AGRICULTURAL UNIVERSITY OF GEORGIA
ASSOCIATION OF PROFESSIONAL CHEMISTS OF GEORGIA

5-th International Conference of Young Scientists
CHEMISTRY TODAY -2016

September 18-21, 2016
Tbilisi, Georgia
Wellcome!

Dear Colleagues,

The Organizing Committee cordially invites you to the 5-th International Conference of Young Scientists (Chemistry Today-2016) which is organized by the Agricultural University of Georgia and Association of Professional Chemists of Georgia.

The conference series “Chemistry Today” is a scientific event that has been established in Georgia since 2011 attracting attendees from various universities of Europe and Asia.

The first three conferences were held in Georgia. The venue of the 4-th conference was Yerevan, Armenia, confirming that conference "Chemistry Today" really became an international famous conference. ICYS-2014 was held on August 18-22, 2014 and was organized by Young Chemists Association of Armenia and Association of Professional Chemists of Georgia.

The 5-th International Conference of Young Scientists will continue the same tradition of the prior Chemistry Today’s, offering a scientific program dealing with the latest developments in new methods in chemistry. The meeting will create an environment for in-depth, informed discussions highlighting the importance of chemistry in the industry and academia. There is also wide space for oral and poster contributions to allow established colleagues as well as young researchers to discuss their latest results and achievements. Besides the scientific aspects of the program, you will have a chance to appreciate the scenes of Georgia and visit historic regions of our country.

It is an honor and challenge for us to organize Chemistry Today-2016 again in Georgia, and we will work hard to ensure a rewarding event, both scientifically and socially.

Chemistry Today -2016 is included in the program of Science and Innovation week - comprising a lot of interesting exhibitions, lectures, presentations, scientific events, etc and organized by Ministry of Education and Science of Georgia.

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Oral Presentations
O1. OPTIMIZATION OF KARONDA WINE PRODUCTION: A RESPONSE SURFACE METHODOLOGY APPROACH

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Underutilized fruits provide a good source of energy, nutrients, vitamins, and minerals. However, most minor fruits have lesser shelf life when compared to other fruits unless they are appropriately preserved. Karonda (Carissa carandas L.), a tropical minor fruit was used for the preparation of red wine. In the present study, Karonda, which is abundantly available in India, was subjected for wine production. The alcohol content of wine varied from 6.0 to 10.98 % depending upon the variable pH (3 to 4) and varying levels of inoculum size (5-15 %). Yeast Saccharomyces cerevisiae NCIM 3215 was used for wine production. The fermentation parameters were optimized by response surface methodology using central composite design. The wine had 10.34 % ethanol content at the end of fermentation with following optimizing conditions 10 % inoculum size, pH 3.5 and temperature of 25°C. Karonda wine was found to be good with respect to colour, taste, astringency and flavour. Biochemical and proximate analysis of karonda pulp and wine were studied. The pulp had total soluble solids of 13.11 °Brix, pH 3.18 and total phenolics 1.01 g/100 mL the wine had total soluble solids of 8.3 °Brix, pH 3.54, total phenolics 0.80 g/100 mL. Heavy metals such as Cu, Mn, Zn and Fe were found in the wine. The karonda pulp and wine was evaluated for its antioxidant activity by 2,2-diphenyl-1-picrylhydrazyl (DPPH)-scavenging assay. The inhibition concentration was 69.00% and 50.10% respectively.

References


O2. RADON IN SOME NATURAL WATER SOURCES

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One of the most actual problems of modern ecology is the control of a radioactive condition of the environment. Now scientists came to the conclusion that the main contribution in population exposure concerns with natural sources, in particular, radioactive gas radon.

Radon gets in the water from environmental soil, and also granites, basalts, sands to which aquiferous layers adjoin. Radon concentration in usually used water is small, but water from some deep wells and artesian wells can contain a lot of radon – from 100 pCi L$^{-1}$ up to 1000000 pCi L$^{-1}$ [1].

Radon dissolved in water operates in two ways. On the one hand, it together with water gets to digestive system, and on the other hand, people inhale radon allocated from water by its utilization.

Breathing radon in indoor air can cause lung cancer. Radon decays into radioactive particles that can get trapped in lungs at the inhalation. Drinking water containing radon also represents a risk of developing of internal organ cancers, primarily stomach cancer [2].

In the present work there are given some results on radon activity in waters of spring sources as well as other sources in the geographical areal of Tbilisi city – the capital of Georgia.

Research objects were various natural sources of water located in the territory of settlements in Tbilisi artesian basin (21 control points). It was investigated water in various types of sources, in particular:

- Springs (WSp-1) in which water was selected directly in spring zone - 6 points;
- Springs (WSp-2) in which water was selected far from spring zone – in pipelines, on sufficiently remote distance - from hundred meters up to several kilometers) - 11 points;
- Rivers (WR) - 3 points;
- Lake (WL) - 1 point.
- Sampling was carried out in special glass containers in capacity 250 mL. Containers were filled with water up to the top and densely closed by a cover.

Table 1-2. Generalized monthly activity of radon (A, Bq L\(^{-1}\)) in surface water of different types, their average (A\(_{av}\)), minimal (A\(_{mn}\)), maximal (A\(_{mx}\)) values, relative standard deviation (RSD), and in the column (Prm) also their averaged values (aver - average, min - minimal, max - maximal) in various control points

<table>
<thead>
<tr>
<th>#</th>
<th>ST</th>
<th>Prm</th>
<th>A, Bq L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WSp-1</td>
<td>aver</td>
<td>96.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>min</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>max</td>
<td>110</td>
</tr>
<tr>
<td>4</td>
<td>WSp-2</td>
<td>aver</td>
<td>13.4</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>min</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>max</td>
<td>27</td>
</tr>
<tr>
<td>7</td>
<td>WR</td>
<td>aver</td>
<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>min</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>max</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>WL</td>
<td>aver</td>
<td></td>
</tr>
</tbody>
</table>

Electronic radon detector RAD7 was used for determination of radon content in water.

For the whole period of observations, it has been received more than 100 values of radon concentration in water samples selected in 21 control points in the territories of Tbilisi artesian basin.
Table 1 shows the generalized monthly activity of radon ($A$, Bq L$^{-1}$) in surface water of different types in various control points for the period January - December, 2013.

1. It was established, that radon content in spring water as well as in water of other types in the areal of Tbilisi city varies in the wide range, in particular;

- in spring water of the first type (samples were selected directly in zone of spring location) is in the limits from several units of Bq L$^{-1}$ (2.7 Bq L$^{-1}$) up to 100 and more (163 Bq L$^{-1}$), with average value of 72.3 Bq L$^{-1}$;

- in spring water of the second type (samples were selected from the pipeline on sufficiently big distance from zone of spring location) is in the limits from 0.1 Bq L$^{-1}$ up to 35.8 Bq L$^{-1}$, with average value of 8.4 Bq L$^{-1}$;

- in river water size of changing makes up from 0.1 up to 7.0 Bq L$^{-1}$ with average value of 2.2 Bq L$^{-1}$. 

<table>
<thead>
<tr>
<th>#</th>
<th>ST</th>
<th>$A_{av}$</th>
<th>$A_{mn}$</th>
<th>$A_{mx}$</th>
<th>RSD</th>
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<tr>
<td></td>
<td></td>
<td>Bq L$^{-1}$</td>
<td>Bq L$^{-1}$</td>
<td>Bq L$^{-1}$</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
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<td>72.3</td>
<td>33.1</td>
<td>99.9</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>20.7</td>
<td>2.7</td>
<td>49.8</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>124</td>
<td>72.9</td>
<td>163</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>WSp-2</td>
<td>8.4</td>
<td>4.8</td>
<td>13.4</td>
<td>34</td>
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<tr>
<td>6</td>
<td></td>
<td>16.2</td>
<td>7.3</td>
<td>35.8</td>
<td>55</td>
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<tr>
<td>7</td>
<td>WR</td>
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<td>0.4</td>
<td>4.7</td>
<td>81</td>
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<tr>
<td>8</td>
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<td>0.9</td>
<td>0.1</td>
<td>2.4</td>
<td>140</td>
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<tr>
<td>9</td>
<td></td>
<td>4.2</td>
<td>0.5</td>
<td>7.0</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>WL</td>
<td>0.2</td>
<td></td>
<td></td>
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</tbody>
</table>
2. It was shown that the majority of the investigated control points on values of radon concentration in surface waters was in the groups with above typical (3-10 Bq L\(^{-1}\)) or high (10-30 Bq L\(^{-1}\)) values of radon activity.

3. It was carried out analysis in which it was shown that the received results for surface waters can be connected with features of geology of these territories; comparison with literary data has been carried out.

References


Multicomponent reactions are one of the main subjects of fundamental research in modern synthetic organic chemistry. Despite the fact that some of them had been discovered many years ago their investigation became a never ending story due to emerged novel catalysts, and methods for the activation and control, such as sonication and microwave irradiation. This creates the possibility to enlarge the reaction scope, control selectivity, and sometimes even to discover new reaction pathways, and obtaining novel unexpected structures.

Biginelli-like condensation utilizing triazoles as a binucleophile has a significant potential to become a powerful tool of diversity-oriented synthesis due to the tunable reaction pathways leading to different chemotypes of products. However, development of synthetic approaches for each chemotype is a challenging task due to the high sensitivity of the reaction, the nature of substrates, and the reaction conditions. Thus the scope and limitations need to be carefully defined in each case.

This study covers several reaction pathways of Biginelli-like three-component condensation utilizing 1,2,4-triazoles and raises the questions of regioand stereoselectivity of the reactions.

The research we wish to present is a continuation of previously published results where several pathways of Biginelli-like condensation were found and the Biginelli-like condensation utilizing 1,2,4-triazole was revised. This opened several directions for further investigations that are going to be implemented within the current study.

In the vast majority of previous works unsubstituted triazole derivatives were
described. To enlarge synthetic capacity of such MCRs it is planned here to introduce another point of diversity into the reaction products by using C-substituted 3-aminotriazoles.

As it was shown by preliminary results Biginelli-like condensation of salicylic aldehyde with triazole and acetone in harsh conditions lead to the formation of benzoxadiazacines with incorporated tetrahydropyrimidine and dihydropyrane cycles [1]. The first report regarding the contained compounds of benzoxadiazacine fragment 1 (Fig. 1), which were obtained by cycloaddition of pyridine and resorcinol was published in 1979 by Girke et al [3]. Later, structurally similar compounds were obtained by intramolecular condensation of Biginelli-like dihydropyrimidines with carbohydrates as aldehyde component [4,5]. Then, it was shown that benzoxadiazacines with methylene bridge can be obtained in one stage by Biginelli reaction with salicylic aldehyde [6,7].

![Figure 1](image1.png)

In general, it can be stated that there are several approaches leading to compounds that contain such conformationally restricted heterocyclic systems. Diversity of such structures is presented in Figure 2.

![Figure 2](image2.png)

In our previous work we have obtained several representatives of benzoxadiazacines 5 (Scheme 1), annulated to triazole, but the only substituent varied was $R_1$ in aromatic ring ($R_2 = R_3 = H$) that is obviously not enough
for further development. Aim of this work is to enlarge the scope of the reaction and to identify its limitations by variation of substituents ($R_1$, $R_2$, $R_3$) in all starting materials (2, 3, 4).

Scheme 1.

This work utilizes modern synthetic approaches (microwave assisted, diversity oriented synthesis) for tasks like the investigation of the compound’s reactivity, selectivity, the synthesis of novel compounds and creates synthetic methodology.

References


O4. COMBUSTION SYNTHESIS OF 2W-Cu & W-3Cu COMPOSITE NANOPOWDERS FROM OXIDE PRECURSORS

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Tungsten-copper pseudoalloys are widely used in the manufacture of electrical contact materials and electrodes, thermal management devices such as heat sinks and spreaders, and conductive inks and pastes for ceramic metallization [1]. W-Cu composite materials have elevated corrosion resistance, controllable thermal expansion coefficient, as well as electrical and thermal conductivities that can be adjusted by change of its composition. This allows to match the thermal expansion coefficient to those of the ceramic substrates used with electronic devices. Besides having improved mechanical properties, these high density samples have higher thermal conductivity which is crucial for the application of W-Cu alloys in electronic industry [2].

In this work for the manufacturing of W-Cu composite materials the self-propagating high-temperature synthesis (SHS) method is applied by using thermo-kinetic coupling approach [3]. Its essence consists in the coupling of low exothermic reduction reaction (MeO+C) with a high caloric (MeO+Mg) one with possible change of reaction pathway. Furthermore, using (Mg+C) combined reducer will allow to control the reaction temperature in a wide range at synthesize of W-Cu composite powders with various composition.
First of all thermodynamic calculations were carried out for $2\text{WO}_3$-$\text{CuO}$-$y\text{Mg}$-$x\text{C}$ and $\text{WO}_3$-$3\text{CuO}$-$y\text{Mg}$-$x\text{C}$ systems to determine optimal conditions for joint and complete reduction of copper and tungsten oxides, aimed at obtaining $2\text{W}$-$\text{Cu}$ & $\text{W}$-$3\text{Cu}$ alloys. For the both systems it is achieveable in a definite area of magnesium and carbon amounts (cross marked on the Fig. 1): at that adiabatic temperature makes $700$-$2000^\circ\text{C}$

Based on the results of thermodynamic calculations magnesio-carbothermic co-reduction of tungsten and copper oxides were performed with such number of reducers corresponding to low temperature area. The effect of reducer’s amount on the behavior and combustion parameters was studied. According to the results the growth of carbon amount leads to a decrease both the combustion temperature and velocity, while increasing of magnesium amount increases the combustion parameters. According to XRD analyses results, the variation of reducers makes possible to completeley reduce the both oxides up to desired $\text{W}$ and $\text{Cu}$ metals. As a result, $2\text{WO}_3$+$\text{CuO}$+$2.7\text{Mg}$+$4\text{C}$ and $\text{WO}_3$+$3\text{CuO}$+$1.7\text{Mg}$+$4.8\text{C}$ compositions

![Figure 1. Thermodynamic analysis results for the $2\text{WO}_3$-$\text{CuO}$-$y\text{Mg}$-$x\text{C}$ system, $P=0.5$ MPa](image)
were selected as optimum and further studies were done with them. According to the gas-chromatography analysis, the main gaseous products are CO and CO$_2$ and CO/CO$_2$ molar ratio for the first mixture, is about 12.3 at $T_c=1300^\circ$C. Then the reaction can be presented by the following equation:

$$2\text{WO}_3+\text{CuO}+2.7\text{Mg}+4\text{C} = 2\text{W}+\text{Cu}+2.7\text{MgO}+3.7\text{CO}+0.3\text{CO}_2$$

For the second mixture ($\text{WO}_3+3\text{CuO}+1.7\text{Mg}+4.8^\circ$C) at experimental conditions CO/CO$_2$ ratio is about 3.1 at $T_c=1200-1250^\circ$C. Note that at lower amount of carbon in the initial mixture the amounts of carbon oxides approach each other.

According to XRD analysis results, after acid leaching the products contain only target metals. Microstructural examinations testify that after acid leaching the combustion products 2W-Cu & W-3Cu contain fine snowflake-like particles up to 30-50 nm in size (fig. 2).

![XRD pattern and microstructure](image)

Figure 2. XRD pattern (up) and microstructure (down) of combustion products for the $2\text{WO}_3+\text{CuO}+2.7\text{Mg}+4$ mixture after acid treatment, $P=0.5$ MPa

Powders Cu:W=3:1 and Cu:W=1:2 were compacted into cylindrical rods by two stage hot explosive consolidation (HEC) technology. At first stage the cylindrical containers filled with nanoscale Cu-W (3:1 & 1:2) blend powders were preliminary compacted at room temperatures with intensity of loading around 5GPa. At second stage the same, preliminary consolidated samples were reloaded at high temperatures between the 700 up to 1000°C with intensity of loading up to 10 GPa. Experiments showed that the combination of SHS and HEC technologies allows to fabricate high dense cylindrical billets near to theoretical density without visible cracks and cavities which is result
of homogenous distribution and size of the W and Cu particles.

Acknowledgements
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References
O5. SYNTHESIS OF POLYSUBSTITUTED FURAN-2(5H)-ONES

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3,4-Disubstituted furan-2(5H)-one fragment is present in many natural, biologically active compounds. In particular, furan-2(5H)-one derivatives containing non-identical aromatic substituents in positions 3 and 4 of the furan ring exhibit various biological activities [1]. An example is the anti-inflammatory drug Rofecoxib [4-(4-methanesulfonylphenyl)-3-phenylfuran-2(5H)-one]. Eutypoid A isolated from the marine mangrove fungus Eutypa sp. (# 424) [2] and gymnoascolides [3] isolated from the Australian soil ascomycetes Gymnoascus reessii and Malbranchea filamentosa IFM41300 are naturally occurring 3,4-disubstituted furan-2(5H)-ones.

Considering the above statements and the fact that our research interests include synthesis of new derivatives of furan-2(5H)-ones, we decided to perform the condensation mentioned below, with the aim of synthesizing the analogous systems, with the perspective of investigation of the biological activities of obtained compounds.

\[
\begin{align*}
R_1 & = \text{Me, Ph; } R_2 = R_3 = \text{Me; } R_2 + R_3 = (\text{CH}_2)_5 \\
R_4 & = \text{Ph, 4-}(\text{NO}_2)\text{C}_6\text{H}_4, 4-\text{(CH}_3\text{O})\text{C}_6\text{H}_4
\end{align*}
\]
For the economy of steps, we performed also the three component reaction between 3-acetyl-4,5,5-trimethylfuran-2(5H)-one, benzaldehyde and malononitrile.

![Chemical reaction diagram](image)

Thus the cyclocondensation of 3-(1,1-dicyanoprop-1-en-2-yl)-4,5,5-substituted furan-2(5H)-ones with arylidenemalononitrile was carried out, and it was shown, that the alternative, three component pathway for obtaining of these products is possible. The biological examinations of these systems are also planned.

References


Tungsten-copper composite materials are engineered materials made from two constituent elements with significantly different physical and chemical properties which remain distinct at the macroscopic and microscopic scale within the final structure. W-Cu composites are made from a refractory phase - tungsten, which possess high strength and low coefficient of thermal expansion, and a Cu-phase having high thermal and electrical conductivity. The combination of these elements optimizes some properties such as ductility, strength, corrosion and wear resistance [1]. In the recent years, W-Cu composites have gained great importance in automotive, electrical, and military industry because of their high thermal conductivity, low thermal expansion, high wear resistance and excellent electrical conductivity. They are used as electrical contacts, resistance welding electrodes, heat sinks, electro-forging dies, packaging materials, and so on. The fabrication of a full density W-Cu composite is very difficult issue. Because of the big difference between melting points of tungsten and copper, there is no overlap of sintering temperature range and no mutual solubility which means poor sinterability. The infiltration of a porous-sintered tungsten skeleton by liquid copper is one of the most common methods for producing W-Cu composite [2]. However, in this method defects like pores, copper lakes, and tungsten agglomerates form easily, so this technique results in a poor quality. Other methods to fabricate W-Cu composites include the following: thermal-mechanical process, metal powder injection molding, hot extrusion, liquid sintering, microwave sintering, etc. Although one of the modern methods in producing composites is energy-efficient combustion synthesis, in which the
particles of obtained material would be partially merged, followed by hot-explosive consolidation of powder.

In this work W-Cu composite preparation was realized particularly from copper tungstates, where W and Cu are chemically bonded and being in the same crystalline structure will promote to the formation of homogeneous microstructure of final product. Copper tungstate was prepared by different ways: (i) calcination of WO₃ and CuO powders with a molar ratio of 1:1 (25.55 wt.% CuO) in air at 700°C for 3 hrs (SSA 1 m²/g); (ii) chemical coprecipitation using sodium tungstate and copper sulfate (22 m²/g), (iii) chemical coprecipitation using ammonium tungstate and copper sulfate (25 m²/g), and (iv) sol-gel method using ammonium paratungstate and copper nitrate (4 m²/g) as precursors. The obtained copper tungstates were characterized by XRD, SEM, IR and adsorption analyses methods. It was shown that more homogeneous CuWO₄ salt with smaller particle size is formed due to chemical precipitation methods (with average particle size less than 100 nm).

The reduction of copper tungstates by means of yMg+xC reducing mixture was investigated in the combustion mode. Based on thermodynamic analysis results experiments were carried out within thermodynamically selected optimal intervals (y=1.5-1.7 moles, x=1.8-3 moles, T_{ad}=1000-1500°C). It was shown that the change of carbon amount in the CuWO₄-1.6Mg-xC system essentially influences on the combustion parameters (T_c and U_c), as well as on the phase composition of combustion products. At that, the increase in x leads to significant decrease in T_c and U_c. At the same time reduction degree of metals increases with the increasing of carbon content, and when the amount of carbon is in the range of 2≤x≤3 combustion product contains Cu, W, Cu₀.₄W₀.₆, and MgO. Byproduct magnesia removed from the target compounds by acid leaching process (10% HCl aqueous solution). Microstructure examinations have shown that the combustion products are homogeneous, without molten areas, and particles are in the submicron range. Gas chromatography analysis results points to formation of CO and CO₂ as gaseous products, where CO exceeds about 5 times CO₂ at the change of carbon amount in the range of x=2-2.5 moles.

W-Cu nanocomposites developed by CS process were subjected to densification into cylindrical rods using hot explosive consolidation (HEC) technology to fabricate high dense cylindrical billets. Preliminary explosive
densification of the nanocrystalline W-Cu precursor powder blend is carried out at room temperature with a loading intensity up to 10GPa to increase the initial density and to activate the particle surfaces in the blend. Already predensified cylindrical rods are reloaded by primary explosive shock wave with a loading intensity near to 10GPa, but at a temperature from 800 up to 1050°C.

The investigations showed that explosive consolidation of CS nanopowders allows to consolidate cylindrical billets near to theoretical density without cracks and cavities. The obtained samples are characterized with good integrity which depends on the distribution and size of the W and Cu particles.

Thus the possibility of complete and combined reduction of copper and tungsten in the CuWO₄-Mg-C system and obtaining of W-Cu powder at certain amounts of reducers was demonstrated for the tungstate obtained by different methods, as well as HEC technology considered as an alternative way to fabricate novel Cu–W compacts with tailored properties.

**Acknowledgements**
The authors gratefully acknowledge the financial support of the International Science and Technology Center (ISTC project #A-2123).

**References**


O7. SYNTHESIS OF 3-AMINO-1-(3,5-DIMETHYL-1H-PYRAZOL-1-YL)-2,7
NAPHTHYRIDINE-4-CARBONITRILES AND 5-HYDRAZINO-3H-
PYRAZOLO[3,4-C]-2,7-NAPHTHYRIDIN-1-AMINES

A. A. Hovakimyan, E. K. Hakobyan, A. G. Nikoghosyan*,
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Condensed derivatives of 2,7-naphthyridines and pyrazoles represent an important and interesting class of nitrogen-containing heterocyclic systems and have been the subject of many studies on account of their pharmacological properties as evidenced by the literature data [1–4] and by the results of our investigations [5–9]. Therefore, the synthesis of compounds, simultaneously containing in their structure the above-mentioned heterocycles appears a very attractive task. Herein we report the synthesis of new 3-amino-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2,7-naphthyridines 3 and pyrazolo[3,4-c]-2,7-naphthyridines 5.

3-Chloro-1-hydrazino-7-methyl-5,6,7,8-tetrahydro-2,7-naphthyridine-4-carbonitriles 1 [8] by refluxing 10 h with acetylacetone gave the 7-alkyl-3-chloro-1-(3,5-dimethyl-1H-pyrazol-1-yl)-5,6,7,8-tetrahydro-2,7-naphthyridine-4-carbonitriles 2; thus realizing an example of the Knorr synthesis of pyrazoles [10]. Further, compounds 2 were reacted with various amines with formation of corresponding 7-alkyl-3-amino-1-(3,5-dimethyl-1H-pyrazol-1-yl)-5,6,7,8-tetrahydro-2,7-naphthyridine-4-carbonitriles 3 in high yields (Scheme 1).

After, with the aim of synthesizing the 5-(3,5-dimethyl-1H-pyrazol-1-yl)-3H-
pyrazolo[3,4-c]-2,7-naphthyridines 4, the 7-alkyl-3-chloro-1-(3,5-dimethyl-
1H-pyrazol-1-yl)-5,6,7,8-tetrahydro-2,7-naphthyridine-4-carbonitriles 2 were treated with hydrazine hydrate in ethanol under refluxing. During the reactions the 7-alkyl-5-hydrazino-6,7,8,9-tetrahydro-3H-pyrazolo[3,4-c]-2,7-naphthyridin-1-amines 5 were obtained in high yields, while compounds 4 were not formed at all (Scheme 2).
1–3. \( R = \text{alkyl}; R^1, R^2 = \text{H, alkyl}; R^1 + R^2 = \text{cycloalkyl}. \)

Scheme 1. Synthesis of 3-chloro-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2,7-naphthyridines 3.

Namely, during the cyclization of the pyrazole ring the nucleophilic substitution of the 3,5-dimethyl-1H-pyrazol-1-yl group, a quite unusual leaving group was observed with formation of 5-hydrazino-3\( H \)-pyrazolo[3,4-c]-2,7-naphthyridines 5. It should be mentioned that, such substitution in the condensed pyridine series, and especially in the 2,7-naphthyridine system is not known. Such substitution has been reported in some tetrazine systems [11].

The structure of the synthesized pyrazolo[3,4-c]-2,7-naphthyridines 5 besides the spectroscopic methods was confirmed by an alternative synthesis from the 1,3-dichloro-2,7-naphthyridines 6 [8] as well as starting from the intermediate 1-hydrazino-2,7-naphthyridines 7 [8] (Scheme 2).

4–7. \( R = \text{alkyl}; R^1, R^2 = \text{H, alkyl}; R^1 + R^2 = \text{cycloalkyl}. \)

Scheme 2. Syntheses of 5-hydrazino-3\( H \)-pyrazolo[3,4-c]-2,7-naphthyridines 5.
The structures of all synthesized compounds were supported by the NMR, IR, MS spectroscopy and by elemental analysis.

This work was supported by the RA MES State Committee of Science, in the frames of the research project № 15T-1D221.

References

O8. ZNO NANOPARTICLES AS HETEROGENEOUS CATALYST FOR SYNTHESIS OF CHROMENE DERIVATIVES

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Chromenes are an important group of compounds that are present in natural compounds because of chemical properties and biological activity [1-3]. The bicyclic ring system of chromenes has been produced by a number of different synthetic methods [4-5]. Many natural and synthetic chromone derivatives have the same biological and pharmacological activities, including anti-vira [6], anti-allergic [7] and neuroleptic activities [8]. Herein, we display an effective synthesis of 9H-furo[2,3-f]chromenes via the reaction of 1-(6-hydroxy-2-isopropenyl-1-benzofuran-yl)-1-ethanone 1, aldehydes 2 and malononitrile or ethyl cyanoacetate 3 in the presence of ZnO nanoparticles under solvent-free conditions at room temperature (Scheme 1).

![Scheme 1](image)

References


O9. SYNTHESIS OF NEW MACROCYCLIC COMPOUNDS VIA CLICK CHEMISTRY

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Nowadays, application of click chemistry in macrocycle syntheses represents a new approach. These reactions include quantitative yields, a high tolerance of functional groups, an insensitivity of the reaction to solvents, irrespective of their protic/aprotic or polar/non-polar character, and reactions at various types of interfaces, such as solid/liquid, liquid/liquid, or even solid/solid interfaces \[1,2\].

\[ \text{alkyne} + \text{azide} \rightarrow \text{macrocyclic compound} \]

The new click synthesis between alkyne and azide compounds, will be carried-out in organic solvent (such as toluene, methanol, and acetone) using Cu(II) derivatives (CuCl, Cu or Cu(II)\textsubscript{SO\textsubscript{4}·5H\textsubscript{2}O/sodium ascorbate) as catalysts. Tertiary amine, (triethylamine, tetramethyl ethylenediamine) will be used to enhance activity of copper catalyst.

References


Posters
PP 1. STEVENS REARRANGEMENT OF AMMONIA SALTS, WHICH CONTAIN PROP-2-IN-1-IL-GROUP

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We studied the Stevens rearrangement of piperidine and morpholine salts, containing carboxymethyl, phenacyl or cyanomethyl group (I-IV) together with prop-2-in-1-il group.

\[
\begin{align*}
\text{I} & : X=O, Y=\text{COPh} \\
\text{II} & : X=\text{CH}_2, Y=\text{COPh} \\
\text{III} & : X=O, Y=\text{COOMe} \\
\text{IV} & : X=\text{CH}_2, Y=\text{COOMe} \\
\text{V} & : X=O, Y=\text{CN} \\
\text{VI} & : X=\text{CH}_2, Y=\text{CN}
\end{align*}
\]

During rearrangement of salts (I, II), which contain phenacyl group, we expected to receive derivatives of furan [1]. Indeed, as a result of rearrangement, we received morpholine- and piperidine- substituted furanes (VII, VIII).

In the case of salts (III-VI) the rearrangement resulted in heterocyclic dienes with substituted methoxymethyl (X, XI) or cyanmethyl (XI-XII) group in \( \alpha \)-position. The said systems can have both E- and Z- configurations, if we take into account the positioning of hydrogen atom and amino groups relative to
central double bond. In that case quite interesting results were obtained during Stevens rearrangement of abovementioned salts.

The configurations of obtained salts were identified using NMR$^1$H, $^{13}$C and NOESY spectroscopy. During rearrangement of salt (IV) with methoxymethyl group dienamine (X) exclusively with Z-configuration of double bond was obtained, while in the case of salt (VI), containing cyanmethyl group, the obtained dyenamine (XI) double bond has E-configuration.

![Diagram of rearrangement process]

In the case of morpholyne group (III, V), (E,Z)-methyl-2-morpho-linopenta-2,4-dienonate (IX) and (E,Z)-2-morpholynopenta-2,4-diennytril (XII) were obtained, as a mixture of Z- and E-isomers, where dominating products was E configuration (61-75%).

![Diagram of rearrangement process]

**References**

Cyclocondensation of 3-cyanofuran-2(5H)-ones with arylidene malononitriles: synthesis of 4-amino-1,1-dimethyl-L-3-oxo-6-aryl-1,3-dihydrobenzofuran-5-carbonitrides

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Isobenzofuran-1(3H)-one skeleton can be found in structure of several biologically active compounds. As an example, the isobenzofuran-1(3H)-one containing natural compound cryphonectric acid is inhibiting the growth of tomato sprouts, and the research for its analogues represents some interest for agriculture. In continuation of our research in obtaining of substituted furan-2(5H)-ones, we investigated the addition-cyclocondensation of 3-cyano-4-methyl-5,5-disubstituted furan-2(5H)-ones with arylidene malononitriles.

The initial cyanolactones were obtained by interaction of corresponding ketoalcohols and ethyl cyanoacetate. They are further reacted with arylidene malononitriles. Reaction includes the intermediate Michael addition and intramolecular cyclization with the elimination of hydrogen cyanide.

Thus we obtained 6 new isobenzofurane derivatives, which will undergo further investigations for their biological activities.
References


SYNTHESIS OF METHYL SULFIDE DERIVATIVES OF COBALT BIS(DICARBOLLIDE)

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Nucleophilic ring opening of cyclic oxonium derivatives of polyhedral boron hydrides is known to be convenient method for synthesis of their various functional derivatives [1,2]. Nevertheless, the ring opening with such week nucleophiles as dialkylsulfides was not described. We found that the 1,4-dioxane derivative of cobalt bis(dicarbollide) reacts with dimethylsulfide giving the corresponding sulfonium derivative \([8-\text{Me}_2\text{S}(\text{CH}_2\text{CH}_2\text{O})_2-3,3’-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1’,2’-\text{C}_2\text{B}_9\text{H}_{11})]\) (Fig. 1) [3].

\[
\begin{array}{c}
\text{Co} \\
\text{O} \\
\text{O} \\
\text{SMe}_2
\end{array} \quad \text{SMe}_2
\]

Figure 1

The treatment of the dimethylsulfonium derivative with stronger nucleophiles results in the partial sulfur demethylation to give podand \([8-\text{MeS}(\text{CH}_2\text{CH}_2\text{O})_2-3,3’-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1’,2’-\text{C}_2\text{B}_9\text{H}_{11})]\), whereas poorly nucleophilic bases, such as t-BuOK, induce the contraction of the side chain with formation of alcohol \([8-\text{HOCH}_2\text{CH}_2\text{O}-3,3’-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1’,2’-\text{C}_2\text{B}_9\text{H}_{11})]\). The alcohol was used for synthesis of a series of other short-spacer functional derivatives \([8-\text{XOCH}_2\text{CH}_2\text{O}-3,3’-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{10})(1’,2’-\text{C}_2\text{B}_9\text{H}_{11})]\) (X = SH, N₃, NH₂) (Fig. 2) [3].

To study effect of thioether substituents on mutual orientation of the
dicarboxylate ligands in cobalt bis(dicarboxylate) we attempted synthesis of isomeric dimethylsulfonium derivatives [8-Me2S-3,3’-Co(1,2-C2B9H10)(1’,2’-C2B9H11)] and [4-Me2S-3,3’-Co(1,2-C2B9H10)(1’,2’-C2B9H11)] and their demethylation (Fig. 3).
Acknowledgements

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References


Indole alkaloids and their synthesized analogues and derivatives are characterized by a sharply expressed multi-physical activity.

Arylindoles are distinguished between the admixtures of indole line. It is approved, that, such admixtures are antidepressant, and analgesic agents, blocker and mediators of central nervous systems. Some of them are used in medical practice for the treatment of malignant tumors. Because of mentions above, there is conducted research about aromatic and heteroaromatic aldehydes. In particular, the unusual deformilation reaction was studied on the example of 3-formyl-2-etoksicarbonilindoles.

The purpose of work was to confirm the mechanism of the reaction intermediate cyclic acetal, or to separate the individual form of the admixture.

In order to synthesize a cyclic acetal, 3-formyl-2-etoksicarbonilindoles was boiled in benzene solution with ethylene glycol, then with a toluenesulfonic acid. Then, ethylene glycol were added ten times more and boiled for a few hours. The reaction did not processed. The same result was received in case of toluenesulfonic acid. The experiment proceeded the same way in toluene solution. The deformilation reaction for this substance was repeated in the conditions proposed by T. Narindoshvili [1]. Aldehyde and
ethylene glycol mixture was heated carefully. The reaction procedure was checked in every 25°C with chromatographic method. The formation of expected cyclical acetal begins on 100°C, but its appropriate spot disappears on 150°C. A similar chromatographic spot is observed in the presence of the trials in toluenesulfonic acid too. Finally the spot disappears too. In any cases there are produced the deformilation products. All attempts to identify the substance of this patent, failed. The authors of article provided the same information [2]. Moreover, in some cases, they tried to separate acetal by the means of distillation, which also failed. They didn’t managed to separate out acetal neither by chromatography, nor by distillation. It’s not surprising, because they point out, that this cyclic acetics are labile and they soon break down either from the aldehyde, or from the production of deformilation products.

References

Elaboration of chemical construction methods of molecular and macro-
molecular structures, including nano\micro-sized ones, on the basis of func-
tional organoelement and organic compounds on synthetic and natural poly-
mer surface allow to impart to polymers such relevant properties as hydro-
phobility, hydrophility, biocidity, repellent properties as well as sorption
activity, flame-resistance and incombustibility, photoluminescent properties
etc. at the very small expense of starting compounds.

Traditional chemical modification of synthetic and natural polymers for
directed changing their properties consist of introduction of different
compounds into the structure of macromolecules or into the bulk of
polymer. A new approach is based on the introduction of such modifiers on
polymer surface by the method of chemical molecular construction of
microamounts of organoelement and organic compounds, resulting in the
formation one or a few molecular layers, including nano\micro-sized ones.

Directed regulation of polymer properties is achieved by means of layers
structure. thickness and quantity variation, as well as their order. Because of
chemical bonds formation, nano\micro-coatings are fixed and held on the
polymer surface. Typical coating thickness range from monomolecular layer
to 10 nm and above.

In case of such organoelement compounds as organosiloxanes with silicon-
bound alkoxy- and silanolic groups, the latter connect to the polymer surface
by means of reaction of alkoxy- and silanolic groups with polymer functional
groups (hydroxylic, carboxylic et al.). If silicon atoms of the first layer bear
carbofunctional groups, such as amino-, epoxy, halide alkyl, olefin etc., their
capability to further chemical transformations can be used for construction
of covalently bonded to the material second-layer nano\micro-sized
coatings on the siloxane layer surface, and for construction of the next
organic, organoelement and inorganic layers. This approach makes it
possible to create new generation of sandwich nanosized hybrid materials with given thickness, composition and structure. As a result, initial polymers with modified surface acquire a complex of necessary physicochemical properties.

Polyorganosiloxane coatings have been synthesized by the molecular assembly method in two stages. At the first stage the immobilization of oligo(chloroalkyl)ethoxisiloxane (I-IX at scheme 1) has been made on the surface of materials by treating them with a solution in an organic solvent or with the water emulsion of oligomer (I-IX) with a specified 0,01; 0,1; 1,0; 3,0%- concentration, with air-drying; after that the modifier was fixed by 100 °C heat-treating during 10 minutes or it was kept in the air at the room temperature during 24 hours. The characteristics of oligomers are given in the article [1].

In the result of the mentioned treating the modifier (I-IX) was covalent fixed on the surface of the material because of the condensation of ethoxygroups of the modifier with the functional groups of polymer material while building an grafted micro/nano-sized polyorganosiloxane coating on the surface (scheme 1).

Scheme 1  

where \( n = 5, x = 1\) (I), 3 (II), 4 (III); \( n = 10, x = 1\) (IV), 3 (V), 4 (VI); \( n = 15, x = 1\) (VII), 3 (VIII), 4 (IX).

The amount of polyorganosiloxane coating on the surface of the material have been defined after the impregnating, drying and thermal treatment according to the increased weight of material expressed in percentages from the initial mass of one. If after a one-time impregnation, drying and thermal treatment of the material the increased weight did not reach the required value, then the impregnation, drying and thermal treatment of the materials have been conducted some times more and it has been continued until an increased weight with the required values was reached.
At the second stage the condensation of the grafted poly(chloroalkyl)organosiloxane coating with 1,6-di(guanidinhydrochloride)hexane in an alcohol solution with the presence of alkali at the room temperature was carried out.

Polymeric thiophene-containing coatings were prepared via curing of thiophene-containing silicones on a 50-μm-thick polyarylate film cast from chloroform.

As the result of a two staged treatment the grafted coatings materials which contain 1,6-di(guanidinhydrochloride)hexane and polythieno[2,3-b] thiophenes groups (scheme 2) were obtained.

![Diagram of chemical reaction]

Scheme 2

The presence of guanidine groups in the coating gives to the material a high biocide activity.

Such coatings are very effective for bacteria E. coli, P. Aeruginosa, fungi Penicillium chrysogenum, Aspergillus niger, yeast spores Saccharomyces cerevisiae, as well as for other bacteria, fungi and yeast spores.

The presence of polythieno[2,3-b]thiophenes groups in the coating gives to the material a high electroluminescent properties.

New approaches and principles of the creating of layered micro/nano-sized
functional polysiloxane coatings of the given structure, composition and texture, which are immobilized on the surface of materials allow to enhance the efficiency of the practical using of such materials, to improve their quality and field-performance data.

Acknowledgements

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References

For many years benzimidazoles are of interest for medicinal chemistry. Among them compounds having antihistamine [1] and antibacterial [1,2] activity is found. Benzimidazole derivatives exhibit cytostatic [1], anesthetic, hypotensive and antipyretic activities [3]. So synthesis of novel benzimidazole derivatives, including annelated polycyclic systems, is very important.

In continuation of our previous investigations on usage of furan compounds for various fused heterocyclic systems synthesis we studied a furan ring recyclization in 1-(5-alkylfuryl-2)benzimidazoles.

Earlier we have used similar compounds bearing methyl group at position 2 of benzimidazole ring for 1-(pyrrol-2-ylmethyl)benzimidazole synthesis [4] (Scheme 1). The method included two stages: furan ring opening to obtain 1,4-diketone unit and N-substituted pyrrole ring formation via an interaction of the diketone with primary amines. We showed that an application of various primary amines (aliphatic or aromatic) allowed preparing a wide range of pyrrolylmethylbenzimidazoles which were hard-to-reach by another ways.

Now we present an original approach to pyrrolo[1′,2′:4,5]pyrazino[1,2-a]benzimidazole derivatives based on an intramolecular recyclization of furan ring. Earlier we have utilized similar strategy for fused pyrrolo[1,2-a][1,4]diazepines [5] and pyrrolo[1,2-a][1,4]diazocines syntheses [6]. The unique feature of both transformations is simultaneous formation of pyrrole and diazepine (or diazocine) ring.

The acid-catalyzed transformation of furan ring in 2-aminomethyl -1-(5-alkylfuryl-2)methylbenzimidazoles proceeds as a domino-process and lead
to new heterocyclic system - pyrrolo[1',2':4,5]pyrazino[1,2-a]benzimidazole. The key stage of the reaction is an intramolecular furan ring recyclization (Scheme 2).

\[ \text{Scheme 1} \]

\[ \text{Scheme 2} \]

\[ X = \text{H, CH}_3, \text{Cl}; R = \text{CH}_3, \text{C}_2\text{H}_5 \]
Structures of all synthesized compounds are proved with NMR spectroscopy and MS data.

The study was supported by The Ministry of education and science of Russian Federation, project 2515.

References

The aim of our research is exploration of the 50 % aqueous solution of N-methylmorpholine N-oxide (NMNO) as an alternative, reusable and ecologically friendly medium for nucleophilic reactions [1-2]. In the current report, we show the possibility of alkylation of phenol with various alkyl halides.

It is known, that phenol behaves as an ambident anion in the alkylation
reactions [3], leading to the formation of O- or/and C- alkylated products [4-6]. The phase transfer catalysis is often used for the alkylation of phenols, however, in some cases, it has a disadvantage of formation of the mixture of products [7-8] so we compared the proposed system in the scope of the selectivity either. The alkylation of phenol with several alkyl halides performed in the system NMMO/water in the presence of potassium hydroxide by the scheme.

As it can be seen from the scheme, all the reactions proceed with good yields and studies of the products show no formation of byproducts, leading to only O-alkylated products, hence the proposed system is a promising alternative for phase transfer catalytic process.

Since the NMMO is not a cheap product, the investigation of the reusability of NMMO/H\textsubscript{2}O system is also a topic of interest for us. The research for reusability was done on the model reaction of alkylation of phenol with allyl bromide, however it was shown, that the secondary utilization of the mentioned solvent system leads to the formation of several byproducts. Aside from O-allylphenol (A) the mono alkylation, with formation of o- and p-allylphenol(B) occurs, along with the formation of O-,C-diallylphenol (C). The products of oxidation (D) of the disubstituted phenols are also found in the mixture of products. The clear mechanisms of these reactions are not
yet understood.

This work is supported by the RA MES state Committee of science, project 15T-1D348.

References


The great importance of uracil and his condensed derivatives are mainly determined by their biological properties, as well as by the structural similarity with natural compounds such, as flavins, deazaflavins, xantines and etc [1]. Many of them possess a wide spectrum of physiological activity-antitumor [2], antiviral [3], antibacterial [4] and etc. Proceeding from these data, in a continuation of our previous research, we performed slightly modified synthesis of new 9,10-substituted pyrimido [4,5-b]quinoline-2,4- (3H,10H)diones (5-deazaflavins) by annulation of 6-aminouracils with 2,3-dimethoxybenzaldehyde[5], providing introduction of the methoxy group at the 9-position. Parallelly we synthesized some new analogues called system 2 for the biological (antitumor and antimicrobial) properties study.

On the other hand 12- or 9,12-substituted benzo[b]pyrimido[5,4-g][1,8] naphthyridine -2,4-diones 3 were obtained by the reaction of cyclocondensation of 6-aminouracils 1 with 2-halogenquinoline-3- and 2-halogeno-7-methylquinoline-3-carbaldehyde. As a trial in the active
molecular design for biologically active substances, we were interested in the
synthesis of pyrimido[4,5-b]quinoline-2,4-diones, selectively substituted on
the phenyl ring or on the 5-position (pyridine ring) without modifying the
pyrimidinedion moiety, by a three-component one-pot reaction, based on
barbituric acid, corresponding aldehydes and anilines. We are used two
aldehydes- in the present study acetaldehyde and aromatic 3,4-
methylenedioxibenzaldehyde (heliotropine).

![Chemical Structures](image)

R=2-MeO, 3-MeO, 4-MeO, 2-NO₂, 3-NO₂, 3-CF₃.

The reactions were carried out by boiling equimolecular amounts of the
starting compounds in acetic acid, DMF or in a mixture of the both solvents.
At the current step of our, research only in the case of acetaldehyde and o-
anizidine expected 5-deazaflavin 4 was isolated. In case of heliotropine, only
a compound 5 was isolated. The character of aniline substituents (electron
donor or electron-withdrawing) has no influence on the cyclocondensation
reaction according to our experimental studies.

The study of this reaction has been continued. Structures of the synthesized
compounds were confirmed by IR and ¹HNMR spectroscopy.

Eventually, we have developed convenient procedures for the synthesis of
new 9, 10- or 9,12- substituted pyrimido[4,5-b]quinoline-2,4-(3H,10H)dio-
des and benzo[b]pyrimido[5,4-g][1,8] naphthyridin-2,4-diones.
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PP 9. THE REACTION OF 1-(PROP-2-YN-1-YL)PIPERIDINE WITH CH-ACIDS

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In previous work in the presence of electrophilic catalyst mercury(II) acetate by development new methods functionalization of terminal alkynes are disclosed new methods of alkylation more substituted atom carbon of triple bond of propargynitrogen-containing compounds with CH-acids to give corresponding 1,3- and 1,5-diketone and keto-enol derivatives[1-2].

It was also interesting to study the acetylenic and cyclic aminic fragments containing substrates, which are the best models to clarify some issues regio-, stereochemistry of mercuration-demercuration reactions.

The interaction between 1-(prop-2-ynyl)piperidine and sodium acetylacetone in the presence of mercury (II) acetate of tetrahydrofuran medium give the positional isomers-3- (3- (piperidin-1-yl) prop-1-en-2 -yl ) pentane-2,4-
dione 3 and 3- (1- (piperidin-1-yl) propan-2-ylidene) pentane-2,4-dione 4 if demercuration of mercury organic intermediate was carried in the presence of systemsodium borohydride/ water. Direction of indicated reaction changes if the demercuration of intermediate compound was implemented by system sodiumborohydride/ 3M NaOH . In this case, it turns out piperidinic ring containing corresponding isomers of unsaturated aminoketone(E)-4-methyl-5-(piperidin-1-yl)pent-3-en- 2-one 5 and (Z)- 4-methyl- 5- (piperidin-1-yl)pent-3-en-2-one 6 . The molecular structure of synthesised compounds confirmed the 1H NMR and MS spectroscopy data. In the 1H NMR spectrum of E and Z isomers of vinylic hydrogen atoms chemical shifts are respectively at 6.22 ppm and 6.4 ppm and in mass spectrum M / Z + = 181 is molecular peak.

Studied the interaction 1-(prop-2-ynyl)piperidine 1 with sodium salt of ethyl esteracetoacetic acid in the presence of mercury (II) acetate. To implement demercuration of mercury organic intermediate compound 7 by the systems sodium borohydride / water and sodium borohydride / 3M NaOH , got derivative of dialkynymercury - bis (3- (piperidin-1-yl) prop-1-ynyl) mercury 8. Obtained dialkynyl substituted mercury compound decompose by hydrochloric acid, leading to propargylpipiridine, but steadily over sodiumborohydride . The structure is confirmed by 1H, 13C NMR, IRand mass spectrometric data.

Thus in the presence of mercury (II) acetate were implemented to develop optimal conditions of new methods functionalization of propargyl and cyclic aminic groupscontaining substrate with C-nucleophiles-acetylacetone ,ethyl ester acetoacetic acid.
References


SYNTHESIS OF NEW HYDRAZONES OF 3-ACETYL-4,5,5-TRIMETHYLFURAN-2(5H)-ONES AND THEIR BIOLOGICAL ACTIVITY

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It is known that compounds containing azomethine functional group possess a high biological activity, including antibacterial, antiviral, antitumor, antioxidant and etc. On the other hand, a number of derivatives of γ-lactones are widely spread in nature and show a high biological activity. The importance of amino acids both in fauna and flora is also beyond doubt.

Based on the aforesaid, the aim of the present work was on the basis of 3-acetyl-4,5,5-trimethylfuran-2(5H)-ones [1] to synthesize new derivatives of amino acids containing azomethine functional group and study their antibacterial activity.

At the first stage of work by interaction of 2-(aryl)-4-aryldene-5(4H)-oxazolones (1) [2] with hydrazine hydrate the corresponding hydrazides – N-(1-aryl-3-hydrazinyl-3-oxoprop-1-en-2-yl)benzamides (2) were synthesized.

\[
\begin{align*}
R=R_1=H, Cl; R_2= 4- \text{CH}_3O- &-C_6H_4^- , 4- \text{Br}-C_6H_4^- , 3- \text{NO}_2-C_6H_4^- .
\end{align*}
\]

Then under microwave irradiation (emission) the reaction of 3-acetyl-4,5,5-trimethylfuran-5(4H)-ones (3) with synthesized hydrazides was studied. The reaction was carried out in glacial acetic acid at 100°C for 30 min. It was established, that the products were the corresponding hydrazones – N-1-aryl-3-oxo-3-(2-(1-(4,5,5-trimethyl-2-oxo-2,5-dihydrofuran-3-yl)ethylidene)-hydrazinyl)prop-1-en-2-yl)benzamides (4).
The antibacterial activity of synthesized hydrazones (4) towards Gram-positive staphylococci (Staphylococcus aureus 209 p, 1) and Gram-negative strains (E. Coli 0-55, Sh. Dysinteriae Flexneri 6858) was tested [3]. The obtained data showed that all tested compounds displayed a weak selective activity against Gram-negative strains, inhibiting the growth of microorganisms in the zone by diameter 9-12 mm.

References

PP 11. SYNTHESIS AND SOME TRANSFORMATIONS OF NEW FUNCTIONALIZED 1,2,4-TRIAZOLES AND 1,3,4-TIADIAZoles

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Derivatives of thiol- and thionsubstituted 1,2,4- triazoles and 1,3,4-thiadiazoles are known for their broad spectrum of biological activities [1-3]. At the same time, bearing some reactive functional groups, they are of interest as substrates for use in molecular design for the linear-coupling or synthesis of condensed heterocyclic compounds. In our previous works we have reviewed a significant antibacterial, hypoglycemic, antitumor activitis of new derivatives of the above - mentioned heterocycles, allowing to study the possible relationship between biological activity and chemical structure of the compounds [4]. In a continuation of our previous works herein we report the synthesis of novel derivatives of sulfanyl substituted 1,2,4-triazoles and 1,3,4- thiadiazoles, containing different pharmacophore groups.

Based on the substituted phenyl-, phenoxyacrylic acids hydrazides, key intermediates - 1,2,4- triazole-3- and 1,3,4- thiadiazole-2-thioles 3,11 were synthesized. From the possible nucleophile centers of the latter towards alkylation with the various halides in alkaline media only thiol groups are involved of form the corresponding sulfanylsubstituted 1,2,4- triazoles and 1,3,4- thiadiazoles 4,12. Absence of the absorption bands of SH- group in the IR spectrum of the compounds 4.12 and the presence of SCH2- groups protons singlets at 3.82-4.20 ppm in the 1HNMR spectrum confirms the course of the alkylation reaction over SH thiol group. The exception was only the alkylation indicates of 1,2,4- triazole-3-thiol 3 (R=3-Br, R`=C6H5, X=O, Y=CH2) with ethylene chlorohydrin, leading to the formation of 3- hydroxy derivative- triazole 5, and not to the target triazole 4 (R``=CH2OH).
where \( R = H, \ 3\text{-Br}, \ 3\text{-MeO}, \ 4\text{-EtO}; \ R = \text{C}_6\text{H}_5, \ \text{C}_6\text{H}_{11}, \ \text{C}_6\text{H}_2\text{CH}_2, \ \text{CH}_2\text{CH} = \text{CH}_2, \ R^\prime = \text{COOEt, CH}_2\text{OH, CONH}_2, \text{COOH}; \ X = \text{O, CH}_2, \ Y = 0, \text{CH}_2. \)

The essence of the transformation the substitution of \(-S^\prime\) group by \(-O^\prime\), caused by intramolecular nucleophilic rearrangement [5], and the cleavage of formed intermediate A. Further investigations showed that aminomethylation and cyanoethylation reaction of 1,2,4-triazole-3- and 1,3,4-thiadiazole-2-thioles takes place exclusively on the \(N^2\) or \(N^3\) endocyclic nitrogen atoms of these heterocycles. Similarly, the latter are reacted with acrylic acid in the conditions developed by us, leading to the corresponding acids 8, 15, the structure of which is confirmed by the counter synthesis acid
hydrolysis of 1,2,4-triazol-substituted propionitriles 7,14. In a continuation of our previous works [6] in the present paper we also reported the electrophil heterocyclization of 5-substituted-4-allil-4H-1,2,4-triazole-3-thioles, leading to the formation of corresponding thiazolo[2,3-C] [1,2,4]triazoles 16.

Some transformations of compounds 16 were studied.

Structure of the synthesized compounds was confirmed by IR, NMR\textsuperscript{1}H spectroscopy analysis.

References

PP 12. SYNTHESIS AND BIOLOGICAL ACTIVITY IN A SERIES PYRIDAZINE DERIVATIVES

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Pyridazine, pyrimidine, [1,3,5]triazine, pyrazole, [1,3,4]oxadiazole and fused [1,2,4]triazolo[4,3-b]pyridazine derivatives represent a wide diversity of biological activity and are used in medical practice and also in agriculture as means of plant protection [1]. In a series of nonfused systems, containing two of mentioned cycles, some substituted pyrazolyl-pyridazines obtained by cyclization of 3-hydrazino-pyridazines have shown hypotensive, anti-inflammatory, antibacterial and antioxidant activities [2-5].

The conventional methods for the synthesis of bi- and triheterocyclic systems in many cases requires the use of organic solvents, prolonged heating, which is associated with the loss of time and energy. In recent years, MW-irradiation method for the synthesis of bioactive heterocyclic compounds has evolved as an effective ecofriendly method [6-10]. MW-assisted synthesis offers several advantages, such as facile work up, shorter reaction time, cleaner products, products selectivity and hence this procedure is consistent with the principles of "Green chemistry".

The purpose of this study was the targeted conventional and MW-assisted synthesis of new previously undescribed compounds with combination of two or three heterocycles in the same molecule and their biological evaluation.

The syntheses were carried out according the following schemes via transformation and further heterocyclization of starting 3,6-dichloropyridazine and 2-N-substituted 6-hydroxy-pyridazin-3(2\textit{H})-ones.
A number of products were also obtained using MW-irradiation procedure. It is found that the application of this method has the greatest advantage
when the conventional methods of synthesis are carried out for a long time and at high temperatures.

The growth-regulating activities of the synthesized compounds were determined in vitro using the methods adopted in phytopathology. To estimate the growth-regulating properties, the activity of the synthesized compounds solutions, emulsions and suspensions in concentrations of 25 and 50 mg/L were compared with IAA solutions in the same concentrations. As a test object the seeds of common bean (Phaseolus vulgaris L.) were chosen. Studies have shown that the synthesized compounds showed growth promoting activity in the range of 65-100% (compared with IAA). Among them, the most promising compounds were selected for further deeper studies and subsequent field trials.

References

The expanding field of carborane chemistry constantly produces new application areas, such as the development of new molecular switches based on transition metal bis(dicarbollide) anions [1-3]. Therefore, stabilization of individual rotamers of transition metal bis(dicarbollide) complexes is of great importance. Such stabilization can be achieved by introduction of substituents which are able to form intramolecular hydrogen bonds between the dicarbollide ligands.

We found that reaction of the methylsulfide derivative of nido-carborane \([10-\text{MeS}-7,8-\text{C}_2\text{B}_9\text{H}_{11}]^-\) with CoCl\(_2\) in water in the presence of sodium hydroxide gives the corresponding complex \([3,3'-(8-\text{MeS}-1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-\) (Fig. 1).

![Figure 1](image1.png)

The similar reaction with asymmetrically substituted nido-carborane \([9-\text{MeS}-7,8-\text{C}_2\text{B}_9\text{H}_{11}]^-\) results in diastereomeric pair of isomers of \([3,3'-(4-\text{MeS}-1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]^-\) which were separated by column chromatography (Fig. 2).
Unfortunately, our attempt to use the same approach for synthesis of similar derivatives of iron bis(dicarbollide) failed. Therefore, we used another route. At the first, we prepared a set of known [4,5] isomeric dimethylsulfonium derivatives of iron(II) bis(dicarbollide) \([3,3'-\text{Fe}(4/8-\text{MeS}-1,2-\text{C}_2\text{B}_{9}\text{H}_{10})_2]\). Their treatment with strong nucleophiles such \(\text{BuSH}, \text{tBuOK}\) results in the partial demethylation of sulfur to give the corresponding di(methylsulfide) derivatives \([3,3'-\text{Fe}(4/8-\text{MeS}-1,2-\text{C}_2\text{B}_{9}\text{H}_{10})_2]^2^-\), which are readily oxidized by air oxygen to give the corresponding paramagnetic iron(III) bis(dicarbollide) derivatives \([3,3'-\text{Fe}(4/8-\text{MeS}-1,2-\text{C}_2\text{B}_{9}\text{H}_{10})_2]^3^-\) (Fig. 3).

Effects of thioether substituents on the mutual orientation of the dicarbollide ligands in the synthesized bis(dicarbollide) complexes as well as some peculiarities of their NMR spectra of will be discussed.
Acknowledgements

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References


SYNTHESIS AND SOME TRANSFORMATIONS OF 5(6)-(1-ADAMANTYL)-2-AMINOBENZIMIDAZOLES

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Some preparations of the adamantane line such as kemantane, bromantane and others restore functional activity of hormone, immune and nervous systems, increase physical and mental activities. In addition, they enhance organism’s resistance on viral and bacterial infections. What is more, compounds with antiviral, antibacterial, anticancer, anticataleptic and other activities have been revealed [1–3]. Because of mentions above, researches indirection of synthesis of adamantane containing benzimidazoles and studies of their pharmacological properties are perspective.

The aim of work was synthesis and some transformation of 5(6)-(1-adamantyl)-2-aminobenzimidazole.

In order to synthesize 5(6)-(1-adamantyl)benzimidazole (2), condensation of 4-(1-adamantyl)-o-phenylenediamine dihydrochloride (1) with formic acid were performed by heating for 7 hours at 95-100°C. By heating of obtained 5(6)-(1-adamantyl)benzimidazole (2) with sulfur mixture on Wood’s metal bath at 260-265 °C for 1.5 hours 5(6)-(1-adamantyl)-2-mercapto benzimidazole (3) was separated, in 95% yield, then was oxidized with hydrogen peroxide in alkaline medium which lead to formation of 5(6)-(1-adamantyl)-2-sulfobenzimidazole (4), in 76% yield. The boiling of 5(6)-(1-adamantyl)-2-sulfobenzimidazole (4) with ammonium acetate in aqueous area for 7-hours, gave 5(6)-(1-adamantyl)-2-aminobenzimidazole (5), in 93% yield. The N-acylation reactions of synthesized 5(6)-(1-adamantyl)-2-aminobenzimidazole (5) with benzoyl chloride and salicyl aldehyde were studied. Relative amide (6) and Schiff Base (7) were formed.
The reaction of 5(6)-(1-adamantyl)-2-aminobenzimidazole (5) with benzoyl chloride in absolute ether area in the presence of triethylamine gave us white crystals of 5(6)-(1-adamantyl)-2-benzo[y]aminobenzimidazole (6), in 70% yield. While 15-hours boiling of 5(6)-(1-adamantyl)-2-aminobenzimidazole with salicyl aldehyde in absolute ethanol area, gave us 5(6)-(1-adamantyl)-2-(2-hydroxybenzyldened)aminobenzimidazole as yellow crystals, in 93% yield.

Chromatographically pure samples are being prepared for studying of biological activity.

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References
Nowadays, the use of azide–alkyne click chemistry in polymer science is a rapidly growing field of research. The mild reaction conditions, functional group tolerance and quantitative yields allow the fast and simple creation of well-defined and complex polymeric structures that were previously unattainable. Since its introduction in polymer science in 2004, the copper(I) catalyzed azide–alkyne 1,3-dipolar cycloaddition has already been exploited for the synthesis of a variety of polymer architectures including end-functionalized polymers, block copolymers, cyclic polymers, graft copolymers, star-shaped copolymers, dendrimers and crosslinked materials [1]. Surprisingly, there are only a few papers [2-5] on the application of azide–alkyne click chemistry in step-growth polymerization as a chain propagation reaction for constructing either AB or AA-BB type polymeric backbones. At the same time, to our best knowledge, there are no examples of the synthesis of classical polymers like aliphatic or aromatic polyesters, polyamides, their copolymers via azide–alkyne click reaction. The state-of-the-art overview given in [5] supports our assessment.

Therefore, this research is dedicated to the obtaining of new biodegradable clicking poly(ester amide)s using copper(I) catalyzed azide–alkyne click cycloaddition-mediated step-growth polymerization. We have synthesized and characterized novel poly(ester amide)s containing triazole units in the backbone via the in situ click reaction of bisethynyl and dibromide compounds in the presence of sodium azide as a tricomponent reaction (Scheme 1).
Scheme 1. Synthesis of clicking poly(ester amide)s

The click step-growth polymerization was carried out in a high polar organic solvent (DMA) using copper(I) iodide as catalyst and triethylamine (NEt₃) as a ligand enhancing the activity of copper catalyst. The polymers obtained after click step-growth polymerization were characterized by FTIR, NMR, GPC, viscometry and DSC.

The resulting poly(ester amide)s could be of interest for various biomedical applications. Furthermore, quaternization of 1,2,3-triazole groups of the polymers will give highly charged cationic biodegradable polymers which can be promising as antimicrobial [6] and gene nonviral intracellular delivery (transfection) agents for the applications in both gene therapy and biotechnology [7,8].

References


PP 16. STUDY PHYSICAL, CHEMICAL AND TECHNOLOGICAL PROPERTIES, AND CHEMICAL COMPOSITION OF CLAYS SPREAD IN ADJARA REGION

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There are a lot of endemic resources in Georgia, which are not only untapped but also not studied. Their study and using methods are one of the most important tasks as in Modern Medicine, also in Cosmetology.

From the Earth’s resource, no one has such a broad, important and versatile use as clays. Clay is widely used in Medicine and Cosmetology – as in the form of nature as processed form, in particular: in Balneology and Resorts Therapy, for treatment of rheumatic and bone-joint disease, various types of skin diseases, besides that it’s very important to use it as the auxiliary means base in various soft and solid drug forms.

In the clay resources, it is particularly interesting in Adjara region. There the local population and a lot of tourists use clay arbitrarily, despite the fact that their chemical composition and medical properties have not been studied and it’s only on the traditional medicine level. In the literature available to us, we have not found the data about the clays research widespread in Adjara Region.

That’s why, one of the most actual problems in medicine and pharmacy is the clays research widespread in Adjara for the purpose of their using in medical and cosmetic practice.

We have studied the physical-chemical and technological features of the clays: phyluration, the, adhesions, congestion, the true, bulk and relative density, fractional compositions etc.

We have determined the chemical composition and the composition of biologically active substances with physical-chemical and instrumental methods of analysis, in particular have carried out the determination of macro and micro elements of clays in Rize (Turkey). There was used EPSILON 5 EDXRF, resulted in a through it was found that in the study samples there are a significant number of macro and micro elements necessary and...
essential for the human organisms.

Petrographic studies and X-ray diffraction were conducted on the base of Mining Geology Faculty of Georgian Technical University. There was used the polarization microscope Amscope PZ300T-5M and DRON-3. Researched of amino acids and fatty acids have been undertaken on the base of Tbilisi State Medical University.

Conduction of the mentioned researches will allow us to develop the nature, healing and cosmetic remedies of accessible and cheap price. Besides that, the above mentioned research will contribute not only to health care, but also in medical and economic Tourism of our country, in particular in popularization and development of the mentioned region, (manufacturing, employment, services, procedures, realization) and so on.

In scientific point of view, there was created the new form of pharmaco therapeutic means that will develop the new technologies and approaches in the field of using the healing clays.
PP 17. SYNTHESIS OF MACROCILYC AZOMETHIN COMPOUNDS

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Cyclic poly azomethine compounds are one of the important dyes of the fluorescent compounds. The compounds are characterized with easy and inexpensive preparation method and flexible technology giving opportunity of further purposeful modification of the properties with easy transformations and have ability to give crown like 32- and more membered poly azomethine macrocycles with hole diameter 1-10 nm and flat structure. Therefore, obtained compounds can be used as nanoparticles [3]. Macrocyclic azometin compounds are synthesised by two different methods [1,2]:

1. The condensation reaction between diamins and aldehids and

\[
\text{OH} \quad \text{OH} \\
\text{\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2} \quad \text{CH}_3\text{OH} \\
\text{OH} \quad \text{OH} \\
\text{\text{CHCl}_3; \text{NaOH}}
\]

2. Between bispenols and diamins with chloroform.

\[
\text{OH} \quad \text{OH} \\
\text{\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2; \text{CHCl}_3} \quad \text{NaOH} \\
\text{OH} \quad \text{OH}
\]

All synthesized compounds are explored by electronic absorption spectra.
References


PP 18. SYNTHESIS OF UNSATURATED BIODEGRADABLE POLY(ESTER AMIDE)s AND STUDY OF THEIR THERMAL AND MECHANICAL PROPERTIES

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Among biomedical polymers of different classes one of the key positions is held by AABB-structure poly(ester amide)s on the basis of natural amino-acids [1-7], which are characterized by interesting complex of properties: high skills of biodegradation and biocompatibility with tissues, hydrophylity, good material properties etc. Getting of even more diverse poly(ester amide)s with predetermined properties is possible via their functionalization, with insertion of chemically active groups, long hydrophilic chain into polymers etc. [8]. One of the prospective ways of polymers functionalization is represented by synthesis of macromolecules containing unsaturated bonds, which contain unsaturated bonds both in main chain and in lateral chains [9].

Taking into account the abovementioned, we set a goal to insert unsaturated bonds into AABB-type poly(ester amide)s with the purpose of their functionalization and respective extension of application area. Introduction of unsaturated bonds into main chain of polymers was implemented by us using fumaric acid – unsaturated dicarboxylic acid that was main monomer of the work [10].

Biodegradable Poly(ester amide)s of different structures, containing unsaturated double bonds in main chain are received: homopoly(ester amide)s (UPEA) with 100% content of fumaric acid residues, unsaturated/saturated poly(ester amide)s (USPEA) with <100% content of fumaric acid residues and saturated co-poly(ester amide)s of L-leucine and L-phenylalanine with 100% content of fumaric acid residues. Their thermal properties are studied with the purpose of determination of application area and possibilities of cross-linking of unsaturated Poly(ester amide)s using UV-irradiation are shown.

We studied thermal and mechanical properties of polymers and that allows us to identify the areas of their application. For instance, biodegradation of
crystalic polymers proceeds at far less rates than of amorphous polymers. Polymers with high vitrification temperatures are prospective compounds in the form of extracted surgical and construction materials, while polymers with low vitrification temperatures are used in the form of artificial leather, stent coating, for getting of medication controlled extraction systems, polymers with good mechanical characteristics are prospective generally as surgical materials, reconstructive orthopedic surgery, for preparation of blood vessels stent etc.

References


Every year ½ of world’s food supply undermines and grazes by plant pests, diseases and weeds. Agricultural and vegetable crops productivity is heavily dependent on the protection against them. For this purpose, combat chemical methods are used. Pesticides are substances meant for attracting, seducing, and then destroying any pest. They are a class of biocide. The most common use of pesticides is as plant protection products (also known as crop protection products), which in general protect plants from damaging influences such as weeds, fungi, or insects. Although pesticides have benefits, some also have drawbacks, such as potential toxicity to humans and another species. Triazole group of Chemicals-Fungicides are actual nowadays.

Here are explored chiral triazoles: Bitetranole, Diclorbutazole, Difenocouzole, Diniconazole, Fenbuconazole, Metconazole, Penconazole, Prothrocouzole, Triadimenole, Triadimefone, Vinclozoline, Itraconazole, Etconazole.

Used mobile phases: Methanol 100%+ Diethylamine 0.1%, Methanol-Water 97-3% + Diethylamine 0.1%, Methanol-Water 95-5%+Diethylamine 0.1%, Methanol-Water 90-10%+Diethylamine 0.1%, Methanol-Water 85-5% + Diethylamine 0.1%, Methanol-Water 80-20%+Diethylamine 0.1%, Methanol-Water 75-25%+Diethylamine 0.1%, Methanol-Water 70-30% + Diethylamine 0.1%.

The separation of enantiomers of 13 triazole derivatives was studied using polysaccharide-based chiral stationary phases and aqueous-organic mobile phases in high-performance liquid chromatography (HPLC). The major emphasis was made on the role of chemistry of a chiral selector and the mobile phase on elution order and separation mechanism of enantiomers.
For the most of chiral triazole derivatives studied the retention and separation factor of enantiomers increased with increasing content of water in the methanol as the mobile phase. An interesting effect was observed for the stereoisomers of difenconazole on the Lux Cellulose-3 column. In particular, in methanol containing 0.1% (v/v) diethylamine all four stereoisomers were baseline separated while separation worsened with increasing content of water and when water content in the mobile phase reached 20% only two separated peaks were observed. For the enantiomers of triadimephone separation of enantiomers increased with increasing content of water in methanol, reached the maximum at 15% water content, then decreased again and disappeared at the water content of 20%. For several analytes with two chiral centers all for stereoisomers were resolved baseline with various combinations of mobile and stationary phases.

References


The ability of C60 fullerene as an electron-deficient olefin is now well accepted. C60 fullerene behaves similar to an alkene with high electron deficiency. Therefore, C60 fullerene eagerly involves in nucleophilic reactions [1,2]. Functionalization of fullerenes denotes a suitable approach to modify their properties. C60 fullerene as an electrophilic compound tends to react with nucleophilic species in 1,2-addition reactions. Furthermore, C60 fullerene readily acts as a dienophile in a [4+2] cycloaddition reactions [3].

In this work, we have chosen ortho-quinone (o-quinone) to functionalized C60 fullerene. Additionally, o-quinone with different four functional groups including -OH, -NH₂, -CN and -NO₂ were used as substituents of C60 fullerene to investigate the influence of donor/acceptor groups on the thermodynamic properties of C60 fullerene.

Density functional theory (DFT) was accomplished to calculate geometry optimizations using B3LYP functional and 6-31G(d) basis set. The adsorption energies (E_{ad}) of pristine, and functionalized o-quinone molecules and C60 fullerene are obtained using equation $E_{ad} = E(\text{Quinone/C60}) - E(\text{C60}) - E(\text{Quinone})$, where $E(\text{Quinone/C60})$ is the energy of the complex between o-quinone and C60 fullerene. The exothermic character of the adsorption process is specified by the negative values of $E_{ad}$. To ensure that our optimized structures are correspond to global minima on the potential energy surface, vibrational frequency calculations have been done.

Among all possible interactions, the most stable complex between o-quinone and C60 fullerene is shown in figure 1. In order to find the adsorption behaviour of o-quinone molecule on C60 fullerene, we calculated $E_{ad}$ for pristine and functionalized o-quinone molecules react with C60 cage.
The negative values of $E_{ad}$ in our results indicates that o-quinone prefers to interact chemically with a carbon-carbon bond in a (6,6)-membered ring of C60 fullerene via its carbonyl groups. Generally, the driving force for [4+2] cycloaddition reaction is the creation of new two $\sigma$ bonds instead of three $\pi$ bonds. Also, by changing the $sp^2$ hybridization to $sp^3$, the strain in the C60 fullerene cage will reduce. The both newly formed bonds of oxygen-carbon are about 1.45 Å, which implies the covalent characteristic of interaction. The adsorption of o-quinone also causes slightly deformation on C60 cage, since as shown in figure 1, the 1.39 Å carbon-carbon bond length in C60 changes to 1.60 Å, after adsorption of o-quinone molecule.

Functionalization of o-quinone by different groups including -OH, -NH$_2$, -CN and -NO$_2$ was performed in para position of o-quinone. The values of $E_{ad}$ for pristine and functionalized o-quinone molecules and C60 are listed in table 1. One can clearly observe the process of increment of $E_{ad}$ by rising the electron withdrawing behaviour of functional groups as followed: -NO$_2$ > -CN > -H > -OH > -NH$_2$. Hence, we comprehend that in this [4+2] cycloaddition reaction, C60 acts as a dienophile in an inverse demand, since electron withdrawing groups make the lowest unoccupied molecular orbital (LUMO) of the diene (o-quinone) sufficiently electron-deficient, and as a result, the highest occupied molecular orbital (HOMO) of C60 (dienophile) can reacts easier with the LUMO of o-quinone. In contrast, the electron donating groups -NH$_2$ and -OH by enlarging the energy differences between LUMO of o-quinone and HOMO of C60, reduce the $E_{ad}$ values to -8.12 and -12.30.
kcal.mol$^{-1}$, respectively. Electron donating groups with lone pairs like -NH$_2$ inactivate the aromatic ring of quinone as an electrophile by increasing the electron density on the ring and reduce the $E_{ad}$ values.

Table 1. The total, adsorption, HOMO and LUMO energies and HOMO-LUMO energy gap of studied systems. HOMO-LUMO energies and gap are in eV.

<table>
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<th>System</th>
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<th>$E_{ad}$(kcal/mol)</th>
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<th>LUMO</th>
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The values of HOMO, LUMO and the HOMO-LUMO energy gap ($E_g$) listed in table 1 show the influence of pristine and functionalized o-quinone adsorption on the electronic structure of C60 fullerene. We obtained $E_g$ for the C60 about 2.76 eV using B3LYP functional, which is in good agreement with other previous theoretical reports [4-6]. The strong electron donating substituents such as -NH$_2$ and -OH decrease dramatically the HOMO-LUMO energy gap, but electron withdrawing groups do not change it. Nevertheless the weakness of the interaction between -NH$_2$ functionalized o-quinone and C60, one may use -NH$_2$ group to engineer the energy gap of C60 fullerene.

References


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Fused thieno[2,3-b]pyridines are ‘privileged medicinal scaffolds’ used for the development of pharmaceutical agents, showing a wide range of pharmacological activities [1]. On the other hand, fused triazoles represent an important and interesting class of nitrogen-containing five-membered heterocyclic systems due to their interesting range of biological activities: anti-inflammatory [2], antimicrobial [3], antifungal [4] and anticancer [5] activities, which makes the study of these compounds an attractive research field. For these reasons, the study of the properties of compounds simultaneously containing the above mentioned heterocycles appears interesting from both a theoretical and a practical point of view.

Taking into account our previous results in the field of condensed triazoles [6–8] some novel substituted thieno[2,3-e][1,2,4]triazolo[4,3-c]pyrimidines have been synthesized thus enlarging the spectrum of new molecules with pharmacological interest.

4-Alkyl(aryl)-7-hydrazino-9-(methylthio)-2,3-dihydro-1H-cyclopenta[4',5']pyrido[3',2':4,5]thieno[3,2-d]pyrimidines 1 [9] by the action of carbon disulfide in pyridine were cyclized into 10-alkyl(aryl)-5-(methylthio)-2,7,8,9-tetrahydro-3H-cyclopenta[4',5']pyrido[3',2':4,5]thieno[2,3-e][1,2,4]triazolo[4,3-c]pyrimidine-3-thiones 2, which were able to show the thiolactam-thiolactim tautomerism via the transfer of a hydrogen atom between the two basic centers. Indeed, the spectroscopic data of compounds 2 showed that the equilibrium favored the thiolactam form. Then, compounds 2 were alkylated by the action of methyl iodide in DMF in the presence of K₂CO₃ at 35–40 °C thus giving the 10-alkyl(aryl)-3,5-bis(methylthio)-8,9-dihydro-7H-cyclopenta[4',5']pyrido[3',2':4,5]thieno[2,3-e][1,2,4]triazolo[4,3-c]pyrimidines 3.
Finally, the reaction of compounds 3 in ethanol with various amines has been examined. As a result of the reactions the corresponding 10-alkyl(aryl)-3-(methylthio)-8,9-dihydro-7H-cyclopenta[4',5']pyrido[3',2':4,5]thieno[2,3-e] [1,2,4]triazolo[4,3-c]pyrimidin-5-amines 4 were obtained in high yields (Scheme).

The structure of compounds 4 (substitution of ‘only’ the SCH$_3$ group on the pyrimidine ring, that is the one linked to the ring more prone to react with a nucleophile) also was established by an alternative synthesis. Thus, at first compounds 2 were reacted with 2-methoxyethylamine thus giving the 10-alkyl(aryl)-5-[(2-methoxyethyl)amino]-2,7,8,9-tetrahydro-3H-cyclopenta[4',5']pyrido[3',2':4,5]thieno[2,3-e][1,2,4]triazolo[4,3-c]pyrimidine-3-thiones 5. Then, the obtained compounds 5 were alkylated with methyl iodide in DMF in the presence of K$_2$CO$_3$ at 35–40 °C yielding compounds 4 (Scheme).

Our investigations have shown that in these systems Dimroth rearrangement was not observed in both an acidic and basic medium probably due to the effect (steric or electronic) caused by the two methylthio substituents present on the triazole and pyrimidine rings (Scheme).


1–5. $R$ = alkyl, aryl; $R^1$, $R^2$ = H, alkyl; $R^1 + R^2$ = cycloalkyl
The structures of all synthesized compounds were supported by the NMR, IR, MS spectroscopy and by elemental analysis.

The synthesized compounds were tested for their possible antimicrobial activity using the agar diffusion method against Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacilli (*Sh. Dysenteriae Flexneri 6858, Eshercchia Coli 0-55*) strains. The experiments revealed that the tested compounds showed moderate antimicrobial activity.

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