

ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ  
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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ХИМИЧЕСКИЙ ЖУРНАЛ  
КАЗАХСТАНА

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CHEMICAL JOURNAL  
of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО  
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ  
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК  
им. А. Б. БЕКТУРОВА»

**1** (61)

ЯНВАРЬ – МАРТ 2018 г.  
ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА  
ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ  
2018

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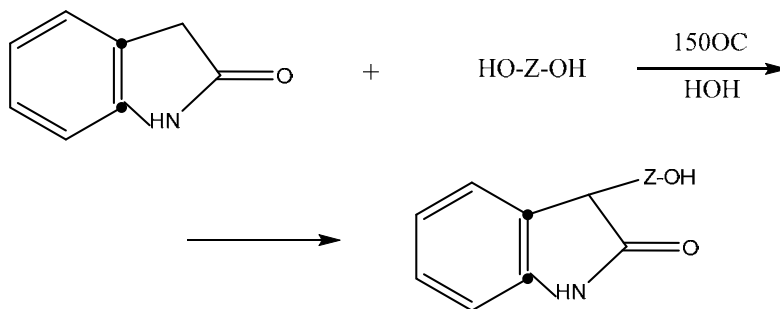
## SYNTHESIS OF DIHYDROXYALKYLCYCLOPENTADIENES

**Abstract.** Alkylation of cyclopentadiene with dihydric alcohols of the C<sub>2</sub>-C<sub>4</sub> series in the presence of an alkaline catalyst in a molar ratio of 1 : 2 in good yield have been carried out. The physico-chemical parameters of the synthesized products are determined. The structure of adducts is confirmed by modern physico-chemical methods of analysis.

**Key words:** alkylation, dihydric alcohols, cyclopentadiene.

It is known that dihydric alcohols can be used as alkylation agents of various classes of organic compounds and the results of similar studies are described in a number of scientific publications [1-14]. These studies describe the use and study of the mechanism of reactions involving alkylating agents used to convert carboxylic acids to esters, phenols to arylphenols, enols to enol esters and thiols to thioethers.

In work [1] a new synthetically convenient method of obtaining compounds interesting from the pharmaceutical point of view, based on alkylation of oxindole with diols, proceeds according to the scheme:



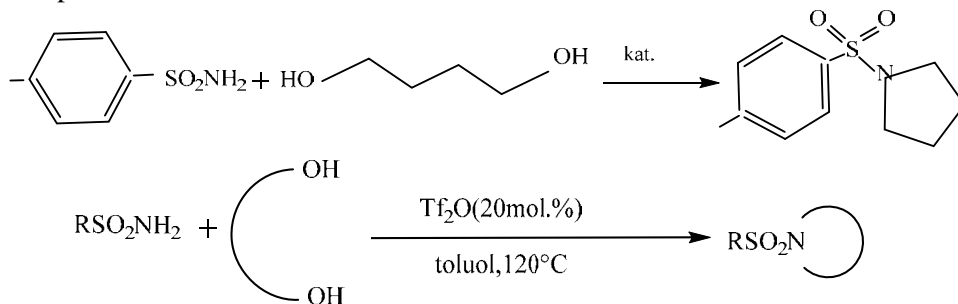
Z = (CH<sub>2</sub>)<sub>7</sub> (yield 66 %)

Z = (CH<sub>2</sub>)<sub>8</sub> (yield 72 %)

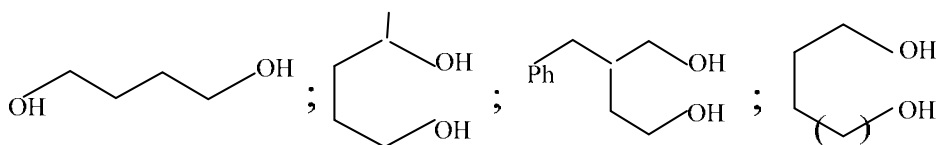
The monoalkylation of aniline and benzylamine with diols has been studied, leading to the formation of important 5-, 6- and 7-membered nitrogen-containing heterocycles used in pharmaceuticals [2].

In work [3] it is reported that sulfonamides are mainly used as antibacterial, diuretic, anticolvus and hypoglycemic drugs. In the alkylation of sulfonamides with 1,4-diols in the presence of trifluoromethanesulfonic anhydride, the reaction

proceeds in moderate conditions in high yields to form N-sulfonylpyrrolidine derivatives, which are the structural basis of a number of biologically active compounds.



Toluene, xylene, DMF, DMSO for 23-57 hours were used as a solvent. The yield of products was 68-96%. The following diols were used:

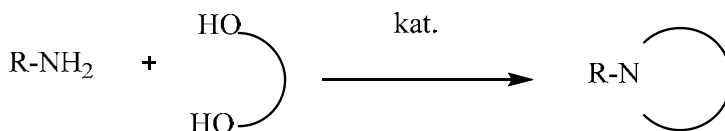


Patent [4] describes a process for the alkylation of ortho-disubstituted phenols with  $\alpha$ ,  $\omega$ -alkanediols containing 3 to 8 carbon atoms in the presence of an alkali metal hydroxide or alkoxide at a temperature of 200 to 300°C with the continuous removal of the by-product of water upon its formation.

The selective N-alkylation of primary amines by diols, promoted by an iridium catalyst supported on a metal oxide [5], was carried out.

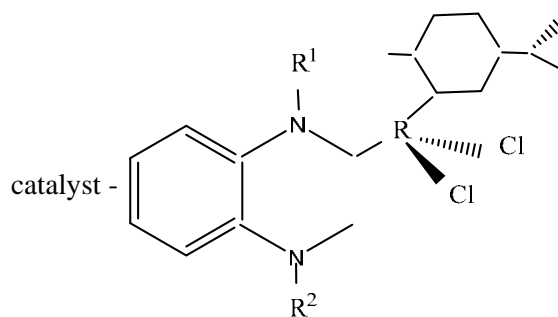
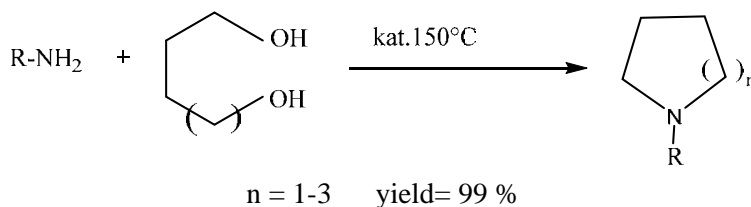
An effective method of N-alkylation of tryptamine and phenethylamine using alcohols and diols as an alkylating agent was proposed [6]. The reaction proceeds through catalytic electron activation involving an iridium catalyst that activates the alcohol by borrowing the hydrogen atom from the substrate, returning it later in the catalytic cycle.

N-alkylation of amines and ammonia with monohydric alcohols and diols has been studied with the aim of obtaining new biologically active compounds in the presence of transition metal complexes (Ir, Ru, Cu, Fe, Pd), in the complex part 2.5 mol. % [Ru (p-cymene) Cl<sub>2</sub>]<sub>2</sub> [7].



The review [8] presents the reactions of hydrogenation, addition, N-heterocyclization, and also alkylation involving alcohols and diols in the presence of an iridium catalyst that acts as a hydrogen acceptor from the alcohols forming iridium hydride, which is the key intermediate.

The simple ruthenium complexes stable to air and moisture, which are effective catalysts for alkylation of amines with the use of alcohols and diols [9], are synthesized according to the scheme:



$R^1, R^2$  – isopropyl, benzyl

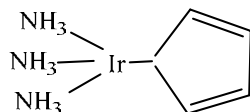
The reaction proceeds at a temperature of  $130^{\circ}\text{C}$  for 18 hours in the absence of a solvent. This environmentally friendly method can serve for the synthesis of pharmaceutically important amines.

Friedel-Crafts alkylation of simple aromatics (toluene, benzene, o-, m- and p-xylenes) by various diols in the presence of very strong trifluoromethanesulfonic acid was studied [10]. It has been found that 1,2- and 1,3-diols lead to the formation of unexpected products of predominantly monoalkylation. Thus, bis (1-methyl-2-phenyl) propyl ester forms in the reaction with 2,3-butanediol, and 2,4-dimethyl-2,4-pentanediol results in the formation of mono- and di-tert-butyl substituted benzenes. Higher homologues of diols, in turn, undergo electrophilic cycloalkylation with the formation of tetralin derivatives with high selectivity and good yields. By-side primary alkylation processes are monoalkylation to form alkylbenzenes and diphenylalkanes.

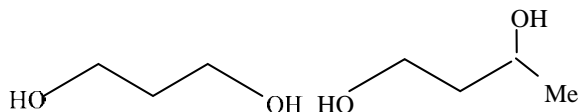
Direct amination of amines by mono- and dihydric alcohols in the presence of complexes of transition metals, in particular Ru, Pd, Ir [11]. However, recently, iron complexes have been used as a catalyst for this purpose. In this paper,

monoalkylation of anilines and benzylamines with diols is carried out, leading to the formation of 5-, 6- and 7-membered heterocycles of nitrogen, which are the structural units of a number of pharmaceutical preparations.

New water-soluble iridium complexes were synthesized and used as a catalyst in the multi-alkylation reaction of aqueous solutions of ammonia with alcohols [12]. It was shown that the catalyst exhibits a high activity in this reaction. When 1,5,9-nonantriol was used, quinolizidine was synthesized.

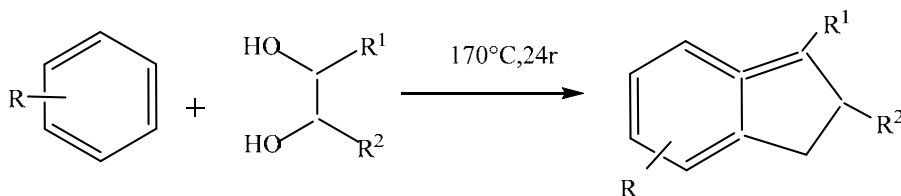


In the work [13] describes the catalytic alkylation of heteroarenes using mono- and dihydric alcohols as soft alkylating agents. The following diols were used:



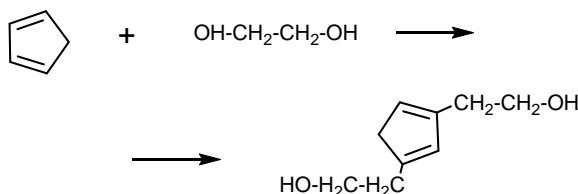
These reactions are the key stages in the synthesis of such drugs as fasudil and mildrinone.

Alkylation of aniline with vicinal diols was carried out in the presence of a catalytic ruthenium complex  $\text{RuCl}_3$  ( $\text{PPh}_3$  or xanthos) [14].



Thus, a review of literary reports shows that dihydric alcohols, as well as their monoatomic representatives, are often used in organic chemistry in alkylation reactions as an alkylating agent.

In this connection, in the continuation of our previous reports [13-16], we carried out the alkylation of cyclopentadiene with dihydric alcohols of the  $\text{C}_2\text{-C}_4$  series in a molar ratio of 1: 2 according to the scheme:



## Experimental part

Physic-chemical parameters of the starting compounds are presented in table 1.

Table 1 – Physicochemical properties of the starting compounds

Compounds	T. melt., °C	T. boil., °C	M <sub>r</sub>	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>
Dicyclopentadiene	32,5	172 (destr.)	132	1.5005	0.8280
Cyclopentadiene	- 97	42	66	1.4450	0.8050
Ethandiol-1,2	- 13.2	197.2	62	1.4319	1.1140
Propandiol-1,2	- 60	187.4	76	1.4326	1.0363
Butandiol-1,4	20	235	90	1.4463	1.0170

The IR spectra of the starting and synthesized compounds were taken on a UR-20 spectrophotometer in the 700-4000 cm<sup>-1</sup> region. NMR<sup>1</sup>H spectra were recorded on a Bruker WP-400 instrument (400 MHz). Chemical shifts are determined with respect to TMS, solvent C<sub>6</sub>D<sub>6</sub>.

The synthesis of the desired products was carried out according to the following procedure. A reaction flask equipped with a mechanical stirrer, a dropping funnel, a Dean-Stark nozzle with a condenser and a thermometer was charged with the calculated amount of the corresponding diol and 87% KOH solution. Before heating, a portion of DCPD was added to the reaction mixture. Then, the heating was adjusted to 200°C. After the water starts to collect in the Din-Stark nozzle, the remaining portion of the calculated amount of DCPD is added dropwise within 1.5 hours. After the end of the addition of the DCPD, the reaction mixture was heated for 4 hours. After cooling, the mixture was washed with water, hexane, dried over MgSO<sub>4</sub> and distilled under vacuum (p = 25 mm Hg). The corresponding di-n-hydroxyalkylcyclopentadiene was obtained.

Physic-chemical parameters of synthesized di-n-hydroxyalkylcyclopentadienes are presented in table 2.

Table 2 – Physicochemical properties of synthesized dihydroxyalkylcyclopentadienes

Compounds	T <sub>boil.</sub> , °C / mm Hg	M <sub>r</sub>	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>
Di-hydroxyethylcyclopentadiene	148-50/50	154	1,4250	0, 9850
Di-hydroxypropylcyclopentadiene	153-55/50	182	1,4435	0,9875
Di-hydroxybutylcyclopentadiene	165-68/50	210	1,4750	0, 9820

Figures 1–3 show IR-spectra of synthesized di-n-hydroxyalkylcyclopentadienes.

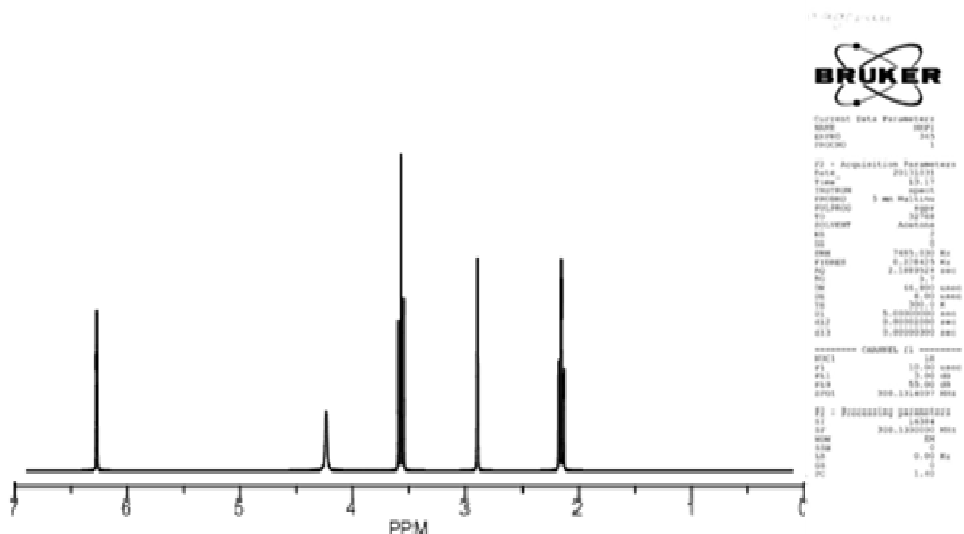


Figure 1 – NMR spectrum of dihydroxyethylcyclopentadiene

In the spectrum, absorption bands characteristic of the CH<sub>2</sub> group in the radical 2.15 (α), 3.55 (β) are observed; CH<sub>2</sub> groups in the 2.90 ppm cycle, as well as for the CH (in the ring) groups, 6.20 ppm. and OH groups 4.20 ppm.

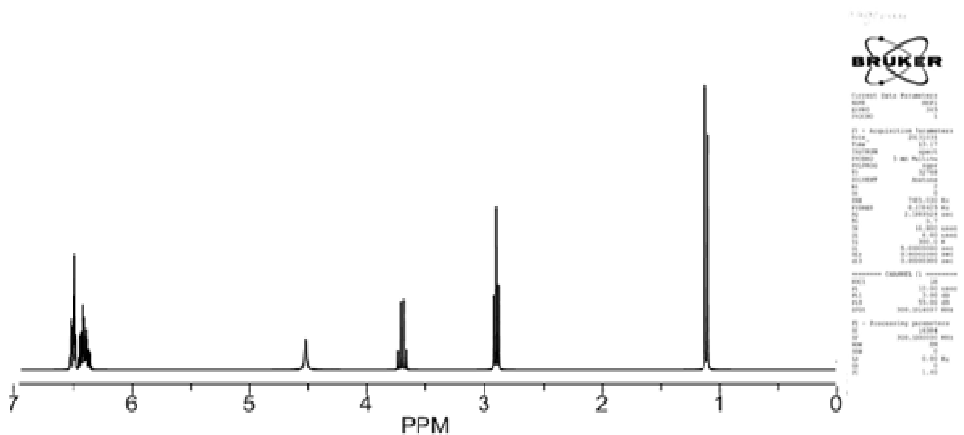


Figure 2 – NMR spectrum of dihydroxypropylcyclopentadiene

In the spectrum, absorption bands characteristic of the CH<sub>2</sub> group in the 2.20 radical are observed, and also for the CH groups (in the cycle), 6.40 ppm, 6.50 ppm. and OH groups of 4.30 ppm.

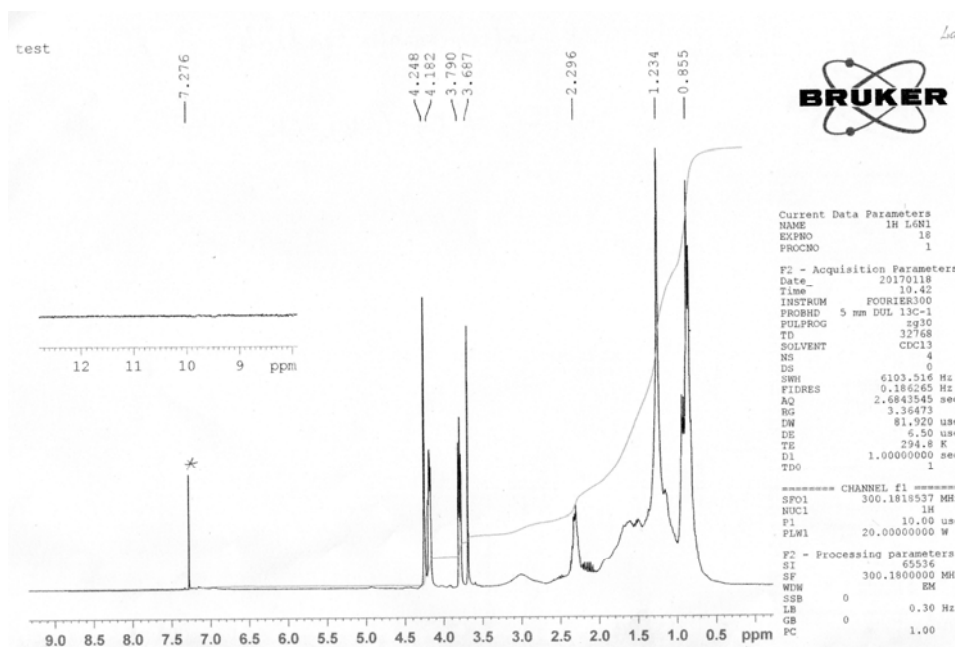


Figure 3 – NMR spectrum of dihydroxybutylcyclopentadiene

In the spectrum, absorption bands characteristic of the  $\text{CH}_2$  group in the radical 2,15 ( $\alpha$ ) are observed; 1,30( $\beta$ ); 1,52( $\gamma$ ); 3,45( $\delta$ ); 1,85( $\alpha$ ); 1, 39( $\beta$ ); 1,56( $\gamma$ ); 3,60( $\delta$ ), and also for the  $\text{CH}_2$  groups (in the cycle) 2.90 ppm, the CH groups (in the cycle) 6.25 ppm, and the OH groups 4.20 and 4.70 ppm.

The compounds obtained are synthones for the synthesis of the corresponding di-*n*-hydroxyalkylcyclopentanes, which can be obtained by hydrogenating the di-*n*-hydroxyalkylcyclopentadienes synthesized in this paper and used as additives to synthetic oils.

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### Резюме

*А. Г. Гасанов, А. М. Мамедова, И. Г. Аюбов, С. Т. Алиева, И. М. Мамедова*

### ДИГИДРОКСИАЛКИЛЦИКЛОПЕНТАДИЕНДЕРДІ СИНТЕЗДЕУ

1:2 мольдік қатынасында сілтілік катализатордың қатысуымен C<sub>2</sub>-C<sub>4</sub> қатарының екіатомды спиртпен циклопентадиенді алкилдеу жүзеге асырылды. Синтезделген өнімдердің физика-химиялық көрсеткіштері анықталды. Аддуктердің құрылымы заманауи физика-химиялық талдау әдістерімен анықталған.

**Түйін сөздер:** алкилдеу, екіатомды спирттер, циклопентадиен.

### Резюме

*А. Г. Гасанов, А. М. Мамедова, И. Г. Аюбов, С. Т. Алиева, И. М. Мамедова*

### СИНТЕЗ ДИГИДРОКСИАЛКИЛЦИКЛОПЕНТАДИЕНОВ

Осуществлено алкилирование циклопентадиена двухатомными спиртами ряда C<sub>2</sub>-C<sub>4</sub> в присутствии щелочного катализатора в мольном соотношении 1:2 с хорошим выходом. Определены физико-химические показатели синтезированных продуктов. Строение аддуктов подтверждено современными физико-химическими методами анализа.

**Ключевые слова:** алкилирование, двухатомные спирты, циклопентадиен.