

Національна академія наук України

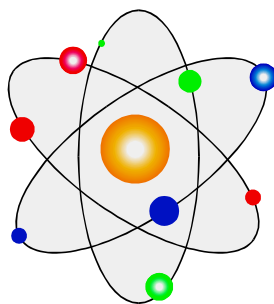


Інститут біоорганічної хімії та нафтохімії
ім. В.П. Кухаря

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ТЕЗИ

Київ

UDC 631.81:631.895

Effective organic and mineral fertilizers – a complex solution for the utilization of local raw materials and a promising direction for the reproduction of soil fertility

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Nowadays, the use of effective organo-mineral fertilizers in agricultural production is one of the main measures for solving the country's environmental and food security. That is why the organic-mineral fertilizers of the new generation were created at the V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine on the basis of recycled vegetable waste, excess silt and deposited BSA sewage sludge. Field research results with corn of the Moskito hybrid confirmed the high agrochemical efficiency of these fertilizers (OMF-I and OMF-II) in 2018. Improvement of the nitrogen-phosphorus nutrition of the experimental plants was due to the use of these fertilizers. The introduction of OMF-I and OMF-II into the corn fertilizer system of the Moskito hybrid affected the improvement of structural yield indicators. Thus, the grain productivity of one plant in the experiment increased by 19–43 %, the mass of 1000 grains by 14–37 %, the weight of cob – by 60–82 % compared with the control where only mineral fertilizers were introduced. With optimal moistening in the reporting year, the roots of the experimental plants pierced the granules, absorbing the biogenic elements not only from the soil solution, but also from the created fertilizers OMF-I and OMF-II. This contributed to obtain an additional harvest of high-quality corn grain – 5.1 t/ha, and increased protein content by 18.5 %. X-ray fluorescence analysis of maize grain confirms that the content of heavy metals in samples for the use of OMF in the field experiment did not exceed the maximum permissible values, and therefore, it may be suitable for food, feed, and technical needs. The conducted field researches confirm that the deposited sewage sludge, processed vegetable waste in the composition of OMF is a valuable raw material for the creation of granular agrochemical-effective fertilizers in order to improve the mineral nutrition of crops, in particular nitrogen-phosphorus, and to improve the humus condition of soils.

UDC 665.753.4:66.095.134

Alkaline synthesis, physicochemical and operational properties of butyl esters of fatty acids on the basis of oil's triglycerides

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When carrying out transesterification (TE) of nature oil triglycerides (TG) by *n*-butanol over KOH, the presence of trace amounts of water limits butyl esters (BE) yields by level 80–85 %, preventing separation of glycerol layer (GL). The mixture of products forms high-stable emulsion, which was interpreted by simultaneous stabilizing action of potassium soaps and mono(di)glycerides. When carrying out TE reaction in water-free conditions over potassium butoxide (KOBu), obtained in original way, the yields of BE higher than 90 % and spontaneous products dividing were managed to get after shortrun stirring at low butanol excess and without reagents heating. Formation of up to three separate GL's depending on TE conditions was observed. One of them was noted to be mixture of only two components, being glycerol and potassium glyceroxide. The ways of formation of the latter were treated on the base of difference in acid strength of glycerol, *n*-butanol and water.

The mechanism of butanol molecule activation and further transformations, when potassium butoxide is used as catalyst, was proposed. Studying of the butanolysis over KOBu, KOH and potassium methoxide indicated, that reaction is described by third-ordered formal kinetic equation. The reaction over butoxide is characterized by highest rate and equilibrium yield of BE (95–96 %).

Generally, it was established, that BE meet the requirements for biocomponents of blended diesel fuels by a number of physicochemical and operating characteristics. According to the results of bench testing, the mixtures based on BE almost do not inferior to petroleum diesel fuel by power characteristics, while exceeding it by environmental performance.

UDC 547.786.541.521.54.057

A new approach to the synthesis of isoxazole-containing thiodiazepine derivatives by ring-closing metathesis reactions

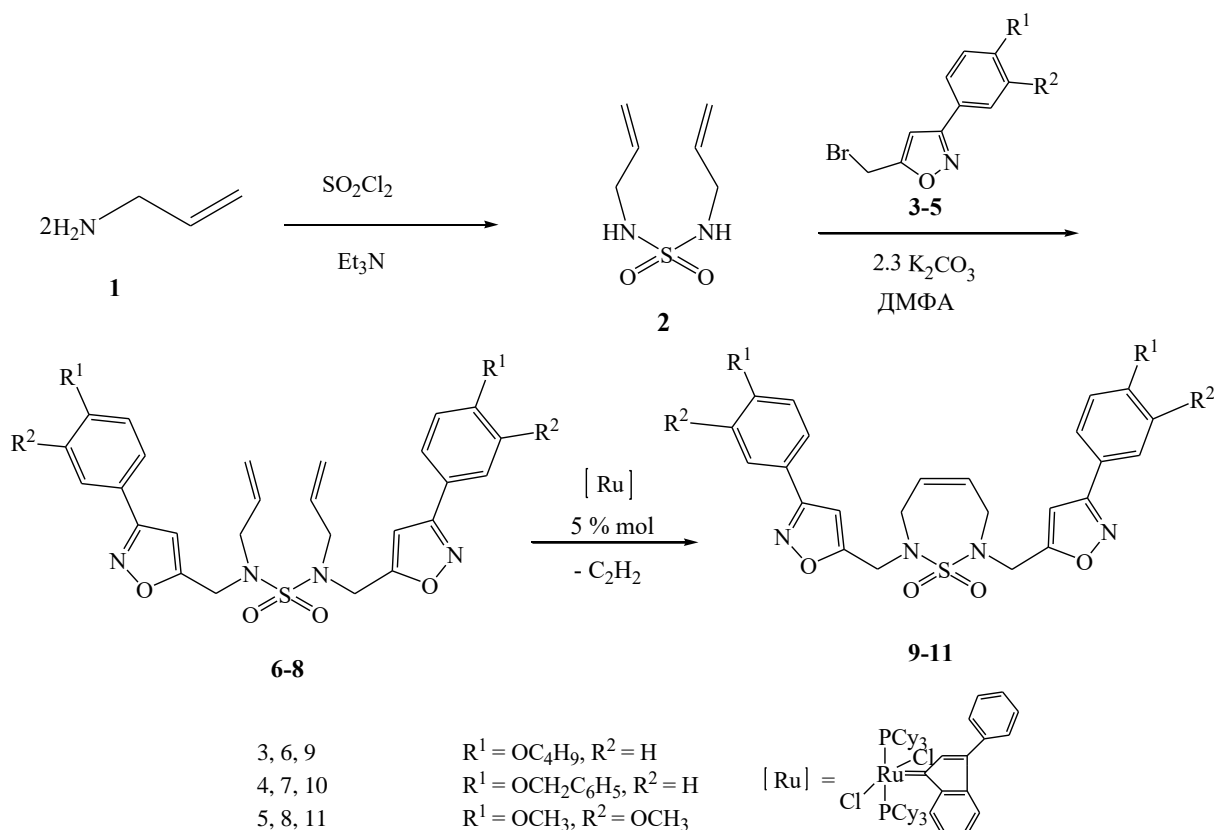
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The sulfamide functional group is present in a number of commercially available and researched drugs, with a wide range of activities. Cyclic sulfamides are also of great interest from the point of view of bioactivity, so it is not surprising that there is the growing interest stimulated by the development of new synthetic methods for their production. It is known that HIV-1 proteinase inhibitors have been found among disubstituted thiodiazepine-containing derivatives. Previously, we have reported about the synthesis of novel thiodiazepine-containing isooxazole derivatives by RCM, performed for the first time using the corresponding isooxazole-containing amines. This message relates to an alternative route of obtaining compounds of this type from the more accessible bromo-derivatives aryl substituted isooxazoles, which has made it possible to significantly optimize and expand the ability to obtain the target derivatives.

For this purpose, we have obtained 1,3-bis-allylsulfodiamide (2) by the interaction of allylamine with sulfuryl chloride in the presence of triethylamine, not previously described in the literature. Isoxazole-containing diallyl derivatives (6–8) have been obtained by alkylation of the source 1,3-bis-allylsulfodiamide with the corresponding bromo isooxazole derivatives in DMF solutions in the presence of 2.3 eq. potassium carbonate at a temperature of 75–80 °C. Diallyl derivatives (6–8) were obtained in 74–83 % yields.



Ring-closing metathesis reactions of the derivatives (6–18) were carried out in solutions of dry degassed dichloromethane in an atmosphere of dry argon at a temperature of 25–30 °C for 8–10 hours using ruthenium carbene catalyst ([Ru]) synthesized by us. The target isooxazole-containing thiodiazepines (9–8) have been obtained in 75–82 % yields. The structure of all new compounds was confirmed by elemental analysis and ¹H, ¹³C NMR spectra. Thus, a new more convenient way of obtaining isooxazole-containing thiodiazepines has been worked out using cycle-closing metathesis reactions, which significantly increase the chances of obtaining thiodiazepine derivatives that are otherwise difficult or impossible to obtain.

UDC 544.47

Toluene with methanol alkylation on the basic FAU zeolite: the effect of $(\text{NH}_4)_2\text{SiF}_6$ modification on product distribution and coking

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The problem of deactivation for catalysts based on microporous materials is of current interest since the deactivation of active sites themselves is accompanied by an active surface reduction through blocking the access to it by coke precursors. This applies mainly to acidic catalysts, on which cracking reactions occur with the formation of a large number of unsaturated hydrocarbon molecules. For basic catalysts, which do not contain Bronsted acid sites (BAS), deactivation through the formation of coke is not considered. The aim of this work was to reveal the influence of active sites of external surface of basic catalyst on product distribution and coking in the reaction of side-chain toluene with methanol alkylation.

It has been found under short contact time that ethylbenzene is a primary product. The leading role of methanol as an alkylating agent and the dehydrocondensation reaction as being dominant in the toluene conversion on the basic catalysts are proposed.

The formation of heavy coke on the outer surface of zeolite microcrystals has been established to cause the loss of activity of basic catalyst of toluene methylation. Removing the appropriate active sites prevents this process. The possibility of coke formation on a strongly basic zeolite catalyst in the absence of BAS has been shown, that initiated by the alkylbenzenes dehydrocondensation with methanol, followed by hardening the products of such transformation.

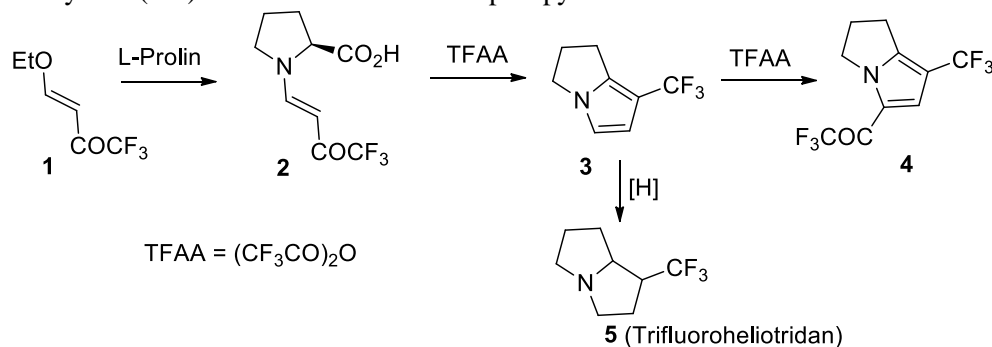
UDC 547.321

Synthesis of trifluoromethyl containing pyrroles

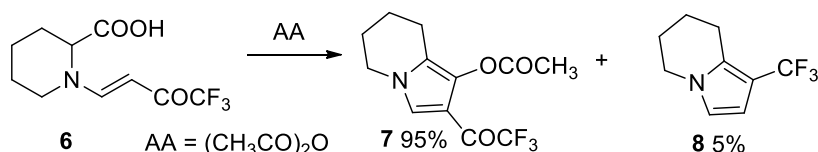
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Fluorocontaining heterocyclic compounds, in particular trifluoromethylpyrroles, are perspective precursors for the synthesis of fluorinated analogues of natural bioactive compounds – pyrrolizidine alkaloids, for example: heliotridane. We have found that the enaminone **2** (readily available from enone **1** and Proline) reacts with trifluoroacetic anhydride (TFAA) and affords trifluoromethylpyrrole **3** in high yield, which can be further trifluoroacetylated by excess of TFAA into pyrrole **4**. The using of acetic anhydride (AA) instead of TFAA afforded pure pyrrole **3** from the enaminone **2**.



At the same time the reaction of the derivative of pipercolic acid **6** with AA gives the mixture of products **7** and **8** with the ratio 95 : 5.



The structure of pyrroles **3**, **4**, **7** and **8** fully assigned by NMR spectroscopy and also X-ray analysis for compounds **4** and **7**. We proposed the mechanism of formation of pyrroles **3** and **7** from enaminones **2** and **6**.

UDC 541.515:547.56:541.128

Mechanisms of inhibition of oxidation of organic compounds by organometallic complexes, carbon and polynuclear nanoscale clusters

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The continued interest in the purposeful search for new more effective oxidation inhibitors (antioxidants), that play an important role in modern technologies of organic synthesis, combustible and lubricating materials, polymers, foodstuffs and chemistry of living organisms, requires a detailed and sophisticated study of the mechanism. In the oxidation of organic compounds with oxygen in liquid media, the process occurs by a chain mechanism with the formation of alkyl and peroxide radicals, which play a major role in the continuation and branching of the chains. The most effective are antioxidants that quickly react with them by breaking the chains.

The report addresses the main classes of effective inhibitors and their mechanisms of action.

The first class is phenols, thiophenols and aromatic amines, which stoichiometrically react with peroxy radicals and are irreversibly consumed in the process of inhibiting the oxidation of compounds.

The second class of compounds are complex compounds that are capable of cyclic regeneration in acts of breaking and branching of chains. Cyclic oxidation breakage mechanisms lead to a significant increase in the stoichiometric inhibition coefficient. The main 19 mechanisms of cyclic breakage of the chains, which are divided into 3 main groups by the nature and participation of the radicals leading the branching are given.

The third class of compounds are cluster compounds whose mechanism of action is divided into three groups:

- reactions that are localized to the metal nucleus and proceed: without changing the metal nucleus of the cluster; by changing the nucleolarity of the cluster metalloid and by changing the spatial structure of the cluster metalloid;
- reactions that are localized to the coordinated cluster ligand;
- reactions occurring on products of homolytic replacement of cluster ligands by free radicals.

The fourth class of compounds are nanoscale spherical carbon clusters whose mechanism of action is inverse and varies depending on the temperature and the solvation shell of the cluster due to the formation of solvate domains.

UDC 621.891:662.754

Nonmonotonicity of concentration dependences of macrophysical characteristics of ethanol solutions on the content of spherical carbon nanoclusters

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Synthesis of spherical carbon nanoparticles is performed by high-frequency bit-pulse method. Non-equilibrium plasma, which is generated by kilohertz bits, allows to draw large volumes of gas into the synthesis process, i.e. to exert a volumetric effect (energy pumping) on the gas environment.

The aim of the study was to investigate the change in refractive index, surface tension and load-bearing capacity of ethanol solution depending on the content of synthesized spherical carbon nanoclusters. According to the results of the work, it is established that the dependencies are non-monotonic: in the area of low concentrations there is a decrease in surface tension and an increase in bearing capacity and refractive index, and when the threshold concentration exceeds 0.01% of the mass, dependencies change to opposite. This dependence inversion can be explained by the transformation of the supramolecular structure of the solution: the breaking of the hydrogen bond network and the formation of supramolecular domains under the influence of the nanoparticles introduced.

The symbathic non-monotonous character of the change of physicochemical properties (refractive index, surface tension, dynamic strength) of ethanol solutions from the concentration of nanospheric polyspheric carbon clusters in them has been established. The occurrence of extrema on these dependences at ultra-low nanoparticle concentrations in the range of units of tens of ppm is shown.