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CYCLIZATION REACTIONS OF QUATERNARY SALTS OF AZAAROMATICS

Wanda Sliwa

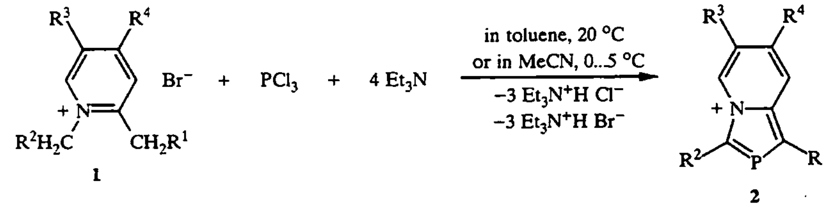
Cyclization reactions of quaternary salts of azaaromatics including inter- and intramolecular condensation as well as radical processes are described.

I. INTRODUCTION

Numerous cyclization reactions of azaaromatic quaternary salts are known [1-10]; they often provide a convenient approach to fused heterocycles. In the continuation of our research concerning azaaromatics [11-14] and their quaternary salts [15-21] we present here chosen examples of cyclization reactions of these compounds. As cycloaddition reactions of azaaromatics cover a large amount of works [22-25], this topic is not included here.

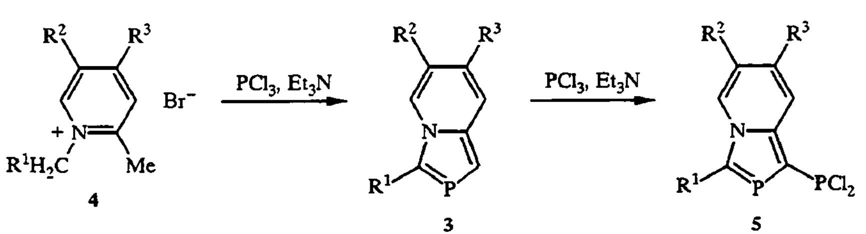
II. INTERMOLECULAR CYCLOCONDENSATION REACTIONS

The [4 + 1] cyclocondensation reaction of 2-alkyl- and 2-aminoazaaromatic salts with suitable phosphorus reagents is a facile synthetic route to a series of annelated azaphospholes with a bridgehead nitrogen atom [1, 26]. The cyclocondensation of 1,2-disubstituted pyridinium bromides (1) with phosphorus trichloride in the presence of triethylamine leads to 2-phosphaindolizines (2). It was observed that the cyclization occurs when both N-methylene and 2-alkyl groups are activated by electron-withdrawing substituents [27, 28].



1, 2 a $R^1 = H$, $R^2 = CN$, $R^3 = H$, $R^4 = Me$; b $R^1 = H$, $R^2 = COOEt$, $R^3 = n\text{-}Bu$, $R^4 = H$; c $R^1 = R^2 = Ph$, $R^3 = R^4 = H$; d $R^1 = 4\text{-}ClC_6H_4$, $R^2 = 4\text{-}NO_2C_6H_4$, $R^3 = R^4 = H$

In order to obtain 1-unsubstituted product (3), an analogous reaction with the use of salt **4** as starting material has been performed [28]. The synthesis of the 1-unsubstituted 2-phosphaindolizine **3** is often accompanied by the formation of 1-dichlorophosphino derivative (5), which is a secondary product arising from the electrophilic substitution of **3** by phosphorus trichloride [29]. When the reaction is carried out in acetonitrile at 0°C, the formation of **5** may be avoided [28].



$R^1 = COOEt$, COPh, $4\text{-}NO_2\text{—}C_6H_4$; R^2, $R^3 = H$, Me, Bu

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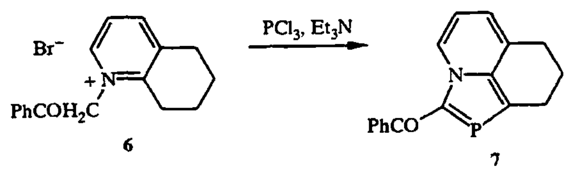
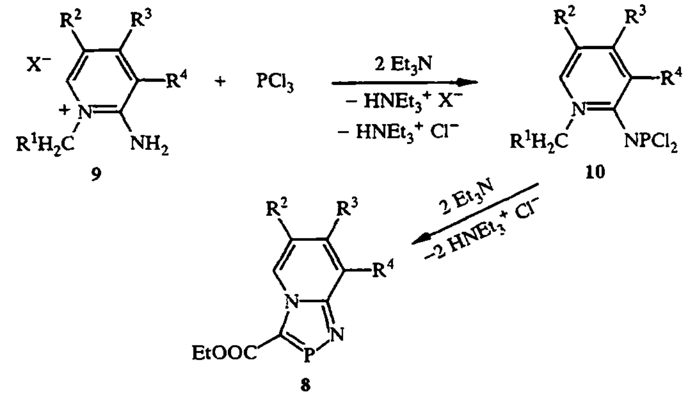
Institute of Chemistry, Pedagogical University, Czestochowa, Poland. Published in Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 23-40, January, 1997. Original article submitted January 31, 1996.

From 5,6,7,8-tetrahydro-1-phenacylquinolinium bromide (**6**) the tricyclic phosphaindolizine derivative **7** is formed [28].



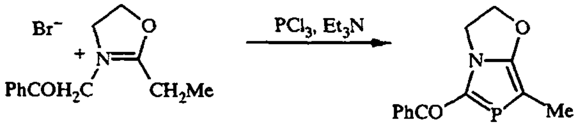
In order to synthesize 3-ethoxycarbonyl-1,4,2-diazaphospholopyridines (**8**), 2-aminopyridinium bromides **9** were treated with phosphorus trichloride and triethylamine; depending on the R^1 substituent, the reaction affords diazaphospholopyridines **8** or stops on the formation of their intermediates, aminodichlorophosphines **10** [30, 31].



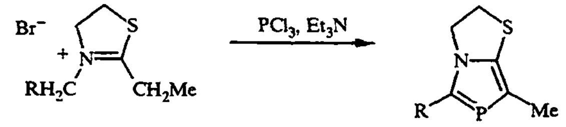
8—10 **a** $R^1 = COOEt$, $R^2 = R^3 = R^4 = H$, $X = Br$; **b** $R^1 = COOEt$, $R^2 = R^4 = H$, $R^3 = Me$, $X = Br$; **c** $R^1 = COOEt$, $R^2 = R^3 = H$, $R^4 = Me$, $X = Br$; **d** $R^1 = COOEt$, $R^2 = Me$, $R^3 = R^4 = H$, $X = Br$; **e** $R^1 = Ph$; $R^2 = R^3 = R^4 = H$, $X = Cl$; **f** $R^1 = 4\text{-}MeC_6H_4$, $R^2 = R^3 = R^4 = H$, $X = Br$

For ring closure, the presence of the electron-withdrawing R^1 substituent, here COOEt, is necessary; then **8a-d** are obtained; however, in the case of R^1 = Ph or 4-MeC_6H_4, the reaction leads only to **10e,f**, respectively [30].

Reactions of this type, proceeding on quaternary salts of heterocycles other than pyridine, should be mentioned here also, for example:

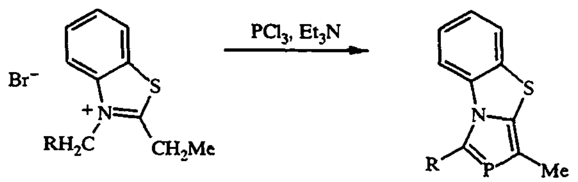


[2, 32]



[2, 33, 34] .

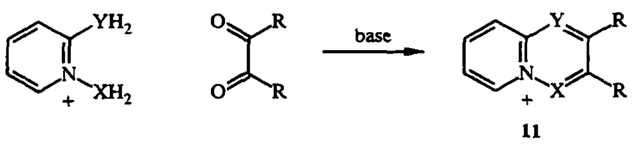
R = 4-MeC_6H_4, COPh, COOEt



[2, 33, 34]

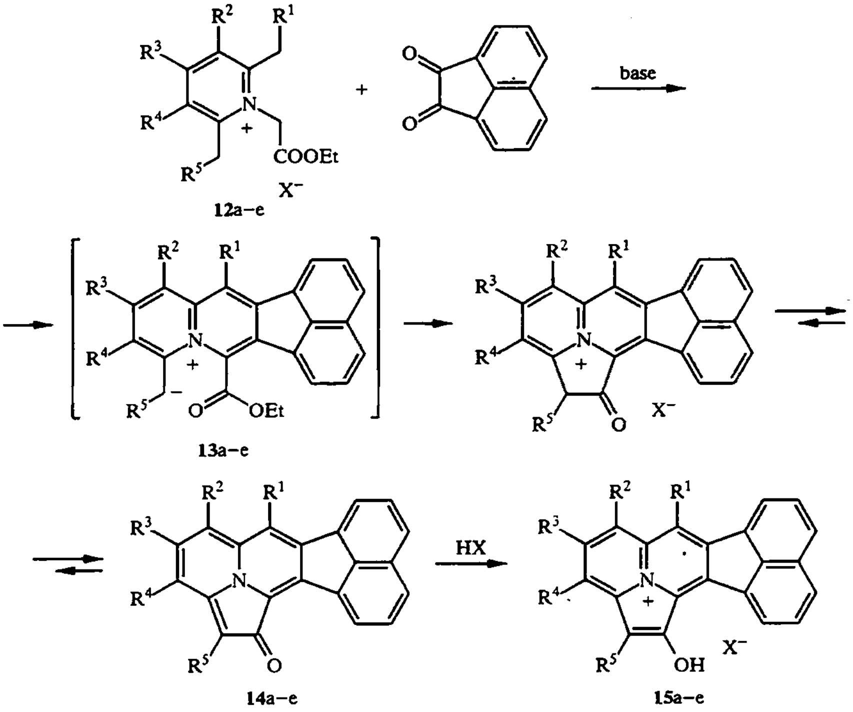
R = CN, COPh, COOEt

Bicyclic systems of the type **11** with bridgehead quaternary nitrogen atom can be easily obtained by the Westphal condensation, i.e., the reaction of 1,2-disubstituted pyridinium salts with 1,2-diketones in the presence of a base [2, 35-37].



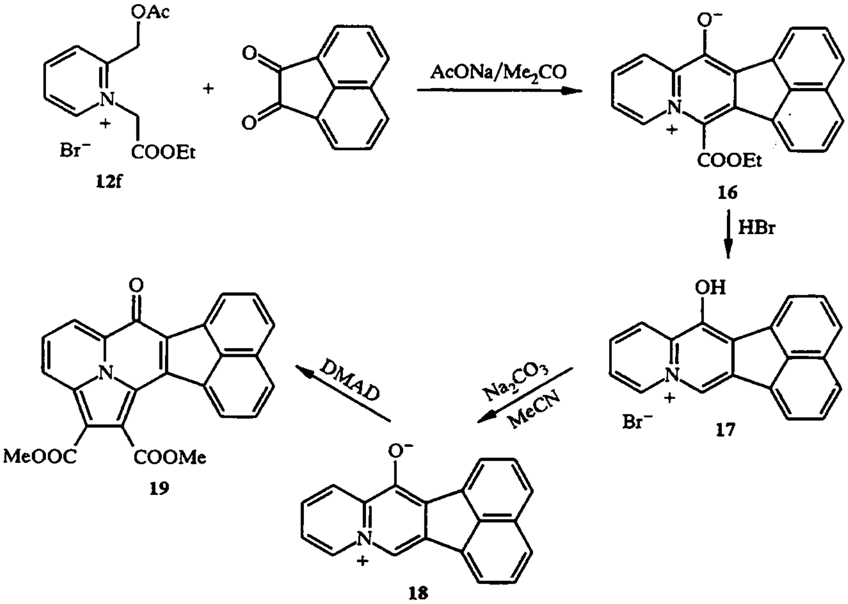
X = C–COOR; Y = C–Alk

The Westphal condensation of pyridinium salts **12a-e** with 1,2-acenaphthenequinone proceeds via zwitterions **13a-e**, undergoing an intramolecular Claisen process to yield cyclazinone derivatives **14a-e** isolated as their hydrobromides **15a-e** [36].



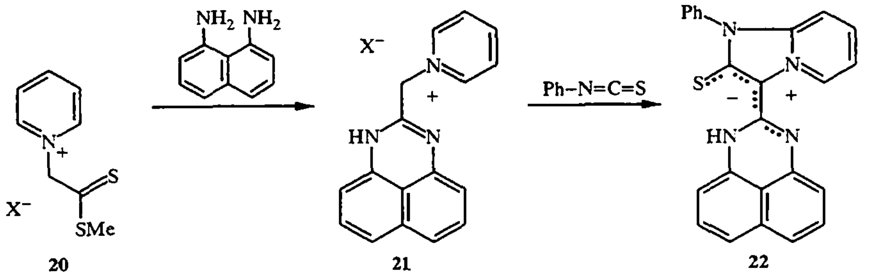
12—15 a $R^1 = R^2 = R^3 = R^4 = R^5 = H$, $X = Br$; b $R^1 = R^2 = H$, $R^3 = Me$, $R^4 = R^5 = H$, $X = Br$;
c $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = R^5 = H$, $X = Br$; d $R^1 = R^2 = R^3 = H$, $R^4 = R^5 = —(CH_2)_3—$, $X = Br$;
e $R^1 = R^2 = —(CH_2)_3—$, $R^3 = H$, $R^4 = R^5 = —(CH_2)_3—$, $X = BF_4$; f $R^1 = OCOMe$,
$R^2 = R^3 = R^4 = R^5 = H$, $X = Br$

The reaction of **12f** with 1,2-acenaphthenequinone affords quinolizinium 1-olate (**16**) converted by 40% hydrobromic acid into **17**. The betaine **18** derived from **17** was submitted to cycloaddition reaction with DMAD resulting in [2.3.3.]cyclazin-6-one **19** [36].



Further examples of Westphal condensation are given in [38].

We should note here also the cyclocondensation of quaternary pyridinium salts **20** with 1,8-diaminonaphthalene resulting in (perimidinylmethyl)-pyridinium salts **21**, converted by treatment with phenyl isothiocyanate into **22** [39].

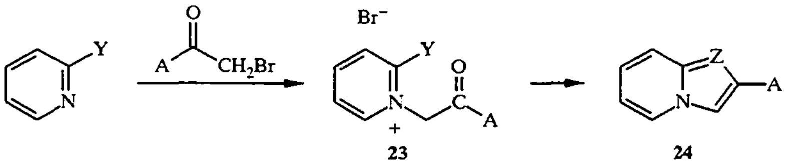


X = I, BF$_4$

III. INTRAMOLECULAR CYCLOCONDENSATION REACTIONS

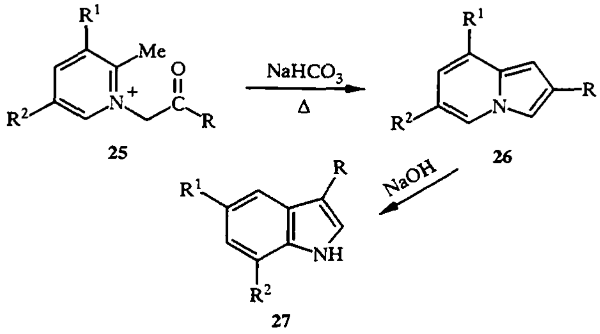
The intramolecular cyclocondensation is another type of cyclization reaction, often used in the syntheses of polyheterocycles.

The reaction of α-picoline or 2-aminopyridine with 1-adamantyl-2-bromomethylketone leads to quaternary salts **23** undergoing the intramolecular cyclocondensation to afford **24a** or **24b**, respectively [40].



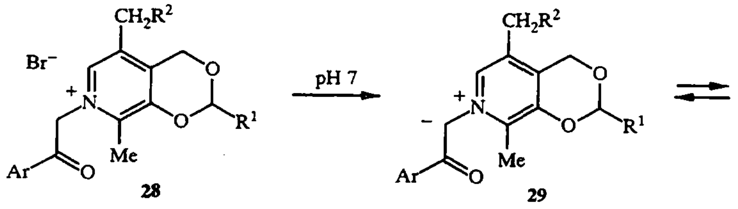
A = adamantyl; 23 a Y = Me, b Y = NH$_2$; 24 a Z = CH, b Z = N

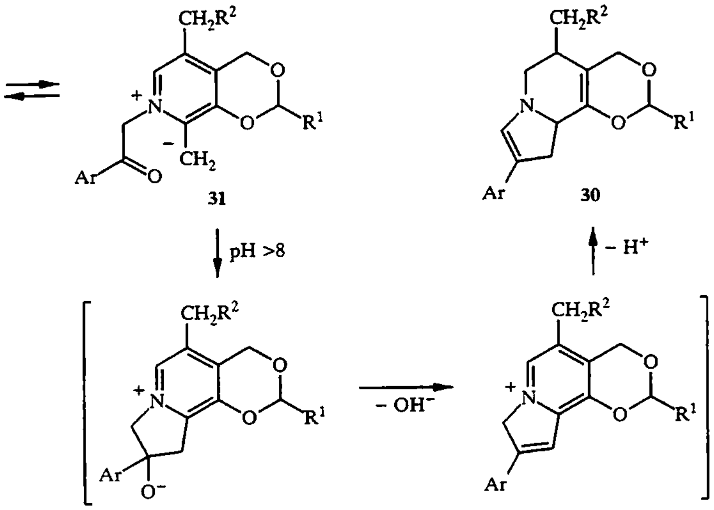
Pyridinium salts **25** were cyclized into indolizines **26** by treatment with NaHCO$_3$. Compounds **26** can be converted by sodium hydroxide into indoles **27** via ring opening and recyclization [41, 42].



R = Me, *t*-Bu, Ph; R^1 = R^2 = H, NO$_2$

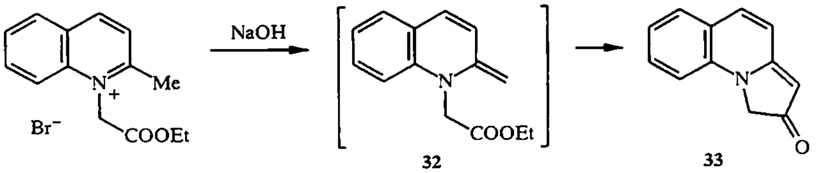
It was observed that quaternary salts **28** at pH ca. 7 (treatment with KHCO$_3$) give ylides **29**, which are stable on storage in air. Systems **28** or **29** at pH 8-10 (treatment with K$_2$CO$_3$) yield 1,3-dioxanoindolizines **30**. The mechanism of this process involves the tautomerization of **29** resulting in zwitterions **31**, which undergo a subsequent aldol condensation [43].



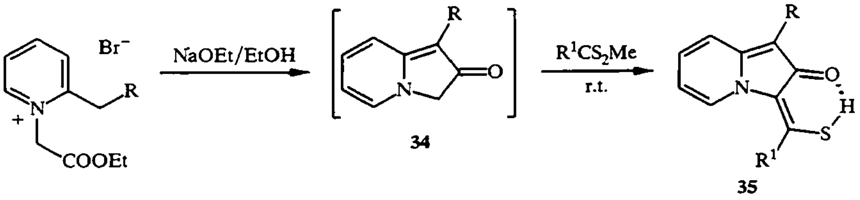


Ar = Ph, 4-BrC$_6$H$_4$; R^1 = H, Me; R^2 = OH, OAc

The reaction of 1-ethoxycarbonylmethyl-2-methylpyridinium bromide with sodium hydroxide in ethanol leads to the formation of enamino ester **32**, rearranging into pyrroloquinolone **33** [44].

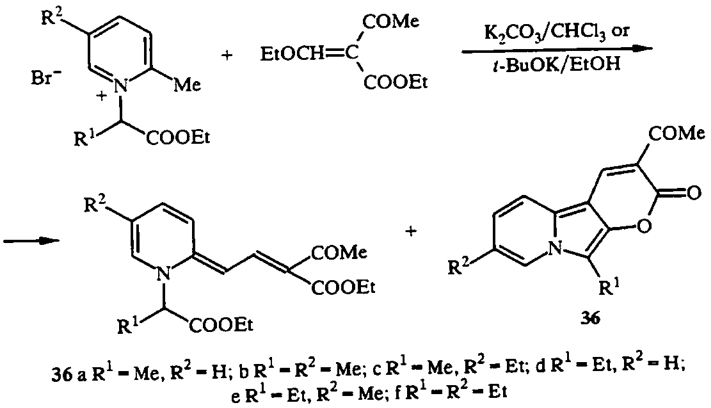


We should mention here also the reaction of derivatives of 1-ethoxycarbonylmethylpyridinium bromide with sodium ethoxide resulting in indolizinones **34**, which when treated *in situ* with methyl dithioacetate or methyl dithiobenzoate afford smoothly mercaptomethyleneindolizinones **35** [45].



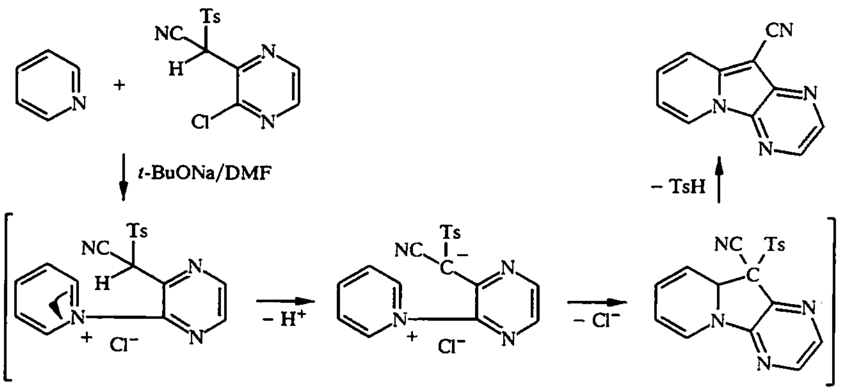
34, **35** a R = R^1 = Me; b R = Ph, R^1 = Me; c R = 4-ClC$_6$H$_4$, R^1 = Me; d R = Me, R^1 = Ph;
e R = R^1 = Ph; f R = 4-ClC$_6$H$_4$, R^1 = Ph

Pyranoindolizinones (**36**) are formed as minor products in the process shown below; the mechanism of this reaction is given [46].

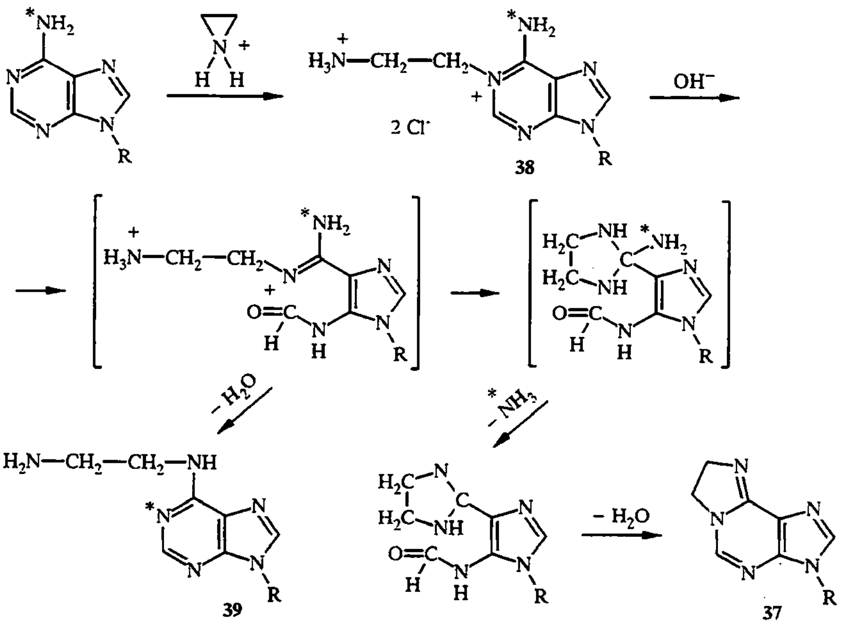


36 a R^1 = Me, R^2 = H; b R^1 = R^2 = Me; c R^1 = Me, R^2 = Et; d R^1 = Et, R^2 = H;
e R^1 = Et, R^2 = Me; f R^1 = R^2 = Et

The following cyclization has been performed [47].



The formation of the tricyclic ethanoadenosine **37** was observed in the Dimroth rearrangement of 1-(2-aminoethyl)adenosine **38** leading to N^6-(2-aminoethyl)adenosine **39** [48, 49]. The proposed mechanism of this reaction is given below.



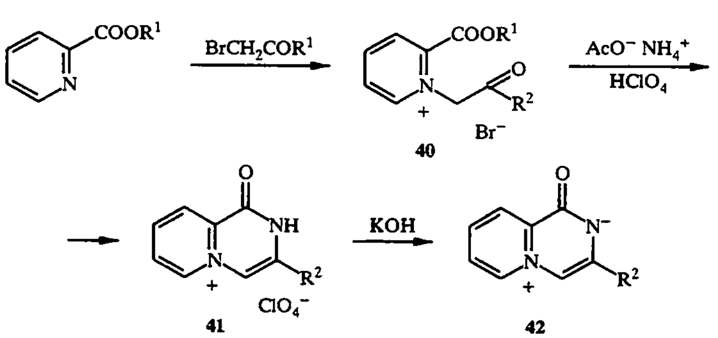
38

39

37

R = *D*-Ribose; N^* = labeled ^{15}N

Pyridinium salts **40** easily undergo ring closure by ammonium acetate to give oxopyridopyrazinium salts **41**. These compounds were converted into stable zwitterionic systems **42** [50].



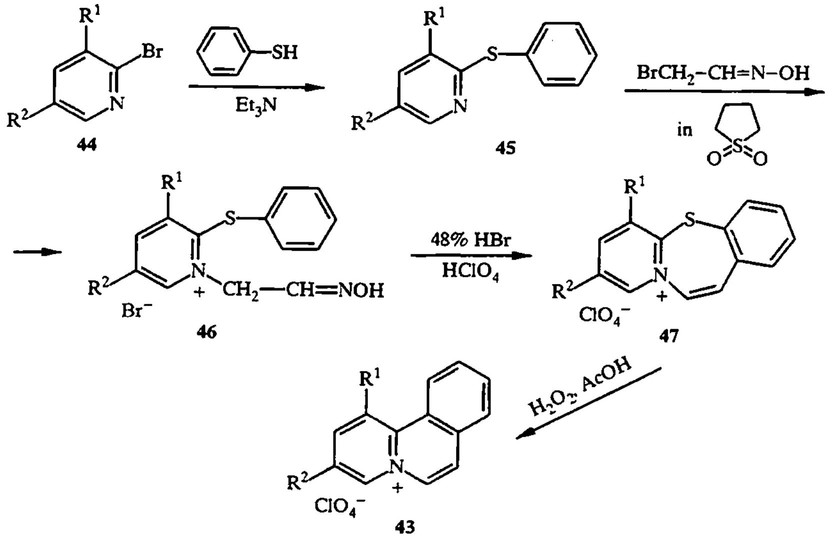
40

41

42

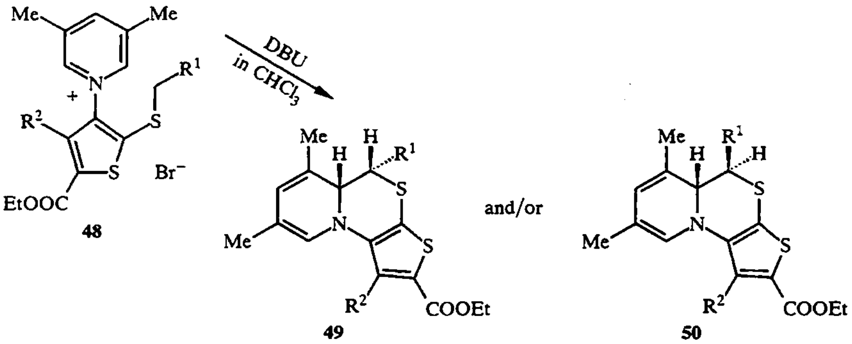
40—42 a R^1 = Et, R^2 = *t*-Bu; b R^1 = Et, R^2 = C_6H_5; c R^1 = H, R^2 = 4-MeC_6H_4; d R^1 = Et, R^2 = 4-BrC_6H_4; e R^1 = H, R^2 = 4-$NO_2C_6H_4$

In order to obtain benzo[*a*]quinolizinium salts **43**, 2-bromopicolines **44** were treated with thiophenol in the presence of triethylamine. The formed 2-(phenylthio)picolines **45** reacted with bromoacetaldehyde oxime in sulfolane to give the quaternary salts **46**. The cyclization of **46** with 48% HBr afforded the thiazepinium salts **47**, which by treatment with 30% H_2O_2 in acetic acid underwent oxidative sulfur extrusion resulting in **43** [51].



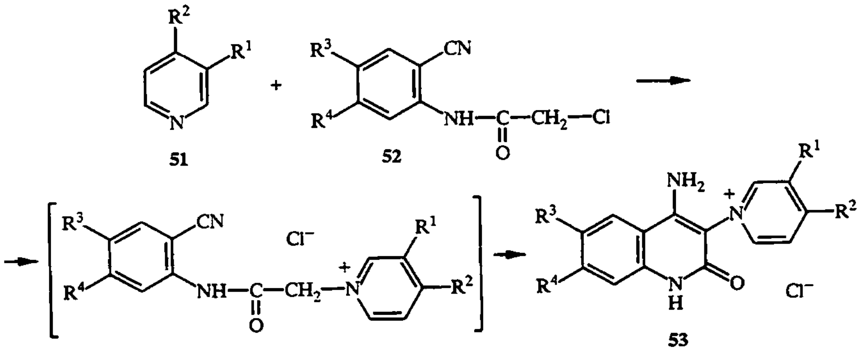
44—48 a R^1 = Me, R^2 = H; b R^1 = H, R^2 = Me

Pyridiniothiophenes **48** submitted to dehydrobromination with DBU afford dihydropyridothienothiazines **49** and/or **50** [52].



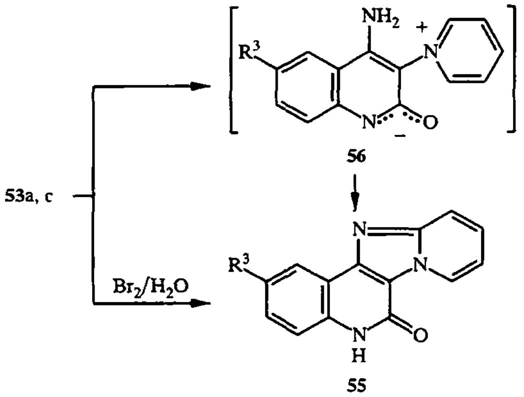
48—50 a R^1 = CN, R^2 = Me; b R^1 = CN, R^2 = Ph; c R^1 = COOEt, R^2 = Me; d R^1 = COOEt, R^2 = Ph

The reaction of pyridines **51** with chloroacetylanthranilonitriles **52** leads to pyridinioquinolinone chlorides **53**; the intermediate pyridinium salts **54** are isolable; however, their isolation is not necessary [53].

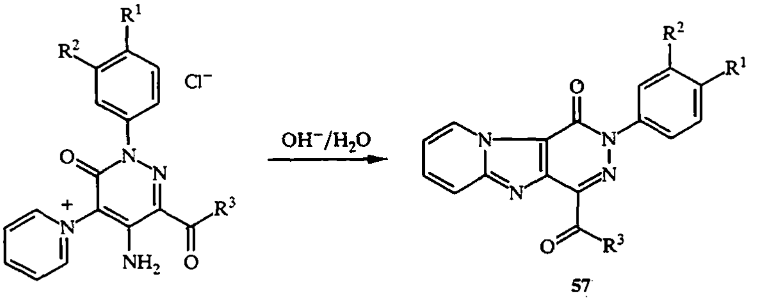


53, 54 a R^1 = R^2 = R^3 = R^4 = H; b R^1 = R^2 = H, R^3 = R^4 = OMe; c R^1 = R^2 = H, R^3 = NO_2, R^4 = H; d R^1 = $CONH_2$, R^2 = R^3 = R^4 = H; e R^1 = H, R^2 = Me, R^3 = R^4 = H; f R^1 = H, R^2 = NH_2, R^3 = R^4 = H; g R^1 = H, R^2 = Me, R^3 = NO_2, R^4 = H

The deprotonation of **53a,c** with ~2 N NaOH yields pyridoimidazoquinolones **55**; the reaction proceeds via pyridinioquinolinolates **56**, immediately undergoing an intramolecular addition of amino group to the pyridinium ring, followed by the dehydrogenation with air oxygen [53, 54]. Compound **55** may also be obtained from **53** by cyclooxidation with bromine [53].



The following reactions involving nucleophilic addition of the amino group to the pyridinium ring and subsequent dehydration lead to stable products **57** [3]:



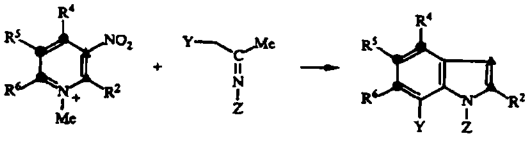
57 a $R^1 = H, R^2 = Me, R^3 = NH_2$; b $R^1 = NO_2, R^2 = H, R^3 = NH_2$; c $R^1 = R^2 = H, R^3 =$ morpholinyl

IV. OTHER CYCLIZATION REACTIONS

The reactions of nitropyridinium salts with ketimines or with a mixture of ketones and amines resulting in polyalkylindoles also belong to cyclization processes. It is a convenient approach to these heterocycles, difficult to obtain by other routes. The process occurs under mild conditions, and the products are easily isolated [55].

The reaction proceeds via the scission of the pyridinium cation at the $C_{(3)}—C_{(4)}$ bond; the $C_{(2)}—C_{(3)}$ moiety of the pyridinium cation is involved in the construction of the pyrrole ring, and the $C_{(4)}—C_{(5)}—C_{(6)}$ moiety forms the benzene ring [55-60].

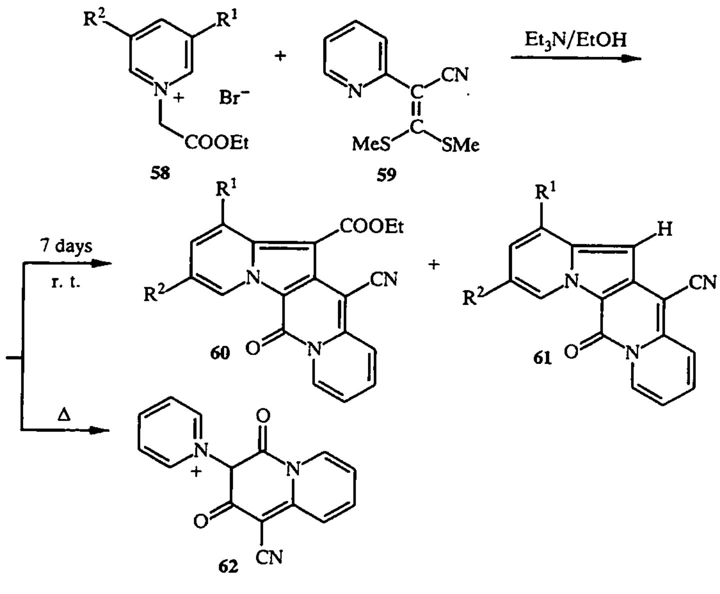
For example,



Y = H, Me; Z = Me; R^2 = H, Me, Et, *i*-Pr; R^4 = H, Me, Et, Pr, *i*-Pr, *t*-Bu, Ph;
R^5 = H, Me, *i*-Pr; R^6 = H, Me, Et, *i*-Pr

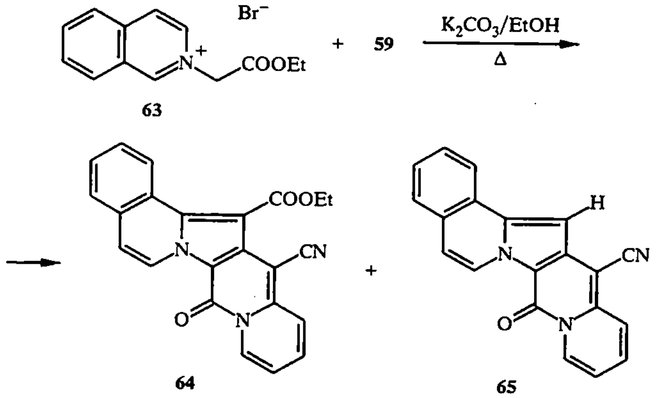
It was established that the quaternary salts bearing bulky substituents such as *i*-Pr or *t*-Bu in positions 2, 4, or 6 also undergo this process; the bulkiness of substituents does not influence significantly the reaction rate [60]. The most convenient are bipolar aprotic solvents such as DMF or DMSO; in nonpolar or protic solvents the reaction is slow [61].

The reaction of pyridinium bromides **58** with pyridylketene dithioacetal **59** [62-65] yielding indolizinoquinolizines **60** and **61** is another example of cyclization of azaaromatic quaternary salts [66, 67]. When the reaction of **58a** and **59** was carried out in refluxing ethanol, only the ylide **62** was formed. The mechanism of the above processes involving double cyclization was proposed.

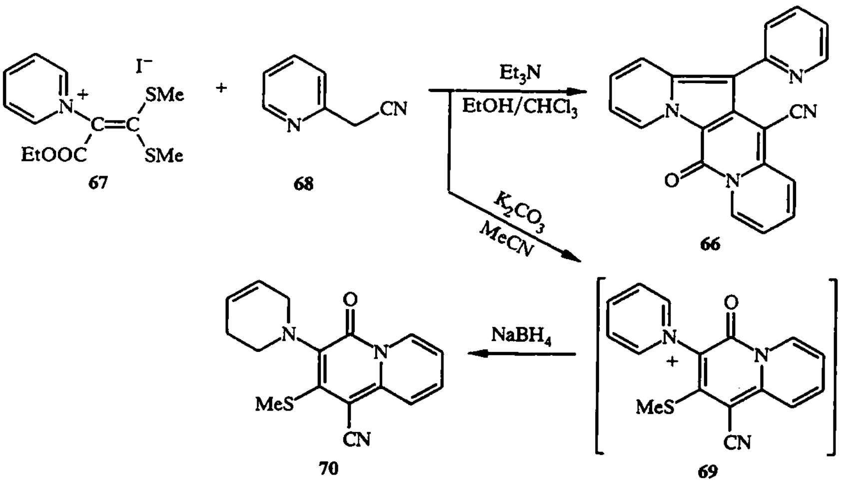


60, 61 a $R^1 = R^2 = H$; b $R^1 = R^2 = Me$; c $R^1 = H$, $R^2 = Me$

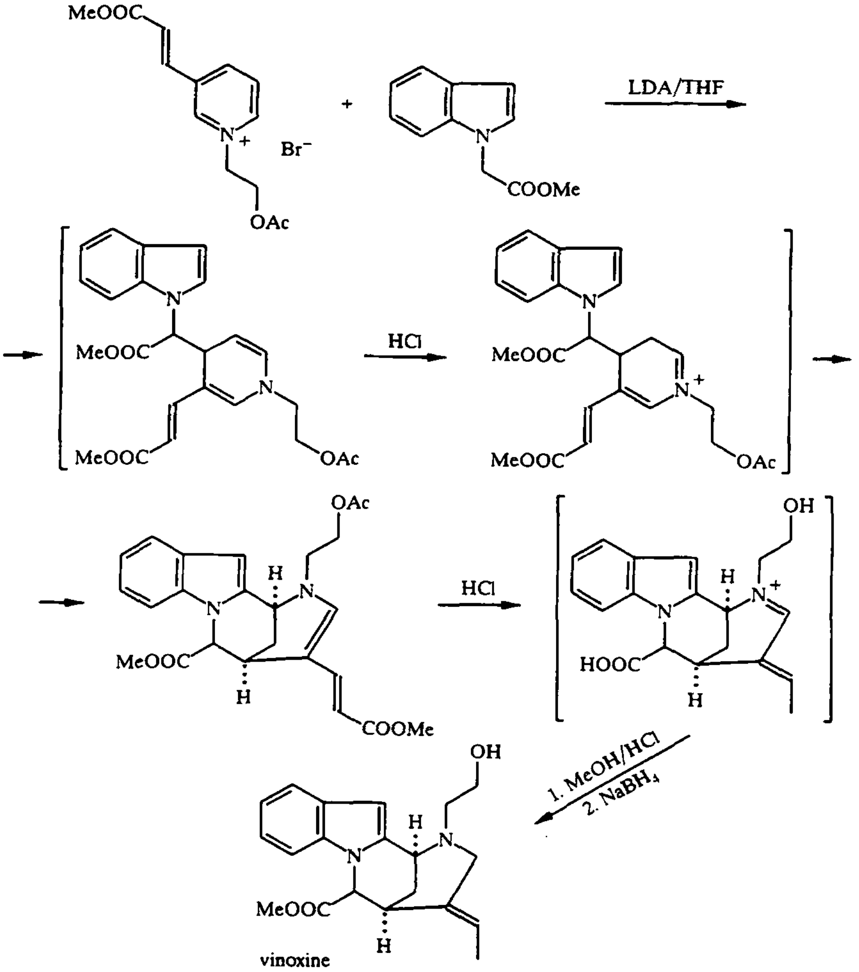
The reaction of isoquinolinium bromide **63** with **59** in the presence of K_2CO_3 in refluxing ethanol affords benzindolizinoquinolizines **64** and **65** [66].



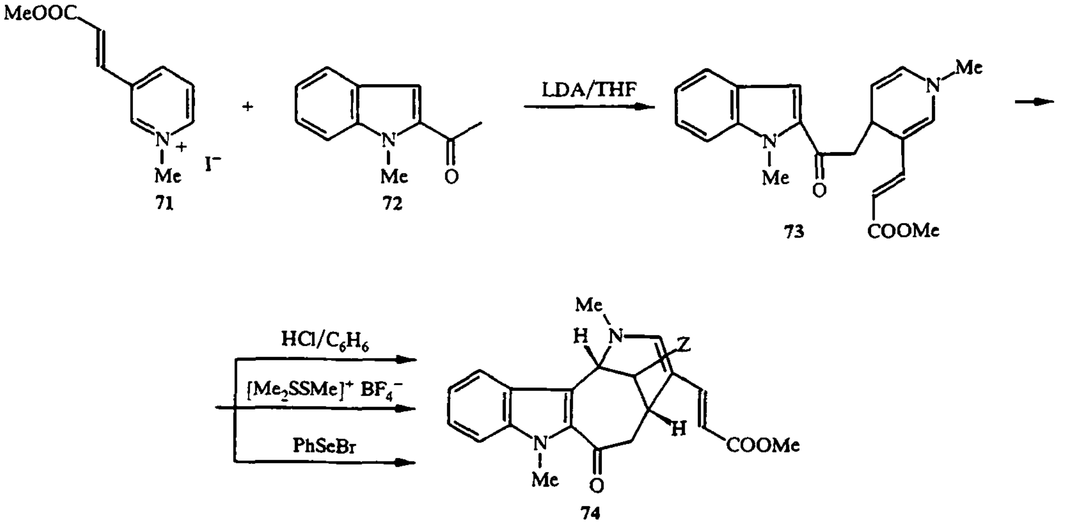
Another approach to indolizinoquinolizines **66** involves the treatment of pyridiniumketene dithioacetal **67** with pyridylacetonitrile **68** in the presence of triethylamine in EtOH/CHCl$_3$. When the reaction of **67** and **68** was carried out in the presence of K_2CO_3 in MeCN, unstable pyridinium oxoindolizine **69** was formed, which by reduction with NaBH$_4$ yielded tetrahydropyridylquinolizine **70** [66].



The nucleophilic addition of stabilized carbon nucleophiles to N-alkylpyridinium salts is used in the synthesis of bridged indole alkaloids [4, 68, 69]. The first total synthesis of the alkaloid vinoxine, using this procedure, is shown below [70-72].



The reaction of the pyridinium salt **71** with enolate derived from acetylindole **72** affords 1,4-dihydropyridine **73**. The treatment of **73** with HCl in benzene solution gives tetracyclic product **74a**, and with [Me_2SSMe]BF_4 or PhSeBr compounds **74b** or **74c**, respectively, are formed [73, 74]. Further treatment of **72c** was useful in the synthesis of methylervitsine [73].

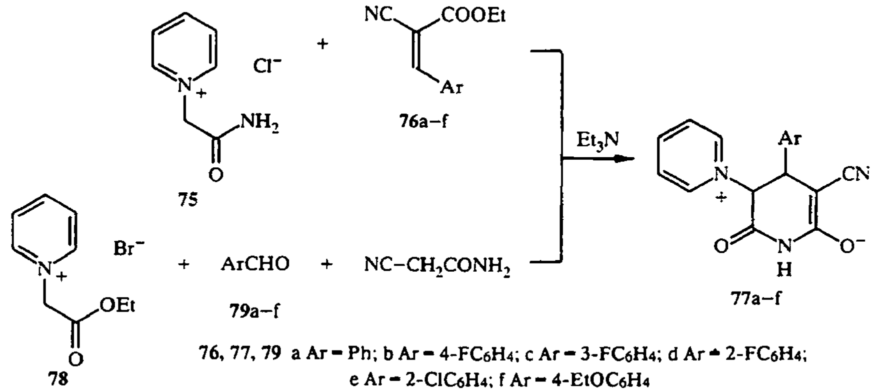


74a Z = H, b Z = SMe, c Z = SePh

Similar reactions of pyridinium salts with other nucleophiles have been studied [75-77].

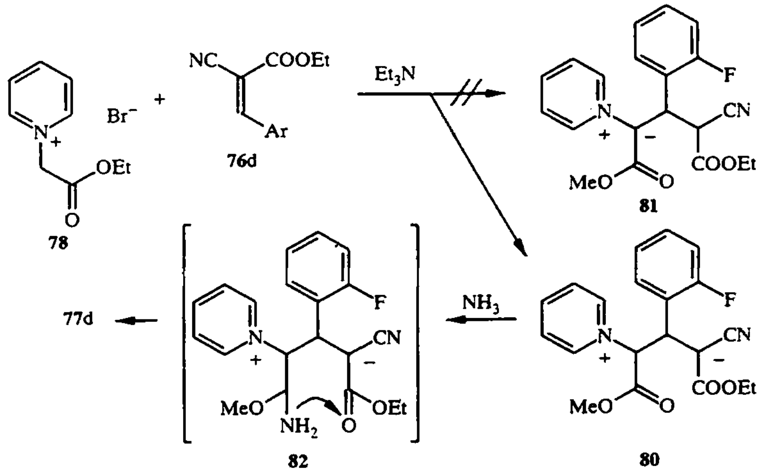
V. CYCLIZATION REACTIONS LEADING TO OLATE INNER SALTS

Reactions of pyridinium salts leading to olate inner salts also deserve attention; some examples will be described here. The reaction of N-carbamoylmethylpyridinium chloride **75** with unsaturated nitriles **76a-f** leads to olate inner salts **77a-f**; they can also be obtained by condensation of N-ethoxycarbonylmethylpyridinium bromide **78** with aromatic aldehydes **79a-f** and cyanoacetamide. Reactions are performed in the presence of triethylamine; pyridinium ylides which are intermediates in these processes undergo Michael addition [78].



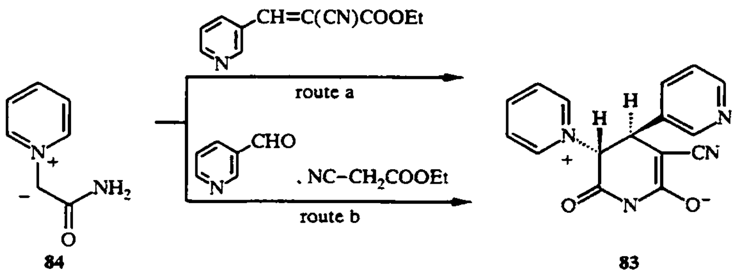
76, 77, 79 a Ar = Ph; b Ar = 4-FC_6H_4; c Ar = 3-FC_6H_4; d Ar = 2-FC_6H_4; e Ar = 2-ClC_6H_4; f Ar = 4-$EtOC_6H_4$

It was established that the reaction of **78** and **76d** in the presence of Et_3N leads to the Michael adduct **80**, i.e., to the pyridinium 1,4-ylide, and not to the ylide **81**. The treatment of **80** with ammonia affords olate **77d** via the intermediate **82**.

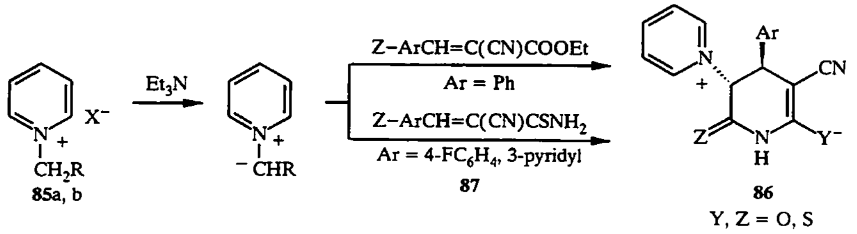


The results of conformational analysis have shown that Michael adduct **80** and olates **77** are formed in a stereoselective way [78].

The pyridinium olate **83** was obtained from pyridinium ylide **84** by two routes (*a*) and (*b*) given below; route (*b*) involving a three-component condensation proved to be a more convenient one [79].

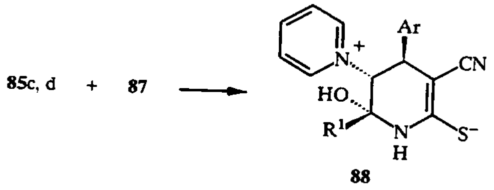


Two following reactions of pyridinium salts **85a,b** leading regio- and stereoselectively to inner salts **86** have been performed [80, 81]:



85 a R = COOMe, X = Br; b R = CONH$_2$, X = Cl; c COMe, X = Br; d COPh, X = Br

When **85c,d** were treated with **87**, the inner salts **88** were obtained [80].

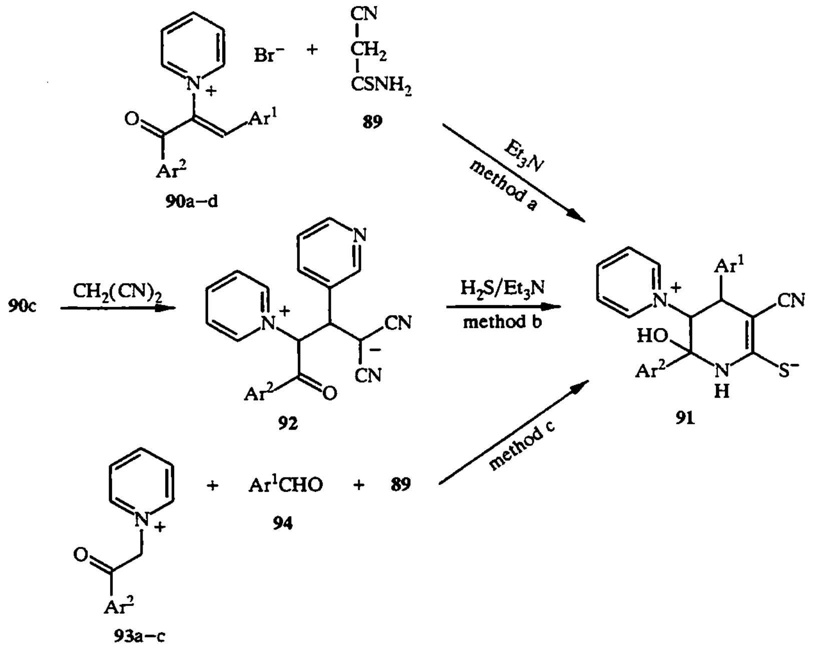


85 c R^1 = Me; d R^1 = Ph

Styrylpyridinium salts where the double bond is activated by the presence of pyridinium cation undergo nucleophilic addition to amines, thioles, and CH-acids; they also have the properties of highly stereoselective dienophiles. Reactions of substituted 1-styrylpyridinium salts with cyanothioacetamide **89** were studied.

When 1-styrylpyridinium bromides **90** react with **89** in ethanol in the presence of triethylamine, (method *a*), thiolate inner salts **91** are formed via Michael addition. The treatment of the ylide **92** (obtained from **90c** and malononitrile) with hydrogen sulfide in the presence of Et$_3$N results also in **91c** (method *b*) [82].

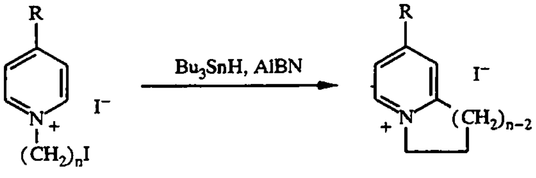
It was found that **91** can be obtained in a more convenient procedure, without the prior isolation of 1-styrylpyridinium salts, simply by condensing pyridinium salts **93a-c**, and aldehydes **94** and **89** (method *c*); the reaction proceeds in a highly stereoselective manner [82].



90—94 a Ar^1 = 4-FC$_6$H$_4$, Ar^2 = Ph; b Ar^1 = 4-BrC$_6$H$_4$, Ar^2 = Ph; c Ar^1 = 3-C$_5$H$_4$N, Ar^2 = Ph;
d Ar^1 = 4-FC$_6$H$_4$; Ar^2 = 4-BrC$_6$H$_4$

VI. RADICAL CYCLIZATION REACTIONS

Intramolecular radical-induced substitution of pyridinium salts **95** resulting in bicyclic compounds **96** proceeds with the use of tributylstannyl radicals, in MeCN/THF [83, 84].

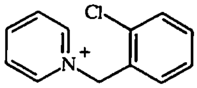


95 **96**

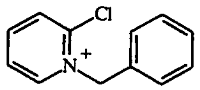
n = 3, 4, 5; R = H, Me

These reactions are of interest for alkaloid syntheses. It is worth noting that in the isolation of products chromatography is not necessary, due to the use of the lipophilic tributyltin hydride as radical source.

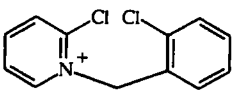
The intramolecular photocyclization reactions of the quaternary pyridinium ions **97-99** have been investigated [5].



97



98

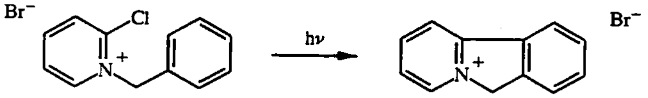


99

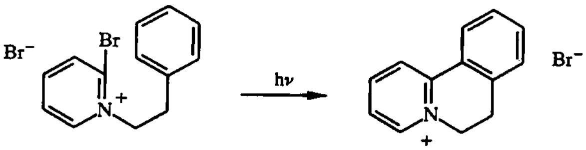
The π-electron density, atom self-polarizability values, as well as free valences on each atom of **97**, **98**, and **99** have been calculated using a simple Hückel method. The photocyclization occurs via radical intermediates by breaking a C—Cl bond.

The C—Cl bond breaking is facilitated by π-complex formation between chlorine atom and the π-electrons of the neighboring ring in the triplet state. When the π-complex is strong, the C—Cl bond breaking is easier, and the photocyclization rate increases [5].

The following photocyclization reactions have been performed:

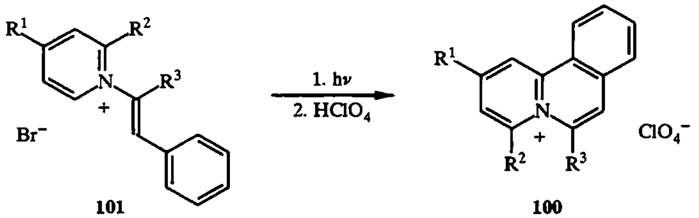


[85]



[86]

Benzo[*a*]quinolizinium perchlorates (**100**) have been obtained by photocyclization of the appropriate N-styrylpyridinium bromides (**101**) in ethanol in the presence of iodine (λ > 280 nm) [51].



101 **100**

100, 101 a R^1 = Me, R^2 = R^3 = H; b R^1 = R^3 = H, R^2 = Me; c R^1 = R^2 = H, R^3 = Me

VII. CONCLUSION

Cyclization reactions of quaternary salts of azaaromatics are a convenient approach to heteropolycycles containing one or more nitrogen atoms. In view of the interesting properties of these compounds, for example, their use as biologically active species, dyes, or redox systems, promising in the construction of electronic devices, their reactions involving cyclization processes deserve attention.

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