

**CHEMISTRY OF HETEROCYCLIC
COMPOUNDS AT THE DEPARTMENT
OF ORGANIC CHEMISTRY, CHEMICAL FACULTY,
M. V. LOMONOSOV STATE UNIVERSITY. (REVIEW)**

M. A. Yurovskaya

This review of achievements in the area of the chemistry of heterocyclic compounds at the Department of Organic Chemistry of M. V. Lomonosov Moscow State University is dedicated to the 250th anniversary of the University and the 75th anniversary of the Chemical Faculty. It contains a brief historical account and information on researches carried out by the team at the Department in recent years.

Keywords: azolidines, azoles, benzisoxazoles, benzodiazepines, benzofurans, benzopyrans, benzotriazoles, furans, furazans, indoles, isoxazoles, phthalocyanines, piperidines, pyrazoles, pyridines, pyrrolopyrazines, tetrazoles, chemistry of heterocyclic compounds.

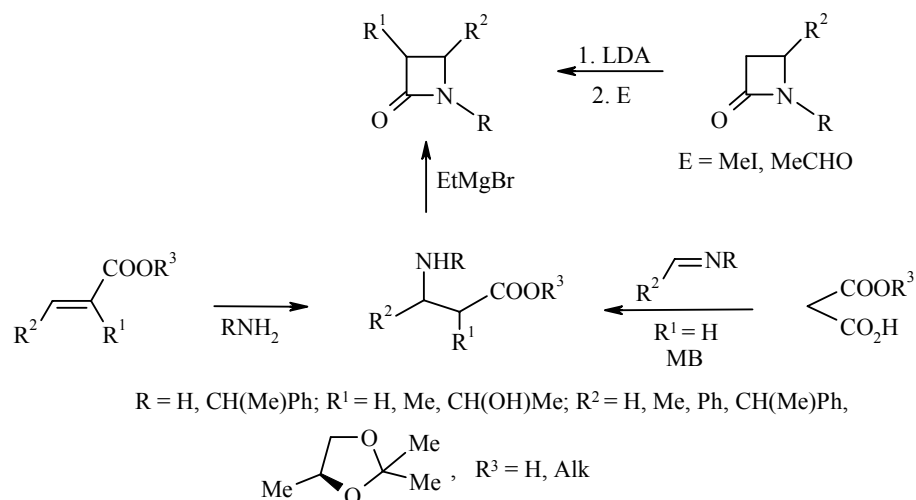
The Department of Organic Chemistry at the Chemical Faculty is one of the leading centers for the development of the chemistry of heterocyclic compounds not only in Russia but also in the world. While speaking of the achievements of the team in recent years it is impossible to ignore the history of developments in this region of organic chemistry at the Department, as was mentioned briefly in the review [1], since it is the continuity and the commendable traditions of recent years that have determined the level of contemporary investigations. The beginning of researches on the chemistry of heterocycles at Moscow State University is closely linked to the name of N. D. Zelinsky, who became interested in this field while still a young chemist undergoing on-the-job training, as it is now customary to say, in the laboratory of the discoverer of thiophene Victor Meyer. It was to compounds of the thiophene series that N. D. Zelinsky's master's thesis defended in 1889 was devoted [2]. In the twenties to forties of the twentieth century at Moscow University N. D. Zelinsky and his students investigated the catalytic hydrogenation and dehydration of a series of nitrogen- and oxygen-containing heterocycles [3]. More recently, at Moscow University the researches into the chemistry of heterocycles have developed widely. It is sufficient to present a list of the famous professors who have successfully worked and are working at the Department in the field of the chemistry of heterocyclic compounds: They include A. N. Nesmeyanov, Yu. K. Yur'ev, R. Ya. Levina, A. P. Terent'ev, A. N. Kost, Yu. S. Shabarov, V. M. Potapov, Yu. K. Novitskii, N. K. Kochetkov, Yu. A. Arbuzov, I. K. Korobitsina, I. I. Grandberg, N. S. Zefirov, L. A. Kazitsina, N. P. Shusherina, L. A. Yanovskaya, V. R. Skvarchenko, N. N. Magdesieva, V. V. Ershov, A. N. Grinev, L. I. Khmel'nitskii, V. G. Yashunskii, M. N. Preobrazhenskaya, Yu. G. Bundel, I. P. Beletskaya, A. M. Yurkevich, P. B. Terentiev, R. S. Sagitullin, N. V. Zyk, I. G. Bolesov, M. A. Yurovskaya,

M. V. Lomonosov Moscow State University, Moscow, Russia; e-mail: yumar@org.chem.msu.ru.
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V. I. Terenin, G. V. Grishina, T. S. Kuznetsova, S. S. Mochalov, N. A. Bumagin, N. V. Lukashov, M. V. Proskurina, and many others. Many of the methods they developed for the synthesis and transformations of heterocycles have become classical methods, and some of the reactions have become named reactions. Traditionally, at the Department throughout the history of its development and up to the present time the chemistry of heterocyclic compounds has been represented by the most varied range of heterocycles, differing in size, and by saturated and aromatic compounds containing widely varying heteroatoms. In this connection we consider it desirable to arrange the material presented in the review according to the character and size of the heterocycle, using separated headings for the universal synthons that are suitable for the formation of a wide range of heterocyclic compounds and for the mass-spectrometric modelling of heterocyclization processes.

SMALL HETEROCYCLES

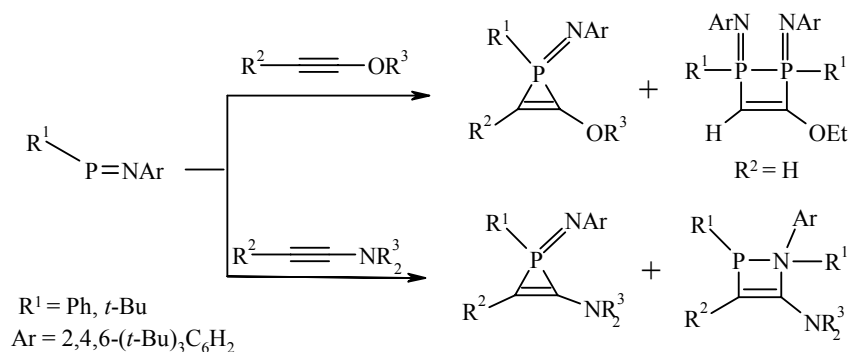
The first investigations on small heterocycles began at the Department in the eighties of the last century (V. M. Potapov, N. N. Romanova, G. V. Grishina, V. A. Budylin). They were concerned with methods for the asymmetric synthesis of azetid-2-ones (precursors of the β -lactam antibiotics) and study of their stereochemistry and biological activity [4-6].



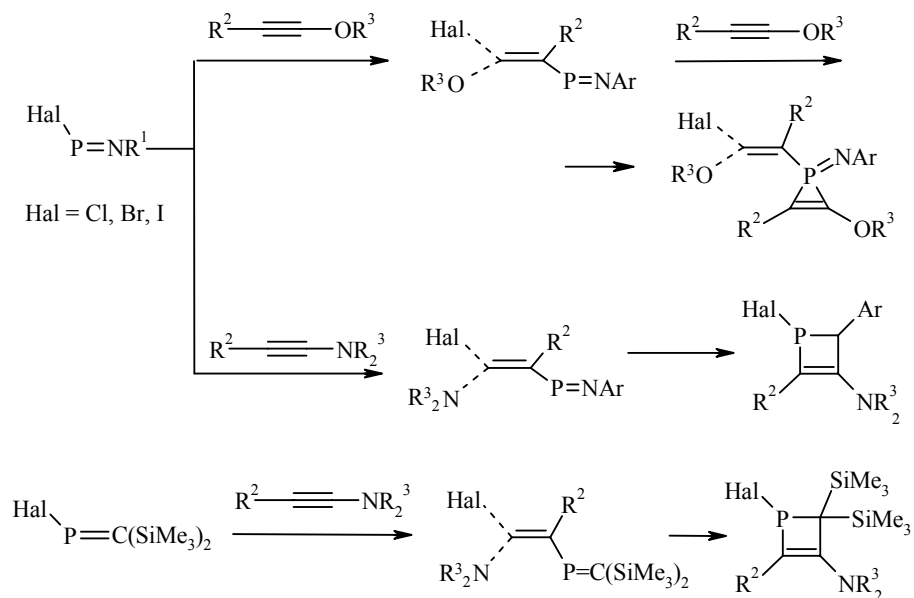
By studying the chiral optical properties of a series of homochiral isomers with one, two, and three asymmetric centers it was possible to make a correlation between the sign of the Cotton effect of the $n \rightarrow \pi^*$ transition of the amide chromophore and the absolute configuration of the *exo*- and *endo*-cyclic carbon stereocenter [7]. Later, the absolute configuration of the chiral centers of liquid (1*S*,4*R*)-1-(1-phenylethyl)-4-methylazetid-2-one proposed as a result of application of the chiroptical correlation method was confirmed by data from X-ray crystallographic analysis, obtained for the crystalline complex formed by an enantiomerically pure *ortho*-palladized matrix with known absolute configuration and a liquid β -thiolactam produced by transformation of the optically active β -lactam (without affecting the asymmetric centers) [8].

By the use of microwave activation (Yu. G. Bundel, N. N. Romanova, and coworkers) in the synthesis of the esters of β -amino acids by the Michael [9] and Rodionov [10] methods it was possible to extend the nature of the substituents R, R¹, and R² and to study the effect of microwave treatment on the direction and stereochemistry of these reactions [11].

In 1990-1999 in the Laboratory of Organoelement Compounds (I. P. Beletskaya, N. V. Lukashov, A. D. Averin) the cycloaddition of derivatives of dicoordinated phosphorus to nucleophilic alkynes, leading to the formation of tri- and tetracoordinated unsaturated phosphorus-containing heterocycles – [2+1] and [2+2] cycloaddition products – was investigated [12-16].



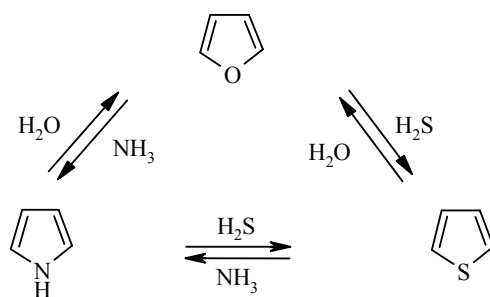
It was shown that the reaction of the halides of dicoordinated phosphorus with 1-alkoxy- and 1-dialkylaminoalkynes leads to regio- and stereoselective addition of the organophosphorus compounds at the triple bond. The obtained adducts are capable of spontaneous cyclization to azaphosphetines or of [2+1] cycloaddition with a second molecule of the alkoxyalkyne [17-21].



FIVE-MEMBERED HETEROCYCLES WITH ONE HETEROATOM AND THEIR CONDENSED ANALOGS

The chemistry of five-membered heterocycles has been a traditional topic for the Department of Organic Chemistry throughout its existence.

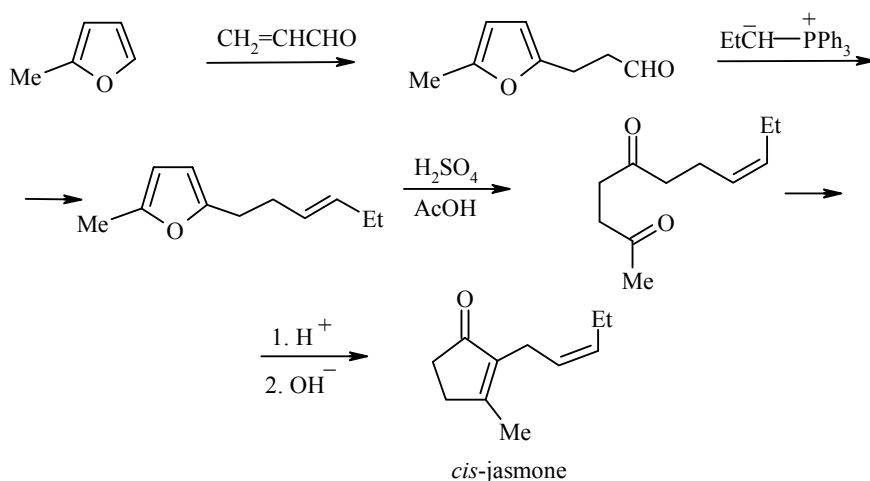
In 1935 Yu. K. Yur'ev discovered the mutual transformation of five-membered heterocycles in the vapor phase (e.g., see [22]), which has been named after him.



Researches by A. P. Terent'ev, L. A. Yanovskaya, and L. A. Kazitsina made the functional derivatives of many heterocycles accessible and led, in particular, to the use of pyridine–sulfur trioxide in organic synthesis as sulfurizing agent, making it possible to obtain the sulfonic acids of pyrrole, indole, furan, and other acidophobic heterocycles [23-25].

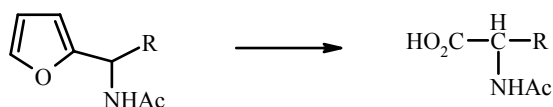
Workers at the Department have made a substantial contribution to the development of furan chemistry. Thus, K. Yu. Novitskii and Yu. K. Yur'ev [26-33] investigated in detail the reactivity of various mono- and bischloromethylfurans in reactions with nucleophilic agents, which provide general convenient methods for the production of functionally substituted furans. In the course of these investigations an instance of an allylic rearrangement of halogenofurans during their reaction with metal cyanides was discovered. The hydroxy- and mercaptoethylamines of the furan series were used for the production of other heterocyclic systems (piperazine, thiomorpholine, oxazolidine, all containing a furan ring). Bischloromethylfurans in turn proved suitable starting compounds for the synthesis of new nitrogen- and sulfur-containing bi- and tricyclic systems with a furan fragment.

In researches by Yu. K. Yur'ev and N. S. Zefirov a new method for the synthesis of carbonyl compounds of this series was developed on the basis of the previously discovered substitutive addition to furan [34-38]. Such carbonylalkyl derivatives of furan have widespread use in organic synthesis and in particular for the production of jasmone [39].

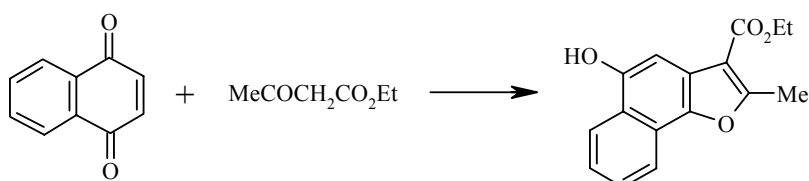


In the case of the adducts from [4+2] cycloaddition to furan derivatives the same authors comprehensively studied theoretical questions associated with the Wagner–Meerwein rearrangement [39-42], homoallylic interaction [43, 44], and stereochemical addition at a double bond [43, 45-47].

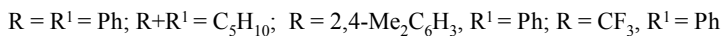
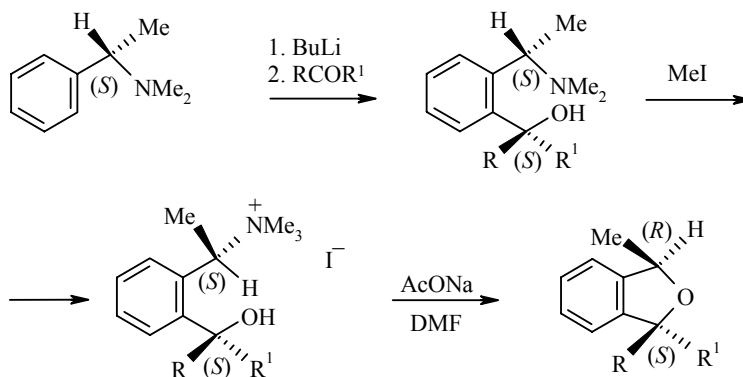
An original method for the synthesis of α -amino acids, including the nonracemic acids, was developed by A. P. Terent'ev and R. A. Gracheva [48-50].



Other subjects of investigation at the Department were benzannelated furans. Thus, A. N. Grinev and A. P. Terent'ev developed an original method for the synthesis of benzofuran derivatives based on the reaction of *p*-quinones with acetoacetic ester [51]. Effective plant growth stimulants were found among the obtained compounds.



In recent years a method was developed under the guidance of assistant professor V. M. Dem'yanovich for the functionalization of *N,N*-dimethyl-1-phenylethylamine through an *ortho*-lithiation stage, and this made it possible to obtain a series of δ -amino alcohols [52], which were used for the synthesis of chiral 1,3-disubstituted 1,3-dihydroisobenzofurans (phthalans). In the reaction of the methiodides of δ -dimethylamino alcohols with sodium acetate in DMF cyclization occurs with the stereospecific formation of optically active phthalans [53]. The dihydroisobenzofuran fragment is encountered in the molecules of some natural and synthetic biologically active compounds. However, there were previously hardly any data on chiral phthalans.



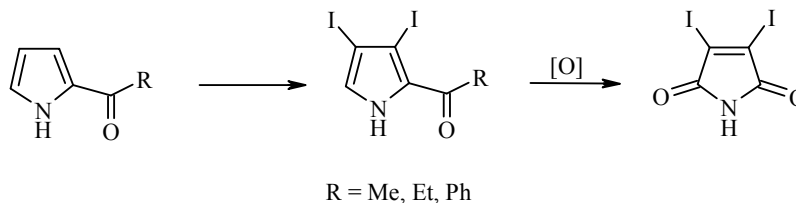
The corresponding phthalan was also obtained during cyclization of the methiodide of diastereomeric [*o*-(1-dimethylaminoethyl)phenyl]trifluoromethylphenylcarbinol ($R = \text{CF}_3$, $R^1 = \text{Ph}$). By X-ray crystallographic analysis of the complex of this phthalan with tricarbonylchromium it was possible to establish that cyclization of the methoxides of δ -hydroxyammonium salts takes place as intramolecular nucleophilic substitution by an S_N2 mechanism, i.e., with inversion of the configuration at the center being attacked [the chiral center of the initial amine, having the (*S*) configuration].

The researches of Yu. K. Yur'ev, L. I. Khmel'nitskii, N. N. Magdesieva, and N. K. Sadovaya made a large contribution to study of the chemistry of the five-membered aromatic heterocycle selenophene, the closest analog of thiophene [54-59]. Thus, a convenient method was developed for the synthesis of selenophene by the reaction of butenes with selenium. Electrophilic substitution reactions in the ring were studied in detail, and this

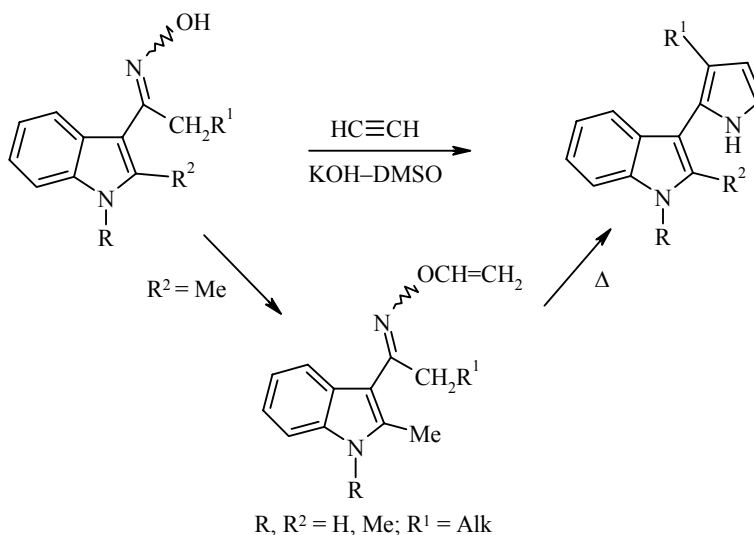
made it possible to synthesize various functional derivatives of the selenophene series, to study their reactivity, and to identify paths for their practical utilization (as antioxidants, complexing agents, physiologically active compounds). As a result of kinetic investigations of mercuration and ion exchange in deuterated derivatives of selenophene it was possible to identify the position of the selenophene in the series of aromatic five-membered heterocycles.

In the region of nitrogen-containing heterocycles a series of fundamental scientific discoveries were made by workers at the Department.

While still quite a young scientist – a student of V. V. Chelintsev – A. P. Terent'ev began investigations in the chemistry of pyrrole [60]. These investigations were mainly concerned with the iodination of 2-acylpyrroles and oxidation of the diiodo derivatives.

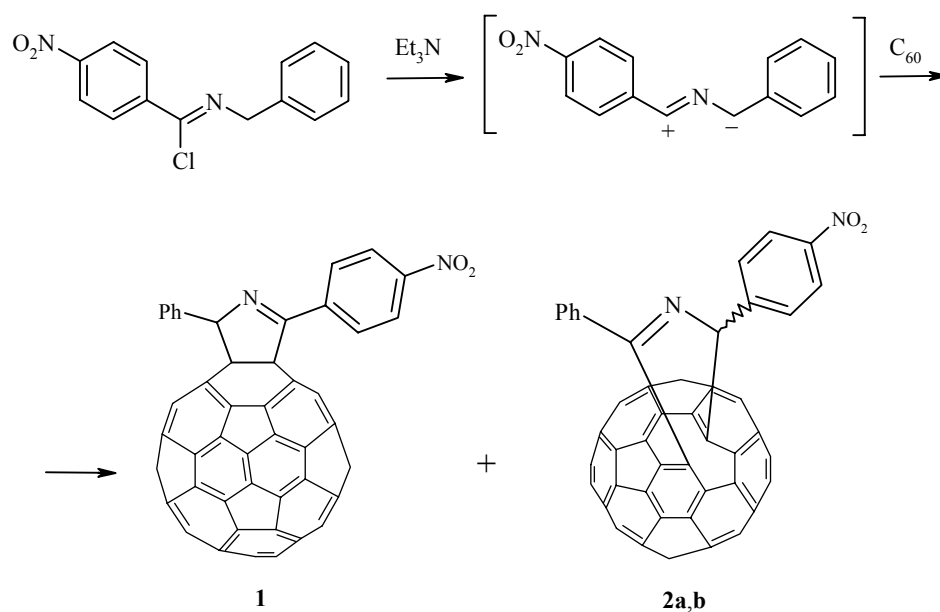


In the eighties during researches by M. A. Yurovskaya's group the Trofimov reaction discovered at that time, i.e., the synthesis of pyrroles from ketoximes and acetylene in superbasic media, was extended to the oximes of 3-acylindoles [61]. This made it possible to synthesize a series of 3-(2-pyrrolyl)indoles and also to demonstrate convincingly the sigmatropic nature of the process during investigation of the thermal transformation of specially synthesized O-vinyl ethers of the oximes to the corresponding pyrroles [62].

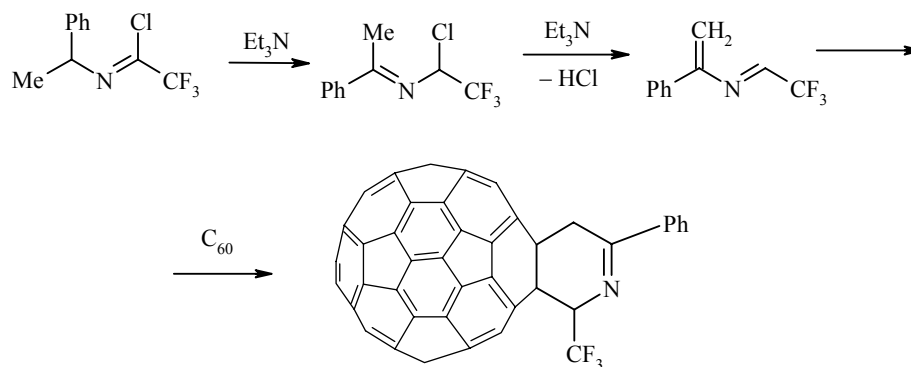


Recently the foundation was set in the Department for a completely new direction – the organic chemistry of buckminsterfullerene[60] derivatives (M. A. Yurovskaya, A. V. Karchava, and A. A. Ovcharenko). These investigations were linked with the development of methods for the annelation of heterocyclic fragments (in particular derivatives of pyrroline) to the fullerene spheroid using cycloaddition reactions. Thus, it was found for the first time that the cycloaddition of 1-(4-nitrophenyl)-3-phenylnitrile ylide, generated *in situ* from N-benzyl-4-nitrophenylimidoyl chloride by the action of triethylamine, leads not only to the formation of [6,6]-closed 1,2-[3,4-dihydro-2-phenyl-5-(4-nitrophenyl)-2H-pyrrolo]fullerene[60] (**1**) but also to a mixture of

diastereomeric [6,5]-open (**2a, b**) fulleroid cycloadducts in a ratio of 2:1. The double bond in the open cycloadducts is located at the α -position in relation to the unsubstituted phenyl ring, whereas in the [6,6]-closed isomer it is at the α -position in relation to the nitrophenyl substituent [63].

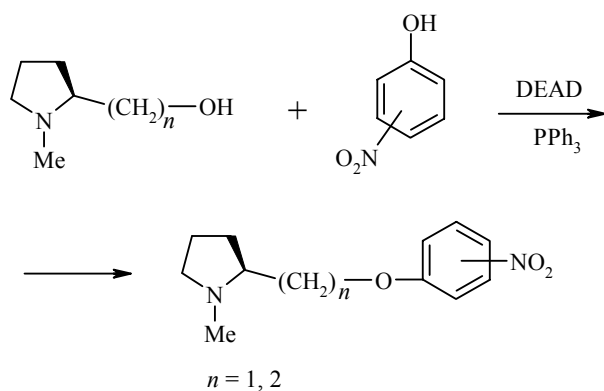


Unexpected results were obtained with N-(1-methylbenzyl)trifluoroacetimidoyl chloride, the dehydrochlorination of which led to the formation of an azadiene instead of the expected nitrile ylide. The azadiene reacted with C_{60} fullerene by a Diels–Alder reaction with annelation of the tetrahydropyridine ring [64].

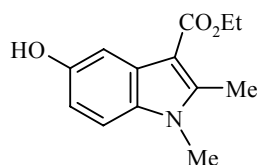


By 1,3-Dipolar cycloaddition of nitrile imines, generated *in situ* by dehydrohalogenation of hydrazonoyl chlorides or by thermal decomposition of 2,5-diaryltetrazoles, it was possible to synthesize a wide range of fulleropyrazolines, in which only the [6,6]-closed isomers were found [65].

At the present time special attention is being paid to the use of chiral pyrrolidine derivatives for the production of potential biologically active compounds. Thus, a method was developed at the Department (N. S. Zefirov, E. D. Matveeva, and T. A. Podrugina) for the synthesis of isosteric analogs of nicotine – calcium channel blockers [66]. These compounds, which are ethers of [*S*(-)-2-(2-pyrrolidinyl)]methanol and 2-[*S*(-)-2-(2-pyrrolidinyl)]ethanol and nitrophenols, were obtained by the Mitsunobu reaction.

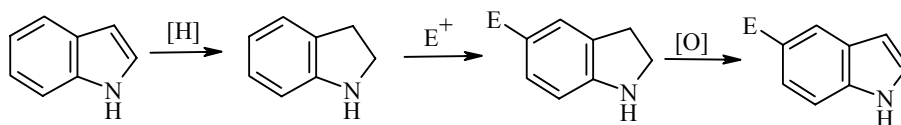


Traditionally, extremely robust investigations into the chemistry of indole have been carried out in the Department (and are being carried out to this day). The method for the construction of an indole ring developed during researches by A. N. Grinev and A. P. Terent'ev and based on the Nenitzescu reaction with the condensation of quinones with aminocrotonic ester and its analogs can be cited as an example [67-72]. These investigations provided the basis for the development of an industrial method for production of the original antihypertensive product Dimecarbin.



Dimecarbin

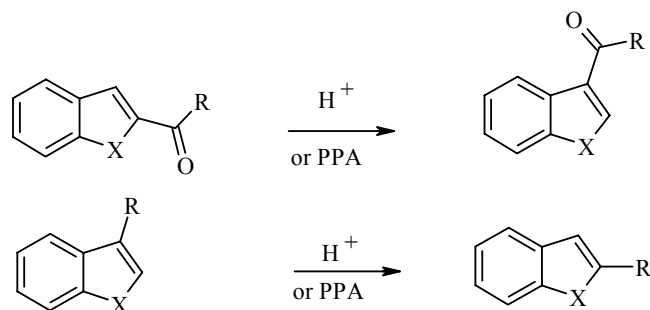
The so-called "indole-indoline" method for functionalization of the benzene ring in the indole bicycle, developed by A. P. Terent'ev and M. N. Preobrazhenskaya [73] and involving successive reduction of indole to indoline, electrophilic substitution in the benzene ring of the indoline (in fact already an analog of a typical alkyaniline), and finally aromatization to the indole derivatives, deserves a special mention.



The greatest contribution to the chemistry of indole came from the work of A. N. Kost and his numerous students (mostly coworkers at the Laboratory of Chemistry and Biological Action of Nitrogen Bases, created by him in 1969 and later renamed Laboratory of Biologically Active Organic Compounds). These researches were involved with the synthetic and theoretical development of the Fischer method for the synthesis of indoles, the creation of new methods for the formation of the indole ring, and more comprehensive study of the chemical characteristics of this heterocycle.

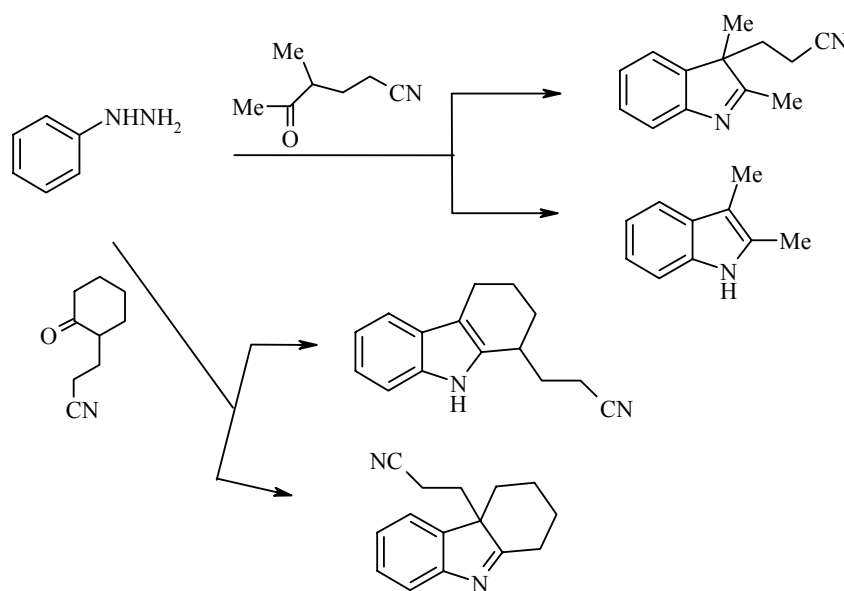
Of great importance for study of the reactivity of indoles were researches by A. N. Kost, L. G. Yudin, and V. A. Budylin on the regioorientation of electrophilic substitution in 2,3-disubstituted indoles in relation to the acidity of the medium [74].

In researches by E. D. Matveeva, V. A. Budylin, and A. N. Kost prototropic processes in the indole series and in the isoelectronic benzofurans and benzothiophenes were studied. It was found that the action of trifluoroacetic acid or polyphosphoric acid on the 2-acyl derivatives of these heterocycles led to intramolecular isomerization to the corresponding 3-isomers and of the 3-alkyl and 3-aryl derivatives to the 2-isomers [75-77].

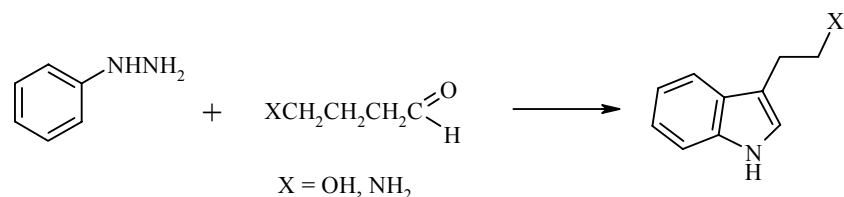


X = NH, O, S; R = Alk, Ar

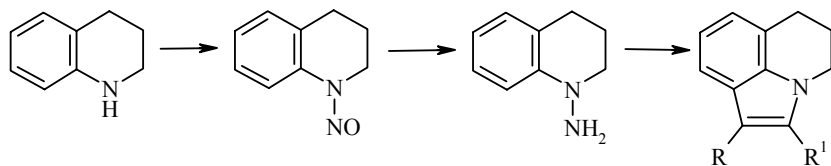
During investigation of further possibilities for the Fischer synthesis of indole A. N. Kost and L. G. Yudin found that keto nitriles can undergo this reaction. Both indole and indolenine nitriles and also substituted indole nitriles can be obtained, depending on the reaction conditions and on the structure of the initial compounds [78, 79].



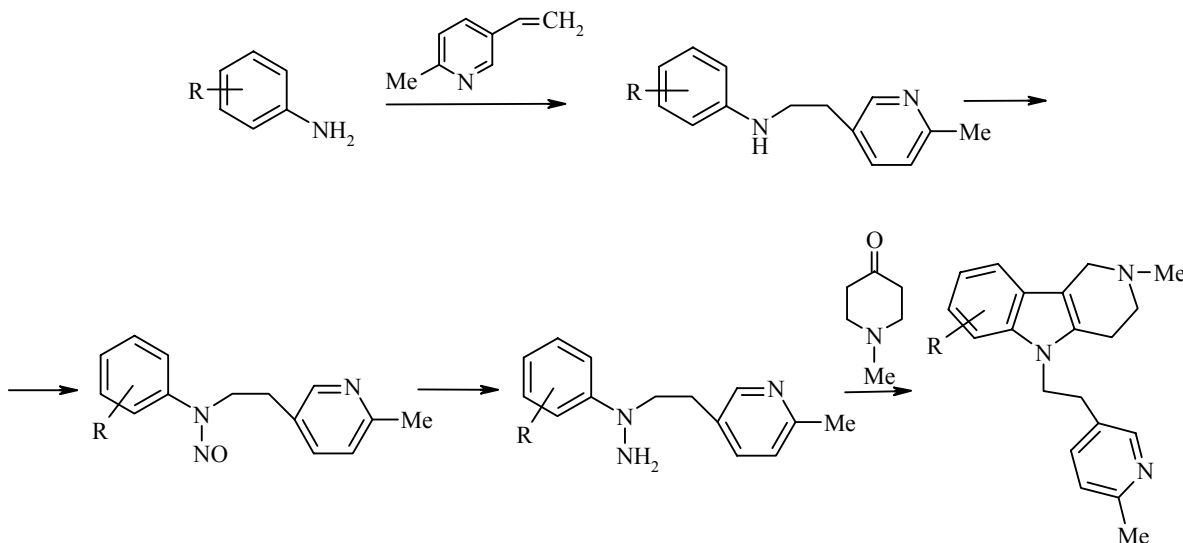
I. I. Grandberg, A. N. Kost, and A. P. Terent'ev proposed a convenient method for the synthesis of 2-methyltryptophols from arylhydrazines and γ -hydroxycarbonyl compounds [80]. Later I. I. Grandberg and coworkers [81] discovered a new simple method for the synthesis of tryptamines based on arylhydrazines and halo- or γ -aminocarbonyl compounds, and this method has not lost its significance to the present day.



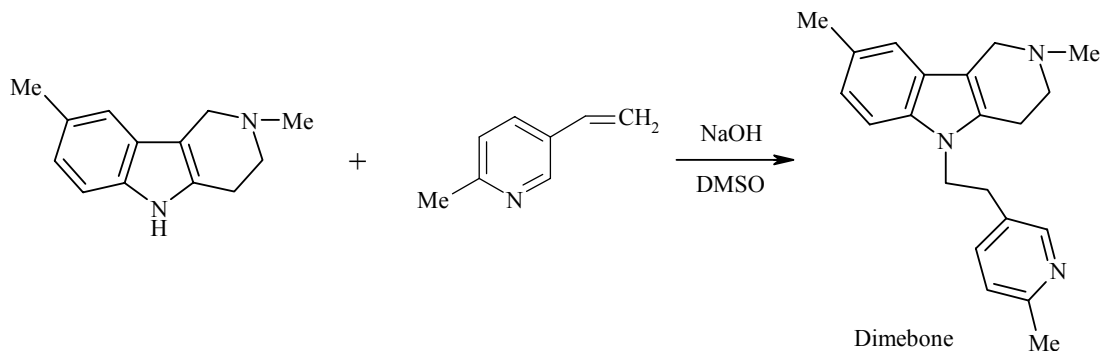
An excellent illustration of the extended possibilities of Fischer indolization is provided by the elegant method for the synthesis of lilolidene structures developed by A. N. Kost, L. G. Yudin, and A. P. Terent'ev [82, 83].



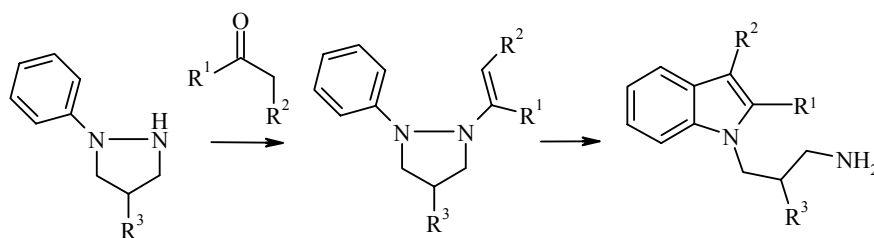
In papers by E. V. Vinogradova, A. N. Kost, and A. P. Terent'ev the Fischer reaction was extended to the production of N-[2-(3-pyridyl)ethyl]-1,2,3,4-tetrahydro- γ -carboline, among which compounds having strong antihistamine activity were found [84-86].



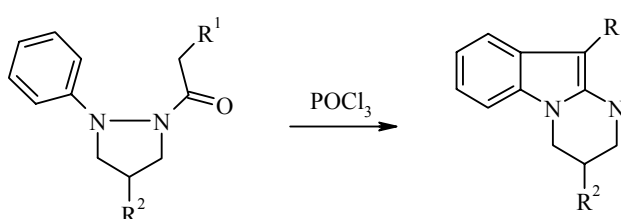
Later, in researches by A. N. Kost and M. A. Yurovskaya an improved method was developed for the synthesis of such structures based on the direct pyridylethylation of tetrahydro- γ -carboline in a superbasic medium. This provided the basis for the creation of a technological scheme for manufacture of the original antihistamine product Dimebone and its introduction into medical practise [87]. A wider spectrum of biological activity has now been discovered, and the product has been patented as an agent for the treatment of Alzheimer's disease [88].



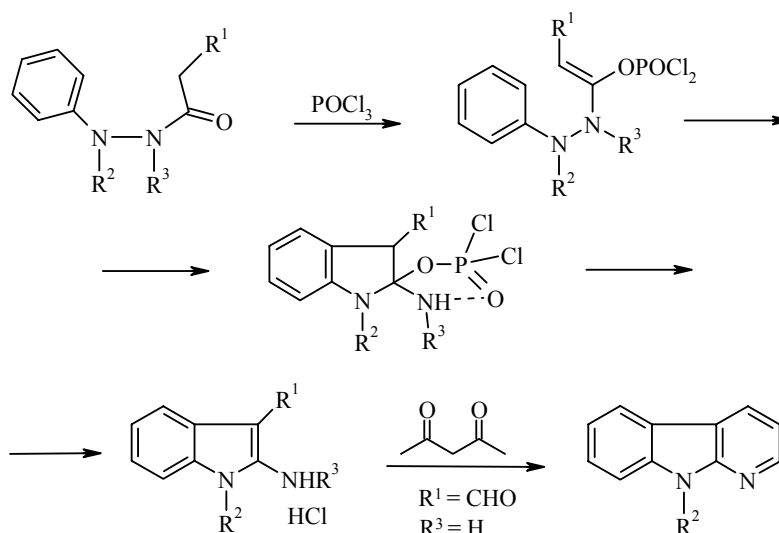
The mechanism of the Fischer synthesis was demonstrated elegantly in papers by A. N. Kost, G. A. Golubeva, L. A. Sviridova, and Yu. N. Portnov. If the cyclic analogs of phenylhydrazines – 1-pyrazolidines – are used in condensation with carbonyl compounds, the "leaving" nitrogen atom remains connected to the indole nitrogen atom by an aminoalkyl chain [89].



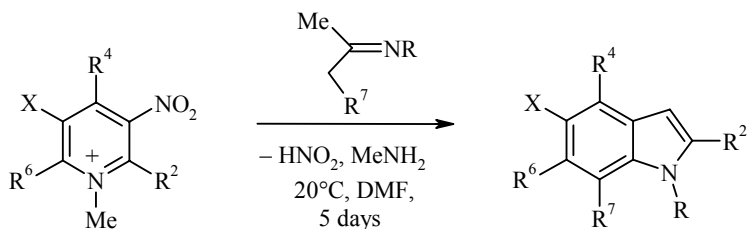
The same authors showed that arylpyrazolidines acylated at the nitrogen atom undergo heterocyclization under the influence of phosphorus oxychloride and form condensed derivatives of indole [90].



Subsequently it was shown that this reaction is general in nature and extends to any β -arylhydrazides of carboxylic acids, leading to a wide range of 2-aminoindole derivatives. This transformation, now known as the Kost reaction [91], has made 2-aminoindole derivatives accessible, and a whole series of further transformations leading to various polyfunctional derivatives of indole and its condensed systems have been realized on their basis.

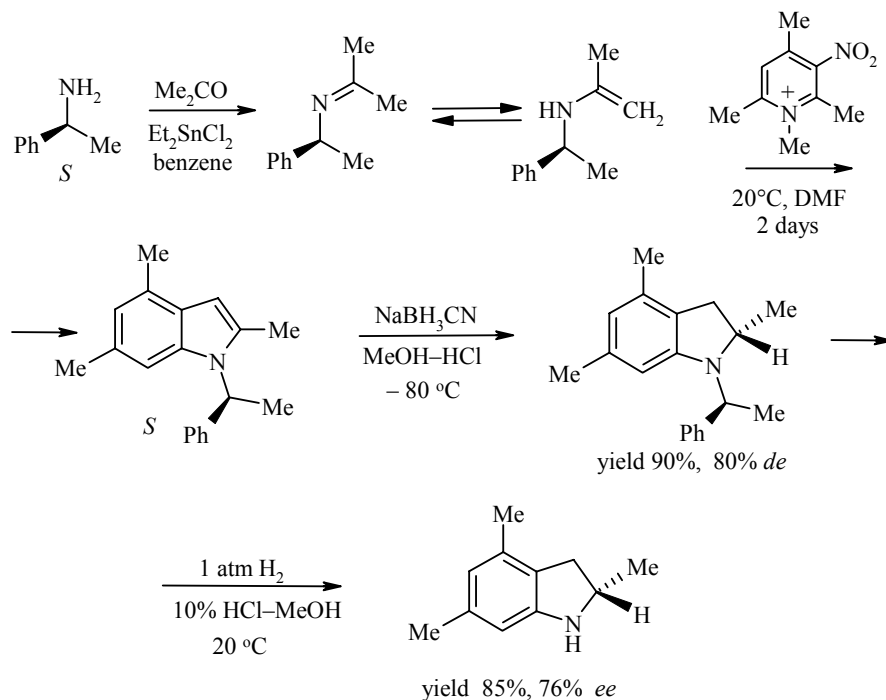


In the last 20 years a new unusual method for the formation of an indole ring, not having analogies in the literature, was discovered (M. A. Yurovskaya and coworkers, Yu. G. Bundel, and S. P. Gromov). It involves the transformation of 3-nitropyridinium salts into indoles by the action of ketimines [92-99].

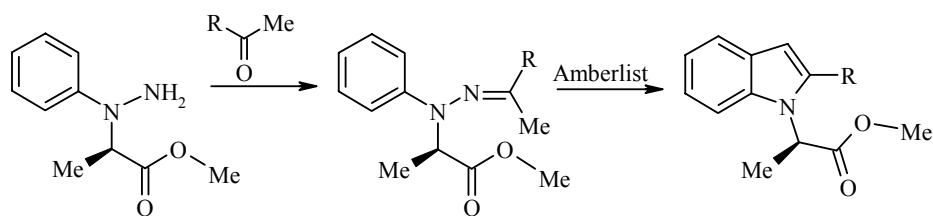


It was found that the synthetic possibilities of this process, which takes place under extremely mild conditions and gives high yields, are not restricted to the synthesis of the various polyalkylindoles themselves but can also be developed further. Thus, it was possible to extend the method to the production of indoles with a functional substituent at position 5 of the indole ring (M. A. Yurovskaya, O. D. Mit'kin, and R. V. Kombarov) [100]. It should be noted that the successful production of indoles with accepting substituents at position 5 by this method requires the addition of a small amount of acid (acetic acid or trifluoroacetic acid) to the reaction mixture to suppress concurrent deprotonation of the α -alkyl substituents of the initial 3-nitropyridinium salt.

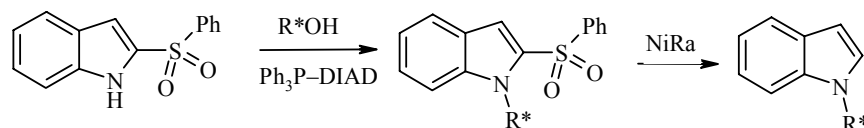
Furthermore, the fact that the source of the substituent at the indole nitrogen atom is the ketimine, established in these researches, made it possible on the basis of this general scheme to propose a new approach to the synthesis of indoles with a chiral substituent at the nitrogen atom using the acetone imines of chiral amines and then reducing such indoles diastereoselectively to indolines (A. V. Karchava and M. A. Yurovskaya) [101].



Recently the same group has proposed two more original methods for the synthesis of indoles containing a chiral substituent at the nitrogen atom. The first uses the Fischer synthesis of indoles based on optically active arylhydrazines [102].

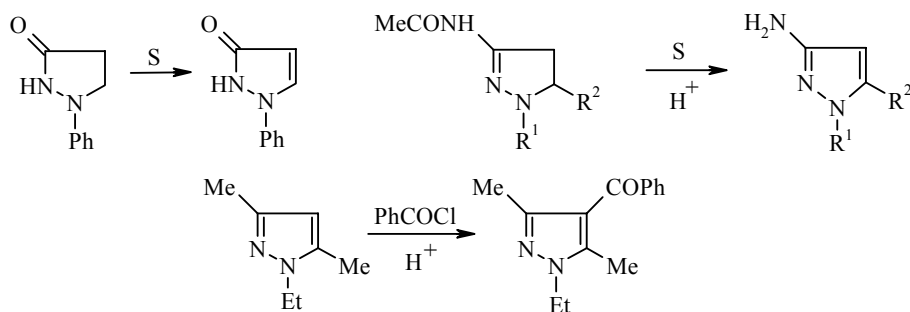


The second is based on the N-alkylation of indoles activated by a 2-phenylsulfonyl substituent with chiral alcohols in the Mitsunobu reaction followed by removal of the activating group [103].

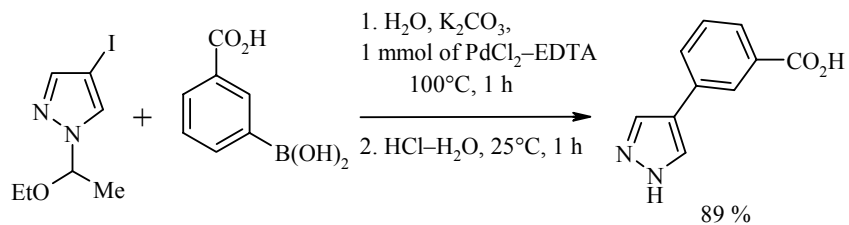


FIVE-MEMBERED HETEROCYCLES WITH SEVERAL HETEROATOMS

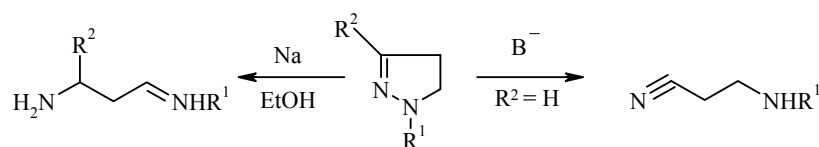
Some of the directions developed historically in the laboratory of A. N. Kost were investigations into the chemistry of organic compounds of hydrazine, including their cyclic analogs – pyrazole and its saturated derivatives. In work by I. I. Grandberg and coworkers methods were developed for the synthesis of functional derivatives of pyrazole both by dehydrogenation of the more readily available compounds of 2-pyrazoline and by direct electrophilic substitution in the pyrazole ring [104].



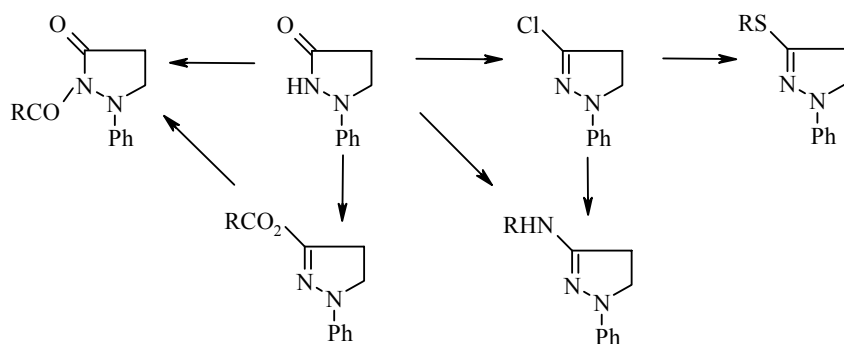
Contemporary methods for modification of the pyrazole ring result from the Department's extensive investigations into metal-complex catalysis. Thus, in the metal-complex catalysis group under the guidance of N. A. Bumagin a highly effective catalytic system was developed on the basis of a palladium complex with ethylenediacetic acid (EDTA). This made it possible to achieve the synthesis of previously difficultly obtainable 4-aryl-substituted pyrazoles with high preparative yields [105].



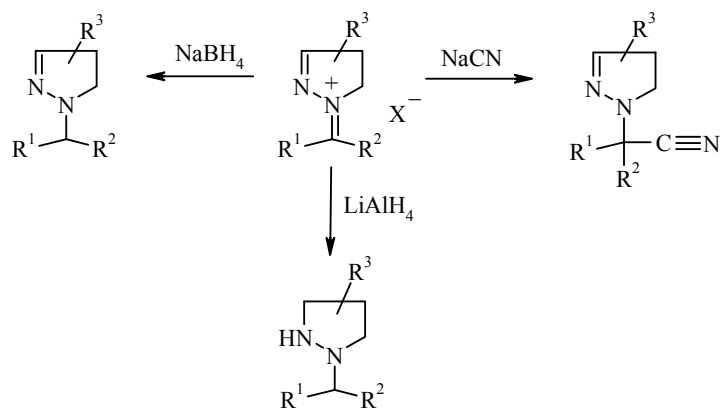
As shown by the researches of workers at the Department (A. N. Kost, G. A. Golubeva, I. I. Grandberg, and Yu. A. Naumov) [106, 107], 2-pyrazolines are characterized not only by transformation to pyrazoles but also by cleavage of the ring leading to polyfunctional compounds, i.e., β -amino nitriles and 1,3-diamines.



In recent years several new preparative methods have been developed on the basis of 3-pyrazolinones for the synthesis of functional derivatives of 2-pyrazolines that are promising for further synthesis (G. A. Golubeva and N. I. Vorozhtsov) [108-110].

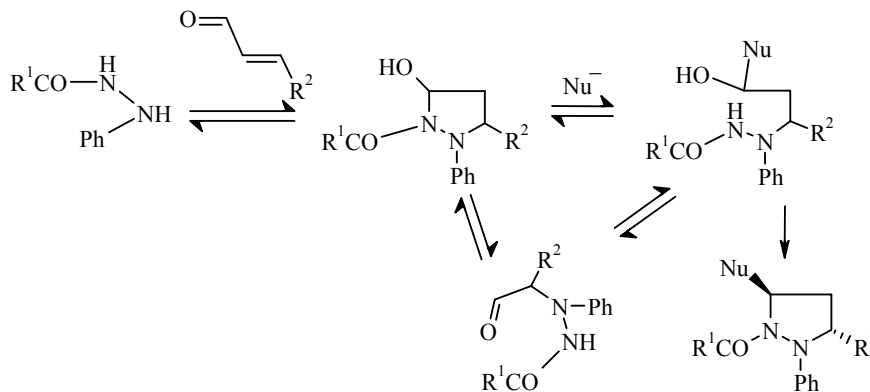


The formation of 1-alkylidene and 1-arylidene salts of 2-pyrazolines activated the C=N bond and made it possible to realize both selective nucleophilic addition at the exocyclic bond with the production of derivatives of 2-pyrazoline and exhaustive reduction of both C=N bonds leading to five-membered saturated pyrazolidines [111, 112].



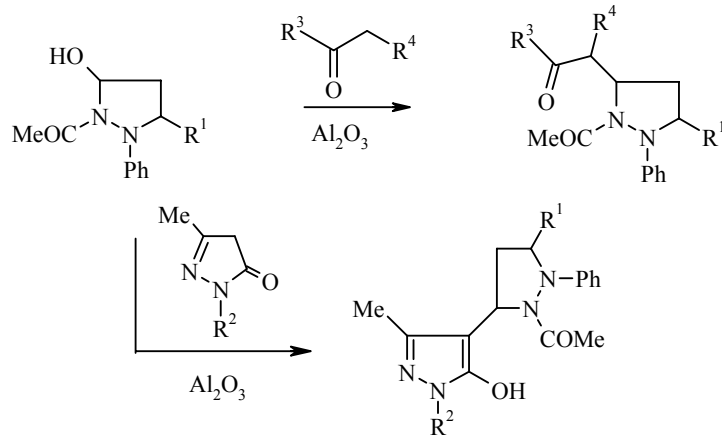
In recent years researches have developed successfully on the chemical transformations in functional derivatives of pyrazolidines. A convenient synthesis was developed in the Department for 5-hydroxypyrazolidines, which proved to be readily obtainable synthons for the production of various functional

derivatives of pyrazolidines by nucleophilic substitution of the semiaminal hydroxyl group. Alcohols, amines, amino acids, hydrazines, thiols, etc. were used as nucleophilic agents, and this made it possible to obtain the corresponding 5-substituted pyrazolidines with the *trans* configuration of the pyrazolidine ring (L. A. Sviridova and S. V. Afanas'eva) [113].



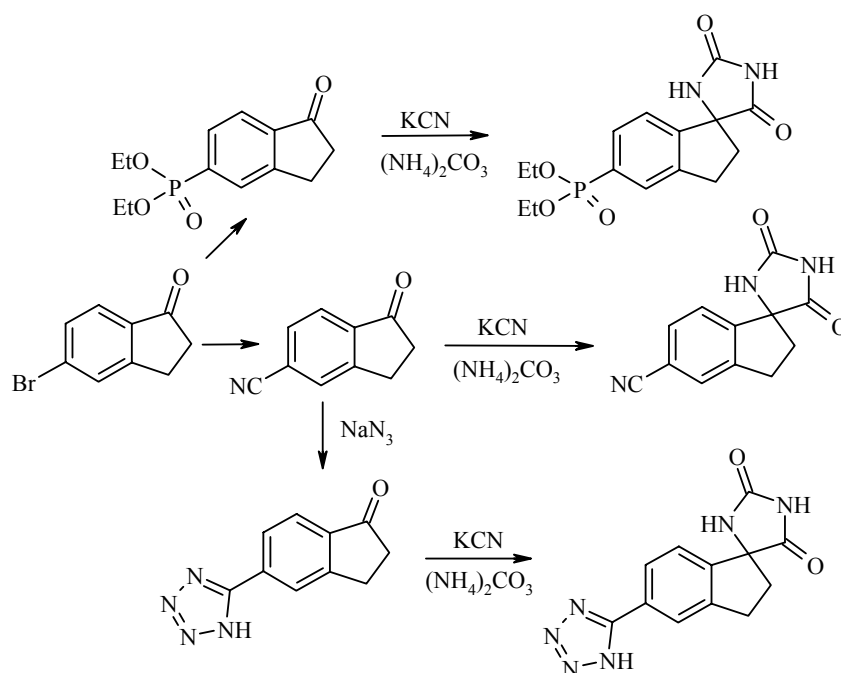
By introducing a natural α -amino acid group at various positions of pyrazolidine it was possible to obtain likely biologically active compounds [114, 115].

The use of CH-acid agents in reactions with hydroxypyrazolidines required the development of special synthetic methods, i.e., to conduct the process at the surface of various adsorbents without a solvent, thereby securing the possibility of generating the reactive particles under mild reaction conditions [116, 117].

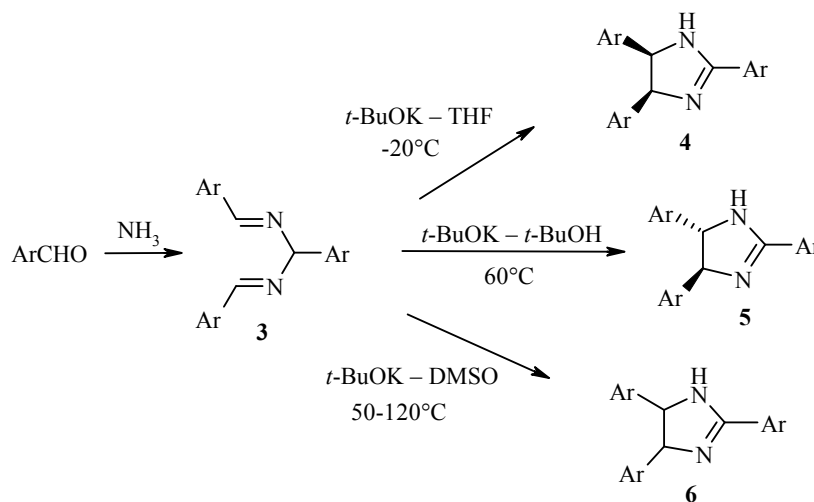


The obtained functional derivatives of pyrazolidine are of great interest not only in respect of their further use in synthesis but also in respect of pharmacology.

In recent years researches have been carried out at the Department on the targeted synthesis of compounds – agonists and antagonists of a series of receptors – for the needs of medicinal chemistry. As an example it is possible to mention the method developed in the Laboratory of Biologically Active Organic Compounds (E. D. Matveeva and T. A. Podrugina) for the synthesis of hydantoin of the indane series – bioisosteric analogs of 1-amino-1,5-indanedicarboxylic acid – an antagonist of group I metabotropic glutamate receptors. Hydantoin containing phosphonate and tetrazole groups in the benzene ring were synthesized [118].

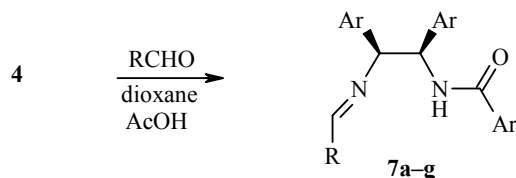


In the Organic Synthesis Laboratory (N. S. Zefirov and M. V. Proskurnina) a stereoselective method was developed for the synthesis of *cis*- and *trans*-2,4,5-triarylimidazolines **5** [119, 120] with preparative yields from aromatic aldehydes.



$\text{Ar} = \text{Ph}, 4\text{-BrC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, 2\text{-thienyl}, 3\text{-O}_2\text{NC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, 2\text{-furyl},$
 $4\text{-(EtO)}_2\text{C}_6\text{H}_3, 4\text{-OCHC}_6\text{H}_4$

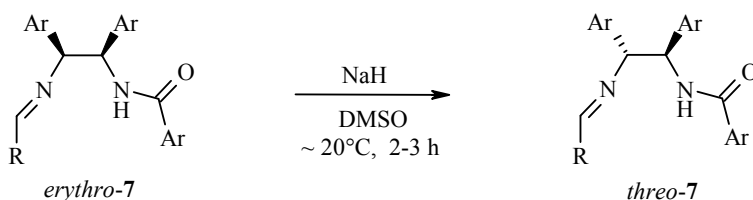
It was shown that *cis*-2,4,5-triarylimidazolines enter into reaction with aromatic aldehydes under the conditions of acid catalysis with the formation of *erythro*- $\text{N}_{(1)}$ -arylidene- $\text{N}_{(2)}$ -aroyl-1,2-diaryl-1,2-ethylenediamines **7**. Ring opening does not occur in *trans*-2,4,5-triarylimidazolines under these conditions [121, 122].



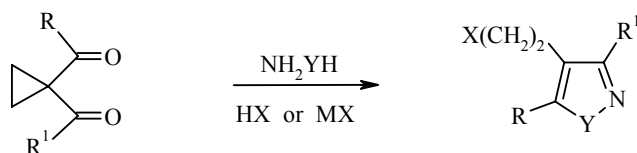
a Ar = R = Ph, **b** Ar = Ph, R = 4-BrC₆H₄, **c** Ar = Ph, R = 4-MeOC₆H₄, **d** Ar = Ph, R = 2-HOC₆H₄, **e** Ar = 4-MeOC₆H₄, R = Ph, **f** Ar = R = 3-O₂NC₆H₄, **g** Ar = R = 4-MeOC₆H₄

The scheme differs favorably from many other methods, since it is possible to obtain unsymmetrical vicinal diamines with differently substituted amino groups. By successive hydrolysis it is possible to modify them independently. The reaction with the aldehyde does not take place in the presence of a stoichiometric amount or an excess of the acid. The reaction is also not catalyzed by mineral acids such as hydrochloric or sulfuric acid.

The production of *trans*-2,4,5-triarylimidazolines according to the scheme presented above in the presence of accepting substituents in the ring is often accompanied by undesirable oxidation by atmospheric oxygen to the corresponding imidazoles. The problem of synthesizing the *threo* isomers of compounds **7a,f,g** was solved on the basis of the ability, first discovered in this group, of the *erythro*-**7a,f,g** compounds to isomerize quantitatively to the corresponding *threo* isomers in superbasic media (*t*-BuOK–DMSO or NaH–DMSO).



In the same laboratory (N. S. Zefirov, T. S. Kuznetsova, and others) during study of the reactivity of 1,1-diacetylcyclopropanes it was found that the reaction of these diketones with derivatives of hydrazine and hydroxylamine takes place with facile nucleophilic opening of the three-membered ring and inclusion of the external nucleophile, including the nucleophilic solvent, in the structure of the product [123-125]. Various aspects of this unusual reaction [123, 125] and its mechanism [126] were studied, and an effective preparative method was developed for the synthesis of 3,5-dialkyl-4-(β-X-ethyl)pyrazoles and isoxazoles.

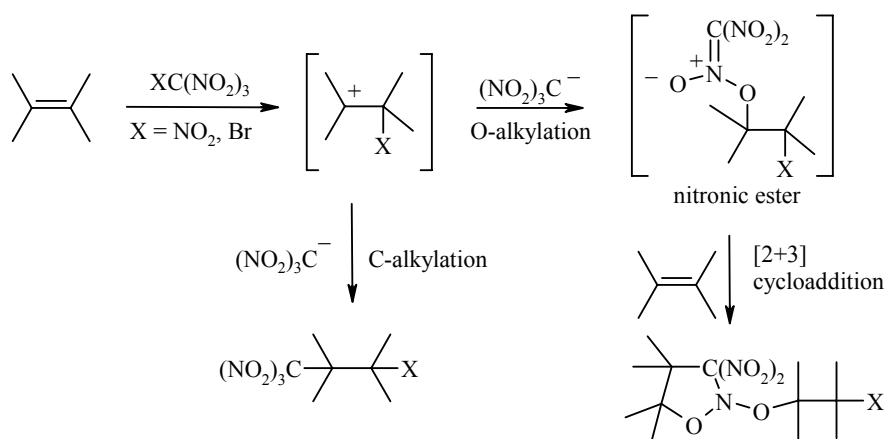


R = R¹ = Me, Ph, 2-Py, *c*-Py; Y = NH, O; X = Cl, Br, I, OMe, OEt, OPh, OAc, NEt₂, piperidyl, morpholyl, *c*-C₅H₁₁NH, *c*-C₆H₁₃NH

In order to produce a series of 4-(β-aminoethyl)pyrazoles, which are prospective biologically active compounds, a synthetic approach was developed on the basis of the alkylation of amines by the halogen derivatives of pyrazoles [127].

During a study of the reaction of tetranitromethane with olefins containing small rings it was shown that the main direction of such a reaction was the formation of 3,3-dinitrooxazolidines of the cyclobutane and cyclopropane series [128, 129]. In a number of cases, however, mainly for olefins containing

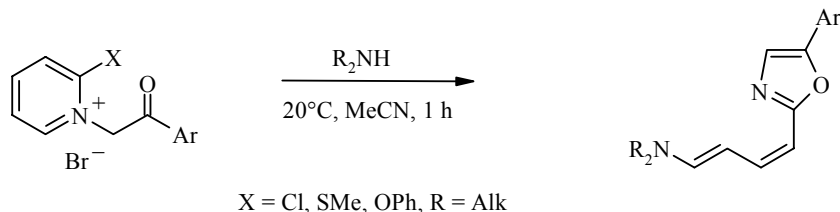
three-membered rings the formation of tetranitropropanes or rearrangement products was observed [130]. Taking account of the published data and also of the authors' results the general scheme of the reaction can be represented as follows:



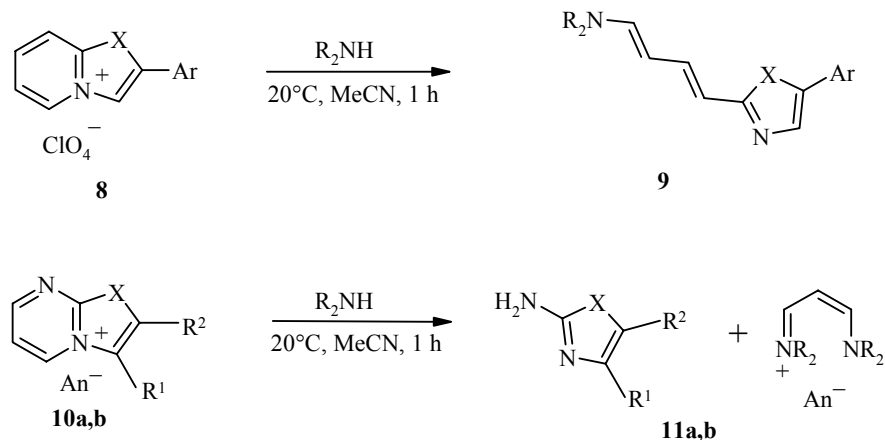
It was shown that the reactions are tandem processes including a sequence of two stages, i.e., *in situ* generation of the nitronic ester and its subsequent [3+2] cycloaddition to the unsaturated compound. Since the steric and electronic demands of the alkene at the first and second stages are different, it seemed possible to make the reaction of tetranitromethane and its derivatives with olefins more universal by using two different alkenes [131-133]. As key olefin for generation of the nitronic ester we successfully used bicyclobutylidene [131, 132], 1-phenyl-substituted cyclopentene and cyclohexene, and 1-methylcyclobutene [133]. Alkenes containing small rings and aromatic, heterocyclic, and electron-withdrawing substituents and also alkynes with electron-donating substituents were used as dipolarophiles.

A three-component one-pot reaction of tetranitromethane or halotrinitromethane with olefins provides a simple preparative method for the synthesis of 3,3-dinitroisoxazolidines of mixed structure. The isoxazolidines are formed with high regio- and in some cases diastereoselectivity. The effectiveness of the method was demonstrated for the case of the synthesis of more than 40 new heterocyclic compounds [131-133].

One of the most elegant approaches to the synthesis of various heterocycles is the transformation of some heterocyclic compounds into others. This method has found widespread use for the production of azoles. Thus, in E. V. Babaev's research group an interesting method was discovered for the production of oxazole derivatives by the recyclization of N-phenacylpyridinium salts containing the leaving group at the α -position.



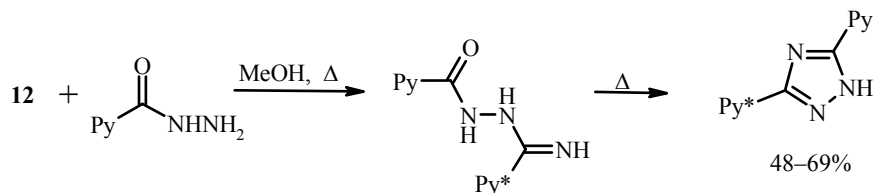
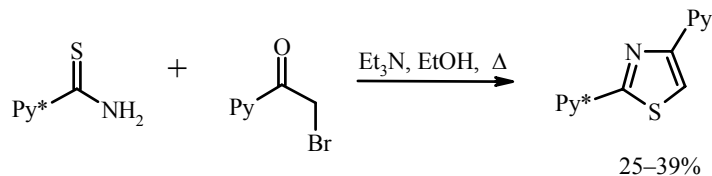
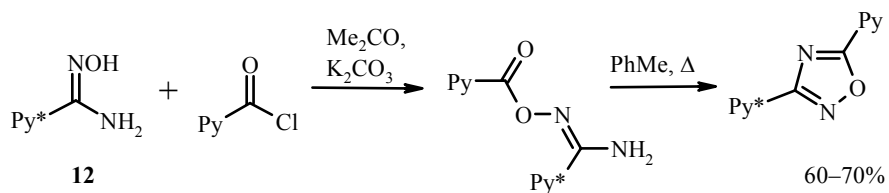
The reaction takes place for 2-chloropyridinium salts [134, 135] and also for the 2-methylthio [136] and 2-phenoxy [137] derivatives. It was shown that the intermediate in this reaction is the oxazolo[3,2-*a*]pyridinium cation **8a** ($\text{X} = \text{O}$), in which the pyridine fragment is opened by the action of the secondary amines; the stereochemistry of the obtained dienes was studied. The corresponding thiazoles **9b** and imidazoles **9c**, containing a diene fragment, can be obtained in a similar way from the condensed azolopyridinium salts **8b,c** ($\text{X} = \text{S}, \text{NMe}$) [138, 139].

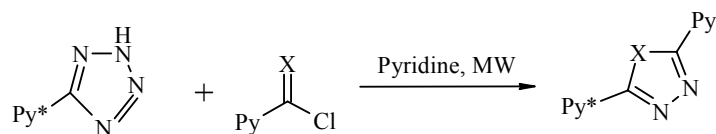
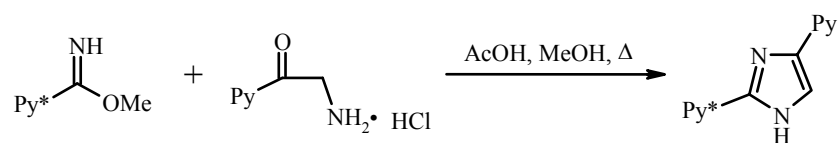


8, 9 a X = O, b X = S, c X = NMe; **10, 11** a X = S, b X = NR

By using the azolopyrimidinium salts **10a,b** in a similar reaction it is possible to obtain 2-aminoazoles **11a,b**, and the second component of the reaction, corresponding to the product from cleavage of the pyrimidine group, can be detected experimentally [140-142].

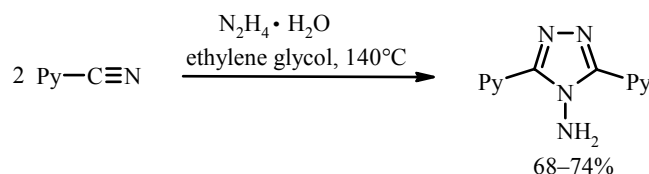
In the Laboratory of Biologically Active Organic Compounds (N. V. Zyk, S. Z. Vatsadze, and V. N. Nuriev) methods are being developed for the synthesis of dipyrindylazoles [143], which have found widespread use in the boundary region of applied organic and coordination chemistry – in the creation of supramolecular assemblies. Various strategic approaches to the synthesis of unsymmetrical and symmetrical dipyrindylazoles were proposed. A method for the production of unsymmetrical azoles (containing two different pyridyl substituents) is a two-component synthesis based on nucleophilic adducts at the cyano group of pyridylcarbonitriles, on the one hand, and acid chlorides, imidoyl chlorides, hydrazides of pyridinecarboxylic acids, or bromoalkyl- and aminoalkyl pyridyl ketones, on the other, leading to the formation a heterocycle from an ambiphilic precursor [143]. Examples of such transformations are given below:



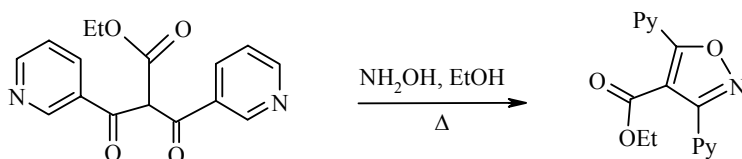


X = O (78–90%), X = *p*-BrC₆H₄N (59%)

The condensation of two molecules of pyridylcarbonitriles was used for the production of symmetrical dipyridylazoles [143].

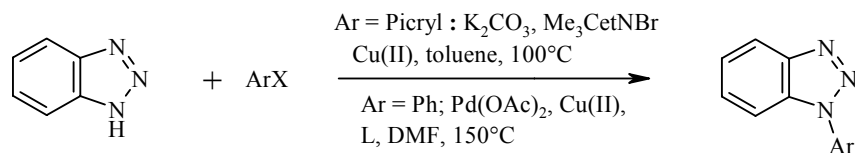


The reaction of a biselectrophilic functionally substituted β -diketone of the pyridine series with bisnucleophilic hydroxylamine made it possible to obtain a symmetrical functionally 3-substituted 3,5-dipyridylisoxazole [140].



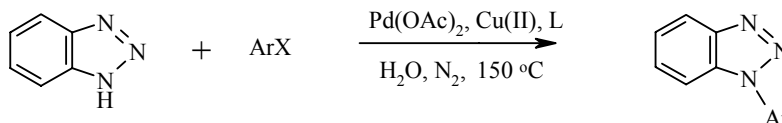
In this way the scientific team obtained a wide range of dipyridyl-substituted azoles, which recommended themselves as prospective ligands for the investigation and creation of supramolecular structures.

In the Laboratory of Organoelement Compounds (I. P. Beletskaya, D. V. Davydov, and others) several methods were developed for the regioselective N-arylation of ambident azoles by the action of aryl halides and iodonium salts. Thus, for example, in the case of activated aryl halides 1-arylbenzotriazoles can be easily obtained under the conditions of phase-transfer catalysis by boiling the reagents in toluene in the presence of copper phenylcyclopropanecarboxylate, which is a convenient source of low-valence copper [144].



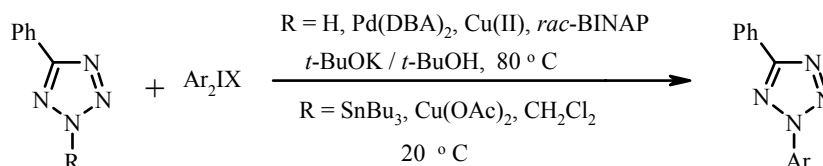
ArX is an activated aryl halide or a nonactivated halide,
Cu(II) is a salt of 2-phenylcyclopropanecarboxylic acid, and L is a diphosphine ligand

For nonactivated aryl halides arylation takes place excellently in DMF with the participation of a palladium catalyst and the same copper salt. The process can be conducted under milder conditions in water with an iodonium salt as arylating agent in the presence of the same catalyst–cocatalyst pair [145].



Cu(II) is the salt of 2-phenylcyclopropanecarboxylic acid, and L is the diphosphine ligand.

The regioselective arylation of benzotriazole by the action of iodonium salts can be carried out without a catalyst by microwave activation of the process in dichlorobenzene [146]. 5-Substituted tetrazoles are arylated regioselectively at position 2 by the action of iodonium salts in the presence of the above-mentioned catalyst–cocatalyst pair in boiling *tert*-butanol [147].



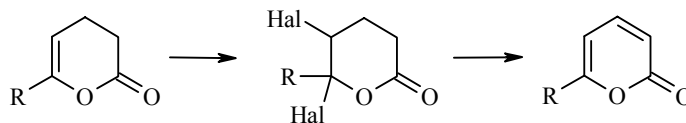
DBA is dibenzylideneacetone, *rac*-BINAP is 2,2-bisdiphenylphosphinobinaphthyl.

With microwave activation the reaction can be conducted in water only in the presence of metallic copper.

Analogous stannylated tetrazoles, formed during the reaction of tributylstannyl azide with nitriles, are easily arylated at room temperature in methylene chloride in the presence of an equivalent of copper acetate [148].

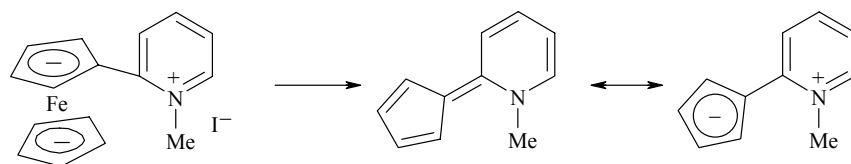
SIX-MEMBERED HETEROCYCLES

The chemistry of six-membered oxygen-containing heterocycles at the Department was studied mainly for the case of α -pyrones. For example, R. Ya. Levina and N. P. Shusherina proposed a method for the production of α -pyrones by halogenation of δ -enollactones followed by dehydrohalogenation of the obtained dihalides [149-151].



Electrophilic substitution (nitration, bromination, sulfonation, chloromethylation) of pyrones and various transformations of carboxylic acid derivatives of this series were also studied in detail [151].

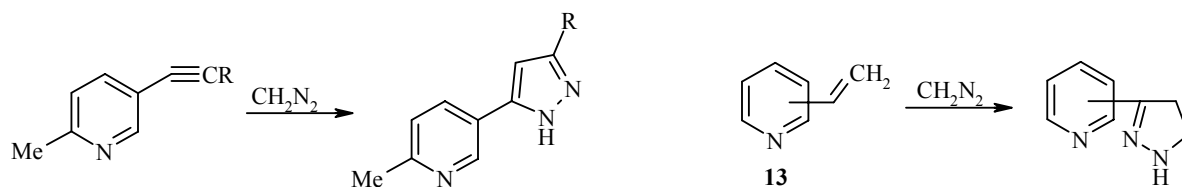
In the sixties A. N. Nesmeyanov and V. A. Sazonova realized the synthesis of heterocyclic derivatives of ferrocene [152, 153]. Further development of these investigations showed that such derivatives of ferrocene (e.g., ferrocenylpyridine methiodide) readily dissociate with the formation of ylides.



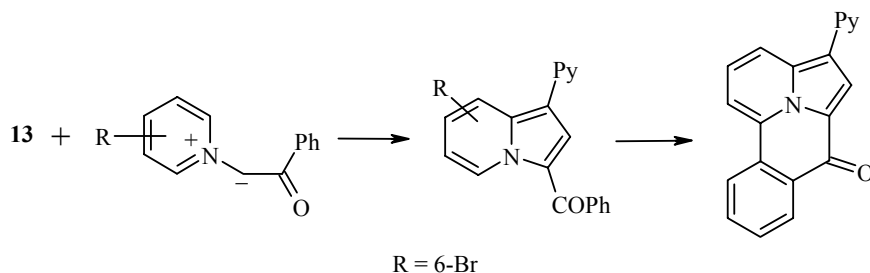
An interesting modern application of pyridine derivatives arose from the fact that dipyriddy-substituted conjugated dienones based on cyclic ketones, for example, proved convenient prospective ligands for the production of coordination polymers. Thus, the derivative of cyclohexanone and pyridine-3-carbaldehyde in reaction with silver nitrate gives infinite polymeric chains of a complex linked by $\text{Ag}\cdots\text{Ag}$ interactions and π - π stacking between neighboring pyridines [154].

At the beginning of the fifties in the Laboratory of Special Organic Synthesis of the Department under the guidance of the young assistant professor A. N. Kost investigations were carried out on the synthetic use of simple but reactive and industrially accessible reagents, such as 2-methyl-5-vinylpyridine (P. B. Terentiev and others). Thus, the latter was converted according to the standard scheme into the corresponding ethynylpyridine, which proved a convenient starting compound for the synthesis of a large number of various structures of the pyridine series: Vinyl alcohols, vinylamines, Mannich bases [155], ethynylcarbinols [156, 157], and alkynylpyridines [158, 159]. Their reduction with NiRa alloy in hydrazine hydrate or with iodine and red phosphorus in an acidic medium followed by oxidation of the 2-methyl group gave natural fuzarinic acid and its various analogs [158-161] (Scheme 1).

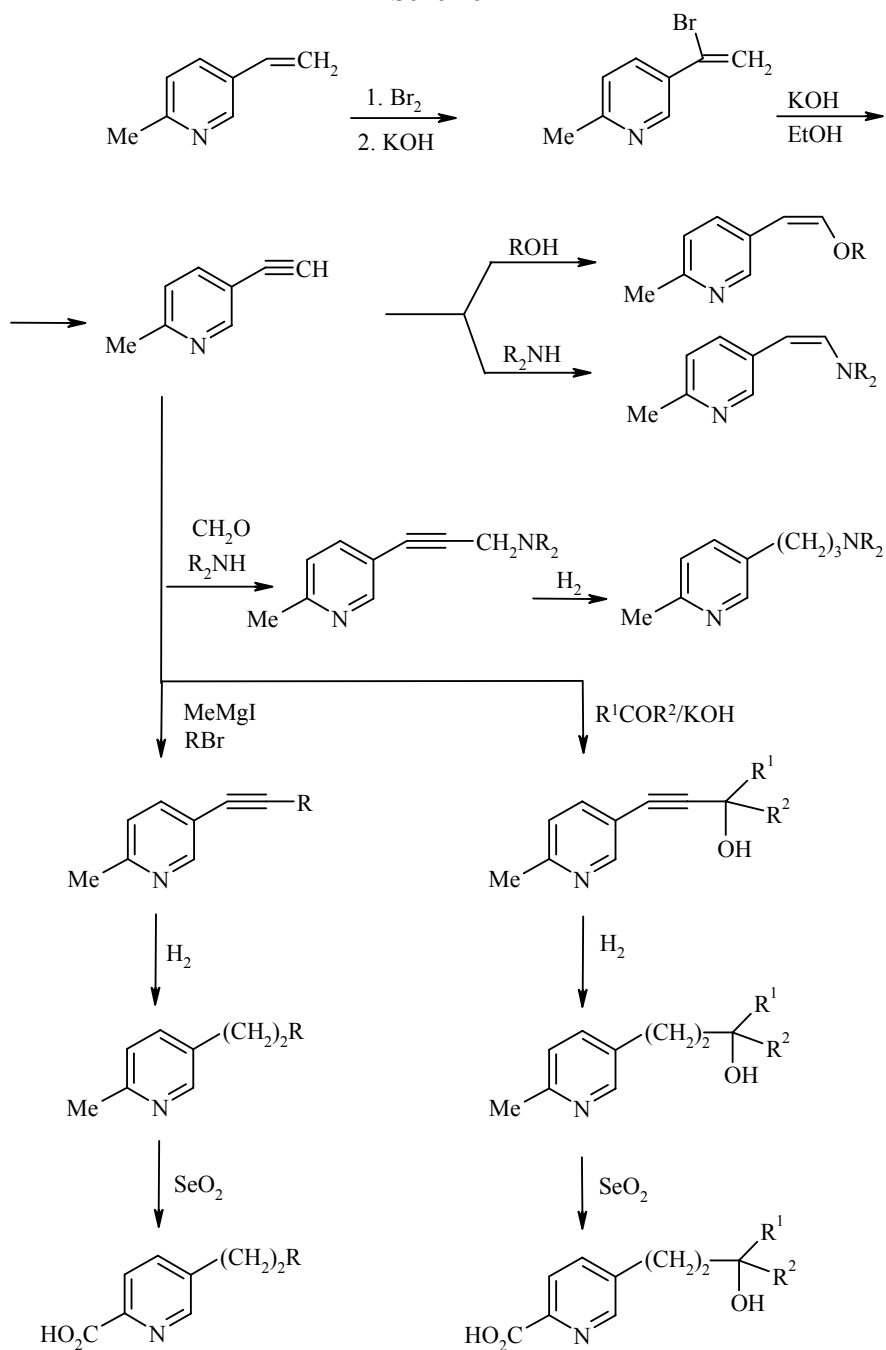
Further investigations (A. N. Kost, P. B. Terentiev, and coworkers) showed that ethynyl- and vinylpyridines were unique synthons for the production of a whole series of new hetarylpyridines and condensed systems. For example, the reaction of ethynylpyridine and its substituted derivatives with diazomethane in a [1,3]-dipolar cycloaddition reaction led to good yields of pyridylpyrazoles [162], while the reaction of diazomethane with isomeric 2-, 3-, and 4-vinylpyridines **13** followed by treatment of the reaction mixture with acetic anhydride made it possible to obtain a series of isomeric 3-pyrazolinylypyridines [163].



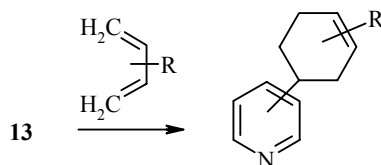
Similarly, the reactions of 2- and 4-vinylpyridines and their pyridyl-substituted analogs with phenacylpyridinium ylides take place by 1,3-dipolar cycloaddition with the formation of substituted 1-aryl-3-pyridylindolizines [164].



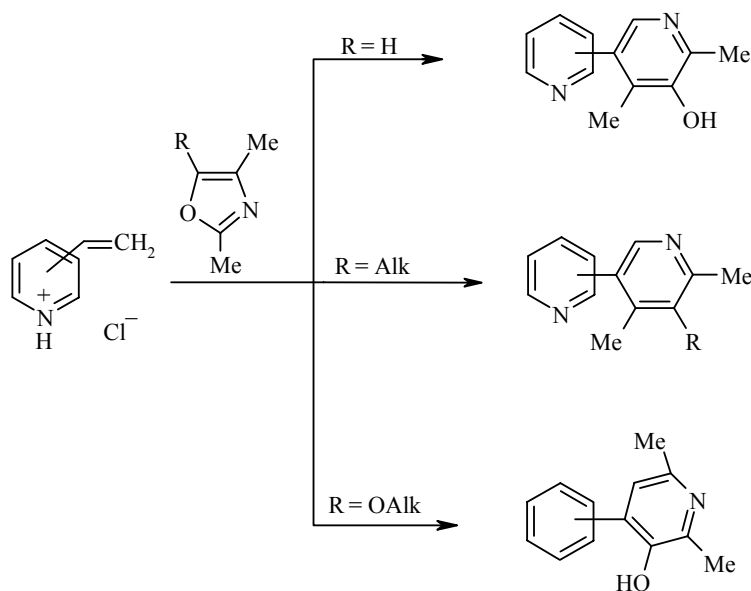
Scheme 1



The reactions of the isomeric vinylpyridines with carbodienes take place in the normal way by a [4+2] cycloaddition mechanism with the formation of the corresponding (3-cyclohexenyl)pyridines [165].

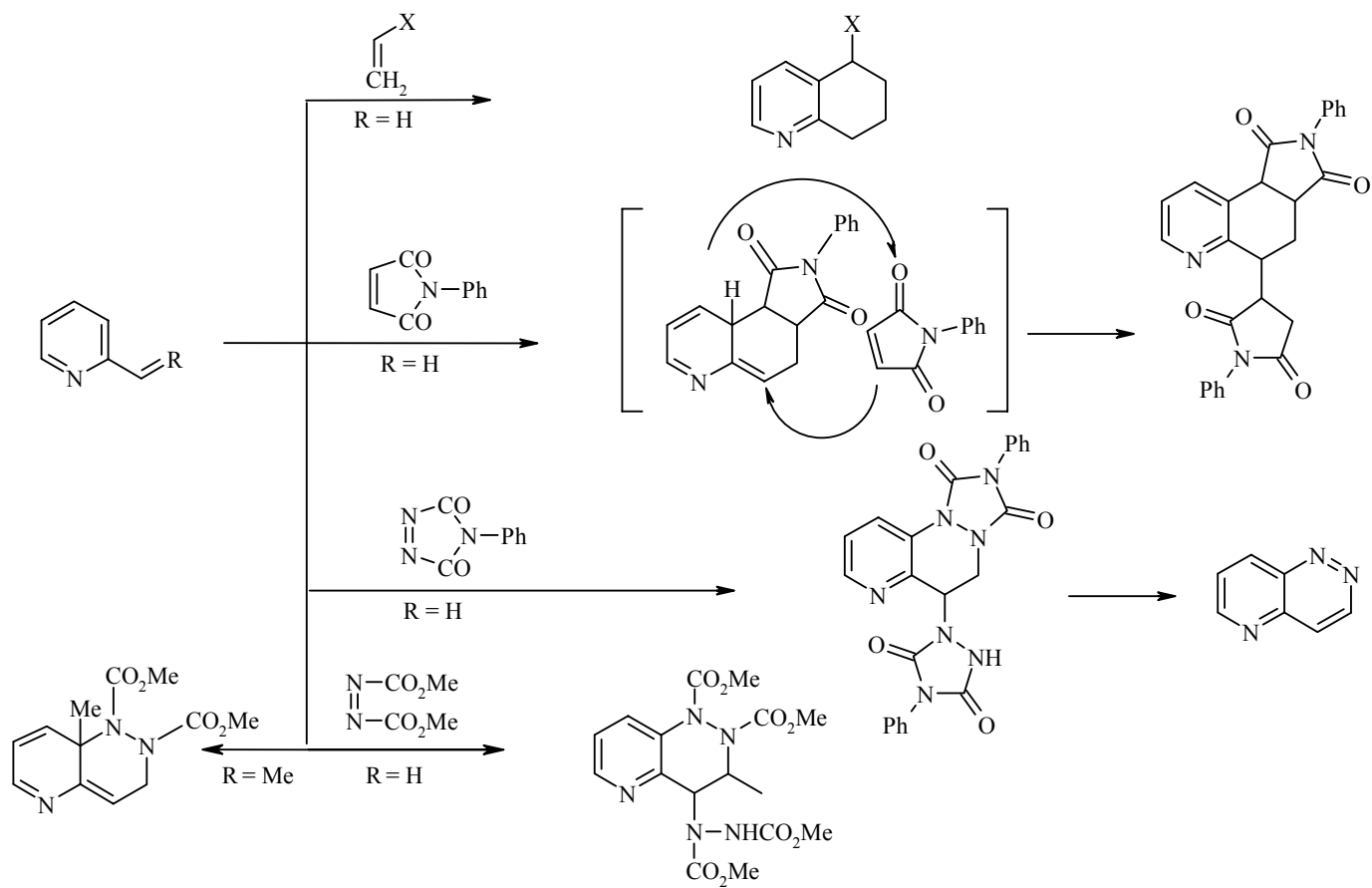


However, the reactions of vinylpyridine hydrochlorides with such heterodienes as oxazoles take place in different ways, depending on the nature of substitution of the latter. Thus, 3-pyridylpyridines are formed during reaction with 5-alkyl-substituted oxazoles, whereas the final products in the reaction with 5-unsubstituted oxazoles are 3-pyridyl-5-hydroxypyridines. It is interesting to note that replacement of the 5-alkyl group in the oxazole by alkoxy also makes it possible to obtain 3-hydroxypyridylpyridines, but the pyridyl radical in this case is at position 4. This type of mutual orientation in oxazoles and vinylpyridines was supported by quantum-chemical calculations [166-168].

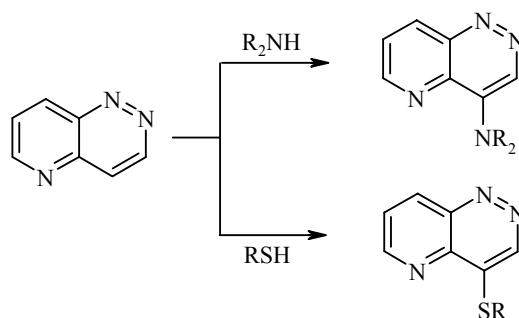


It should be mentioned that from 1967 the structure of most of the above-mentioned compounds and previously synthesized compounds of the pyridine series has also been proved by detailed analysis of their mass spectra [169-174]. These works lay the foundation for the mass-spectrometric investigations (P. B. Terentiev) at the Faculty's Department of Organic Chemistry [167, 168].

It was found that vinylpyridines can react not only as dipolarophiles or dienophiles but can also in a number of cases react with known dienophiles. Here the vinyl group and the heteroaromatic C=C bond play the role of diene. Thus, when 2-vinylpyridine hydrochloride is heated with its own base cyclodimerization occurs, and 5-(2-pyridyl)-5,6,7,8-tetrahydroquinoline is formed [175]. The dimeric processes in other isomers and also the cross-reactions of a mixture of two isomeric vinylpyridines take place similarly, and quantum-chemical calculations make it possible to predict the preferential formation of specific regioisomers [176]. Acrylic acid derivatives can also act as dienophiles in reactions with vinylpyridines. More active dienophiles, such as N-phenylmaleimide, react with 2-vinylpyridine with the initial formation of the partially hydrogenated pyrrolo[3,4-*f*]quinoline system. The latter, however, quickly reacts with a new molecule of the dienophile in a substitutive addition reaction, leading to the 8-substituted product. The reaction of vinylpyridines with azodicarboxylic ester [177-179] and N-phenyltriazolinedione [180] goes in an absolutely identical manner. When boiled in hydrazine hydrate the adducts here with the last dienophile undergo solvolysis, decarboxylation, and oxidative aromatization and form the previously unknown 5-azacinnoline.

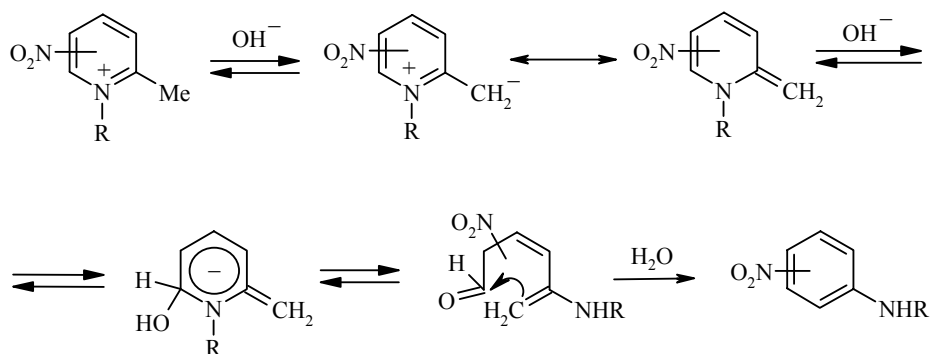


This compound proved extremely reactive and gave good yields of 4-amino- and 4-alkylthio-5-azacinnolines respectively when simply boiled with aliphatic amines [181] or mercaptans [182]. The role of catalyst here is played by the pyridine nitrogen atom.



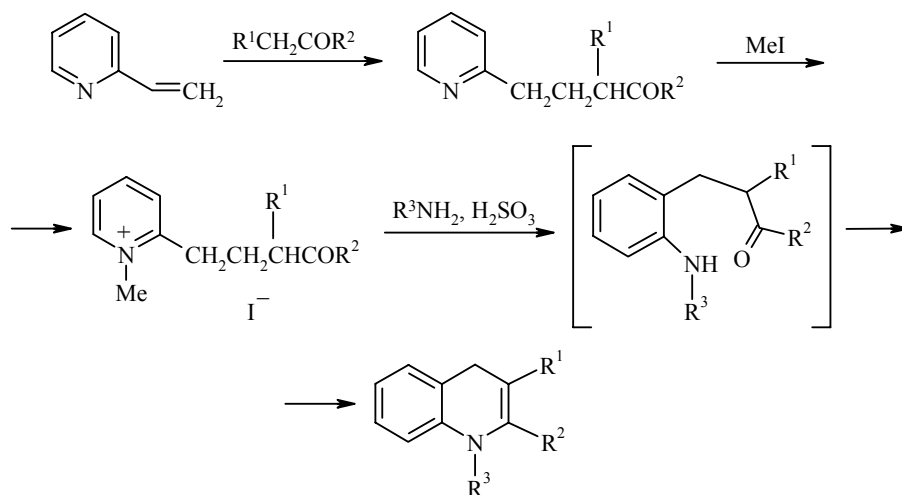
It should also be mentioned that researches on diene synthesis have also been a traditional subject in the Department. Thus, outstanding pioneering work on the Diels–Alder reaction of diene hydrocarbons with nitroso compounds, leading to derivatives of 1,2-dihydro-1,2-oxazine, was carried out in the fifties by Yu. A. Arbuzov [183].

In the seventies at the Department of Organic Chemistry there was a momentous event – the isomerization/recyclization of α -methylnitropyridinium salts to anilines by the action of bases [184], called "the Kost–Sagitullin rearrangement," was discovered (and registered as discovery No. 205).

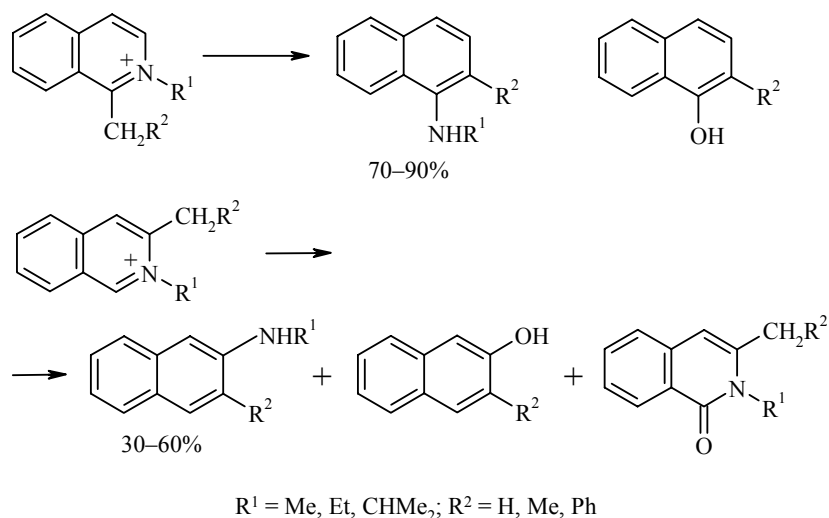


Pyridinium substrates not activated by accepting substituents undergo the same recyclization under the influence of the sulfite ion, and this substantially extends the applications of this reaction.

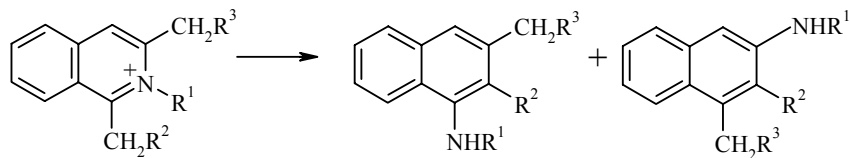
A development of the Kost–Sagitullin reaction was the recyclization of the quaternary salts of pyridylethylated carbonyl compounds. It is known that 2-vinylpyridine reacts readily with aliphatic alicyclic and aliphatic aromatic ketones. It was established that when the methiodides of such pyridylethylated ketones are heated in a tube with the sulfites of primary amines they undergo recyclization to 2-(3-oxoalkyl)anilines. The latter undergo spontaneous cyclization to 1,4-dihydroquinolines, and they partly disproportionate to the corresponding quinolines and tetrahydroquinolines [185-187]. Chromatomass-spectrometric analysis of the reaction mixtures showed that apart from the above-mentioned compounds they also included tetralones not containing nitrogen, the formation of which clearly arises from partial hydrolysis of the intermediately formed imines.



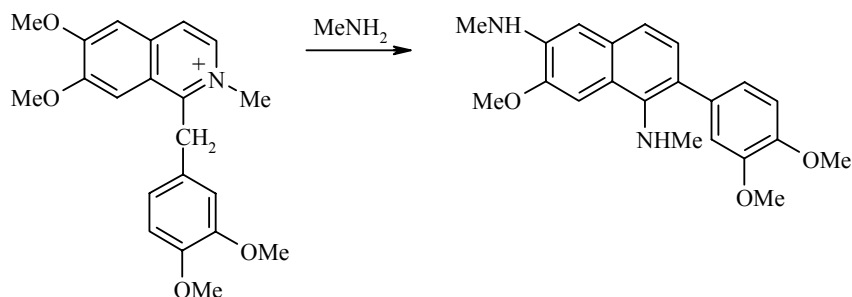
Alcohol solutions of alkylamines were used as nucleophiles for the recyclization of the isoquinolinium salts. Here, the 1-alkylisoquinolinium salts rearrange to 1-alkylaminonaphthalenes, while the 3-alkylisoquinolinium salts rearrange to 2-alkylaminonaphthalenes [188, 189].



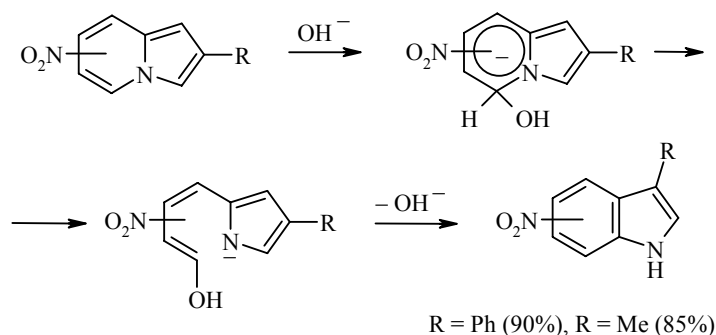
If an aqueous solution of the alkylamine is used as recyclization agent, the corresponding naphthols are formed in addition to the aminonaphthalenes, while in the case of the 3-alkylisoquinolinium salts the main direction of the reaction is oxidation to isoquinolines. Recyclization of the 1,3-dialkylisoquinolinium salts leads to a mixture of the isomeric 1-aminonaphthalenes (30-60%) and 2-aminonaphthalenes (7-40%). The preferred formation of the 1-aminonaphthalenes agrees with the data from quantum-chemical calculations [190].



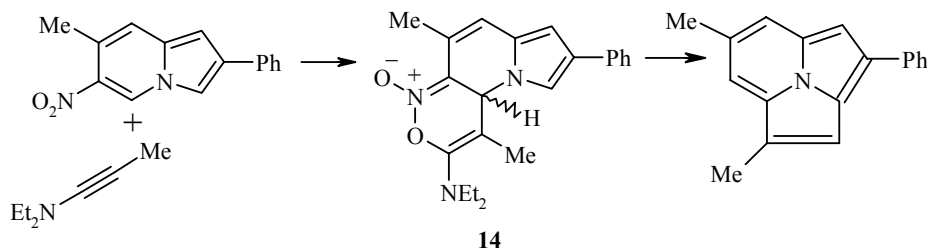
Nucleophilic substitution of the methoxy group by the methylamino group [191-194] was detected during the recyclization of 6-methoxyisoquinolinium salts by the action of methylamine. An excellent example of this is the recyclization of papaverine methiodide [194].



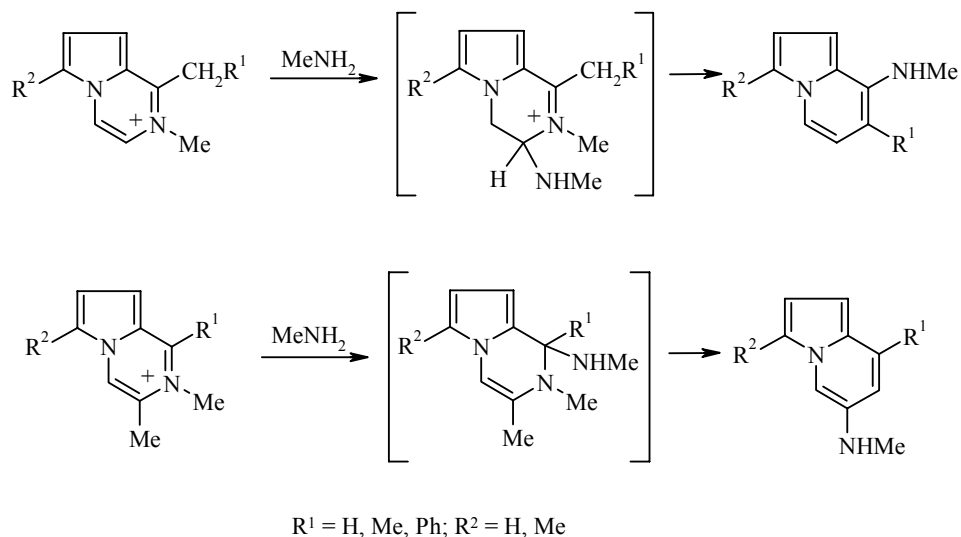
Further investigations showed that recyclization with cleavage of the C–N bond and the formation of a new C–C bond is a common phenomenon for condensed heterocycles with a bridging nitrogen atom. An example of this is the recyclization of indolizines that are activated by the presence of a nitro group in the six-membered ring of the indolizines to nitroindoles. This reaction, discovered in 1976 by A. N. Kost and coworkers [193-197] for the case of the rearrangement of 3-methyl(phenyl)-5(7)-nitroindolizines to 3-methyl(phenyl)-5(7)-nitroindoles, opened a new page in the chemistry of indolizines, which previously had extremely limited applications.



It was concluded on the basis of detailed quantum-chemical investigations [198] that an essential condition for recyclization of indolizines to indoles is the presence of a substituent with electron-withdrawing character no weaker than that of the nitro group at position 6(8) of the indolizine. In the course of this work a wide range of electrophilic substitution reactions in the indolizine ring was investigated [198]. In general, the investigations in the chemistry of indolizines involved study of the π -amphoteric characteristics of the 6(8)-nitroindolizines [199, 200]. One of the most interesting recent results was the discovery of an unusual cycloaddition in such systems [201-203] with the experimental detection of a stable intermediate **14**.

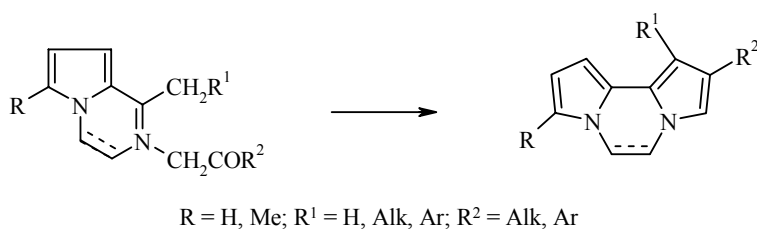


Other representatives of condensed heterocycles with a bridging nitrogen atom, painstakingly investigated in V. I. Terenin's group, are derivatives of pyrrolo[1,2-*a*]pyrazine [204-206]. This heterocyclic system is interesting in that it contains two nitrogen atoms, each of which is capable of participating in recyclization. Rearrangement with participation of the N₍₂₎ atom must take place similarly to the rearrangement of isoquinolinium salts and requires the presence of a methyl or methylene group in the α -position to this nitrogen atom. Depending on the presence of an alkyl substituent at position 1 or 3, the recyclization products will be the respective 8- or 6-aminoindolizines:

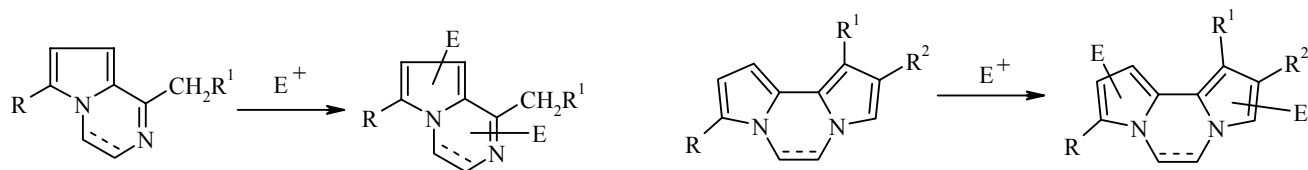


The N₍₄₎ atom is bridging, and rearrangement with its participation must take place similarly to the rearrangement of indolizines with the formation of 6-azaindoles. Such a direction is not, however, realized in practise.

In addition, pyrrolo[1,2-*a*]pyrazinium quaternary salts proved suitable starting compounds for the production of tricyclic nitrogen-containing heterocycles both with π -electron-excessive and with π -electron-deficient rings, dipyrrolo[1,2-*a*;2',1'-*c*]pyrazines, and their 5,6-dihydro analogs.

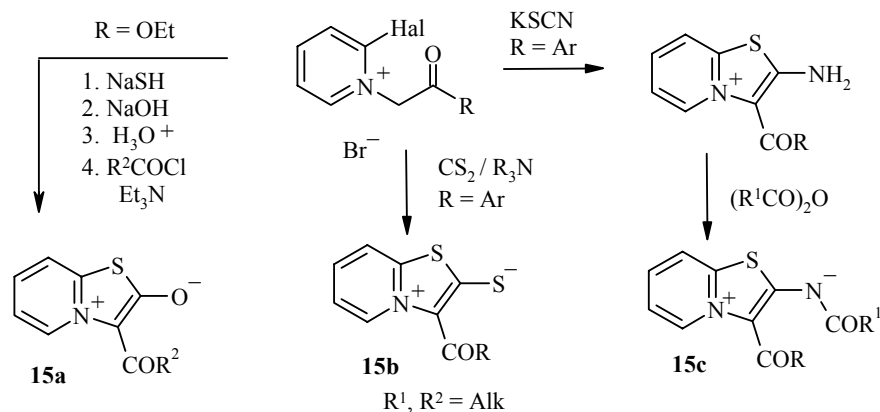


In V. I. Terenin's group the behavior of pyrrolo[1,2-*a*]pyrazines [207, 208] and dipyrrolo[1,2-*a*;2',1'-*c*]pyrazines [209-216] in electrophilic substitution reactions (protonation, acylation, aminomethylation, nitration, formylation, phosphorylation) was investigated systematically.

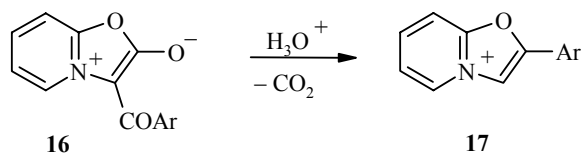


Preparative methods were developed for the synthesis of various derivatives of pyrrolo- and dipyrrolopyrazines containing formyl, acyl, and nitro groups. Various amides, phosphine sulfides, Mannich bases, and azo dyes of the dipyrrolopyrazine series were synthesized.

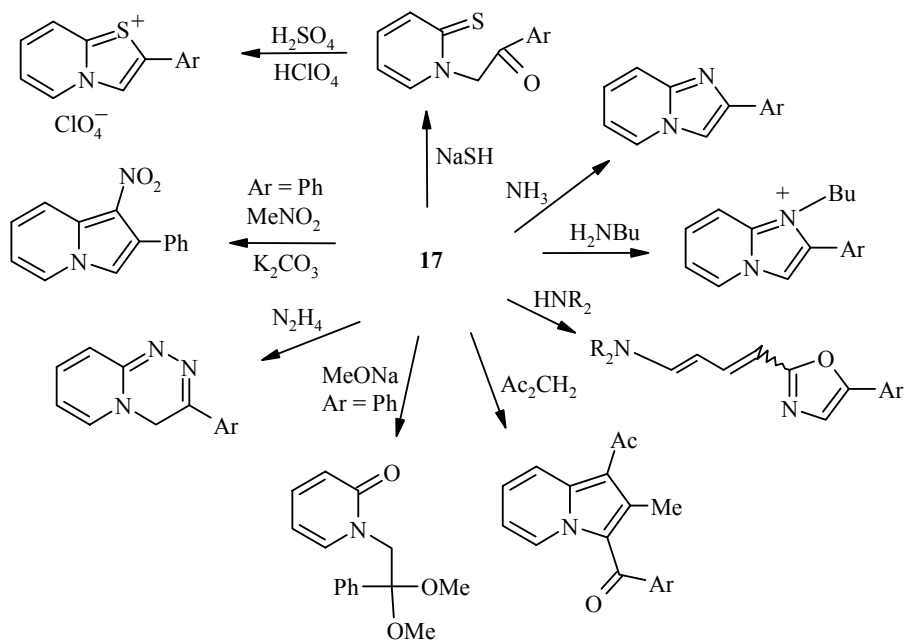
In E. V. Babaev's group synthetic approaches to the construction of previously unknown condensed analogs of munchnone in the thiazolopyridine series were investigated systematically [217-219]. Abnormally stable mesionic olates **15a**, thiolates **15b**, and imidates **15c** were discovered.



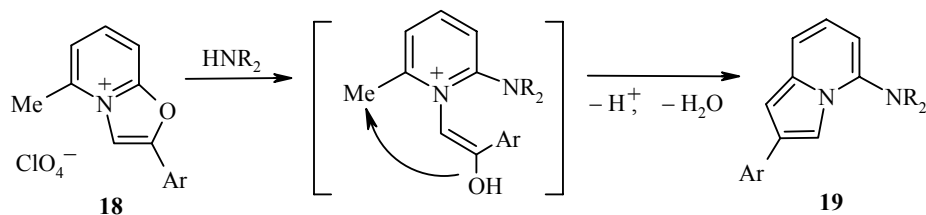
Under the influence of acids the structurally similar mesionic 2-olates of the oxazolopyridinium series **16** undergo cleavage of the oxazolone fragment and recyclization to aromatic oxazolo[3,2-*a*]pyridinium cations **17** [219, 220]



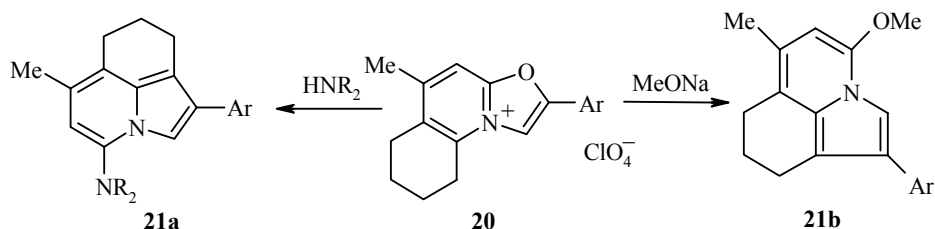
The obtained salts **17** in turn are capable of transformation both of the pyridine ring and of the oxazole rings and are the precursors of a large series of heterocycles with a bridging nitrogen atom [221-226].



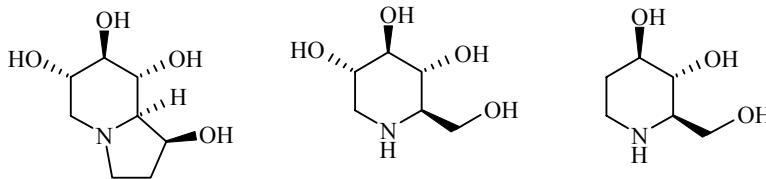
As demonstrated by E. V. Babaev and coworkers [227-231], an unusual type of recyclization of the oxazole ring to a pyrrole ring with the formation of indolizines **19** is observed in the reactions of the cation **18** (a homolog of the cation **17**) with secondary amines.



The obtained indolizines **19**, which are difficult to obtain by other methods, are biologically active and bind selectively with β_2 -adrenoreceptors. By further enlargement of the range of systems capable of such recyclization it was possible to realize the unusual transformation of angular tricyclic cations **20** to the *peri*-condensed systems **21** [232,233].

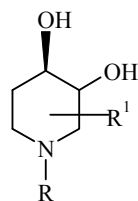


The unflagging interest in the stereoselective synthesis of natural and synthetic derivatives of piperidine is due to their great potential of biological activity. Great attention has recently been attracted to polyfunctionalized piperidines, which represent the building blocks for the production of natural compounds having important biological characteristics. This determines the enormous interest displayed toward the diastereo- and enantioselective synthesis of the derivatives of piperidine and its analogs. In this connection G. V. Grishina's group have carried out extensive investigations into polyhydroxylated piperidines, which are the simplest aza sugars with an interesting pharmacological effect, including an increase in the glucose level of the blood, suppression of the development of metastasis in cancerous diseases, and inhibition of the replication of viruses.



Castanospermin alkaloids

The aim of the latest researches of this group is to seek and create new anti-HIV agents. As a result it was found that the racemic and chiral N- and C-substituted *trans*-3,4-dihydropiperidines **22a-l** are low-toxicity compounds that exhibit high *in vitro* anti-HIV activity.

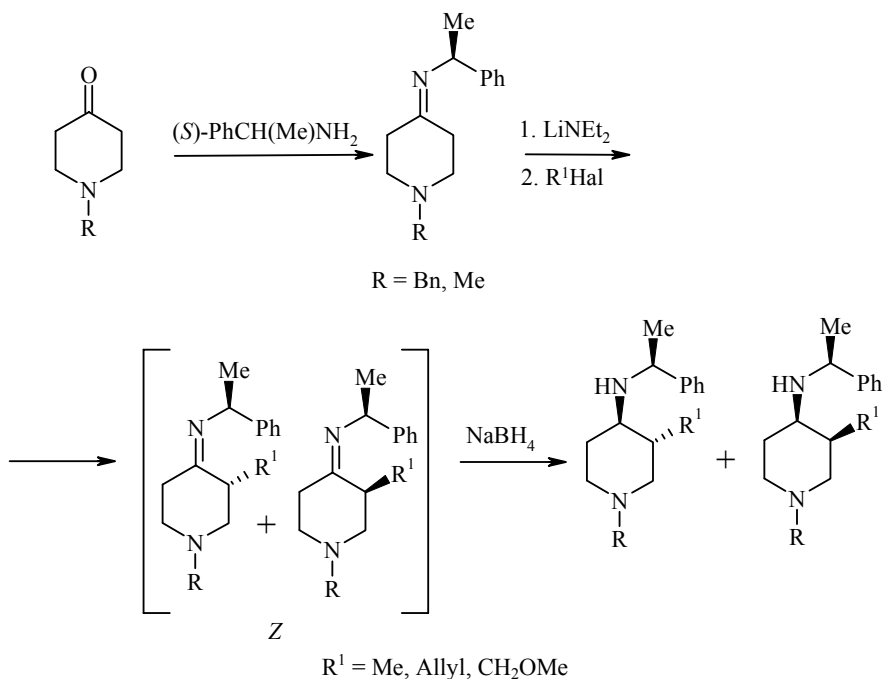


22a-1

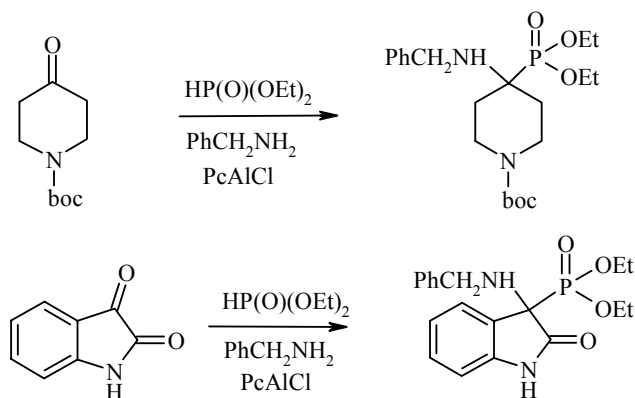
22 a R = R¹ = H; **b** R = Me, R¹ = H; **c** R = Et, R¹ = H; **d** R = *n*-Pr, R¹ = H;
e R = *n*-Bu, R¹ = H; **f** R = Bn, R¹ = H; **g** R = Bn, R¹ = 6-Me; **h** R = Bn, R¹ = 3-Me;
i R = Bn, R¹ = 4-Me; **j** R = Bn, R¹ = 4-Ph; **k** R = (CH₂)₂OH, R¹ = H; **l** R = MeCHPh, R¹ = H

On this basis the *trans*-3,4-dihydropiperidine fragment must be regarded as an anti-HIV pharmacophore [234-236]. The compounds, which exhibit the highest anti-HIV activity and minimal cytotoxicity (leader compounds) are of interest for in-depth study, in particular, of the mechanism of their biological action.

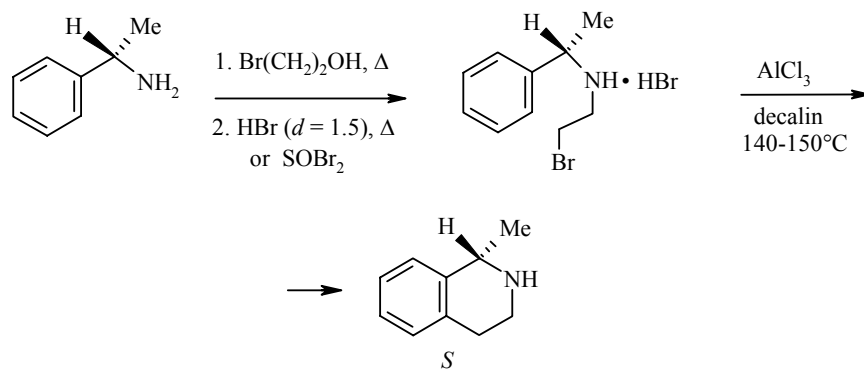
Another possibility for functionalization of the piperidine ring is the development of an asymmetric synthesis for the chiral nonracemic *cis* and *trans* isomers of 4-aminopiperidines. It was shown the previously unknown optically pure *trans*-(3*R*,4*R*) isomers with a diastereomeric excess (*de*) > 99% and a diastereomeric pair of *cis*-(3*S*,4*R*) and *cis*-(3*R*,4*S*) isomers with *de* up to 71% of 1,3-dialkyl-N-[(1*S*)-1-phenylethyl]-4-piperidylamines are formed with yields of 46-90% during successive lithiation and alkylation by the alkyl halides of chiral imines with the formation of the *Z*-(3*S*-3-alkyl- and *Z*-(3*R*)-3-alkylimines and their subsequent reduction with sodium borohydride in ethanol. The whole sequence of reactions is conducted without isolation of the intermediate compounds.



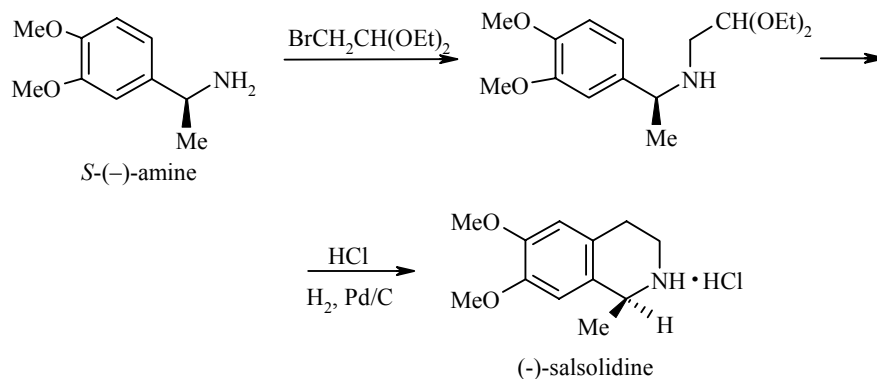
In E. D. Matveeva's group a method was developed for the synthesis of α -aminophosphonate on the basis of N-Boc-piperid-4-one using metal-containing phthalocyanines as catalysts. A similar method was used for another heterocyclic ketone isatin. These aminophosphonates are bioisosteric antagonists of glutamate receptors [237].



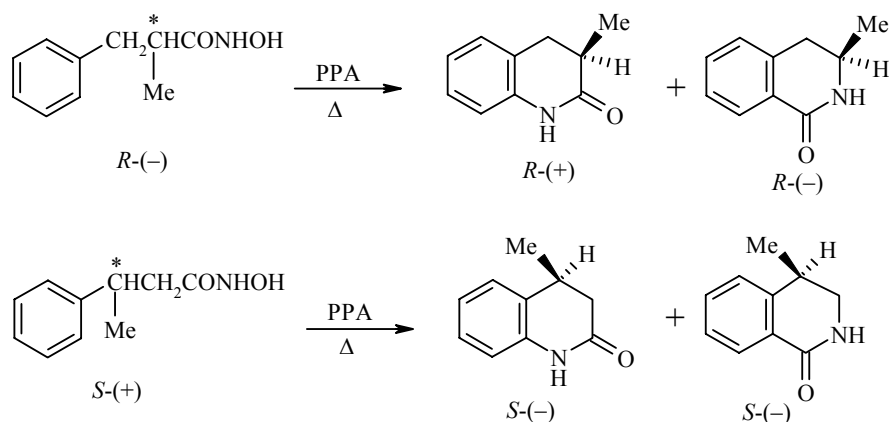
A large series of researches at the Department on chiral tetrahydroquinolines and isoquinolines was associated with the name of V. M. Potapov. He was the first in our country to adopt and bring into research practise of the sixties the new physicochemical method spectropolarimetry, which is an irreplaceable tool in work with complex natural and synthetic optically active substances. Under his leadership various types of chiral heterocycles based on optically active arylalkylamines and arylalkylcarboxylic acids were synthesized, and methods for the production of some of them were developed in the Laboratory of Special Organic Synthesis (V. M. Potapov, V. M. Dem'yanovich, and others). Thus, optically active 1-methyl-1,2,3,4-tetrahydroisoquinoline was obtained from 1-phenylethylamine, which is readily available in the form of both enantiomers, according to the following scheme [238-240]:



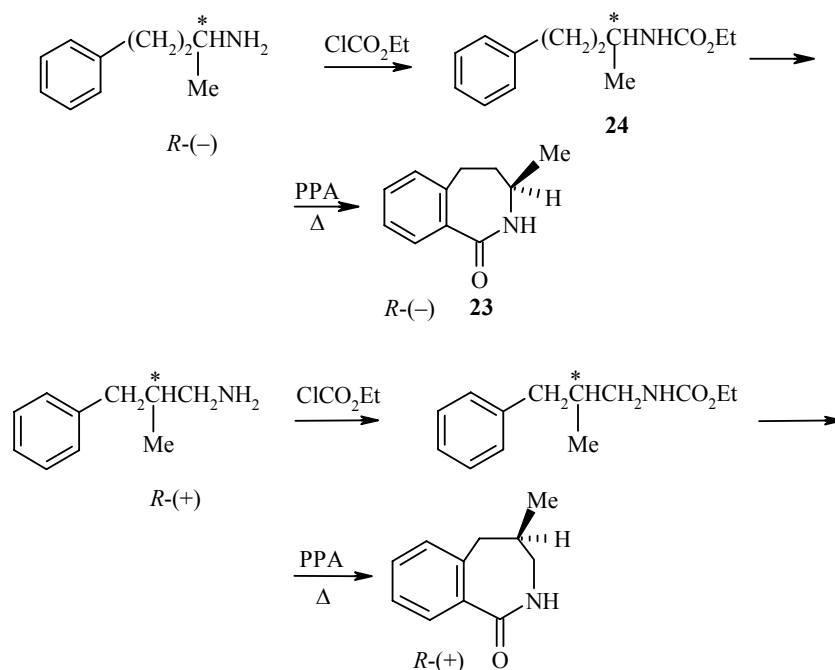
In the Laboratory methods were developed for the cleavage of a series of substituted phenylethylamines, which can be used for the synthesis of other tetrahydroisoquinolines. Thus, the natural alkaloid salsolidine was synthesized from 3,4-dimethoxy-substituted α -phenylethylamine [241].



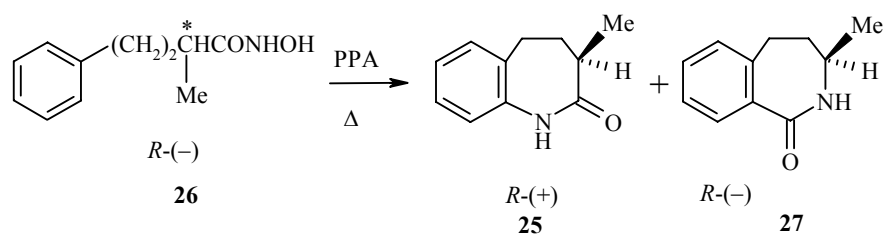
To study the correlations between structure and chiral optical characteristics a series of chiral benzolactams with various lactam ring sizes and with the asymmetric center at various positions were synthesized [242-249]. Six-membered benzolactams of the anilide and benzamide type were obtained by intramolecular amidation of the respective optically active hydroxamic acids [242, 243].



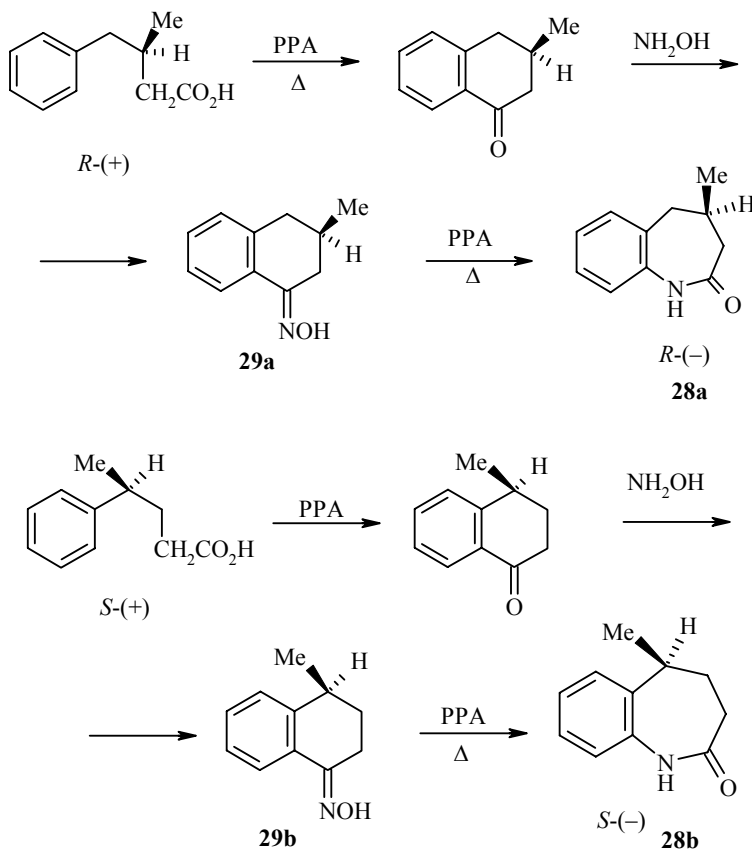
Various methods were used for the synthesis of optically active seven-membered benzolactams, depending on the position of the asymmetric center and the type of conjugation of the chromophoric system. Compounds of the benzamide type **23** were obtained by cyclization of the urethanes **24** of the respective optically active amines [244].



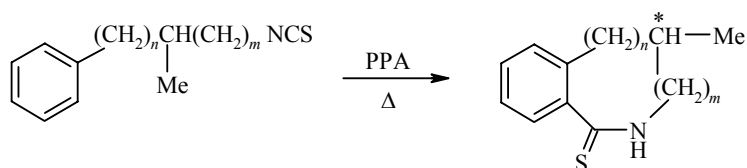
A benzolactam of the anilide type **25**, containing an asymmetric carbon atom at the α -position to the amide group, was obtained by intramolecular amidation of the optically active hydroxamic acid **26**, and the obtained mixture of isomeric lactams **25** and **27** was separated by chromatography on silica gel [243].



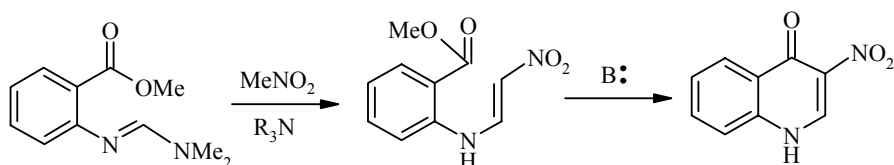
Benzolactams of the anilide type **28a,b**, containing an asymmetric carbon atom at the β - and γ -positions to the amides group, were obtained by Beckmann rearrangement of the oximes of the corresponding substituted tetralones **29a,b** (obtained from the optically active carboxylic acids) [244-246].



A series of chiral benzothiolactams were also synthesized by cyclization of the corresponding optically active isothiocyanates [247-249].

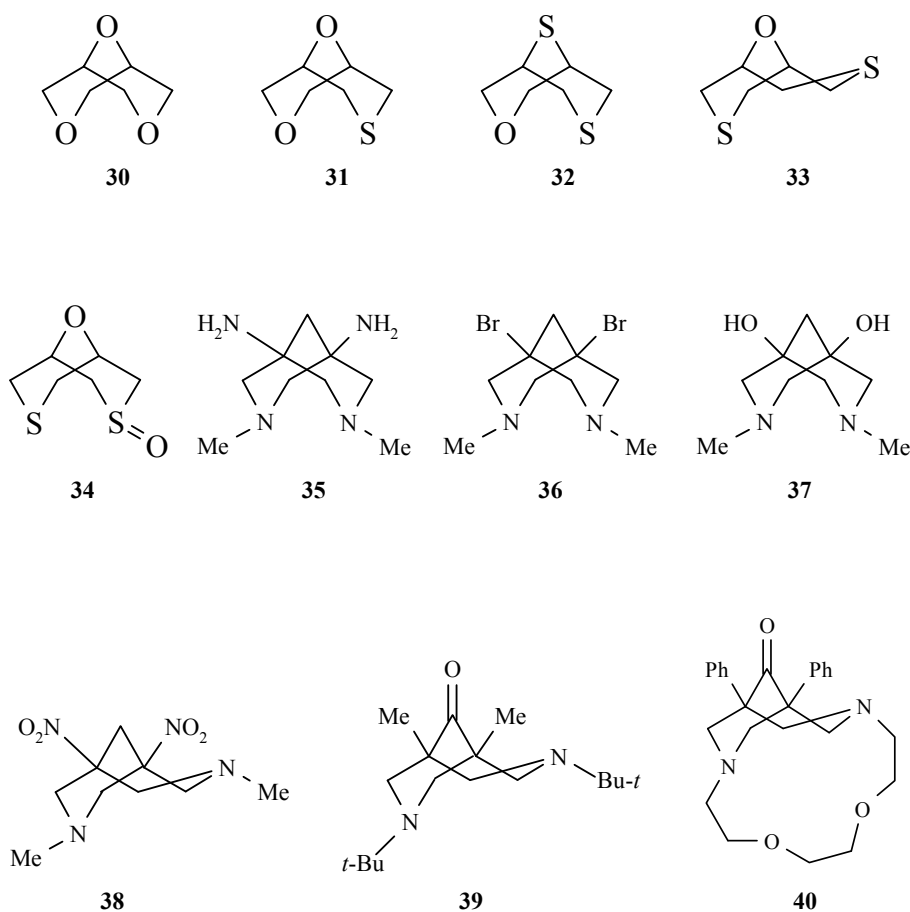


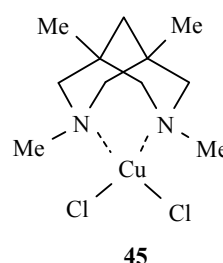
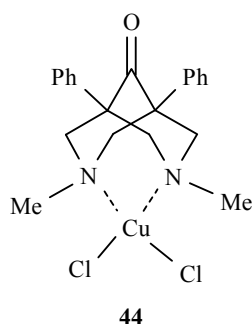
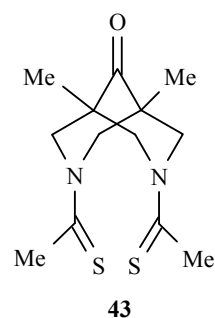
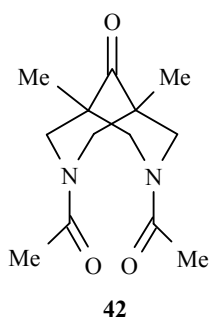
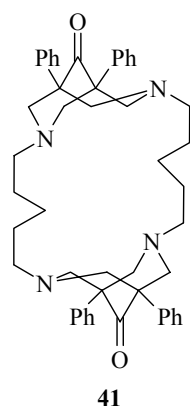
A new method for the construction of a quinoline ring by " β -insertion" of nitromethane was realized by E. V. Babaev [250-252]. Until recently there has been no such plan for the 5+1 assembly of a heterocycle in reviews and monographs on methods for the synthesis of a pyridine ring.



MACROHETEROCYCLES

For many years in the laboratory of N. S. Zefirov investigations were carried out on the synthesis and conformational analysis of the heteroanalogs of saturated bicyclic compounds, chiefly heterobicyclo[3.3.1]nonanes [253]. Investigation of the conformational behavior of a series of 3,7,9-triheterobicyclo[3.3.1]nonanes **30-33** (X-ray and NMR) [254-257] made it possible to discover the anomalous conformational behavior of compound **33**, where the *chair-boat* conformation predominates in contrast to compounds **30-32**. (For the "through bond" effect in this series of compounds, see [258]; the review [259] was devoted to the problem of conformational effects and, in particular, the "hockey stick" effect.) It is interesting to note that the corresponding sulfoxide **34** adopts the *chair-chair* conformation [257].





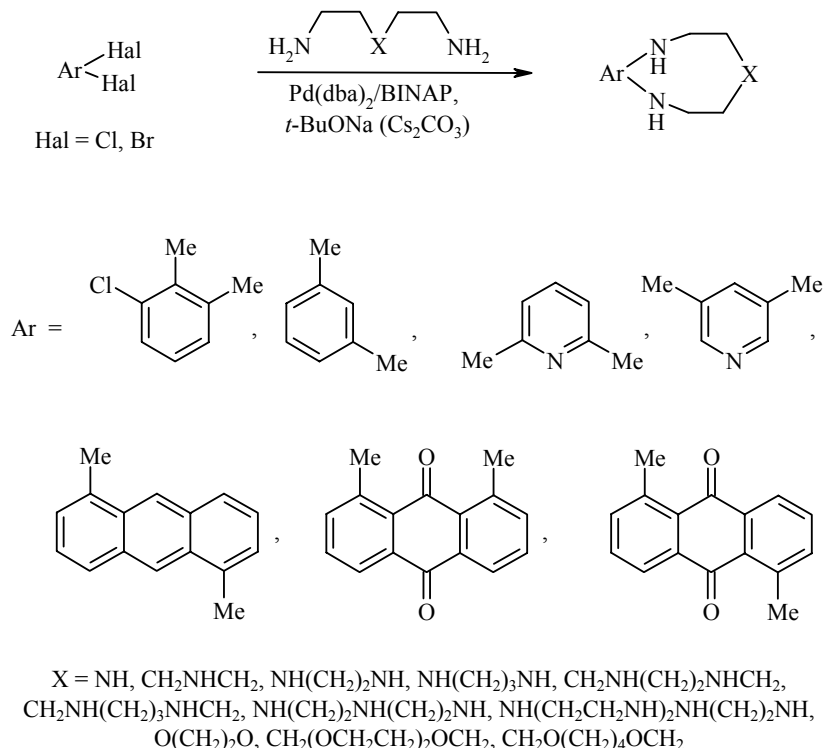
By further investigation it was possible to find a whole series of anomalies in the conformational behavior of 3,7-diazabicyclo[3.3.1]nonanes: The wholly expected *chair-chair* conformation is preferred for compounds **35-37** [260], whereas the presence of the nitro groups at positions 1,5 leads to the preferred *chair-boat* conformation for compound **38** [261]. The introduction of a carbonyl group at position 9 also leads to predominance of the *chair-boat* conformation (e.g., for compound **39**) [262], and the *chair-boat* conformation predominates even in cases where the bicyclo[3.3.1]nonan-9-one fragment is present in the tricyclic [263] and pentacyclic [264] structures **40** and **41**. If, however, the nitrogen atoms at positions 3 and 7 become amide or thioamide nitrogen atoms (compounds **42** and **43**) [265], the *chair-chair* conformation is more stable. Derivatives of 3,7-diazabicyclo[3.3.1]nonane and 3,7-diazabicyclo[3.3.1]nonan-9-one have good complexing characteristics, and here the bicyclo[3.3.1]nonane framework in the complexes always adopts the form of a double chair with the free electron pairs of the nitrogen atoms close (e.g., compounds **44** [266] and **45** [267]). The structure of all the above-mentioned compounds was confirmed by X-ray crystallographic analysis.

Beginning in 1999 investigations were also carried out at the Laboratory of Heteroorganic Compounds (I. P. Beletskaya and A. D. Averin) on the synthesis of nitrogen- and oxygen-containing macrocycles using palladium-catalyzed intramolecular diamination of diaryl halides. In this period methods were developed for the synthesis of macrocycles containing such aromatic fragments as benzene, anthracene, anthraquinone, and pyridine. Triamines, tetramines, pentamine, hexamine, and dioxa- and trioxadiazines were used as aminating agents [268-271] (Scheme 2).

In the course of these researches macrocycles containing several aromatic and polyamine fragments and having up to 60 atoms in the ring were also synthesized.

Phthalocyanines and their complexes have recently attracted the attention of many research workers on account of their clearly defined electrochromic and semiconducting characteristics and also their unique spectral characteristics, which open up new fields of application. Many of these characteristics show up particularly clearly in diphthalocyanines. In spite of the fairly large volume of papers in this region of the metal complexes of phthalocyanines, many aspects of this type of compound are insufficiently reliable and often contradictory.

Scheme 2



The principal task of L. G. Tomilova's group is the targeted synthesis of new symmetrically substituted compounds and study of their characteristics with the aim of establishing a "structure–property" relation. (The principal publications on the group's research are in [272-277].)

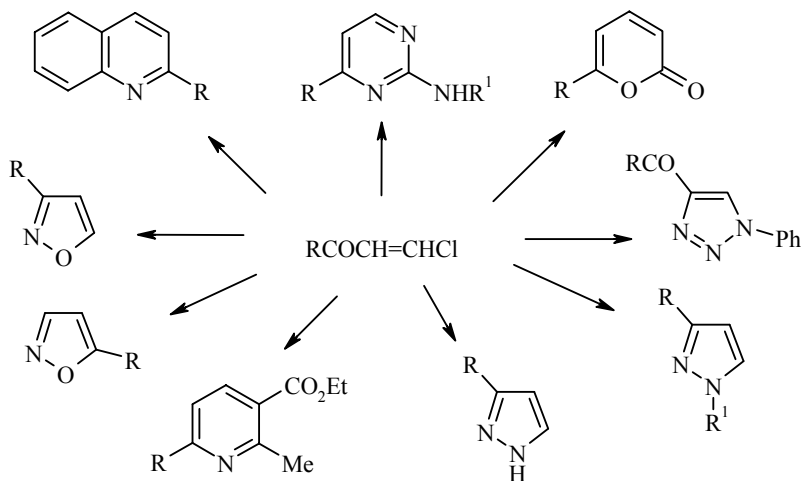
The targeted synthesis of new functionally substituted phthalocyanines and their related macrocyclic complexes of *d* and *f* elements was undertaken. Their structure was studied using X-ray crystallographic analysis, and the relationships between structure and catalytic characteristics in the transition from the planar to the sandwich-like and binuclear structures were established.

For this purpose new synthetic approaches were worked out for the production of various phthalocyanine complexes. For instance, with microwave radiation it is possible to simplify the synthesis considerably, reducing the time from several hours to a few minutes. This approach made it possible to synthesize for the first time phthalocyanines with sandwich structures with a high degree of purity and binuclear phthalocyanines with various structures.

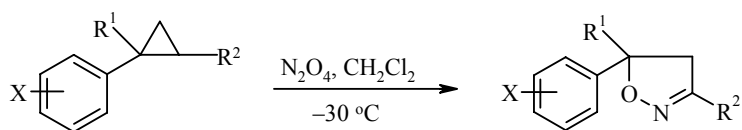
Recently this group showed that the mono- and diphtalocyanine complexes of certain transition and rare-earth metals can be used as catalysts for the reaction of carbon dioxide with epoxides, leading to the formation of cyclic alkylene carbonates. On the basis of the obtained binuclear complexes ion-selective electrodes were developed for the recognition and specific bonding of dicarboxylic acids, amino acids, and their esters. A method was proposed for the reduction of aromatic nitro compounds to the corresponding amines using phthalocyanine complexes as catalysts. The technology of a continuous catalytic method for the conversion of carbon dioxide into propylene carbonate was developed and prepared for practical utilization.

UNIVERSAL SYNTHONS FOR THE PRODUCTION OF VARIOUS TYPES OF HETEROCYCLES

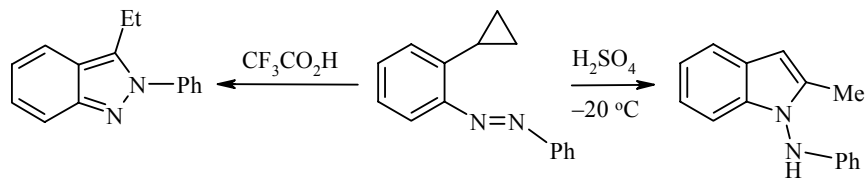
A general method for the synthesis of various five- and six-membered heterocyclic systems (pyrazole, triazole, pyridine, quinoline, pyrimidine, isoxazole, and others) was developed as far back as the fifties by A. N. Nesmeyanov and N. K. Kochetkov on the basis of alkyl and aryl β -chlorovinyl ketones – the products from the condensation of acetylene with acid chlorides in the presence of aluminum chloride [278-286].



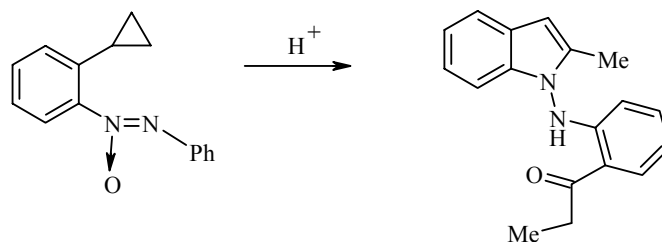
These traditions of creating universal synthons are still being developed in the Department to this day. Thus, one of the promising trends in the synthesis of nitrogen- and oxygen-containing heterocyclic compounds, which was first identified in the Laboratory of Organic Synthesis at the Department of Organic Chemistry (Yu. S. Shabarov, S. S. Mochalov, and A. N. Fedotov) in the seventies to eighties of the last century, involved both the use of the phenylcyclopropanes themselves as synthons and the acid- and base-catalyzed transformations of functionally *ortho*-substituted arylcyclopropanes and the products from their primary rearrangements and isomerizations. One of the paths for the production of heterocyclic compounds is direct single-stage synthesis from arylcyclopropanes [287-296]. Thus, the action of N_2O_4 on substituted arylcyclopropanes leads to the production of 5-arylisoxazolines [287, 288].



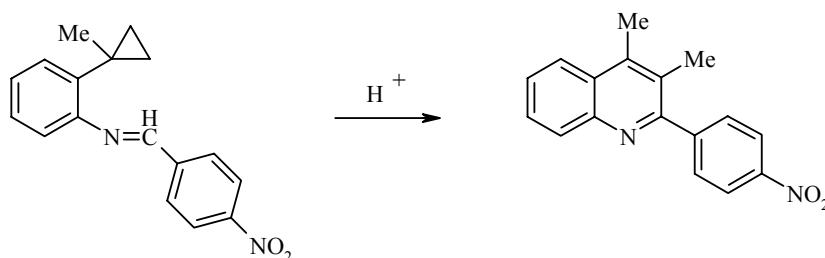
Depending on the employed acidic agent, *o*-cyclopropyl-substituted azobenzenes are capable of forming both N-phenylaminoindoles [289] and N-phenylindazoles [290, 291].



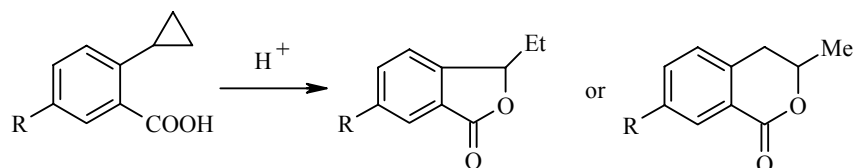
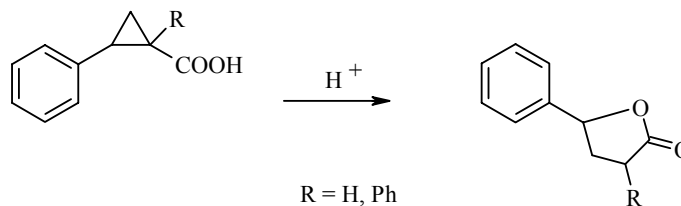
The use of alkoxy compounds based on the above-mentioned azobenzenes in this reaction leads to N-(*o*-acylphenyl)aminoindoles [289].



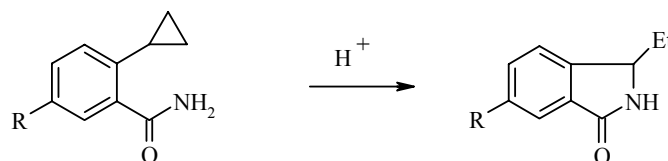
By acid-catalyzed cyclization of the benzylidene derivatives of *o*-cyclopropylaniline it is possible to produce a quinoline ring [292].

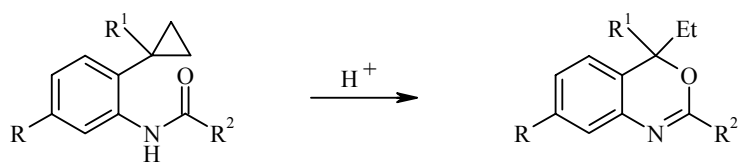


If phenylcyclopropylcarboxylic acids are used it is possible to produce a phenyl-substituted five-membered lactone ring [293], while the presence of a carboxyl group at the *ortho* position to the cyclopropane substituent makes it possible to annelate five- and six-membered rings to the benzene ring [294].

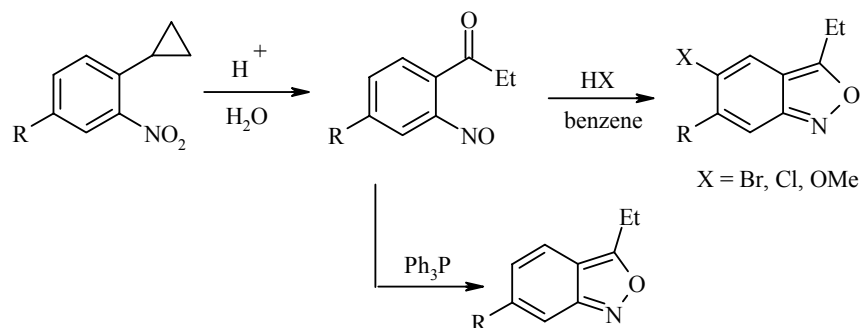


Replacement of the carboxyl group by carbamoyl leads to the formation of the respective lactams [295], and if there is an aminoacyl group in the *ortho* position derivatives of 1,3-benzoxazines are formed [296].

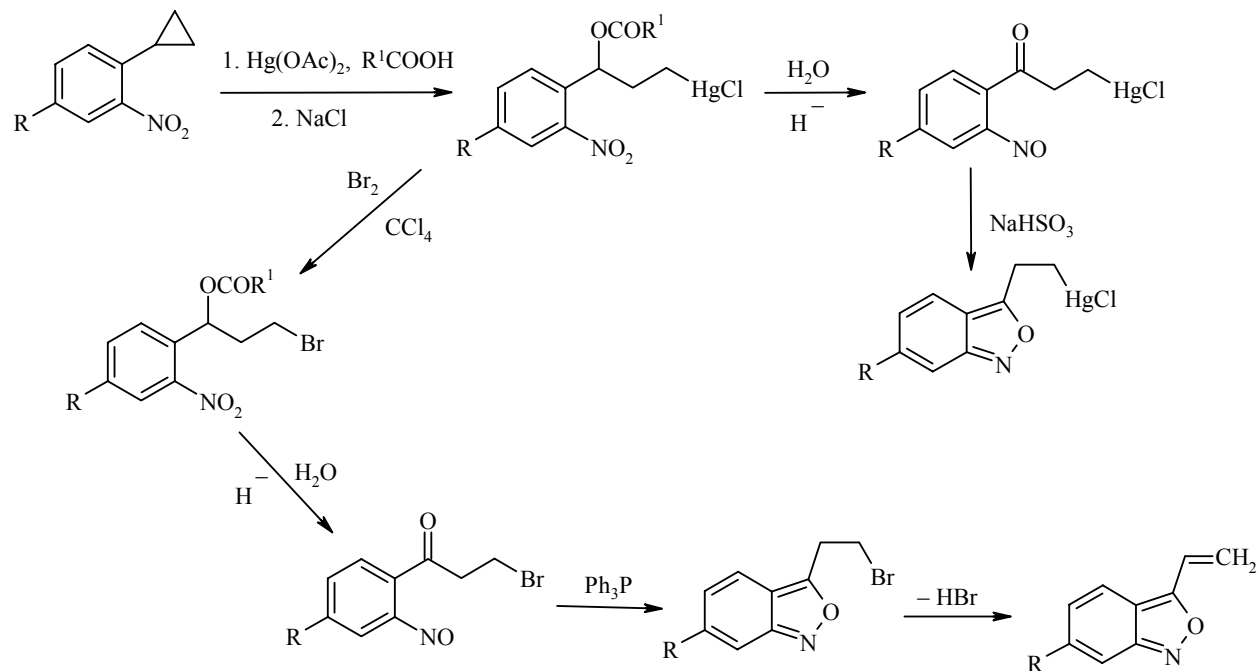




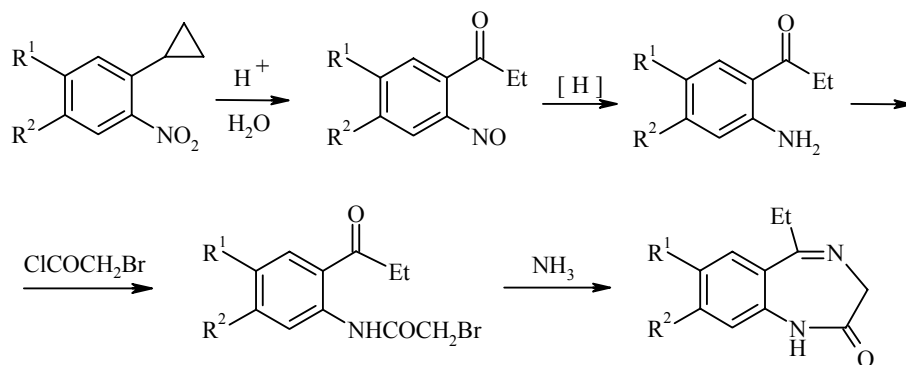
Another path to the formation of various heterocyclic systems involves the use of products from the primary transformations of functionally substituted arylcyclopropanes as substrates [297-310]. Such functionally substituted compounds include primarily *o*-nitrophenylcyclopropanes, the acid-catalyzed transformation of which to *o*-nitrosoacylbenzenes creates great possibilities for various heterocyclizations. For example, the use of HX [297-299] or triphenylphosphine [300] as cyclizing agent leads to the formation of benzisoxazoles. The X⁻ enters at the stage of stabilization of the benzenonium ion, formed during the formation of the heterocyclic ring.



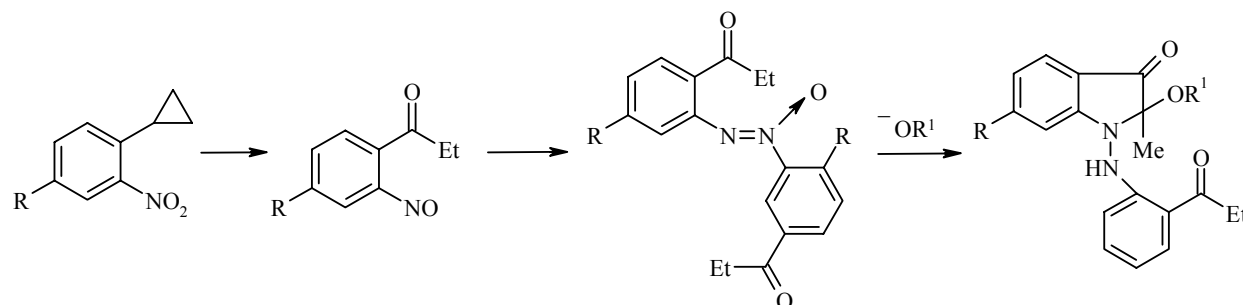
A different path to benzisoxazoles substituted in the benzene and five-membered rings involves prior opening of the cyclopropane by the action of mercury acetate and organic acids. This multistage transformation takes place according to the following scheme [303-306]:



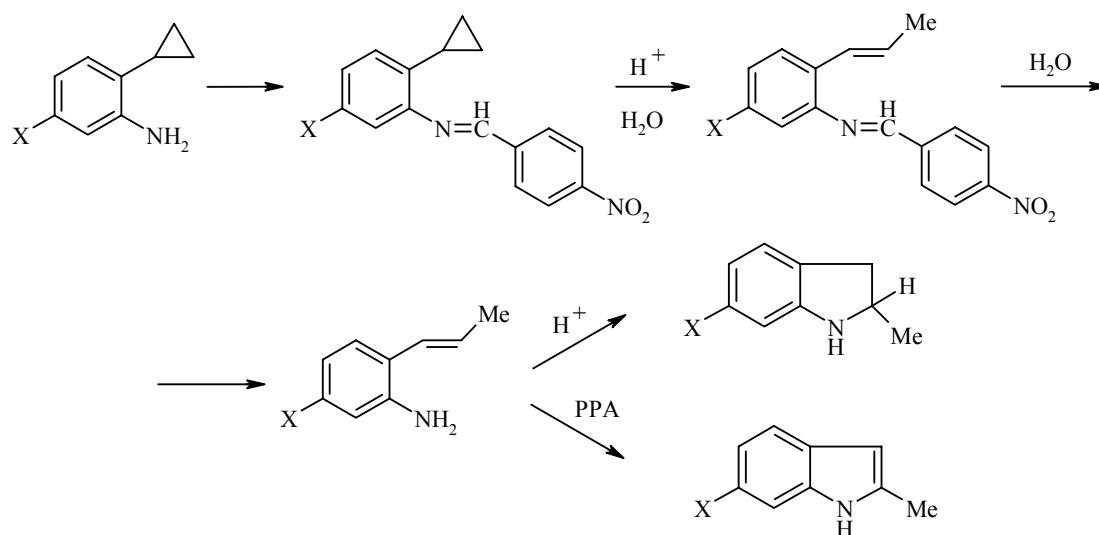
The successive reduction of *o*-acylnitrosobenzenes to the corresponding anilines, acylation with bromoacetyl chloride, and condensation with ammonia lead to the synthesis of derivatives of 1,4-benzodiazepin-2-ones [307-308].



The intramolecular cyclization of azoxybenzenes, synthesized from *o*-nitrosoacylbenzenes, by the action of alkoxide ions leads to the production of complex derivatives of indoxyl [309].

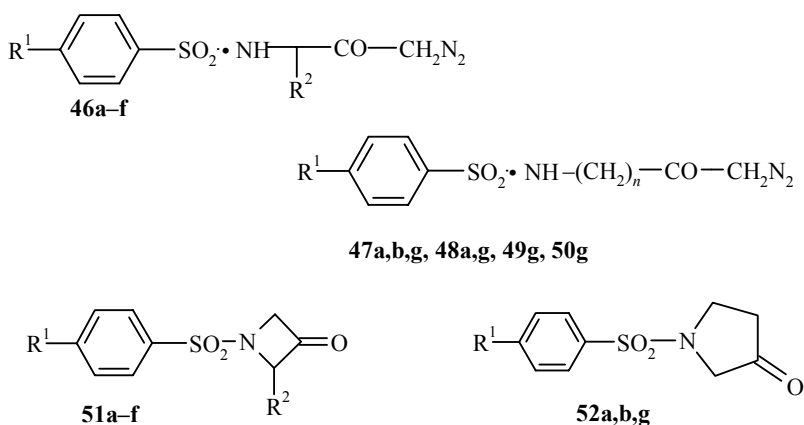


A series of successive transformations – introduction of *p*-nitrobenzylidene protection into *o*-cyclopropylanilines, cleavage of the cyclopropane substituent, removal of the protecting benzylidene group, and finally acid cyclization – leads (depending on the nature of the acid catalyst) to derivatives of 2-methylindole [311] or 2-methylindoline [310].



MASS-SPECTRAL MODELLING OF HETEROCYCLIZATION PROCESSES

In the Department at the beginning of the eighties (A. T. Lebedev and others) researches were started on the mass-spectrometric modelling of heterocyclization. Diazo ketones were the first type of compounds studied in this way. It was shown, for example, that α -diazo- ω -arylsulfonylaminoalkan-2-ones, reacting with acids, are transformed into heterocyclic systems. Similar processes were observed for the compounds in the gas phase. Tandem mass spectrometry with collision activation was used to obtain reliable evidence for cyclization of the molecular ions of α -diazo- ω -arylsulfonylaminoalkan-2-ones **46-50** under the conditions of electronic (EI) and chemical ionization (CI) to the corresponding N-substituted azetidin-3-ones and pyrrolidin-3-ones.

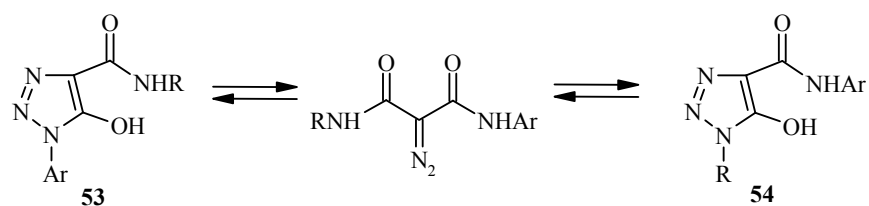


a $R^1 = R^2 = H$; **b** $R^1 = Me, R^2 = H$; $R^1 = OMe, R^2 = H$; **d** $R^1 = Cl, R^2 = H$; **e** $R^1 = R^2 = Me$;
f $R^1 = Me, R^2 = Et$; **g** $R^1 = Br$; **47** $n = 2$; **48** $n = 3$; **49** $n = 4$; **50** $n = 5$

It was shown that under the conditions of EI and CI α -diazo- ω -arylsulfonylaminoalkan-2-ones **46-50** undergo cyclization with elimination of a nitrogen molecule to the corresponding N-substituted azetidin-3-ones and pyrrolidin-3-ones much as occurs in solution during catalysis by acids. Heterocycles with ring sizes of more than six atoms are not formed. Cyclization of the diazo ketones **46-50** under the conditions of CI with ammonia takes place in the same way as in solution in the presence of sulfuric acid, and comparison of the quantitative characteristics showed that CI secures optimum conditions, compared with EI, for study of the processes in the acid-catalyzed cyclization of diazo ketones.

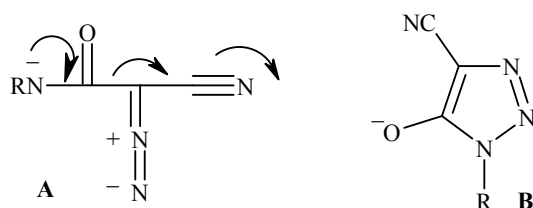
In the eighties a series of papers was published in Chemistry of Heterocyclic Compounds on cyclization leading to the formation of furans, oxazines, and thiazines. The accumulated material from the mass spectrometry of diazoketones under the conditions of electronic and chemical ionization demonstrated the similarity between the monomolecular reactions in the gas phase of the mass spectrometer and during acid-alkali catalysis in solutions. This made it possible to propose mass-spectrometric modelling for predicting the direction of the chemical reactions initiated by acids and bases. A series of heterocyclic systems were synthesized on the basis of the mass-spectrometric predictions. The advances made in this direction were summarized in the review [312].

The next type of compound studied in the course of mass-spectral modelling was diazoamides. In solutions these compounds can be transformed into the isomeric triazoles. For example, the isomeric 4-carboxamido-5-hydroxy-1,2,3-triazoles **53** and **54** easily change from one to the other in solution.



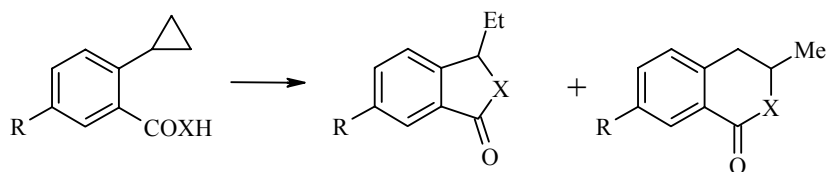
It was shown [313] also that 4-carboxamido-5-hydroxy-1,2,3-triazoles are transformed in the gas phase of the ion source in much the same way as in solution.

Negative-ion mass spectrometry with soft ionization was used to model the reaction conditions for the isomerization of 2-cyano-2-diazoacetamides to 4-cyano-5-hydroxy-1,2,3-triazoles by the action of alkalis. The aim of the investigation of the spectra of the deprotonated molecular ions (chemical ionization with ammonia) of 2-cyano-2-diazoacetamides (**A**) and 4-cyano-5-hydroxy-1,2,3-triazoles (**B**) was to determine whether their mutual transitions occur in the gas phase [314].



The investigations showed that the ions (**A**) undergo fragmentation, having previously isomerized to the 1,2,3-triazole ion (**B**), i.e., cyclization of the 2-cyano-2-diazoacetamides to the isomeric 4-cyano-5-hydroxy-1,2,3-triazoles occurs under the conditions of the mass-spectrometric experiment in the gas phase. Consequently, there is a direct analogy between the behavior of the deprotonated compounds (**A**) in the gas phase and their neutral precursors in the alkaline solution.

The *ortho*-substituted phenylcyclopropanes were interesting compounds for comparison of the intramolecular processes in the gas phase and in solution. For example, *o*-carboxy- and *o*-carboxamidocyclopropylbenzenes undergo cyclization under the action of sulfuric acid with the formation of a mixture of five- and six-membered heterocycles.



Unfortunately, the establishment of thermodynamic equilibrium was an extremely slow process. The amounts of the isomeric heterocycles only stopped changing 2-3 months after addition of the acid. The ratio of the isomers was determined by the nature of the heteroatom ($X = O, NH$) and the substituent R in the benzene ring. Mass spectrometry proved an extremely convenient fast method for predicting the yields of the isomeric heterocycles. The intensity ratios of the key peaks in the electron impact spectra of the cyclopropanes corresponded with an accuracy of 3-5% to the ratio of the isomeric products after the establishment of equilibrium in the solution [315].

Comparison of the mechanism of cyclization in the gas phase of the mass spectrometer and in the solution was continued on a large group of N -(*o*-cyclopropylaryl)acetamides, N -(*o*-cyclopropylphenyl)-benzamides, and N -[*o*-(1-methylcyclopropyl)phenyl]benzamides. Whereas cyclization of the former in the mass

spectrometer led to the formation of 1-ethyl-3-methyl-1H-benzoxazines, the cyclization of cyclopropylphenylbenzamides led to the formation of both 3-aryl-1-ethyl-1H-benzoxazines and 5-ethyl-2-oxobenzodiazepines. A methyl group at position 1 of the small ring prevents the formation of the latter, making only the formation of benzoxazines possible. On the basis of the mass-spectrometric data it was assumed that the analogous cyclization processes would occur with these compounds in solution during their reaction with sulfuric acid. The predictions were confirmed by chemical experiment. Both N-(*o*-cyclopropylphenyl)benzamides and N-[*o*-(1-methylcyclopropyl)phenyl]benzamides, reacting with sulfuric or trifluoroacetic acid, are converted into 3-aryl-1-ethyl-1H-benzoxazines with yields of 70-90%, whereas 5-ethyl-2-oxobenzodiazepines in trace quantities were only detected for N-(*o*-cyclopropylphenyl)benzamides [316].

Apart from these compounds the reactions of a series of ylides, substituted polyhalopyridines, heterocyclic tertiary amines, sultins, and other compounds in solution and in the mass spectrometer were also studied [317].

Thus, all the information presented above indicate that the chemistry of heterocyclic compounds has been successfully developed at the Department of Organic Chemistry in the Chemical Faculty of M. V. Lomonosov Moscow State University. Our department has always been and still remains one of the world's leading centers in the chemistry of heterocyclic compounds.

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