Scientific Heritage of Academician N. N. Vorozhtsov at the Present Stage of Research at the Novosibirsk Institute of Organic Chemistry of Siberian Branch of the Russian Academy of Sciences

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Abstract

Scientific Heritage of N. N. Vorozhtsov first of all includes the development of all the scientific directions outlined by him during establishment of the Institute. This review deals with the analysis of the major results obtained in these directions, mainly during the recent years. These works are connected with chemistry of aromatic and heterocyclic compounds, mechanisms of the reactions of nucleophilic and electrophilic substitution, perfluoroarene chemistry, chemistry of natural compounds, and synthesis of functional materials.

Key words: nucleophilic substitution, electrophilic substitution, metal complex catalysis, isomerization, 1,2-shift, carbocations, cation radicals, heterocyclic compounds, fluoroaromatic compounds, light-sensitive materials, dendrochemistry, biologically active compounds, stable nitroxide radicals

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INTRODUCTION

Creative work of Academician N. N. Vorozhtsov occupies a worthy position in the history of science in our country. It holds the greatness of Russian traditions in organic chemistry and enriches it with discovery and development of the new research areas.

The scientific interests of Academician N. N. Vorozhtsov, realized in his creative heritage, became the seed from which all the research directions of the scientific school founded by him had germinated and developed at the Novosibirsk Institute of Organic Chemistry.

Aromatic nucleophilic substitution attracted rapt attention of N. N. Vorozhtsov during the whole his creative life as one of the main tracks from basic arenes to their functional derivatives. The results obtained in this area were of prime importance for the formation of modern overview about the mechanism of metal complex catalysis in aromatic nucleophilic substitution. The entire set of regularities revealed by N. N. Vorozhtsov and his collaborators when investigating the reactions of nucleophilic substitution, and the relevant experimental approaches developed during the investigations had created a powerful potential for thorough advance in the chemistry of fluoroaromatic compounds.

The brightest page of the scientific creative work of N. N. Vorozhtsov is the extensive series of investigations carried out by him and his followers in the area of the chemistry of fluoroaromatic compounds, due to which N. N. Vorozhtsov went into the history of science as the founder of this scientific direction in our country.

Recognizing the importance of isomerization of aromatic compounds opening the possibilities of transition from the isomers primarily formed in the reactions of electrophilic substitution into less available ones, N. N. Vorozhtsov performed thorough investigation of the processes of isomerization of organic compounds. The works of N. N. Vorozhtsov and his co-workers on isomerization of aromatic compounds that comprised one of the principal directions of his research were dealing with revelation of the major laws and intimate mechanisms of the process of substituent migration.

One of the "side" results obtained by him together with his outstanding follower V. A. Koptyug became the starting point for the development of the scientific direction connected with the synthesis of imidazole derivatives and stable nitroxide radicals starting from α -hydroxylaminooxims.

The flora of Siberia is the richest source of biologically active compounds, due to which N. N. Vorozhtsov had laid the foundations for the powerful development of works on dendrochemistry and chemistry of natural biologically active compounds for the subsequent years.

N. N. considered the outcome in applied developments finding various applications in industry and agriculture as one of the most important goals and tasks for conducting fundamental research.

DEVELOPMENT OF THE METHODS OF FUNCTIONALIZATION OF AROMATIC COMPOUNDS

Reactions of nucleophilic substitution

One of the main aspects of research carried out by N. N. Vorozhtsov and his co-workers in the area of aromatic nucleophilic substitution was investigation of the mechanism of catalysis of these compounds by copper compounds, which had become the subject of his Doctoral dissertation [1]. He proved that the catalytic effect is due to the formation of the active intermediate complex, and proposed its structure providing coordination of copper cation with the halogen atom to be substituted. However, the alternative version of selective activation of the carbon-halogen bond was not excluded in this situation. Recently, within the framework of subsequent development of this fundamental result, for ammonolysis of polyfluorochlorobenzenes as an example, the assistance of electron-donating substituent - para-





Scheme 2.

amino group - to catalysis was discovered. This confirmed the relevance of N. N. Vorozhtsov's ideas concerning the nature of the active intermediate (Scheme 1) [2].

Within the framework of investigation into metal complex activation of substrates in aromatic nucleophilic substitution, alkoxydefluorination of aryl fluorides under the action of alcohols, catalysed by dication of pentaalkylcyclopentadienylrhodium, was thoroughly investigated. The mechanism involving *p*-coordination of the substrate with the catalyst, and the structure of the active catalytic complex were fully proven. The effect of this coordination was shown to be close to the effect of three *ortho/para* nitro groups in non-coordinated arene (Scheme 2) [3–7].

In the investigations of aromatic nucleophilic substitution, N. N. Vorozhtsov and his followers paid much attention to the problem of the effect of solvent. One of the last achieved results became establishment, for alkoxydefluorin aiton as example, of exclusively high activity of charged nucleophilic agents in liquid ammonia (Scheme 3), which is due to the aprotic nature of ammonia. The factors determining the competition between nucleophilic and protophilic attacks in the reactions of polyfluoroarenes were revealed, laboratory technologies of obtaining a number of important semi-products on the basis of the discovered effect were developed [8–10].

As long ago as in the 50es of the past century, N. N. Vorozhtsov had been successfully

NMR and kinetic investigation:

- Comprehensive confirmation of the mechanism.
- Establishment of the effect of coordination on the rate fo nucleophilic substitution of fluorine atoms.





developing the methods of nitroarene fictionalisation [11]; this direction further developed at the Institute. For example, during the recent years, the quantitative data on the selectivity of substitution of nitro group and fluorine atom in some *meta*-substituted arenes under the action of charged O- and Snucleophilic agents were obtained. It was established that a decrease in the basicity of a nucleophilic agent and temperature rise cause an increase in the rate of nitro group substitution in comparison with fluorine atom under the conditions of entropy control of the reaction (Scheme 4) [12, 13].

In the area of aromatic nucleophilic substitution, much attention had been paid during the last 40 years to the possibility of realization of arene reactions with nucleophilic agents according to the single electron transfer mechanism (SET mechanism). Recently, facts confirming the assumption that the mechanism of these reactions changes from S_N Ar to the nonchain SET (Scheme 5, routes c and b, respectively) were established. Thus, the possibility of



Scheme 3.



Scheme 6.

he realization of SET mechanism is evidenced by the obtained correlation (see Scheme 5, Eq. 1 and the diagram) between Bronsted coefficient (Eq. (2)) and the coefficient of reaction rate dependence on the potential of nucleophil oxidation $E_{\rm ox}$ (Eq. (3)). So, it is evident that the potential of nucleophil oxidation is connected with the internal barrier of the reaction [14].

Generation and reactions of anion intermediates

N. N. Vorozhtsov started the investigation of aromatic nucleophilic substitution, the logical continuation of which became the studies of the nature, structure and reactivity of anion intermediates formed during these processes. As time was going by, these studies formed a separate area: investigation of the mechanistic and synthetic aspects of the reductive activation of functionalised arenes. One of the most recent results is the development of reductive condensation of aromatic nitriles and synthesis of polycyanodiaryls that are practically important but difficultly accessible using other routes (Scheme 6) [15–17].

Isomerization of aromatic compounds

At that time, industrial organic chemistry had been far from what we call now green chemistry, so N. N. Vorozhtsov paid much attention to the investigation of isomerization of the compounds of aromatic series. For instance, together with V. A. Koptyug who had been postgraduate student at that time, for isomerization of α -methyl- and α -chloron aphthalenes as examples, N. N. Vorozhtsov established with the help of radiotracer method that these processes follow the intermolecular route [18, 19]. The stage of 1,2-shift of the migrating group in carbocation intermediates - arenonium ions plays the key role in these processes. Indubitable achievement of N. N. Vorozhtsov is recognition of the fact that the characteristics of degenerate processes are very important for the description of the reactions of this kind. The problem of revealing these characteristics was successfully solved by the outstanding scientist V. A. Koptyug and his co-workers. They succeeded in performing the multistage synthesis of toluene selectively labeled with the radioactive carbon isotope ¹⁴C and demonstrated that degenerate isomerization actually occurs and proceeds, similarly to non-degenerate processes (Scheme 7, upper row) through intermolecular 1,2-shifts of the methyl group [20].

In order to get a thorough insight into isomerization processes and develop approaches to control them, it was necessary to reveal the regularities of the key stage: 1,2-shift in carbocation intermediates (Scheme 8). Using the physical methods, first of all nuclear magnetic resonance, the scientific school of V. A. Koptyug accumulated a large amount of experimental



Scheme 8



Scheme 9

data on the rates of degenerate rearrangements of "long-living" carbocations that serve as the model of carbocation intermediates [21]. The obtained kinetic data were compared with the results of quantum chemical calculations and thus received theoretical verification. It is appropriate to mention here that N. N. Vorozhtsov paved the way for the application of physical methods: he paid special attention to this aspect when organizing research at the Institute.

In the course of this direction, the authors of one of the recent works [22] dealing with the studies of the mechanism of electrophilic fluorination of aromatic compounds with NF reagents stated that the reaction of deuterated benzene with 1-fluoro-4-chloromethyl-1,4-diazoniuabicyclo[2.2.2]-octane bistetrafluoroborate (F-TEDA-BF₄) is accompanied by isomerization *via* 1,2-shifts of hydrogen or deuterium atoms (Scheme 9). This confirms the formation of arenonium intermediates during fluorination of benzene.

Along with the reactions involving isomerization of aromatic compounds, essential synthetic potential belongs also to the reactions of carbocation cyclization that are used in industrial processes. An example may be the production of anthraquinone and 2chloroanthraquinone (Scheme 10) [23]. The conventional process is characterized by very large amount of acid liquid wastes (up to 20 t/t of target product). In our institute, the process of obtaining anthraquinone and its 2-Xsubstituted derivatives was developed; instead



Scheme 10.

of liquid acids, it involves activated clay, which has improved the ecological characteristics of the process substantially [24].

Synthesis and reactivity of organofluoric compounds

N. N. Vorozhtsov was founder of the chemistry of fluorinated aromatic compounds in our country. Under his supervision, the reaction of hexachlorobenzene with potassium fluoride without using any solvent was carried out in our institute in 1963; the major products of this reaction were hexafluorobenzene and chloropentafluorobenzene (Scheme 11) [25, 26]. Decafluorodiphenyl, octafluoronaphthalene [27], decafluoropyrene [28], difluoroanhydrides of tetrafluorophthalic [29] and tetrafluoroterephthalic acids [30, 31] were successfully obtained using a similar route. An access to the synthesis of basic perfluoroarenes allowed the fundamental research of this interesting but relatively poorly investigated (at that time) class



Scheme 11.

of compounds to be launched in our institute and in our country. The 1,3,5-isomer that is extremely valuable for further synthesis may be successfully isolated from the mixture of isomeric trifluorotrichlorobenzenes formed in this reaction (see Scheme 11) [32].

Another important problem was the search for ways of the application of the mixture of isomeric dichlorotetrafluorobenzenes for which no use could be found for a long time. It was shown recently that isomeric mercapto derivatives are formed under the action of KSH on this mixture (Scheme 12) [33]. Their subsequent chlorination resulting in the replacement of mercapto group for chlorine leads to the formation of individual and not less valuable 1,2,4trifluorotrichlorobenzene with the 90 % yield.

A method of obtaining chlorin ated and brominated polyfluoroaromatic compounds through co-pyrolysis of polyfluoroarenethiols, polyfluorohetarenethiols with chlorine or bromine in a flow system has been developed recently. This method was successfully used to transform the corresponding polyfluoroarenethiols into chloro- and bromopentafluorobenzenes, *para*-substituted chlorine- and bromine-containing tetrafluorobenzenes, heptafluorotoluenes, 2,4-bis-(trifluoromethyl)- and 2,5-bis(trifluoromethyl)chlorobenzenes and the corresponding bromobenzenes (Scheme 13) [34, 35].

Together with German scientists, a new method has been recently developed to obtain perfluoroaromatic organozinc compounds from perfluoroarenes under the action of zinc in the presence of tin chloride in dimethylformamide (Scheme 14) [36]. This result opens the possibilities for extensive investigation of the chemical properties of these reagents and for their use in synthesis.



Scheme 12.

 $\label{eq:ar_FSH} \begin{array}{c} \mathrm{Ar_FSH}_{\frac{\mathrm{Hal}_2}{400-500~^{\circ}\mathrm{C}}} & \mathrm{Ar_FHal} \\ \mathrm{Hal} = \mathrm{Cl}, \ \mathrm{Br} \end{array}$

Yield of target products: Cl (84–95 %), Br (68–91 %) Purity of reaction products 96–99 %



Scheme 13.



Scheme 14.

Highly reactive and easily accessible polyfluorinated 2,4-cyclohexadienones, for which the methods of synthesis were developed in our institute, turned out to be promising with respect to the synthesis potential. One of the characteristic reactions of these compounds is cycloaddition. Due to the high regio- and stereoselective interaction with acetylenes and the possibility of further modification and splitting of cycloadducts, these compounds may become the basis for obtaining fluorinated arylacetic acids. The use of olefins as dienophils allows one to obtain fluorinecontaining cyclohexene- and anthraquinone carboxylic acids, while their interaction with diazoalkanes results in the formation of cyclopropanoic derivatives (Scheme 15) [37-62]. At the juncture of the directions connected with the investigation of cationoid reactions and polyfluorinated aromatic compounds, we observed the rise and intense development of the investigation of long-lived polyfluorinatedarenonium and aryl methyl (in a broad sense) cations and cation-radicals that may be generated from polyfluoroarenes using different methods (Scheme 16) [63–65].

The regularities of cationoid skeleton rearrangements of perfluorinated benzocycloalkenes and their carbonyl derivatives are under intense investigation during the recent years. These reactions may result in cycle broadening, in the transformation of carbonyl groups into difluoromethylene groups with the



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formation of the corresponding perfluoroaromatic compounds, isomerization of fluorinated indanedions into 3-methylenephthalides, and isomerization into isochromenones (Scheme 17) [66–68].

N. N. Vorozhtsov paid much attention to the development of methods for obtaining fluorinecontaining heterocyclic compounds. As a matter of fact, thus he united research in the area of polyfluoroaromatic compounds with his longstanding interest to heterocyclic compounds springing from his graduate work carried out by him under the supervision of A. E. Chichibabin. Further development of this direction by the followers of N. N. Vorozhtsov showed that the reactions of polyfluoroaromatic compounds containing the reactive imidoylchloride group -N=CCl with arenes in the presence of $AlCl_3$ opens the new possibilities for the synthesis of fluorinated five- and six-membered N-heterocyclic derivatives (Scheme 18) [69].

On the basis of aminoiminohexafluorindenes the synthesis of polyfluorinated 1,3-diazafluorenes, their di- and tetrahydro derivatives was carried out for the first time. In addition, the first representatives of formerly unknown polyfluoro-2-thia-1,3-diazafluorenes were obtained (Scheme 19) [70-72].

Within the framework of polyfluoroaroamtic direction, the processes of selective hydrodehalogenation of polyfluoroarenes based on reductive activation have been under intense investigation during the recent years. These processes allow one to follow a short route to obtain incompletely fluorinated arenes that are difficultly available but important for fine organic synthesis. One of the newest results achieved in this direction is the discovery of the possibility of selective *ortho*-defluorination of the acetyl derivatives of polyfluoroarylamines (Scheme 20) [73–76]. This result opens an unexampled short way to previously poorly studied polyfluorobenzoazaheterocycles.

SYNTHESIS AND PROPERTIES OF HETEROCYCLIC COMPOUNDS

Methods of the synthesis of various functional derivatives of six-membered nitrogencontaining heterocycles including pyrimidine



Scheme 17.



Scheme 18.





Scheme 19.



Scheme 20.

were under development for many years at Novosibirsk Institute of Organic Chemistry under the supervision of another outstanding follower of N. N. Vorozhtsov, Corresponding Member of the Academy of Sciences V. P. Mamaev. During the recent years, Mamaev's followers synthesized for the first time a number of diaryl-substituted 5-nitrodihydropyrimidinones that exhibited high antiarhythmic activity exceeding the activity of known antiarhythmics (Scheme 21) [77-80]. The synthesized compounds are evident candidates for advanced biotesting and subsequent introduction into practical medicine. Original synthesis methods were developed for various functional derivatives of pyrimido[4,5-b]indole that are of interest as potential antiasthmatics, neuro- and hepatoprotecting means [81, 82].

At present, the scientific foundations of the new section in the area of heterocyclic compounds are laid: chemistry of 12π -electron formally antiaromatic 1,3,2,4-benzodithiadiazines. The methods of synthesis were developed; molecular structure was studied in the gas phase and in the crystal state. For these compounds, the structural dichotomy was discovered (the heterocycle may be either plain or bent), the features of π -electron structure were established. The heteroatomic reactivity of 1,3,2,4benzodithiadiazines was investigated; as a result, new chemical reactions were proposed (Scheme 22) [83].

Investigating the properties of α -halogenated ketone – tetralone derivative – with nucleophilic reagents, N. N. Vorozhtsov and his followers discovered that this compound is easily transformed into α -hydroxylaminooxime (Scheme 23) [84]. This fact became a stimulus for intense and fruitful development of the chemistry of previously uninvestigated compounds of this type [85–93].

On their basis, synthesis methods were developed for a broad range of various heterocyclic compounds many of which had been in accessible before that (Scheme 24). The broad development of works on the synthesis and application of stable imidazoline nitroxide radicals should be mentioned specially; these compounds today comprise a separate and intensively developing area of investigation [94–97].

Development of the chemistry of α -aminooximes in the series of the derivatives of natural terpenoids allowed one to perform the synthesis of polyheteroatomic macrocyclic



Scheme 21.



Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

structures and chiral nanocycles that are of interest for use as optically active ligands for coordination chemistry and enantioselective molecular recognition (Scheme 25) [98-100].

CHEMISTRY OF NATURAL COMPOUNDS

The flora of Siberia is the richest source of biologically active compounds. In this connection, when organizing NIOCh, N. N. Vorozhtsov paid much attention to setting and development of research in the area of dendrochemistry. Now this research area is considered as the direction of special importance at our institute. As a result of the systematic investigation of turpentine and extractives of terpene series from coniferous trees, a scheme of low-waste integrated processing of all the valuable turpentine components was developed (Scheme 26) and highly efficient preparations for agriculture and cosmetic industry were obtained [101–104].

Methods of isolation of the compounds shown in Scheme 27 have been well developed by present, which made them readily available. Due to this, many compounds extracted from plants were subjected to chemical transformation for the purpose of changing or enhancing their biological activity [105].

For instance, alkaloid lappaconitine (Scheme 28), the active component of the antiarhythmic preparation allapinin – is today manufactured at the experimental works of NIOCh, SB RAS.

New transformations of labdanum diterpenoid – lambertianic acid – were discovered, leading to the formation of the corresponding heterocyclic derivatives that are analogues of





Scheme 29.

natural antitumour, antiviral and antimicrobial agents (Scheme 29) [106–108].

SYNTHESIS OF LIGHT-SENSITIVE MATERIALS

Another very important direction set by N. N. Vorozhtsov and oriented at a broad range of applications (for example, as light-sensitive materials) is the synthesis of dyes based on naphtha- and anthraquinones (Scheme 30). As a result of these investigations, the synthesis of photoresists for the production of circuit boards was carried out [109–113].

Recently, the works on the synthesis of thioflavilium IR dyes (Scheme 31) with different absorption wavelengths were developing; these dyes found application in manufacturing thin films for optical discs [114, 115].

Another type of dyes – quinocyanines – was used to obtain J-aggregates in thin films.



[O]	Yield, %
K ₃ Fe(CN) ₆	38 - 85
$\rm FeCl_3$	11
$(\mathrm{NH}_4)_2\mathrm{Ce}(\mathrm{NO}_3)_6$	11
$(NH_4)_2S_2O_8$	10
HIO_3	41 - 93

But

But



Ålk'

Scheme 32.

Alk

 I^-

To order aggregation and structure, long alkyl substituents were introduced into the structure (Scheme 32) [116, 117].

One more direction connected with the synthesis and application of dyes is holographic photopolymer materials [118–120]. At present, these developments are passing the stage of technological workup for the goal of coming to the industrial level.

SYNTHESIS OF HIGHLY EFFICIENT POST-METALLOCENE CATALYSTS OF OLEFIN POLYMERISATION

Another example of the development directed at the industrial application may be the synthesis of highly efficient postmetallocene catalysts of olefin polymerisation. Systematic investigations aimed at the development of new catalysts showed the promising character of structural modification of known catalysts of olefin polymerisation based on bis(arylimino)acenaphthene complexes of nickel. Due to this structural modification that involves the introduction of cycloaliphatic substituents into the *ortho*-position of the aryl ring bound to the imine group, the obtained catalysts exhibit high activity at temperatures 70-90 °C. So, the possibility to broaden the temperature range of efficient use of catalysts based on these complexes for obtaining polyolefins with high molecular mass was demonstrated (Scheme 33) [121–129].

A group of new complexes of ferrous chloride with oligomeric bis(imino)pyridine ligands



Scheme 33.

Multifunctional complexes



Scheme 34.



Scheme 35.

containing cyclopentyl and cyclohexyl substituents in the *ortho*-position of the phenyl ring was synthesized (Scheme 34) [130].

It was discovered that the multifunctional complexes differ substantially from their monofunctional analogues. For instance, oligomeric complexes of ferrous chloride are characterized by higher efficiency, which allows one to decrease the concentration of the catalyst used. The activity of polyfunctional catalytic systems remains almost constant with an increase in polymerisation temperature to 90 °C. At the same time, the activity of the catalytic system based on oligomeric complexes increases with an increase in polymerisation temperature from 30 to 90 °C (taking into account a decrease in the solubility of ethylene with temperature rise). A very important advantage of the new catalysts is also not so sharp decrease of molecular mass of polyethylene with an increase in process temperature to 90 °C. The molecular mass of resulting polyethylene is almost the same at 50 and 70 °C; only with temperature rise from 80 to 90 °C it decreases to 20 000-14 000.

A method of synthesis of the new complexes of titanium chlorides was developed; it is based on the interaction of $Ti(O^{i}Pr)_{2}Cl_{2}$ with phenoxyimine ligands. The latter are characterized by different combinations of bulky substituents and are formed in the interaction of the corresponding 3,5-disubstituted salicylic aldehydes with various primary amines (Scheme 35) [131–133].

The features of ethylene polymerisation within temperature range 30-70 °C were investigated using the catalytic systems based on the synthesized complexes activated with methylalumoxane; the regularities of the effect of ligand structure on the catalytic activity of the complexes and on the properties of the formed polymer were established. Polyethylene samples obtained in the presence of the studied catalysts possess linear structure and high crystallinity.

CONCLUSION

Thus, all the directions set by N. N. Vorozhtsov when organizing the Institute were successfully continued and became the welldeserved contribution into the development of both the fundamental research in organic chemistry and applied achievements that are used in industry and agriculture.

Acknowledgements

The author thanks V. D. Shteingarts, V. G. Shubin, V. M. Vlasov, L. S. Kobrina, T. D. Petrova, A. V. Tkachev, O. P. Shkurko, A. V. Zibarev, A. Ya. Tikhonov, V. V. Shelkovnikov and I. I. Oleinik for participation in the present work.

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