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**ТЕЗИ**

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**Novel metal complexes of Schiff bases  
as multifunctional additives for alternative fuels**

*Ye.O. Bozhko, Ye.V. Sheludko, R.S. Zhyla, V.S. Pilyavsky, Ye.V. Polunkin*

*Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine, Kyiv  
Department of homogeneous catalysis and additives to petroleum products*

Metal complexes of Schiff bases have a number of valuable properties that determine their practical applications in various fields of science, technology and medicine.

We have synthesized some metal salen complexes. These types of compounds are effective antioxidants. On the basis of antioxidative studies it is clear that the copper (II) azomethine complex acts catalytically. The chain termination of organic compounds oxidation occurs repeatedly ( $f > 350$ ). For instance, the inhibitory efficiency rate ( $f_{k_{ROO}}$ ) of Cu complex of N-salicylidene-4-octyloxyaniline are given in Table. The initiated oxidation of benzyl alcohol used as a model reaction ( $W_i = 2,98 \cdot 10^{-8}$  mol/(l·s), 50 °C).

Inhibitor	$f_{k_{ROO}}, 10^5, 1/(\text{mol}\cdot\text{s})$
N-(4-hydroxysalicylidene)-4-octyloxyaniline (1)	0,07
bis [N-salicylidene-4-octyloxy] copper (II) (2)	9,8
2,6-bis(1,1-dimethylethyl)-4-methylphenol (3)	0,26

Comparing their activity, we found that the complex (2) greatly exceeds the known acceptor peroxide radicals (3).

The findings reveal that the introduction of carboxyl groups in the structure of the ligand compared with other groups greatly enhances the value of the critical load indicator substrate (ethanol, fuel E-85) with the addition of complexes. Thus, for complexes Cu, Zn, La with hydrocarbon substituents increase the critical load factor is 1,6, and for compounds containing –COOH and –OH groups in their structure, this figure rises up to 2,5.

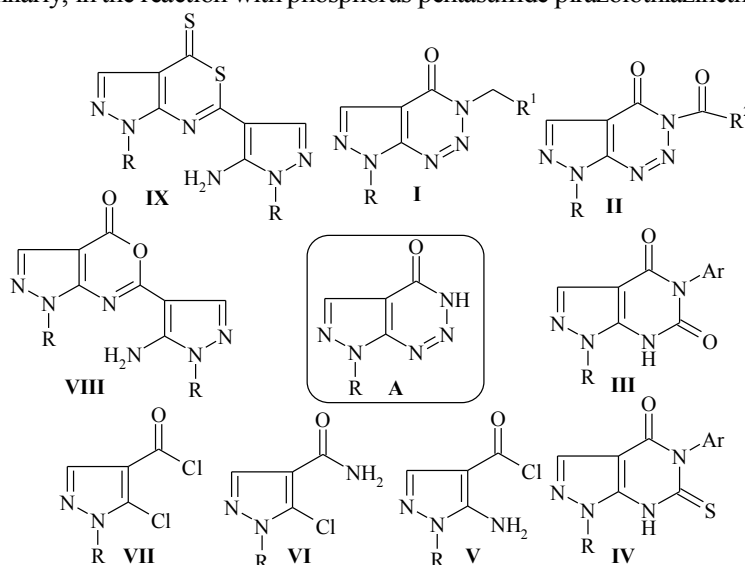
Schiff bases metal complexes could be used as an antioxidant and wear-reducing additives for alternative motor fuels.

## Properties of Pyrazolo[3,4-D][1,2,3]triazin-4-ones and products of their transformation

*A.O. Gurenko, B.M. Khytova, S.V. Klyuchko, V.S. Brovarets*

*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of chemistry of bioactive nitrogencontaining heterocyclic bases*

In this paper the synthetic potential of insufficiently studied pirazolotriazines **A** is considered. Pirazolotriazines **A** were prepared by diazotization of 5-amino-4-carboxamide pyrazoles with aqueous sodium nitrite. Pirazolotriazines are regioselectively alkylated and acylated at center N-3 to form the structures **I**, **II**. Heating of compounds **A** with isocyanates and isothiocyanates results in triazine ring destruction and formation of substituted pyrazolopyrimidine **III** and pirazolothio-pyrimidines **IV** respectively. Treatment of pirazolotriazines **A** with thionyl chloride, leads to acid chlorides **V** and the amide **VI** depending on reaction conditions. As a result of interaction of compounds **A** with phosphorus oxychloride, acid chloride **VII** is formed. Heating of pirazolotriazines **A** with phosphorus pentoxide in dioxane leads to the formation of substituted pirazolooxazines **VIII**. Similarly, in the reaction with phosphorus pentasulfide pirazolothiazinethiones **IX** are formed.



## Focusing of protons' current by weak magnetic field

*P.Y. Yevdokimov, R.V. Korzh, V.A. Bortyshevskiy*

*Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine,  
Laboratory of Zeolite Catalysts and Sorbents*

Here we study the possibility of focusing the current of protons in solids by weak magnetic field with intensity of 1.3 T. Protons were obtained by the electrolysis of a 5 % aqueous solution of  $H_2SO_4$ . They were transported through the proton conductor based on Nafion-117 introduced into pores of tubes from alumina-zirconium ceramics. The collective cathode was made in the form of a cylinder or cone. These forms of cathodes were selected for the following reasons. A positive charge moving in an electric field  $E$  and a constant magnetic field  $B$  is acted by the Lorentz force which curved the trajectory of the proton. This curvature in terms of the cylindrical cathode causes the protons to pass through an uniform electric field around. The vector of Lorentz force is directed from the plane of the drawing. When using the cathode as a cone, proton moves in a nonuniform electric field.

The results of current-voltage tests have shown that the study proton conductor has two zones of proton conductivity: low potential at 0,3–0,75 V with the change of the conductivity of 2–2,5 orders, and high potential at 1,5–3,0 V with the conductivity rise to 1–1,5 orders. The application of the perpendicular magnetic field regardless of its direction encourages sensitivity to changes in low potential region. These results give a positive assessment for the possibility of creating the sources of currents of protons, which could be regulated and focused by electric and magnetic fields, for new catalytic processes.

## Perspectives of bioethanol using in biodiesel synthesis

S.O. Zubenko

*Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine,  
Department of Catalytic Synthesis*

The fuels of the biological source base are as the alternative to the usual petroleum fuels. Biodiesel is produced as a rule by methanol homogeneous catalytic transesterification of vegetable oils and the fats. The using of bioalcohol for biodiesel synthesis makes the raw materials for its production fully renewable. Today bioethanol is the most utilized bioalcohol in the world. Simultaneously *n*-butanol using as a transesterification agent have been proposed by some researchers.

Now *n*-butanol production becomes in new wave of development. Modern technologies of biobutanol synthesis allow producing relatively cheap alcohol.

The principal scheme of production of butyl esters of fatty acids of vegetable oils on the base of literature data has been proposed. The process includes fermentation of natural materials like halm with butanol, ethanol and acetone mixture production. Nowadays technologies of the butanol separation allow obtaining pure alcohol. There are two ways of glycerin as by-product of transesterification applying: its fermentation for biobutanol production or its acetalization by acetone to produce solketal, which can be use as fuel additive.

Transesterification of linseed oil by *n*-butanol have been studied. The investigation has been carried out in a wide range of reaction conditions: temperature (20–80 °C), reaction time (1–6 hours), alcohol/oil molar ratio (5–10) and amount of catalyst KOH (1–2 wt. %). The best yield of esters (87,5 %) has been obtained at 20 °C, 2 % KOH, 6 hrs., alcohol/oil molar ratio 10.

Therefore, biobutanol can be considered as a perspective alcohol for more careful investigation as transesterification agent for biodiesel production.

UDC 541.49:541

## Study of the complexation of Calix[4]arene hydroxymethylphosphonic acid with amino acids and N-acetyltryptophan amide by RP HPLC

O.I. Kalchenko<sup>1</sup>, S.O. Cherenok<sup>1</sup>, R.V. Rodik<sup>1</sup>, Y. Mely<sup>2</sup>, V.I. Kalchenko<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry, National Academy of Sciences of Ukraine  
02660, Murmanska str. 5, Kyiv, 94, Ukraine, E-mail: oik@ioch.kiev.ua*

<sup>2</sup>*Universite de Strasbourg, 74, Laboratoire de Biophotonique et Pharmacologie UMR CNRS,  
Strasbourg, Route Du Rhin, 60024, BP, 67401 Illkirch Cedex, France*

Calixarenes and their derivatives are widely used as a molecular platforms on the design of the artificial receptors for the recognition and binding of organic substrates [1–3]. The calixarene hydroxymethylphosphonic acid (CPA) complexation with amino acids and N-acetyltryptophan amide (NATA) were studied. The binding constants of the CPA complexes with amino acids and NATA (20000–40000 M<sup>-1</sup>) were calculated.

It was established that CPA is an effective receptor for the recognition and binding for amino acids and NATA. The influence of the nature of the substituents in the amino acid molecules on the binding constants of CPA inclusion complexes was studied. The correlation of the binding constant values with the Log P of amino acids has been made. CPA is an effective binder of the amino acids and NATA in water solution. These results provide the foundation for the design of the protein inhibitor (by Trp residue) that will block the activity of the HIV virus in the human body. The study of CPA in molecular recognition and binding of Trp residues in proteins is in progress.

1. O. Kalchenko, S. Cherenok, R. Rodik, A. Drapailo, S. Miroshnichenko, V. Kalchenko. *Phosphorus, Sulfur, Silicon*, 2011, **186**, 898.

2. O. Kalchenko, S. Cherenok, O. Yushchenko, V. Kalchenko. *J. Incl. Phenom.*, 2013, **76**, 29.

3. O. Kalchenko, A. Drapailo, S. Shishkina, O. Shishkin, S. Kharchenko, V. Gorbachuk, V. Kalchenko. *Supramol. Chem.*, 2013, **25**, 263.

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## Autohydrolysis of pentosecontaining raw material

*D.S. Kamenskyh, T.V. Tkachenko, V.O. Yevdokymenko, D.A. Matviychuk, V.I. Kashkovskiy*

*Institute of Bioorganic Chemistry and Petrochemistry, Kyiv  
Department of Organic and Petrochemical Synthesis*

Now biomass is one of the main promising sources of energy and raw materials. Since Ukraine is agriculture country the best raw materials for autohydrolysis are agriculture waste e.g. straw, corn cobs, different plants stalks etc. The 80 mil. ton they one were formed in 2012 year.

We were worked out and assembled laboratory equipment on this investigation stages. Corn cobs composition was identified. It was ascertained that they consist of carbohydrates, cellulose and lignin 0,8, 43, 41 % (as weight percent of dry samples) respectively. It should be noted that particle size of original herbaceous lignocellulosic biomass hadn't effect on final product. Dependence of corn cobs autohydrolysis versus contact time was investigated at 200 °C and pressure by saturated vapor or excess argons pressure from bottle. Extremal dependence of sugars and lignin amount versus contact time was obtained. Ceiling amount of sugars and minimum lignin observed at a 30-minute processing of raw materials in the reactor at 200 °C was established. The use of excessive pressure is shown achieves a greater degree of release of soluble carbohydrates compared with data for the reaction without excessive pressure.

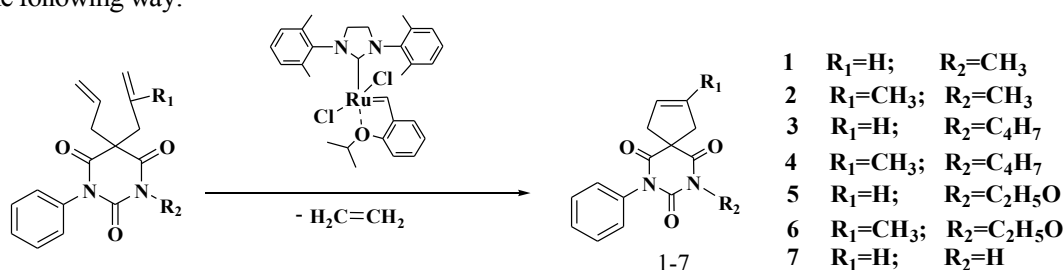
UDC 547.854.5+54.057

## The new spirocycloalkenic N-aryl-N'-alkylpyrimidine-2,4,6-trione derivatives synthesis by means of ring-closing

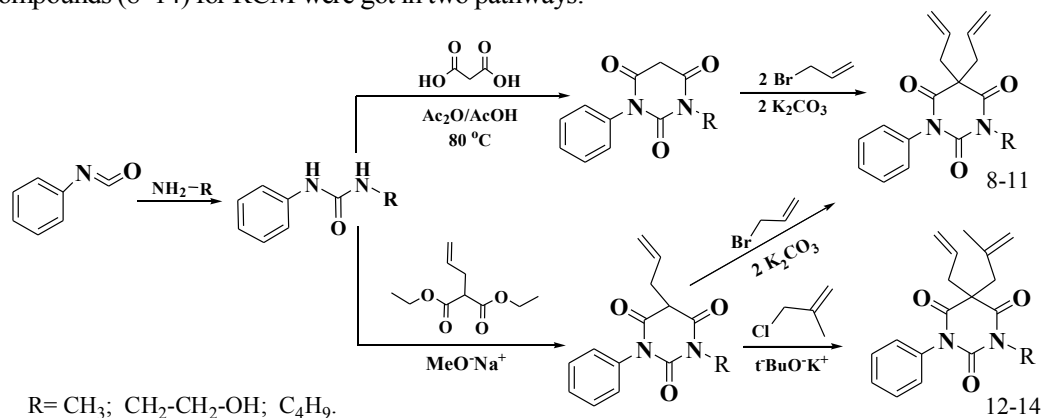
*N.I. Kobyzhcha, V.M. Holovatiuk, Yu.V. Bezugly, V.I. Kashkovsky*

*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of organic and petrochemical synthesis*

It has been synthesized the new series of 5-spiropyrimidine-2,4,6-triones (1–7) via ring-closing metathesis reactions (RCM) in the following way:



Starting compounds (8–14) for RCM were got in two pathways:



The structures of all new synthesized compounds were verified by NMR spectroscopy (1H).

The virtual screening of resulting products (1–7) was realized by means of Prediction Activity Spectra for Substances program. The obtained data were shown, that the aforementioned compounds could be testosterone 17beta-dehydrogenase (NADP+) inhibitors, anaphylatoxin receptor antagonist, kidney function stimulant also they may have antieczematic and other biological activities with a high probability.

## Development model system for determining of influence of physiological activity substances on key enzymes of oxylipin synthesis

*V.M. Kopich, G.I. Kharitonenko, T.D. Skaterna, O.V. Kharchenko*

*Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine  
02660, Kyiv-94, Murmanskaya str. 1, Ukraine, kopich@bpci.kiev.ua*

It was investigated the influence of brassinosteroids, abscisic acid, lysophospholipids, phosphatidic acid, 13-hydroperoxide linoleic acid on 9- and 13-lipoxygenases activity, key enzymes of oxylipin synthesis *in vivo* and *in vitro* model systems. Determined value  $V_{max}$ ,  $[S]_{0,5}$  and  $h$  for lipoxygenase oxidation of linoleic acid with and without of 50  $\mu\text{M}$  lysophosphatidylinositol are  $114,04 \pm 25,8$  and  $3,29 \pm 0,08$   $\mu\text{mole}/\text{min}$ ;  $0,48 \pm 0,05$  and  $0,12 \pm 0,002$   $\text{mM}$ ;  $2,44 \pm 0,05$  and  $3,81 \pm 0,14$  respectively. In model systems of mechanical wounding on potato tubers *in vivo* under conditions of exogenous 1  $\mu\text{M}$  linoleic acid 13-hydroperoxide application was found a significant decrease in lipoxygenase oxidation velocity and biotransformation of linoleic acid 13-hydroperoxide. It was determined the inhibitory effect of 10  $\mu\text{M}$  phosphatidic acid on linoleic acid 13-hydroperoxide biotransformation. To significant changes in the activity of plant 9- and 13-lipoxygenase at low temperature, high salt concentration and under exogenous 1  $\mu\text{M}$  24-epibrassinolide and 10  $\mu\text{M}$  abscisic acid influence were founded. Obtained results indicate on possibility to involve lysophospholipids, brassinosteroids, lipoxygenase primary metabolites to regulation of lipoxygenase cascade and communication between multiple signaling pathways of plant cells.

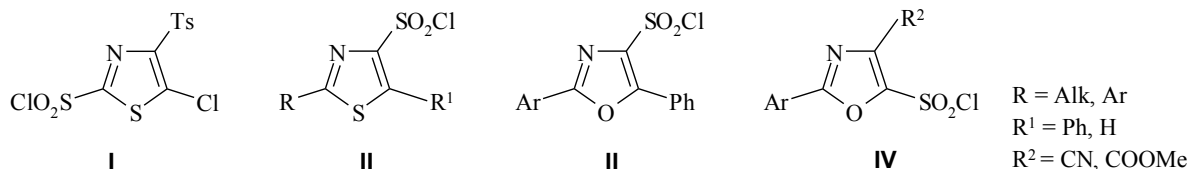
UDC 547.787+547.853+548.737

## Synthesis and properties of new 1,3-thiazol- and 1,3-oxazolesulfonylchlorides and their derivatives

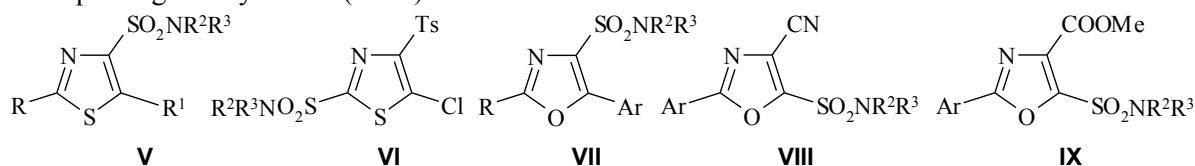
*A.M. Kornienko, S.G. Pilyo, V.M. Prokopenko, V.S. Brovarets*

*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of Chemistry of Bioactive Nitrogencontaining Heterocyclic Bases*

We developed preparative syntheses of 1,3-thiazol- and 1,3-oxazolesulfonyl-chlorides (I - IV).

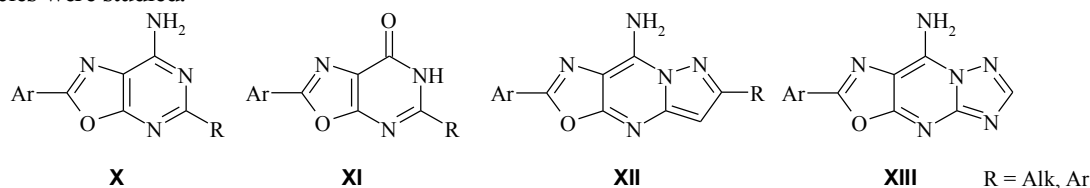


Corresponding sulfonylamides (V-IX) were also obtained.



$\text{NR}^2\text{R}^3 = \text{NH}_2, \text{NHCH}_2\text{Ph}, \text{NHPh}, \text{NMe}_2, \text{N}(\text{CH}_2)_5, \text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$

Reactions of 2-aryl-4-cyano-1,3-oxazol-5-sulfonylchlorides and 2-aryl-1,3-oxazol-4-methoxycarbonyl-5-sulfonylchlorides with amidines, aminopyrazoles and aminotriazole with formation of bicyclic (X, XI) and tricyclic (XII, XIII) azaheterocycles were studied.



Species with high antivirus and anticancer activity were found among synthesized compounds.

## Influence of conditions of the zeolite X ammonium hexafluorosilicate modification on the toluene with methanol alkylation

*M.M. Krylova, Yu.G. Voloshyna, V.V. Ivanenko, O.P. Pertko, L.K. Patrylak, K.I. Patrylak*

*Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv,  
Department of Catalytic Synthesis*

Styrene is the most desired product of the toluene with methanol side-chain alkylation reaction. The reaction proceeds over the base catalysts like low silica alkaline-exchanged zeolites, but with utterly low selectivity. Xylene isomers concurrently appear on the such contacts as the result of ring alkylation.

The aim of the work is to evaluate the selectivity of the toluene with methanol alkylation reaction, realized over zeolite X modified with ammonium hexafluorosilicate under different conditions.

The catalysts preparation includes the ammonium hexafluorosilicate treatment of zeolite X in aqua or ammonium acetate medium following by ion exchange with  $\text{KNO}_3$  or  $\text{KOH}$  and then the samples obtained were impregnated with 10 % wt.  $\text{CsNO}_3$ . The catalysts have been tested in the micro pulse setup at 400–500 °C (carrier gas – helium, toluene : methanol molar ratio 2 : 1).

It was determined that ammonium hexafluorosilicate modification causes rise of the catalyst activity in comparison with such for the unmodified sample. Side-chain alkylation occurs exclusively on the modified in aqua medium catalysts. Such catalysts produce in 3–11 times more styrene than sample modified in ammonium acetate. Moreover, the significant increase of styrene:ethylbenzene ratio in the products has been observed. Therefore, the ammonium hexafluorosilicate treatment in the aqua medium following by ion exchange with both  $\text{KNO}_3$  and  $\text{KOH}$  and cesium impregnation seem to be the most effective catalyst modification procedure.

UDC 544.032.7

## Hybrid nanocomposites of conducting polymers for ammonia and amines detection

*S. Mikhaylov<sup>1,2</sup>, A. Pud<sup>1</sup>, J.-L. Wojkiewicz<sup>2</sup>, P. Coddeville<sup>2</sup>*

*<sup>1</sup>Institute of Bioorganic Chemistry and Petrochemistry NAS of Ukraine,  
Chemistry of functional materials department*

*<sup>2</sup>Mines Douai, Département Sciences de l'Atmosphère et Génie de l'Environnement (SAGE)*

The detection of ammonia and amines gases is an important challenge at present time. Specifically clinical diagnostics, agriculture, industrial processes, environment protection need compact, sensitive and cost-effective solutions in the matter. As a response to this challenge we focus our work on the development of polyaniline (PANI) and polypyrrole (PPy) based hybrid nanostructured composites with high sensitivity to ammonia and amines at concentrations down to low ppb level. Unlike their neat components, these new nanocomposites, made through combination of PANI or PPy with semiconducting metal oxide nanoparticles, exhibit synergistic effect due to specific chemical and physical interactions along polymer-oxide interfaces existing inside the nanocomposite. The used fabrication protocols involved simple one-step chemical aniline or pyrrole polymerization in the presence of  $\text{TiO}_2$  nanoparticles under action of oxidant  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or  $\text{FeCl}_3$  respectively. In case of aniline the dodecylbenzenesulfonic (DBSA) and laurilsulfate (LSA) acids were used as dopants. This approach allowed formation of nanocomposites with core-shell morphology. The influence of the polymerization conditions and dopant nature on key properties of the target nanocomposite materials was investigated. The composition, structure and core-shell morphology of the synthesized nanocomposites was confirmed by FTIR, XRD and TEM methods. The  $\text{TiO}_2$ -PANI/DBSA and  $\text{TiO}_2$ -PANI/LSA nanocomposites showed highest and reproducible responses to ammonia, methylamine (MA) and trimethylamine (TMA) gases even at low concentrations (down to 200 ppb).

## Using of heteropolyacid catalysts in the process of glucose and cellulose conversion

*D.V. Molodyy, L.V. Golovko*

*Institute of bioorganic chemistry and petrochemistry of the NAS of Ukraine,  
laboratory of sorbents and supports*

Dehydration of glucose and cellulose in an aqueous solution in hydrothermal condition with presence or absence of heteropolyacid catalysts was investigated.

The method of temperature programmed desorption of ammonia from the surface of catalysts was confirmed the superacid grade of catalytic centers of the synthesized hybrid catalysts. The Keggin structure of heteropolyacid in the composition of hybrid catalysts was confirmed by IR spectroscopy.

It was showed that at the equal conditions of conversion on hybrid catalysts the depth of transformation of glucose considerably exceeds conversion of cellulose. The catalytic activity of hybrid catalysts  $H_3PW_{12}O_{40}/SiO_2$  in 2–2,5 times higher than the activity of pure  $H_3PW_{12}O_{40}$ . The ratio of the reaction products was almost equal in presence and absence of hybrid catalysts.

It was shown that temperature dependence of 5-hydroxymethylfurfural yield as a result of conversion reaction of glucose has extreme character with a maximum at the temperature of 190 °C.

UDC 547.814.5

## Synthesis of isoflavone Mannich bases and their transformation

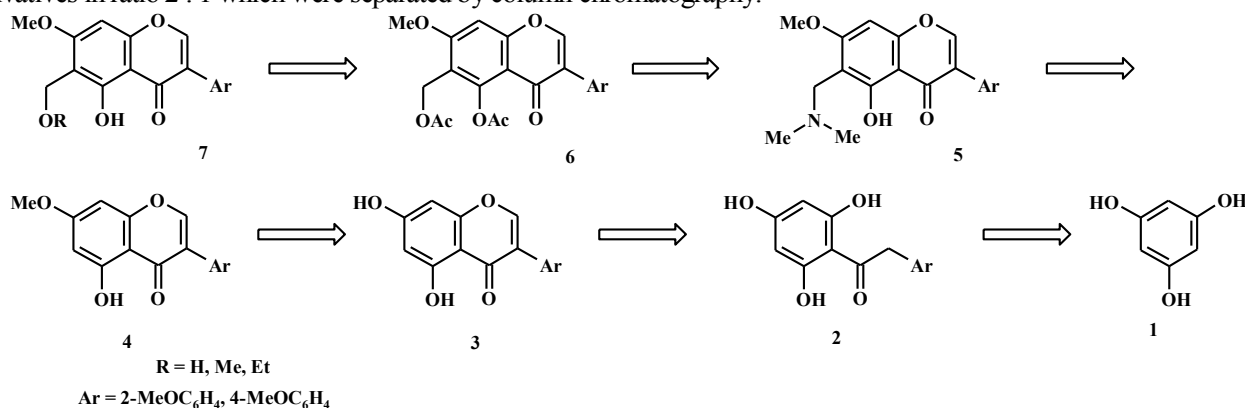
*G.P. Mrug<sup>1</sup>, S.P. Bondarenko<sup>2</sup>, M.S. Frasinuk<sup>1</sup>, O.M. Vasylenko<sup>1</sup>*

*<sup>1</sup>Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv,  
Department of nitrogen-contain heterocyclic compounds;*

*<sup>2</sup>Kyiv Taras Shevchenko National University, Kyiv*

Chromane alkaloids and their synthetic analogues play significant role for the development of the new type of drugs. We studied synthesis the aminomethyl- and (alk)oxymethyl derivative of 5-hydroxy-7-methoxy- and 7-hydroxy-5-methoxyisoflavones as alkaloid and synthetic flavones analogues, which possess CDK1 inhibition, and there are promising anticancer compounds.

Thus, the aminomethylation of 7-hydroxy-5-methoxyisoflavones led to formation of 8-aminomethyl derivatives only. The aminomethylation of regioisomeric 5-hydroxy-7-methoxyisoflavones **4** led to formation of 6- and 8-aminomethyl derivatives in ratio 2 : 1 which were separated by column chromatography.



Interaction of the synthesized Mannich bases **5** with acetic anhydride/potassium acetate were synthesized di-O-acyl 5-hydroxy-6-hydroxymethyl-7-methoxyisoflavone **6** derivatives. The deacylation of these compounds in alcohol led to formation of unexpected 6-alkoxymethyl derivatives **7**. Cristatein and its derivatives were synthesized by hydrolysis of compounds **6** in water-dioxane mixture. The synthesized compound structures were confirmed by 2D NMR spectroscopy (COSY, NOESY, HMBC etc. methods).

UDC 547.786.541.521.54.057

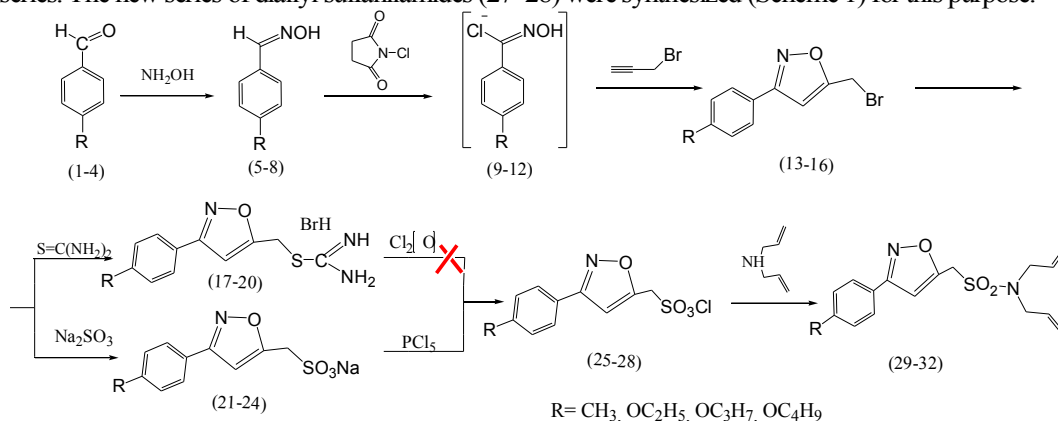
## Synthesis of new pyroline containing isoxazole derivatives by ring-closing metathesis reactions

*O.V. Pavliuk, Y.V. Bezugly, V.I. Kashkovsky*

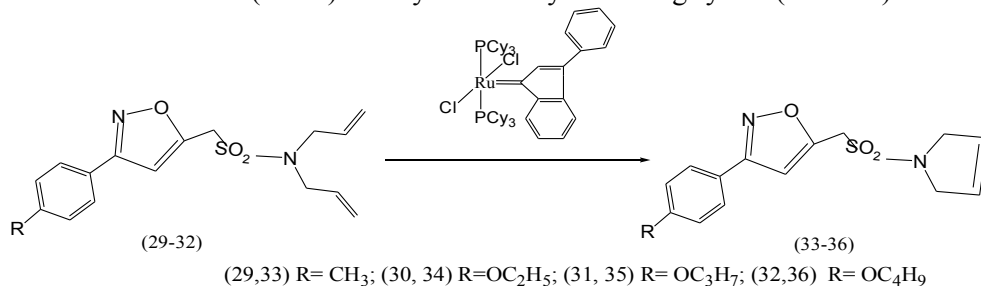
*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of organic and petrochemical synthesis*

Sulfonamides and their isoxazole derivatives, have recently attracted much attention of researchers as objects for pharmacological investigations. A number of biologically active compounds has been identified among this class of substances and some of which have already found practical use as commercially available pharmaceutical drugs.

We investigated the possibility of using ring-closing metathesis reactions for synthesis of new pyroline containing sulfonamides of isoxazole series. The new series of diallyl sulfanilamides (27–28) were synthesized (Scheme 1) for this purpose.



Later, by means of reacting of the sulfonamides (29–32) with 1 mole% ruthenium carbene catalyst (Ru) new sulfonylamide derivatives of Isoxazole (33–36) were synthesized by us with high yields (85–90 %)



The structures of all new compounds were verified by <sup>1</sup>H NMR spectroscopy.

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## Dynamic Phenomena in Zeolites

*O.P. Pertko, K.I. Patrylak*

*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine,  
Department of Catalytic Synthesis*

Zeolites are well known modern catalysts of carbonium ion petroleum-refining processes. Their catalytic properties depend from the nature of exchanged cations and generated acid sites. Since zeolites characterize by developed porous structure and molecular sieve effect, availability of active sites is a key point for catalytic conversion. Therefore, any information about the cation distribution and behavior within the zeolite framework is of great importance.

The aim of presented work is to use ammonia TPD method to determine the localization of the cations in the zeolite structure. As the research object the simplest zeolite form NaY has been selected.

Experiment procedure consists in zeolite sample (0,1 g) dehydration (up to 380 °C), ammonia adsorption at 200 °C, ammonia thermoprogrammed desorption (200–500 °C) and sample rehydration. After that, the experiment was repeated.

Absolutely different ammonia thermodesorption in the thirty consecutive experiments from the being dehydrated-rehydrated NaY zeolite has been revealed. This picture has been explained by changing the current location of the cations in the zeolite structure.

The zeolite was considered as the system of point charges which according Earnshaw's theorem cannot has the energy minimum, and so any negligible action can turn out the zeolite from the state of unstable equilibrium. Therefore, such dynamic phenomena as permanent motion of exchange cations is the condition of zeolite structure stability.



UDC 547.321

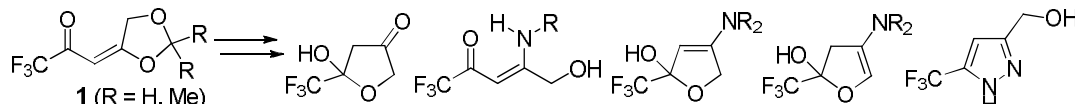
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## First example of [3+2] intramolecular cyclization with new fluorocontaining cyclopentenones formation

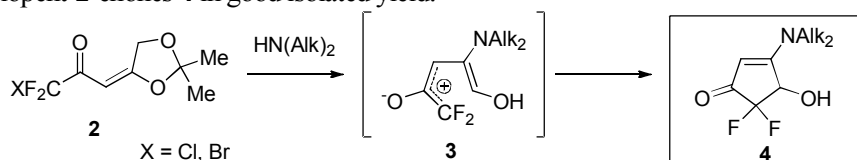
*K.V. Tarasenko, V.E. Ivasyshyn, I.I. Gerus, V.P. Kukhar*

*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of Fine Organic Synthesis*

Recently we have developed the synthesis of new type of fluorinated **enones** – **cyclic enones 1** bearing additional protected hydroxymethyl function, that was successfully utilized in various synthetic purposes. For example, some of CF<sub>3</sub> containing products were obtained:



Now we have synthesized new **cyclic enones 2** bearing (chloro,bromo)difluoromethyl groups (CClF<sub>2</sub> or CBrF<sub>2</sub>) and unexpectedly found that the reaction of the **enones 2** with an excess of secondary amines afforded to 3-dialkylamino-5,5-difluoro-4-hydroxycyclopent-2-enones **4** in good isolated yield:



We propose that the formation of new C–C bond is a result of previously unknown [3+2] intramolecular cyclization of an intermediate **3**. The *gem*-difluorocyclopentenones **4** are versatile intermediates to synthesize a wide variety of difluoromethylene analogues of biologically interesting compounds.

UDC 544.72

## The effect of carrier on the conductivity of proton conductors based on nafion

*D.O. Trepyadko, R.V. Korzh, V.A. Bortyshevskiy*

*Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine,  
Laboratory of Zeolite Catalysts and Sorbents*

The purpose of our study was the investigation of the influence of the structure of the organic carriers for the conduction of proton conductors based on Nafion 117.

It was developed and designed the installation for the measurement of total and proton conductivity of proton conductors with length up to 25 cm in the temperature range from 15 to 200 °C at atmospheric pressure and relative humidity of 100 %. The proton conductor was made by coating from a solution of Nafion 117 of the prepared media with structures shown in Table.

Table. Organic carriers for proton conductors based on Nafion 117

Fiber	polyethylene terephthalate	poly-para-phenylen terephthalamid	cellulose
Formula			
Tensile strength, kgf/mm <sup>2</sup>	17.2	362.0	43.0
σ of proton conductor carried on, S/cm	1.3×10 <sup>-1</sup>	1.4×10 <sup>-2</sup>	1.7×10 <sup>-1</sup>

The developed experimental setup will allow the further simplifying of the search for the optimal proton conductor. Last one would provide the proton transport in particular, and hydrogen at all, at long distances to the necessary places, and most importantly, in controlled amounts.

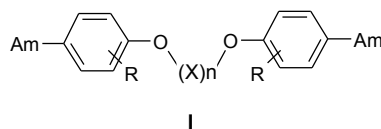
## Development of non-peptide inhibitors of furin

*T.V. Osadchuk<sup>1</sup>, O.D. Fedoryak<sup>1</sup>, V.V. Kyslyy<sup>1</sup>, O.P. Kozachenko<sup>1</sup>, V.S. Brovarets<sup>1</sup>, V.K. Kibirev<sup>2</sup>*

<sup>1</sup>*Institute of bioorganic chemistry and petrochemistry, National Academy of Sciences of Ukraine, Kiev*

<sup>2</sup>*Palladin Institute of biochemistry, National Academy of Sciences of Ukraine, Kiev*

Furin is a proprotein convertase that is a member of a family of serine proteases. The purpose of the work is design and synthesis of new non-peptide furin inhibitors. The best results were obtained with bis-amidinohydrazone derivatives (**I**). The inhibition mechanism was found to be competitive and mixed.



The antifurin activity was shown to grow with the increase of the length and hydrophobicity of the bridge. The most active compounds containing in the bridge the lipophylic benzene cycle was found to inhibit the activity of furin with  $K_i \approx 0,50 \mu\text{M}$ . The docking of these compounds into active center of furin was performed.

Also the derivatives of thiazines were studied as inhibitors of furin.

## Methanol production under mechanochemical activation of the catalyst

*N. Khimach<sup>1</sup>, S. Melnykova<sup>1</sup>, I. Polunkin<sup>1</sup>, V. Kremenitsky<sup>2</sup>*

<sup>1</sup>*Institute of Bioorganic Chemistry and Petrochemistry of NAS, Ukraine*

<sup>2</sup>*Technical centre of National Academy of Sciences of Ukraine*

One of the ways of improving the performance of catalytic processes is using the technology of continuous (uninterrupted) mechanical activation of the catalyst in situ under conditions of "mechanochemical Catalysis" (its variation – aerosol nanocatalysis AnC) in vibroreactor.

The advantage of mechanochemical catalysis is continuous dispersion of the catalyst to particles of 5–200 nm in size with simultaneous restoration of the active surface, formation of defects of the structure and decreasing the activation energy of the adsorbed reactants.

In the submitted paper the impact of mechanochemical activation (MCA) of the industrial copper-zinc-alumina oxide catalyst SNM-U (Ukraine) on the process of conversion of syngas to methanol is represented.

The experiment was carried out in statically circulating installation with non gradient reactor in the temperature range of 140–260 °C at atmospheric pressure. The reactor was filled with dispersive material for 50 % and a small amount (0,32–2,5 g/l<sub>reactor</sub>) of shredded catalyst SNM-U with the initial particle size of  $\approx 200$  microns.

The impact of temperature and catalyst contents in reactor on syngas conversion to methanol has been investigated.

It has been determined that mechanochemical activation of catalyst causes lowering of the initiation temperature of the reaction for approximately 40 °C – from 200 to 160 °C.

There is an essential increase of specific reaction rate (capacity of catalyst), selectivity for the main components, carbon conversion level and also decrease of the velocity of side reactions with the lowering of catalyst concentration in the reactor from 2,5 to 0,32 g/l of reactor.

Productivity (0,16 g/g<sub>cat.</sub> per hour) under the catalyst concentration in reactor of 0,32 g/l is only 4 times less than the best results of the commercial tests of SNM-U catalyst at the temperature of 220–260 °C and the pressure of 9 MPa.

The research of compositional change of the initial and target products during the time of experiment confirms the correctness of the mechanism of reaction of methanol synthesis from syngas proposed by A.Ya. Rozovskyy and et al. for the copper–zinc–alumina–oxide catalysts.

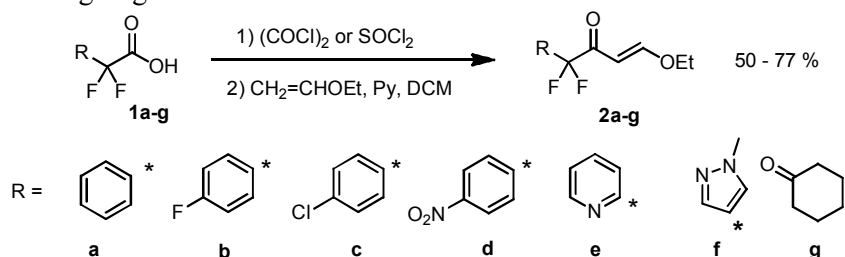
Results of the research illustrate the advantages of mechanochemical method of synthesis gas conversion to methanol: simplification of the flowsheet; lowering of initial temperature of the reaction; possibility of carrying out the reaction at atmospheric pressure; significant decrease in value of the catalyst per unit volume of reactor; overall cost reduction of the process of synthesis gas conversion to methanol.

## Synthesis and investigation of physicochemical properties of new difluoromethylene bearing enones

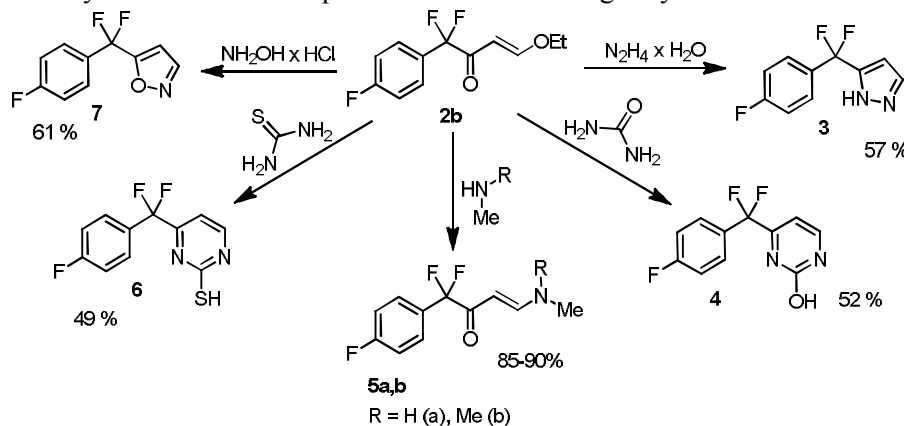
*M.Ya. Bugera, V.E. Ivasyshyn, K.V. Tarasenko, I.I. Gerus*

*Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine, Kyiv  
Department of Fine Organic Synthesis*

The finding new fluorine-containing synthons is the main subject of the department №01 of IBPC NUAS, and now we have synthesized a series of difluoromethylene bearing enones **2a-g**, using difluoroacetic acids **1a-g** with aryl, hetaryl and alkyl substituents as the starting reagents.



Powerful synthetic possibilities of the compounds **2** were shown by the example of enone **2b**: various heterocyclic compounds bearing difluoromethylene link at a desired position were obtained in good yields.



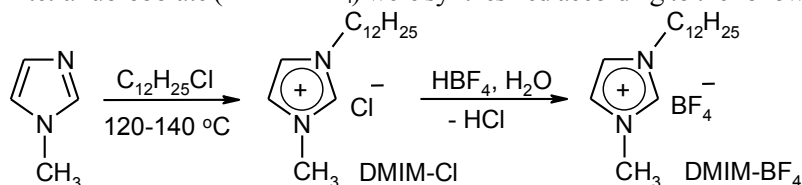
## Antimicrobial properties of imidazolium ionic liquids and their complexes with $\beta$ -cyclodextrin

*<sup>1</sup>D.M. Hodyna, <sup>1</sup>L.E. Kalashnikova, <sup>1</sup>L.O. Metelytsia, <sup>1</sup>S.P. Rogalsky,  
<sup>1</sup>O.P. Tarasyuk, <sup>2</sup>L.V. Kobrina, <sup>2</sup>S.V. Riabov*

*<sup>1</sup>Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine  
<sup>2</sup>Institute of Macromolecular Chemistry, NAS of Ukraine*

Ionic liquids (ILs) are considered as novel promising biocides due to the broad spectrum of their antimicrobial activity, as well as anti-biofilm activity. The goal of current research was to estimate antimicrobial properties and ecotoxicity of ILs comprising 1-dodecyl-3-methylimidazolium cation.

Water soluble IL, 1-dodecyl-3-methylimidazolium chloride (DMIM-Cl) and water immiscible 1-dodecyl-3-methylimidazolium tetrafluoroborate (DMIM-BF<sub>4</sub>) were synthesized according to the following scheme:



Inclusion complexes of ILs with  $\beta$ -cyclodextrin (CD) were obtained in water-ethanol (1 : 1) mixture and characterized by IR-spectroscopy.

Both ILs and their complexes with CD were found to have excellent anti-microbial activity against *Staphylococcus aureus* (ATCC-25923), *Escherichia coli* (ATCC-25922), *Pseudomonas aeruginosa* (ATCC-27853), *Candida albicans* (M 885 ATCC 10231) and *Candida albicans* (clinical isolate) strains.

Acute toxicity ( $LD_{50}$ ) of samples on a model of hydrobiont Zebrafish (*Danio rerio*) was registered for DMIM-Cl – 5 mg/l, DMIM-Cl with  $\beta$ -cyclodextrin – 40 mg/l, DMIM-BF<sub>4</sub> – 7 mg/l, DMIM-BF<sub>4</sub> with  $\beta$ -cyclodextrin – 100 mg/l. Thus, the obtaining of IL-CD complexes is effective approach to reduce the toxicity of IL biocides keeping strong antimicrobial activity.

UDC 547.854.5+54.057

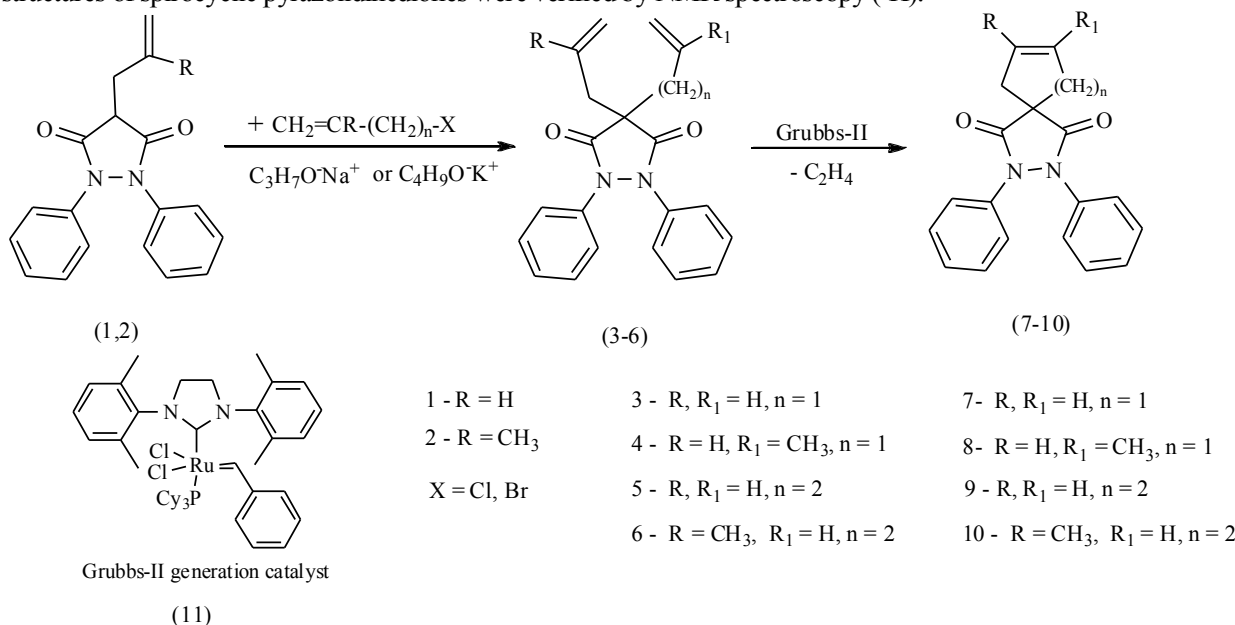
## The new spirocycloalcanic pyrazolidine-3,5-dione derivatives synthesis by means of ring-closing metathesis

*V.M. Holovatiuk, Yu.V. Bezugly, V.I. Kashkovsky*

*Institute of Bioorganic Chemistry and Petrochemistry NAS Ukraine,  
Department of organic and petrochemical synthesis*

A lot of different pyrazolidine-3, 5-dione containing compounds were shown to be used in biology, pharmacology and medicine very actively. Therefore, this type of heterocyclic systems is interesting object for further research in the area of chemistry and biology.

The new spirocyclic unsaturated 1, 2-diphenylpyrazolidine-3, 5-diones were synthesized by ring-closing metathesis reaction. It should be noted, that metathesis transformations were carried out in the presence of ruthenium containing carbene complex – Grubbs second generation catalyst (11) (3 mol. %) in dry dichloromethane (0.5 N solution) at 41 °C for 1 hour. All new products were purified by column chromatography and the yields of obtained compounds were scope of 70–90 %. The structures of spirocyclic pyrazolidinediones were verified by NMR spectroscopy (<sup>1</sup>H).



It was carried out the computing analysis of synthesized products by means of Prediction of Activity Spectra for Substances program and resulting unsaturated spirocyclic pyrazolidinediones were found to have some biological activities, such as CYP2A8 substrate, testosterone 17 $\beta$ -dehydrogenase (NADP<sup>+</sup>) inhibitor, L-glutamate oxidase inhibitor, anti-inflammatory activity etc.