Nagorskaya, and others studied for the first time the equilibrium diagram of the Al–Be–Mg system, and also investigated the nature of crystallisation in beryllium-rich alloys of various systems (Be–Nb and Be–Re).

A series of important studies has been carried out by A. F. Kapustinskii on the dependence of the energetics of chemical reactions on the positions of the elements in the Periodic System. He made a systematic survey of the thermodynamic properties of the sulphides of various metals, and put forward a convenient simplified equation for calculating crystal lattice energy as a function of the valencies and radii of the ions forming it.

A valuable contribution to the thermodynamics of inorganic compounds, particularly the halides and oxides of the rare elements, was made by the work of S. A. Shchukarev.

The theoretical principles of chemical bonding in inorganic compounds has been developed by Ya. K. Syrkin and M. E. Dyatkina. A theory of directed valencies and a theory of the valency states of atoms in molecules have been developed, and the interactions of atoms with electrons have been studied from the viewpoint of quantum mechanics. Systematic studies of the valency states of both transition and non-transition elements have made it possible to reach a number of conclusions of importance for inorganic chemistry. In particular, the electronic structure of the tetrahedral oxoanions of the transition metals has been studied. Quantum-chemical calculations of the energies of inorganic compounds have made it possible to make predictions regarding the covalent character of the bonding in crystals; this is extremely significant for an understanding of the semiconducting properties of various inorganic substances.

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In the fifty years for which the Soviet State has been in existence, inorganic chemistry has grown in the Soviet Union, together with the whole of chemical science. As can be seen from this necessarily brief review, considerable progress has been made in many important fields of the development of modern inorganic chemistry. However, the great task which stands before us—the construction of communism by the first workers' state in the world—is increasing to an even greater extent the need for the extensive utilisation of science as a direct productive force in society. The potential possibilities provided by inorganic chemistry in this respect are unusually great: inorganic polymers, laser crystals, refractory and super-hard materials, materials for superconductivity, and many other valuable materials can be provided only by inorganic chemistry.

Our country's anniversary is inspiring Soviet inorganic chemists to new scientific efforts and achievements!

U. D. C. 547

SOVIET ORGANIC CHEMISTRY AFTER 50 YEARS

N. S. Zefirov

Russian organic chemistry long ago won an honourable place in world science. The names of A. M. Butlerov, V. V. Markovnikov, N. N. Zinin, E. E. Vagner, and N. N. Men'shutkin have acquired a wide repute. Russia had strong chemical schools; in this connection special mention must be made of the Kazan' chemical school, which has produced a great number of brilliant organic chemists, to whom world science must be obliged for the greatest scientific achievements.

Despite this, it has fallen to the Soviet land after half a century to make the most grandiose work on the development of chemical science and industry. Before the revolution chemical science had developed only in individual scientific centres and the number of chemists with higher education amounted to not much more than 1000; the organic chemical industry was practically non-existent.

Fifty years later a powerful chemical industry has been created in our country. In the USSR a series of new means of production—coal tar chemicals, aniline dyes, petrochemical, chemico-pharmaceutical, etc.—have been set up where there was literally an empty place. This enormous construction required great forces in assimilating even the experience gained abroad. In addition our country developed novel solutions for various problems in the construction of a chemical industry. The clearest example is the organisation of the production of synthetic rubber, which was the first in the world.

The rapid development of the organic chemical industry in the USSR was based on the experience and traditions of Russian, and then Soviet, organic chemistry. On the other hand, with the development of the chemical industry, organic chemistry obtained a new firm foundation. After years of Soviet power, having opened wide the doors of educational establishments, there grew up in our land an enormous army of organic chemists. A marked extension of the "geography" of organic chemistry resulted—in addition to Moscow, Leningrad, Kazan', Kiev, Tomsk, Khar'kov, Odessa, and Riga, there are now large scientific centres at Gor'kii, Kuibyshev, Novosibirsk, Irkutsk, Vladivostok, Erevan, Tbilisi, Baku, Tashkent, etc.

It is impossible to list all who took part in this. We will only note that during the years of Soviet power new scientific schools have developed which are of worldwide repute and which determine the development of individual branches of organic chemistry not only in our own country but throughout the world. In this connection mention must be made of the school of N. D. Zelinskii, who tackled many problems of the chemistry of hydrocarbons and organic catalysis; the school of A. E. Favorskii and S. V. Lebedeva, who developed the chemistry of unsaturated aliphatic compounds; the school of A. E. Chichibabin, celebrated for their investigations in the field of heterocyclic compounds; the school of A. N. Nesmayanov, who worked at large classes of organoelemental compounds and moulded this division of organic chemistry into an independent field; the school of A. E. Arbuzov, whose studies in the field of the chemistry of organophosphorus compounds are well known.

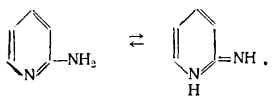
The basis of organic chemistry, as for any other science, are its theoretical concepts. Russian chemists have always paid special attention to the fundamental rules. It is sufficient to name A. M. Butlerov, who created the structural theory, V. V. Markovnikov, well-known for the principal investigations into problems of the mutual interaction of atoms in a molecule, N. N. Menshutkin former pioneer of the use of kinetic methods of investigation in organic chemistry. This tradition lives on today.

A distinguishing feature of modern organic chemistry is the wide use of methods of mixed sciences—physics and biology. Undoubtedly the achievements of Soviet chemists

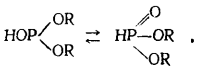
in the fields of physical chemistry, the chemistry of polymers, and chemical physics have significantly enriched organic chemistry both as regards understanding the significance of chemical changes and also from the methodological point of view. An examination of this question goes beyond the bounds of the present review; however, in this connection mention must be made of the development of the kinetics and theory of chain processes in the studies of N. N. Semenov and his school, the works of V. A. Kargin, V. V. Korshak, S. S. Medvedev, B. A. Dolgoplosk, N. S. Enikolopyan, G. L. Slonimskii in the field of polymer chemistry; the work of V. V. Voevodskii and P. A. Blyumenfel'd on the use of the EPR method; the quantum-mechanical studies of Ya. K. Syrkin, M. E. Dyatkina and others; work on X-ray structural analysis by A. I. Kitaigorodskii and others; M. G. Gonikberg and B. S. El'yanov's studies of reactions at high and superhigh pressures; the electrochemical work of A. N. Frumkin and his school; studies in the field of photochemical processes made by A. N. Terenin; and those of S. G. Mairanovskii in the field of polarography.

A. N. Bakh's work on oxidation in biological systems, the biochemical studies of I. E. Severin, A. N. Belozerskii, and A. S. Spirin, and the work of M. M. Dubinin and I. A. Rappoport on chemical mutagens are of great importance.

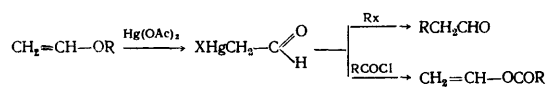
Soviet organic chemistry has great fundamental achievements in various fields of theoretical organic chemistry connected with the study of tautomerism and dual reactivity, the mechanisms of organic reactions, skeleton rearrangements, stereochemistry, etc. As is well known, the phenomenon of tautomerism—equilibrium isomerism—was first considered by A. M. Butlerov. The work on the problem of tautomerism and the closely connected problems of dual reactivity began more than a century ago and is still continuing. Soviet chemists have paid great attention to this problem. Thus Chichibabin discovered the tautomerism of 2-aminopyridine [1]:



A. E. Arbuzov studied an interesting new form of tautomerism by the example of dialkyl phosphites [2,3]:



The work of A. N. Nesmeyanov and M. I. Kabachnik is of special importance in this field. Nesmeyanov's school made extensive studies of the dual reactivity of organometallic compounds in the absence of tautomerism. Thus Nesmeyanov, Freidlina, and Borisov obtained many unsaturated compounds of mercury, gallium, lead, and antimony, capable of a dual reaction and named "quasicomplex" compounds by virtue of the easy elimination of the unsaturated compound under the action of complexing agents [4,5]. Nesmeyanov and Lutsenko found a very clear instance of dual reactivity of non-tautomeric substances in the compound β-chloromercuriacetaldehyde [7-9]:



Subsequently Nesmeyanov and Sazonova studied the geometrical isomers of (β,β-diphenylpropionyl)mesitylene enolates, which enabled them to draw conclusions about the absence of a tautomeric equilibrium between the metal enolates and the keto-form and the C-alkyl forms which were obtained on carrying out the reaction with "transfer of the reaction centre" [10-12]. In this series of investigations the regions of tautomerism and dual reactivity were first demarcated; it was shown that the latter is wider than the former: dual reactivity is a more general property of compounds with conjugated bonds. In these investigations the conjugation of triple bonds was extensively examined. Subsequently Nesmeyanov and Kabachnik surveyed the experimental results on the problem of the relation between dual reactivity and tautomerism [13]. It was shown that it is possible for two series of derivatives to be formed from a single form; here dual reactivity is the consequence of the special electronic structure of the conjugated system (for example, πσ-conjugation). The reactions of πσ-conjugated systems are now being broadly studied by I. F. Lutsenko (see p. 835). It is interesting to note that the fragmentation decomposition in the reactions of carbonium ions which has been widely studied by Grob's school [14] is evidently a further development of the ideas about πσ-conjugation [15]. The problems of dual reactivity were recently studied by Novikov and Tartakovskii by the example of trinitromethane derivatives [16]. A new approach to the problem of dual reactivity of the enolates of acetoacetic ester is being developed by Reutov, Beletskaya, and Kurts with the use of the concept of "nucleophilic cooperation" in reactions of organometallic compounds (see p. 819). [17]

The greatest achievement in the field of tautomerism proper is connected with the work of M. I. Kabachnik and his school. By applying the Brønsted equation to prototropic tautomeric equilibria, Kabachnik developed a quantitative theory of tautomerism [18,19]: he derived fundamental relationships which were governed by the position of the tautomeric equilibrium as a function of acidity:

$$K_T = \frac{k_{a_I}}{k_{a_{II}}} \frac{f_I}{f_{II}}$$

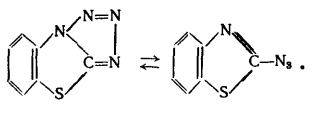
and which reflect the effect of the medium on the position of the equilibrium:

$$pK_{TS_I} = pK_{TS_{II}} + \text{const}\ .$$

These two fundamental equations enabled an explanation to be found for such dependences as the relation of acidity to enolisability, and gave a theoretical explanation for empirical relations found earlier, for example, the formulae of Meyer and Dimrot [18-21]. Kabachnik, with his students Ioffe, Mastryukova, Polikarpov, and Gilyarov, made a detailed investigation of the problems of the tautomerism of keto–enols, lactim–lactams, organophosphorus thion–thiols, diaryl- and amidodialkyl-phosphites, and phosphamidines [22-26]. By using the quantitative relationships found by M. I. Kabachnik, Sheinker studied the tautomerism of various heterocyclic compounds, such as acylaminopyridines, aminothiazoles, etc. [27,28]

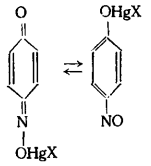
The use of correlation ratios enabled Kabachnik and Mastryukova to explain the departure from a simple linear relationship of the Hammett type for tautomeric systems and to derive a new equation with the aid of which equilibrium constants could be calculated [29].

Of the other studies in the field of tautomeric changes mention must be made of Postovskii's study of tetrazole–azide tautomerism [30]:



We note also the work of Novikov, Fainzil'berg, and Tartakovskii on acid equilibrium for polynitroalkanes, where the absence of the formation of an aci-form was demonstrated[31].

Of great fundamental interest is metallotropy, which was discovered and studied by Nesmeyanov and Kravtsov by the example of mercurated nitrosophenols[32,33]:



The study of the mechanisms of organic reactions is one of the key questions of organic chemistry; almost every organic chemist encounters these problems to some extent. The many investigations cannot be listed here and we will discuss the work of the main theoretical schools.

The most diverse problems of physical organic chemistry and the reaction mechanisms were studied in the work of O. A. Reutov, O. P. Beletskaya, and their students. Their main research deals with the mechanisms of electrophilic substitutions, by the example of organomercury compounds. Combined investigation of the stereochemistry (begun together with A. N. Nesmeyanov)[34] and kinetics of substitution of saturated organomercury compounds allowed a rule to be formulated about the retention of configuration in reactions which proceed by an S_E2 mechanism[34-39]. This rule can now be used to find the configuration of various functional derivatives of mercury[40,41].

The kinetic study of electrophilic substitutions of organomercury compounds of the aliphatic, aromatic, and alkenic series allowed general rules to be found for electrophilic substitutions at carbon atoms in various states of hybridisation. It was shown that a change in the structure or medium leads to a change in the bimolecular mechanism of the reaction to a unimolecular type S_E1.[37,42-44] A type S_E1 mechanism could be realised for all the types of carbon atom studied. It is especially interesting that the configuration at an alkenic carbon atom is retained, in accordance with the Nesmeyanov–Borisov rule, which will be discussed below, not only in S_E2 reactions, but also in reactions which take place by an S_E1 mechanism.

As a result of a study of much experimental material, the concepts of "inner" and "outer" nucleophilic catalysis have been created and it has been shown that catalysis of the latter type plays the decisive part in the realisation of electrophilic substitutions in several asymmetric organomercury compounds. This concept evidently has general significance in the reaction of organometallic compounds[33]. We note here that similar ideas about the role of complex formation for reactions of organoelemental compounds are being developed by Okhlobystin[45].

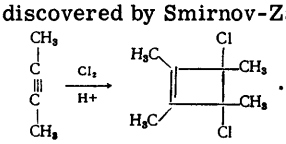
O. A. Reutov, I. P. Beletskaya, and K. P. Butin investigated the mechanisms of polarographic reduction of various types of organomercury compounds and showed the possibility of correlating the parameters of the electrolytic reduction $\alpha E_{1/2}$ of the symmetrical organomercury compounds R_2Hg with the pK_α of the corresponding hydrocarbons R–H. On the basis of the correlation obtained, a most complete scale of the acidity of hydrocarbons was compiled[46]. In this connection note must be taken of the systematic studies of the polarography of organic compounds made by Mairanovskii[47] and Stradin'[48].

Shatenshtein and coworkers undertook a very extensive investigation to find the acidities of hydrocarbons with the aid of a study of reactions of isotopic exchange in the ammonia–potassium amide system[49,50]. In these papers the view was first expressed that isotopic exchange reactions and metallation reactions belong to a general type of protophilic reactions in which the limiting stage is the loss of a proton and the formation of a carbanion. With the works of Shatenshtein a systematic investigation began into the influence of the solvent and the structural factors in various anionic reactions (isotopic exchange, metallation, Wurtz reaction, the formation of anion-radicals) and the exceptional role of specific solvation in all the processes studied has been demonstrated.

It is difficult to overestimate the value of isotopic methods to study the mechanisms of the reactions. The founders of this method in the USSR were A. I. Brodskii, G. P. Miklukhin, and A. I. Shatenshtein. We will also mention the systematic investigations on deuterio-exchange in hydrocarbons carried out by Kursanov, Setkina, and Parnes[51,52]. Many of the studies of these investigators were devoted to an investigation of hydride transformations. Mention must also be made of the work of Gragerov on the mechanisms of reactions by an isotopic method[53,54].

Under the direction of B. A. Arbuzov an extensive research was mounted to study organic compounds by physicochemical methods. Thus with the aid of parachor measurements B. A. Arbuzov succeeded in showing a series of details of the structure of esters of phosphoric, orthocarbonic, orthosilicic, formic, and phosphinic acids, and in studying the nature of the intermolecular interaction. Some interesting studies of reactions were made by the thermographic method. Together with Vereshchagin, systematic investigations were made into the configuration of addition products of diene synthesis by the dipole moments method[55]. Finally, B. A. Arbuzov and Yu. Yu. Samitov were the pioneers in the USSR in the use of the NMR method[56,57] in organic chemistry. Many series of papers by these authors deal with the study of conformations of α-oxides of the terpene series, 1,3-dioxanes, cyclic sulphites, etc.

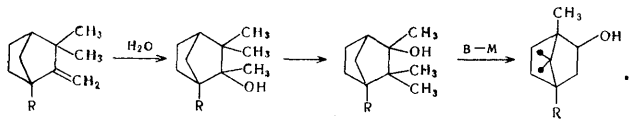
A systematic kinetic study of additions to alkenes was undertaken by E. A. Shilov and his student Smirnov-Zamkov. The study of these processes allowed Shilov to formulate the general principle of reactions proceeding through cyclic transition states[58,59]. The important role of termolecular complexes in heterolytic reactions was clearly demonstrated for the first time in the works of this school. The dimerisation of alkynes during chlorination is a very interesting reaction discovered by Smirnov-Zamkov[60]:



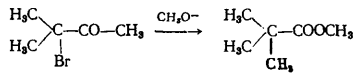
Such non-thermal reactions for cycloaddition are of great synthetic and theoretical interest.

Correlation equations are now widely used for solving many theoretical problems connected with reaction mechanisms. Pal'm[61] gave a theoretical basis for the principle of the linearities of free energies which lies at the basis of these equations. The correlation equations thus obtained were widely used for solving detailed problems of electronic structure, reactivity, and transmission of electronic effects by A. N. Nesmeyanov, E. G. Perevalova, S. I. Gubkin, M. I. Kabachnik, T. A. Mastryukova and V. A. Gilyarov, L. M. Litvinenko, Yu. A. Zhdanov, and V. I. Minkin.

Chemists have always been interested in rearrangements. Russian scientists have made a large contribution to this field of organic chemistry, and it is sufficient to remember the "celebrated" rearrangements of Wagner, Arbuzov, and Dem'yanov. Nametkin and his students discovered a new skeletal rearrangement, which is named after this investigator [62]:



The rearrangement of halogeno-ketones discovered by Favorskii [63] and bearing his name [64] is of enormous synthetic value:

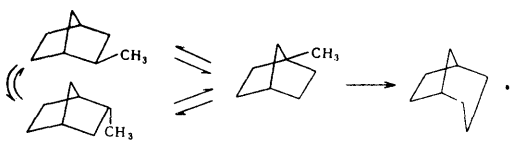


This rearrangement is widely used for the synthesis of various polycyclic and frame structures; it will be remembered that the synthesis of cubane includes a Favorskii rearrangement at two stages [65].

It is not accidental that Favorskii's students have paid great attention to studying skeleton rearrangements and related processes. The extensive investigations in the field of molecular rearrangements made by Danilov, Venus-Danilov [66], and Temnikova [67] are well known.

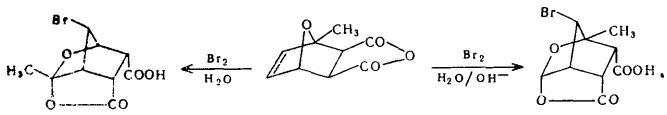
In recent years great attention has been paid to detailed aspects of the mechanisms of skeleton rearrangements. Thus Reutov and Shatkina have shown that in the deamination of propylamine a skeleton rearrangement does not take place; the observable distribution of an isotope tracer shows only the occurrence of a 1,3-hydride displacement [68]. Subsequently Reutov and Bundel' made a detailed study of carbonium ion rearrangements [69,70].

Plate, Belikova, and Mil'vitskaya [71-73] investigated the rearrangement of bicyclic hydrocarbons under the influence of acid, alkaline, and metallic catalysts. As an example we give the isomerisation of 2-methylnorbornane, which proceeds by the scheme:

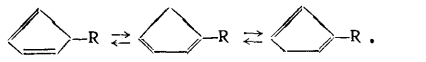


In a similar way the rearrangement of bicyclic hydrocarbons with eight and ten carbon atoms was studied in a similar manner [74].

Yur'ev and Zefirov studied several problems connected with the factors which determine the skeleton rearrangement in additions at a double bond and during the opening of α-oxides [75,76]:



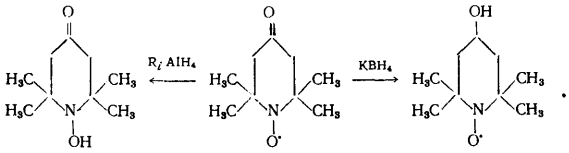
V. A. Mironov and A. N. Elizarova made interesting investigations in the field which is now unified under the name "valency tautomerisation and isomerisation". They studied the migration of double bonds in cyclopentadiene and its various homologues and showed that at low temperatures (depending on the type and extent of substitution) substituted cyclopentadienes—including deuteriocyclopentadiene—can exist as one of the isomers with a fixed position of the double bonds. On raising the temperature the double bonds migrate, and for substituted cyclopentadienes this leads to structural isomers:



Such isomerisation takes place in stages, and in several instances separate structural isomers can be isolated. It is interesting that the diene synthesis of cyclopentadienes with maleic anhydride can proceed without isomerisation of the double bonds [77,78].

Mention must be made of the theoretical studies of N. N. Vorozhtsov, Jnr. and V. A. Koptyug on rearrangements in aromatic systems. Extensive use of physical methods and particularly labelled atoms and NMR made possible a detailed investigation of various rearrangements in aromatic systems connected with the migration of a proton, or alkyl groups, and the explanation of the part played by acid catalysts. The extensive use of kinetic methods enabled several results of prime importance to be obtained on the mechanisms of the nucleophilic replacement of halogen, sulpho-, and nitro-groups. Of special interest is the study of the migration of methyl groups in polymethylbenzenonium ions [79,80].

The important role of free radicals in the most diverse chemical processes is now widely known. Note that in the field of the chemistry of stable free radicals a great part was played by the work of A. E. Chichibabin of the pre-revolutionary period. Work on the synthesis and study of the properties of stable radicals has continued ever since; in this connection note can be taken of Neiman and Rozantsev's work on the chemistry of iminoxyl free radicals [81]. These authors were the first to show the possibility of effecting the chemical conversions of these compounds without utilisation of the unshared electron:



Unstable free radicals were studied long ago by the school of N. N. Semenov. Thanks to these investigations the kinetics of chain gas reactions have been investigated in much greater detail than any other class of organic reactions.

The investigation of liquid-phase radical reactions began in the USSR with the works of Razuvaev and Koton by the example of the thermal decomposition of organomercury compounds [82]. Subsequently G. A. Razuvaev systematically studied the most diverse problems connected with the chemistry of free radicals in solution. As sources of free radicals, the photolysis and thermolysis of organic derivatives of lithium, zinc, mercury, aluminium, titanium, silicon, tin, and lead were studied [83-85]. Problems connected with the mechanism of the oxidation of organic derivatives of magnesium, zinc, cadmium, boron, aluminium, and mercury were investigated.

A long series of papers by R. Kh. Freidlina and coworkers was devoted to the study of the rearrangement of radicals in solutions. Until these appeared the very possibility of

skeleton isomerisations of radicals in solution was doubted. The investigations of Nesmeyanov and Freidlina showed that the CCl_3 group is active in reactions of a homolytic nature[86]. In a detailed study of the chlorination of hydrocarbons many instances were found of homolytic rearrangements, for example:

$$CCl_3CBr{=}CH_2 \rightarrow CCl_2{=}CCl{-}CH_2Br\ .$$

Subsequently the general character of homolytic rearrangements was discovered[87]. It is interesting that homolytic rearrangements with the 1,2-migration of chlorine were observed in the polymerisation of trichloroethylene[88].

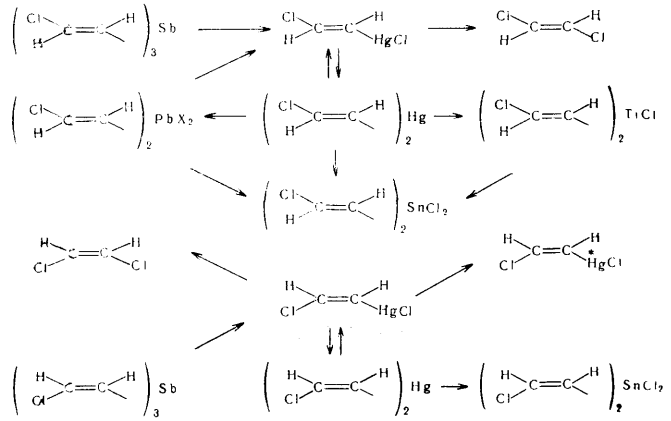
In addition, Reutov and Shatkina found that the propyl radical formed in the thermal decomposition of butyryl peroxide labelled in the α position undergoes rearrangement (to 4% extent), with 1,3-migration of hydrogen[89]:

$$CH_3CH_2\overset{14}{C}H_2\cdot \rightarrow \cdot CH_2CH_2\overset{14}{C}H_3\ .$$

Stereochemical studies carried out in the Soviet Union deal with the most varied aspects of this subject. Here the work of A. P. Terent'ev and his students must be mentioned first of all. Thus Terent'ev and Klabunovskii showed the possibility in principle of carrying out an asymmetric catalytic synthesis on the laevo- and dextro-crystalline modifications of quartz[90,91]. In the studies of Terent'ev and Potapov the spectropolarimetric method was used for the first time in the USSR to investigate the most varied compounds (nitrogen-containing heterocycles, Schiff bases, etc.)[92-95]. In investigating the rotatory dispersion (RD) of Schiff bases these authors observed a complex relation between the form of the RD curves and the solvent. This relation was used to explain detailed features of the structure of a series of compounds distinguished by solvation, etc. Spectropolarimetry was successfully used in association with reduction methods for the analysis of perfumery and food products.

Reference must also be made to the work of Kamai and Klabunovskii on the separation of arsenic derivatives by adsorption on quartz[96,97]; Levchenko and Kozlov separated derivatives of tetra-substituted sulphur into antipodes[98].

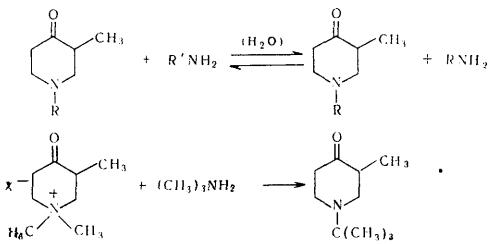
The stereochemistry of electrophilic substitution was examined in detail by A. N. Nesmeyanov. From extensive experimental material Nesmayanov and Borisov showed that homolytic and electrophilic substitutions at an alkene carbon atom proceed with retention of the configuration[99-104]:



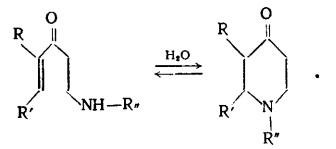
The stereochemical studies of O. A. Reutov in the field of electrophilic substitutions have been mentioned above.

Nazarov, Kucherov, and their students made a series of investigations into the steric and structural directionality of the reactions of the diene synthesis[105]. Subsequently V. F. Kucherov, N. Ya. Grigor'ev, V. M. Andreev, E. P. Serebryakov, and A. S. Onishchenko extensively studied the influence of conformational factors on the conjugation of unsaturated groupings in cyclic systems, on the direction of the initial attack in additions at a multiple bond in mono-, di-, and tri-cyclic systems, and studied the stereochemistry of epoxidation and bromination of derivatives of norbornene, cyclohexene, unsaturated derivatives of decalin, hydrindane, etc.[106-108]

Kucherov and Mistryukov investigated the influence of conformational equilibrium on the reactivity of piperidine derivatives[109-111]. They found an "amino-exchange" in piperidines which is unique in the ease of reaction[111]:

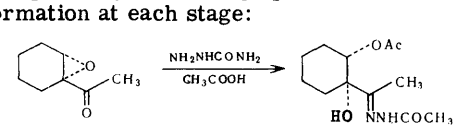


Mistryukov made a detailed investigation of the reversible cyclisation of $\alpha\beta$-unsaturated amino-ketones as a function of the substituent[112]:



The studies of V. F. Kucherov, A. V. Semenovskii, and V. A. Smit on the acid cyclisation of isoprenoids is of special interest. They succeeded in selecting experimental conditions (nitroalkanes, 100% sulphuric acid) such that the cyclisation takes place with high yield and is structurally unambiguous. By selecting catalysts which initiate cyclisation the authors could ensure a completely stereospecific process at all centres and hence model the process of the biological cyclisation of terpenoids[113].

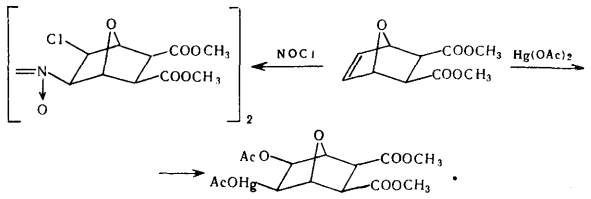
The stereochemical studies of A. A. Akhrem and his coworkers mainly developed in two directions. On the one hand there was the stereochemistry of nucleophilic addition at a carbonyl group. Akhrem and Kamernitskii examined much experimental material for the influence on the stereochemistry of nucleophilic addition of such factors as the conformation of the initial molecule, the dipole–dipole interaction of the functional groups and attacking agent, etc.[114,115]. The second direction is connected with a study of the interesting reaction of cis-opening of an α-oxide ring in keto-oxides under the action of various nucleophilic agents. Study of the mechanism of this reaction showed that this is probably a two-stage process with reversal of the conformation at each stage:



This reaction is used in steroid chemistry[116,117].

Yur'ev and Zefirov[118,119] studied the stereochemistry of the addition of electrophilic agents at a double bond in the 7-oxabicyclo[2,2,1]heptene system. They found an instance

of the cis-addition of weak electrophilic agents to the double bond:



A survey of the information on stereochemistry and the direction of electrophilic addition allowed these authors to advance the general concept of the dependence of the products of addition on alkene type, the electrophilic nature of the attacking agent, the nucleophilic nature of the anion, the polarity of the solvent, and additional stabilisation of the intermediate carbonium ion form of the substituent [119-121].

The studies of M. M. Shemyakin and L. D. Bergel'son showed that the stereochemical course of a Wittig reaction depends on the experimental conditions. The authors developed a variant of this reaction which leads almost exclusively to *cis*-alkenes. Subsequently this reaction was widely used for the synthesis of various natural unsaturated fatty acids [122], for example:

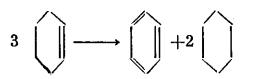
$$CH_3[CH_2]_nCHO + (C_6H_5)_3P{=}CH[CH_2]_7COOCH_3 \rightarrow CH_3[CH_2]_n{-}CH{=}CH{-}[CH_2]_7COOCH_3$$

The foundation for the chemistry of hydrocarbons was laid in our country by the investigations of the school of N. D. Zelinskii and A. E. Favorskii. Zelinskii's work in this field was extremely varied. Use of a combination of chemical and physicochemical methods allowed N. D. Zelinskii, S. S. Nametkin, N. I. Shuikin, and Yu. K. Yur'ev to study the composition of petroleums from all the main oil-bearing regions of our country. Inter alia they improved the old methods of refining and processing petroleum and developed methods new in principle, which allowed it to be converted into a promising starting material for the synthesis of various functional derivatives. The whole variety of these compounds was united by Zelinskii by the expression "products of the highest chemical value obtainable from petroleum hydrocarbons".

Kazanskii and Plate [123,124] discovered the reaction for C_6-dehydrocyclisation of alkanes in the presence of Pt/C. Similar reactions were effected simultaneously at higher temperatures by Moldavskii and Kamusher [125] on Cr_2O_3 and by Karzhev [126] on Cr–Cu phosphate catalyst. These reactions and their mechanism were thoroughly studied by Kazanskii and Zelinskii with the participation of Plate, Liberman, Sergienko, Rozengart, and others [127]. Active catalysts were found [128] which enabled benzene to be made industrially from petroleum hexane [129]. Kazanskii and Liberman discovered and studied in detail the C_5-dehydrocyclisation of alkanes into cyclopentanes [130]. Khromov together with these authors [131] found that 8-, 9-, and 10-membered rings are capable of transannular C_5- and C_6-dehydrocyclisation.

A new reaction for the hydrogenolysis of a 5-membered ring was effected by Kazanskii, Plate, and Zelinskii [132] and subsequently studied in detail [133].

Zelinskii discovered, and together with Pavlov, Kazanskii, and Levina [134] investigated, the reaction of "irreversible catalysis"—the redistribution of hydrogen in partly hydrogenated six-membered rings, with the simultaneous formation of more saturated six-membered and benzene rings. Gryaznov [135] studied the mechanism of these processes:



A reaction discovered by Zelinskii as long ago as 1911, the dehydrogenation of cyclohexanes, individually and in petroleum fractions, on Pt, Pd, and Ni/Al_2O_3 catalysts, found by him then for vapour-phase hydrogenation, has been thoroughly studied [134-138]. Yu. K. Yur'ev, P. P. Borisov, I. N. Tits-Skvortsova, N. I. Shuikin, R. Ya. Levina, A. F. Plate, A. M. Rubinshtein, Ya. I. Denisenko, and G. D. Gal'pern participated in these investigations. This is one of the reactions which lie at the basis of the well-known process of "platforming".

By studying the kinetics and mechanism of dehydrogenation of cyclohexanes, Balandin created the multiplet theory of catalysis, making use initially of the principle of structural [139-141], and then also energetic, correspondence between the reagents and catalyst [140], which stimulated work on the determination of the energies of the bonds between the reacting atoms and catalysts (Tolstopyatova [142] and Kiperman [143]). It was shown that [144-147] that reactions on oxides proceed by a doublet scheme with edge orientation of the ring, unlike the reactions on platinum and palladium, which proceed by a sextet model with planar orientation of the ring.

There have been very extensive investigations of the dehydrogenation of alkanes and alkenes to dienes, alkylbenzenes, and styrenes and also cyclopentanes to cyclopentenes, and further to cyclopentadienes. Zelinskii, Balandin, Marushkin, Bogdanova, Shcheglova, Isagulyants, Kazanskii, Sterligov, Shuikin, Smirnov, Lavrovskii, Lyubarskii, Sergienko, Rapoport, and others participated in these studies [148-161].

Liquid-phase hydrogenation catalysis is widely represented in the research of Zelinskii [134] and his school (Kazanskii, Sokol'skii, Freidlin [162-167]). The investigations of Levina and Skvarchenko [168,169] and also Kazanskii and coworkers [170,171] on reduction by hydrogen at the "moment of liberation" touch on this work.

The isomerisation of cyclic hydrocarbons under the action of Lewis acids—$AlCl_3$ and $AlBr_3$—was investigated by Zelinskii and Turova-Polyak [172-175], and Plate [71,74] investigated that of bicyclic hydrocarbons. Topchiev, Paushkin, A. D. Petrov, Sergienko, A. A. Petrov, and others studied the isomeric transformations of aliphatic hydrocarbons [148,176-179]. The work begun in our country by Ipat'ev [180] on the conversion of hydrocarbons under pressure, was continued in particular by Shuikin, Novikov, Minachev, and others [181-185] with the use of new catalysts. Gonikberg [186] studied the reactions of hydrocarbons and their derivatives, especially those with steric hindrance, under very high pressures. The alkylation of hydrocarbons was widely investigated by Topchiev, Yu. G. Mamedaliev, G. M. Mamedaliev, Lavrovskii, Shuikin, Viktorova, Panchenkov, Paushkin, Tsukervanik, Freidlin, and others [187-197]. The work on the cracking and pyrolysis of hydrocarbons begun even before the revolution and developed during its first years by N. D. Zelinskii was continued by Byzov, Lebedev, Topchiev, Voevodskii, and also by Lavrovskii and Brodskii, Agafonov, Topchieva, Paushkin, Panchenkov, and others [198-210]. After the pioneering investigations of A. N. Bakh in the field of the oxidation of hydrocarbons, important contributions were made by N. N. Semenov, N. M. Emanuel', S. S. Medvedev,

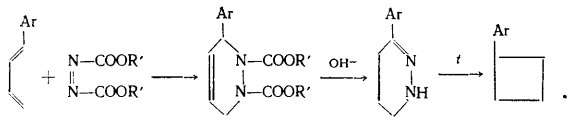
S. S. Nametkin, A. N. Bashkirov, and V. V. Kamzolkin, K. I. Ivanov, D. S. Velikovskii, K. K. Dubrovai, I. P. Losev, P. A. Moshkin, S. Z. Roginskii, and L. Ya. Margolis, P. V. Zimakov, V. Ya. Shtern, N. I. Chernozhukov, S. E. Krein, V. K. Tsyskovskii, and others[211-214].

In the field of polymerisation and condensation we will note the reaction of cross-dimerisation of acetylene into 2-methylpropene (Petrov[215]), and the dimerisation of ethylene (Eidus, Kazanskii and coworkers[216-223]).

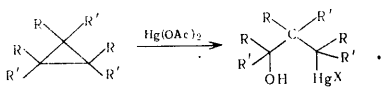
Physical and physicochemical investigations of catalysts for hydrocarbon conversions are represented in the works of Rubinshtein and coworkers[224,225] the rules for reactions in a monolayer in the studies of Vasserberg[226], and the stereochemical aspects of catalysis in those of Klabunovskii[227]. Klabunovskii's studies of the regularity of the configurational correlations in asymmetric catalysis are of great interest[227].

The work in the field of small rings is of great theoretical importance. N. M. Kizhner developed the celebrated method of synthesis of cyclopropanes through pyrazolines from $\alpha\beta$-unsaturated carbonyl compounds. In a long series of papers Levina and Shabarov studied the conjugation of a three-membered ring with a benzene ring[228].

Levina and Shabarov developed an original method for the synthesis of arylcyclobutanes on the basis of a diene synthesis with azodicarboxylic ester[228]:

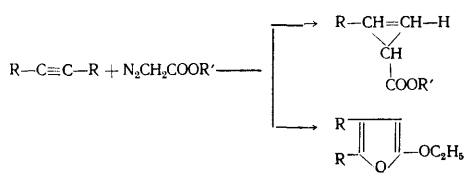


A study of the chemical and physical properties of derivatives of small rings enabled the specific characteristics of their electronic structure to be distinguished clearly. The especially marked relationship between cyclopropanes and alkenes was demonstrated by Levina in studying the opening of a three-membered ring by mercury salts[229]:



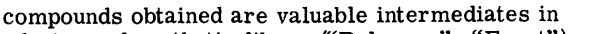
Here we can add the work of Kazanskii and Lukina on the study of the hydrogenolysis of small rings[229a].

Here mention must also be made of the work of D'yakonov and coworkers on the synthesis of derivatives of cyclopropane and cyclopropene on the basis of the reactions of diazo-compounds with alkenes[230]. The synthesis of cyclopropenes by the reaction of diazoacetic ester with acetylenes by the scheme[231]:

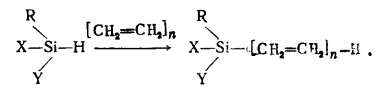


is especially interesting.

A. N. Nesmeyanov and R. Kh. Freidlina have shown that the telomerisation of alkenes with carbon tetrachloride and chloroform allows various $\alpha\alpha\alpha\omega$-tetrachloroalkanes to be obtained; these are intermediates in the synthesis of ω-amino-acids. Subsequently, R. Kh. Freidlina, L. I. Zakharkin, and V. N. Kost made a detailed investigation of the production of aminoheptanoic and aminononanoic acids according to the scheme:

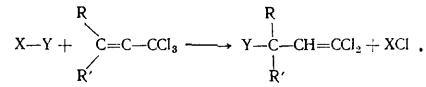


The compounds obtained are valuable intermediates in the manufacture of synthetic fibres ("Pelargon", "Enant"). Methods were also developed for the synthesis of α-amino-acids of the most varied structures and also thiols, sulphides, sulphenyl chlorides, and sulphonic acids. The compounds obtained are of undoubted interest as plasticisers, perfumes, lubricants, and intermediates for organic synthesis[232-237]. This reaction is especially interesting for the synthesis of organosilicon compounds. It was found that alkenes undergo telomerisation with silanes containing an Si–H bond, as follows[238]:



The peculiarity of this reaction is that it takes place in the absence of initiators at 300°C and a pressure of 100–500 atm (thermal telomerisation). It was found subsequently that the addition of silicon hydrides to alkenes is catalysed by various compounds such as metal carbonyls, zirconium and titanium tetrachlorides, etc.

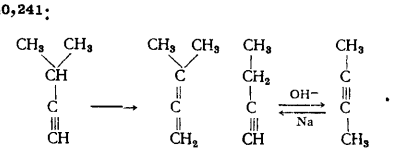
Of great significance in principle is an investigation, completed in connection with the study of telomerisation, into the chemical properties of compounds with the groupings CCl_3, CCl_3CHCl, $CCl_2{=}CH$, $CCl_3{=}C$, etc., and, in particular the action of various nucleophilic, electrophilic, and radical agents on these groupings. For example, it was shown that the action of nucleophilic agents on compounds with the $C{=}C{-}CCl_3$ grouping proceeds with rearrangement by the scheme[232]:



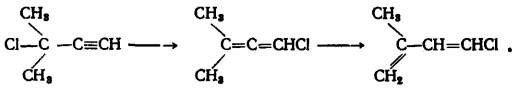
Finally, it is impossible to omit the extensive investigations of I. L. Knunyants in the field of polymer chemistry. In 1942–43, together with Rogovin and Rymashevskaya he first described the polymerisation of caprolactam into caprone. Later Knunyants proposed a new method of synthesis of adipodinitrile by the hydrodimerisation of acrylonitrile[239]. This method has great prospects in the production of nylon.

A very large group of papers by Soviet chemists is connected with the reactions of diene hydrocarbons, the greatest practical interest being in the investigations in the field of polymerisation, which started from the classical works of A. M. Butlerov. The development of this field of organic chemistry in the Soviet period is mainly associated with the name of Butlerov's student A. E. Favorskii, who created one of the largest chemical schools. His students included such celebrated chemists as Zh. I. Iotsich, S. V. Lebedev, I. N. Nazarov, M. F. Shostakovskii, V. A. Mokievskii, S. N. Danilov, T. A. Favorskaya, R. S. Zal'kind, B. V. Byzov, A. E. Porai-Koshits, and others.

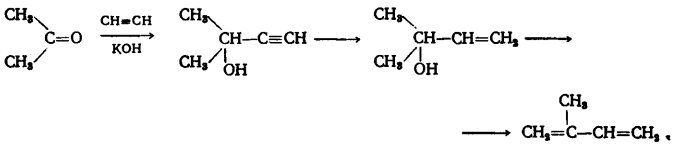
Even in the pre-Octobrian period Favorskii discovered the celebrated rearrangements of unsaturated compounds: acetylene–allene and the prototropic rearrangements of acetylenes[240,241]:



T. A. Favorskaya made thorough investigations of the acetylene–allene and allene–diene rearrangements of acetylenic halides, leading to chloroprene[242]:

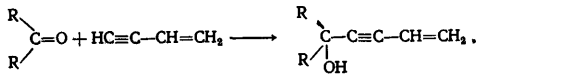


A. E. Favorskii discovered the reaction of alkaline condensation of acetylene with ketones, which made the alcohols of the acetylenic series readily accessible. A method of synthesising isoprene was developed on the basis of this reaction:

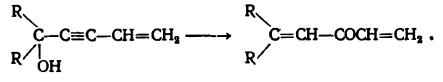


Subsequently this reaction was extensively used in the works of I. N. Nazarov and his students (V. F. Kucherov, L. D. Bergel'son, I. V. Torgov, A. A. Akhrem, I. L. Kotlyarevskii, and S. A. Vartanyan).

By using vinylacetylene as the acetylenic component in the Favorskii reaction, I. N. Nazarov succeeded in obtaining extremely reactive vinylethynylcarbinols:

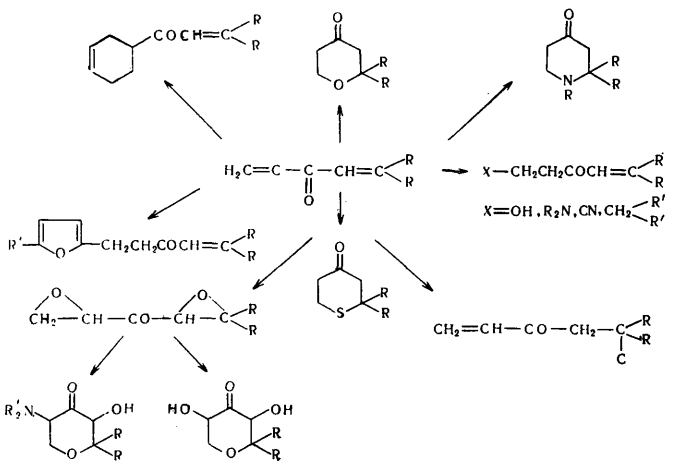


These compounds found practical application for the preparation of the so-called "carbinol glue". Vinylethynylcarbinols readily isomerise under the action of mercury salts into divinyl ketones:



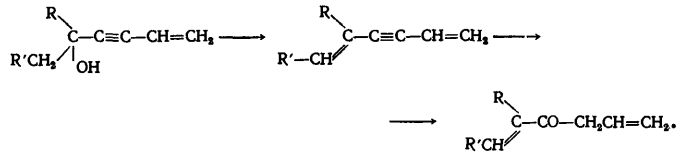
The latter were used for the synthesis of the most varied compounds[242–245], including those of the heterocyclic series, as Scheme 1 shows.

Scheme 1

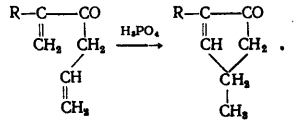


These studies of Nazarov and coworkers are well known and have been reviewed on several occasions[243]. Among the compounds obtained on the basis of the divinyl ketones are valuable pharmaceutical preparations—Promedol and Isopromedol[245].

The dehydration of vinylethynylcarbinols, leading to divinylacetylenic hydrocarbons, and the subsequent hydration of the latter leads to allyl vinyl ketones, which are very reactive compounds[243,246]:



The cyclisation of allyl vinyl ketones under the action of acids leads to cyclopentenones:



Further development of this work consisted in the use of cyclopentenones in a diene synthesis to obtain polycyclic structures related to the steroids. These investigations served as the start of chemical research in the field of the synthesis and modification of steroids, which is developing successfully at the present time (A. A. Akhrem, I. V. Torgov, and S. N. Ananchenko).

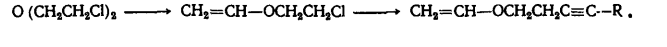
Mention must also be made of the work of Nazarov[247], Yanovskaya[248], and Mikhailov and Povarov[249–251] on the study of the condensation of acetals with vinyl esters which allowed various poly-unsaturated compounds similar in structure to the carotenoids to be obtained.

Favorskii and Shostakovskii developed a new method for the synthesis of vinyl ethers involving the reaction of acetylene with alcohols in the presence of alkali[252]:

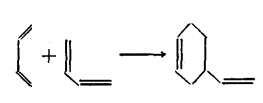


The chemistry of vinyl ethers was subsequently studied extensively by M. F. Shostakovskii. The hydrolysis, addition, and polymerisation of vinyl ethers was studied and a series of compounds was obtained which could be used as pharmaceutical preparations and solvents[253]. Shostakovskii and Prilezhaeva studied vinyl sulphides[254].

The work of Shostakovskii and Vlasov[255,256] on the production of polyfunctional vinyl ethers is especially interesting, for example[255]:

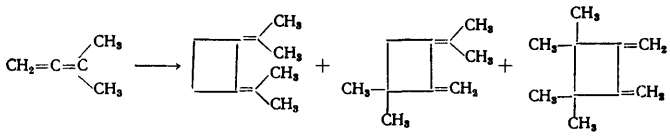


Another direction in the chemistry of diene hydrocarbons is associated with the name of S. V. Lebedev. Even in the pre-Octobrian period he began to study polymerisation processes; he investigated the polymerisation of 16 derivatives of divinyl. During this he formulated, long before the work of Diels and Alder, the principle of the condensation of diene hydrocarbons according to the scheme of the diene synthesis[257]:



We also note that cycloaddition leading to cyclobutanes[258] —a reaction now being widely studied—was also investi-

gated by Lebedev by the example of the dimerisation of allenes[257]:



Without exaggeration it can be said that until recently Lebedev's results on allene chemistry remained the main information in this field.

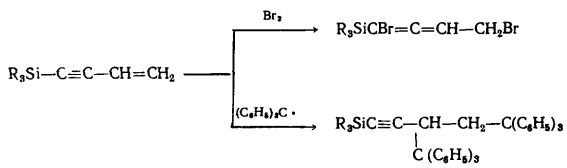
However, S. V. Lebedev's greatest contribution is connected with the creation of the synthetic rubber industry in the USSR. Lebedev and his students developed a single-stage catalytic method for the synthesis of divinyl from alcohol; simultaneously a method was developed for polymerisation by use of metallic sodium. The synthetic rubber industry created by the Soviet state on the basis of Lebedev's work has now attained great success and completely satisfies the requirements of the country's national economy.

The Lebedev process has now been considerably improved as a result of the work of his students, among whom were A. I. Yakubchik, D. M. Slobodina, M. D. Gordina, S. A. Subbotina, Yu. A. Gorina, and I. A. Volzhinskii.

Various types of polymerisation of unsaturated compounds are now widely studied in various centres of the USSR and their consideration goes beyond the bounds of the present review. We will note only the work of Dolgoplosk on stereospecific polymerisation[259,260], that of Klebanskii on chloroprene rubber[261], that of Shilov and coworkers on the mechanism of polymerisation on Ziegler catalysts[262], and also the studies of the coworkers of the Yaroslavl' Scientific Research Institute for Monomers, Fel'dblyum and Obeshchalova[263].

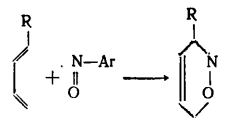
Many papers have been devoted to the study of the chemical properties in connection with the practical use of unsaturated hydrocarbons and in particular additions, the diene synthesis, 1,3-dipolar cycloaddition, etc.

First of all here we must note the extensive series of papers by A. A. Petrov who studied the addition of a wide variety of reagents, to diene, enyne, and diyne hydrocarbons[264-267]. The enyne derivatives of silicon are of especial interest; for them it was shown that the decisive factor which determines the direction of addition is $p_\pi d_\pi$-conjugation of the silicon atom and the double bond:

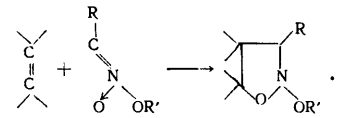


A. A. Petrov studied many acetylene derivatives of tin, phosphorus, and boron; they developed new methods of obtaining organophosphorus heterocycles based on the condensation of phosphides with dienes and $\alpha\beta$-unsaturated carbonyl compounds. As a result of studying the ionic telomerisation of unsaturated compounds with halogen derivatives, he developed an industrial method for the synthesis of citral from isoprene.

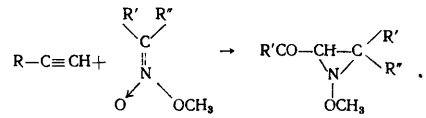
We note also here the work of Kazanskii and Levina on the hydrogenation of diene systems[268], that of Nazarov and Titov on the diene synthesis[269], that of Babayan on the synthesis of nitrogenous compounds from 1,3-dichlorobutane[270], that of B. A. Arbuzov and Konovalov on finding the mechanism of the diene synthesis[271]. A. N. Nesmeyanov and Yu. A. Arbuzov showed that aromatic nitroso-compounds can be used as the dienophile in the diene synthesis[272]:



The original reaction of 1,3-dipolar addition was discovered by Novikov and Tartakovskii, who used esters of the *aci*-form of nitro-compounds as the "1,3-dipole" [16]:



This reaction has been extended to a wide circle of alkenes and dienes. The reaction of acetylenes with these 1,3-dipoles leads to the production of aziridines by the scheme:



Machinskaya and Barkhash extensively studied methods of obtaining and the use in synthesis of the enol acetates of carbonyl compounds[273].

There is also the work of Perekalin[274] and Novikov and coworkers in the field of unsaturated nitro-compounds[275].

The development of the chemistry of aromatic compounds has been continually associated with the aniline dye and phamaceutical chemical industries. In this field, more than in any other, the main forces were directed towards assimilating the experience of foreign chemistry. M. I. Kabachnik took part in interpretation of the structure and the organisation of production of the first cyanine dyes. Conspicuous parts in the development of aniline dye chemistry were played by N. N. Vorozhtsov, Snr., N. N. Vorozhtsov, Jnr., A. E. Porai-Koshits, A. I. Kiprianov, and I. I. Levkoev. Soviet scientists paid special attention to the prolems of the theory of the colour of dyes. In this connection there is work of Izmail'skii on mesomerism[276], which in many respects preceded later ideas of foreign scientists; the work of Ioffe in the field of rhodamine dyes[277]; and that of Levkoev and Vompe, where problems of the dependence of the colour of cyanine dyes on the basicity of the heterocyclic nuclei were examined[278,279]. The work of A. I. Kiprianov is of great importance for the creation of a theory of colour. Critical problems of his work on the relation of the structure and colour of a dye are: the investigation of the influence of steric hindrance, the presence of polar substituents, and the absence of symmetry in the structure of the molecule and also the solvatochroism which is connected with this question. The concept he introduced of the dependence of the colour of polymethylene dyes on the equivalence of bonds in the chromophore of a dye was confirmed by studies in the field of unsymmetrical cyanine dyes. For the latter Kiprianov introduced the "hypsochromic shift" rule according to which with increase in the difference in the basicity or polarity of the terminal units of a chromophore there is an increase in the displacement of the absorption maximum towards shorter wavelengths from the arithmetic mean of the two corresponding symmetrical

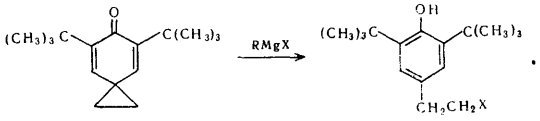
dyes[280]. Note also the work of A. I. Kiprianov on the synthesis of "Sanazine", a homologue of the natural antibiotic pyocyanine.

In addition to direct practical tasks Soviet chemists solved a series of questions of principle in the field of aromatic compounds. Here we must refer to the work of Vorozhtsov, Snr., and Bogdanov in the field of the chemistry of naphthalene derivatives[281,282], A. E. Porai-Koshits and B. A. Porai-Koshits on the structure and tautomerism of dyes, diazo-compounds, the mechanism of diazotisation, etc.[283], and that of Ioffe on the synthesis of binaphthyl derivatives[284].

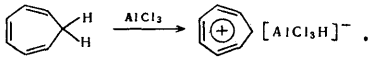
The work of Zeide and Dubinin on aromatic musks[285], and that of Rodionov on derivatives of opianic acid[286] belong to this field. Of the latter, there is special interest in the work of Belov and Kheifits on the alkylation of bicyclic terpenoids with phenols, which leads to the production of valuable perfumery preparations[287,288]. These reactions are interesting also from the theoretical standpoint, since the alkylation is accompanied by complex skeleton rearrangements and 2,6-hydride displacements.

Mention must also be made of the new method of synthesis of aromatic compounds developed by R. Ya. Levina and V. P. Skvarchenko. These authors found that addition products from the diene synthesis with maleic anhydride readily aromatise on heating with phosphorus(V) oxide; this method was used successfully to make homologues of benzene, naphthalene, anthracene, fluorene, and polynuclear aromatic hydrocarbons[289].

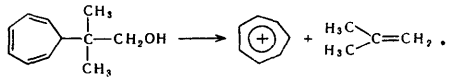
A long series of studies of the field of sterically hindered phenols was made by Ershov and Volod'kin[290,291]. By a large number of examples it was shown that *o,o*-di-t-butylphenol readily forms quinolide structures under the action of various electrophilic reagents. The authors have extensively investigated the dienone–phenol rearrangements that take place in this. The dienone–phenol rearrangement of spirane systems which they studied is especially interesting. For example, under the action of a Grignard reagent 4,6-di-t-butylspiro[2,5]octa-3,6-dien-5-one reacts with cleavage of a C–C bond to form derivatives of phenol by the scheme[290]:



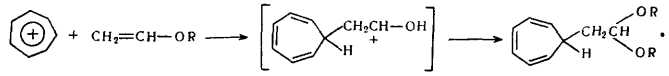
The problem of the structure of aromatic compounds and the reasons for their special properties is one of the central problems of theoretical organic chemistry. The development of quantum mechanics has significantly altered our views on the problem of aromaticity and has enabled a great number of compounds belonging to the class of non-benzenoid aromatic compounds (concerning π-complexes see below) to be obtained. The most important results in this field were obtained by D. N. Kursanov and M. E. Vol'pin. As they showed, under the action of the most varied electrophilic agents cycloheptatriene forms a tropylium salt by the scheme[291,292]:



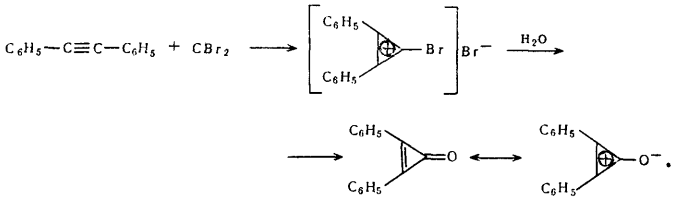
The formation of tropylium can take place even with fission of the C–C bond. For example, 2-cycloheptatrienyl-2,2-dimethylethanol decomposes extremely readily in the presence of acids with the formation of tropylium salts[294]:



As a result of the work of D. N. Kursanov and M. E. Vol'pin the "tropylation" reaction can be used as a means for determining reaction mechanisms. For examples, these authors studied the possibility of a carbonium ion being formed in the reactions of acetals, for which they carried out the reaction of the stable tropylium ion with ethyl vinyl ether, which confirmed the possibility of an acetal condensation by a carbonium ion scheme[295]:



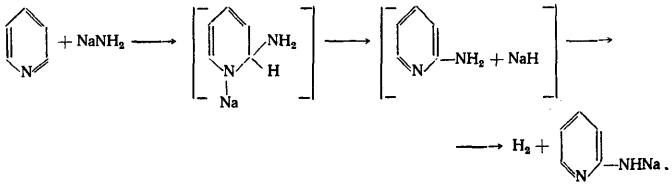
Another interesting direction of Kursanov and Vol'pin's work is connected with a three-membered aromatic system—diphenylcyclopropenone—which they succeeded in obtaining in the reaction of dichloro- and dibromo-carbene with tolane[296]:



As Syrkin and Shidlovskaya's investigation showed, diphenylcyclopropenone has a very high dipole moment, 5.08 D.[296] Of the other work on non-benzenoid aromatic compounds we will mention the investigations of Yashunskii and Kholodov on the chemistry of sydnones[297].

The chemistry of heterocyclic compounds is developing in our country at an explosive rate. Investigations in this field of organic chemistry enable new regularities in the behaviour of organic compounds to be discovered and facilitate the development of new theoretical concepts. On the other hand the enormous practical value of these investigations as a basis for creating new pharmacological preparations, dyes, plant growth regulators, and intermediates for fine organic synthesis is quite evident.

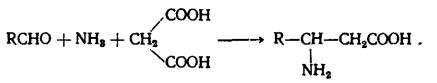
In this field it is necessary above all to refer to the investigations of A. E. Chichibabin. In 1914 Chichibabin and Zeide discovered the reaction of the amination of pyridine and its derivatives under the action of sodium amide, which has been given the name "Chichibabin reaction" in world literature[298–300]:



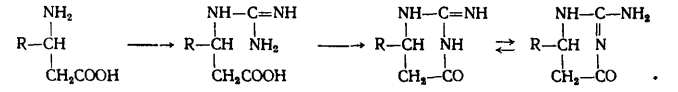
In the subsequent studies of Chichibabin and his school (O. A. Zeide, A. V. Kirsanov, I. L. Knunyants, N. N. Vorozhtsov, Z. V. Benevolenskaya, and A. F. Egorov) the chemistry of the amino-derivatives of pyridine, quinoline, pyrimidazole, and other heterocyclic systems was widely developed[299,300].

However, the chemistry of heterocyclic compounds underwent the greatest development in the post-war years; the chemists working in this field constitute one of the largest groups of Soviet organic chemists. The progress in this field is also shown by the appearance of the journal "Khimiya Geterotsiklicheskikh Soedinenii" [Chemistry of Heterocyclic Compounds] (published in Riga). Such great scientists as A. N. Nesmeyanov, V. M. Rodionov, I. L. Knunyants, Yu. K. Yur'ev, N. K. Kochetkov, amongst others, worked or are working in this field.

Rodionov developed a convenient method of synthesising β-amino-acids by the scheme [301,302]:

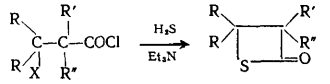


From β-amino-acids, V. M. Rodionov and coworkers synthesised various types of heterocyclic compound, such as glyoxalidones, pyrimidones, dihydrouracils, etc. As an example there is the synthesis of aminodihydropyrimidine [302]:



The first period of work of I. L. Knunyants was devoted to investigations in the field of the chemistry of nitrogen-containing heterocyclic compounds. He obtained various derivatives of alkylaminopyridines and also pyridine analogues of the dyes of the di- and tri-phenylmethane series. Mention must be made of the investigations in the field of cyanine dyes and also in that of acridine, on the basis of which the industrial production of Acrichin [atebrin] was organised.

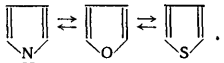
Knunyants and Lin'kova discovered a new class of four-membered heterocyclic system—β-propiothiolactone [303,304]. The most convenient method of synthesising derivatives of this class consists in the reaction of the acid chlorides of β-halogenocarbonyl compounds with hydrogen sulphide in the presence of triethylamine [303]:



Knunyants and coworkers effected a peptide synthesis based on β-thiolactones [305]. Knunyants and Kil'disheva studied the mutual relation of oxazolones and pseudo-oxazolones (2,4-disubstituted) and developed methods of establishing their structure [306].

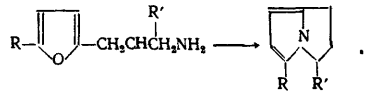
Together with Kil'disheva, Knunyants synthesised a large class of compounds containing a bis-β-chlorovinyl grouping and peptide chains which led to the creation of new mutagens, original cancerolytic preparations.

In 1935 Yur'ev discovered the reaction which bears his name, the interconversion of heterocycles under conditions of vapour-phase catalysis over aluminium oxide [307]:



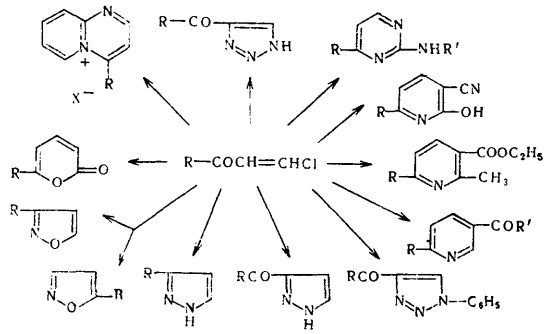
The conversion of the fully hydrogenated derivatives of these aromatic compounds takes place especially readily. In the extensive series of works of Yu. K. Yur'ev and coworkers (E. G. Vendel'shtein, I. K. Korobitsyn, and K. Yu. Novitskii) were synthesised a great number of varied heterocyclic systems [308].

A very interesting intramolecular variant is the Yur'ev reaction (Sorm, Ponomarev) which leads to a pyrrolizidine derivative [309,310]:

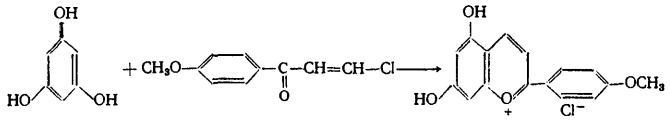


A general, unusually fruitful method of synthesis of a variety of heterocyclic compounds was developed by Nesmeyanov and Kochetkov on the basis of alkyl and aryl 2-chlorovinyl ketones—products of the condensation of acid chlorides with acetylene in the presence of aluminium chloride [311-313]. Scheme 2 shows the extensive theoretical possibilities of this method.

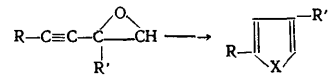
Scheme 2



Note that the reaction of β-chlorovinyl ketones with phenols takes place with the formation of benzopyrylium salts; in this way a natural anthocyanidin methyl ether, hesperidin, was synthesised from phloroglucinol and *p*-methoxyphenyl chlorovinyl ketone [314]:



Another general method of synthesis of various five-membered heterocyclic compounds was developed by Perveev and coworkers on the basis of acetylenic epoxides [315,316]

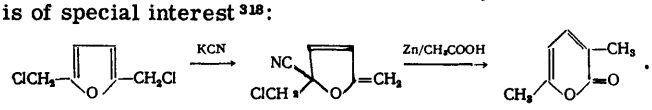


where X = NH, NR, S, O, Se.

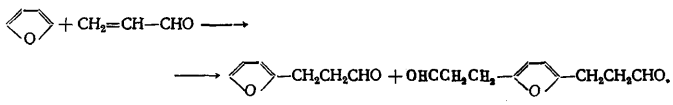
The general nature of this reaction was confirmed by the synthesis of many representatives of furan, thiophen, pyrrole, and selenophen.

Furan chemistry was extensively developed in the studies of Soviet investigators, this being directly connected with the problem of the use of pentosan-containing raw materials, the primary product of the treatment of which is furfural.

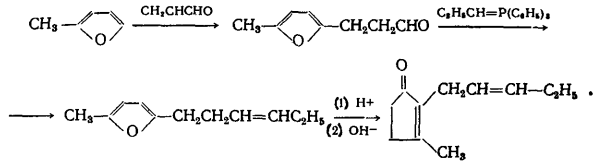
A great contribution was made in this region by Yu. K. Yur'ev and his school (K. Yu. Novitskii, N. K. Korobitsyna, N. S. Zefirov, V. P. Volkov, and M. A. Gal'bershtam). Yur'ev and Novitskii synthesised the most varied bifunctional derivatives of furan from bis(chloromethyl) derivatives of furan [317,318]. The example of an allyl rearrangement in the furan series which was found by these authors is of special interest [318]:



In 1938 Sherlin and Berlin and their coworkers showed that $\alpha\beta$-unsaturated carbonyl compounds react with furan by a substitutive addition[319]:



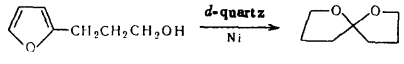
This reaction was subsequently studied by several authors[243]; however, only Yur'ev and Zefirov showed the general nature of this reaction[320]; it is now widely used for the synthesis of a variety of furan derivatives[321,322]. For an illustration we give the synthesis of jasmone, carried out by Yur'ev and Zefirov on the basis of this reaction[323]:



There is also the work of Yur'ev and Korobitsina on the synthesis of heterocycles from 3-keto- and 3,4-diketotetrahydrofurans[324], that of Yur'ev and Zefirov in the field of diene synthesis in the furan series[325], and that of Yur'ev and Gal'bershtam on the kinetics of the solvolysis of chloromethyl derivatives of heterocycles[326].

A great investigation on the synthesis, reactions, and practical applications of furan derivatives was carried out under the direction of S. A. Giller. Among the works of his school there are the development of a method of contact vapour-phase decarbonylation of furfural into furan (Karmil'chik[327]), the industrial synthesis of maleic anhydride from furfural (Shimanskaya[328]), work on the synthesis of physiologically active substances based on nitrofurans[329-331]; the alkylation of furan with alkenes (Berzin'[332]). The work of Stradin' and Giller on the polarography of the nitroderivatives of the furan series is especially interesting; it was shown that it was possible to study intermediate radicals by the EPR method[48,333].

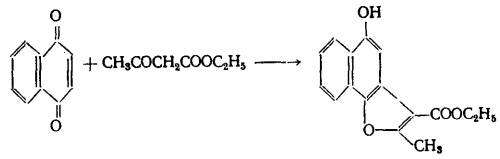
Ponomarev made extensive investigations in the field of furan chemistry[334]; the main directions were connected with a study of the catalytic hydrogenation of these compounds. We may note also Ponomarev and coworkers' study of the synthesis of optically active dioxaspirononanes from derivatives of tetrahydrofuran by the scheme[335]:



The hydrogenolysis of furan compounds was widely studied by N. I. Shuikin and his coworkers I. F. Bel'skii, R. A. Karakhanov, and V. M. Shostakovskii. They studied synthetically the catalytic hydrogenation of furan derivatives of the most diverse types, the isomerisation of γ- and δ-oxides, and the thermal and catalytic conversions of 2,5- and 2,3-dihydrofurans[336-338].

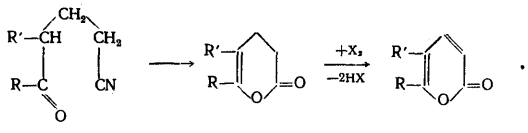
Mndzhoyan and coworkers[339-341] carried out systematic investigations to find physiologically active substances in the furan series. They tackled the problem of the chloromethylation of furan derivatives, on the basis of which they obtained an antitubercular preparation "Armazid" and a preparation against glaucoma "Dimefur". There are also papers by Nazarova[342], and Moshkin and Lutkova[343].

In the benzofuran field, mention must be made of the work of Terent'ev and Grinev, who developed a convenient method for the synthesis of the compounds of this series from p-quinones and acetoacetic ester[344]:



The compounds obtained were effective plant growth stimulators.

Levina and Shusherina developed a new method for the synthesis of 2-pyrones on the basis of δ-enol-lactones[345]:



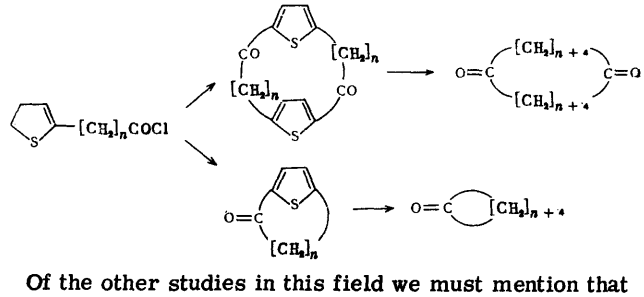
Subsequently these authors made detailed studies of electrophilic substitutions in the pyrone series and also investigated various conversions of the derivatives of this series. Zakharkin and Sorokina developed a new method for the synthesis of 2-pyrones based on the condensation of dichloroacrylaldehyde with compounds having a labile hydrogen atom (acetoacetic ester, pyrotartaric acid)[346]. Zhdanov and Dorofeenko synthesised pyrylium salts[347].

A new method for the sulphonation of acidophobic heterocyclic compounds was developed by Terent'ev and Kazitsina[348]. The sulphonation of furan, pyrrole, and their derivatives takes place smoothly under the action of pyridine–sulphur trioxide and leads to the mono- or the di-sulphonic acid, depending on the conditions.

Thiophen chemistry has formed the subject of broad systematic investigations by Ya. L. Gol'dfarb and his coworkers. The work on the synthesis of sulphides of the thiophen series has acquired an extensive scope; an effective method has been found for their synthesis from lithium derivatives of thiophen. A further development of these studies was the synthesis and study of conversions in the thiophen series[349].

Another type of reaction widely studied by Ya. L. Gol'dfarb, L. I. Belenkii, and coworkers is reduction desulphurisation. The removal of sulphur from thiophen derivatives by Raney nickel leads to aliphatic compounds. The use of this reaction enabled many difficultly accessible types of aliphatic and cyclic compounds to be obtained.

Among the compounds synthesised in this way are ketones from 14 to 17, 20, 26, and 28 carbon atoms in a ring; exaltone and dihydrocivetone were synthesised[349,350]. The following examples can serve as an illustration:



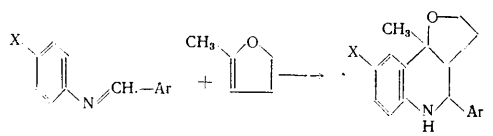
Of the other studies in this field we must mention that of Yur'ev, Elyakov, and Belyakova on the actylation of thiophen with silicoanhydrides[351,352], that of Tits-Skvortsova

and Danilova[353], and also Obolentsev on the destruction of thiophanes[354], and that of Yur'ev and Rozantsev on the synthesis of standard thiophanes[355].

The electrophilic substitutions and reactivity of selenophen derivatives and their synthesis have been extensively studied by Yur'ev, Magdesieva, and Sadova[356,357].

Some of the studies in the field of nitrogen-containing heterocycles were considered above. There are also the work of Putokhin on the application of Den'yanov's ring enlargement reaction to heterocycles[358], that of Chumakov on the synthesis of pyridines from 2-alkoxy-3,4-dihydropyranones[359], that of Kozlov on the synthesis of quinolines from aromatic amines and acetaldehyde[360], that of Pushkareva on the study of derivatives of quinaldine and acridine[361], that of Vanag on the synthesis of complex heterocyclic systems from β-dicarbonyl compounds[362,363], Rubtsov's synthesis of bicyclic compounds with a nitrogen atom at the head of the bridge[364], that of Yakhontov on azaindoles[365], Grigorovskii's study of the chemistry of the luminescent reactions of lucigenin[366], Prostakov's synthesis[367] of pyridine derivatives from piperidones, and Vompe's[368] synthesis of pyridine and quinoline derivatives.

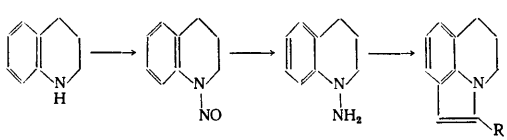
Povarov and Mikhailov developed a method of synthesising tetrahydroquinolines from alkyl vinyl ethers[241-251,369], for example:



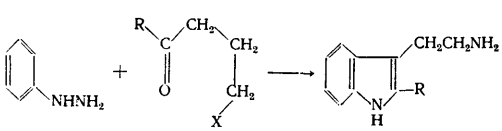
As is well known, indole derivatives play a large part in biochemical processes, therefore the great interest of Soviet chemists in studying derivatives of this class is understandable. A large number of investigators have studied the Fischer reaction. As long ago as 1910, Arbuzov and Tikhvinskii showed that this reaction can be catalysed by additions of copper, zinc, or platinum chlorides[370,371]. By using this reaction, N. N. Suvorov developed a method of synthesis of a known root formation stimulator for plants—3-indolylbutyric acid. Suvorov's work played an important part in establishing the mechanism of the Fischer reaction[372,373].

Kost and Yudin found that δ-ketonitriles can take part in the Fischer reaction and, depending on the conditions, nitriles of the indole or indolenine series are obtained[374].

These authors developed an elegant method for the synthesis of lilolidene structures by the scheme[375]:



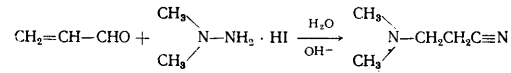
Grandberg developed an original method for the synthesis of important biogenic amines from arylhydrazones and γ-carbonyl compounds; an example is the synthesis of tryptamine[376]:



Of the other methods for building the indole ringe mention can be made of the work of Terent'ev and Grinev on the development of the Nenițescu reaction[344].

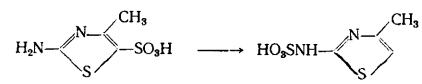
The extensive investigations of Kochetkov, Khomutova, and Sokolov were devoted to a study of isoxazole derivatives[377]. Electrophilic substitution in the izoxazole series was studied for a great number of examples.

A. N. Kost and I. I. Grandberg made a great contribution to the chemistry of heterocyclic derivatives of hydrazine. They developed a method for the synthesis of pyrazolines from azines, methods of dehydrogenating pyrazolines to pyrazoles[378], after which systematic investigations were begun into the chemistry of pyrazole[379]. Grandberg's investigations of the basicity of pyrazole systems include a series of general rules for the transfer of electronic influences through a pyrazole ring and the study of the influence of various factors (including conformational) on the conjugation of unsaturated groupings[380]. In papers of Ioffe and Zelinin[381] and also Grandberg the rearrangement of pyrazolines into nitriles was described; it is known in the literature as the "aminonitrile rearrangement"[382]. An example is the reaction of acrylaldehyde with dialkylhydrazines[383]:

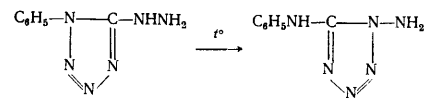


Several papers have dealt with the limits of applicability of this rearrangement[381-384]. Grandberg investigated the rules affecting the course of the reaction with breaking of the N–N bond and showed the genetic relationship of the aminonitrile rearrangement with other reactions of hydrazine derivatives[384].

I. Ya. Postovskii made an large contribution to the chemistry of heterocycles with two heteroatoms. He made a detailed study of the sulpho-derivatives of thiazole, and during this found an interesting example of the isomerisation of aminosulphonic acids into sulphaminic acids[385]:



Postovskii discovered the unique reaction of thermal isomerisation of 5-hydrazino-1-phenyltetrazole into aminoanilinotetrazole by the scheme[386]:



There are also the studies of Grinshtein and Chipen on aminotriazoles[387]; Mushkalo on benzothiazine, thiazoline, and thiazolidine[388]; Elina and Magidson on *N*-oxides of quinoxaline and pyrazine[389]; and Zhiryakov on thienothiazole and thienopyrrolenine[390].

The chemistry of natural products and their analogues was begun in the investigations of A. E. Chichibabin, V. M. Rodionov, I. L. Knunyants, and N. A. Preobrazhenskii. We will note in this connection the studies of Knunyants, Chelintsev, and Magidson on the synthesis of antimalarial substances[391,392], and the synthesis of Vitamin B_1 by Chelintsev and Benevolenskaya[393].

The synthetic chemistry of natural products was broadly developed in the studies of N. A. Preobrazhenskii and his students (R. P. Evstigneeva and N. K. Sarycheva). The work on the synthesis of pilocarpine, begun by A. E. Chichibabin, was successfully finished by the complete synthesis of this

compound[394]. Later Preobrazhenskii was the first to effect the complete syntheses of emetine, cinchonamine, curarine[395], and to create the industrial methods for the production of arecoline, cocaine, and pilocarpine. Work on the synthesis of important triglycerides of vegetable oils (linseed, soybean, cocoa bean oil) was developed on a wide front. These investigations led to the development of methods for the synthesis of saturated and unsaturated fatty acids (lauric, linolic, linoleic, arachidonic). A series of phosphatides and plasmogens entering into the composition of the brain and spinal cord was obtained from them[396].

N. A. Preobrazhenskii and R. P. Evstigneeva's work on the synthesis of porphyrins is of special interest. The authors developed original synthetic approaches to the synthesis of compounds of this type and began to study the natural chromoproteins[397]. Industrial methods of synthesising Vitamins A, B_1, B_2, B_6, PP, and E were developed under N. A. Preobrazhenskii's leadership.

In the field of vitamin chemistry (apart from the work noted above) mention must also be made of Berezovskii's investigations[398].

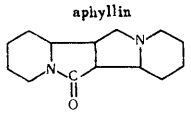
The work in the terpene field is directly connected with the use of turpentines and galipot, A. E. and B. A. Arbuzov[399] and Pigulevskii[400] made extensive investigations into the composition of turpentines.

The catalytic rearrangement of pinene into camphene, discovered by Tishchenko, gave a possibility of organising the production of camphors from turpentine[401].

We have already noted the work of S. S. Nametkin and his students on skeletal rearrangement. Extensive investigations in the terpene field were carried out by B. A. Arbuzov, who discovered the rearrangement of pinene into alloöcimene, and, with Z. G. Isaeva, studied the properties of terpenic α-oxides in detail; B. A. Arbuzov conclusively established the structure of levopimaric acid[402].

A great range of investigations into alkaloid chemistry was reached in the work of A. P. Orekhov and his students. In these studies about eight hundred native alkaloid-bearing plants were examined, from which about fifty new alkaloids were isolated[403]. The structure of a significant proportion of them was established, and in several instances was confirmed by synthesis. The structure and pharmacological value of the alkaloid anabasine, first isolated by Orekhov and Men'shikov[404,405], are generally known. Of the other alkaloids, we note aphylline, lupinine, convolamine, and salsoline[405,406]:

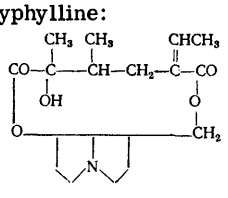
aphyllin



salsolin



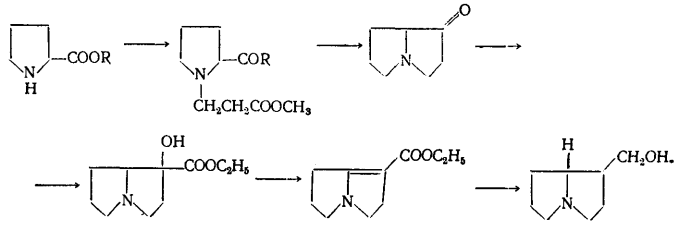
Especially interesting investigations were made by A. P. Orekhov and his student G. P. Men'shikov in the field of alkaloids of the heliotridane group. As was established by the work of these investigators, the alkaloids heliotrine, trichodesmine, platyphylline, etc. are derivatives of nitrogen-free branched unsaturated hydroxy-acids and alcohols of the 1-methylpyrrolizidine[407]. We give as an example the structure of platyphylline:



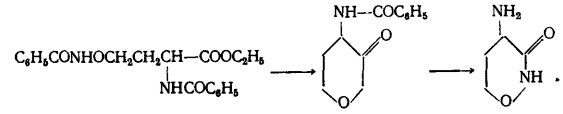
Investigations of alkaloids have been successfully carried out in the Uzbek SSR by Yunusov and Sadykov. A. S. Sadykov isolated about 100 alkaloids from the plants of Central Asia, about half of these for the first time; he made extensive investigations in the field of synthesis of alkaloids and the establishment of their structure. We mention also the series of studies by Sadykov into the reactivity of bipyridyls[408].

However, there has been an especially intensive development of the chemistry of natural compounds in the last decade. This found expression in the creation of the Institute for the Chemistry of Natural Compounds (IKhPS) and in the organisation of the journal "Khimiya Prirodnykh Soedinenii" [Chemistry of Natural Compounds]. The work of two schools is of the greatest value here: those of N. K. Kochetkov and M. M. Shemyakin.

N. K. Kochetkov dealt with most diverse problems of the chemistry of natural compounds. Thus, Kochetkov and A. M. Likhosherstov developed methods for the synthesis of pyrrolizidine bases and acids, entering into the composition of the heliotridane series of alkaloids. An example is the synthesis of isoretronecanol effected by these authors[409,410]:



In the studies of Kochetkov, Khomutov, Karpeiskii, Budovskii, and Severin[411] methods were developed for the synthesis of cycloserine and its analogues with the aim of studying the connection between structure and physiological activity of this antibiotic. As a result of the study of the mechanism of physiological action of cycloserine it was shown that it is a powerful inhibitor of the enzymes of nitrogen exchange, the co-enzyme of which is pyridoxal phosphate. Physiological activity is also exhibited by homocycloserine, which was synthesised by the scheme[412]:



The mechanism of the physiological action of this antibiotic was subsequently studied in greater detail by Khomutov[413].

A large series of papers by N. K. Kochetkov is devoted to carbohydrate chemistry. On the one hand work in the field of monosaccharide chemistry developed over a wide front. Thus, Kochetkov studied the problems of the bromination of monosaccharides by complexes of bromine with phosphorus(III) derivatives and hence found an original approach to the production of deoxysugars[414]. Kochetkov and O. A. Chizhov found a new analytical method for determining monosaccharides with the use of fragment mass spectrometry. The combination of this method with that of the methylation with trideuteriomethyl iodide enabled the sequence of bonds in oligosaccharides to be established[415,416]. Undoubtedly this method has great prospects for finding the structure of oligo- and poly-saccharides.

Of the work in the polysaccharide field we note the investigation of Kochetkov and Derevitskaya on the isolation and

characteristics of the polysaccharides of the group of substances present in blood[417].

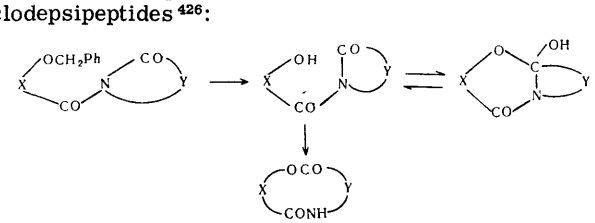
Many of the papers of N. K. Kochetkov and his coworkers (A. Ya. Khorlin, V. E. Vas'kovskii, Yu. S. Ovodov, O. A. Chizhov, and A. V. Bochkov) concern the study of natural glycosides. The first studies dealt with the isolation and establishment of the structure of the oligosides of Manchurian aralia [*Aralia mandschurica* Rupr. et Max. (Ed. of Translation)][418,419]. Kochetkov and G. B. Elyakov began the work on the isolation and characteristic of the ginseng [Panax ginseng C. A. Mey (Ed. of Translation)] alkaloids. G. V. Elyakov and coworkers have recently isolated glycosides (named panaxosides A–G) from gin seng roots, have established their main structure, and for several of the panaxosides have studied their detailed structure. It has been found that the panaxosides are oligosaccharides with 5–9 monosaccharide residues and a genin–panaxdiol–terpineol dammaranic series[420]. Now G. B. Elyakov, V. E. Vas'kovskii, and Yu. S. Ovodov have investigated physiologically active compounds isolated from marine organisms.

In conclusion we will note the work of Kochetkov and Budovskii on the chemistry of the nucleic acids[421]. Methods were developed for the selective splitting of heterocyclic nuclei entering into the composition of the nucleic acids (hydroxylamine method) which enabled original chemical approaches to studying the structure of these important biopolymers to be found.

The first studies of M. M. Shemyakin and his school in the field of the chemistry of natural compounds were devoted to the synthesis of the antibiotic levomycetin. The synthesis of racemic levomycetin—sintomycin—forms the basis for the industrial production of this antibiotic[422,423]:

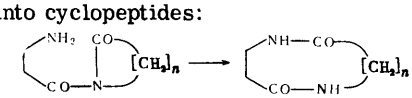
$$NO_2C_6H_4COCH_2NH_2 \cdot HCl \rightarrow NO_2-C_6H_4-\underset{NHCOCHCl_2}{COCHCH_2OH} \rightarrow NO_2C_6H_4\underset{OH}{CH}-\underset{NHCOCHCl_2}{CHCH_2OH} \cdot$$

The series of papers by Shemyakin, Ovchinnikov, and their students deals with the depsipeptides[424,425]. The first direction is connected with the synthesis of natural antibiotics depsipeptides (the enniatins A, B, C, sporidesmolide, *o,o'*-diacetylserratomolide, etc.), and inter alia for some of them earlier formulae were corrected. There was also a very interesting study of the influence of conformational factors on the cyclisation of depsipeptides[425]. The second direction (M. M. Shemyakin, V. K. Antonov, and A. M. Shkrob) is connected with the study of oxacyclols. In these authors' research it was found that oxacyclols obtainable by the spontaneous isomerisation of *N*-hydroxyacylamines and sometimes existing in tautomeric equilibrium with them, are capable of irreversible isomerisation into cyclodepsipeptides[426]:



where X = CH_2 or $[CH_2]_2$; Y = $[CH_2]_3$, $[CH_2]_4$, $[CH_2]_5$, or $[CH_2]_{11}$.

The azacyclols formed as a result of the isomerisation of *N*-aminoacyl-lactams are unstable and spontaneously are converted into cyclopeptides:



Possibly the rearrangements of the hydroxy- and aminoacylamides are some of the possible methods for the biosynthesis and transformation of peptides and depsipeptides.

A long series of papers by M. M. Shemyakin, M. N. Kolosov, and their students (Yu. A. Berlin, I. G. Bolesov, and V. V. Onoprienko) is connected with the establishment of the structure of antibiotic substances. Several years' investigations into syntheses[427] in the tetracycline field culminated recently in the complete synthesis of this antibiotic[428]. In the studies of this group methods were developed for the isolation and purification of antitumour and antivirus antibiotics of microbial origin—olivomycin, aburamycin, abicaviromycin, and the structure of some of them was established completely. In their studies these investigators discovered important relations between the structure and activity of a series of antibiotics and alkaloids, and showed the active centres and structural elements of the molecules which secured the biological activity at the cell and sub-cell levels. We note also the method developed by M. N. Kolosov for the synthesis of the analogues of chloroamphenicol. Here mention must also be made of Khokhlov's work on the isolation of new antibiotics[429].

We record also the work of V. P. Kucherov and coworkers (Gurevich, Grigor'ev, Serebryakov) on the development of methods for the isolation and synthetic modification of the gibberellins[430].

In the studies of Si. Zav'yalov and his coworkers (V. I. Gunar, M. P. Unanyan, and E. P. Gracheva) isoprenoids (for example, phytol) and homosteroids were synthesised from dihydroresorcinol. By use of the Deakin–West reaction the biogenetically similar synthesis of desthiobiotin was effected. Methods were developed for the synthesis of thymine, orotoic acid, 6-methyluracil, and 1,3-oxazines, the direct amination of uracils was achieved, and the selective *N*-glycosidation of silver salts of uracils[431,432].

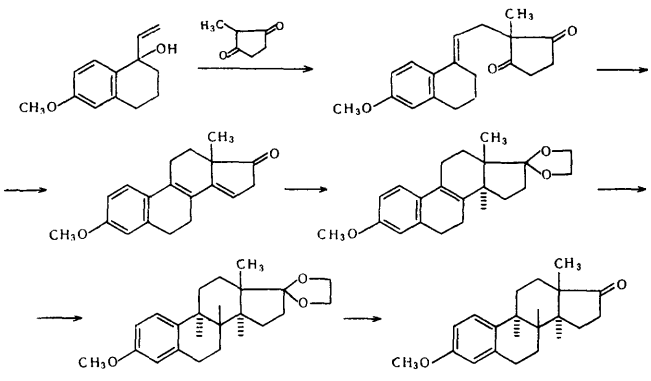
The study of amino-acids, polypeptides, and proteins has been greatly developed in our country. Synthetic investigations in the field of amino-acids is connected in principle with the problem of artificial food. Among these studies we will note the investigations of Feofilaktov[433], Terent'ev[434], and Belikov[435].

The work in the protein field was begun in the USSR by Zelinskii, Sadikov, and Gavrilov[436,437]. The present investigations in this field deal with the most varied aspects of this problem, starting at the synthesis of peptides and ending with the problems of the biosynthesis of protein; a detailed examination of these studies is impossible within the space allotted to the present review. We will only note the work of Kaverzneva[438] and Khurgin[439] on the kinetics of certain hydrolytic conversions of peptides, that of Botvinnik and Avaeva in the field of peptides containing hydroxyamino-acids[440,441], those of Stepanov in the field of pepsin[442], that of Silaev and Poddubnaya on antibiotics of a peptidal nature[443,444], that of Poroshin and Shibnev[445], and also Debabov in the field of peptides isomorphous with collagen[446].

Mention must be made of the work of Prokof'ev, Shabarova, and Bogdanov[477] in which various aspects of the nucleic acid chemistry were examined, and problems of the protein–nucleic acid bond were dealt with. In a long series of studies Prokof'ev and Shvachkin succeeded in synthesising various pyrimidylamino-acids (including natural ones)[448].

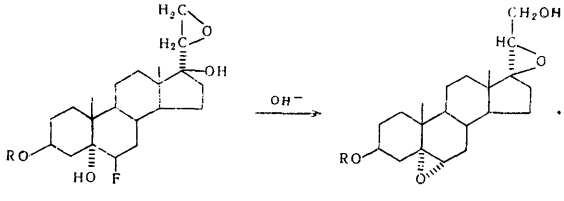
As already mentioned above, the first studies in the field of steroids were undertaken by I. N. Nazarov. These were continued by Torgov and his students Ananchenko, Leonov,

and Zakharychev[449-451]. The greatest achievement of this group must be considered to be the complete synthesis of oestrone from vinylmethoxymethyltetralol by the scheme:



This method of synthesising oestrone also achieved recognition abroad, as is shown by the work on its subsequent improvement and introduction, carried out in the USA, Federal Republic of Germany, and Japan. We note also that some of the intermediate compounds in this synthesis can be used for the synthesis of other steroidal compounds, and in particular, the heart aglycones.

Interesting investigations in the steroid field were made by A. A. Akhrem and coworkers (A. V. Kamernitskii, I. G. Reshetova, V. N. Dobrynin, and A. M. Moiseenkov). In the studies of this group the interesting migration of an oxide ring under alkaline conditions was discovered[452], the stereochemistry of the Favorskii rearrangement was studied by the example of steroidal dibromoketones[453], new reactions were found for the closing of epoxide rings in the steroid series, and methods were developed for the synthesis of highly active analogues of steroids with a broken ring B[454,455]. As an example we will give an interesting migration of the epoxide ring in alkaline medium[455]:



The great development of the boundary regions with inorganic chemistry is characteristic of modern organic chemistry. This is connected with the great practical value of organoelemental materials, and, in particular, fluoro-organic compounds and organosilicon materials, with the exceptional importance of organometallic compounds for synthetic purposes, and with their important use as catalysts for the most varied processes, including polymerisations. We must mention the development of the production of organometallic antidetonators, of selective organophosphorus fluorinating agents, of highly effective insecticides, of organosilicon and fluoro-organic heat-resistant materials, rubbers, and synthetic fibres. Organometallic compounds are of great significance for theoretical investigations. Even in the last century A. M. Butlerov and A. M. Zaitsev extensively used organozinc and organomagnesium compounds for synthetic purposes; in the prerevolutionary period P. P. Shorygin discovered important reactions for metallation. A. E. Arbuzov is rightly considered a pioneer in the field of the organic chemistry of phorphorus.

However, the greatest development in organoelemental chemistry occurred only in the thirties and forties and has continued to develop explosively to the present day. The fundamental achievements in this field and essentially also the creation of the enormous divisions of the chemistry of organoelemental compounds are connected with the school of A. N. Nesmeyanov, who has raised a great pleiad of students, among whom we can mention O. A. Reutov, N. K. Kochetkov, R. Kh. Freidlina, A. E. Borisov, I. F. Lutsenko, L. G. Makarova, L. I. Zakharkin, K. N. Anisimov, V. A. Sazonova, E. G. Perevalova, N. A. Vol'kenau, T. P. Tolstaya, N. S. Kochetkova, M. I. Rybinskaya, S. P. Gubin, V. N. Drozd, Yu. A. Ustynyuk, and A. V. Grib.

Great achievements in this field are linked with the school of K. A. Kochetkov, among whose students were M. M. Nad', N. I. Sheverdina, T. S. Talalaev, A. P. Skoldinov, and N. N. Zemlyanskii.

The broadest investigations in the field of phosphorus chemistry were undertaken by A. E. Arbuzov's school: G. Kh. Kamai, A. N. Pudovik, A. I. Razumov, V. S. Abramov, K. V. Nikanorov, and N. I. Rizpolozhenskii; by the school of M. I. Kabachnik: T. A. Mastryukova, S. T. Ioffe, V. A. Gilyarov, K. V. Matsuro, A. E. Shipov, and N. N. Godovikov; and also by the school of A. V. Kirsanov.

The chemistry of fluoro-organic compounds is rightly connected with the name of I. L. Knunyants and his students: B. L. Dyatkin, L. S. German, Yu. A. Cheburkov, G. A. Sokol'skii, and R. N. Sterlin.

Organic derivatives of almost all the elements of the Periodic System have been investigated by Soviet scientists to some extent.

Extensive investigations in the field of organoelemental chemistry embracing a considerable part of Mendeleev's Table have been made by the foremost Soviet organoelemental chemist, A. N. Nesmeyanov. Of course many of his investigations extend beyond the boundaries of organoelemental chemistry and concern general questions of organic chemistry, and many of these have been considered above.

One of the principal directions of Nesmeyanov's work is the development of a new method for the synthesis of organometallic compounds on the basis of binary diazonium salts. This reaction, which appears in all the textbooks and bears the name of its discoverer, was successfully used for the synthesis of the most varied derivatives of mercury, tin, lead, bismuth, thallium, arsenic, antimony, and zinc[456-458]:

$$(ArN_2X)_m \times MX_n + \frac{2m}{p} \times M' \rightarrow Ar_mMX_{n-m} + \frac{m}{p} M'X_p + N_2 .$$

The mechanism of the decomposition of binary diazonium salts in the presence of reductants has been studied and it has been shown that these processes are homolytic in nature and constitute one of the most important paths for the development of the chemistry of free radicals and homolytic processes.

Nesmeyanov and coworkers (L. G. Makarova and T. P. Tolstaya) investigated the possibility of using the heterolytic decomposition of diazonium salts for synthetic purposes. The investigation of this type of decomposition of diazonium salts gave results far removed from the framework of organometallic chemistry and led to the creation of new types of organoelemental compound with unusual valency.

In this way diarylchloronium, diarylbromonium, and triaryloxonium salts were obtained[459-462]:

$$C_6H_5N_2BF_4 + C_6H_5Cl \rightarrow (C_6H_5)_2Cl \cdot BF_4 + N_2 ,$$
$$C_6H_5N_2BF_4 + C_6H_5Br \rightarrow (C_6H_5)_2Br \cdot BF_4 + N_2 ,$$
$$C_6H_5N_2BF_4 + C_6H_5{-}O{-}C_6H_5 \rightarrow (C_6H_5)_2O \cdot BF_4 + N_2 .$$

Study of the chemical properties of the latter and in particular, the orientation in electrophilic substitution (nitration takes place in the *para*-position) led to the hypothesis of a new "oxane" valence state for the oxygen atom[463-465]. The results of an investigation of the mechanism of decomposition of the salts of aromatic onium compounds[466] are of great interest.

Subsequently Reutov and Ptitsyna developed a method for the synthesis of organic compounds of bismuth, tin, mercury, and antimony through diaryliodonium salts[467,468].

A. N. Nesmeyanov showed that on reaction with metal salts aliphatic diazo-compounds could form organometallic compounds[469-471]. For example, the reaction between diazoacetic ester and mercury(I) chloride is[469]:

$$4N_2CH_2COOC_2H_5 + 3HgCl \rightarrow 2CH_2ClCOOC_2H_5 + Hg(CCl{-}COOC_2H_5)_2 + N_2 .$$

Diazomethane reacts with mercury salts to give various products according to the ratio of the reagents[470,471]:

$$CH_2N_2 + HgX_2 \rightarrow XCH_2HgX \xrightarrow{CH_2N_2} XCH_2HgCH_2X .$$

Subsequently, studies of Braz, Yakubovich, and Ginsburg showed that this reaction is general—halogeno-derivatives of arsenic, antimony, bismuth, thallium, etc. were obtained[472,473].

Another method for the synthesis of onium compounds based on an exchange reaction was developed by Nesmeyanov, R. Kh. Freidlina, and E. M. Brainina. Thus the reaction of *trans*-di-2-chlorovinylmercury with iodine trichloride leads to dichlorovinyliodonium salts[474].

An interesting group of compounds is those provisionally termed "reverse onium compounds", where the multivalent atom is part of the anion, not the cation. Thus Nesmeyanov and Sazonova developed the synthesis of tetra-arylboric acids by the scheme[475]:

$$4RMgX + KBF_4 \rightarrow [R_4B]K + 4MgXF .$$

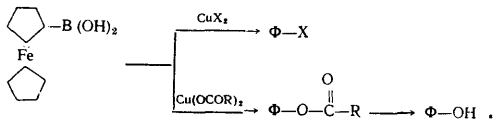
The compounds obtained are of interest as analytical reagents.

Nesmeyanov and coworkers[476-478] developed general methods for obtaining titanium compounds of the general formula $(RO)_nTiX_{4-n}$, where $n = 1, 2, 3, 4$, and X = Cl, Br; obtained titanium(III) compounds in the pure state, and obtained lower polyalkoxytitanoxanes.

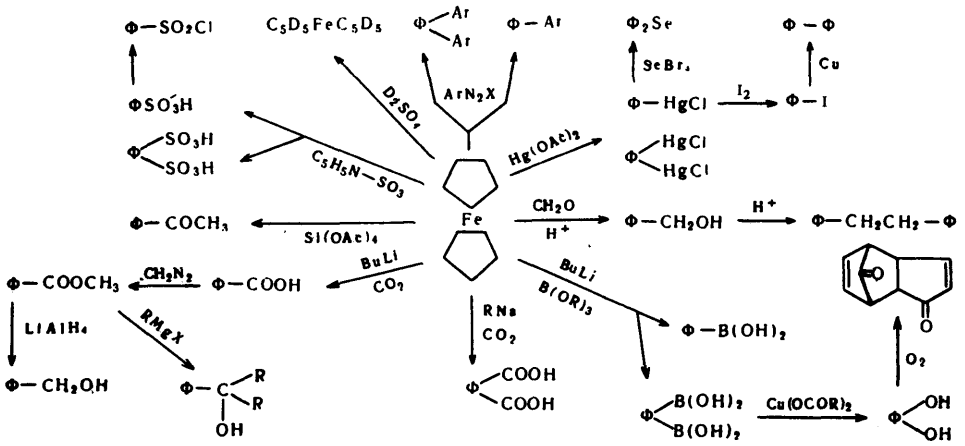
A. N. Nesmeyanov studied the reaction of chelate compounds of iron, zirconium, etc.[479]

As is well-known, the discovery of ferrocene heralded a flood of work in the field of π-complexes, deepened our knowledge of the nature of the chemical bond, and stimulated work on the ligand field theory and also synthetic investigations in the field of metal carbonyls. In our country the main studies in this region are connected with A. N. Nesmeyanov. Nesmeyanov, Perevalova, Gubin, and Ustynyuk began extensive investigations into ferrocene chemistry[480,481]. Scheme 3 shows the results of the studies of the reactions of aromatic substitution in the ferrocene nucleus.

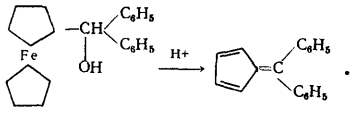
Nesmeyanov and Gubin[482] studied the oxidation potentials of ferrocene derivatives which enabled them to show the nature of the transfer of electronic effects through the ferrocene nucleus, In a series of papers Nesmeyanov, Perevalova, and Ustynyuk studied the influence of the ferrocene nucleus on the stabilisation of neighbouring carbonium, carbanionic, and radical centres[483]. The principal results were obtained by A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd. The elegant use of ferrocenylboric acids led to the production of such basic derivatives as hydroxyferrocene and halogenoferrocenes by the scheme[484]:



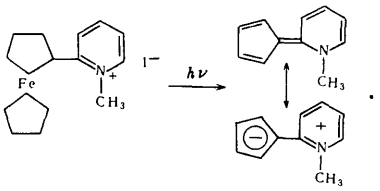
Scheme 3



These investigators studied ferrocenyldiazonium salts, nitrogen derivatives of ferrocene[485]. In studying ferrocenyldiphenylmethanol it was shown that the decomposition of the ferrocene to the fulvene by the following scheme is possible in principle[486]:



Nesmeyanov and Sazonova found a unique reaction of the photochemical decomposition of the ammonium derivatives of ferrocene by the scheme[487]:



Subsequently Nesmeyanov undertook extensive investigations of other types of π-complexes and in particular the π-complexes of palladium of σ- and π-bound cyclopentadienyl derivatives of various elements[488-490].

A. N. Nesmeyanov and K. N. Anisimov made extensive investigations into the synthesis of derivatives of metal carbonyls. Thus methods were developed for synthesising the carbonyls of chromium, molybdenum, and tungsten. Mixed carbonyls with two metal atoms in the molecule were synthesised, for example, $(CO)_5Mn-Re(CO)_5$ [491] and also some π-complexes, for example, π-cyclopentadienylcarbonylironchlorogermane by the scheme[492]:

$$\pi\text{-}C_5H_5Fe(CO)_2Cl + HGeCl_3 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2GeCl_3 + HCl$$

and cyclopentadienyldicarbonylniobiumtolane[493].

Of the works of other authors we note the investigations of Ya. K. Syrkin and I. I. Moiseev in the field of the π-complexes of palladium[494]. Of special interest are the investigations of M. E. Vol'pin and V. B. Shur in which the bonding of nitrogen by use of metallic π-complexes was shown to be possible in principle. For example, in the reaction of nitrogen with phenyl-lithium and cyclopentadienyl derivatives of titanium ammonia is obtained[495,496].

The work of Vol'pin and Shur give a powerful impulse to the investigation of the most diverse aspects of the chemistry and physical chemistry of molecular nitrogen; inevitably these ideas were immediately taken up and are being vigorously developed by a large number of investigators both in the USSR[497] and abroad[498].

K. A. Kocheshkov carried out extensive investigations in the field of organoelemental compounds. His first studies were made with A. N. Nesmayanov and concerned the extensive synthetic possibilities of the Nesmeyanov reaction. Kocheshkov's subsequent work was extremely varied and touches on many elements of the Periodic System. Thus, Kocheshkov and Sheverdina[499] made a detailed study of the metallation of aromatic hydrocarbons already discovered by Shorygin. It is interesting that a method was developed for the direct introduction of thallium into aromatic compounds[500]:

$$CH_3OC_6H_5 + Tl[OOCCH(CH_3)_2]_3 \rightarrow n\text{-}CH_3OC_6H_4Tl[OOCCH(CH_3)_2]_2 + (CH_3)_2CHCOOH.$$

Kocheshkov and Nesmeyanov studied a large number of reactions of double exchange of organometallic compounds; these reactions are a convenient method for making organoelemental compounds from readily accessible organomercury compounds[501-503]. Individual organomagnesium compounds were obtained in this way[503].

Sheverdin and Kocheshkov isolated individual mixed organozinc and organocadmium compounds and studied their properties in detail[504]: Kocheshkov and coworkers made a detailed study of organolithium compounds[505,506], on which basis an elegant method was developed for the synthesis of primary amines by the scheme[506]:

$$2RLi + CH_3ONH_2 \rightarrow R{-}NHLi + RH + CH_3OLi\ .$$

We note also the work of Kocheshkov and Zemlyanskii on the synthesis of plumboxanes and stannoxanes[507].

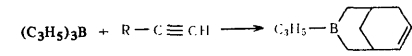
The interest in boron derivatives is due to the ever-increasing practical use of its derivatives. Undoubtedly there is also theoretical value in the chemistry of boron especially for dealing with problems of the nature of the chemical bond.

The greatest progress in boron chemistry was obtained, in the works of L. I. Zakharkin and coworkers (V. I. Stanko, O. Yu. Okhlobystin) and of B. M. Mikhailov and coworkers (Yu. V. Bubnov, V. A. Dorokhov, L. S. Vasil'ev).

In the studies of Mikhailov's group a path was developed for the synthesis of various derivatives of boron(III): trialkyl- and triaryl-borons, various oxygen-, sulphur-, and nitrogen-containing derivatives[508-511]. The study of mutual interchanges between different classes of organoboron compounds led to the discovery of the catalytic influence of the B–H bond on the exchange of radicals at the boron atom[510,511].

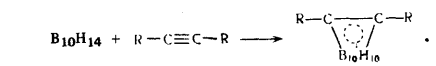
In Mikhailov's work great attention was paid to the study of the complex-forming ability of organoboron derivatives, with extensive studies of borenium and boronium compounds[508,512,513], neutral complexes, inner complexes[514,515], and also the effect of radicals at the boron atom on complex formation.

Special emphasis must be placed on certain aspects of the use of boron compounds in organic synthesis. Thus, extensive study of the derivatives of diborane, mercaptoborane, and aminoboranes made it possible to develop convenient methods for the synthesis of diols, alkenes with a known position of the double bond, and methylenecyclanes[516]. Of especial interest is the new reaction found by Mikhailov and Bubnov between triallylboron and acetylene[517]:



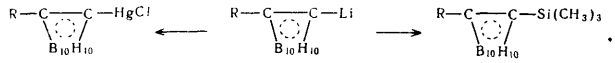
Study of the allyl derivatives of boron showed that these compounds exhibit reversible "valency isomerism" (proceeding according to the scheme of the allyl rearrangement)[518].

Zakharkin and coworkers synthesised some interesting compounds from acetylene derivatives and decaborane—they belonged to the group of carboranes, barene, and its derivatives[519]:

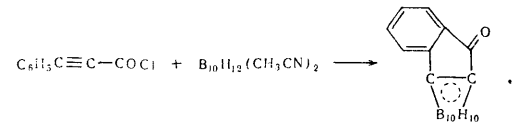


Barene has a high thermal stability; it is stable in relation to the action of alkalis and acids. It has been shown that the barene nucleus exhibits a pronounced electron-withdrawing effect: it hinders electrophilic addition to unsaturated derivatives and makes possible the metallation of the C–H bond[520,521]. A long series of papers by this group

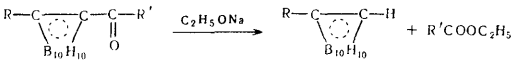
of investigators was concerned with the metallation of barenes. The carbonisation of Grignard reagents gave barenylcarbonic and acetic acids. From the lithium derivatives they synthesised a series of organoelemental compounds of the barene series containing phosphorus, silicon, tin, and mercury [520-523]:



An interesting property of disubstituted barenes is the ease with which intramolecular cyclisations take place. For example, the reaction of phenylpropynoyl chloride with bis(acetonitrile)decaborane(12) gives a cyclic ketone by the scheme [522,523]:

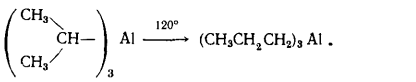


By the examples of esters of barenedicarboxylic acids and barenyl phenyl ketones it was shown that under the action of sodium ethoxide a C–C bond is broken [524,525]:



From the other studies of this group we note the work of Zakharkin and Strunin on the synthesis of organomagnesium compounds in ether-free media [526].

The chemistry of organoaluminium compounds has also been investigated by L. I. Zakharkin and O. Yu. Okhlobystin. For example, they made a detailed investigation of the reducing properties of di-isobutylaluminium hydride [527], and studied the exchange reactions between trialkylaluminiums and halides of mercury, phosphorus, boron, and lead [528,529]. These authors discovered the interesting reaction of the thermal isomerisation of isoalkylaluminium compounds into compounds with a straight chain [530]:

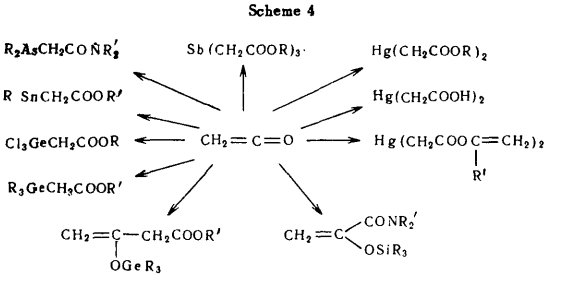


Of the elements of Group IV (of course, excepting carbon) the organic chemistry of silicon has been most developed.

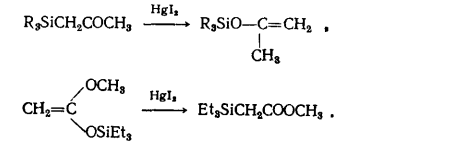
K. A. Andrianov can with justice be called the founder of the chemistry of organosilicon compounds in the USSR. Andrianov and his school studied problems of the synthesis of organosilicon monomers, ways of converting them into polymers, investigation of the properties of the polymers and materials based on them. Under Andrianov's guidance methods were developed for the vapour-phase synthesis of alkyl- and aryl-chlorosilanes, and also the theory of this process. The investigations of Andrianov and his school embrace the problems of the formation of polyorganosiloxanes of various types, the discovery of the laws of the formation of organosilicon polymers and oligomers, the study of hydrolytic polycondensation, the catalytic polymerisation of derivatives of inorganic rings and the establishment of mechanisms of these reactions, and the study of the physicochemical, mechanical, and dielectric properties of the polyorganosiloxanes. Andrianov and coworkers made extensive investigations into the synthesis of polymers with inorganic chain molecules which include (in addition to oxygen and silicon atoms) atoms of aluminium, boron, titanium, tin, phosphorus, and nitrogen. Andrianov and Khananashvili [531] examined theoretically the problem of the possibility of constructing polymers with inorganic chain molecules; they found the factors which influence the ability of the elements to form inorganic rings, framed with organic or organoelemental groups. The investigations of Andrianov and his school formed the basis for the creation of the organosilicon compounds industry.

Extensive investigations in the field of organoelemental compounds of Group IV were made by I. F. Lutsenko and his students (Yu. I. Baukov, V. L. Foss, S. V. Ponomarev, M. A. Kazankov, and Z. V. Kraits). They showed the great possibilities for the synthesis of various derivatives of silicon, germanium, and tin on the basis of keten, diketen, and enol acetates of carbonyl compounds [532-535]. They studied the conversions shown in Scheme 4.

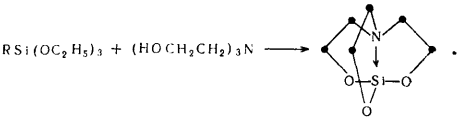
Scheme 4



In continuation of the earlier work of A. N. Nesmeyanov and I. F. Lutsenko mentioned above, a detailed study was made of the dual reactivity of α-mercurated and α-stannated compounds. This resulted in the production of a series of organoelemental *O*- and *C*-derivatives of vinyl esters of carboxylic acids, vinyloxysilanes, and phosphoric and phosphonic acids. Especially important results were obtained for derivatives of silicon and phosphorus, since here success was achieved in observing the conversion of the *O*- and *C*-forms. The greatest interest is in the isomeric conversions of organosilicon derivatives of acetone and methyl acetate, catalysable by mercury(II) iodide, which were discovered by Lutsenko and Baukov [535]:



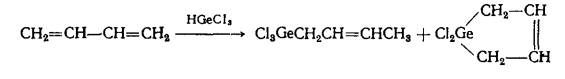
M. G. Voronkov completed successful investigations in the field of the chemistry of "atranes"—unique cyclic systems containing in a ring an atom of an element and a nitrogen atom. Silatranes are readily obtained by the reaction [536]:



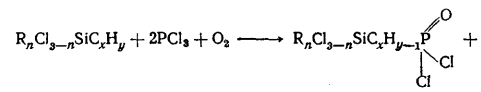
It is interesting that these compounds exhibit a definite physiological activity. In addition to silatrane, Voronkov and coworkers have synthesised boratrane, alumatrane, etc. [536].

A general property of all the "atranes" is strong coordination between the nitrogen and element atoms.

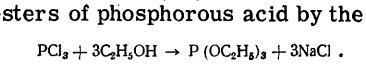
V. F. Mironov made extensive studies of the addition of silicon and germanium hydrides to unsaturated compounds [537,538]. Of especial interest is the reaction of trichlorogermane with dienes, leading to cyclic compounds [539]:



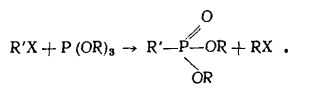
We note also the work of E. A. Chernyshev on the synthesis of compounds containing silicon and phosphorus [540]:



The chemistry of organophosphorus compounds was successfully developed in Kazan' by A. E. Arbuzov, B. A. Arbuzov and their students. As long ago as 1903 A. E. Arbuzov synthesised esters of phosphorous acid by the reaction:

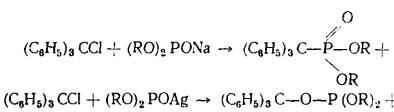


By studying the reaction of alkyl halides on the compounds he had obtained, A. E. Arbuzov discovered the rearrangement which bears his name [541]:



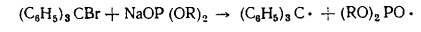
This reaction has proved to be one of the most important synthetic methods in organophosphorus chemistry. It has been used in the synthesis of esters of alkylphosphonic and dialkylphosphinic acids, phosphonocarboxylic acids, phosphonoketones, mixed oxides of tertiary phosphines, etc.; over 700 examples of this rearrangement have now been described [542,543].

A. E. Arbuzov and B. A. Arbuzov made a detailed study of the reaction of the metallic derivatives of dialkyl phosphites with triphenylmethyl halides. This reaction proceeds differently depending on the metal and halogen [544,545]:

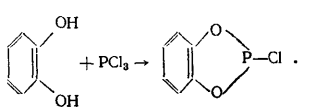


In addition, there are the studies of A. E. and B. A. Arbuzov on the structure of the so-called "Boyd's acid chloride". Of the two structures ascribed to this compound, $(C_6H_5)_3CPOCl_2$ and $(C_6H_5)_3COPCl_2$, the former was selected on the basis of a detailed experimental investigation.

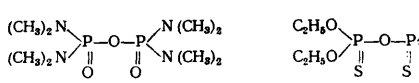
In studying the conversions of "Boyd's acid chloride", A. E. Arbuzov and B. A. Arbuzov developed an interesting method for obtaining free radicals according to the scheme [544,545]:



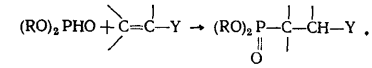
Some of the most interesting directions in A. E. Arbuzov's investigations are the synthesis of cyclic esters of phosphorous acid. A particularly detailed study was made of catecholphosphorochoridite, readily obtained by the reaction [546]:



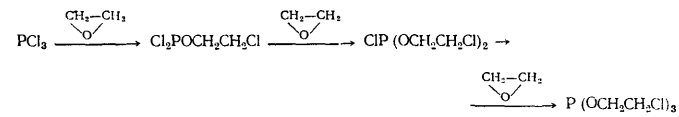
A large group of investigations by A. E. and B. A. Arbuzov are concerned with derivatives of pyrophosphoric acid [547], and are highly active insecticides. They include the well-known agricultural poisons "Oktametil" and "Ditiofos":



New preparations for the treatment of glaucoma ("Armin", "Fosarbin") were obtained. Of the relatively new achievements of the Kazan' school we will mention the discovery by B. A. Arbuzov and A. N. Pudovik of the addition of dialkyl phosphites to unsaturated compounds with an activated multiple bond; this reaction has been extensively studied by Pudovik and coworkers [548,549]:

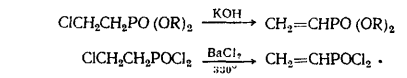


An original development in the chemistry of organophosphorus compounds occurred in the work of M. I. Kabachnik and his students, who found that the reaction of ethylene oxide with phosphorus(III) chloride leads to the synthesis of chloroethyl derivatives of phosphorous acid by the scheme [550]:



In subsequent papers, both of Kabachnik and of other authors (G. Kamai), the general nature of this reaction was demonstrated. On the basis of the chloroethyl derivatives various phosphorus(V) compounds were obtained (with the aid of the Arbuzov rearrangement).

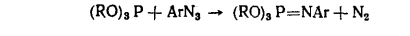
There is general interest in the production of esters of vinylphosphonic acid [551]:



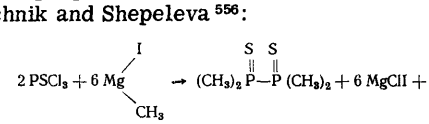
The vinyl compounds obtained are interesting as monomers for the production of incombustible polymers.

In Kabachnik's investigations chloromethyl derivatives of phosphonic acids were obtained [552], esters of α-ketophosphonic acids were studied [553], and the synthesis of organothiophosphorus compounds by the reaction of phosphorus sulphides with alcohols was investigated [554].

Kabachnik and Gilyarov showed that the reaction of aryl azides with phosphorus(III) derivatives, which proceeds by the scheme [555]:



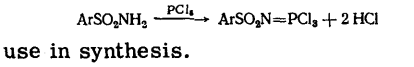
is general, and can be recommended as a method for determining phosphorus(III). We note also that the reaction for the preparation of tetramethyldithiodiphosphyl found by Kabachnik and Shepeleva [556]:



is now the best method for the synthesis of compounds of the tetra-alkyldithiophosphyl series.

Kabachnik has recently carried out extensive investigations on conjugation in non-coplanar systems containing phosphorus, and in particular, in phosphazocyanines [557].

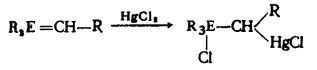
Mention must also be made of the work of Kirsanov and Derkach on the synthesis of trichlorophosphazosulphonaryls and trichlorophosphazocyls [558,559]:



and their use in synthesis.

G. Kamai has studied the chemistry of organoarsenic compounds [560]. There is also the work of O. A. Reutov and N. A. Nesmeyanov on the yields of arsenic and phosphorus [561]. In these studies it was found that the yields readily add

mercury(II) chloride to form unusual addition products, which exhibit "quasicomplex properties":



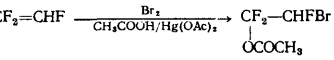
These compounds are fairly stable and may find applications in syntheses as "conservation" Wittig reagents.

We will mention also the systematic studies of E. G. Nifant'ev on methods of phosphorylation of polyols, monosaccharides, and polysaccharides [562].

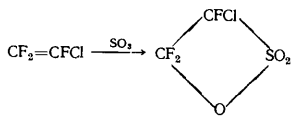
The greatest developments in the organic chemistry of fluorine have been in the research of I. L. Knunyants and his students [563,564]. The main direction of the work of this school was connected with showing the reactivity of fluoroalkenes, in studying the nature of the double bond in fluoroalkenes and the mutual influence of the groups in fluorinated derivatives of the most diverse classes. The rules for the electrophilic and nucleophilic addition in the fluoroalkene series were studied for a wide range of compounds.

There is special interest in the work of Knunyants and his students (B. L. Dyatkin, L. S. German, Yu. A. Cheburkov, and G. A. Sokol'skii) on the chemistry of fluoroacrylates, the chemistry of perfluoronitroso- and perfluoronitrocompounds, and on the study of reactions involving conjugated addition to fluoroalkenes.

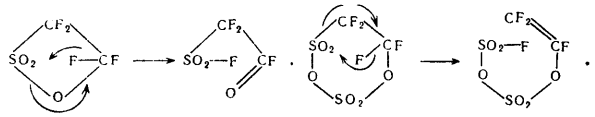
For example, Knunyants and his coworkers showed that hydrogen-containing alkenes, such as $CF_3CH=CH_2$ or $CF_2=CHF$ react with bromine in acetic acid in the presence of mercury(II) acetate or sulphate to form bromohydrins [565]:



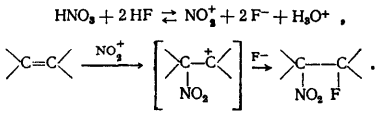
Fluoroalkenes readily add sulphur trioxide to form cycloaddition products of β-sultones [566]:



The development of the chemistry of fluorinated sultones led to the discovery of interesting isomerisations, which probably proceed through a "bicyclic mechanism" [567]:



I. L. Knunyants has made extensive studies of the nitrofluorination of fluoroalkenes, which proceeds by the scheme [568]:



This reaction was first effected by Titov by the example of tetrafluoroethylene [569].

It is impossible to omit the work of Knunyants and Sterlin on the synthesis and investigation of the properties of perfluorovinylmercury [570].

Of the other work in this field we note the investigations of I. V. Martynov and Yu. L. Kruglyak on the nitration of fluoroalkenes by a sulphuric–nitric acid mixture [571] and that of A. Ya. Yakubovich's study of nitrosation [572].

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Obviously, within the framework of a journal article it is impossible to review thoroughly all the great achievements of Soviet organic chemists. However, even in this brief survey the enormous attainments of Soviet scientists in the most diverse branches of science are evident. This guarantees future progress in organic chemistry in our country.

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