SYNTHESIS OF NITROGEN-CONTAINING CONDENSED HETEROCYCLIC COMPOUNDS BY CATALYTIC DEHYDROCYCLIZATION OF SUBSTITUTED PYRIDINE BASES (REVIEW)

N. S. Prostakov and A. V. Varlamov

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Reactions involving the catalytic dehydrocyclization of synthetically accessible substituted pyridine bases, as a result of which condensed nitrogen-containing heterocyclic compounds containing three, four, and five rings are formed, are examined.

The method of dehydrocyclization is used to obtain many aromatic compounds, including those produced on an industrial scale. However, its use in the synthesis of heterocyclic compounds has been limited in the past [1] and remains so at the present time. Dehydrocyclization is carried out under various conditions (pyrolysis, UV irradiation, oxidative dehydrocyclization), but dehydrocyclization in the presence of catalysts is most promising. On active dehydrogenating catalysts the reaction usually proceeds selectively, and the significantly lower temperature as compared with pyrolysis limits side processes (destruction, coke formation). A peculiarity of this reaction is the use, as the starting substances, of compounds into which the functional groups that are necessary for intramolecular ring closing have not been previously introduced.

A nitrogen-containing six-membered ring is a fragment of many synthetic and natural physiologically active compounds, and catalytic dehydrocyclization in conjunction with selective hydrogenation of the pyridine fragment of condensed nitrogen-containing heterocycles with retention of the benzene fragments [2, p.37] may therefore serve as a convenient method for obtaining heterocyclic systems of synthones for their construction that are similar to alkaloids.

The first data on the syntheses of nitrogen-containing heterocycles (pyridines, indoles, carbazole) via pyrolysis, as well as by the use of catalysts, are presented in [1]. In the present review we discuss synthesis by the catalytic dehydrocyclization of various condensed polynuclear nitrogen-containing heterocyclic compounds, chiefly on the basis of substituted pyridines. The latter have become accessible substances owing to the development of methods for their synthesis from γ-piperidones [3], as well as via the Chichibabin reaction using a cadmium calcium phosphate catalyst [4].

Azafluorenes

The cyclodehydration of phenyl-substituted pyridinecarboxylic acids is the principal method for the synthesis of azafluorenes. 1,3-Dimethyl-2-azafluorenone was first obtained from 2,6-dimethyl-4-phenylpyridine-3-carboxylic acid [5]. The development of the chemistry of azafluorenes commenced with this research. However, the use of the indicated method is limited because of the low degree of accessibility of the starting compounds and the low yields of the desired products, and azafluorenes have therefore remained virtually uninvestigated compounds.

The development of the chemistry of azafluorenes in the last 20 years involves the use of catalytic dehydrocyclization for obtaining them. Aryl-substituted pyridine bases containing, as a rule, a methyl group in the ortho position relative to the aryl radical served as the starting compounds. The use of pyridine bases with different relative orientations of the aryl and methyl radicals in the ring has made it possible to synthesize all of the isomeric (with respect to the position of the nitrogen atom) azafluorenes. 3-Methyl-2-azafluorene was the first representative of azafluorenes obtained by catalytic dehydrocyclization [6]. The reaction was carried out on a K-16 dehydrogenating catalyst at 500-520°C with 2,5-dimethyl-4-phenylpyridine as the starting compound. 2-Azafluorene was similarly obtained from 3-methyl-4-phenylpyridine [7].

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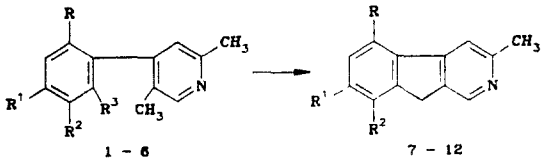
R=CH$_3$, H

The pyrolytic dehydrocyclization of 2,5-dimethyl-4-phenylpyridine on quartz proceeds only at temperatures above 600°C. At 700°C 3-methyl-2-azafluorene was obtained in 4% yield, whereas its yield was 20% in the case of catalytic dehydrocyclization [6]. Dehydrocyclization of this pyridine base also occurs in the presence of iodine at 500-600°C; exhaustive iodination of the methylene group of the resulting azafluorene occurs in this case. Subsequent alkaline treatment of the reaction products leads to 3-methyl-2-azafluorenone in 23% yield [7].

Polymethyl-substituted 2-azafluorenes were also obtained by catalytic dehydrocyclization. The synthetically accessible 2,5-dimethyl-4-arylpyridines with different positions of the methyl groups in the benzene ring were used for their synthesis [8-10].



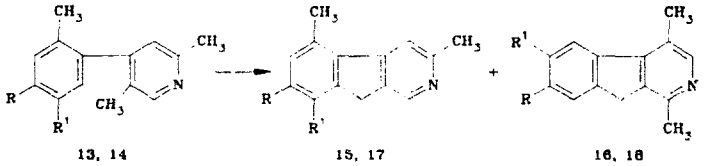
1 - 6 7 - 12

1, 5—7, 11, 12 R=CH$_3$, 2—4, 8—10 R=H; 1, 2, 7, 8 R^1=H, 3—6, 9—12 R^1=CH$_3$; 1, 3, 6, 7, 9, 12 R^2=H, 2, 4, 5, 8, 10, 11 R^2=CH$_3$; 1—5 R^3=H; 6 R^3=CH$_3$

Di-, tri-, and tetramethyl-substituted 2-azafluorenes were obtained in 18-34% yields. The positions of the methyl groups in azafluorenes 7-12 were established by PMR spectroscopy [9, 10].

The stereospecificity of the dehydrocyclization was established in the case of the synthesis of azafluorenes 8 and 10. Splitting out of hydrogen occurs from the ortho position of the aryl radical relative to the methyl group. The theoretically possible 2-azafluorenes with different positions of the methyl groups in the phenylene ring [in the $C_{(6)}$ position in the case of pyridine 2 and in the $C_{(6)}$ and $C_{(7)}$ positions in the case of pyridine 4] were not isolated. The dehydrocyclization of pyridine base 6 to azafluorene 12 is accompanied by demethylation as a result of hydrogenolysis.

The dehydrocyclization of 2,5-dimethyl-4-(2',4'-dimethylphenyl)- and -4-(2',5'-dimethylphenyl)pyridines (13 and 14) proceeds in two directions. In one of them azafluorenes 15 and 17 are formed as a result of splitting out of hydrogen from the β-methyl group of the pyridine ring and the ortho position of the aryl radical. In the second hydrogen is split out from the β position of the pyridine ring and the o-methyl group of the aryl radical to give azafluorenes 16 and 18. The individual isomers were isolated from the reaction mixtures by crystallization [11].

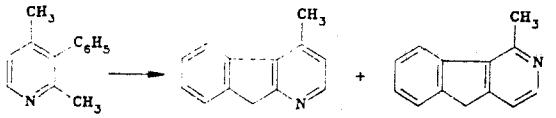


13, 14 15, 17 16, 18

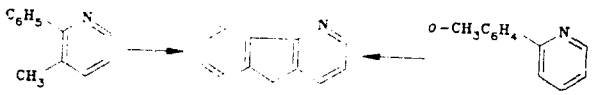
13, 15, 16 R=CH$_3$, R^1=H; 14, 17, 18 R=H, R^1=CH$_3$

The dehydrocyclization of 4-(o-tolyl)-2,6-diphenylpyridine proceeds unambiguously via the second pathway to give 1,3-diphenyl-2-azafluorene [12].

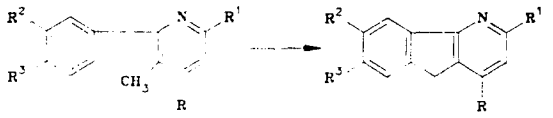
1-Azafluorene was obtained in 24% yield by catalytic dehydrocyclization (at 520-540°C) of 2-methyl-3-phenylpyridine [13]. As expected, in the case of 2,4-dimethyl-3-phenylpyridine the dehydrocyclization proceeds with the participation of both the α- and γ-methyl groups. Only the 1-azafluorene was isolated in individual form from the resulting mixture of 4-methyl-1-azafluorene and 4-methyl-3-azafluorene by chromatography [13]. 3-Azafluorenes are unstable substances that are readily oxidized. 3-Azafluorene itself was isolated in 9% yield in the dehydrocyclization of 4-methyl-3-phenylpyridine [14]. 2,4-Diphenyl-3-azafluorene was obtained in 18% yield in the dehydrocyclization of 3-methyl-2,4,6-triphenylpyridine [15]. 3-Azafluorenes with aryl substituents in the pyridine ring are relatively stable.



4-Azafluorene was obtained for the first time in ~20% yield from 3-methyl-2-phenylpyridine, as well as from 2-(o-tolyl)pyridine, by catalytic dehydrocyclization (560-570°C) [16].



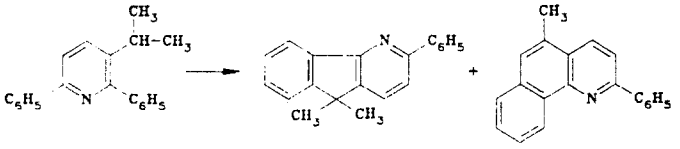
A series of methyl-substituted 4-azafluorenes was similarly obtained [17, 18]. The alkaloid "onikhin" (23) was synthesized in 29% yield [18].



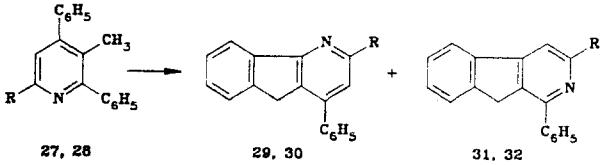
19 - 22 23 - 26

19, 23 R=CH_3, 20—22, 24—26 R=H; 19, 21—23, 25, 26 R^1=H, 20, 24 R^1=CH_3; 19, 20, 22—24, 26 R^2=H, 21, 25 R^2=CH_3; 19—21, 23—25 R^3=H; 22, 26 R^3=CH_3

The dehydrocyclization of 3-n-propyl-2,6-diphenyl- and 2,4,6-triphenylpyridines is accompanied by hydrogenolysis, evidently with splitting out of ethane from the starting compounds or intermediates; 3-phenyl- and 1,3-diphenyl-4-azafluorene, respectively, were isolated [19]. In the dehydrocyclization of 3-isopropyl-2,6-diphenylpyridine at 530-540°C splitting out of hydrogen occurs from both the methyl group and methylidyne group of the isopropyl radical. The two reaction pathways are realized with approximately equal degrees of probability; 9,9-dimethyl-3-phenyl-4-azafluorene (24%) and 5-methyl-2-phenylbenzo[h]quinoline (32%) are formed [19].



Both possible dehydrocyclization pathways are realized in the catalytic transformations (550-560°C) of 3-methyl-2,4,6-triphenylpyridine (27) and 3,6-dimethyl-2,4-diphenylpyridine (28); mixtures of 1,3-disubstituted 4- and 2-azafluorenes (29 and 31, 30 and 32), which can be separated by fractional crystallization of mixtures of the corresponding picrates, are formed [12, 16].

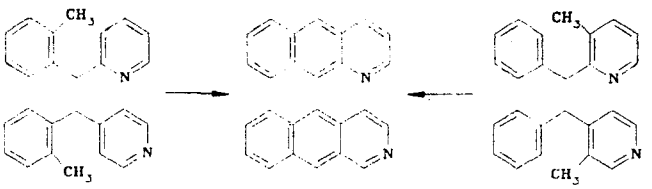


27, 28 29, 30 31, 32

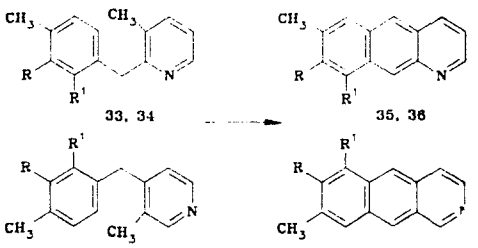
27, 29, 31 R=C_6H_5, 28, 30, 32 R=CH_3

Benzo[g]quinolines and Benzo[g]isoquinolines

The catalytic synthesis of these heterocyclic compounds was first described in [20]. A mixture of benzo[g]quinoline and benzo[g]isoquinoline was obtained from a mixture of α and γ-(o-xylyl)pyridine on a copper catalyst at 580-590°C.



The same compounds are formed in catalytic transformations of a mixture of 3-methyl-2- and -4-benzylpyridine on a K-16 catalyst at 560°C [21]; the products were obtained in 3% and 38% yields, respectively. The higher yield of benzo[g]isoquinoline is due to preponderance of the γ isomer in the starting mixture of methylbenzylpyridines [22, 23]. Methyl-substituted benzo[g]quinolines and benzo[g]isoquinolines were similarly obtained from mixtures of 3-methyl-2(4)-arylmethylpyridines [21].



33, 34 → 35, 36

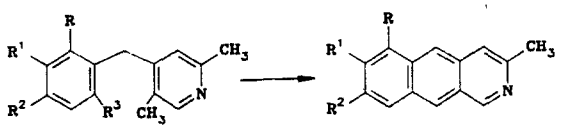
37, 38 → 39, 40

33, 35, 37, 39 R=CH_3, R¹=H; 34, 36, 38, 40 R=H, R¹=CH_3

Demethylation products were also obtained in the dehydrocyclization of pyridine bases 34 and 38. In the case of benzo[g]quinoline 36 demethylation occurs in the $C_{(9)}$ position, whereas in the case of benzo[g]isoquinoline 40 demethylation occurs in the $C_{(6)}$ position.

Dehydrocyclization with the participation of the methyl group of the benzyl radical and the β position of the pyridine ring was realized for a mixture of 2- and 4-(2',4'-dimethylbenzyl)pyridine. 7-Methylbenzo[g]quinoline and 8-methylbenzo[g]isoquinoline were obtained in 4% and 29% yields, respectively; this is approximately equal to the ratio of the benzylpyridines in the starting mixture [21].

Benzo[g]isoquinolines with methyl substituents in the pyridine and phenylene rings were obtained in up to 40% yields in the catalytic dehydrocyclization of 2,5-dimethyl-4-arylmethylpyridines [24-26].

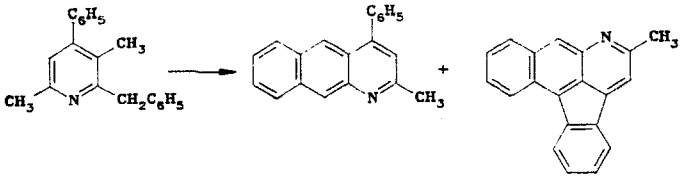


41 - 46 → 47 - 52

41—45, 47—51 R=H; 46, 52 R=CH_3; 41—44, 46—50, 52 R¹=H; 45, 51 R¹=CH_3; 41, 47 R²=H; 42, 45, 46, 48, 51, 52 R²=CH_3; 43, 49 R²=C_2H_5; 44, 50 R²=$(CH_3)_2CH$; 41—45, R³=H; 46 R³=CH_3

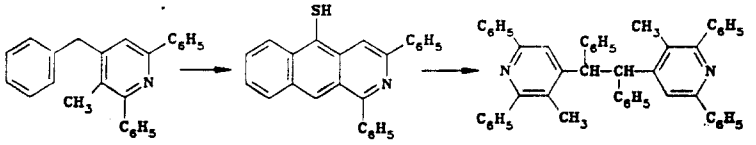
Demethylation in the mesityl radical evidently precedes cyclization of pyridine base 46. The yield of 52 is less than 1%. 3-Methylbenzo[g]isoquinoline (47) was obtained directly from a mixture of 1,2,5-trimethyl-4-benzyl-3-piperideine and -benzyl-4-piperideine on a K-16 catalyst at 480-500°C; N-demethylation, dehydrogenation of the nitrogen-containing ring, and dehydrocyclization also occurred. However, the yield of 47 was only 6% [24].

The dehydrocyclization of 3,6-dimethyl-4-phenyl-2-benzylpyridine (620°C, K-16) proceeds in both the phenyl and benzyl radicals. A mixture of 2-methyl-4-phenylbenzo[g]quinoline(23%) and 7-methyl-6-azabenzo[f]fluoroanthene (6.2%) is formed as a result [27].



The ratio of these dehydrocyclization products depends on the reaction temperature. The yield of 2-methyl-4-phenylbenzo[g]quinoline decreases with an increase in the temperature, whereas the yield of 7-methyl-6-azabenzo[f]fluoranthene increases. At 500-510°C the yield of the benzoquinoline is higher by a factor of 10, whereas at 620°C it is higher by a factor of four than the yield of the azabenzofluoranthene. The benzoquinoline, which is then converted to the azabenzofluoranthene as a result of dehydrocyclization, is evidently formed in the first step. An increase in the temperature favors the occurrence of this second step.

Dehydrocyclization of 3-methyl-2,6-diphenyl-4-benzylpyridine also occurs in the presence of sulfur at 300-305°C; the principal product (in 33% yield) is 10-mercapto-1,3-diphenyl-2-azaanthracene. The same compound is formed in lower yield (10%) under the same conditions from 1,2-diphenyl-1,2-bis(3'-methyl-2',6'-diphenyl-4'-pyridyl)ethane [28].

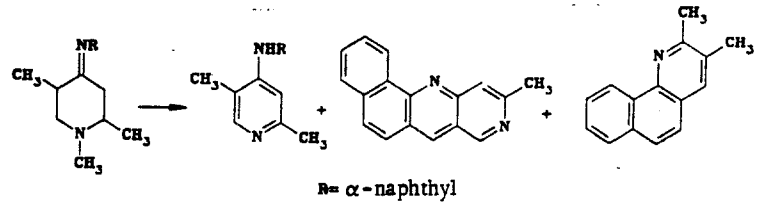


A similar mercapto derivative is not formed when 1,3-diphenyl-2-azaanthracene is fused with sulfur. The incorporation of sulfur in the azaanthracene ring evidently occurs in the dehydrocyclization and dehydrogenation steps.

The relative accessibility of methylpyridines and the arylmethyl-substituted pyridine bases obtained from them makes it possible to recommend catalytic dehydrocyclization as a preparative method in the synthesis of substituted benzo[g]quinolines and benzo[g]isoquinolines.

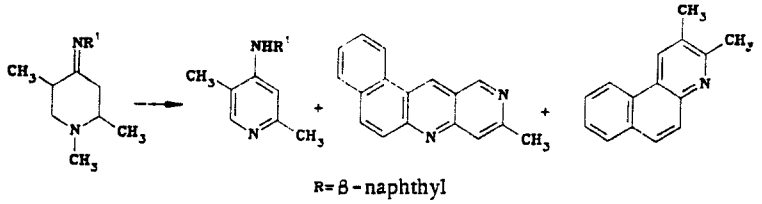
Azaphenanthrenes, Indenoquinolines, Isoquinolines, and Naphthonaphthyridines

N-(2,5-Dimethyl-4-pyridyl)-α-naphthylamine, 9-methylnaphtho[1,2-b][1,6]naphthyridine, and 2,3-dimethyl-4-azaphenanthrene are formed on a K-16 catalyst at 380-420°C from a Schiff base – N-(1,2,5-trimethyl-4-piperidylidene)-α-naphthylamine – as a result of concerted and consecutive dehydrogenation and N-demethylation of the piperidine ring, hydrogenation of the imine bond, and dehydrocyclization [29].



R= α-naphthyl

N-(2,5-Dimethyl-4-pyridyl)-β-naphthylamine, 9-methylnaphtho[2,1-b][1,6]-naphthyridine, and 2,3-dimethyl-1-azaphenanthrene were obtained under similar conditions from N-(1,2,5-trimethyl-4-piperidylidene)-β-naphthylamine [30].

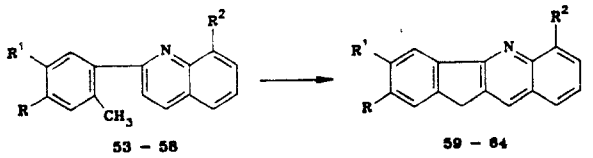


R=β-naphthyl

The principal products of these catalytic transformations are dimethyl-substituted azaphenanthrenes (in 18% and 22% yields, respectively). Prostakov and coworkers [29] have pro-

posed a scheme for their synthesis. The naphthonaphthyridines that are formed in the dehydrocyclization of the pyridylnaphthylamines are hydrogenated in the methyl-substituted pyridine ring under the reaction conditions, after which the hydrogenated products undergo thermal decomposition to give azaphenanthrenes and ethylamine. In [31] it was shown that stepwise decomposition with the formation of less condensed dialkyl-substituted hydrocarbons occurs in the destructive hydrogenation of condensed hydrocarbons – phenanthrene, anthracene, chrysene, etc.

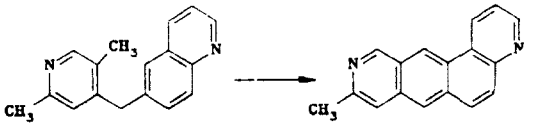
11H-Indeno[1,2-b]quinoline and its methyl-substituted analogs were obtained in higher than 30% yields in the catalytic transformations [K-16, 540-580°C) of 2-aryl-substituted quinolines or mixtures of them with the corresponding 1,2-dihydro derivatives [32].



53 – 58 59 – 64

53, 59 R=R¹=R²=H; 54, 60 R=CH₃, R¹=R²=H; 55, 61 R=R²=H, R¹=CH₃; 56, 62 R=R¹=H, R²=CH₃; 57, 63 R=R²=CH₃, R¹=H; 58, 64 R=H, R¹=R²=CH₃

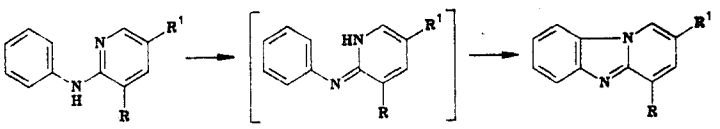
The dehydrocyclization of (2,5-dimethyl-4-pyridyl)(6-quinolyl)methane takes place in the $C_{(5)}$ position of the quinoline fragment with the formation of angular 9-methylisoquinolino[7,6-f]quinoline (in 6% yield) [33].



2-Methylbenzo[b][1,6]naphthyridine was isolated in low yield on the same catalyst at 600°C as a result of the dehydrocyclization of 2,5-dimethyl-4-phenylaminopiperidine [24].

Pyrido[1,2-a]benzimidazoles

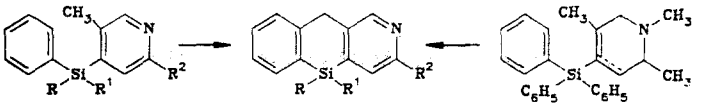
The known syntheses of pyrido[1,2-a]benzimidazole are multistep processes or are based on compounds that are difficult to obtain. An unusual dehydrocyclization pathway – N-dehydrocyclization leading to pyrido[1,2-a]benzimidazoles – was observed in a study of the catalytic transformations of α-phenylaminopyridines at 560-580°C. Pyrido[1,2-a]benzimidazole is formed in 27% yield from α-phenylaminopyridine under these conditions. A similar transformation was also realized in the case of 5-methyl-2-phenylaminopyridine, as a result of which 2-methylpyrido[1,2-a]benzimidazole was obtained in 22% yield. Under the same conditions the dehydrocyclization of 3-methyl-2-phenylaminopyridine proceeds via two pathways. In addition to 4-methylpyrido[1,2-a]benzimidazole, the normal dehydrocyclization product – benzo[b][1,8]naphthyridine – was also studied. It is possible that this reaction proceeds through the imine form of α-phenylaminopyridines [34, 35].



R=R¹=H; R=H, R¹=CH₃; R=CH₃, R¹=H

Dihydrosilaazaanthracenes

Prior to the publication of studies by Prostakov and coworkers [36-40], no information regarding these heterocyclic compounds was available. 3-Methyl-4-triorganosilylpyridines served as the starting substances in the catalytic synthesis of 9,10-dihydro-10-sila-2-azaanthracenes. The dehydrocyclization was carried out on a K-16 catalyst at 520-580°C. The desired products were obtained in 17-35% yields.

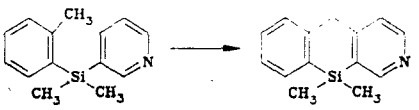


R^2=H, R=R^1=CH_3; R=CH_3, R^1=C_6H_5; R^2=CH_3, R=R^1=C_6H_5

3-Methyl-10,10-diphenyl-9,10-dihydro-10-sila-2-azaanthracene was obtained in one step from a mixture of isomeric Δ^3- and Δ^4-piperideines, bypassing the step involving the preparation of the corresponding pyridine base. However, the yield of the desired product in this case did not exceed 2%.

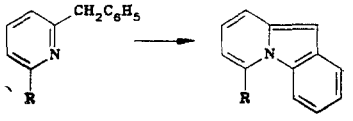
In addition to the K-16 catalyst, the 119 P catalyst (composition: 5% Cr_2O_3, 5% "polirit," 1% K_2O, and 89% γ-Al_2O_3), which was found to be more effective, has been used to obtain dihydrosilaazaanthrancenes [41].

The isomeric (relative to the above-presented dihydrosilaazaanthracene with respect to the position of the nitrogen atom) 9,9-dimethyl-9,10-dihydro-9-sila-2-azaanthracene was obtained by dehydrocyclization of 3-dimethyl(o-tolyl)silylpyridine at 550-570°C (in 18% yield).



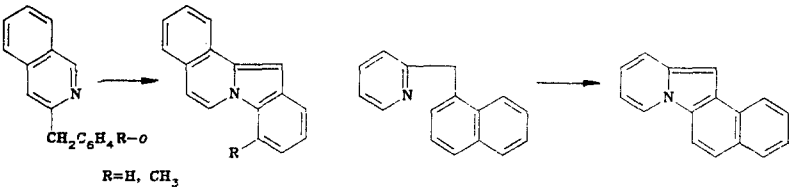
Benzo- and Dibenzoindolizines and Isoindoloquinoxalines

α-Benzyl-substituted compounds – pyridine bases, quinoline, isoquinoline, and o-tolylpyrazine – have been used for the synthesis of these heterocyclic compounds by dehydrocyclization. Cyclization takes place at the nitrogen atom of the azine fragment. This dehydrocyclization pathway was first observed by Braun [42]. Benzo[b]indolizines were obtained in 40% yields in the dehydrocyclization of 2-benzyl- and 2-methyl-6-benzylpyridine on a copper catalyst at 590°C.



R=H; CH_3

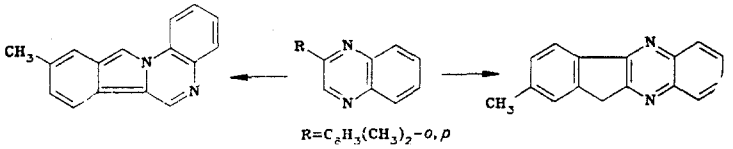
Under similar conditions dibenzo[b, g]indolizines were symthesizedfrom 1-benzyl- and 1-(o-methylbenzyl)isoquinoline, and naphtho[1,2-b]indolizine was obtained from 2(α-naphthylmethyl)pyridine.



R=H, CH_3

Dehydrocyclization under conditions of vapor-phase pyrolysis on quartz at 675-700°C proceeds via the same pathway [34, 43, 44]. Benzo- and dibenzoindolizines are formed in 40% and 70% yields, respectively, in the pyrolysis of similar compounds.

Two substances, viz., a product of dehydrocyclization at the nitrogen atom – 9-methylisoindolo[2,3-a]quinoxaline – and a product of dehydrocyclization in the $C_{(3)}$ position of the quinoxaline fragment – 8-methylindeno[1,2-b]quinoxaline – were obtained from 2-(2',4'-dimethylphenyl)quinoxaline under conditions of catalytic dehydrocyclization [34].



R=$C_6H_3(CH_3)_2$-o,p

Only products of dehydrocyclization in the β position of the azine fragment are formed in the pyrolysis of 2-(o-tolyl)pyridine and 2-(o-tolyl)-pyrazine. 4-Azafluorene and 1,4-diazafluorene were obtained in 9% and 23% yields, respectively, in this case [44].

The thorough research of Mlochowski [45] was devoted to the chemistry of diazafluorenes.

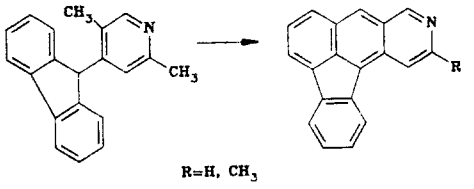
Azabenzofluoranthenes, Pyridofluoranthenes, and Pyridoazafluoranthenes

These nitrogen-containing heterocyclic compounds, which have five condensed rings, were obtained in the catalytic dehydrocyclization on a K-16 catalyst of substituted pyridine bases, as well as 2-azafluorene [27, 46-49].

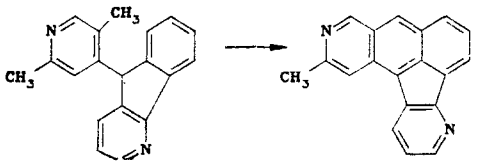
At 500-510°C 7-methyl-6-azabenzo[f]fluoranthene was obtained from 3,6-dimethyl-4-phenyl-2-benzylpyridine in 0.6% yield, whereas at 620°C it was obtained in 6.2% yield. In this case, in addition to 7-methyl-6-azabenzo[f]fluoranthene, 6-azabenzo[f]fluoranthene is formed in appreciable amounts (4.8%) as a result of demethylation. The principal product of this reaction is 2-methyl-4-phenylbenzo[g]quinoline, which is eviently a precursor of azabenzofluoranthene [27].

The general character of this dehydrocyclization pathway was demonstrated in the case of the transformations of 3-methyl-2,6-diphenyl-4-benzylpyridine on a K-16 catalyst at 540-550°C; 1,3-diphenyl-2-azaanthracene (7-13%) and 6-phenyl-5-azabenzo[f]fluoranthene (18-21%) were obtained from it [49]. It is interesting that other possible cyclization products (3-methyl-1-benzyl-2-azafluorene and 1-benzyl-3-phenyl-4-azafluorene, respectively) were not isolated in these two cases.

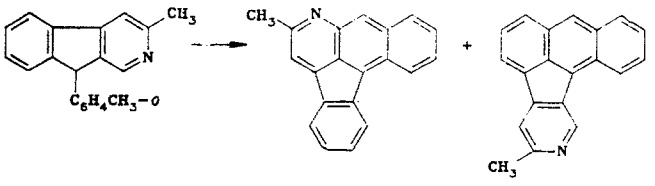
2-Methylpyrido[4,5-a]fluoranthene and the product of its demethylation were obtained in low yields in the dehydrocyclization of 9-(2',5'-dimethyl-4'-pyridyl)fluorene under similar conditions [46].



2-Methyl-9-azapyrido[4,5-a]fluoranthene is formed in the dehydrocyclization (500-520°C) of 9-(2',5'-dimethyl-4'-pyridyl)-4-azafluorene [47].



The dehydrocyclization of 3-methyl-9-(o-tolyl)-2-azafluorene proceeds via both possible pathways with splitting out of hydrogen from both the $C_{(1)}$ position and the $C_{(8)}$ position of the azafluorene fragment. 2-Methyl-3- and 9-methyl-8-azabenzo[f]fluoranthene were isolated in the experiment [48].

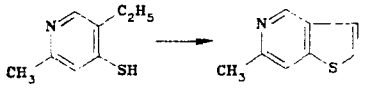


The heterocyclic compounds described in this section, which were obtained by catalytic dehydrocyclization, were previously unknown. They were isolated from the reaction products in insignificant yields; this is evidently associated with the complexity of the structure of their molecules. The 1-azafluoranthene skeleton is the basis of a number of alkaloids [50, 51], and systematic studies to elucidate the optimal conditions for the synthesis of each of

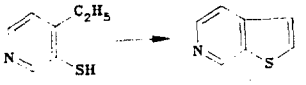
these heterocycles are therefore necessary in the search for biologically active compounds in the future.

Azabenzothiophenes

Azabenzothiophenes are obtained by the catalytic dehydrocyclization of pyridinethiols containing an ethyl radical in the ortho position relative to the thiol group. Chromium and copper oxides applied to carbon are used as catalysts. The reaction is carried out at 425°C [52, 53]. 6-Methyl-5-azabenzothiophene is formed in 20-25% yield in the dehydrocyclization of 2-methyl-5-ethylpyridine-4-thiol.



6-Azabenzothiophene was simlarly obtained in 50% yield from 4-ethylpyridine-3-thiol.



The relatively low yield of 6-methyl-5-azabenzothiophene as compared with 6-azabenzothiophene is due to coking and, chiefly, to hydrogenolysis at the C—S bond. It is assumed that the thione form of the pyridinethiols undergoes hydrogenolysis more readily than the thiol form. As a consequence of this, the hydrogenolysis of pyridine-4-thiols, which can exist in the thione form, proceeds to a greater extent than in the case of pyridine-3-thiols.

The information regarding the syntheses of nitrogen-containing heterocycles by means of catalytic dehydrocyclization that is presented in this review constitutes evidence for the promising character of its utilization. In many examples of appropriately substituted pyridine bases it has been demonstrated that it has general character. Thanks to its use, isomeric (with respect to the position of the nitrogen atom) azafluorenes, benzoquinolines (isoquinolines), azabenzofluoranthenes, pyridobenzimidazoles, azabenzothiophenes, and other compounds, as well as the previously unknown dihydrosilaazaanthracenes, have become accessible for researchers.

Catalytic dehydrocyclization has thus far been studied only as a method for the synthesis of various heterocycles. The selection of catalysts for effecting it has not been distinguished by scientific substantiation. The catalysts have been selected in analogy with the catalysts for the dehydrogenation of aliphatic and carbocyclic compounds. There has not yet been any research dealing with the study of the mechanism of dehydrocyclization and the effect of the nature and structure of the catlayst on its direction, whereas a knowledge of these principles is important in the development of a specific method for the synthesis of heterocycles with certain structures.

Advances in the area of synthesis by means of catalytic dehydrocyclization will obviously also stimulate research in these directions.

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REACTION OF β-ARYLACRYLOXIRANES WITH PHENYL AZIDE. SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF β-PHENYLAMINO-β-ARYLACRYLYLOXIRANES

A. M. Zvonok, N. M. Kuz'menok, and L. S. Stanishevskii

UDC 547.824'724'555.1'391.1'422.22-31.07:541.124

The reaction of β-arylacrylyloxiranes with phenyl azide by refluxing in dioxane or toluene leads to β-phenylamino-β-aryl-acrylyloxiranes. Epoxypropionyl- and β-hydroxypropionyltriazoles are also isolated when the reaction is carried out in the dark without heating. It is shown that β-phenylamino-β-arylacrylyloxiranes undergo cyclization to 3(2H)-furanones in an acidic medium, whereas they are converted to 2,3-dihydro-4-pyridones under basic-catalysis conditions.

Epoxypropionylpyrazolines, which were found to be convenient starting substances for the synthesis of compounds of the bipyrazole and pyrrolidino[1,2-b]pyrazole series, were previously obtained in a study of the cycloaddition of diazo compounds to β-arylacrylyloxiranes [1, 2]. In a continuation of our study of the cycloaddition of 1,3-dipoles to β-arylacrylyloxiranes and in order to synthesize functionally substituted ketones of the heterocyclic series we have investigated the reactions of β-arylacrylyloxiranes with phenyl azide and some synthetic possibilities of the resulting β-phenylamino-β-arylacrylyloxiranes.

We have established that the reaction of β-arylacrylyloxiranes Ia-f with phenyl azide by refluxing in an aprotic solvent (dioxane, toluene) for 15-20 h leads to epoxy enamino ketones II and V-IX (in 50-75% yields), the structures of which were confirmed by the results of elementary analysis and IR and PMR spectral data (Table 1), as well as by alternative synthesis of II from β-phenylpropionyloxirane Ig. The existence of enamino ketones II and V-IX in the cis-s-cis-chelate-bonded form is in agreement with the set of spectral data, viz., the chemical shift of the NH proton (12.05-12.20 ppm), as well as the characteristic frequencies of vibrations of NH, C=O, and C=C bonds at 3170, 1610, 1605, 1590, and 1560 cm^{-1} [3].

For the isolation and identification of the intermediates formed during the described reaction, epoxy enone Ia was maintained with phenyl azide in dioxane at room temperature in

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