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DIAZAPYRENES.* (REVIEW)

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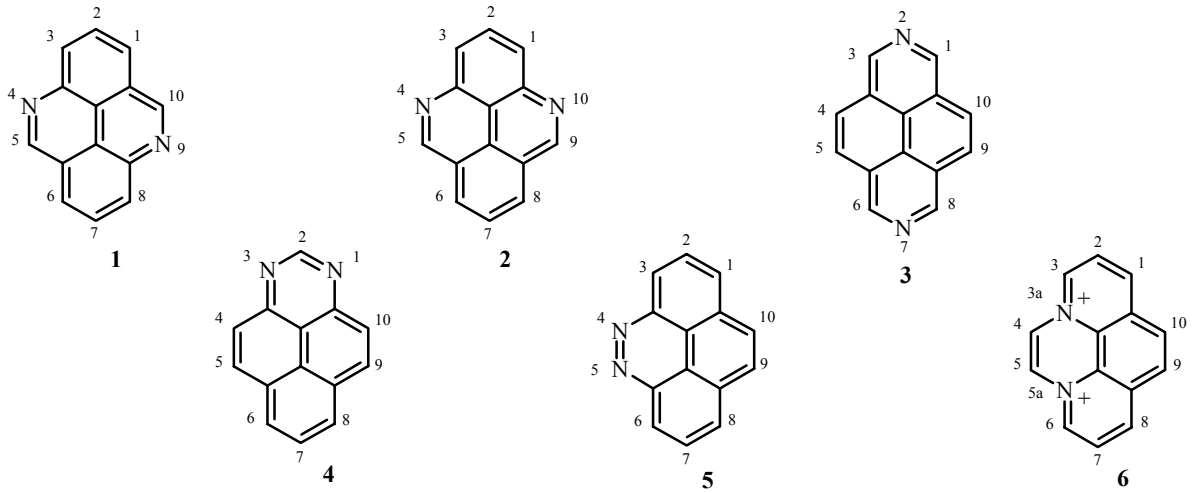
Published data on methods for the synthesis of isomeric diazapyrenes and their properties are reviewed.

Keywords: diazapyrenes, diazapyrenium cations.

Diazapyrenes represent a potentially numerous but not very well studied class of heteroaromatic compound. The existence of 15 isomeric bases of this type differing in the mutual arrangement of the nitrogen atoms around the pyrene ring and also 20 monocations and six dications with a bridging nitrogen atom is theoretically possible. Of all these systems at present only the 4,9- (**1**), 4,10- (**2**), 2,7- (**3**), 1,3- (**4**) and 4,5-diazapyrenes (**5**) and also the 3a,5a-diazoniapyrene dication (**6**) are known:



The interest in diazapyrenes is due not only to general theoretical considerations (aromaticity, the mechanism of electrophilic substitution, the stability of the radical-ions, etc.) but also to applied considerations. Recently the intercalatory characteristics of the derivatives **1** and **3** have been actively studied. 2,7-Diazapyrene cations were inserted into the double helix of DNA and led to its effective photocleavage [1, 2]. A series of oligodeoxynucleotides containing 2,7-diazapyrene [3] and new agents for the selective alkylation of DNA [4] were obtained. Papers [5-8] were devoted to study of the mechanism of intercalation. There have also been reports on the analgesic activity [9] and the semiconducting [10] and photophysical [11] characteristics of the derivatives **3**; dispersants for pigments in nonaqueous media have been patented [12], and a novel luminescent material with high sensitivity to oxygen has been produced [13].

* Dedicated to the 65th birthday of our tutor Prof. A. F. Pozharskii.

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The most recently discovered intercalators include the derivatives **1** [14, 15]. Their recently discovered anticancer activity is in fact explained by this property.

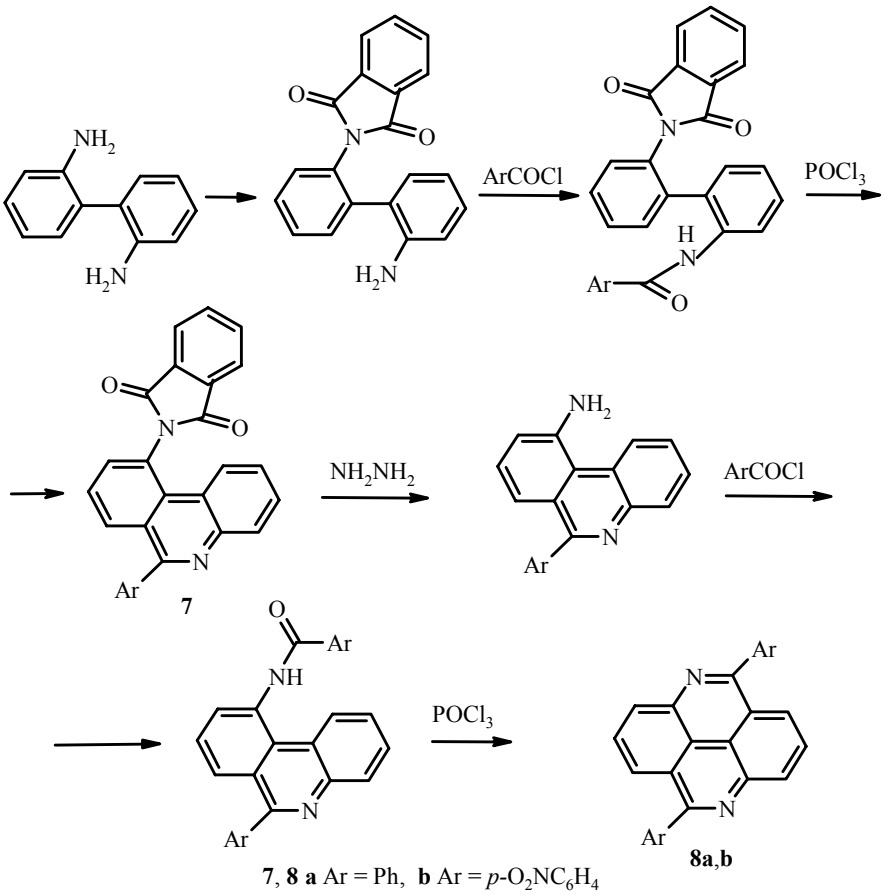
Further interest in polynuclear systems containing diazapyrenes arises from the development of supramolecular chemistry. For example, a molecular switch modelled on the 2,7-diazapyrenium cation was recently proposed [19].

The present review represents the first attempt to summarize published data on methods for the synthesis of compounds **1-6** and their derivatives and properties. It uses the now universally accepted substitutive aza nomenclature [20], although different names were used for these compounds in the early papers.

1. SYNTHESIS

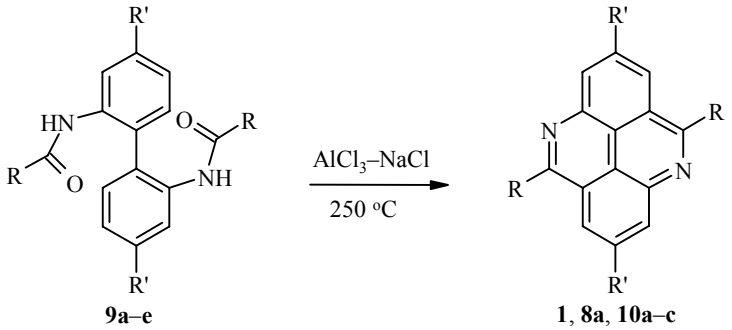
1.1. 4,9-Diazapyrenes

The first directed synthesis of 4,9-diazapyrenes appeared in 1952, when the 5,10-diaryl derivatives **8a**,**b** were obtained from 2,2'-diaminobiphenyl by a multistage scheme [21].



7, **8** **a** Ar = Ph, **b** Ar = *p*-$O_2NC_6H_4$

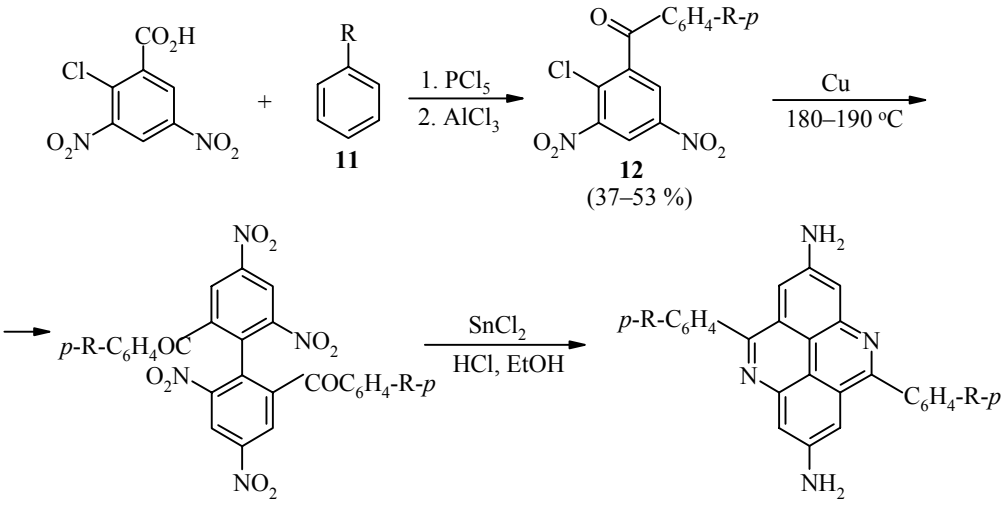
The key stages of cyclization leading to compounds **7** and **8** were realized by boiling (16 h) the respective substrate with phosphorus oxychloride in nitrobenzene. It was subsequently possible to combine these stages by fusion of the respective diamides with an $AlCl_3$–NaCl mixture at 250°C. Thus, the unsubstituted compound (**1**), its 5,10- and 2,7-dialkyl derivatives **10a-c** [22-25], and also 5,10-diphenyl-4,9-diazapyrene **8a** [26] were obtained from the 2,2'-diacylaminobiphenyls **9a-e**.



9a–e **1**, **8a**, **10a–c**

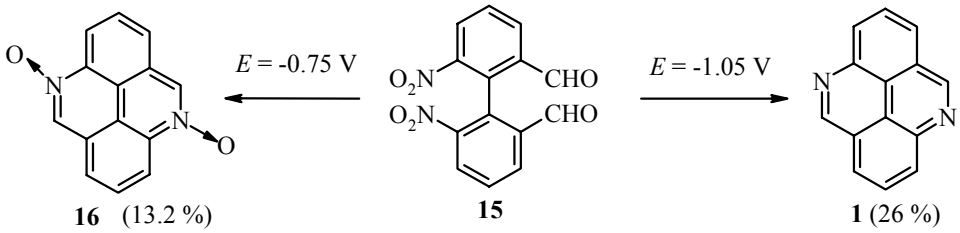
1, **9a** R = R' = H; **9b**, **10a** R = Me, R' = H; **9c**, **10b** R = H, R' = Me; **9d**, **10c** R = Et, R' = H; **8a**, **9e** R = Ph, R' = H

2,7-Diamino-4,9-diazapyrenes **14** were synthesized according to the following scheme [21]:



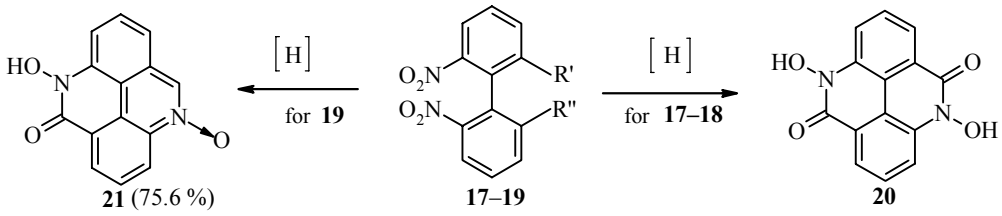
The ketones **12** were obtained by Friedel–Crafts acylation of compounds **11** with 2-chloro-3,5-dinitrobenzoyl chloride. The key stage – the synthesis of 2,2'-diaroyl-4,4',6,6'-tetranitrobiphenyls (**13**) by the Ullmann method – was modified by the authors [21] and gave good yields.

The electrochemical reduction of 6,6'-diformyl-2,2'-dinitrobiphenyl (**15**) gives a small yield of 4,9-diazapyrene **1** or its N,N'-dioxide **16**, depending on the conditions [27]:



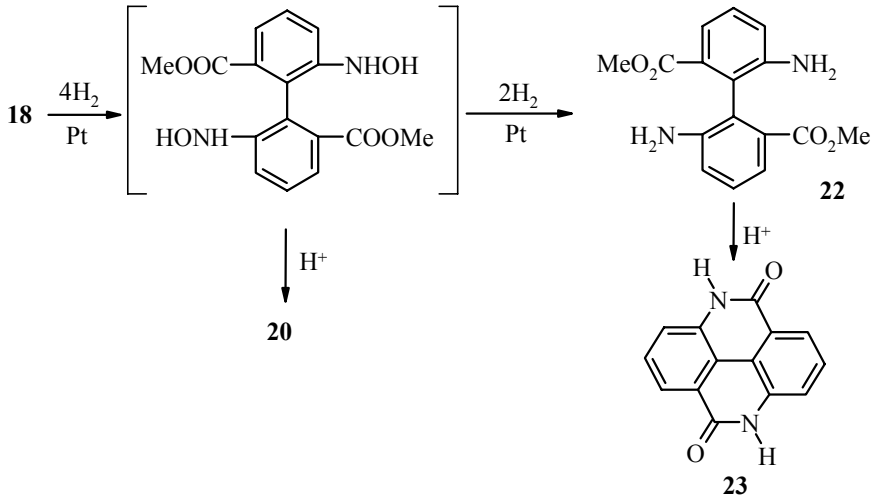
16 (13.2 %) **15** **1** (26 %)

Electrolytic reduction of the biphenyls **17-19** gave the N-hydroxy derivatives of 4,9-diazapyrene **20** and **21** [27]:

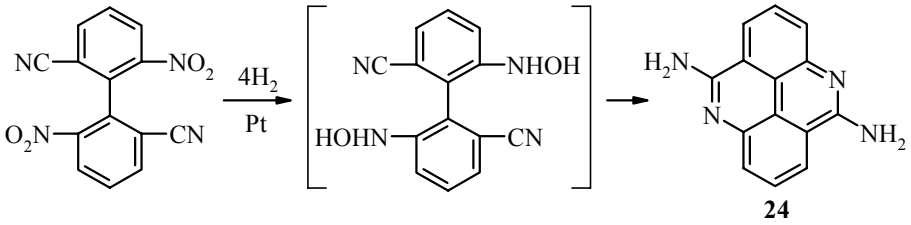


17 R' = R" = CO_2H **18** R' = R" = CO_2Me **19** R' = CHO, R" = CO_2H

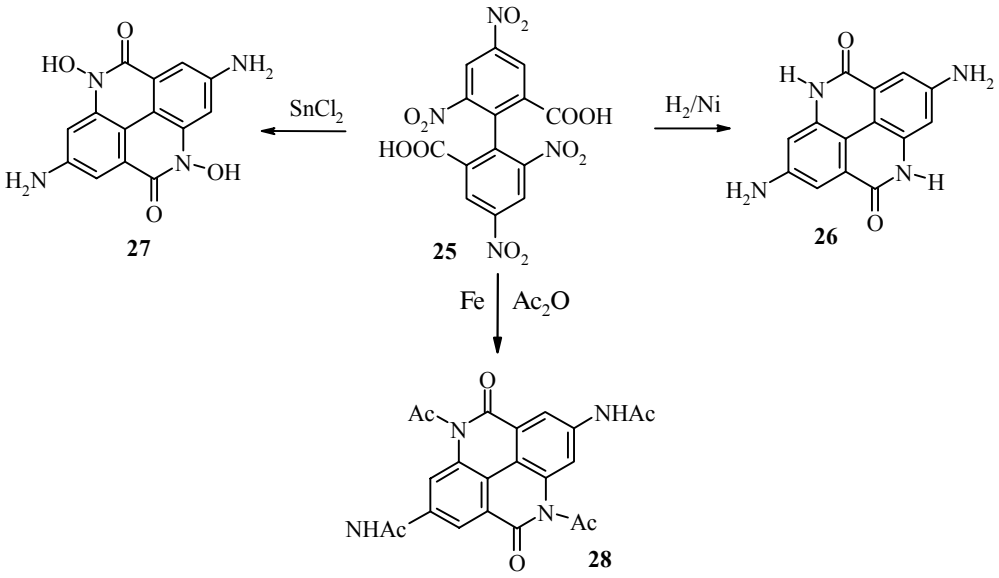
The dihydroxamic acid **20** was also obtained by reduction of the biphenyl **17** with zinc and ammonium chloride in ethanol [28] and also by catalytic hydrogenation of the diester **18** in an acidic medium; in the absence of the acid the reduction leads to 2,2'-diamino-6,6'-dimethoxycarboxylbiphenyl **22**. The latter readily undergoes cyclization to 4,5,9,10-tetrahydro-4,9-diazapyrene (**23**) when heated with mineral acid [29]:



5,10-Diamino-4,9-diazapyrene (**24**) was obtained from 2,2'-dinitro-6,6'-dicyanobiphenyl under the same conditions [28].

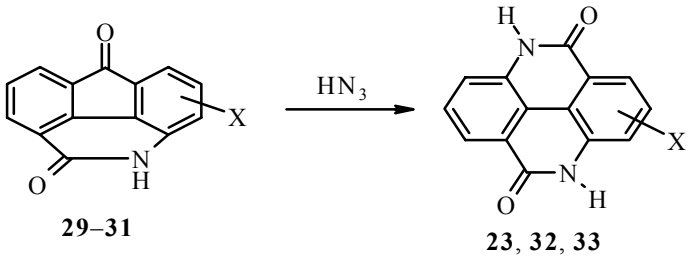


A method was proposed for the synthesis of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (**26**) and its 4,9-dihydroxy derivative **27** from 4,4',6,6'-tetranitrodiphenic acid (**25**), which was obtained with a yield of up to 90% by the nitration of diphenic acid [30]. Christie and Kenner [31] reduced compound **25** with stannous chloride and erroneously assigned the product the structure of **26**. Half a century later Dokunikhin and coworkers established that the compound was in fact the N,N'-dihydroxide **27** [32].



The diamine **26** was obtained by catalytic reduction of **25** [30]; the tetraacetyl derivative of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene **28** was obtained by the action of iron in acetic anhydride [30].

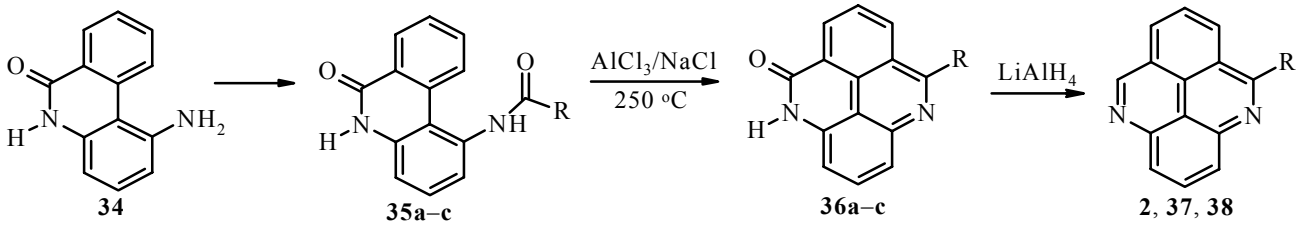
It was reported that compound **23** and its 1- and 3-nitro derivatives **32** and **33** can be obtained from compounds **29-31** by the Schmidt reaction [33].



23, **29** X = H; **30**, **32** X = 1-NO_2; **31**, **33** X = 3-NO_2

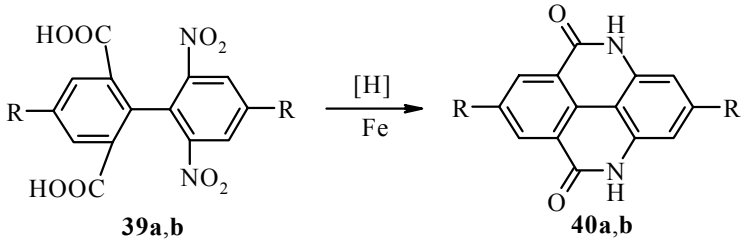
1.2. 4,10-Diazapyrenes

1-Aminophenanthridone **34** became the starting compound for the synthesis of 4,10-diazapyrene **2** and its 5-substituted derivatives **37** and **38** [34]. The amides **35a-c** were obtained from it, and their fusion with an ACl_3–NaCl mixture led to the 5-oxo-4,5-dihydro-4,10-diazapyrenes **36a-c**. Reduction of the latter with lithium aluminum hydride gave the diazapyrenes **2**, **37**, and **38** with yields of 81-92%.



2, **35a**, **36a** R = H; **35b**, **36b**, **37** R = Me, **35c**, **36c**, **38** R = Ph

The reduction of 2',6'-dinitro-2,6-dicarboxybiphenyls **39** is accompanied by cyclization with the formation of 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrenes **40a**,**b** [35]:



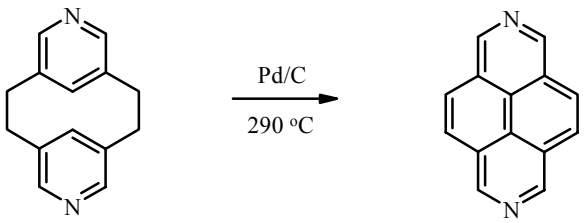
39a,**b** **40a**,**b**

39, **40 a** R = H, **39 b** R = NO_2; **40 b** R = NH_2

The bisdiazonium salt formed from the diamine **40b** was reduced with sodium hypophosphite in an acidic medium to compound **40a**.

1.3. 2,7-Diazapyrenes

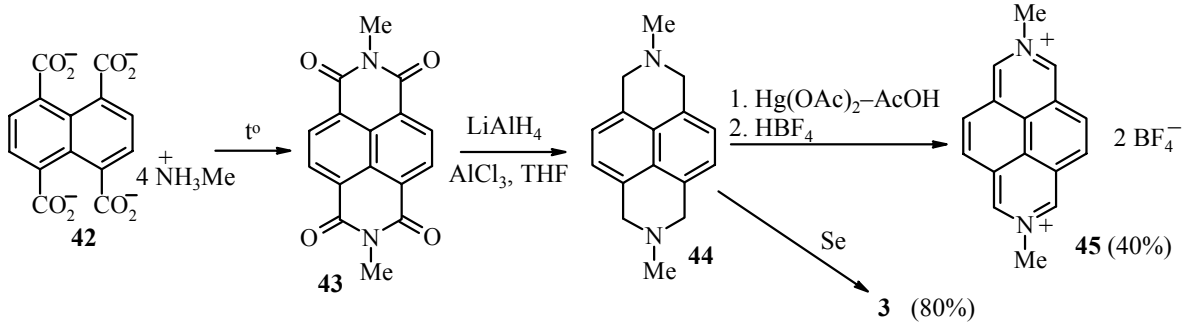
2,7-Diazapyrene **3** was synthesized in 1968 by two methods. The first, which is rather of theoretical interest, involved dehydrogenation of [2.2](3,5)pyridinophane (**41**) by heating with palladium on carbon [36].



41 **3** (30 %)

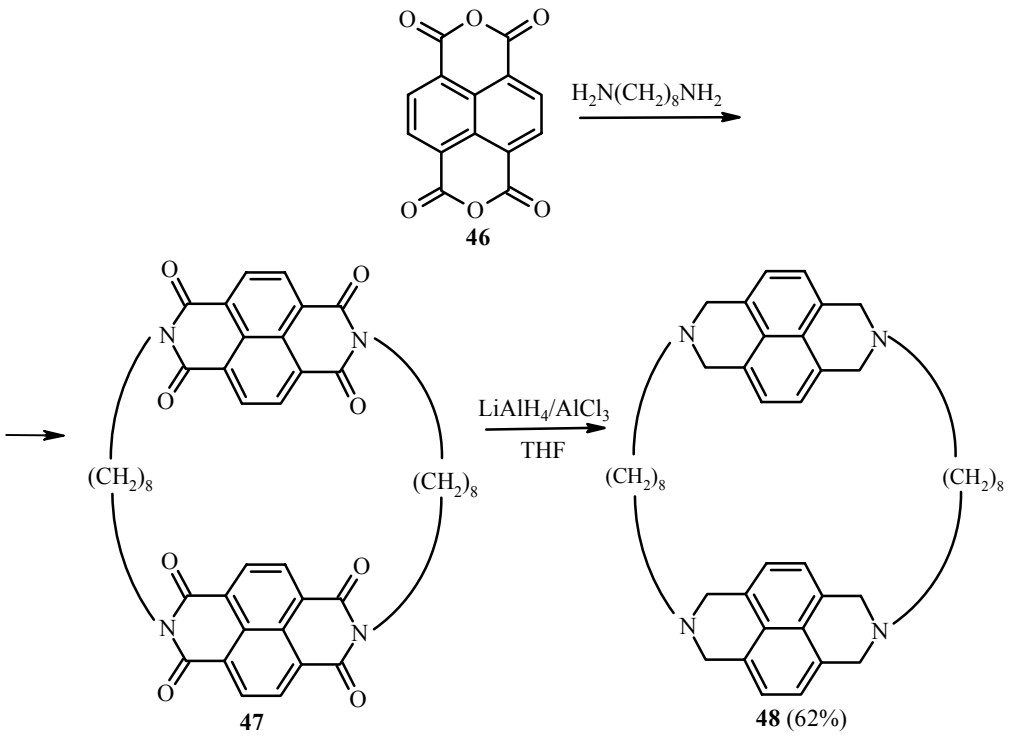
The initial compound **41** was obtained earlier from 3,5-di(chloromethyl)pyridine with a yield of ~2% [37].

The second method was based on the commercially obtainable 1,4,5,8-naphthalenetetracarboxylic acid or its derivatives. Thus, N,N'-dimethyl-1,2,3,6,7,8-hexahydro-2,7-diazapyrene (**44**) was obtained by transformation of the tetra-N-methylammonium salt **42** into the diimide **43** followed by reduction with lithium aluminum hydride [38, 39]. When it was heated with selenium, oxidative dealkylation occurred with the formation of 2,7-diazapyrene **3**; oxidation of the diamine **44** with mercury diacetate of N-bromosuccinimide followed by treatment with HBF_4 led to the salt **45**. It is possible to demethylate the diamine **44** with palladium on carbon at 300-310°C, but the yield of the 2,7-diazapyrene in this case is only 23% [40].



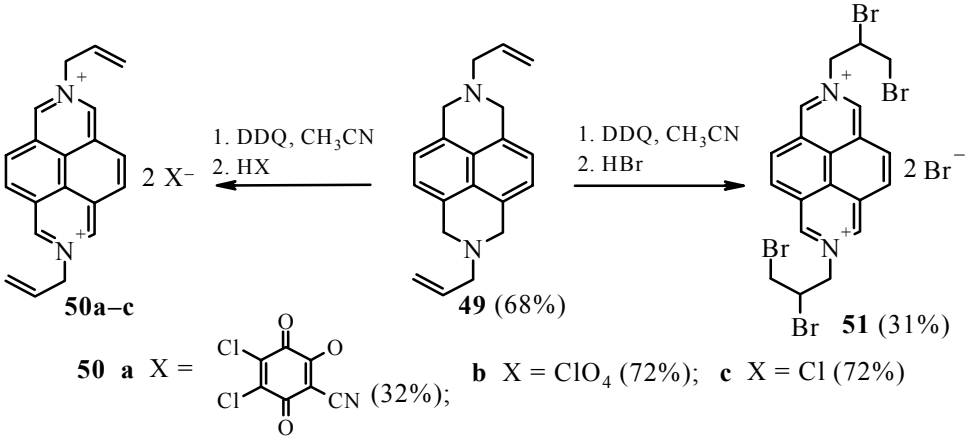
42 **43** **44** **45** (40%) **3** (80%)

1,4,5,8-Naphthalenetetracarboxylic dianhydride (**46**) has most often been used for the synthesis of the diimides **43** [40, 41]. It was converted by the action of 1,8-diaminooctane into the macrocyclic tetraimide **47** with a yield of 10% [42]. The tetraimide was then reduced with lithium aluminum hydride to compound **48**.



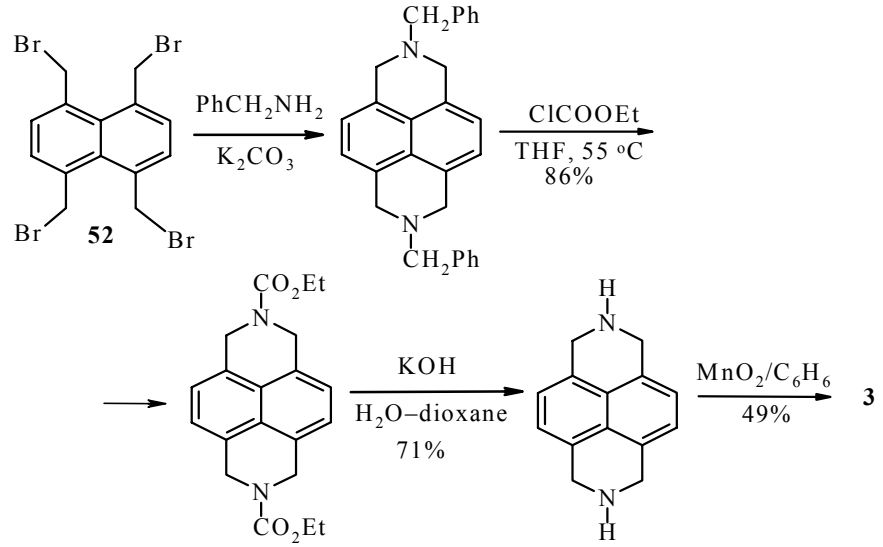
The *syn* and *anti* rotamers of N,N'-bis(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxydiimide were obtained by the action of 2-*tert*-butylaniline on the dianhydride **46** and were separated [43].

The oxidation of the N,N'-diallyl derivative **49** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave a good yield of the corresponding dication **50** [41]. The nature of the counterion in this case depends not only on the acid used to treat the reaction mass but also on the solvent used for crystallization of the crude product. If the reaction is conducted in a $CH_3OH–H_2O$ mixture, the counterion in the obtained red crystalline substance **50a** is the anion of 5,6-dichloro-2-cyano-3-hydroxy-1,4-benzoquinone irrespective of the acid used in the concluding stage. The formation of such an anion is explained by hydrolysis of one of the cyano groups [44].



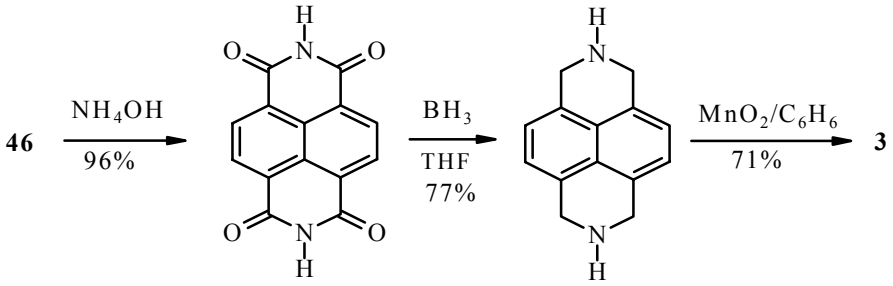
On the other hand, if the crystallization is conducted in anhydrous acetonitrile, the product is the N,N'-diallyl-2,7-diazapyrenium diperchlorate (**50b**) or the dichloride (**50c**), depending on the acid used after oxidation. Finally, if the oxidation with DDQ is accomplished by treatment with HBr, the Br^- anion is oxidized by the unreacted DDQ to Br_2, and the final product is N,N'-bis(2,3-dibromopropyl)-2,7-diazapyrenium dibromide (**51**).

The authors in [45] synthesized 2,7-diazapyrene **3** from 1,4,5,8-tetrakis(bromomethyl)naphthalene (**52**) according to the following scheme:



A disadvantage of this method is the relatively poor accessibility of compound **52**, which is obtained in three stages from 1,4,5,8-naphthalenetetracarboxylic acid [46].

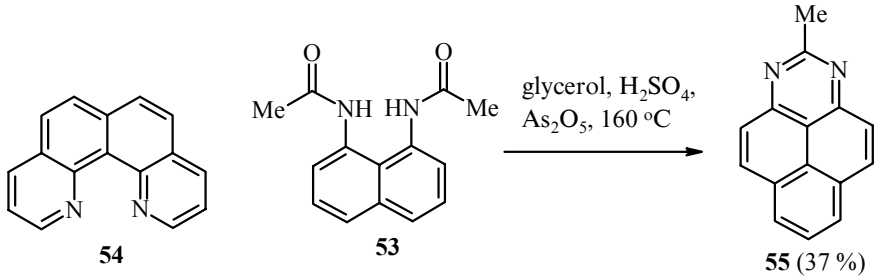
A convenient method was recently proposed for the synthesis of compound **3** in three stages starting from the dianhydride **46** [47]:



The increase in the yield of 2,7-diazapyrene at the concluding stage compared with the previous method [45] is explained by additional extraction of the product from the surface of the MnO_2.

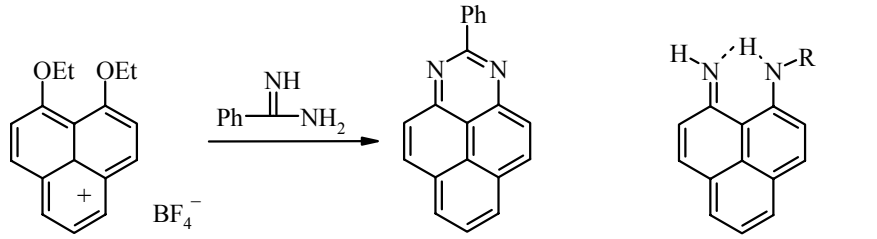
1.4. 1,3-Diazapyrenes

Skraup condensation of N,N'-diacetyl-1,8-naphthylenediamine (**53**) gave a product that was initially assigned the structure of quino[7,8-*h*]quinoline (**54**) [48]. More recently, however, the authors [49] established that it was in fact 2-methyl-1,3-diazapyrene (**55**):



54 **53** **55** (37 %)

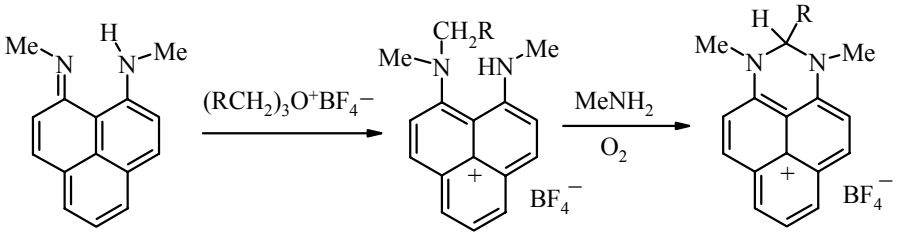
2-Phenyl-1,3-diazapyrene (**57**) was obtained by the action of benzamidine on 1,9-diethoxyphenalenium tetrafluoroborate (**56**) [50]:



56 **57** (85%) **58a**,**b**

58 a R = H; **b** R = Me

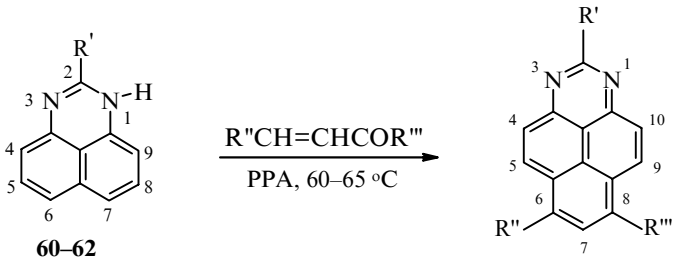
A good precursor for 1,3-diazapyrene **4** could be the long ago described 9-aminophenalenone imine **58a** [51], but no attempts at its cyclization have been reported. At the same time the N-methylated amino imine **58b** was used for the production of 1,3-dimethyl-1,2-dihydro-1,3-diazapyrenium salts **59a**,**b** [52].



58b **59a**,**b**

59 a R = H; **b** R = Me

A convenient starting compound for the synthesis of 1,3-diazapyrenes was the perimidine **60**. A special feature of its structure is the strong displacement of the π-electron cloud from the heterocycle to the naphthalene fragment of the molecule, as a result of which it enters readily into electrophilic substitution (see the reviews [53, 54]). Annelation of the 6,7-*peri* ring to the molecule **60** is possible with double electrophilic attack at these positions, which requires the use of 1,3-bifunctional electrophiles. In fact, 6,8-di- or 2,6,8-trisubstituted 1,3-diazapyrenes **63** are formed in the reaction of the perimidines **60**-**62** with α,β-unsaturated ketones in PPA [55, 56]. The reaction takes place as double C-alkylation of the perimidines by chalcones followed by dehydration and spontaneous oxidation (cf. the facile autooxidation of the dihydro derivatives of 1,3,6,8-tetraazapyrene [57, 58].

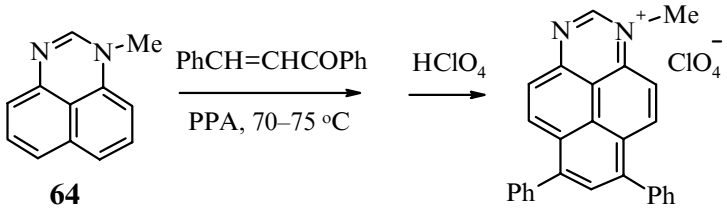


60–62 **63a–f, 4**

63 a-d, **f** R' = H, **e** R' = Me; **a**,**c-f** R'' = Ph, **b** R'' = Me; **a**, **b**, **e**, **f** R''' = Ph, **c** R''' = 4-BrPh, **d** R''' = 4-MeOPh; **4** R' = R'' = R''' = H, yield, %: **63 a** 36, **b** 29, **c** 32, **d** 40, **e** 27, **f** 25, **4** 27

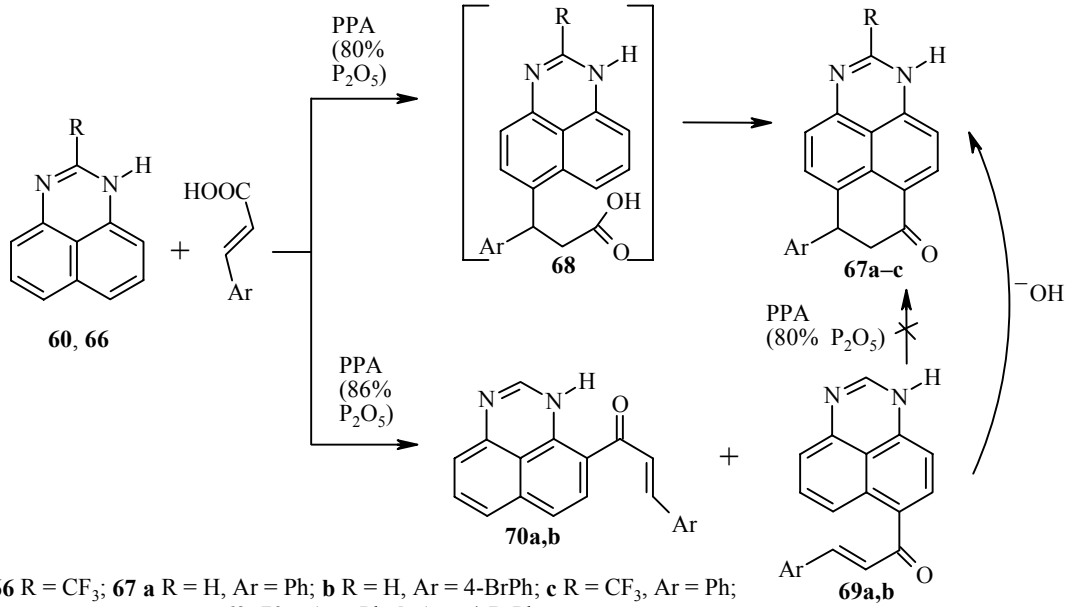
The synthesis of 1,3-diazapyrenes **63a**,**b**,**e**,**f** was also realized under the conditions of alkaline catalysis (180-185°C, sodium glycolate in ethylene glycol) [59], which suggests 1,6-ambident character for the anions **60**-**62**. Unsubstituted 1,3-diazapyrene **4** was obtained by the reaction of **60** with glycerol in PPA at 180-190°C [56]. Essentially, the reagent in this case is acrolein formed *in situ*.

The reaction of 1-methylperimidine (**64**) with benzylideneacetophenone in PPA is also accompanied by aromatization; the salt **65a** was isolated in the form of the perchlorate [60].



64 **65a** (73 %)

The reaction of the perimidines **60** and **66** with cinnamic and *p*-bromocinnamic acids in standard PPA (80% P_2O_5) at 45-70°C results in the formation of 2-R-8(6)-aryl-6(8)-oxo-1,6,7,8-tetrahydro-1,3-diazapyrenes **67** with yields of up to 61% [61-63]. However, if the P_2O_5 content of the PPA is increased to 86% the direction of the reaction changes in so far as the 6(7)-cinnamoylperimidines **69a**,**b** together with a small amount of the 4(9) isomers **70a**,**b** are formed [61, 63].

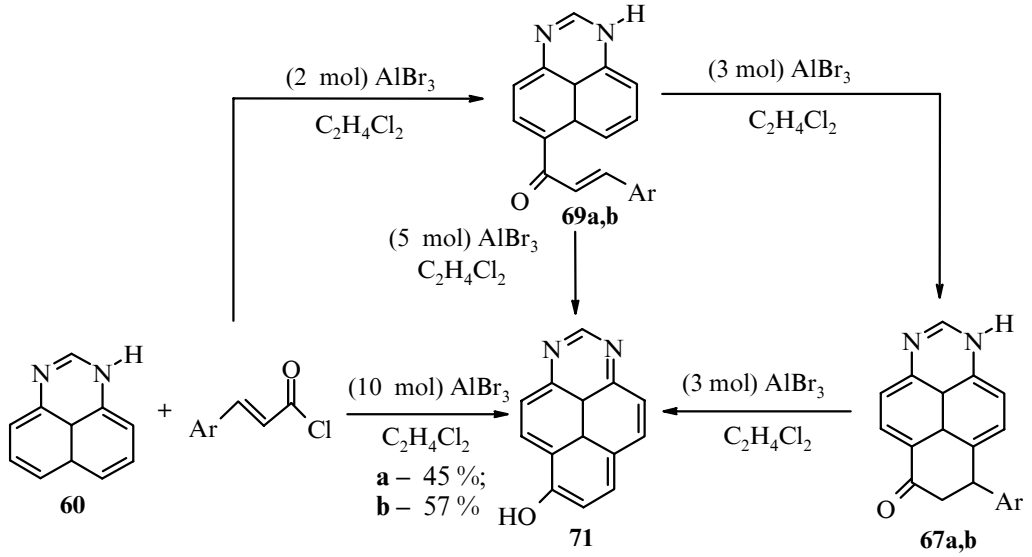


60, **66** **68** **67a–c** **70a,b** **69a,b**

66 R = CF_3; **67 a** R = H, Ar = Ph; **b** R = H, Ar = 4-BrPh; **c** R = CF_3, Ar = Ph; **69**, **70 a** Ar = Ph; **b** Ar = 4-BrPh

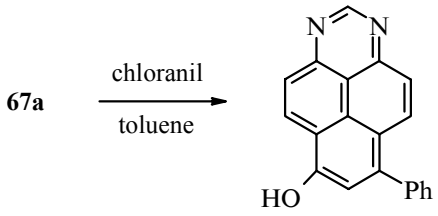
Since compounds **69a**,**b** do not undergo cyclization under the conditions of the synthesis of **67**, the latter are formed in PPA by alkylation of the perimidines by the ambident cinnamoyl cation and subsequent intramolecular acylation of the acid **68** at the neighboring *peri* position. At the same time cyclization of compounds **69a**,**b** takes place when they are boiled with potassium hydroxide in ethylene glycol with the formation of compounds **67a**,**b** [64].

If the cyclization of compounds **69a**,**b** is conducted in the presence of $AlBr_3$, the only product is 6-hydroxy-1,3-diazapyrene (**71**) [62]. The same compound is formed in one pot during the reaction of compound **60** with both cinnamoyl and *p*-bromocinnamoyl chlorides under Friedel–Crafts conditions.

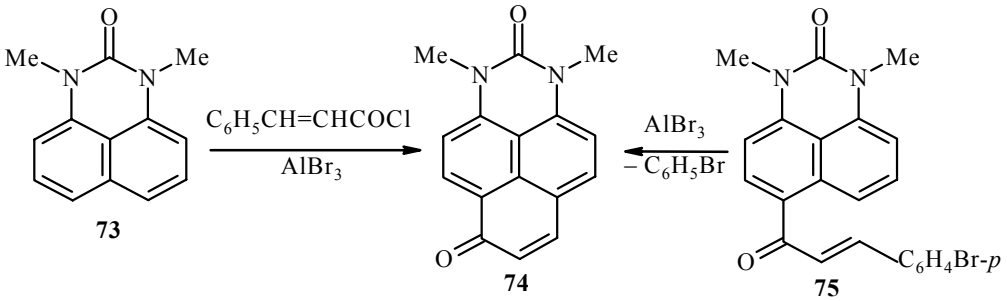


a Ar = C_6H_5; **b** Ar = *p*-BrC_6H_4

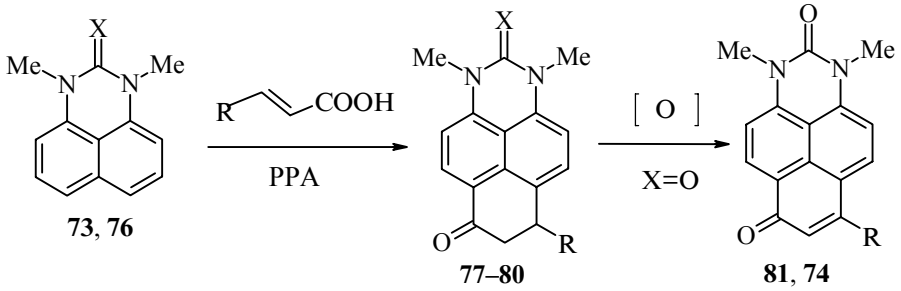
The transformation includes an acylation stage, intramolecular alkylation, and subsequent dearylation. It was found that not only **69a**,**b** but also **67a**,**b** form **71** under the same conditions (dichloroethane, room temperature, an excess of $AlBr_3$) [63]. Its analog – 6-hydroxy-8-phenyl-1,3-diazapyrene (**72**) – was obtained by dehydrogenation of **67a** [63]. It was established by spectral methods that compounds **71** and **72** exist exclusively in the tautomeric 6-hydroxy form of 1,3-diazapyrene.



The acylation of 1,3-dimethylperimidone (**73**) with cinnamoyl chloride in chloroethane in the presence of an excess of $AlBr_3$ leads at once to 2,6-dioxo-1,3-dimethyl-1,2,3,6-tetrahydro-1,3-diazapyrene (**74**) [63]. Compound **74** was also obtained from 6-*p*-bromocinnamoyl-1,3-dimethylperimidone **75**.



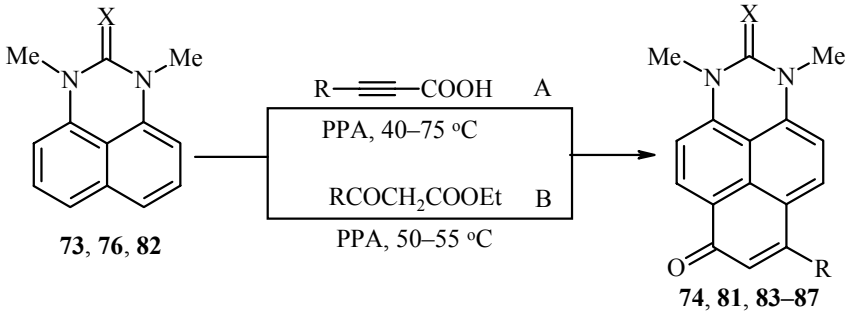
The acylation of 1,3-dimethyl-substituted perimidone **73** and 2,3-dihydroperimidine **76** with cinnamic and acrylic acids in PPA takes place already at 40-55°C and leads to the formation of 6-oxo-1,3-dimethyl-1,2,3,6,7,8-hexahydro-1,3-diazapyrenes **77** and **78** and their 2-oxo analogs **79** and **80** [65]:



77 X = 2H, R = H; **78** X = 2H, R = Ph; **79** X = O, R = H; **80** X = O, R = Ph;
81 R = Ph; **74** R = H

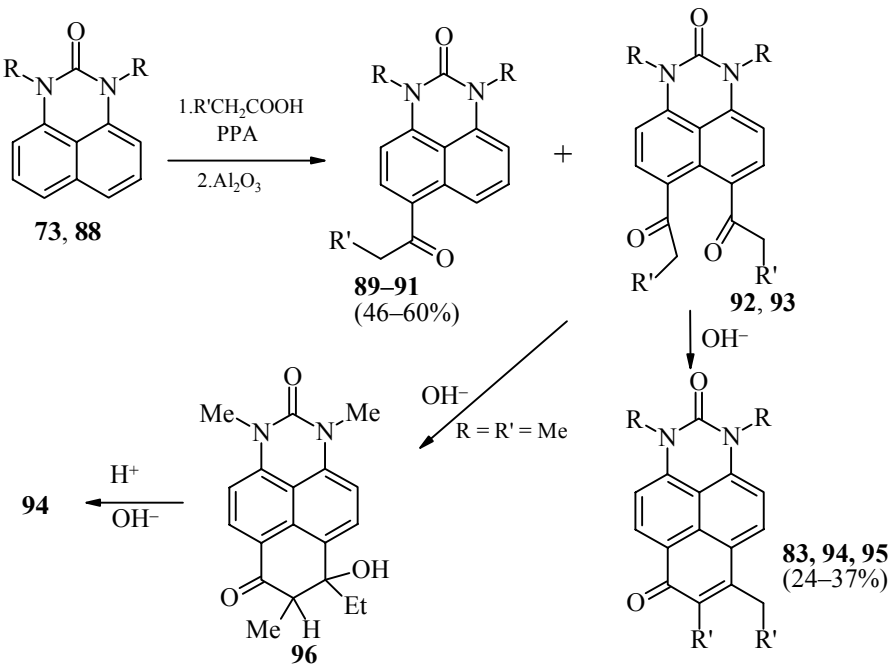
The dehydrogenation of **79** and **80** gave compound **74** and 1,3-dimethyl-2,6-dioxo-8-phenyl-1,2,3,6-tetrahydro-1,3-diazapyrene (**81**). The last compound was also obtained by the direct reaction of compound **73** with cinnamic acid in PPA at 130-135°C [65].

The reaction of 1,3-dimethyl-substituted perimidone **73**, thioperimidone **82**, and 2,3-dihydroperimidine **76** with propiolic acids [66] or with the esters of β-keto acids [65, 67] in PPA takes place extremely readily and leads to the corresponding 1,3-diazapyrenes:



73, **74**, **81**, **83** X = O, **76**, **84**, **86** X = 2H, **82**, **85**, **87** X = S; **74** R = H, **81**, **84**, **85** R = Ph,
83, **86**, **87** R = Me; yield, % (method of synthesis): **74** 13 (A); **81** 72 (A), 58 (B); **83** 83 (B); **84** 50 (A),
85 14 (A); **86** (B); **87** (B)

During the acylation of 1,3-dialkylperimidones **73** and **88** by aliphatic acids in PPA a mixture of 6-mono- and 6,7-diacyl derivatives **89**-**91** and **92**, **93** respectively is formed. The latter in the presence of basic catalysts, e.g., during separation on Al_2O_3, readily undergo cyclization, forming 1,3-dialkyl-2,6-dioxo-1,2,3,6-tetrahydro-1,3-diazapyrenes **83**, **94**, and **95** [65, 68]. The unstable product **96** from aldol condensation of **93** was also isolated.

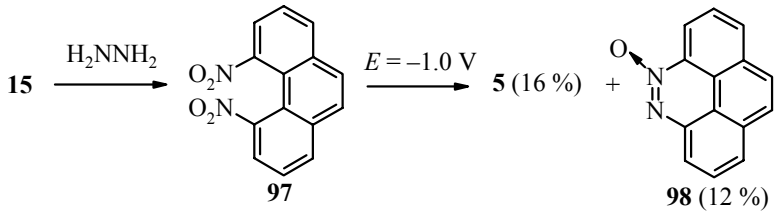


89, **92**, **83** R = Me, R' = H; **90**, **93**, **94** R = R' = Me; **91**, **95** R = Et, R' = H

Good synthons for the synthesis of 1,3-diazapyrenes from perimidine were β-diketones. However, the reaction of **60** with acetylacetone in PPA only begins above 100°C; its only product was 4(9)-acetylperimidine (yield 10%) [56].

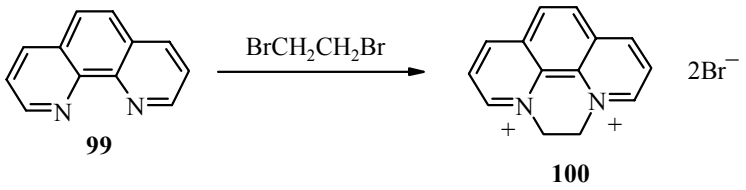
1.5. 4,5-Diazapyrenes

The reaction of compound **15** with hydrazine hydrate leads to the formation of 4,5-dinitrophenanthrene (**97**), the electrochemical reduction of which gives a mixture of the diazapyrene **5** and its mono-N-oxide **98** [27].

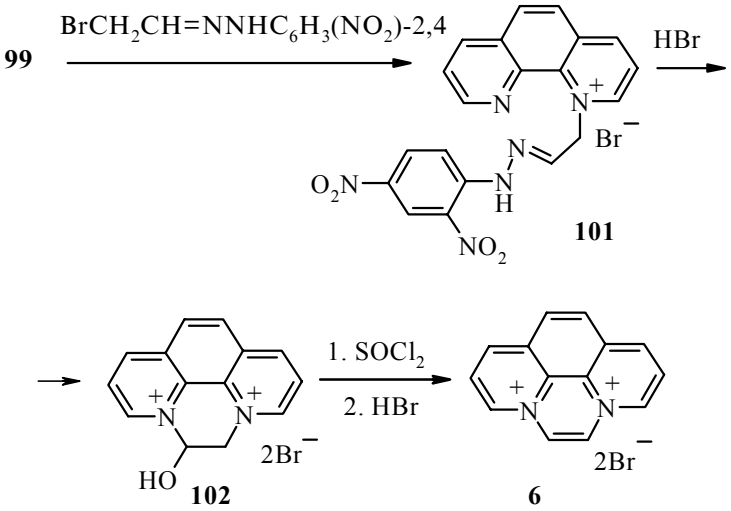


1.6. The 3a,5a-Diazoniapyrene Dication

It was found that 1,10-phenanthroline (**99**) undergoes double quaternization with 1,2-dibromoethane, forming 4,5-dihydro-3a,5a-diazoniapyrene dibromide (**100**) with a yield of 70% [69]. (The yield was subsequently increased to 80% [39].)

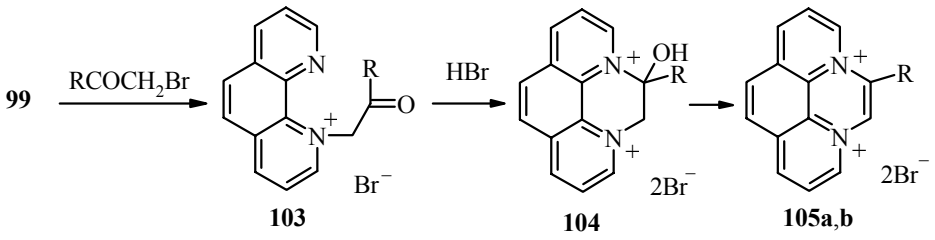


The aromatic dication of compound **6** was synthesized in three stages [70]. The reaction of the phenanthroline **99** and bromoacetaldehyde 2,4-dinitrophenylhydrazone gave the monoquaternary salt **101**, which was converted by heating with an excess of concentrated hydrobromic acid into the dication **102**. The dibromide **6** was obtained when **102** was boiled with an excess of thionyl chloride followed by treatment with HBr.



Compound **6** is stable in aqueous solution but quickly decomposes in the presence of bases with the formation of products with unestablished structure.

The salts **105a**,**b** were synthesized by an analogous scheme through the formation of compounds **103** and **104** [71].



105 a R = Me; **b** R = *p*-MeC_6H_4

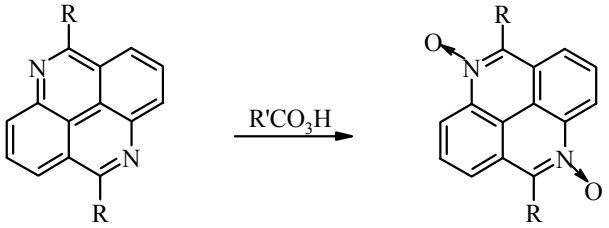
2. PROPERTIES

The synthesized diazapyrenes **1**-**5** and their simple derivatives are crystalline substances with high melting points. The basicity has only been determined for the 4,9 isomer **1**: pK_a 10.40 (MeCN) [72]. The results of investigation of 2,7-diazapyrene and its cations by linear and circular dichroism are given in [5, 73, 74], and

the emission fluorescence spectrum of compound **3** is given in [75]. A crystallographic investigation of the 5,10- and 2,7-dimethyl derivatives of 4,9-diazapyrene **10a**,**a** [23] made it possible to establish for them a β-type of crystal packing similar to the graphite structure and characterized by strong π,π-interaction.

2.1. Oxidation

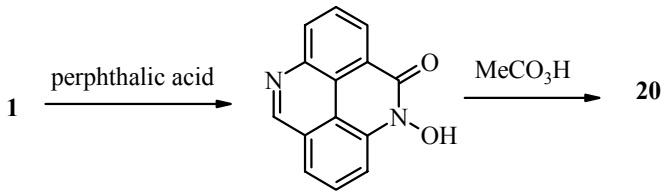
The 5,10-dimethyl- and 5,10-diphenyl-4,9-diazapyrenes **10a** and **8a** are oxidized smoothly to the di-N-oxides **106** and **107** by peracetic or perphthalic acid [26]. Attempts to obtain the mono-N-oxide led to the formation of a mixture of the dioxide and the initial diazapyrene.



8a, 10a **106, 107**

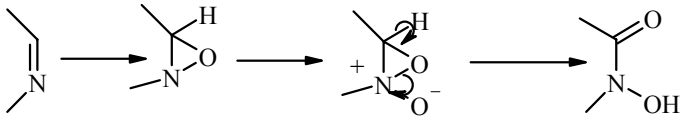
106 R = Me, **107** R = Ph

However, the oxidation of 4,9-diazapyrene **1** itself with perphthalic acid leads to the formation of the monohydroxamic acid **108**, which is converted by the action of peracetic acid into the dihydroxamic acid **20** [76]. (For its acid–base equilibrium, see [77].)

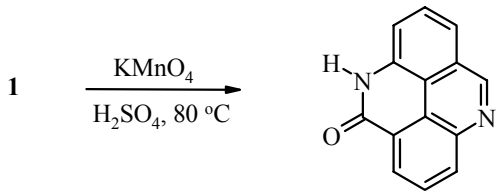


108

The formation of compounds **108** and **20** is explained by the anionic character of the 4,5- and 9,10-bonds in 4,9-diazapyrene, which was later confirmed by calculations [72]. (In pyrene they also have a significant degree of double bond character [78].) In the opinion of the authors [76], attack by the peracid at the C=N bond gives oxaziridine, which is then oxidized to oxaziridine N-oxide, and after rearrangement the hydroxamic acid is formed:

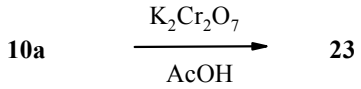


Attempts to oxidize 4,9-diazapyrene **1** by hydrogen peroxide were unsuccessful [22], whereas quinoline under these conditions is transformed into quinolinic acid [79]. During the oxidation of 4,9-diazapyrene **1** with potassium permanganate in an acidic medium 5-oxo-4,5-dihydro-4,9-diazapyrene (**109**) is formed with a 44% yield [76]:

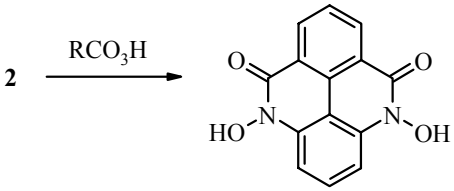


109

The oxidation of 5,10-dimethyl-4,9-diazapyrene **10a** by potassium bichromate in glacial acetic acid leads to 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene **23** (cf. the oxidation of 9-methylphenanthridine to phenanthridone [80]).

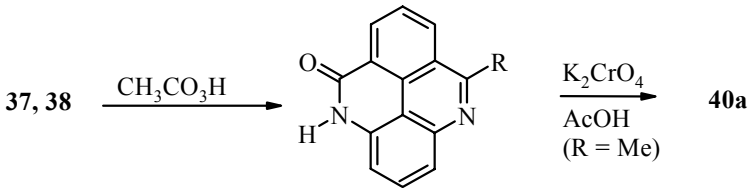


Like the 4,9 isomer, during the action of peracids 4,10-diazapyrene **2** forms the N,N'-dihydroxy-5,9-dioxo-4,5,9,10-tetrahydro derivative **110** [34].



110

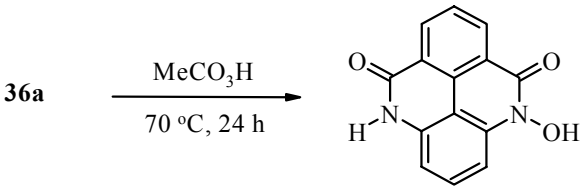
However, during the oxidation of 5-methyl- or 5-phenyl-4,10-diazapyrenes **37** or **38** with peracetic acid the corresponding monoamides **36b**,**c** were obtained instead of the N-oxides [34].



36b,c

During further oxidation of 9-methyl-5-oxo-4,5-dihydro-4,10-diazapyrene **36b** with potassium bichromate in acetic acid the diamide **40a** is formed [34].

Compounds **36b**,**c** and **40a** do not react with peracetic acid, but the diazapyrene **36a** is oxidized to 4-hydroxy-5,9-dioxo-4,10-diazapyrene (**111**) [34].

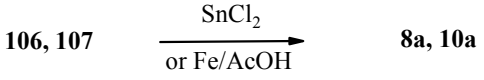


111

2.2. Reduction

Special investigations have not been carried out on the chemical reduction of aromatic diazapyrenes. It is only possible to mention the stability of the 4,10-isomers **2**, **37**, and **38**, since they are not reduced by an excess of $LiAlH_4$ [34].

The di-N-oxides of 5,10-dimethyl- and 5,10-diphenyl-4,9-diazapyrenes **107** are deoxidized by tin chloride or, better, by iron in acetic acid to the initial diazapyrenes [26].

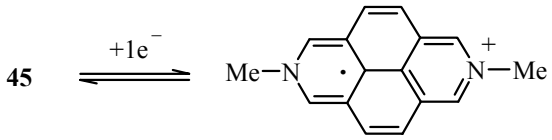


106 R = Me, **107** R = Ph

Compounds **108** and **20** are N-deoxidized by the action of iron in acetic acid or of hydrazine at Raney nickel with the formation of the monoamide **109** or the diamide **23** respectively [76]:

The N,N'-dihydroxy derivative of the 4,10-diazapyrene series **110** is reduced similarly [34].

The electrochemical and photochemical reduction of the N,N'-bismethyl dication of 2,7-diazapyrene **45** has been studied intensively. It was found that it readily undergoes one-electron reduction with the formation of the stable radical-cation **112** [39, 81]:



112

A comparative polarographic study of 4,4'-dipyridinium, phenanthrolinium, and 2,7-diazapyrenium bissalts showed that reduction takes place in two stages, while the dication **45** has not only the lowest reduction potentials but also forms the most stable radical-cation. In aprotic solvents (DMF, MeCN) both stages are reversible, whereas in water only the first is reversible [81].

Under the influence of light the dication **45** is capable of oxidizing donor organic substrates (tertiary amines, alcohols, glucose, etc.), being converted into the radical-cation **112** [82]. The solution is soon decolorized by the action of atmospheric oxygen, and the spectrum of the initial dication is restored. However, with more prolonged irradiation or during electrochemical reduction different particles are formed; the reaction with oxygen is greatly retarded and is not fully reversible. The ESR spectrum was measured for the radical-cation **112** [83].

Comparative data on the polarographic reduction of 4,9-diazapyrene and other polycyclic nitrogen-containing compounds in anhydrous DMSO and DMF were given in [84, 85]. The polarographic reduction of the dications **100** and the diazoniapyrene **6** [81] in aprotic polar solvents takes place in two one-electron stages, where the second stage is irreversible.

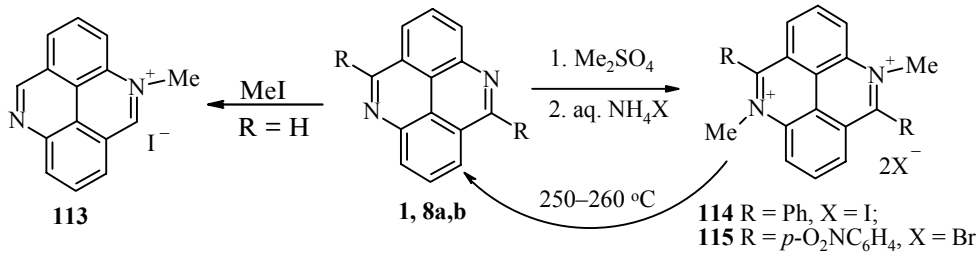
During treatment of aqueous solutions of the dibromides **100** and **6** with zinc dust a red or violet color, attributed to the formation of radical-cations, develops [69, 70]. After removal of the reducing agent and shaking in air the color in the case of the dibromide **100** disappears as a result of oxidation of the radical-cation

to the initial compound. However, in the case of the dibromide **6** the initial salt is not regenerated. Polarographic reduction of the dication **6** in water also leads to its irreversible decomposition [81].

There are data on the spectral characteristics of the radical-anion of N,N'-bis(2,5-di-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxydiimide, produced by its electrochemical reduction [86].

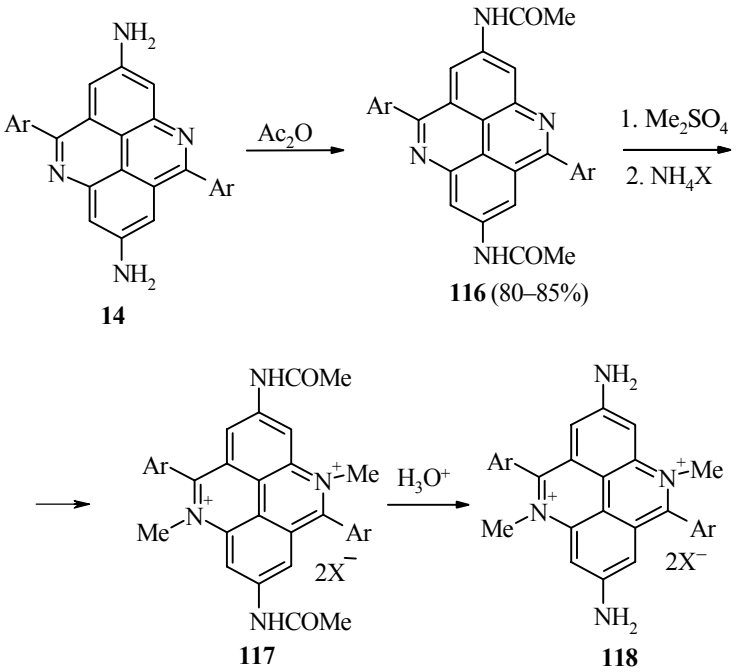
2.3. Quaternary Salts of Diazapyrenes

The monoquaternary salt **113** was obtained with a yield of 70% by boiling 4,9-diazapyrene **1** in an excess of methyl iodide [26]. When 5,10-diaryl-4,9-diazapyrenes **8a**,**b** were heated with an excess of dimethyl sulfate in nitrobenzene with subsequent exchange of the counterion the bisquaternary salts **114** and **115** were obtained [21]. Above 250°C they are demethylated with the formation of the initial diazapyrenes.



Dimeric 4,4'-*m*- and 4,4'-*p*-xylylenebis-4,9-diazapyrenium salts were recently synthesized [14].

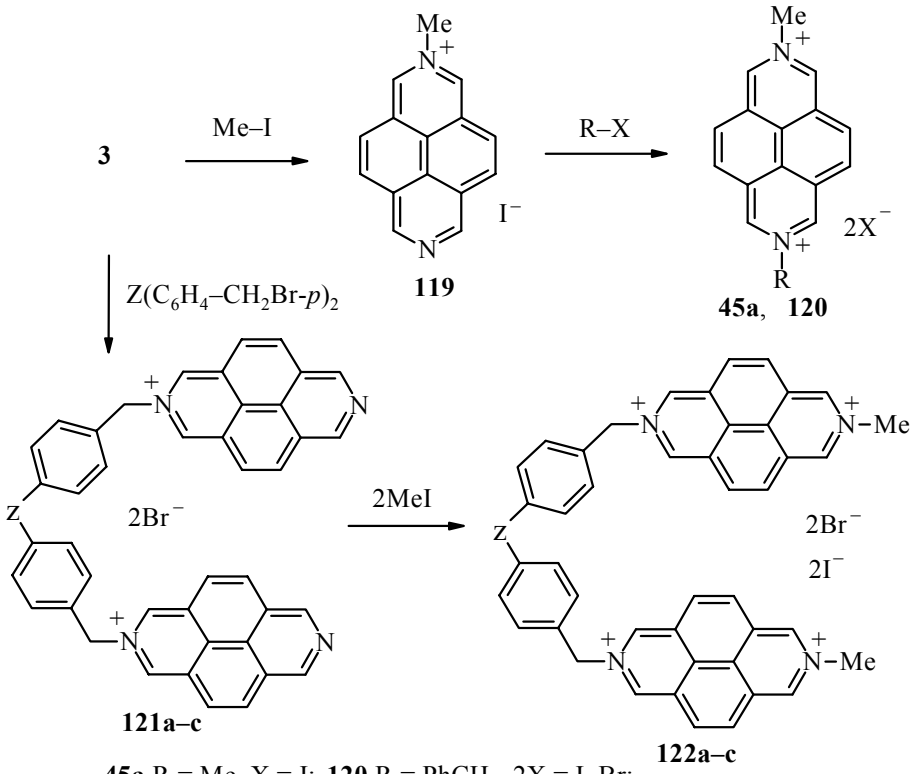
The diacetyl derivatives **116** obtained from the diamines **14** give the salts **117** during quaternization and the salts **118** after hydrolysis [21].



Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-MeOC_6H_4

With methyl iodide 4,10-diazapyrene forms a monoquaternary salt [34].

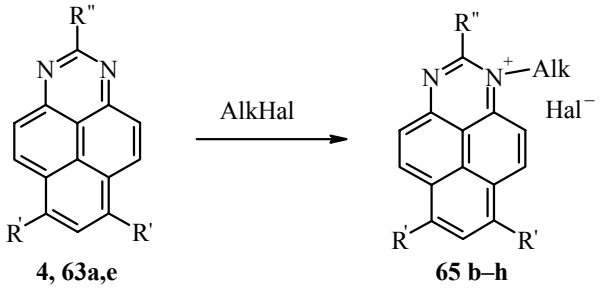
The diazapyrene **3** reacts with trimethyloxonium tetrafluoroborate and forms the salt **45** (84%) [38]. The latter is dealkylated when heated with potassium iodide in triethylene glycol with the formation of 2,7-diazapyrene (50%). The action of methyl iodide on compound **3** in chloroform gave the monomethyl salt **119**. Further methylation or benzylation gave the symmetrical **45a** and unsymmetrical **120** bisquaternary salts of 2,7-diazapyrene [82].



45a R = Me, X = I; **120** R = $PhCH_2$, 2X = I, Br;
121, 122 a Z = CH_2; **b** Z = O; **c** Z = Me_2C

The dimeric dication **121a** was obtained with a yield of 70% by the reaction of bis[4-(bromomethyl)phenyl]methane with a 2.2 molar excess of 2,7-diazapyrene. The dications **121b**,**c** were synthesized similarly. They were converted by the action of an excess of methyl iodide into the dimeric tetracations **122** [82]. Catenanes and rotaxanes containing the 2,7-diazapyrenium dication were recently synthesized [87].

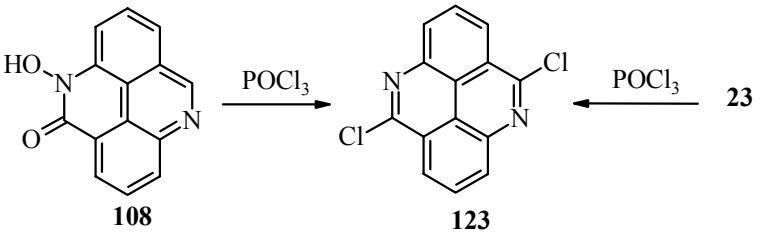
Quaternization of the symmetrical 1,3-diazapyrene **4** and **63a**,**e** with an excess of alkyl halides leads to 1-alkyl-1,3-diazapyrenium salts **65b-h** [60]. (For the synthesis of **65a**, see section 1.4.)



65 b, **c** R' = H, **d**-**h** R' = Ph; **b**-**g** R'' = H, **h** R'' = Me; **b**, **d**, **h** Alk = Me, **c**, **e** Alk = Et, **f** Alk = Bn, **g** Alk = All; **b**-**e**, **h** Hal = I, **f** Hal = Cl, **g** Hal = Br

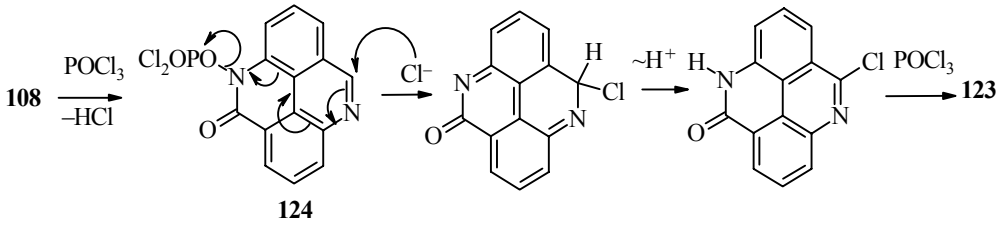
2.4. Nucleophilic Substitution Reactions

5,10-Dichloro-4,9-diazapyrene (**123**) was unexpectedly obtained during the reaction of 4-hydroxy-5-oxo-4,5-dihydro-4,9-diazapyrene (**108**) with phosphorus oxychloride in dimethyl- or diethylaniline [76]. The same compound is formed during the action of phosphorus oxychloride on the diamide **23**:



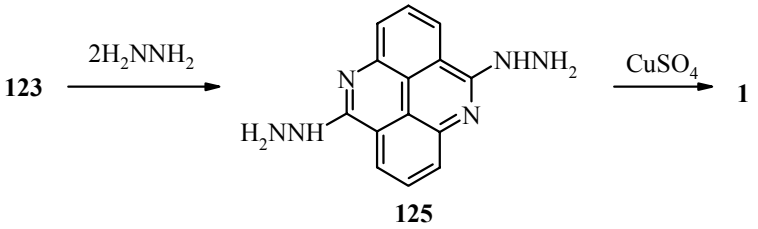
108 **123**

The key stage in the transformation **108** → **123** is presumably *tele*-nucleophilic attack [88] by the chloride anion at position 10 of the intermediate **124**.



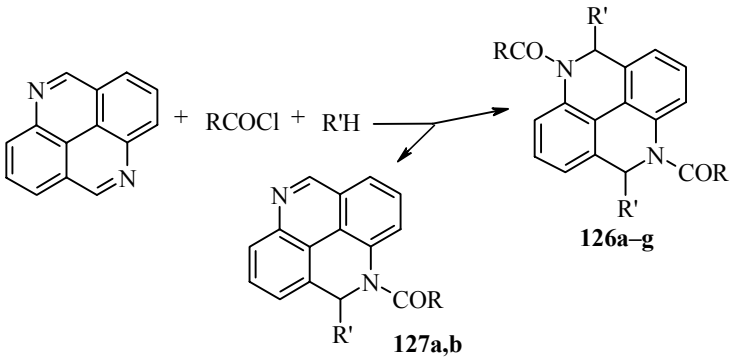
124

Compound **123** was converted into 4,9-diazapyrene **1** through the dihydrazine derivative **125** with subsequent oxidative elimination of the hydrazino groups [76]:



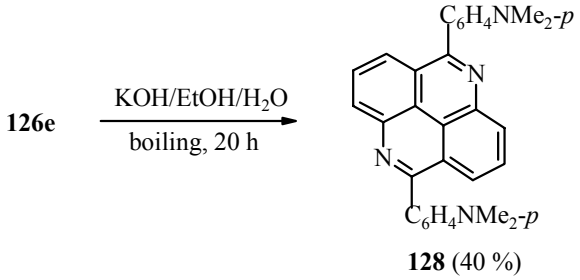
125

The hetarylation of donor substrates by the N-acylium salts of 4,9-diazapyrene, formed *in situ*, was studied [72]. It was found that 5,10-disubstituted 4,9-diacyl-4,5,9,10-tetrahydro-4,9-diazapyrenes **126** are formed during the reaction of a mixture of **1** and acyl halides with π-excessive aromatic substrates. The authors in [72] consider that this is the first example of double hetarylation in the series of diazines. Incidentally, the formation of the monosubstituted compounds **127** was observed in two cases.



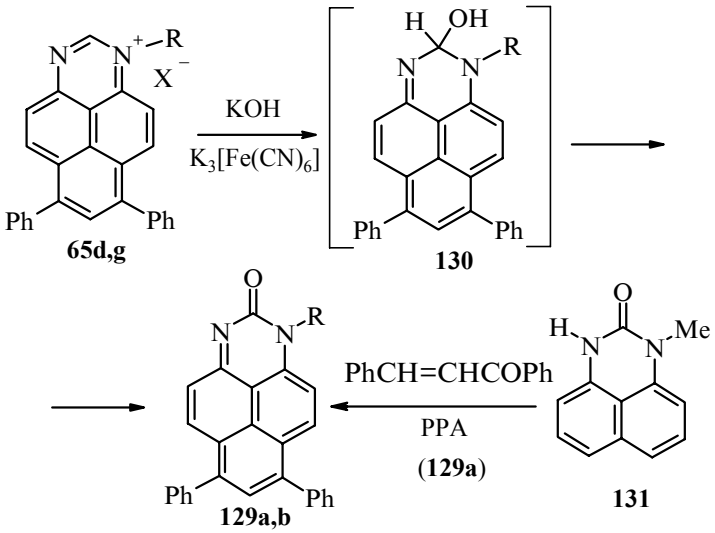
126 a, c–g R = Ph, **b** R = Me; **a** R' = 3-indolyl (60%); **b** R' = 3-indolyl (50%); **c** R' = 1-methyl-3-indolyl (43%); **d** R' = 2-methyl-3-indolyl (45%); **e** R' = $C_6H_4NMe_2$-*p* (51%); **f** R' = 1-methyl-2-pyrrolyl (50%); **g** R' = 1-phenyl-2-pyrrolyl (40 %); **127 a** R = Ph, R' = $CH_2COC_6H_5$ (35%); **b** R = Ph, R' = 5-methyl-2-furyl (50%)

After prolonged boiling in a water–alcohol solution of alkali compound **126e** undergoes aromatization in addition to hydrolysis on account probably of oxidation by atmospheric oxygen, and compound **128** is formed [72].



128 (40 %)

During treatment of the 1,3-diazapyrenium salts **65d**,**g** with aqueous alkali in the presence of $K_3[Fe(CN)_6]$ the 1-alkyl-6,8-diphenyl-1,2-dihydro-1,3-diazapyren-2-ones **129a**,**b** were isolated with yields of 85 and 32% respectively [60]. Clearly, as also in a series of other azaaromatic cations [89], the reaction takes place through the formation of the pseudobase **130** and its subsequent oxidation. Compound **131** was also obtained in PPA [60].



129 a R = Me; **b** R = All

Reversible formation of pseudobases was recently detected in aqueous solutions of mono- and bisquaternary 4,9-diazapyrenium salts [14].

2.5. Electrophilic Substitution Reactions

It was established that the diazapyrenes **1** and **2** are extremely inert toward electrophilic agents. Thus, compound **1** could not be brought into nitration and bromination in sulfuric acid [22], although quinoline is easily nitrated under the same conditions [90]. Attempts at the bromination of compound **2** always led to isolation of the initial compound. Nitration also does not occur either with potassium nitrate in concentrated sulfuric acid at 100°C or with fuming nitric acid in acetic anhydride [34]. The behavior of other aromatic diazapyrenes toward electrophiles has not been reported.

Diazapyrenes with donating substituents enter readily into nitration. Thus, 1- and 3-mononitro, 1,8- and 3,8-dinitro, 1,3,6- and 1,3,8-trinitro, and 1,3,6,8-tetranitro derivatives are obtained from the diazapyrene **23**, depending on the concentration of the nitric acid; the 1-nitro, 1,3-dinitro, and 1,3,7-trinitro derivatives were synthesized from **40a** [33]. Reduction of the nitro derivatives gave the corresponding amines [91]; some transformations of the amines of the 4,9-diazapyrene series were studied [30, 92].

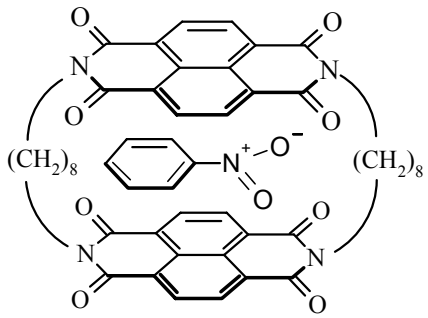
2.6. Complex Formation

The bonding interaction of anionic substrates with the 2,7-diazapyrenium cations **45a** and **120-122a** was investigated by spectral methods. When they are present in aromatic polycarboxylates in aqueous solutions of **45a** and **120-122a** an upfield shift (up to 2 ppm) of the signals of the aromatic protons is observed. This was attributed by the authors of [82] to the formation of stable radical-cation associates. The complexes are formed by partial charge transfer in so far as their formation is accompanied by a change in the color of the solutions of **45a** and **120-122a** with the addition of donating molecules. It was found that the complexes of the dimeric cations **122a** are at least 10 times more stable than those of the monomeric dications **45a** and **120**.

Compared with the 4,4'-bipyridyl dication, its 2,7-diazapyrenium analog forms a much more stable complex with aliphatic amines [93, 94] and aromatic π-donors [19].

A series of other examples of complex formation through covalent interaction have been described. Thus, colorless crystals containing one solvent molecule were obtained during the recrystallization of the tetraimide **47** from nitrobenzene. It was shown by X-ray crystallographic investigation [42] that this was an inclusion compound **47a** containing a nitrobenzene molecule in the inner cavity.

The alicyclic analogs **47** form similar compounds. It was established, for example, in [43] that whereas the *anti* rotamer of N,N'-bis(2-*tert*-butylphenyl)naphthalene-1,4,5,8-tetracarboxydiimide readily forms a compound of the "guest–host" type with various guest molecules the *syn* rotamer does not form such compounds.

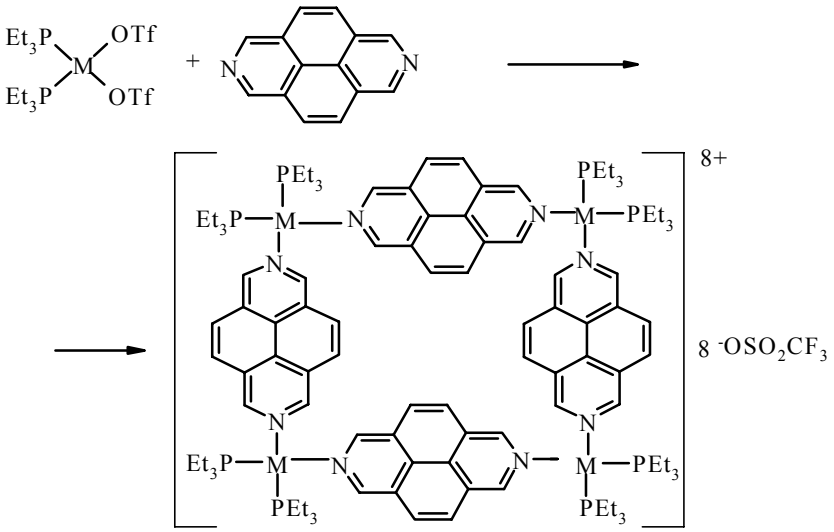


47a

Aspects of the formation of aggregates in solutions of the N,N'-diallyl-2,7-diazapyrenium dication with various counterions were discussed in [41]. The formation of various associates between the N,N'-dibutyl-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene molecules in alcohol solution at low temperatures was detected in [95]. It was found that after rapid cooling to 77 K the associates have a sandwich structure, but after slower cooling they take the form of a "step" ("foot" structure; angle between the planes of the molecules ~90°C).

The metal complexes of 2,7-diazapyrene **3** with $W(CO)_5$ [96] and with Cu(I) and Ag(I) ions, for example, were actively studied [97, 98]. Elaborate complexes, in which compound **3** acts as bridging ligand between the complex-forming metal cations, were obtained [99]. The authors of [100] measured the rate constant of intramolecular electron transfer from iron to cobalt in the complex $(NH_3)_5Co(III)LFe(II)(CN)_5$, where L is compound **3**.

During reaction with the planar *cis*-bistriflate complexes of platinum and palladium in nitromethane at room temperature 2,7-diazapyrene undergoes self-assembly, forming high yields of macrocyclic cationic structures **132a**,**b** [40], which are extremely stable crystalline substances soluble in organic solvents.



132a,b

132 a M = Pt (85%); **b** M = Pd (91%)

On account of the high positive charge (8+) they are effective acceptors for electron-excessive "guest" substrates [40]. Other metal macrocycles of 2,7-diazapyrene with platinum(II) and palladium(II) complexes are known [101].

CONCLUSION

In the absence of a systemic approach to the development of methods for the synthesis of diazapyrenes and investigation of their chemical properties the significant number of papers devoted to their scientific and practical use will in our opinion stimulate the interest of organic chemists in these heterocycles, which envisions progress in this region of organic chemistry in the coming years.

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