Національна академія наук України

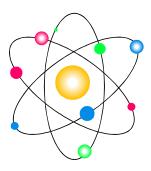


Інститут біоорганічної хімії та нафтохімії

XXXIII наукова конференція з біоорганічної хімії та нафтохімії

Присвячується 100-річчю Національної академії наук України

16-17 травня 2018 р.



ТЕЗИ

Київ

УДК 631.81:631.895

Evaluation of the role of organic raw material as part of organo-mineral composition on growth processes and physiological activity of roots of winter wheat

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The thermal method of utilization of urban sewage sludge and plant wastes with high content of active silicon into organo-mineral composition (OMC) was developed for the purpose of recycling phosphorus from the first one mentioned above in order to optimize phosphorus nutrition of plants. It was indicated on the prospects of the compatible application of these components as part of composition preparation in order to mobilize low solubility phosphates, which form the base of the phosphate soil fund. The results of researches with determination of efficiency of use of composition preparations with silicon-based component confirm the positive influence on root formation, absorption capacity of plants to use hard-soluble phosphate of sediment ash. The growth of phosphorus plant uptake rates by up to 85 % for the use of OMC can be explained by the additional absorption of phosphorus by the root system with increased surface area, absorbing activity and accelerated mobilization of absorbed compounds. Such an effect of OMC is very important, especially in the first stage of organogenesis, because plants are in dire need and actively absorb of available phosphate compounds during this period. The way of using non-traditional diverse raw materials sources for the production of agrochemical effective fertilizers is quite justified, especially in the current state of limited resource, economic and agricultural possibilities.

УДК 547.321

New fluoro-containing synthons and its using for synthesis of potential bioactive compounds

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Difluoromethylene-containing compounds are of interest to researchers in medical and bioorganic chemistry, thus the development of new effective methods for obtaining them is one of important task fluoroorganic chemistry.

Ethyl bromodifluoroacetate (EBDFA) is a usefull starting compound for the preparation of CF_2 -containing substances. Using EBDFA we performed multigram-scale synthesis of 2,2-difluoro- and 3,3-difluoro-analogues of important neuro-transmitter γ -aminobutyric acid (GABA). The key stages of synthesis were the addition of EBDFA to benzyl acrylate and ethyl vinyl ether. Also we used EBDFA for preparation of series aryl difluoromethylene ethoxyvinyl ketons. The latter are convenient substrate for different heterocyclizations, which afford new compounds like Ar(Het)-CF₂-Het' – potential substances for medical investigations.

BnO₂C
$$\downarrow$$
 3 steps \downarrow 5 steps \downarrow 5 steps \downarrow 5 steps \downarrow 4 \downarrow 5 steps \downarrow 5 steps \downarrow 5 steps \downarrow 5 steps \downarrow 6 steps \downarrow 6 steps \downarrow 7 steps \downarrow 7 steps \downarrow 8 steps \downarrow 8 steps \downarrow 9 steps \downarrow 9 steps \downarrow 1 steps \downarrow 1 steps \downarrow 1 steps \downarrow 2 steps \downarrow 1 steps \downarrow 2 steps \downarrow 3 steps \downarrow 3 steps \downarrow 3 steps \downarrow 3 steps \downarrow 6 steps \downarrow 6 steps \downarrow 7 steps \downarrow 7 steps \downarrow 8 steps \downarrow 9 steps \downarrow 1 steps \downarrow 1 steps \downarrow 1 steps \downarrow 2 steps \downarrow 2 steps \downarrow 1 steps \downarrow 1 steps \downarrow 2 steps \downarrow 2 steps \downarrow 3 steps \downarrow 2 steps \downarrow 2 steps \downarrow 3 steps \downarrow 3 steps \downarrow 3 steps \downarrow 2 steps \downarrow 3 steps \downarrow 3 steps \downarrow 2 steps \downarrow 3 steps \downarrow 2 steps \downarrow 3 steps \downarrow 2 steps \downarrow 3 steps \downarrow 3 steps \downarrow 2 steps \downarrow 3 steps \downarrow 4 steps \downarrow 5 steps \downarrow 6 steps \downarrow 7 steps \downarrow 6 steps \downarrow 7 steps \downarrow 8 steps \downarrow

UDC 547.1'1+547.466+547.787

New phosphono-peptido-mimetics: synthesis and properties

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New strategy for the synthesis of a variety biologically active derivatives of α -aminophosphonic acids, phosphorylated peptides and phosphono-peptido-mimetics have been developed.

This method is based on the property of the 4-phosphorylated 5-amino-1,3-oxazole ring to be disclosed in acidic medium. Substances with high vasodilator activity and low toxicity have been founded among the synthesized peptidomimetics.

UDC 661.123;661.682;661.689

Production of carbide and amorphous silicon dioxide from biodiversity materials

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The widespread use of inorganic compounds of silicon, such as silicon dioxide and carbide, in various industries, still leaves open the question of creating an effective technology for obtaining these high purity materials. One of the promising sources of silicon-containing compounds is rice husk, which in turn belongs to agricultural waste. Annually in Ukraine, it is formed by about 75 thousand tons.

This work aimed to create a flexible technological scheme for the integrated processing of human-made wastes to produce useful products.

An amorphous silicon dioxide has been synthesized. It has the shape in the form of globules of an average size of 250 nm and the content of the main component at 99.9995 %.

The technology of obtaining silicon carbide in the form of particles (average diameter 10–15 microns) of the right form sticks (average length 220–250 microns) and fibre-like structure (diameter of thread 800 nm) is worked out. According to IR spectroscopy, it was found that the formation of carbide from amorphous silicon dioxide, previously obtained from rice husks, begins at a temperature of 1500 °C and above. The X-ray phase analysis confirmed the 100% presence of silicon carbide with a cubic structure with a content of 99.9998 % for the main component.

UDK 547.571+547.592.12

Preparative Aerobic Oxidation with N-Hydroxyphthalimide in Trifluoroacetic Acid

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Partial oxidation of toluene to benzaldehyde represents a formidable challenge both for the laboratory and industry as over-oxidation to benzoic acid dominates already at the moderate conversions of starting material.

We found, that *N*-hydroxyphthalimide (NHPI) as a catalyst and NaNO₂ as promoter in highly polar trifluoroacetic acid at room temperature can selectively oxidize methylarenes to corresponding benzaldehydes under high conversions of starting material. With nitric acid as promoter oxidations of cyclohexane, adamantane, diamantane, and 3-oxadiamantane gave, respectively, adipic acid, 1-hydroxyadamantane, 1-hydroxydiamantane, and 9-hydroxy-3-oxadiamantane with up to 90 % selectivity.

The density functional theory computations at the M06-2X and B3LYP-D3 levels demonstrate that the polarized transition structure (TS) for the hydrogen abstraction from toluene and benzyl alcohol with highly electrophilic PINO-radical is substantially stabilized by non-covalent interactions (π - π stacking). Such additional stabilization is not present in the TS for the H-abstraction from benzaldehyde thus retarding its over-oxidation to benzoic acid.

UDC 577.151.042

Synthesis and testing the non-peptide inhibitors of furin and investigation of the effect of reactivity environment components on its activity

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Screening some flavonoids and derivatives of azoles was performed to develop the new non-peptidic inhibitors of human proprotein convertase furin. We found out that these compounds, which did not contain positively, charged groups in the molecule, can interact with the enzyme and inactivate it. We carried out synthesis, docking and testing of antifurine activity of some aromatic amidinohydrazones with several amidinohydrazone groups (Am-groups) in the benzene rings. It was shown that the inactivation efficiency of furin by bisamidinohydrazones depends on the position of the Am-groups in the aromatic cycle, hydrophobicity of the linker, which interconnected benzene rings and replacing the hydrogen atom of the Am-group for methyl. The most effective inhibitor of synthesized derivatives ($K_i \sim 50 \text{ nM}$) was a compound with three positively charged groups in the molecule.

The influence of the reaction environmental factors (organic solvents and ions) on the furin activity was investigated, and found that Cs^+ , Mg^{2+} , Sr^{2+} , Cd^{2+} in the presence of Ca^{2+} (1mM) activated furin, but their affinities in comparison with Ca^{2+} were reduced by 18–150 times. The study of the influence on the enzyme of dielectric permeability of the medium, which polarity was changed by adding to the reaction mixture of organic solvents at concentrations of 0–30 %, showed, that the highest stability of furin was observed in DMSO solutions. It decreased in the series of organic solvents: DMSO >dioxane> ethanol > isopropanol > acetone.

УДК 547.321

Synthesis and properties polyfluorocontaining enones and its using for potential bioactive compounds preparation

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Structural design of fluorinated synthons among α,β -unsaturated ketons – enones like 1, power building blocks for synthesis of fluorocontaining potential bioactive compounds is actual. We have found that the excess of trifluoroacetic anhydride reacts with ortoacetates and previously unknown trioxobicycles 2 were afforded instead of expected enones 1.

Trioxobicycles 2 are hidden bis-trifluoroacetyl acetates and react easily with ammoniac, hydrazines and ureas with bis-trifluoromethyl containing heterocycles formation. Ester function in some pyrazoles and pyrimidine was transformed into trifluoromethyl group.

UDK 620.952

Receiving mixed fuel and biochar from biomass wastes

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The work is aimed at creating mixed fuels capable of expanding the range of products for the fuel market by attracting into their composition, in addition to the energy potential of plant biomass, the potential of organically produced waste which, when permanently stored and stored, presents an environmental hazard to the environment, namely sieges of municipal wastewater treatment facilities, the utilization of which is a problem, as well as coal dust, which in large quantities accumulates on Heat power station and lignin-sludges of cellulose production.

The resulting samples of mixed fuel are characterized by humidity not exceeding 15 %, ash content up to 8 % and calorific value of $15-21 \,\mathrm{MJ/kg}$.

Biogoil was obtained from a variety of biomass (cane, sorrel horse, millet, corn cobs, corn stalks), which was subjected to short-term heat treatment (1–3 min) in an inert nitrogen atmosphere at temperatures from 250 to 400 °C. The solid fuel thus obtained has a calorific value in the range of 21–24 MJ / kg and is characterized by low ash content, which allows it to be used not only for energy generation, for example in metallurgy, but also in industrial production, as a source of carbon.

UDC 547.541.521+547.787

Synthesis, *in vitro* and *in silico* studies of new 4,5-difunctionalized 1,3-oxazole derivatives

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The new 1,3-oxazole derivatives with nitrile or sulfonyl groups in position 4 of oxazole ring, and amino- or mercaptogroup, as well as sulfonyl or sulfinyl fragment in the position 5 have been synthesized. The introduction of electron-acceptor groups into the ring position 5: SO₂ (compounds 1 and 2) and SO (compound 3) has been shown to increase the antitumor and antiviral activity, which may be related with the increased binding energy of the ligand to the target.

This energy and the mathematical expression of biological activity are proportional to the value of the donor-acceptor parameter φ_0 which connected with the relative position of the frontier levels (HOMO, LUMO) in the conjugated systems, and for the oxazole derivatives this value is less than 0.5.

UDC 547.787.1

Synthesis of new azaheterocycles based on condensation products of carbonic acid amides with chloral or phenylglyoxal

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Nitrogen-containing heterocycles are the components of most natural and synthetic modern drugs. In order to obtain biologically active nitrogen-containing heterocycles, acyclic reagents – enamides (I) and α -chloralkylamides (II) were used as starting compounds.

R = H, Alk, Ar, Het; (f) = CN, C(O)OAlk, Alk = Me, Et.

Thus, on the basis of enamides (I), it have been prepared substituted 5-hydrazino-oxazoles (III), 4-oxazolecarboxylic acids (IV) with N- and S-substituents at the 5th position of oxazole ring, sulfonylchlorides (V) and (VI), sulfamides on their basis, oxadiazoles and thiadiazoles (VII) with amino acid fragment, nitrogen-containing bicyclic and tricyclic condensed systems (VIII-X).

The synthesized substances exhibited high biological activity.

UDC 547.854.5+54.057

Synthesis of new derivatives pyrimidintrione by ring-closing metathesis reactions

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A large number of 5-spiro-2,4,6-pyrimidintriones derivatives have been reported to possess biological activities that include anti-inflammatory activity, analgesic, antiviral and others.

Herein we want to report a synthesis of new spiropyrimidintriones by ring-closing metathesis reactions using a ruthenium-carbene catalyst (Grubbs-Hoveyda).

The chemical structures of the new synthesized compounds and their purity were confirmed by ¹H, ¹³C NMR spectral data, mass spectrometry and elemental analysis.

It should be noted that obtained spyrocyclic pyrimidinetrione derivatives have an unsaturated bond which can be chemically transformed to various functional groups to enhance or impart of biological properties.

UDC 577.1+577.11+577.2+581.1

Study of the effect of derivatives of pyrimidine on acceleration of the growth and development of pea plants during the vegetation period

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An actual problem for the modern agrarian sector is the development of new growth regulators for important agricultural crop – pea (*Pisum sativum* L.) cultivated in different countries around the world. Currently, the growth regulators of natural and synthetic origin are widely used in the agriculture to improve the growth and development of pea plants during the vegetation period and increase their yield. However, the great theoretical and practical interest is the elaboration of new ecologically safe plant growth regulators created on the base of low molecular weight five and six-membered heterocyclic compounds which are known to be used as a herbicides and plant growth regulating substances.

The main aim of our work was to study the stimulating effect of low molecular weight heterocyclic compounds, derivatives of pyrimidine synthesized at the Institute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine, on growth and development of pea (*Pisum sativum* L.) cultivar L35/11 middle stalwart bewhiskered during the vegetative period. It was found that the biometric indices of 21-day-old pea seedlings grown on water solution of chemical compounds, derivatives of pyrimidine used at the concentration 10^{-8} M exceeded the biometric indices of control plants grown on distilled water in average: at the 13-24 % – by the length of the main root, and at the 12-37 % – by total number of roots. The highest growth stimulating activity revealed the chemical compounds, derivatives of dihydroimidazo[1,2-c]pyrimidine, their activity was differentiated depending on the substituents in their chemical structure. Obviously, that the high growth regulating activity of the investigated chemical compounds, derivatives of pyrimidine is explained by their auxin-like and cytokinin-like stimulating action on the plant cell enlargement, proliferation and differentiation, which are the main processes of plant growth and development.

The obtained results confirmed the possibility of the application in the agricultural practice of derivatives of pyrimidine used at the concentration 10^{-8} M to improve the growth and development of pea (*Pisum sativum* L.) cultivar L35/11 middle stalwart bewhiskered during the vegetation period.

UDC 544.433.3+547.21

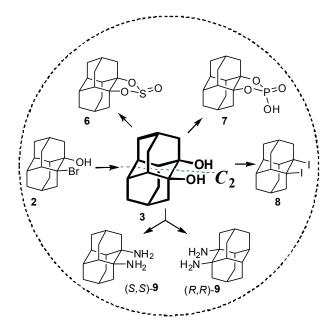
Preparation of novel diamantane derivatives via retro-barbier fragmentations

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Functionalized diamondoids provide exceptional combination of valued properties for the preparation of new building blocks and construction of new materials due to their multivalency, topological rigidity, chemical stability, and size/shape-particle control.

We present a simple and general route to previously unavailable vicinal diamondoid bis-derivatives based on the retro-Barbier fragmentation of readily available 1-hydroxydiamantane (1) followed by cage reconstruction[1]. The reaction of 1 with bromine in chloroform in presence of potassium carbonate gives 1-hydroxy-2-bromodiamantane (2) as the main product together with minor amounts of dihydroxydiamantane (3), bromoprotodiamantanone (4), and bromooxahomodiamantanol (5).



Compounds **2** and **3** display distinct reactivity and we were able to prepare a series of 1,2-disubstituted diamantanes (6-9). The C_2 -symmetric 1,2-diaminodiamantane (9), which may be viewed as analogue of conformationally-flexible 1,2-diaminocyclohexane – was separated to S,S-9 and R,R-9 enantiometric forms with ees > 97%.

The 1,2-substituted diamantanes thus obtained are attractive for various applications, particularly as chiral auxiliaries for asymmetric synthesis and components of metal-based antitumor agents. The extension of this reaction towards the bridge tertiary hydroxydiamantanes have also shown to be promising strategy for the synthesis of stable diamantane cage fragmentation products. The latter are viewed as versatile precursors of currently inaccessible heterodimondoids.

1. Fokin, A.; Pashenko, A.; Bakhonsky, V.; Zhuk, T.; Chernish, L.; Gunchenko, P.; Kushko, A.; Becker, J.; Wende, R.; Schreiner, P., *Synthesis*, 2017. **49** (09): p. 2003–2008.

UDC 547.786.541.521.54.057

Synthesis of new thiodiazepine derivatives of isoxazoles by ring- closing metathesis reactions

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Sulfonylamides are one of the important classes of bacteriostatic antibiotics that are widely used in medicine. Cyclic sulfanilamides are very promising from the standpoint of bioactivity. Thus, in particular, HIV-proteinase inhibitors were found among thiodiazepine derivatives.

On the other hand, there are considerable interest in derivatives of thiodiazepines in which there are isoxazole substituents, since this fragment is present in many molecules of biologically active substances, and those formed as a result of ring-closing metathesis reactions of the N, N' disubstituted derivatives of thiodiazepines, open up wide possibilities for further functionalization by double bonding of different pharmacophore groups.

In order to study the possibilities of obtaining such derivatives and develop methods for their synthesis, we have worked out a convenient way of obtaining a number of amines of the isoxazole series (5–8) by the Delepin reaction.

By this way of interaction of the latter with sulfuryl chloride in dichloromethane at a temperature of about 0 °C, corresponding sulfodiamides of the isoxazole series (9–12) were obtained in 66–76 % yields. Diallyl derivatives (13–16) were obtained by alkylation of the corresponding sulfodiamides (9–12) with allyl bromide in solutions of DMF in the presence of 2.5 eq. potassium carbonate at a temperature of 75–80 °C. Diallyl derivatives (13–16) were obtained in 73–81 % yields.

Ring- closing metathesis reactions of the derivative (13–16) were carried out in solutions of dry degassed dichloromethane in the atmosphere of dry argon at a temperature of 25–30 $^{\circ}$ C for 8–10 hours using a ruthenium-carbene catalyst ([Ru]) synthesized by us. Targeted isoxazole-containing thiodiazepines (17–20) were obtained in 74–85 % yields. The structure of all new compounds is confirmed by the data of elemental analysis and 1 H, 13 C NMR spectra.

Thus, a convenient way of obtaining sulfodiamides of the isoxazole series was worked out, and a number of new potentially biologically active isooxazole derivatives of thiodiazepines were synthesized for the first time by ring- closing metathesis reactions.

UDC 662.756.3+547.264+66.095.134

Peculiarity of alkali transesterification of oil by butanol-1 and products separation

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Synthesis of fatty acids butyl esters (FABE) by transesterification of triglycerides on KOH leads to yields no higher than 80–85 % and isn't followed by separation of products into glycerol and ester layers. It can be due to formation of reverse micelles, consisting of hydrophilic glycerol/water core surrounded by soap and monoglyceride molecules. Such type of colloid system is characterized by very high stability.

Using of self-prepared anhydrous solution of potassium butoxide in butanol eliminates the saponification process and leads to high FABE yields (90–95 %) and spontaneous glycerol separation. It is due to much less stability of system, containing micelles formed by glycerol surrounded only by monoglyceride molecules.

The yield of FABE continues to rise also throughout 24 hours of settling of reaction products, attended with glycerol separation. Glycerol layer collects alkali catalyst from reaction mixture. About 50 % of catalyst transfers to glycerol layer at first 12 minutes of reaction. At the same period of time increasing of FABE yield and growth of glycerol layer amount slow down sufficiently. Glycerol settled within 24 hours collects additional 20–30 % of catalyst to provide its amount in ester layer at range 20–30 % from loaded.

IR-spectra of settle glycerol layer is identical to IR-spectra of pure glycerol, which proofs soap, glycerides and ester absence. Chromatographic analyses show 78 % of glycerol, 2 % of butanol and trace amount of FABE. The counted quantity of potassium glyceroxide is about 20 %, due to potassium amount is 6.4 %. Potassium glyceroxide has poor solubility in non-polar reaction media, and mixture of glycerol and glyceroxide forms glycerol-glyceroxide layer.

УДК 547.571+547.592.12

Transformation of aromatic derivatives catalytized by basidiomychetous enzymes

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One of the key requirements of modern industrial organic chemistry is environmental safety. The most successful examples of environmental-friendly transformations are natural processes that continuously proceed in all organisms with the participation of biocatalysts, namely enzymes, and are characterized not only by exceptional safety and balance, but also by extraordinary efficiency under normal conditions. Among the diversity of biocatalysts, special attention is focused on the enzymes of basidiomycota, which are capable to decompose complex biopolymers, in particular lignin, and utilize it as a source of energy. Recently, we have discovered the potential of the above-mentioned enzymes for selective aerobic CH-oxidation of alkanes, the most complex objects in organic synthesis, utilizing the basidiomycetous fungus *D. albidofuscus* [1]. The next stage of the study was the oxidation of toluene under the developed conditions.

In the reaction medium, oxidation products of the methyl group, namely benzyl alcohol and benzaldehyde, as well as a mixture of cresols and phenol, were detected. The formation of the last product is unexpected, and the possible ways of its formation under these conditions are currently being investigated.

1. Zhuk, T. S.; Goldmann, M.; Hofmann, J.; Pohl, J. C. S.; Zorn, H., Preparative aerobic oxidations with basidiomycetous enzymes: CH-functionalization of adamantane. *J. Molec. Catal. B* **2015**, *122*, 87–92.

УДК 665.372 + 665.765

Metallurgical antifriction grease on basis of the transformed product of phosphatide concentrate

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Phosphatide concentrate is a by-product of vegetable oil production, with no clear ways to conversion it or use it. On the other hand, metallurgical greases are produced in our country in an insufficient quantity, have an oil base, which entails a number of resource and environmental problems. In this regard, the main focus of the study was to develop a method for the use of phosphatide concentrate as a raw material for the production of metallurgical greases, as well as to compare the properties of the resulting substances with known industrial products with a view to their replacement.

The proposed method includes the amidation of a phosphatide concentrate from oxyethylene ethylenediamine at a temperature of 170–180 °C. for 5–6 hours with the release of the product. In the second step, the necessary components were added to the resulting product, carbonatation was performed, and the prepared grease was produce. The process of carbonatation is quite widely known in the literature, so we took two of the most common methods and obtained samples of metal-lurgical greases.

Today, the most common metallurgical greases are complex lithium and complex calcium greases, for this reason they were used as a comparison.

| Name of indicator, unit of measure | Test method | Complex Li | Complex Ca | Obtained greases | |
|---|-----------------|----------------------|----------------------|----------------------|--------------------|
| | | grease | grease | Prototype 1 | Prototype 2 |
| Dropping point, °C | GOST 6793 | > 230 | > 230 | > 250 | > 250 |
| Penetration at 25 °C (worked 60 strokes), | GOST 5346 | | | | |
| mm·10 ⁻¹ | 0031 3340 | 330 | 263 | 294 | 285 |
| Ultimate strength at 20 °C, Pa | GOST 7143 | 240 | 200 | 325 | 345 |
| Shell Roll Stability (60 °C, 6 h). | ASTM D1831, | | | | |
| Failure index, (Κφ), % | (mod. UkrNDINP | 96,9 | 84,8 | 60,0 | 52,1 |
| | "MASMA") | | | | |
| Tribological characteristics on FBM: | | | | | |
| – critical load, N | GOST 9490 | 921 | 1039 | 1646 | 1646 |
| welding load, N | | 1646 | 2323 | 2546 | 2938 |
| Water-washout (79 °C, 1 h), % | ASTM D1264 | 1,0 | 7,5 | 2,7 | 2,5 |
| Increase acid number (150 °C, 10 h), | GOST 5734 | 1,20 | 1,65 | 0 | 0 |
| mg KOH/g | 0031 3734 | 1,20 | 1,03 | U | U |
| Protective properties under dynamic conditions. | UkrNDINP | | | | |
| Corrosion rate, mm/year | "MASMA" | | | | |
| | "Dinacorrotest" | 3,9×10 ⁻⁴ | 9,3×10 ⁻⁴ | 3,4×10 ⁻⁴ | $3,5\times10^{-4}$ |

Test results indicate the possibility of using phosphatide concentrate as a raw material for the production of metallurgical greases to replace existing commercial products.

UDC 547.422.02+547.412.722+547.597

C_s-trishomocubane-based epoxides transformations induced by BF₃·Et₂O

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It was found that epoxy-derivatives **1**, based on pentacyclo[$5.4.0.0^{2.6}.0^{3.10}.0^{5.9}$]undecane (C_s -trishomocubane) hydrocarbon cage, in presence of BF₃ etherate at -80 °C isomerized to the kinetical mixture of products with *endo-C_s*-trishomocubyl-8-carbaldehyde as major component. At the same time, in these conditions, a significant amount of D_3 -trishomocubane fluoroal-cohol **3** is formed, whose structure was determined by NMR and X-Ray analysis. Mixture obtained in abovementioned conditions at elevated temperatures in the presence of BF₃ etherate gives thermodynamically favored *exo-*aldehyde (**2**) exclusively.

Although 1,2-fluoroalcohols are common byproducts in rearrangement reactions of epoxides in the presence of BF₃ etherate, in very few cases formation of 1,3-fluoroalcohols is mentioned. Transformation of 3 into exo-2 is the first case of more stable D_3 -trishomocubane hydrocarbon cage isomerization to less favorable C_s -trishomocubane. The result of established quantum-chemical calculations shows an existence of common zwitter-ionic intermediate for all the products of reaction (aldehydes 2 and fluoroalcohol 3). However, calculated activation barrier of reverse aldehyde to zwitter-ion transformation was high enough for explanation of thermodynamical product (exo-2) formation.

UDC 621.351

Carbon carriers obtained by the method of template synthesis as the basis of catalytic systems

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In recent decades the nanostructured carbon materials have been intensively developed and studied. Some of them have already been introduced into production. Nanoporous carbon adsorbents have been received by method of template synthesis, using commercial silica gel SG-60 which is now widely used in biochemistry as a template. Methods of chemical modification of surface of nanoporous carbon adsorbents by precursors of various nature have been developed. It has been shown that after chemical modification of the surface, the latter is very highly specific and the synthesized carbon adsorbents, by others parameters, completely meet requirements of biochemists to such type of materials. Highly effective methods of mono- and polylayer modification of the high-porous nanostructured carbon materials that enable preparation of highly effective adsorbents, catalysts and other materials to be applied in modern biochemistry, biotechnology, pharmacology and liquid chromatography have been developed. Chemical modification of surface of nanostructured carbon materials by organic polylayers confers the necessary specificity to the material surface with preservation of high values of the surface activity. Content and thermo stability of carbon materials functional groups have been studied depending on conditions of their oxidation on the surface of nanoporous materials with friable and compact structure of carbon framework, active carbon on synthetic and natural base and the nonporous colloidal graphite. Calculation of activation energy of oxides thermal destruction on the carbon surface with carbon dioxide emission has been carried out by Cvetanovic method. Thermogravimetric studies of nanoporous carbon materials have been carried out. The main purpose of thermogravimetric studies of the synthesized and initial samples of nanoporous carbon materials was to establish of their thermal stability and, if possible, to obtain mathematical relationships that describe them.