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SYNTHESIS OF AZA- AND POLYAZA-PYRENES (REVIEW)*

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Published data on methods for the synthesis of mono-, di-, tri-, and tetraazapyrenes are reviewed.

Keywords: azapyrenes, diazapyrenes, triazapyrenes, tetraazapyrenes, polyazapyrenes.

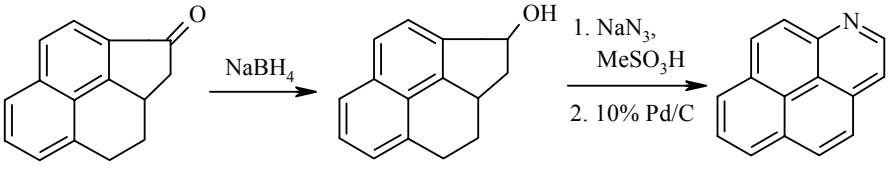
It is theoretically possible to envisage about 300 isomeric aza- and polyazapyrenes with the nitrogen atoms at various positions around the periphery of the pyrene ring and also many mono- and dications with a bridging positively charged nitrogen atom. At present, according to our data, only a small number of these aromatic nitrogen heterocycles have been synthesized.

The attention paid to azapyrenes is due both to theoretical aspects (aromaticity, thermodynamic stability, the mechanism of electrophilic and nucleophilic substitution, the stability of the radical-ions, etc.) and to the results of applied studies. In particular, the change of the biological activity with the inclusion of nitrogen atoms in the pyrene ring, i.e., the transition from pyrene to its aza and polyaza analogs, is of undoubted interest. Thus, whereas the monoazapyrenes found in natural subjects [1-4] exhibit mutagenic and carcinogenic activity [5] the derivatives of the most investigated 4(9)- and 2,7-diazapyrenes exhibit analgesic [6] and antiviral and antibacterial [4] activity, and also anticancer activity [8-10]. The mechanism of such activity is usually attributed to their known ability to act as intercalators [11-20]. Polyazapyrenes are actively used in supramolecular chemistry for the construction of molecular devices [21], compounds with topological bonding [22], molecules of the "host–guest" type [23], and macrocomplexes with the cations of transitional metals [24, 25].

In this review the generally accepted substitutive aza nomenclature [26] is used for these compounds, although other names were used in the earlier papers.

1. AZAPYRENES

1-Azapyrene **3** was first obtained in 1986 according to the following scheme [27]:



1 **2** **3**

* Dedicated to the 70th jubilee of A. F. Pozharskii.

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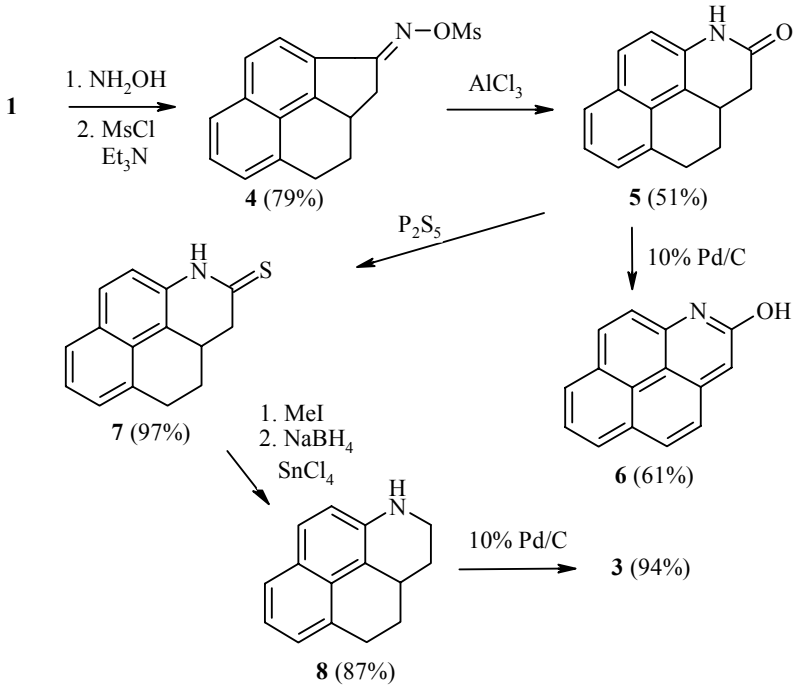
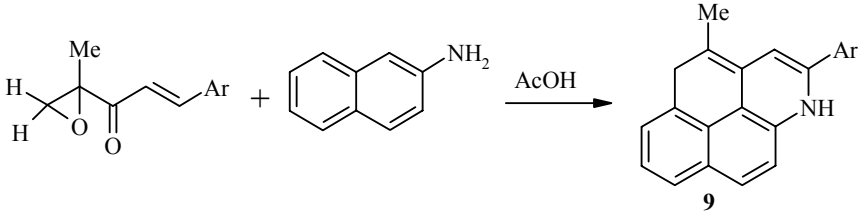
The ketone **1** was synthesized in three stages from dihydrophenalene. The alcohol **2**, obtained by the reduction of the ketone **1**, was then used in a modification of the Schmidt reaction [28]. The 4,5-dihydro-1-azapyrene formed here was dehydrogenated, without isolation, with palladium on charcoal. However, the yield of the Schmidt reaction was very low, and the overall yield was only 1%.

Another approach to the synthesis of 1-azapyrene used by the authors in [27] was more successful. The oxime and then its mesylate derivative **4** were obtained from the ketone **1**. Compound **4** underwent a Beckmann rearrangement with $AlCl_3$ with ring enlargement and the formation of the lactam **5**.



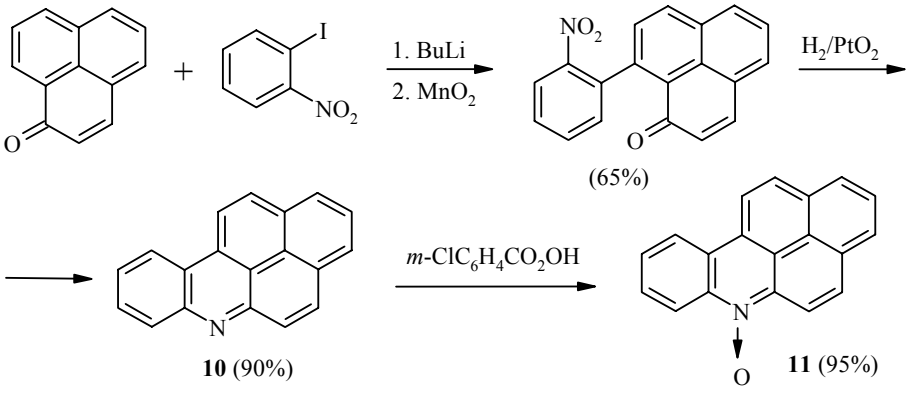
An attempt at the dehydrogenation of compound **5** by the action of Pd/C led to 2-hydroxy-1-azapyrene (**6**). The amide **5** was then converted into the thioamide **7**; quaternization of the latter followed by reduction of the methylthio derivative gave the amine **8**. Aromatization of the amine **8** took place smoothly with the formation of the required 1-azapyrene **3**.

In 1995 a report appeared on a single-stage method for the synthesis of 2-aryl-1,5-dihydro-1-azapyrenes **9** starting from β-naphthylamine [29]. Reaction of the latter with the oxirane derivative of the α,β-unsaturated ketone takes place in glacial acetic acid at room temperature in an atmosphere of argon and gives high yields of compounds **9**. However, nothing has been reported about attempts at their aromatization.

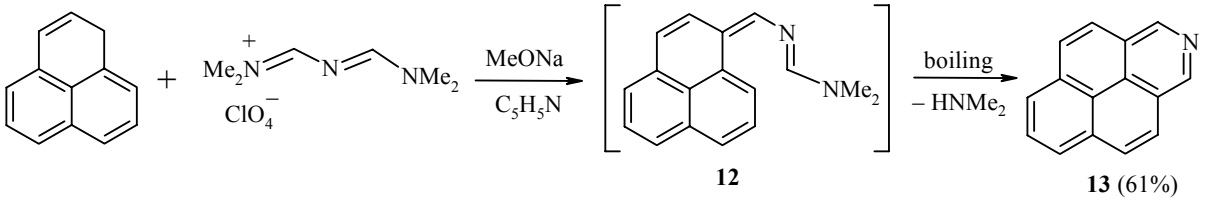


Ar = Ph (91%); 4-MeC_6H_4 (93%); 4-$EtOC_6H_4$ (95%); 4-ClC_6H_4 (96%)

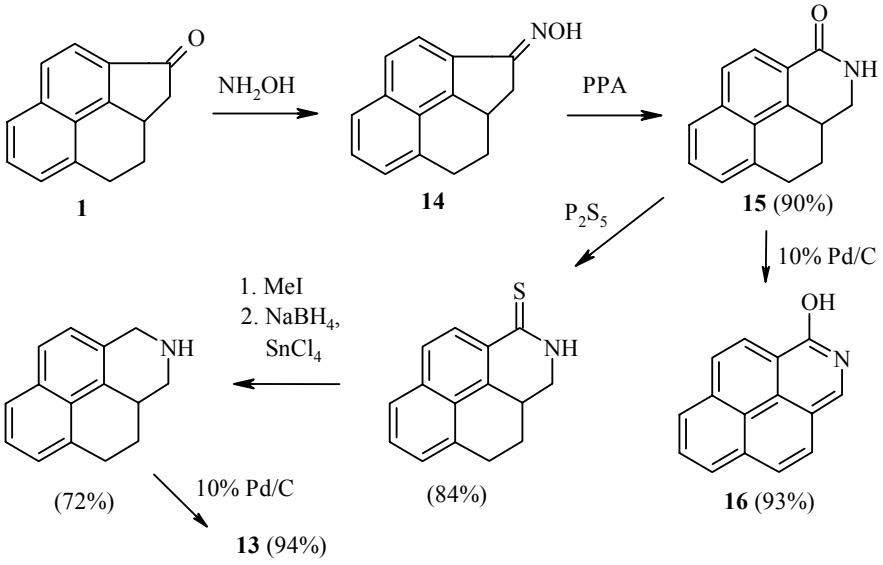
The benzo[*a*] analog of 1-azapyrene **10** was obtained from phenalenone and *o*-iodonitrobenzene with subsequent reductive cyclization [30]. Its N-oxide **11** was obtained by the action of *m*-chloroperbenzoic acid.



2-Azapyrene **13** was first obtained by the reaction of phenalene with 3-dimethylamino-2-aza-propenylideneammonium perchlorate and sodium methoxide in pyridine [31]. The amine **12** formed at the first stage presumably undergoes cyclization to 2-azapyrene **13** when heated. The synthesis of the salt 2-methyl-2-azapyrenium iodide was also reported.

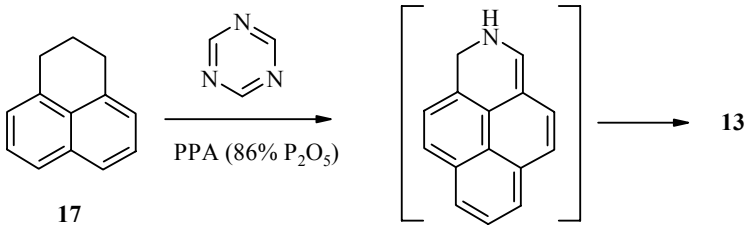


The scheme presented below was worked out by the authors in [27] for the synthesis of 1-azapyrene. Unexpectedly, however, the key stage – the Beckmann rearrangement of the oxime **14** formed from the ketone **1** as a 9:1 mixture of *syn* and *anti* isomers – led in polyphosphoric acid (PPA) not to the expected arylamide but exclusively to the alkylamide **15**.



The transformations that followed were similar to those carried out by the authors of this paper for the synthesis of 1-azapyrene (see above). As a result 2-azapyrene **13**, 1-hydroxy-2-azapyrene (**16**), and other partly hydrogenated derivatives were obtained.

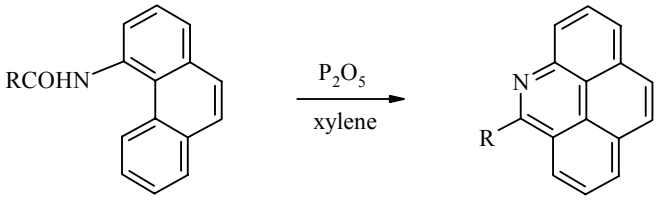
A new method was recently developed for the *peri* annelation of a [*c*,*d*]pyridine ring to phenalenes, heterophenalenes, and their dihydro derivatives [32]. It involves the action of *sym*-triazines on the substrate in polyphosphoric acid. Thus, 2-azapyrene **13** was obtained from dihydrophenalene **17** in one pot with a yield of 74%.



17 **18**

In the course of the reaction the intermediate **18** undergoes spontaneous dehydrogenation. This method proved extremely productive for the synthesis of other polyazapyrenes.

4-Azapyrene **20a** and its 5-substituted derivatives **20b**,**c** were obtained by cyclodehydration of the 4-acylamidophenanthrenes **19a-c** by the action of phosphorus pentoxide in boiling xylene [33].



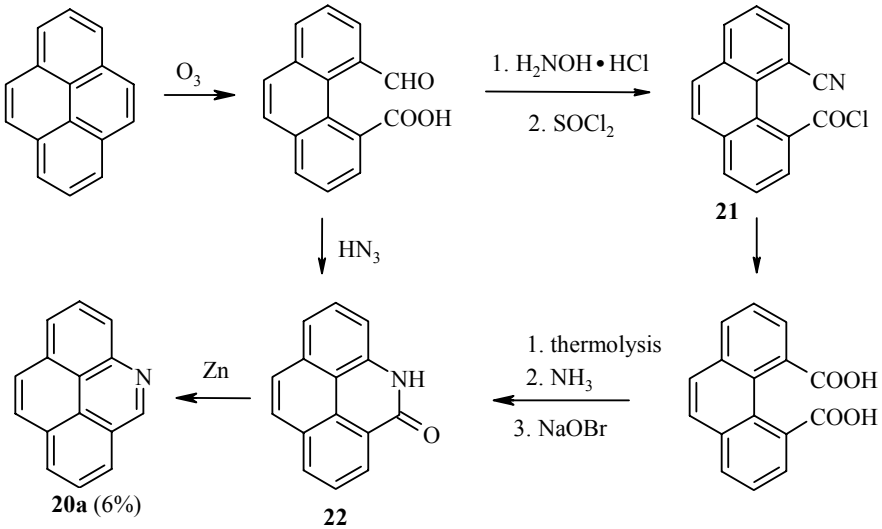
19a–c

19 a R = H, **b** R = Me, **c** R = Ph

20a–c

20 a (33%), **b** (47%), **c** (the yield was not)

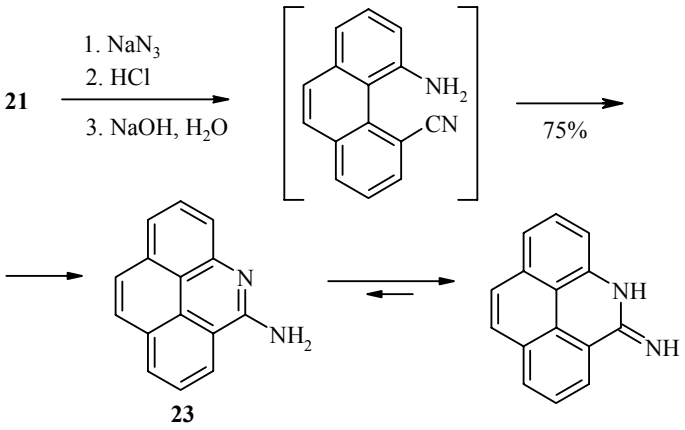
The synthesis of 4-azapyrene **20a** and 4,5-dihydro-4-azapyren-5-one (**22**) from pyrene was realized by the authors of [34] according to the following scheme:



21

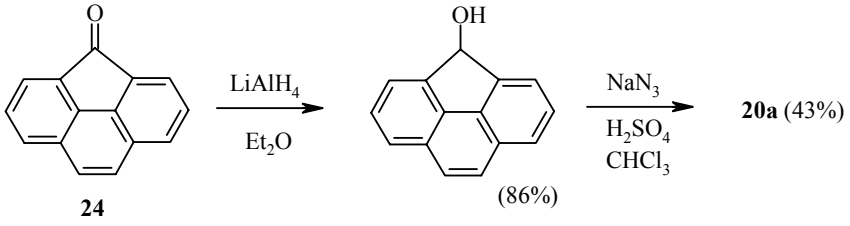
20a (6%) **22**

5-Amino-4-cyanophenanthrene, which undergoes spontaneous cyclization with the formation of 5-amino-4-azapyrene (**23**), was also obtained from compound **21** [34].

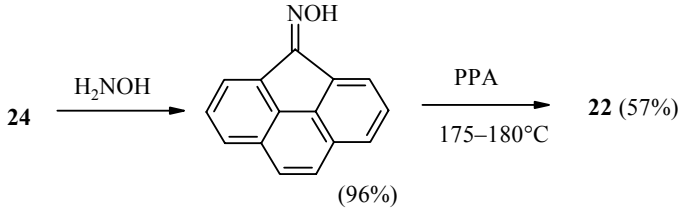


From the UV spectra the authors of [34] conclude that the reaction product exists in the imino form.

Another approach to the synthesis of 4-azapyrene **20a** was demonstrated in [35]. It was produced from cyclopentano[*def*]phenanthren-4-one in two stages, i.e., reduction of the ketone **24** to the corresponding alcohol followed by the action of sodium azide and concentrated sulfuric acid in chloroform.

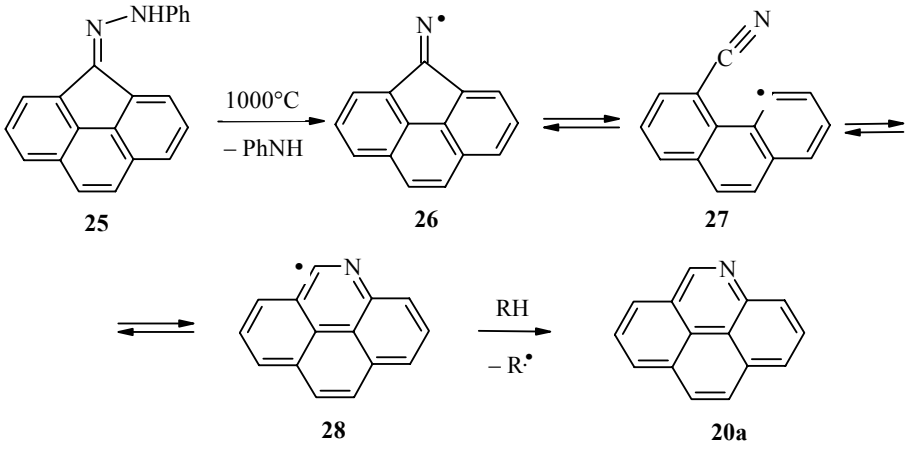


Another pathway – the production of the oxime from the ketone **24** followed by brief heating in PPA – led to a Beckmann rearrangement with ring enlargement and the formation of compound **22** [35].



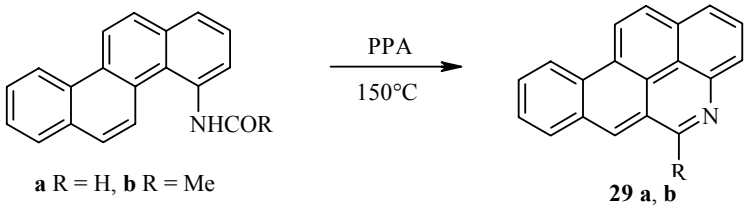
In [35] it was noted that according to IR and NMR spectroscopy compound **22** does not contain significant amounts of the enolic tautomer, i.e., 5-hydroxy-4-azapyrene.

German researchers [36] showed that 4-azapyrene (in the original paper it was called benzo[*lmn*]phenanthridine) was formed with an unexpectedly high yield (72%) during brief high-temperature pyrolysis (1000°C, 0.3 sec) of the phenylhydrazone of cyclopentano[*def*]phenanthren-4-one (methanophenanthrenone) (**25**). The authors assume that the process takes place by a radical mechanism according to the following scheme.



The ketiminyl radical **26** generated under these conditions undergoes reversible opening of the five-membered ring with the formation of a radical of the phenyl type **27**. The most unusual, according to the authors, is the intramolecular addition of the radical **27** to the nitrogen atom of the nitrile group with the formation of the imidoyl radical **28**.

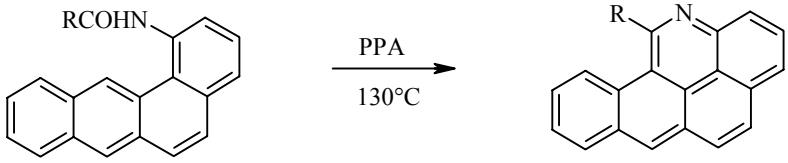
The benzo[*i*], benzo[*h*], and benzo[*a*] analogs of 4-azapyrene (**29a**,**b**, **30a**,**b**, and **31a**,**b**, respectively) were obtained by multistage syntheses, the concluding stage of which was cyclodegradation of the corresponding amides by the Bischler–Napieralski method by heating in polyphosphoric acid [37].



a R = H, **b** R = Me

29 a, **b**

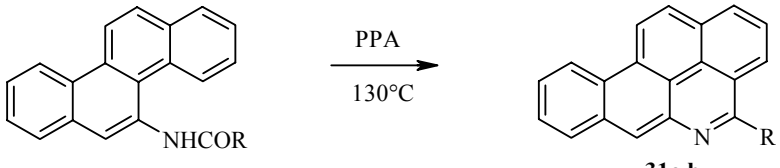
29 a (66%), **b** (59%)



a R = H, **b** R = Me

30a,**b**

30 a (80%), **b** (53%)



a R = H, **b** R = Me

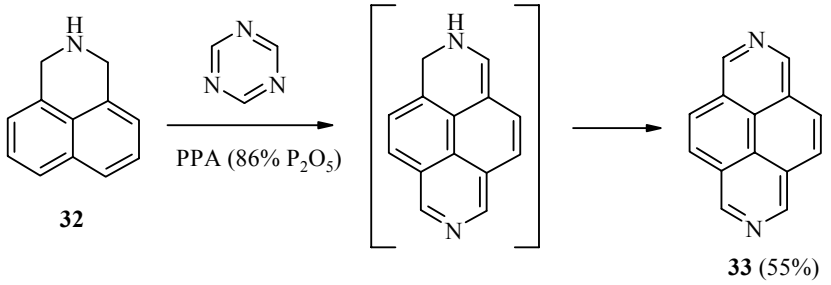
31a,**b**

31 a (75%), **b** (80%)

2. DIAZAPYRENES

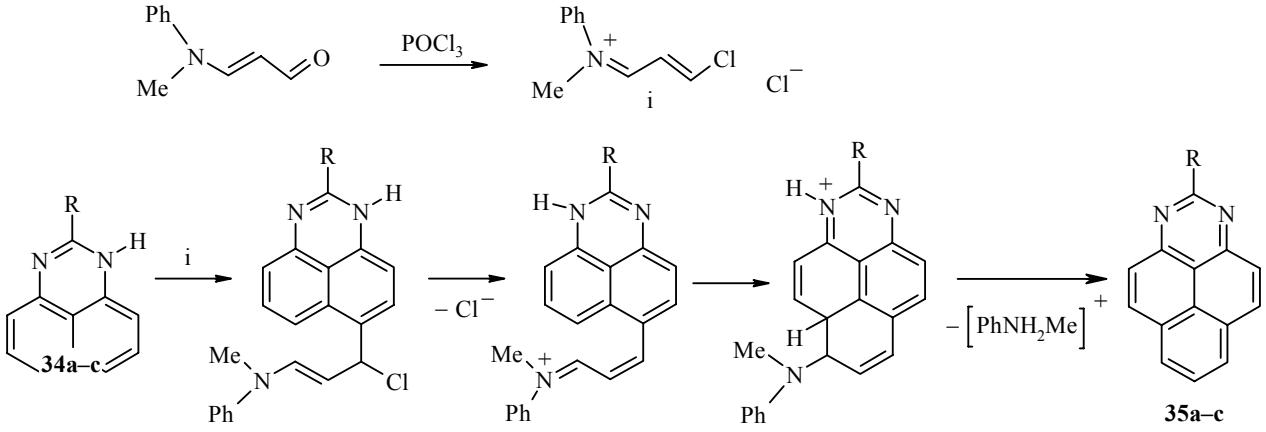
The synthesis and properties of diazapyrenes were described in our previous review [38], and only new data on their production are therefore given here.

Like 2-azapyrene 2,7-diazapyrene **33** was synthesized from dihydroazaphenalene **32**, using the *sym*-triazine – PPA system [32].



32 **33** (55%)

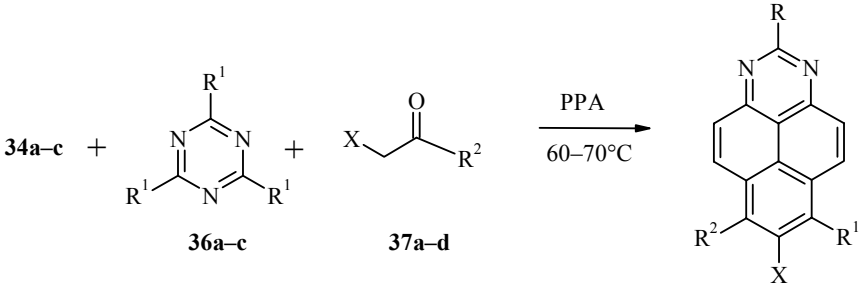
Two new methods were developed for the synthesis of 1,3-diazapyrenes from perimidines. The first of them involves the action of the Vilsmeier reagent, formed by the vinylog of N-methylformanilide, on the perimidines **34a-c** [39].



34a–c **35a–c**

34, **35 a** R = H, **b** R = Me, **c** R = Ph

The second method is the three-component reaction between the perimidines **34a-c**, 1,3,5-triazines **36a-c**, and carbonyl compounds **37a-d** in polyphosphoric acid, which gives a moderate yield of the corresponding 1,3-diazapyrenes **38a-j** [40] (Table 1).



34a–c **36a–c** **37a–d** **38a–j**

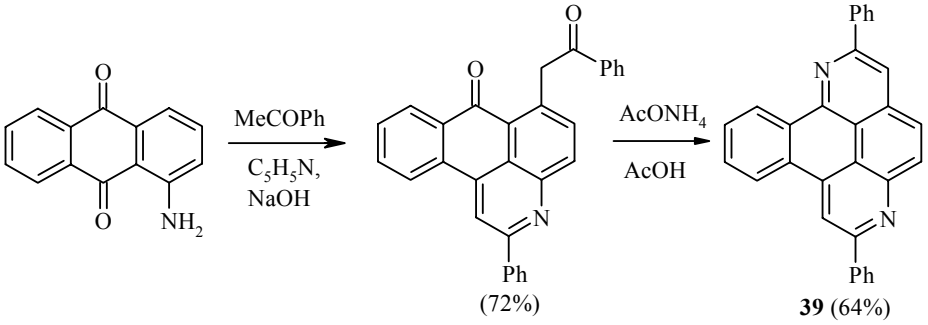
36 a R^1 = H; **b** R^1 = Me; **c** R^1 = Ph

TABLE 1. The Synthesis of 1,3-diazapyrenes **38a-j** from Perimidines **34a-c**

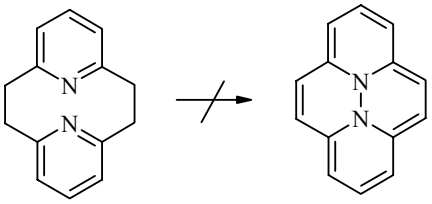
R	R^1	R^2	X	Product	Yield, %	R	R^1	R^2	X	Product	Yield, %
H	H	Me	H	**38a**	47	H	Me	Ph	H	**38f**	73
H	Me	Me	H	**38b**	45	H	Ph	Ph	H	**38g**	43
H	H	Ph	H	**38c**	75	Me	H	Me	CO_2Et	**38h**	57
H	H	Me	COMe	**38d**	57	Ph	Ph	Ph	H	**38i**	51
H	H	Me	CO_2Et	**38e**	43	H	Me	Me	COMe	**38j**	37

The mechanism proposed by the authors for this unusual transformation was presented in [40].

1,6-Diazapyrene has so far been unknown. However, its benzo analog 2,7-diphenyl-1,6-diazabenzo[*e*]pyrene (**39**) was obtained by the condensation of acetophenone with 1-aminoanthraquinone under the conditions of alkaline catalysis followed by cyclization of the product by boiling with ammonium acetate in acetic acid [41].



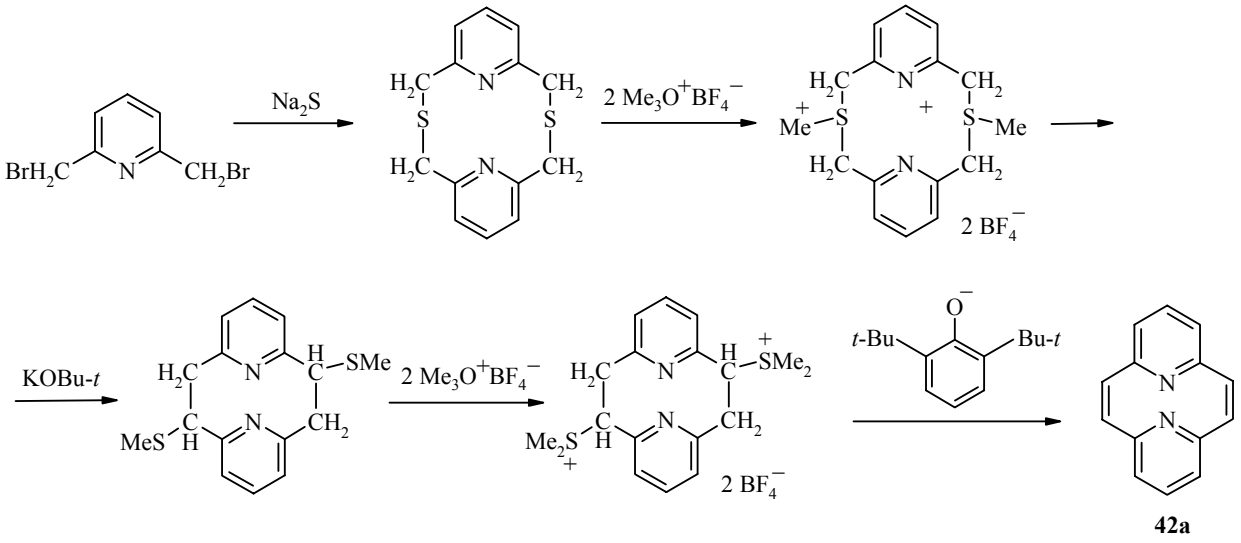
In the second half of the twentieth century attempts were made at the synthesis of 10b,10c-dihydro-10b,10c-diazapyrene **41**. This compound was of great theoretical interest since it contained 14 peripheral π electrons, which corresponded to the Hückel rule, and it could consequently have aromaticity. In addition, the potentially possible existence of valence tautomerism between **41** and **42**, which would link cyclophane and cyclazine systems, was suggested. However, an attempt to obtain **41** from the synthesized [2,2](2,6)pyridinophane (**40**) was unsuccessful [42].



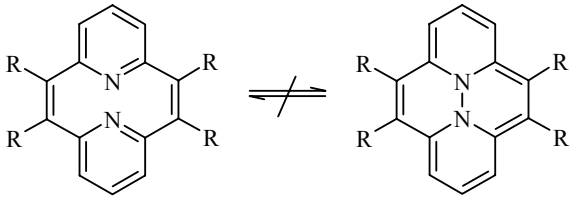
40 **41**

In 1970 the valence isomer of 10b,10c-dihydro-10b,10c-diazapyrene – [2,2](2,6)pyridinophane-1,9-diene (**42a**) – was obtained for the first time by a multistage synthesis [43]. The synthesis of this compound is of separate interest in that it demonstrates the possibility of transformation of a sulfide bond (C–S–C) into a carbon–carbon double bond (C=C).

Compounds **42b**,**c** were later synthesized by a different method [44]. It was found, however, that none of the [2,2]metacyclophanes **42a-c** undergoes spontaneous acid-catalyzed or photoinduced transformation into the valence isomer 10b,10c-diazapyrene **41**.



Quantum-chemical calculations also showed that **42** is more stable than **41** [43].

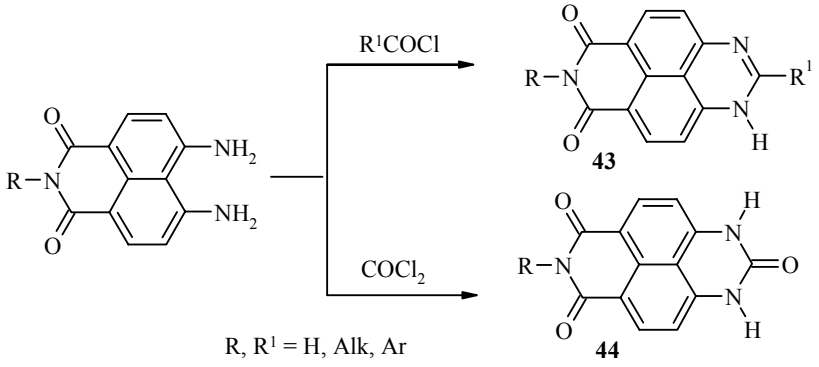


42a–c **41a–c**

41, 42 **a** R = H, **b** R = Cl, **c** R = SCH_2Ph

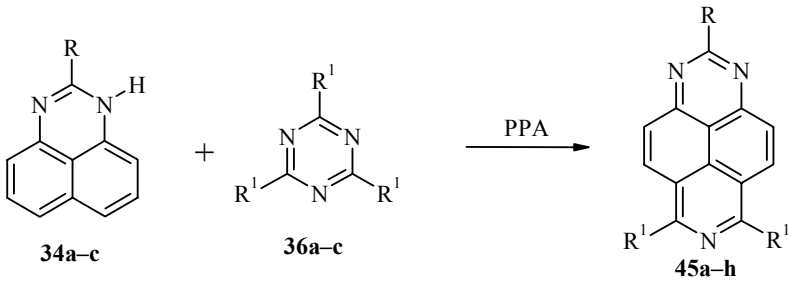
3. TRIAZAPYRENES

Partly hydrogenated derivatives of 1,3,7-triazapyrene **43** and **44** were synthesized by a multistage method, the concluding stage of which was the cyclization of 4,5-diaminonaphthylimides [45, 46].



R, R^1 = H, Alk, Ar

Aromatic 1,3,7-triazapyrenes **45a-h** were obtained recently by the reaction of perimidines **34a-c** with 1,3,5-triazines **36a-c** in polyphosphoric acid [32] (Table 2).



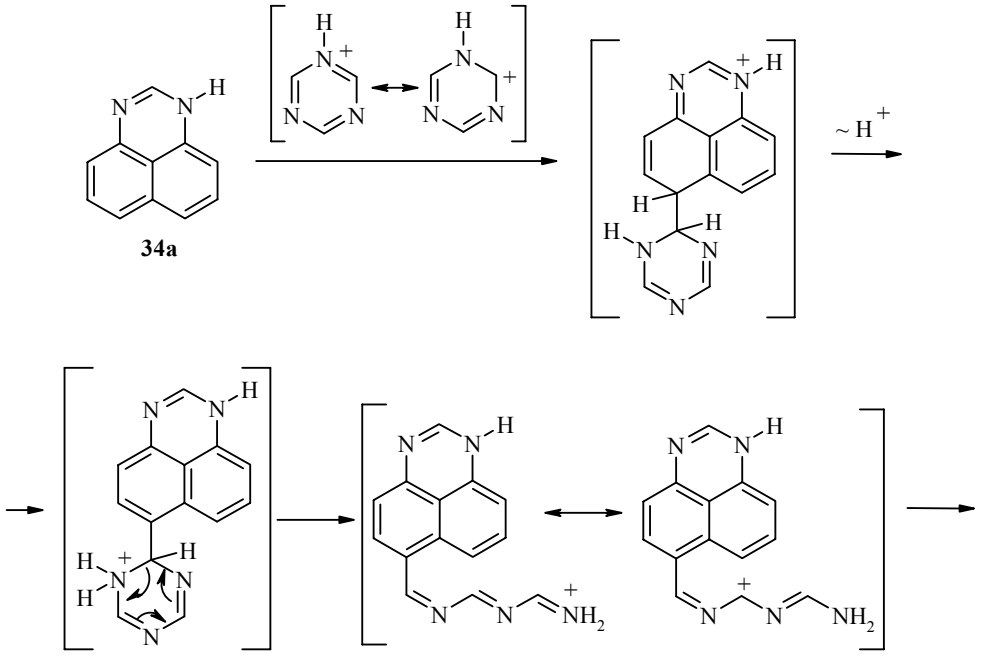
34a–c **36a–c** **45a–h**

TABLE 2. Synthesis of 1,3,7-Triazapyrenes **45a-h**

Product	R	R^1	Yield, %	Product	R	R^1	Yield, %
45a	H	H	63	**45e**	Me	Me	52
45b	Me	H	55	**45f**	Ph	Me	60
45c	Ph	H	56	**45g**	H	Ph	78
45d	H	Me	72	**45h**	Ph	Ph	40

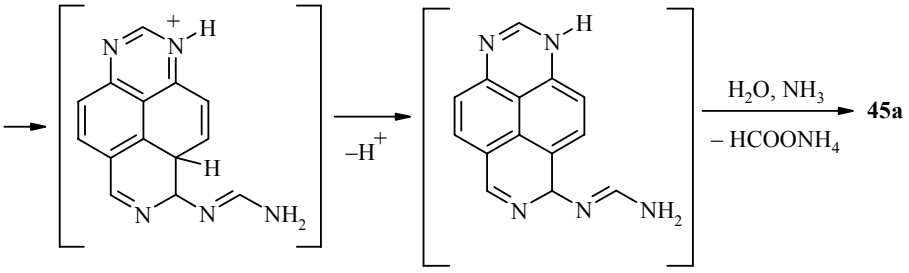
It should be noted that whereas the reactions of the perimidines with the triazine **36a** take place at 100°C more severe conditions are needed for its substituted derivatives **36b**,**c** (140 and 180°C respectively).

In the opinion of the authors [32] the most likely mechanism for the reaction of the perimidines with triazine (in the case of the formation of **45a**) involves electrophilic attack on **34a** by the 1,3,5-triazinium cation at position 6(7), opening of the triazine ring with formation of intermediate **46** and its subsequent cyclization at the *peri* position. Aromatization of **47** takes place by elimination of the amidine, which undergoes hydrolysis during isolation.



34a

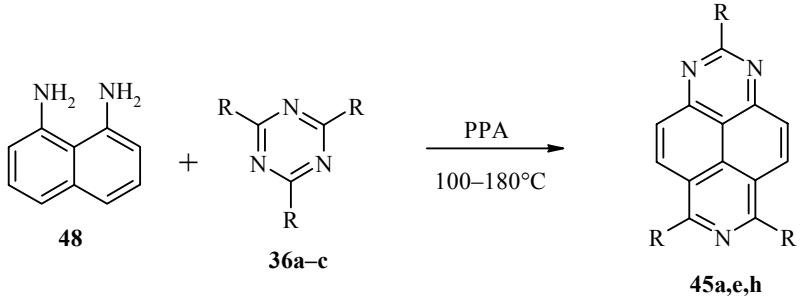
46



47

As established somewhat earlier, at a lower temperature the perimidines are formylated (acylated) in the 1,3,5-triazine–PPA system as a result of hydrolysis of intermediates of the **46** type or their precursors [47] during isolation. This confirms indirectly the mechanism proposed for the formation of 1,3,7-triazapyrenes from perimidines.

Earlier it was reported that the reaction of 1,8-diaminonaphthalene **48** with 1,3,5-triazine **36a** without a catalyst leads to perimidine [48]. However, when the diamine **48** was heated with the triazines **36a-c** in polyphosphoric acid above 100°C the only reaction products were 1,3,7-triazapyrenes **45a**,**e**,**h** [49].

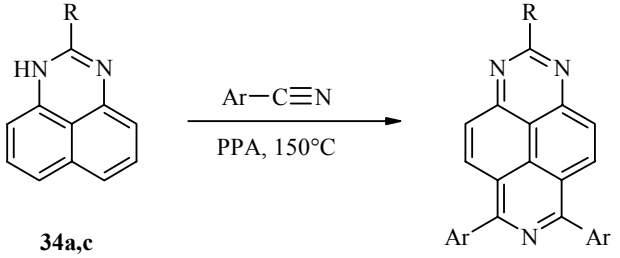


48 **36a–c** **45a,e,h**

a R = H, **e** R = Me, **h** R = Ph

It was not possible to stop the reaction at the formation of the corresponding perimidines since it does not take place at lower temperatures. In other words the process is limited by the stage of initial cyclization of the diamine **48**; it then goes according to the scheme presented above.

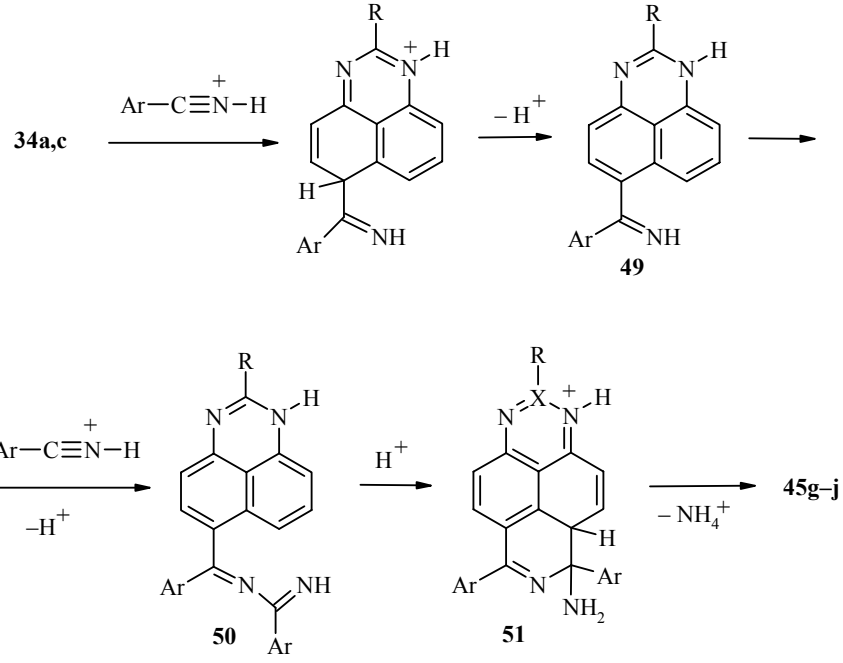
An attempt at the acylation of the perimidines **34a**,**c** with an excess of the nitriles of aromatic acids in polyphosphoric acid ended unexpectedly – the only products in this case were the corresponding 1,3,7-triazapyrenes [50].



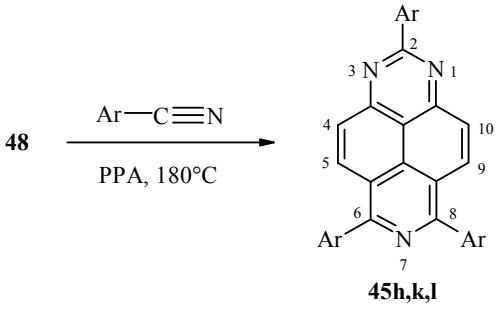
34a,c **45g–j**

45 g R = H, Ar = Ph (68%), **h** R = Ar = Ph (30%), **i** R = H, Ar = 4-BrC_6H_4 (77%),
j R =H, Ar = 4-$O_2NC_6H_4$ (49%)

The mechanism of this transformation probably involves regioselective attack by the nitrylium cation initially at position 6(7) of the compound **34a**,**c** and then at the nitrogen atom of the ketimine **49** with the formation of the intermediate **50** and its subsequent cyclization at the *peri* position. Aromatization of **51** takes place by elimination of an ammonium cation.

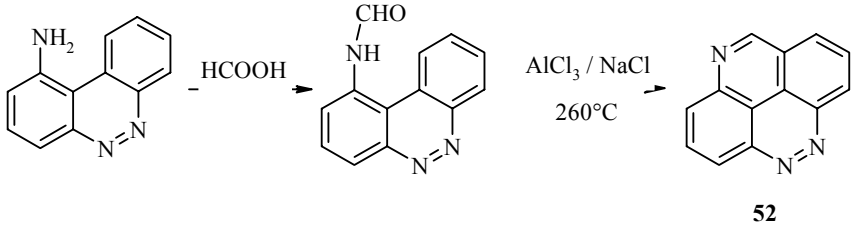


The reaction of 1,8-diaminonaphthalene **48** with aromatic nitriles in polyphosphoric acid also resulted in the formation of the corresponding 2,6,8-triaryl-1,3,7-triazapyrenes **45h**,**k**,**l** [48].



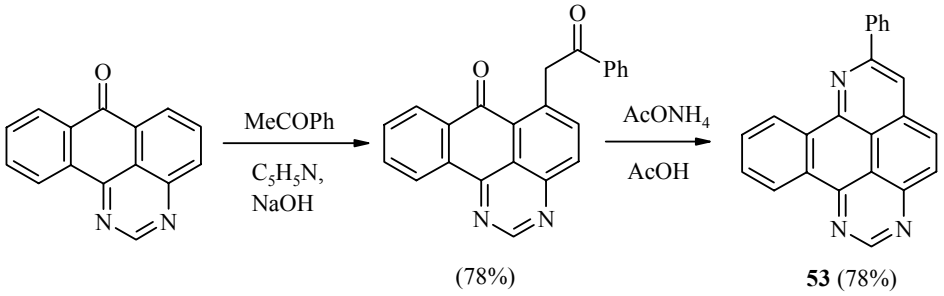
45 h Ar = Ph (35%), **k** Ar = 4-BrC_6H_4 (24%), **l** Ar = 4-$O_2NC_6H_4$ (27%)

4,5,9-Triazapyrene (**52**) was first obtained according to the following scheme [45]:



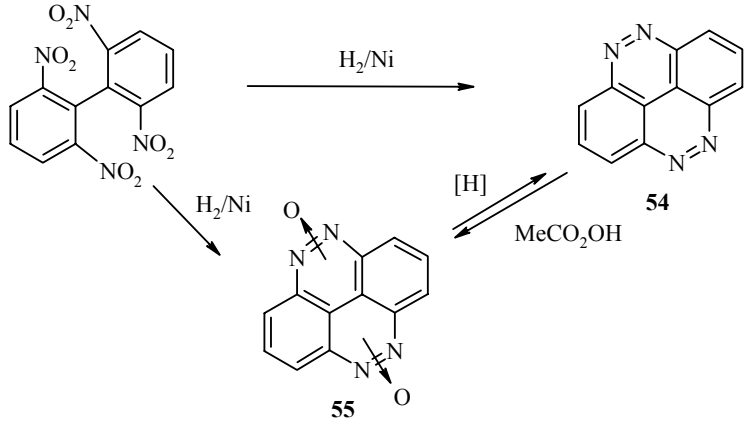
The concluding stage – condensation of 1-formamidobenzo[*c*]cinnoline – takes place under more severe conditions.

7-Phenyl-1,3,8-triazabenzo[*e*]pyrene (**53**) was produced by the condensation of acetophenone with 7H-benzo[*e*]perimidin-7-one under the conditions of alkaline catalysis followed by cyclization of the product by boiling with ammonium acetate in acetic acid [41].



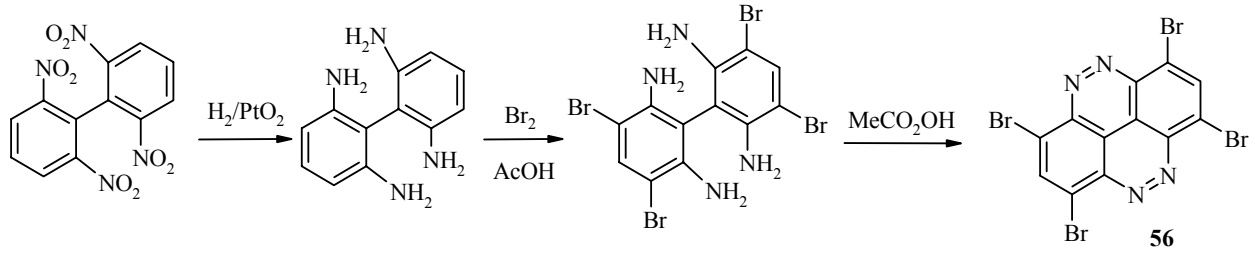
1.4. Tetraazapyrenes

The synthesis of 4,5,9,10-tetraazapyrene (**54**) was first achieved by the hydrogenation of 2,2',6,6'-tetranitrobiphenyl [52].



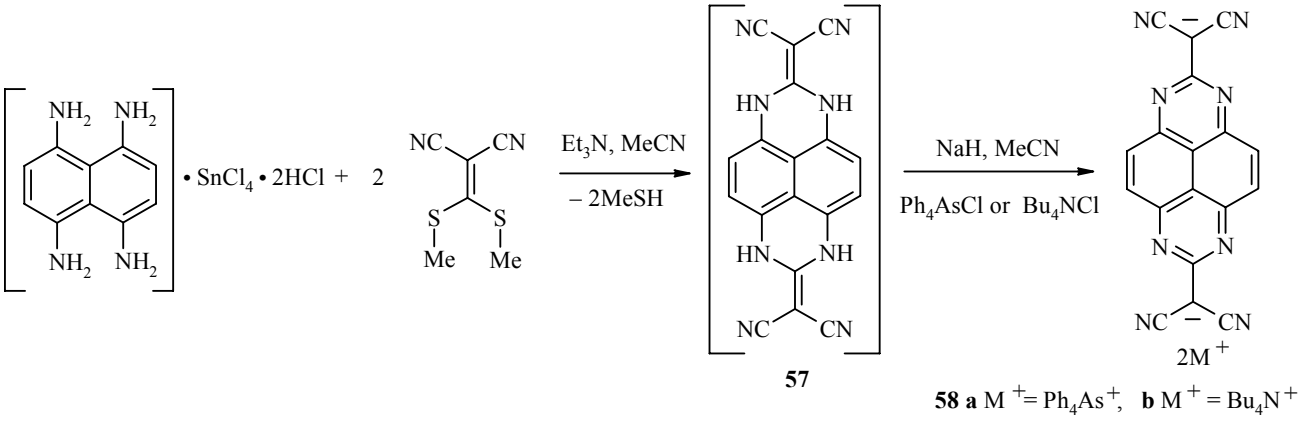
It was later found [53] that the main product under milder conditions was a mixture of tetraazapyrene di-N-oxides **55**, which after further hydrogenation or reduction by the $SnCl_2$/HCl system gave tetraazapyrene **54**. On the basis of the UV and IR spectra the authors considered that **55** was a mixture of the 4,9- and 4,10-N-oxides. In turn the tetraazapyrene **54** was readily oxidized by peracetic acid to the di-N-oxides **55** [53].

1,3,6,8-Tetrabromo-4,5,9,10-tetraazapyrene (**56**) was synthesized from 2,2',6,6'-tetranitrobiphenyl according to the following scheme [54]:



A large series of 1,3,6,8-tetraaryl-4,5,9,10-tetraazapyrenes were obtained in a similar way [54].

In [55] it was reported that the double tin salt of 1,4,5,8-tetraaminonaphthalene, obtained from 1,4,5,8-tetranitronaphthalene [56], in reaction with 1,1-bis(methylthio)methylenemalononitrile forms a complex reaction mixture presumably containing a derivative of 1,3,6,8-tetraazapyrene **57**.

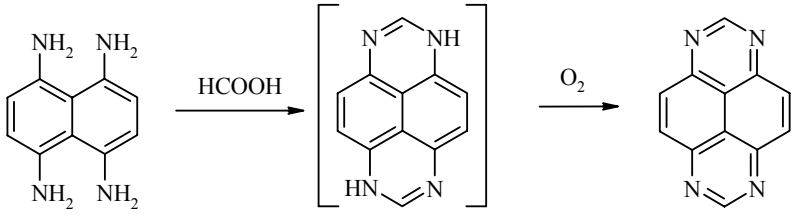


57

58 a $M^+ = Ph_4As^+$, **b** $M^+ = Bu_4N^+$

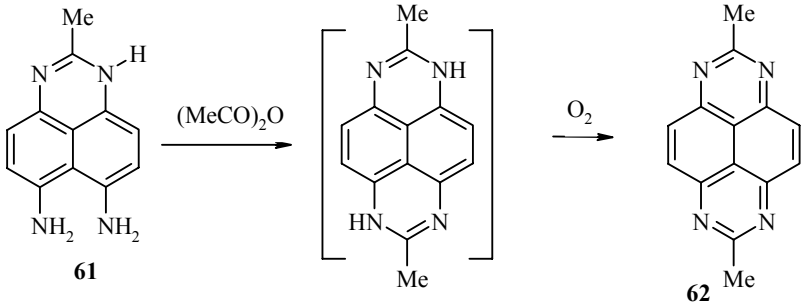
Since it was not possible to isolate the product from it in any way the authors treated the reaction mass with sodium hydroxide in the presence of ammonium or arsonium salts. The products of these transformations were the extremely stable salts **58a**,**b** with an organic dianion. The dianion **58** was so stable that attempts to oxidize it by chemical means were unsuccessful; it was oxidized electrochemically in a single stage to the corresponding radical-ion and reduced to a relatively stable radical-trianion.

When heated with formic acid 1,4,5,8-tetraaminonaphthalene forms the red diperimidine **59**, which is oxidized extremely readily by atmospheric oxygen to the scarcely greenish 1,3,6,9-tetraazapyrene **60** [57, 58].



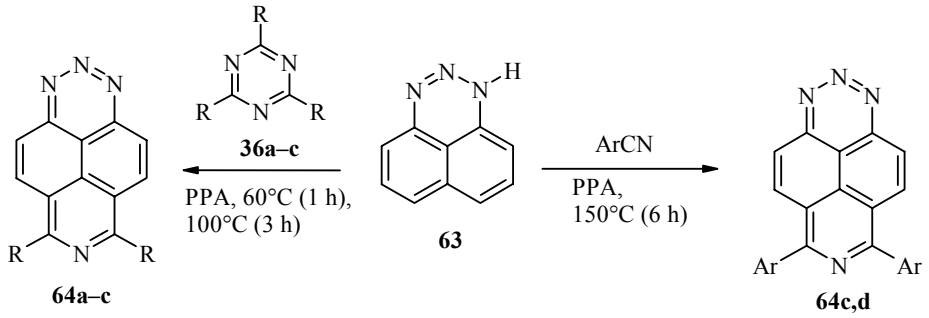
59 **60**

2,7-Dimethyl-1,3,6,8-tetraazapyrene (**62**) was obtained by the reaction of 6,7-diamino-2-methylperimidine (**61**) with acetic anhydride [59, 60].



61 **62**

1,2,3,7-Tetraazapyrenes **64a-d** were synthesized by the reaction of 1H-naphtho[1,8-*de*]triazine [1,2,3-triazaphenalene (**63**)] with 1,3,5-triazines or aromatic nitriles in polyphosphoric acid [32, 50, 61].



64 a R = H (68%), **b** R = Me (55%), **c** R = Ph (58%); **c** Ar = Ph (61%),
d Ar = 4-$O_2NC_6H_4$ (23%)

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