ХИМИЧЕСКИЕ НАУКИ

SYNTHESIS OF 1,3,2-DIOXOAZAPHOSPHOLANES

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1. INTRODUCTION

The chemistry of phospholanes gained broad development first of all due to their many useful properties as the readily available intermediate monomeric substances with functional groups and various heteroatoms, and also having particular biological properties [1,2]. Phospholane cycle is a part of the biologically active synthetic material. In addition, it is a structural basis of many antimicrobic tools, thus researchers` interest in these sysQtems is caused [3-5].

With the purpose of obtaining new 1,3,2-dioxoazaphospholanes, the following compounds are used as starting reagents: ethylene glycol, phosphorus trichloride, alcohols, monoethanolamine vinyl ether (2-(ethenyloxy)ethan-1-amine). These substances are readily available monomers of chemical production. They are not waste products, but are monomers for obtaining different chemicals. The novelty of this work is that in order to obtain new phospholanes for the first time we used vinyl monoethanol amine ether. For the first time we obtained 1,3,2-dioxoazophospholanes.

The aim of this work was to develop preparative aspects of the formation reactions of phospholane series compounds at interaction of chlorine-containing phospholanes with monoethanolamine vinyl ether, which would extend preparative capabilities using a known method, and obtain previously unknown 1,3,2-dioxoazaphospholanes. Chlorides of ethyleneglycol phosphorus acid were taken as initial reagents. They were obtained by phosphorylation of ethylen glycol by means of phosphorus trichloride according to the scheme:

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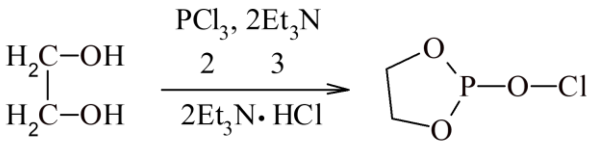

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(1)

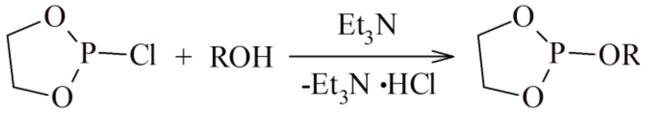
In the series of phosphorous organic compounds, 1,3,2-dioxoazaphospholanes have a huge potential as a synthetic materials, and are interesting objects to study different types of biological activities.

In the course of the experiment, we have successively obtained the compounds indicated in the article.

2. RESULTS AND DISCUSSION

The foundation of researches in the field of 1,3,2-dioxaphospholane is laid in Arbuzov and Kabachnik's works [6,7].

We investigated reactions of alkyl-1,3,2-dioxophospholanes with monoethanolamine vinyl ethers, which, in the result, leads to formation of series of 1,3,2-dioxophospholanes vinyl ethers derivatives. Firstly we synthesized 2-chloro-1,3,2-dioxaphospholane [8], and further corresponding alkyl-1,3,2-dioxaphospholanes were obtained on its basis according to the following scheme:



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(2)

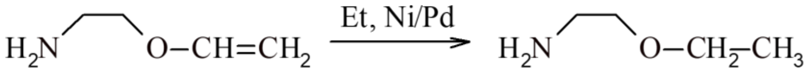
$R = C_2H_5$, n - C_3H_7, i - C_3H_7, n - C_4H_9

In order to obtain polyfunctional derivatives of phosphorous acid diols, in our investigations we used the chemical monomer of series of amino alcohols vinyl ethers - monoethanolamine vinyl ether.

Due to the presence of amino- and vyniloxi groups these compounds have a great sinthetic potential of amines and vinyl ethers.

Vinyl ethers and their derivatives are of great interest as monomers for sinthesis of polyfunctional compounds, which are widely used as chemotherapeutic drugs, plymer materials, pesticides, plant growth stimulators.

In the industry, ethoxyethylamine were obtained by catalytic hydrogenation on the basis of monoethanolamine vinyl ether. Ethoxyethylamine were used in synthesis of antidiabetic medicines. The scheme of this medicinal preparation is given below:



(3)

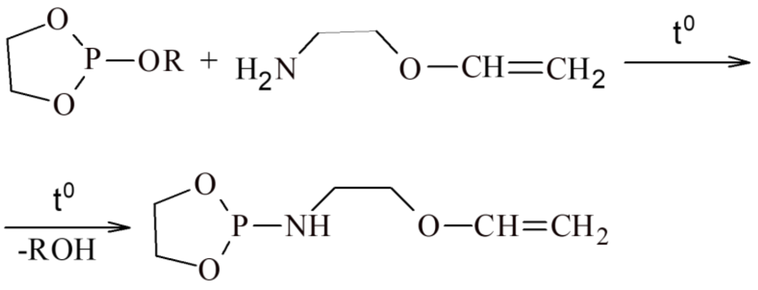
The synthesized vinyl ethers of Schiff bases are of interest as polyfunctional monomer compounds for the development of the theory and practice of functionally substituted vinyl ethers of amino alcohols, and for the further development of targeted methods of new biologically active derivatives synthesis on their basis having a set of properties that are important for practical applications.

The researches of properties of a number of Schiff bases containing amino groups, various on character, [8-14] were conducted in order to clarify the relationship between the structure and reactivity of vinyl ethers of amino alcohols.

Studying the properties and synthetic opportunities of amino alcohols vinyl ethers and their derivants, the researches of properties of a monoethanolamine vinyl ether monomer in reactions with phosphoric acid diols were continued.

Earlier we studied condensations of monoethanolamine vinyl ether with various carbonyl compounds, the corresponding Schiff bases were received [15-23].

With a view to expand the series of polyfunctional and heteroatom-containing derivatives of amino alcohols vinyl ethers, including monoethanolamine vinyl ether, the series of derivatives of 1,3,2-dioxophospholanes vinyl ethers was sinthesized in the result of interaction between alkyl-substituted diols of phosphorous acid with monoethanolamine vinyl ether (2-(ethenyloxy)ethan-1-amine):



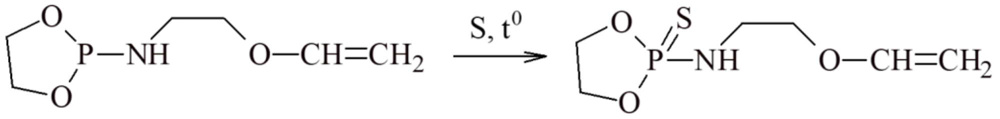
(4)

$R = C_2H_5, n - C_3H_7, i - C_3H_7, n - C_4H_9$

Molecules of 1,3,2-dioxaphospholane vinyl ethers derivatives contain reactive secondary amino groups and vinyloxy group.

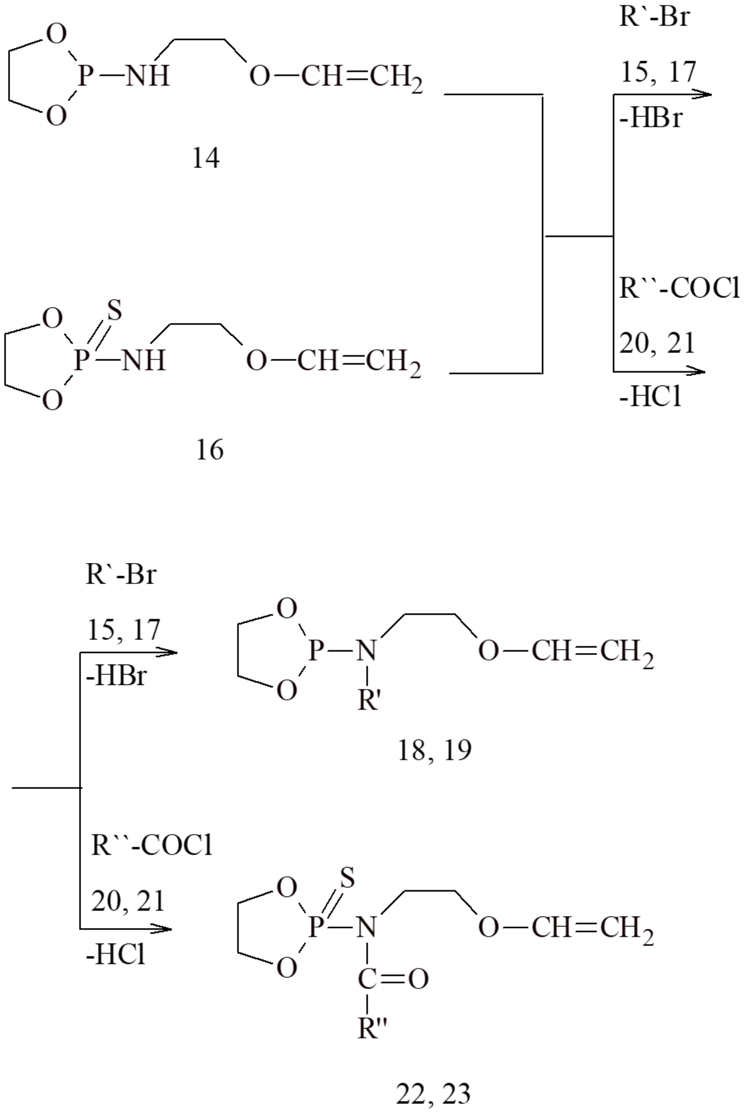
The presence of a trivalent phosphorus of dioxaphospholane cycle and the double bond in vinyloxy group causes high reactivity. Thus, organic phosphorus compounds containing R-C-N, P-O-C fragments deserve attention as effective bioactive, flotation and complexing agents. These compounds possess unique reactivity due to the mutual influence of geminal nitrogen and phosphorus atoms.

Due to our research interests in the field of organophosphorus compounds chemistry [8-10], we conducted the reaction of N-vyniloxiethyl-1,3,2-dioxaphospholane with elemental sulfur, which resulted in the corresponding synthesized thiophospholane:



(5)

Reactions of alkylation and acylation were carried out in order to elucidate the reactivity of synthesized 1,3,2-dioxathiophospholanes. As a result, the corresponding alkyl and acyl derivatives of phospholanes were obtained:

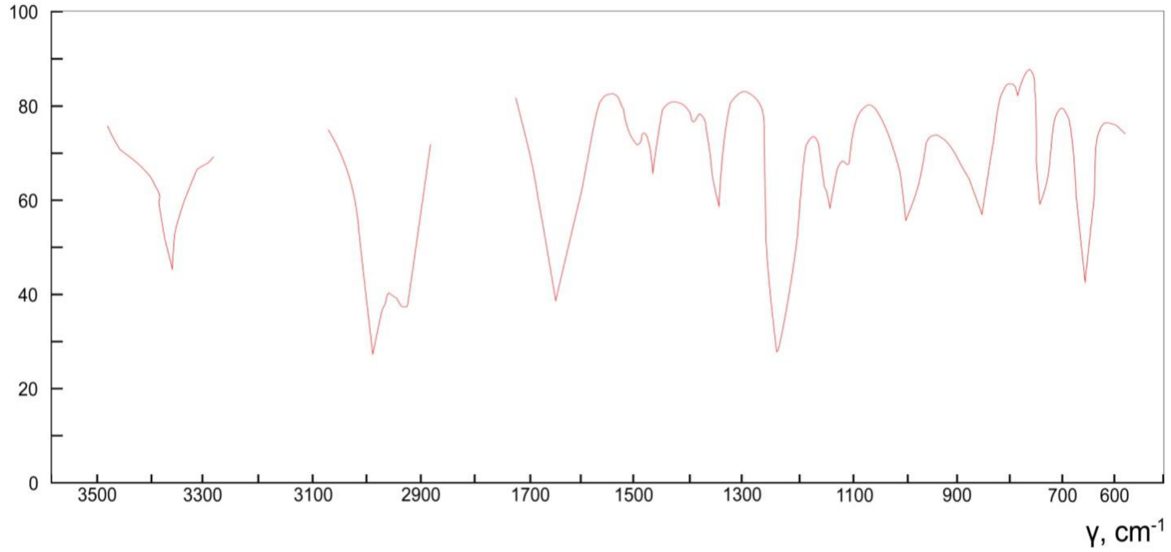


(6)

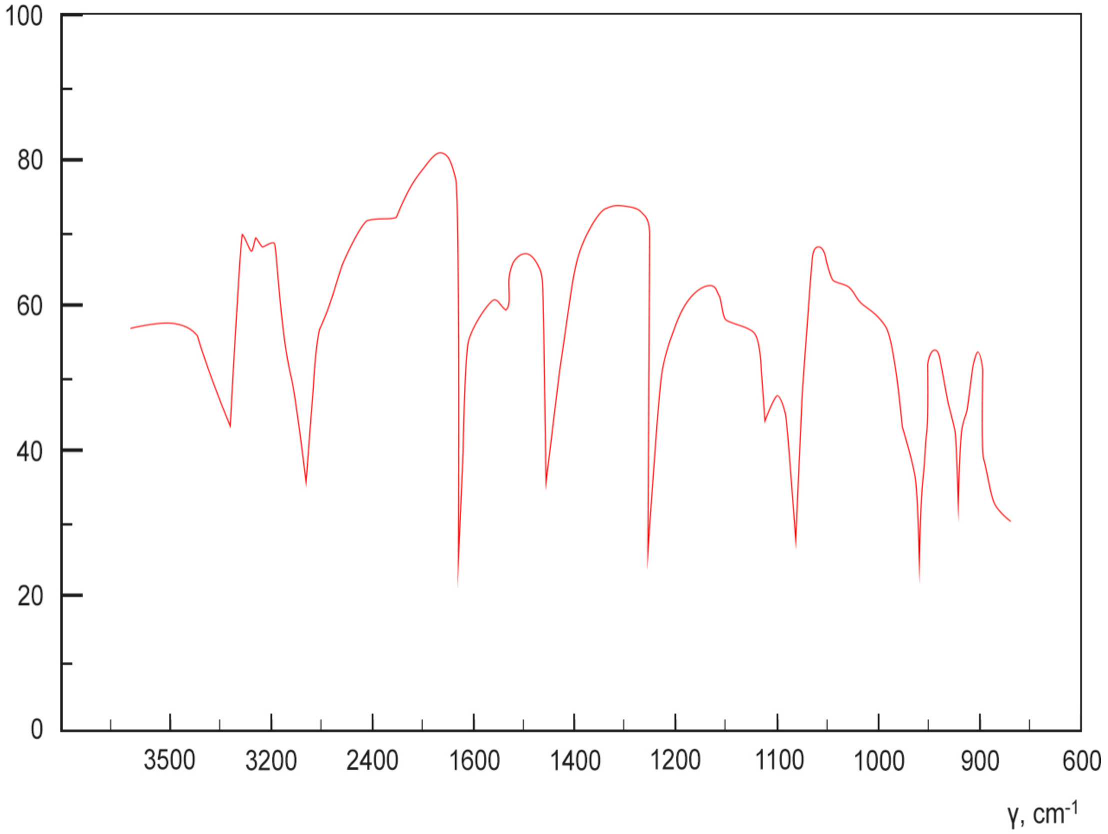
R` = C_2H_5, n - C_3H_7, R`` = CH_3, C_2H_5

The structure of the obtained substances confirmed by 31P NMR and IR spectroscopy. IR spectra (δ): P=S (630-650), P-N (890-920), P-O-C (1135-1180), C=C (1605-1625), N-H (3260-3280).

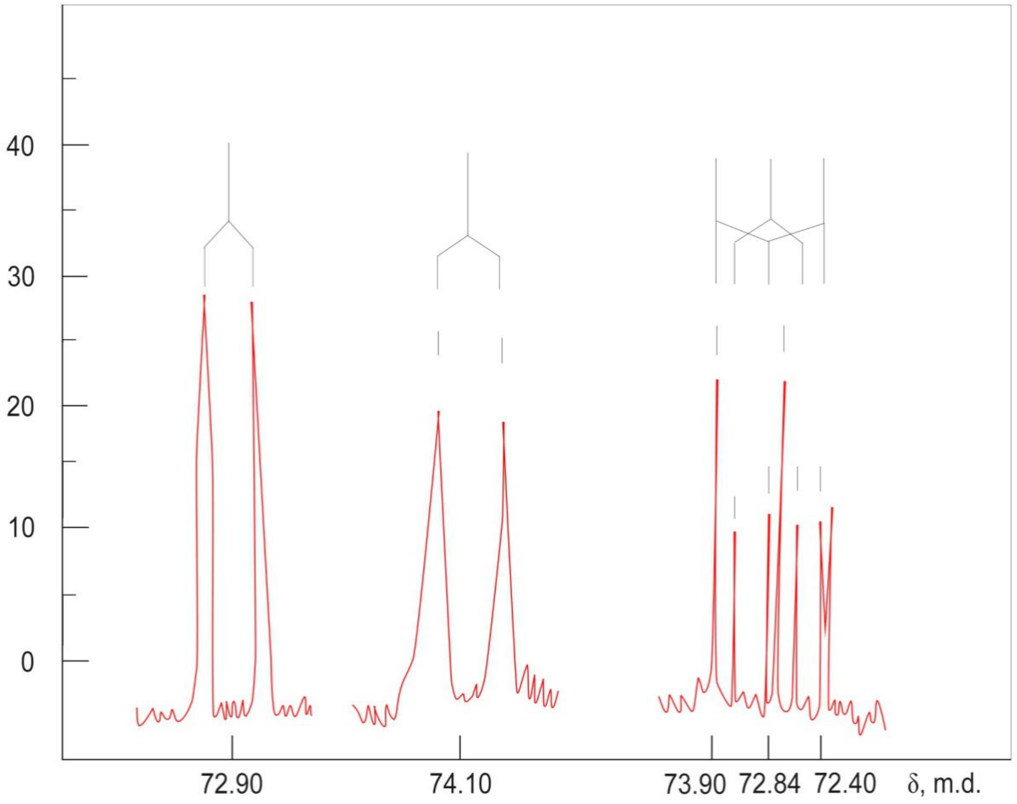
31P NMR spectra -(1H) [, ppm.[: Pr n 72.40 (s), Pr iso 72.84(s), Bu n 72.90(s), Pr iso PP piperidyl-74.10(s), Bu n PP piperidyl 73.90(s).



Picture 1: IR-spectrum of O,O-dipropyl(N-2- vinyloxy)ethylamidophosphorus.



Picture 2: IR-spectrum of o-butyl(piperidyl)-N-2-(vinyloxyethylamido)-thiophosphorous.



Picture 3: NMR ^{31}P spectrum of O-i-propyl-[N-2-vinyloxyethylamid]thiophosphorus.

IR spectra were obtained on a spectrophotometer UR-20. 31P NMR spectra were recorded on the instrument "Bruker WP-200 SY" (81.01 MHz, the standard - 85% H_3PO_4).

Currently, the biological activity of the compounds is studied by computer prediction, structure is studied by the quantum chemistry method.

3. EXPERIMENTAL SECTION

3.1 O.O-Dipropyl - {N-2-(vinyloxy), ethylamido}thiophosphate

4.55 g (0.025 moles) of thiophosphite O,O-dipropyl was added to benzene solution of 2.17 g (0.025 moles) of monoethanolamine vinyl ether, 2.5 g (0.025 moles) of triethylamine, and 3.84 g (0.025 moles) of CCL_4 under stirring and a temperature of 18^{o}C. Hydrochloride of triethylamine precipitated in process of cooling of a reaction mixture. The sediment was filtered, then the filtrate was boiled out in vacuo, the rest was investigated on a chromatograph with a column with a silica gel, eluent - hexane - acetone (3:1).

O,O-diisopropyl-, O,O-dibutyl-, O-isopropyl (piperidyl) [N-2-vinyloxyethylamido]thiophosphate and O-butyl (piperidyl) [N-2-vinyloxyethylamido]thiophosphate were received similarly.

The purity of the compounds and the reactions were monitored by TLC on Silufol UV 254 plates in specified eluents systems. The manifestation was carried out with iodine vapor.

^{31}P NMR spectra was recorded on the "Bruker WP-200SY" device with an operating frequency on nuclei ^{31}P 81.01 MHz; external standard - 85% solution of H_3PO_4.

3.2 Synthesis of 2-chloro-1,3,2-dioxaphospholane

50 ml of anhydrous ether, 9.3 g of ethylene glycol and 22.0 g of pyridine were placed in the reaction flask. 20.62 g of phosphorus trichloride was added to the reaction mixture with stirring at a temperature of from -16 to -17^{o}C. After the addition of phosphorus trichloride at room temperature, the solution was left with stirring for about 1.5 hours. During the reaction, the pyridine hydrochloride formed. The ether solution of 2-chloro-1,3,2-dioxaphospholane was isolated by filtration. Further desired product 2-chloro-1,3,2-dioxaphospholane was obtained by simple distillation. Boiling point = 56^{o}C, =1.4917. Molecular Weight = 126.49. Gross formula – $C_2H_4PO_2Cl$.

3.3 Synthesis of 2-alkoxy-1,3,2-dioxaphospholanes

3.3.1 Synthesis of 2-ethoxy-1,3,2-dioxaphospholane

30 ml of absolute diethyl ether, 1.72 g of ethanol, and 2.96 g of pyridine were placed in a reaction flask. 4.74 g of 2-chloro-1,3,2-dioxaphospholane was dropped into the reaction mixture with stirring. The reaction flask was cooled with a mixture of ice and salt to +3 - -6^{o}C degree. During the reaction, the pyridine hydrochloride formed. After filtration ether solution of 2-ethoxy-1,3,2-dioxaphsopholane was obtained. Desired product was obtained with distillation. The purity of product was checked with TLC. Properties of 2-ethoxy-1,3,2-dioxaphsopholane: boiling point is 51.0-51.5^{o}C, =1.4395, =1.1317. Gross formula – $C_4H_9PO_3$.

2-propoxy-1,3,2-dioxaphospholane, 2-isopropoxy-1,3,2-dioxaphospholane, 2-butoxy-1,3,2-dioxaphospholane were synthesized under similar condition.

3.3.2 Synthesis of 1,3,2-dioxaphospholane amide ether

1.07 g of desired product was obtained from 1.01 g of 2-ethoxy-1,3,2-dioxaphospholane and 0.64 g monoethanol amine vinyl ether in a dry diethyl ether environment. The purity of the product was checked with TLC. The folllowing system of eluants was used: chloroform:acetone (1:1), =1.4435, =0.1928. Gross formula: $C_6H_{12}NPO_3$.

3.3.3 Syntheses of 1,3,2-thiophospholane

25 ml of benzene and 0.023 g of elemental sulfur were placed into the reaction flask. Then it was heated to the full dissolution of sulfur in benzene. After that, the flask was cooled. Then, 0.12 g of 1,3,2-dioxaphospholane amide ether was added to the reaction mixture. The product was heated at a temperature of 76°C for 30 minutes. The resulting product was then left at room temperature for 25 minutes. After that, benzene was removed from the mixture. The resulting product 1,3,2-dioxathiophospholane is a dark gray liquid. The refractive index is 1.4650. The gross formula is $C_6H_{12}NO_3PS$. The product dissolves well in ethanol, chloroform and acetone. It does not dissolve in petroleum ether, diethyl ether and toluene.

3.3.4 Synthesis of the acyl derivative of the 1,3,2-dioxaphospholane amide

25 ml of absolute diethyl ether, 0.17 g of the 1,3,2-dioxaphospholane amide ether, 0.10 g of triethylamine were placed in the reaction flask. Further, 0.07 g of acetyl chloride was added to the ether mixture through a dropping funnel with stirring. In this case precipitation is observed. The precipitate of triethylamine hydrochloride was filtered off. Then, diethyl ether was removed. The purity of the product were checked by thin layer chromatography. A clear liquid product, 1,3,2-dioxaphospholane N-acetyl-amide ester, was obtained. = 1.4541. Gross formula: $C_6H_{10}NPO_3$.

3.3.5 Synthesis of alkyl derivatives of 1,3,2-dioxaphospholane amide ether

Under similar conditions, 1.67 g of the reaction product, N-ethyl amide ether, was isolated in the medium of the absolute ether from the Grignard reagent (0.6 g of magnesium and 2.7 g of ethyl bromide), 1.4 g of 1,3,2-dioxaphospholane amide ether. = 1.4445. The gross formula is $C_8H_{16}O_3PN$.

The IR spectra of the compounds obtained exhibit characteristic absorption regions (cm^{-1}) (δ): PN (870-925), P=S (680-710), C=O (1640-1660), CN (1495-1580) , -OC=C- (1460-1480), POC (1100-1165).

In ^{31}P NMR there is one singlet in the region -60÷63 ppm.

4. CONCLUSION

In the process of phosphorylation of ethylene glycol in the presence of phosphorus trichloride and alcohols, cyclic alkyl derivatives of phospholanes were synthesized. And on the basis of cyclic phospholanes and vinyl ether monoethanol amine, amine derivatives of phospholanes were first obtained. Subsequently, cyclic amino derivatives of phospholanes undergo an acylation reaction. In the result, acyl derivatives of cyclic phospholanes and their thio derivatives were synthesized.

The importance from the theoretical point of view of the amino derivatives of cyclic phospholanes are promising chemical monomers. Since the molecule contains vinyloxy and a secondary amine group. 1,3,2-dioxoazophosphlanes form a class of biologically active substances and can have antibacterial properties.

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ИЗОТОПНАЯ СЕЛЕКТИВНОСТЬ ГИДРАТАЦИИ ПЕРОКСИДА КАЛЬЦИЯ

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THE ISOTOPIC SELECTIVITY OF THE HYDRATION OF CALCIUM PEROXIDE

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АННОТАЦИЯ

Экспериментально показано, Что при взаимодействии с водой, загрязненной тритием, безводный пероксид кальция проявляет изотопную селективность, формируя гидратную оболочку образующегося труднорастворимого октагидрата кальция из протиевой воды и оставляя тритиевую воду в жидкой фазе.

ABSTRACT

It has been shown experimentally, that during an interaction with water, contaminated with tritium, anhydrous calcium peroxide exhibits isotopic selectivity, forming a hydrated shell of the produced insoluble calcium octahydrate from protium water and leaving tritium water in the liquid phase.

Ключевые слова: Пероксид кальция, гидратация, изотопная селективность, Фукусима
Keyword: Calcium peroxide, hydration, isotopic selectivity, Fukushima

Для разделения изотопов водорода известны многие методы, основанные на различиях свойств их соединений, таких как температура плавления и кипения, потенциал ионизации и др. [2, 3]. Реализация этих в принципе несложных подходов требует, однако, сравнительно непростой аппаратуры, использования дорогих катализаторов на основе палладия или платины, больших затрат труда, времени и электроэнергии.

В настоящей работе описываются результаты исследования взаимодействия безводного пероксида кальция (ПОК) с водой, загрязненной тритием. Известно [1], что при гидратации ПОК образуется труднорастворимый октагидрат пероксида кальция (ОГ ПОК) $CaO2{\cdot}8H2O$.

Пероксид кальция – продукт крупнотоннажного производства химической промышленности. Его использование основано, главным образом, на способности испускать кислород при медленном разложении:

$$CaO_2 + H_2O \rightarrow Ca(OH)_2 + \tfrac{1}{2}O_2$$

Кислород in statu nascendi воздействует на корневые системы растений, что ведет к повышению урожайности почв, может обеззараживать воды и почвы и имеет множество других областей применения.

В экспериментальной работе использовался технический ПОК, синтезированный в Институте Общей и Неорганической Химии РАН и содержащий довольно высокий процент примесей (до ~40%), таких как карбонат и оксид кальция и др.

Как показали экспериментальные исследования авторов, при добавлении безводного ПОК к воде, содержащей тритий, для формирования гидратной оболочки ПОК использует только молекулы протиевой воды. В результате удельная активность трития в жидкой фазе над осадком ОГ ПОК повышается с увеличением массы добавляемого ПОК (Рисунок 1).