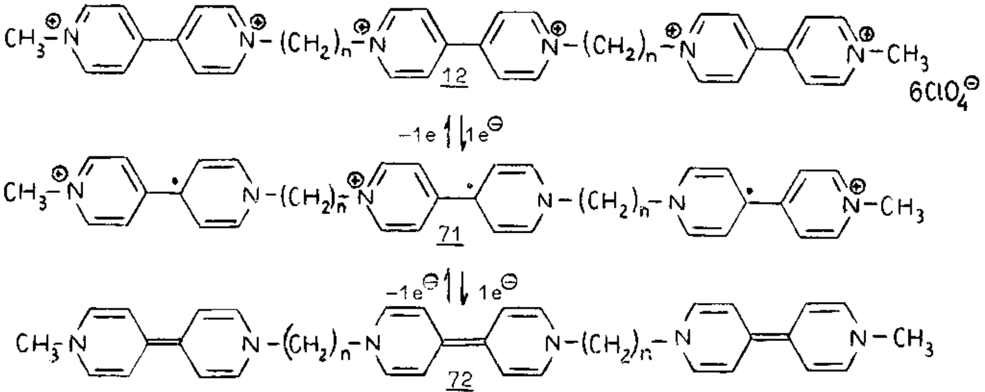


66 67 68

The polarographic reduction of 15 leads presumably to 69 and 70, while 12 gives rise to 71 along with 72, and 16 forms triradical cation of type 71 (H for Me).

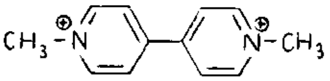


15 69 70



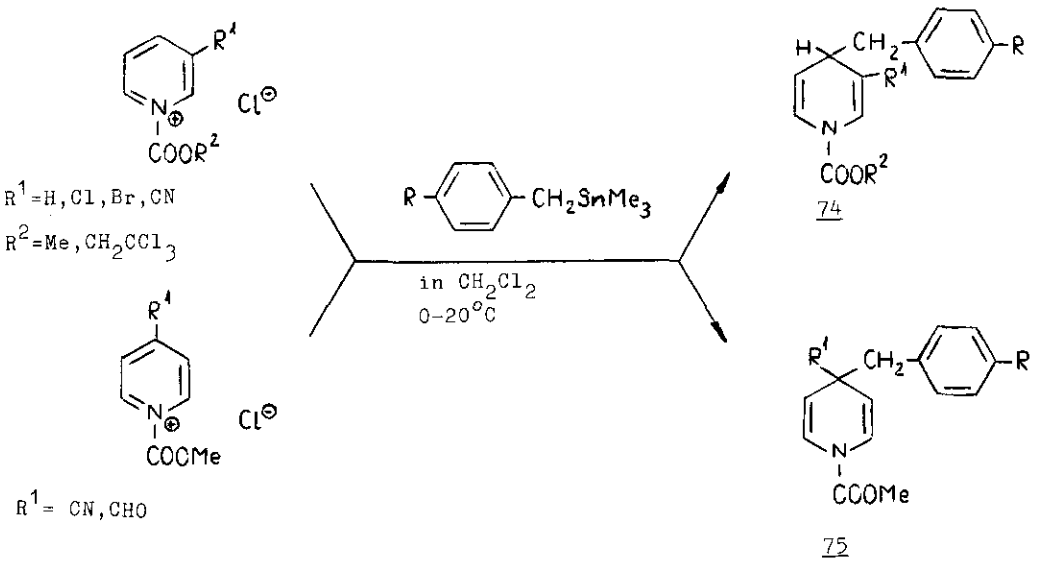
12 71 72

Two diquaternary salts 15a,b and two hexaquaternary salts 12a,b as well as paraquat 73, on treatment with zinc dust in aqueous solution give intense violet colorations due to the formation of the radical species 69 and 71.When the reducing agent was removed and the solutions were shaken in air the deep colorations disappeared, suggesting that the one-electron transfer from 15 to 69 and the three-electron transfer from 12 to 71 are reversible [36].

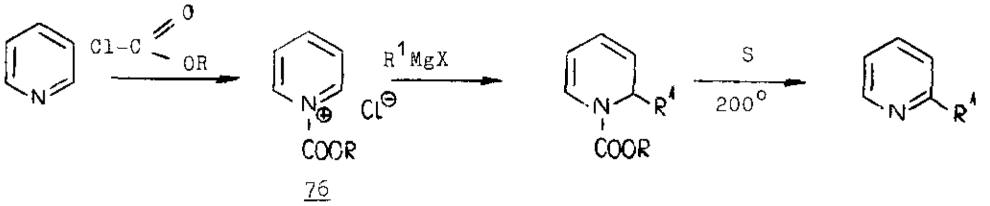


73

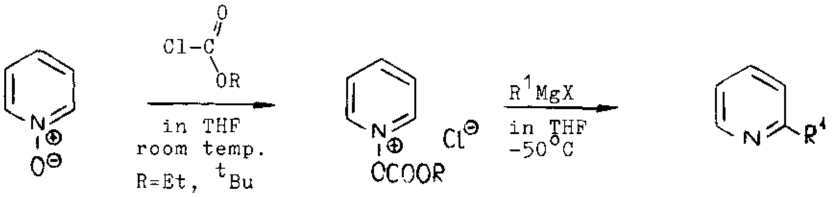
Benzyltin reagents add to N-acylpyridinium salts in a high regioselective fashion to give 4-benzyl-1,4-dihydropyridines 74 and 75, difficult to obtain on other routes [62].



*N-Carboalkoxypyridinium salts 76 can serve for the synthesis of* 2-substituted pyridines by the addition of Grignard reagents, followed by oxidation of the formed dihydropyridines with elemental sulphur at 200°C [63,64].

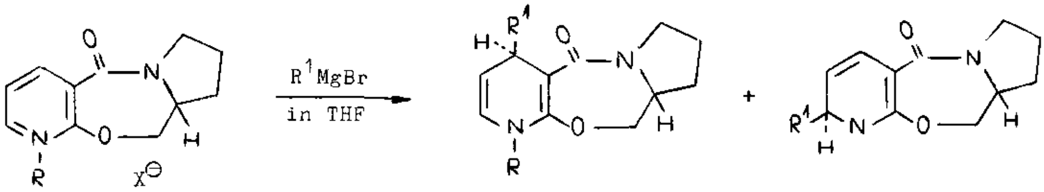


However having in view drastic conditions and relatively poor regioselectivity of this procedure, the one pot synthesis with a high regioselectivity by starting from pyridine N-oxide has proved to be more favorable.
Simple addition of isobutyl or ethyl chloroformate to pyridine N-oxide gives rise to the unstable 77 (more stable in the case of $R = {}^{i}Bu$ than R = Et) in a form of a suspension which is then treated directly with a Grignard reagent[65].



77 $R^1$ = aryl, alkenyl, alkynyl

Quaternary salts 78a,b derived from pyridooxazepinone undergo addition of Grignard reagents to give 79 as the major product; in this compound the group $R^1$ is oriented anti to the hydrogen atom at the chiral center of the L-prolinol residue[66].

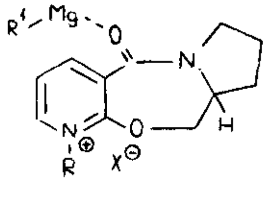


78a, b

79

a R=Me, X=I $R^1$=Ph,$CH_2$=CH-
b R=$PhCH_2$, X=Br $Me_2CH$-$CH_2$

The high regio- and stereoselectivity of this reaction may be due to coordination between Grignard reagent and the amide oxygen atom, as shown in 80 .

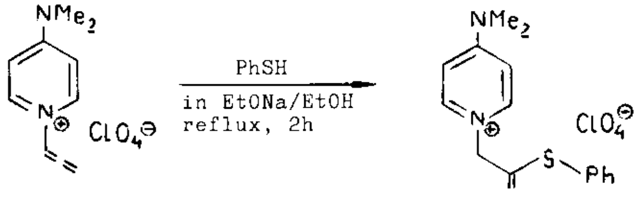


80

## 3. OTHER TYPES OF REACTIONS

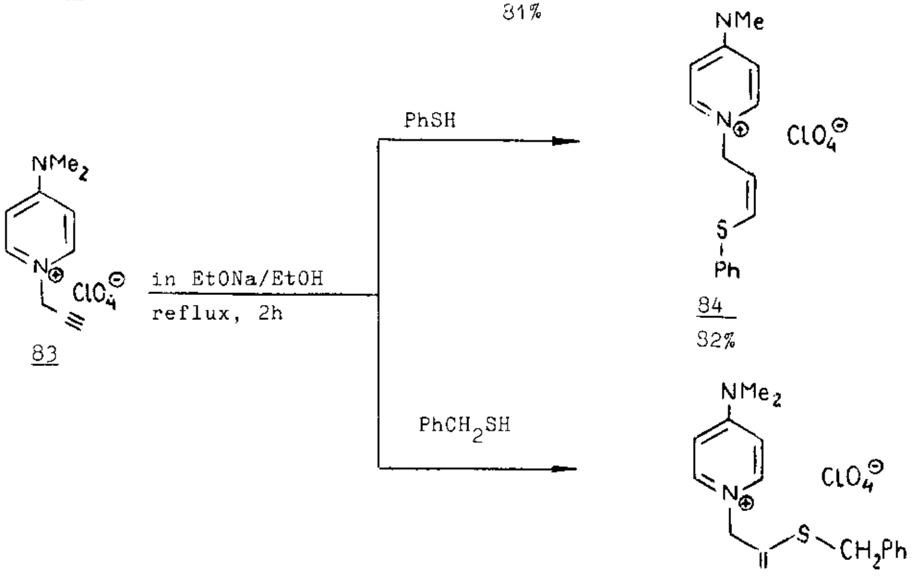
In the study of quaternary salts, the addition of sulphur nucleophiles to multiple bonds activated by an adjacent pyridinium moiety has been examined[67]. There was shown that 81 added thiophenol at the C-2 affording vinyl sulfide 82a, while in the case of 83 under the same conditions the addition proceeded at the C-3 to give 84 .

However, when benzyl mercaptan of thiophenol was used, under the same conditions, 83 gave only the C-2 addition product 82b.



81

82a
81%

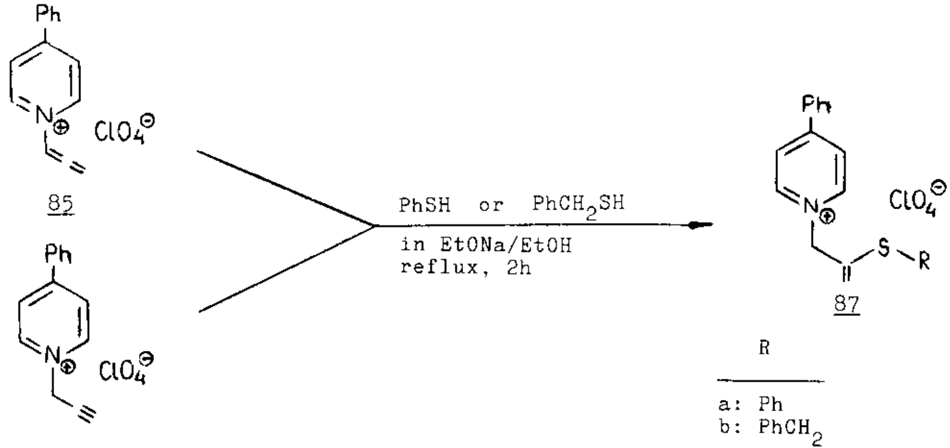


83

84
82%

82b
76%

Under analogous conditions, the treatment of 85 and 86 with thiophenol or with benzyl mercaptan led exclusively to C-2 addition products 87a,b.



85

86

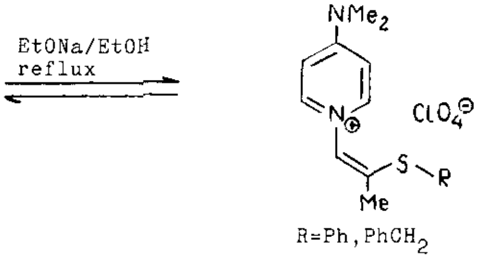
87

R
a: Ph
b: $PhCH_2$

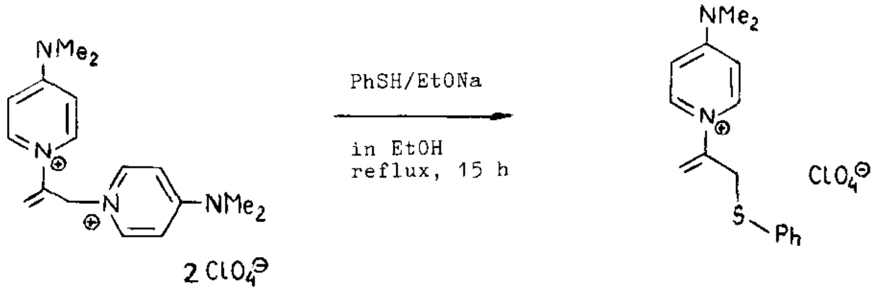
The observation that the C-3 addition took place only in the case between 83 and thiophenol can be explained by a competition between addition and base-catalyzed propargyl-allene rearrangement.

On heating in EtONa/EtOH, the vinyl sulfides 82a,b underwent partial isomerization [67].

82 a,b



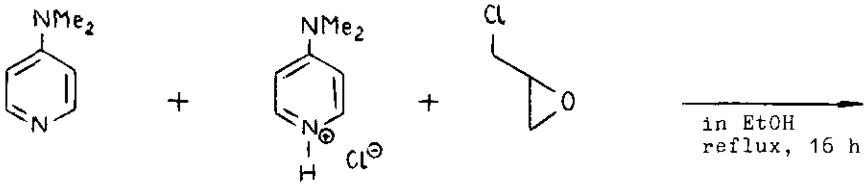
In the study of bis pyridinium salts there was shown that 88 [68] when treated with thiophenol in EtONa/EtOH produced the vinyl pyridinium salt 89 .

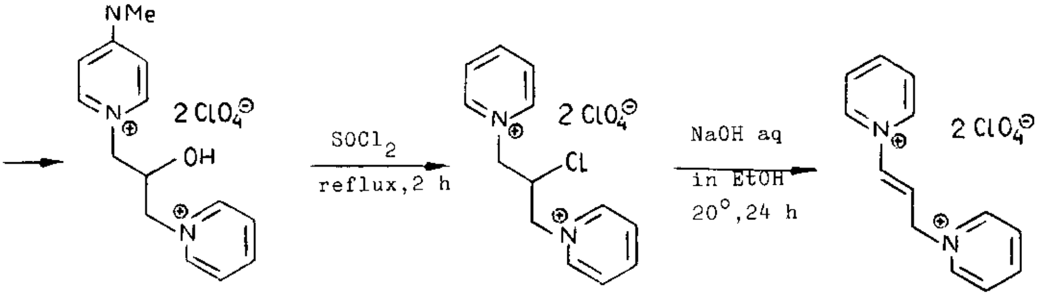


88

89
61%

The reaction of 4-(dimethylamine) pyridine with its hydrochloride and epichlorohydrin gave rise to 90, which was readily converted by thionyl chloride into the chloro derivative 91, and further to 1,3-disubstituted propene 92 [67] by elimination of HCl with aqueous NaOH.



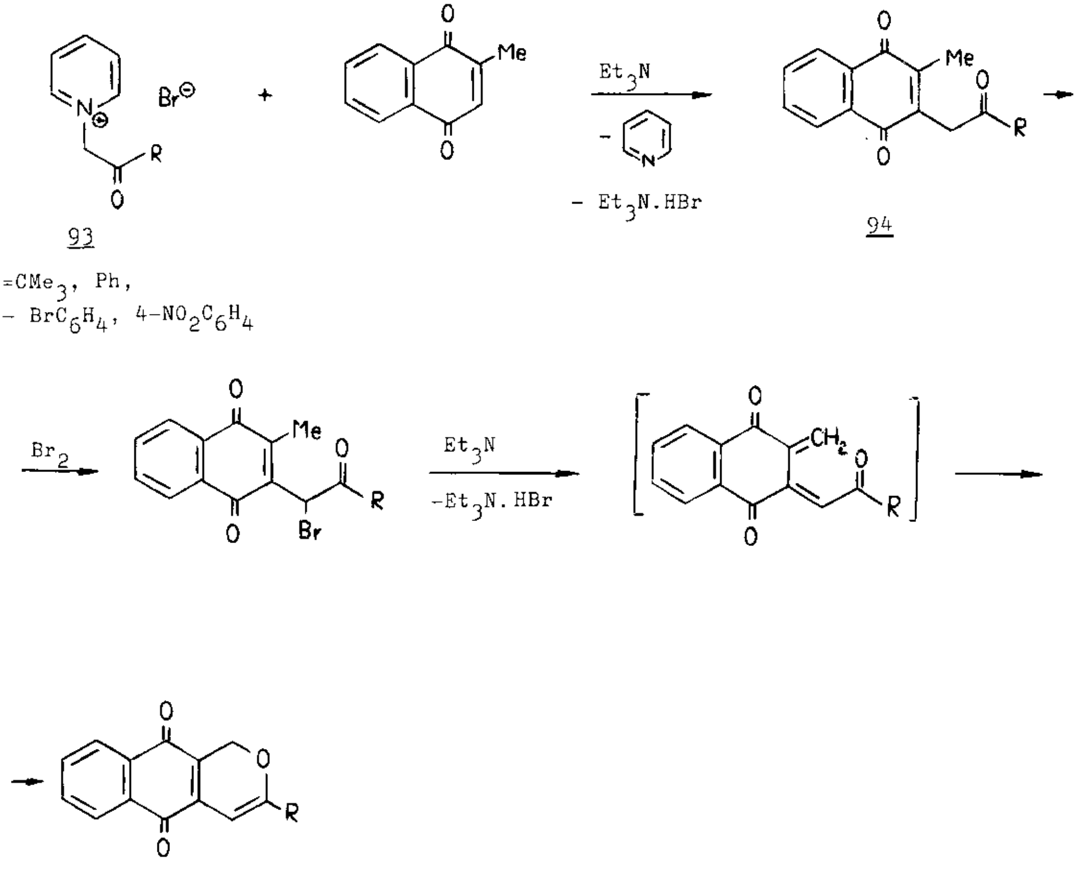


90
77%

91
80%

92
76%

Pyridinium N-ylides generated from quaternary salts 93 by treatment with triethylamine convert 2-methyl-1,4-naphthoquinone into 3-(acylmethyl) derivatives 94; these compounds by bromination and subsequent dehydrobromination undergo cyclization to 95, giving a variety of colours in acid media.[69,70].



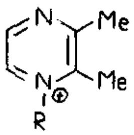
93

R=CMe$_3$, Ph,
2- BrC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$

94

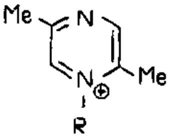
95

In deprotonation reactions of pyrazinium ions 96 and 97, the activation by adjacent alkyl substituents, and deactivation by more distant alkyl substituents has been discussed in terms of polar effects, as well as of ring strain and inter-alkyl interactions [29,30,71,72]; the influence of used bases such as carboxylate ion, aniline and pyridine derivatives has been investigated, too[73].



96

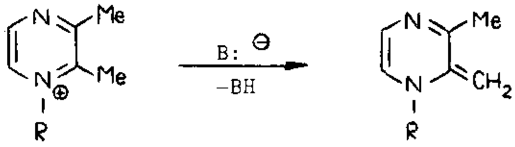
R=Me,Et,$^i$Pr



97

R=Me,Et

For instance:

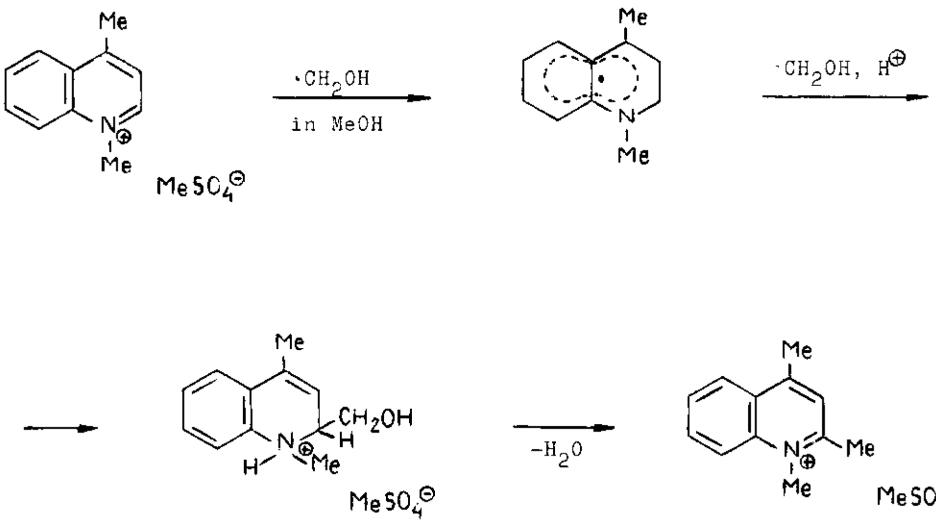


The radiation-induced methylation of quinolinium salts with methanol has been performed. Hydroxymethyl radicals playing important role in this reaction can be produced by the UV-irradiation of acetone in methanol[74,75].

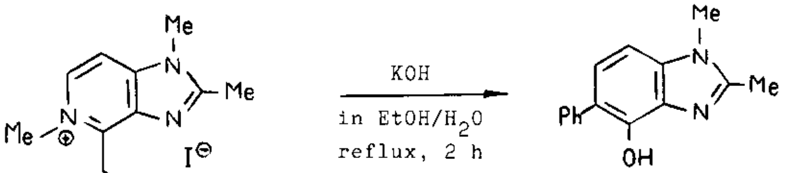
$$CH_3COOCH_3 \xrightarrow{h\nu} {}^1(CH_3COCH_3)^* \longrightarrow {}^3(CH_3COCH_3)^* \longrightarrow$$

$$\xrightarrow{CH_3OH} CH_3\dot{C}(OH)CH_3 \quad + \ \bullet CH_2OH$$

The methylation reaction proceeds as follows:



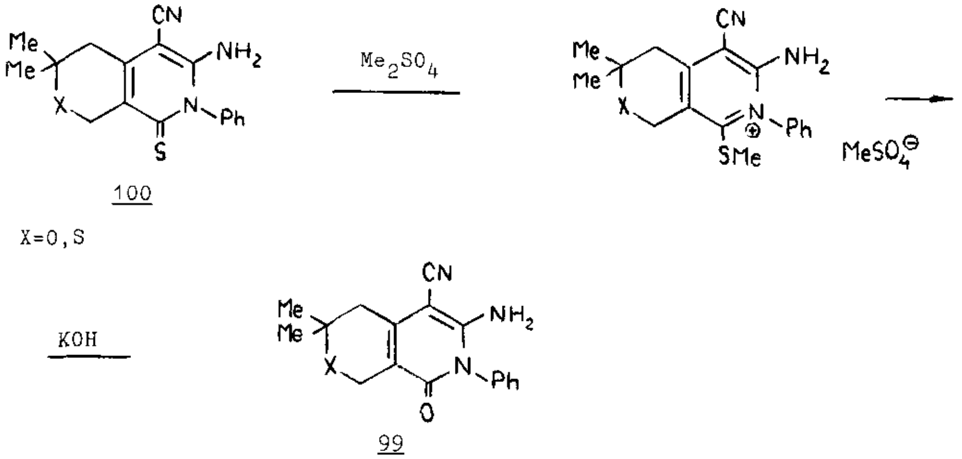
Among a variety of recyclizations of quaternary salts[76], an unprecedented example is the synthesis of substituted benzimidazole 98, otherwise difficult to obtain [77]. The pyridine-into-benzene ring transformation proceeds via an open-chain intermediate.



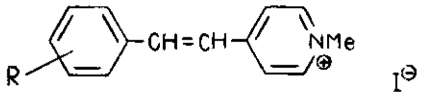
98

95%

In order to obtain 99, the thiones 100 were converted into the corresponding quaternary salts and hydrolyzed next [78].



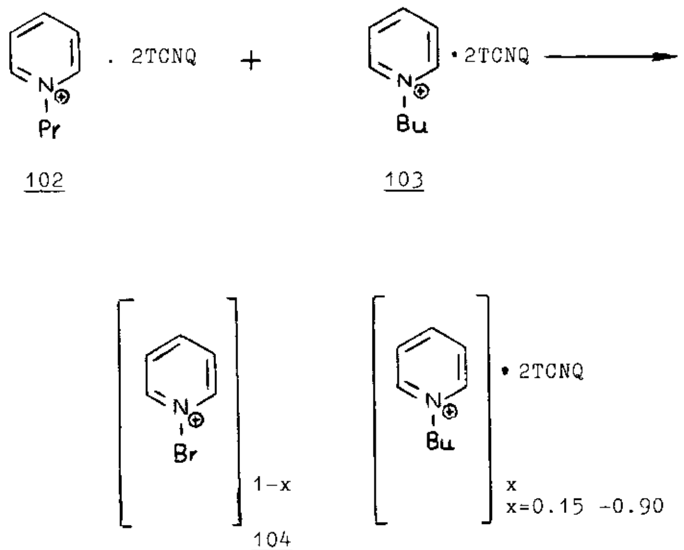
The kinetics of epoxidation of N-methyl-4-styrylpyridinium iodides 101 with alkaline hydrogen peroxide in aqueous solution has been investigated spectrophotometrically, and its mechanism was proposed [79].



101

R=H, Me, OMe, $NO_2$, F, Cl, Br

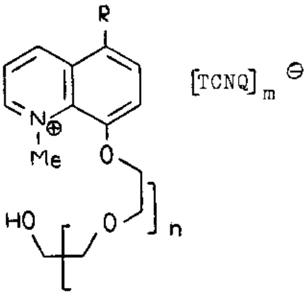
In the search of organic semiconductors salts 102 and 103 were mixed and molded at 6 tons/cm$^2$ to give 104 [80].



102 103

104

The radical-anion TCNQ salts 105 have been obtained from appropriate quinolinium salts and the influence of substituent on their conductivity was discussed [81].



105

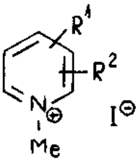
|   | R | n | m |
|---|---|---|---|
| a | H | 0 | 1 |
| b | H | 0 | 2 |
| c | H | 1 | 2 |
| d | Cl | 0 | 2 |

## IV. PHYSICOCHEMICAL PROPERTIES

The structures of a series of N-methylpyridinium cations 106 were calculated by GEOMO RV, utilizing semiempirical MINDO/3 SCF procedures [82]. A very good correlation was obtained between calculated energy of methylation and Brown´s experimental heats of tetrafluoroboronation for the same pyridines.

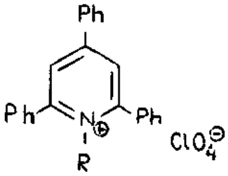
The electronic and luminescence spectra of 107 have been recorded and the results interpreted in correlation values calculated by SCF PPP method [83].

For N-methylides 108 the electronic structures have been calculated by CNDO/2 procedure ; a linear correlation between charges of nitrogen atoms and binding energies measured by ESCA method has been established [84].



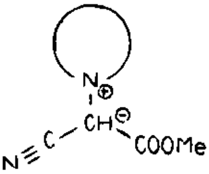
106

$R^1, R^2$ =Me,Et,$^i$Pr, $^t$Bu



107

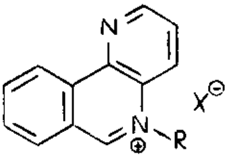
R=Me, Ph



108

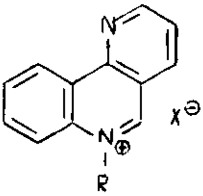
 = pyridine, isoquinoline, pyridazine, phthalazine, cinnoline

Investigating benzo [h] naphthyridinium salts excitation energies and oscillator strength values for cation components of 17 abc and 18 abc , as well as of 109 abc and 110 abc , have been calculated within limited CI-PPP method, and a very good agreement of experimental and calculated UV-VIS spectral data has been obtained [6,10,11].



109

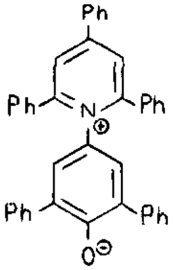
| | R | X |
|---|---|---|
| a | Me | I |
| b | $CH_2COOEt$ | Br |
| c | $CH_2COPh$ | Br |



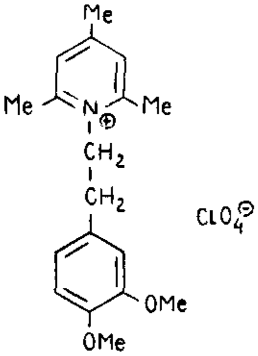
110

In the study of solvent polarity in highly aqueous mixed solvents, the Dimroth-Reichard $E_T$ (30) parameter has been used; its numerical value is the transition energy of the longest wavelength absorption of 2,6-diphenyl-4-(2,4,6,triphenyl-1-pyridinio)phenoxide 111 [85-87].

Pyridinium perchlorate 112 was investigated by fluorescence and electrogenerated chemiluminescence ; the observed long-wave absorption can be explained by formation of an intramolecular electron donor-acceptor complex [88].



111

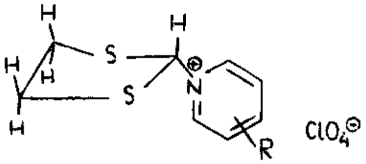


112

Among spectroscopic studies of N-substituted quaternary salts the $^{13}C$ NMR data of N-acetylpyridinium chloride are reported [89].

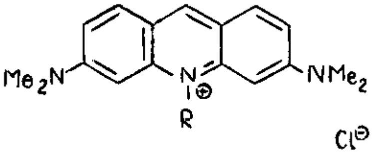
Rates of dissociation of the C-N bond in substituted 1-(1,3-dithiolan-2-yl)pyridinium perchlorates 113 have been determined by the dynamic $^{1}H$ NMR technique. There was shown that the dissociation proceeds via the $S_N2$ mechanism, the perchlorate ion acting as a nucleophile [90].

The kinetics and thermodynamics of the dimerization of Acridine Orange 10-alkyl derivatives 114 have been investigated by spectrophotometry and temperature - jump method. $^{1}H$ NMR data show that the planes of two component molecules in the dimer are parallel [91].



113

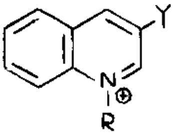
R=H,4-Me,4-MeO



114

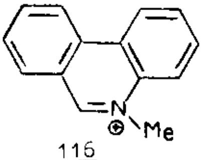
R=$C_nH_{2n+1}$ (n=1,2,3,5,8)

In the study of tunneling theories, the observed and calculated kinetic isotope effects for hydride-transfer reactions of 115 and 116, analogues of $NAD^+$, have been discussed. The results suggest, that the large-curvature tunneling needs to be considered in hydrogentransfer reactions [92].



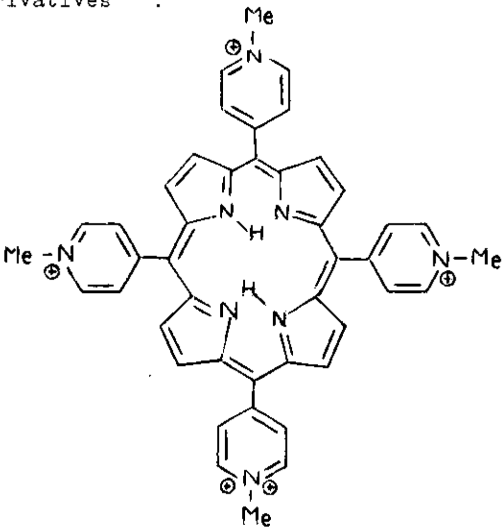
115

R=Me, $PhCH_2$ Y=CN, $CONH_2$



116

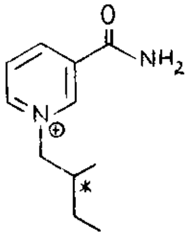
Describing physicochemical properties of pyridinium salts, there ought to be mentioned here resonance Raman spectra of porphine 117 and of its metalated (Mn,Fe, Co, Ni, Cu, Zn, Ag ) derivatives [93].



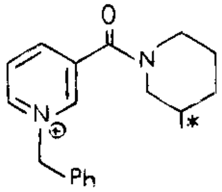
117

## V. BIOLOGICAL ACTIVITY

Among investigations of diphosphopyridine dinucleotide models, reduction reactions of chiral 118 and 119 with sodium dithionite leading to the corresponding 1,4-dihydro derivatives have been performed [94].

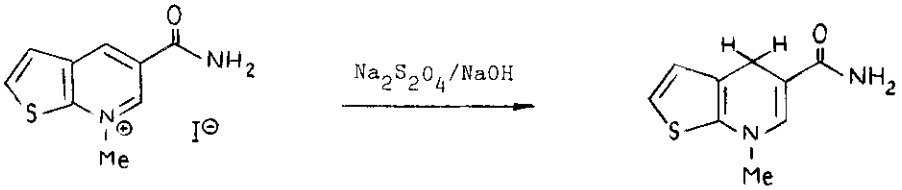


118

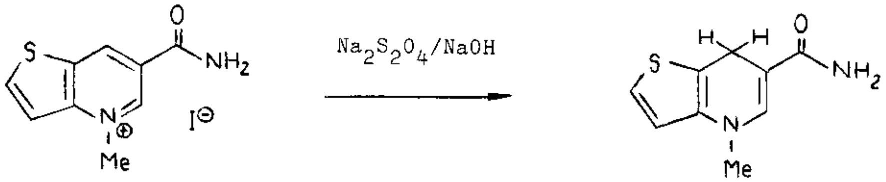


119

Non water-sensitive NADH models 120 and 121 have been submitted to the following reactions: [95].

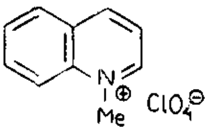


120

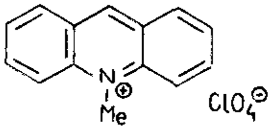


121

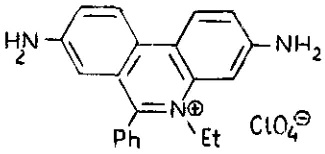
In investigations of surfactant molecules there has been shown that the binding between heterocyclic cations 122 and 123 with anionic sodium dodecyl sulfate can serve as a model for similar attractions between cationic heterocyclic dyes such as ethidium ion 124 and the strong electric field associated with the anionic phosphate groups of DNA [96,97].



122



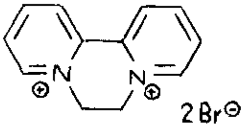
123



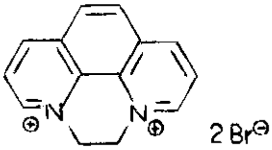
124

ethidium

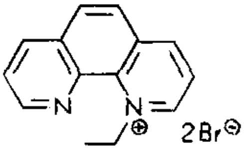
Studies of DNA intercalating agents have shown that 125 and 126 do not possess these properties. This is due to their torsional angles of 20° (125)and 8° (126) between two pyridinium moieties in each molecule, while 127 where the torsional angle is only 2° can intercalate with DNA [98].



125

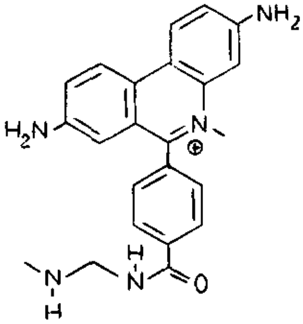


126

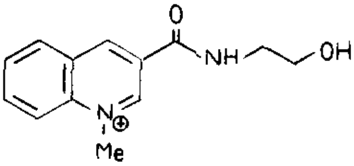


127

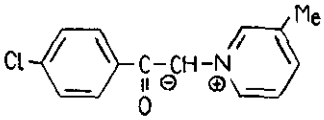
As DNA intercalators can be also applied the redox systems of the type 64/65 [33,36] *or the crown ethers incorporating a substituted phenanthridinium ion* 128 [99].



128



129



130

In the investigation of drug-DNA affinities, there was observed that 117 and its metal derivatives can either bind to the phosphate backbone of DNA via electrostatic interaction with the charged N-methylpyridinium groups or intercalate in a manner similar to amino acridines. Compounds of this type have biological activity, and some of them show antineoplastic properties [93].

Studying benzo[h] naphthyridines there was found that their N-substituted quaternary salts, for instance 17 and 18 , show antibacterial and antifungal activities [10].

## VI. APPLICATIONS

Among pyridinium salts of some practical value one can mention 1-acylpyridiniums 2-5 possess acylating properties; the kinetics of acylation of p-nitroaniline with these compounds were examined by conductometry and UV spectroscopy methods[26].

An example of a new class of chiral detergents is 1; the formation of single micelles from 1 was studied with the CD and UV spectroscopy, and the results were compared with its 1-methyl analogue, a nonmicelle-forming salt [25].

Photoreduction of keto carboxylic acid derivatives to hydroxy acid derivatives performed with sodium thiosulphate, for instance of methyl benzoylformate to the corresponding mandelate, may be catalyzed by photosensitising micelle incorporating 129 [100]. The redox systems of the type 64/65 [33] are of interest as bielectronic mediators [101, 102]; they can also find application as components of electrochromic memory display devices [36,103] as well as of redox active membranes [104].

Studying properties of cation-exchange membranes, the electrodialysis in the presence of N-dodecylpyridinium bromide, as well as its analogues 10 and 11 was performed ; there was observed that during this process the $p_{Na}^{Ca}$ was decreased and the electric resistance strongly increased [32].

The ylide 130 can be used as an accelerator in the polymerization of styrene [105] and as a radical initiator for homopolymerization of vinyl acetate, with methyl acrylate or methyl methacrylate [106,107], as well as for copolymerization of acrylonitrile with styrene [108].

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