SÍNTESE DO 2-(2'- ACILOXI-ETÓXI) CLORETO DE ETILA E SUA INTERAÇÃO COM AMIDOS E RODANÍDEOS DE METAIS ALCALINOS

SYNTHESIS OF 2- (2' – ACYLOXY-ETHOXY) ETHYL CHLORIDE AND THEIR INTERACTION WITH AMIDES AND ALKALI METAL RHODANIDES

СИНТЕЗ 2- (2' - АЦИЛОКСИ-ЭТОКСИ) ЭТИЛХЛОРИДОВ И ИХ ВЗАИМОДЕЙСТВИЕ С АМИНАМИ И РОДАНИДАМИ ЩЕЛОЧНЫХ МЕТАЛЛОВ

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RESUMO

Este trabalho tem como objetivo estudar a reação de substituição nucleofílica do átomo de cloro em 2-(2'-aciloxi-etoxi) etilcloreto com aminas e um íon rodanida e desenvolver métodos de síntese de 2-(2'-aciloxi-etoxi) etilcloreto, rodanidas e seus derivados anteriormente desconhecidos na literatura especializada. Na molécula de cloridrina de dietilenoglicol há dois centros de reação que permitem a realização de reações de substituição nucleofílica, bem como reações que os promovem com reagentes eletrofílicos. Os autores realizaram diversas experiências para acilação de cloridrina de dietilenoglicol com ácidos carbônicos, reações de substituição nucleofílica de o átomo de cloro em 2-(2'-aciloxi-etoxi) etilcloreto com várias aminas, bem como sintetizou-se o éter cloracetoxietílico de ácido rodano acético. Ao estudar a substituição nucleofílica de 2-(2'-aciloxi-etoxi) etilcloreto com o íon rodanida, descobriu-se que apenas o átomo de cloro foi substituído. A possibilidade da substituição nucleofílica da clorohidrina de etileno foi mostrada através do exemplo de N-metil e N-etilanilinas. Descobriu-se que o grupo hidroxila do dietilenoglicol poderia reagir com os ácidos carbônicos na presença de catalisadores e, portanto, estimular a esterificação. Verificou-se que a substituição nucleofílica do átomo de cloro em 2-(2'-aciloxi-etoxi) etilcloreto com o íon rodanida corre suavemente na presença de iodeto de potássio atuando como um ativador e que o grupo aciloxi não é afetado. Descobriu-se que o papel primário na substituição nucleofílica de halogenetos de alcóxialquilo é desempenhado pela basicidade das aminas e pela essência e posição dos substituintes em relação ao grupo alcóxilo do átomo de halogênio.

Palavras-chave: cloridrina de dietileno glicol, substituição nucleofílica, acilação, produtos químicos reativos, espectros.

ABSTRACT

This work is aimed at studying the reaction of nucleophilic substitution of the chlorine atom in 2-(2'-acyloxy-ethoxy) ethylchlorides with amines and a rhodanide ion and developing methods of synthesizing a 2-(2'-acyloxy-ethoxy) ethylchlorides, rhodanides, and their derivatives previously unknown in specialized literature. In the chlorohydrin molecule of diethylene glycol, there are two reaction centers that allow carrying out nucleophilic substitution reactions, as well as reactions that promote them with electrophilic reagents. The authors carried out several experiments for acylating diethylene glycol chlorohydrine with carbonic acids, reactions of nucleophilic substitution of the chlorine atom in 2-(2'-acyloxy-ethoxy) ethylchlorides with various amines as well as synthesized the chloracetoxethyl ether of rhodane acetic acid. While studying the nucleophilic substitution of

2-(2'-acyloxy-ethoxy) ethylchlorides with the rhodanide ion, it was discovered that only the chlorine atom was replaced. The possibility of the nucleophilic substitution of the ethylene chlorohydrine was shown by the example of N-methyl and N-ethylanilines. It was discovered that the hydroxyl group of diethylene glycol could react with carbonic acids in the presences of catalysts and, therefore, encourage esterification. It has been found out that the nucleophilic substitution of the chlorine atom in 2-(2'-acyloxy-ethoxy) ethylchlorides with the rhodanide ion goes smoothly in the presence of potassium iodide acting as an activator and that the acyloxy group is unaffected. It has been discovered that the primary role in the nucleophilic substitution of alkoxyalkylhalides is played by the basicity of amines and the essence and position of substituents relative to the alcoxyl group of the haloid atom.

Keywords: *diethylene glycol chlorohydrine, nucleophilic substitution, acylation, reactive chemicals, spectra.*

АННОТАЦИЯ

Целью исследования является изучение реакции нуклеофильного замещения атома хлора в 2-(2'-ацилоксиэтокси) этилхлоридах аминами и роданид-ионом, выяснение факторов, влияющих на ход реакции и реакционную способность, разработка методов синтеза неизвестных в литературе 2-(2'-ацилоксиэтокси) этилхлоридов, роданидов и их ацилпроизводных. В молекуле хлоргидрин диэтиленгликоля имеются два реакционных центра, позволяющие провести реакции нуклеофильного замещения, а также способствующие их реакции с электрофильными реагентами. Авторы провели эксперименты по ацилированию хлоргидрина диэтиленгликоля карбоновыми кислотами, провели реакции нуклеофильного замещения атома хлора 2-(2'-ацилоксиэтокси) этилхлоридов различными аминами и синтезировали хлорацетоксиэтиловый эфир родануксусной кислоты. При изучении реакции нуклеофильного замещения 2-(2'-ацилоксиэтокси) этилхлоридов роданид-ионом было обнаружено, что замещению подвергается исключительно атом хлора. Возможность нуклеофильного замещения атома хлора этиленхлоргидрина была показана на примерах N-метил- и N-этиланилинов. Было выявлено, что гидроксильная группа хлоргидрина диэтиленгликоля способна вступать в реакцию с карбоновыми кислотами в присутствии катализаторов, приводя к образованию сложных эфиров. Найдено, что нуклеофильное замещение атома хлора 2-(2'-ацилоксиэтокси) этилхлоридов роданид-ионом протекает гладко в присутствии активатора – иодистого калия. Установлено, что при этом ацилоксигруппа не затрагивается. Выявлено, что при нуклеофильном замещении алкоксиалкилгалогенидов аминами основную роль играет основность аминов, природа и местоположение заместителей по отношению к алкоксильной группе атома галоида.

Ключевые слова: *Хлоргидрин диэтиленгликоля, нуклеофильное замещение, ацилирование, реагенты, спектры.*

1. INTRODUCTION

Haloid alcohols and esters are interesting, simple, and convenient models for studying the reactive ability of separate function groups as well as their reciprocal influence. The influence of function groups on the reactive ability of haloid esters strongly shows depending on their remoteness. Halogen is very active in the α position to the ester group, relatively inert in the β position, whereas γ haloid esters hardly differ from halogen alkanes in terms of reactive ability. Despite the inert behavior of the haloid atom, β haloid esters can enter into various reactions of substitution. A special interest is awakened by β haloid esters because they can turn into epoxy compounds with a very strong reactive ability (Pokonova, 1966).

The chemistry of chlorohydrines additionally containing an ether link is still understudied despite the presence of a chlorine

atom, a hydroxyl group, and an ether component in their molecules, which makes chlorohydrines chemically interesting. That is why the study of reactions of 2-(2'-acyloxy-ethoxy) ethylchloride (diethylene glycol chlorohydrine) awakes an undoubted theoretical interest. In addition, diethylene glycol chlorohydrine is the waste of ethylene chlorohydrine production and can serve as the original compound for synthesizing multifunction substances (Pokonova, 1966, 1982).

In the literature about β haloid alcohols, the reactions of nucleophilic substitution of the chlorine atom of ethylene chlorohydrine are studied in more detail. The interaction between ethylene chlorohydrine and nucleophilic reactive chemicals may form the oxide of ethylene that reacts with amines, or else the chlorine atom is directly replaced with the nucleophilic residue (Pokonova, 1982). Usually, the reaction is carried out in abundance of amine or in the presence of bases necessary for binding released hydrogen

chlorine. The salts being formed can catalyze the process. Products of various types of substitution may form depending on the existence and kind of substituents in the nitrogen atom and also in the benzene cycle, i.e., one or two chlorine atoms from two ethylene chlorohydrine atoms of the primary amino group can enter into the reaction. The reaction of ethylene chlorohydrine with primary amines is also attended by the cyclization of the formed intermediate compounds to respective 1,4-piperazines (Pokonova, 1982).

The nucleophilic substitution of the ethylene chlorohydrine atom (primary, secondary, tertiary) has been investigated in sufficient detail. The reactions were carried out both, in the presence and absence of alkali agents at variable temperatures and duration (Traven, 2008; Ivanov, 2006; Knoop, 1989; Nenicescu, 1962; Berezin, 2003; Elderfield, 1961; Temnikova, 1968; Gorodiov and Petrov, 1966; Gilmanov *et al.*, 2013). Sometimes, water was used to prevent secondary processes. The nucleophilic substitution of the chlorine atom in ethylene chlorohydrine with aniline leads to N- β -oxyethyl aniline (Nenicescu, 1962). High product output is observed during the heating for 15 minutes at the boiling point of the reaction mixture (see Eq. 1).

The temperature rises to 180°C decreases the target product output because the chlorine atom is replaced with the second molecule by formed N- β -oxyethylaniline, which leads to N, N' - bis- (β -oxyethyl)aniline. The bis-product formation process is suppressed, and the target compound increased in volume by adding water. In this case, a high degree of substitution is observed when an aniline/ethylene chlorohydrine ratio of 1:1 is used (Shorygin and Beglov, 1936).

Although water leads to an increased output of the resultant, it partially hydrolyzes ethylene chlorohydrine to ethylene glycol. Hydrolysis was prevented by means of alkali metal hydroxides and carbonates (Petrov *et al.*, 1954). However, this method applies only to an excessive amount of aniline (aniline/ECH = 2:1). In the absence of the specified reactive chemicals, aniline reacts even with ethylene chlorohydrine excess (aniline/ECH = 2:1) and thus forms N- β -oxyethylaniline.

To carry out the secondary nucleophilic substitution, the reaction mixture was neutralized with caustic alkali after the end of the reaction (Petrov *et al.*, 1953). As noted above, the reaction of aniline and other amines with ethylene chlorohydrine can develop in two ways, i.e., with

the formation of ethylene oxide in the absence or presence of alkalis, which was pointed out in works (Petrov *et al.*, 1953; Tulyaganov, 1972); ethylene chlorohydrine reacts with amines and forms the respective amino alcohol. The same authors admit that the direct nucleophilic substitution of the chlorine atom of ethylene chlorohydrine is possible. According to the kinetic research of the reaction of aniline and other amines, it develops with the direct substitution of a chlorine atom with an amino group.

According to the literature data on studying the nucleophilic substitution of the chlorine atom of ethylene chlorohydrine, the reaction speed depends mainly on the amino group basicity, which has to do with the electron essence of the substituent in the benzene ring, which increases or decreases the amino group basicity. Electron-donating substituents favor nucleophilic substitution, whereas substituents with a negative J effect, especially in the meta position relative to an amino group, inhibit the course of this reaction. It should also be noted that ethylene chlorohydrine can react with primary aromatic amines also in the form of ethylene oxide, in which case nucleophilic substitution occurs by directly substituting the chlorine atom. According to the available data on nucleophilic substitution of ethylene chlorohydrine with aromatic amines with electron-acceptor substituents, this reaction develops with difficulty, which is due to the low basicity of the specified amines. The possibility of nucleophilic substitution of the chlorine atom of ethylene chlorohydrine was shown by the examples of N-methyl and N-ethyl anilines. To carry out the reaction of a secondary amine, it is often necessary to use a double excess of a respective amine; moreover, this requires following harder conditions (160°C, 7 hours) (Lattes and Verdier, 1965).

Usually, ethylene chlorohydrine does not react with tertiary amines. However, the literature does provide data on the reaction of dimethyl aniline with ethylene chlorohydrine attended by the removal of one of the two methyl groups in the form of chloride methyl. The reaction develops at 190-200 °C, and N - β -oxyethyl - N - methyl aniline forms (Lattes and Verdier, 1965) (see Eq. 2).

It follows from the presented literature overview that the nucleophilic substitution of the chlorine atom of ethylene chlorohydrine with secondary and tertiary amines develops in harder conditions and usually results in a mixture of mono- and bis-products.

The nucleophilic substitution of the chlorine atom of 2-methoxy ethylchloride with aromatic amines was considered in works (Mirzaev, 1987; Dustmukhamedov, 1973). The interaction between aryl amides and various alkoxy ethylchlorides was studied. For example, the substitution of the chlorine atom of 2-ethoxyethylchloride with aniline takes four to five hours with the mixture heated at the reaction mixture boiling point. The nucleophilic substitution of the haloid atom of 2-alkoxyethyl chloride with substituted anilines was carried out in the presence of catalysts and acceptors of hydrogen chloride at 90- 150°C (Katsonovu and Airo, 1976; Kataku, 1985; Dustmukhamedov *et al.*, 1989). To keep the reaction going, it is necessary to apply an equimolecular amount of a strong base. Sometimes, alkoxy alkyl chlorides interact with substituted anilines under pressure and at heating (Buhman *et al.*, 1980; Arkhipov *et al.*, 2000; Abraham and Grellier, 1976).

The exposed literature data allow concluding that the main role in the nucleophilic substitution of alkoxyalkyl halides with amines is played by the basicity of amines, essence, and position of substituents relative to the alcoxyl group of the haloid atom (Bennur *et al.*, 1975; Korzhenevskaya and Titov, 1988; Korzhenevskaya and Kalmitskiy, 1987). According to some authors, the reactive capacity of arylamines interacting with alkoxyalkyl halides stems mainly from their basicity and steric factors, without taking into account physical, chemical characteristics of N - β - alcocyl arylamines. This is one of the crucial factors, especially for explaining side processes, in particular, the formation of dialcoxy-alkylamines and 1,4-diaryl piperazines. In the literature, there are also data on the basicity of N - β oxy-, - alkoxy-alkyl and also N -alkyl anilines (Korzhenevskaya *et al.*, 1991; Dustmukhamedov *et al.*, 1989). Thus the study of chemical transformations of the specified compounds, synthesis of diverse multifunction substances, and search for highly efficient acyl aniline acyloxyethoxyethyl (aryloxypropyl) preparations are relevant to research tasks.

The work conducted involved studying the acylation and alkylation of N-2-(2'-acyloxyethoxy)ethylarylamines with various acylation agents, 1,2-dibromethane, and epichlorohydrine leading to multifunction derivatives in different positions. They awake interest as original substances for synthesizing various compounds.

N-2-(2'- acyloxyethoxy)ethyl anilines are alkylated with methyl iodide with difficulty even

with potassium iodide and sodium carbonate contained in dimethyl formamide, which is due to the low boiling point of methyl iodide. The attempts to release the resultants were unsuccessful (Alfred and Klaus-Gürgen, 1982; Zhanaliyeva, 1994).

The interaction of N-2-(2'-acyloxyethoxy)ethyl anilines with 1,2-dibromoethane results in the formation of N,N'-diphenyl-N,N'-di-(2-acyloxyethoxyethyl) ethylene diamines, though with low outputs of 21 to 23 %. This reaction was carried out in the presence of alkali metal iodides as catalysts and sodium carbonate as an acceptor of haloid hydrogen in dry dimethylformamide.

In terms of physical-chemical characteristics and spectral data the synthesized compounds tallied with N, N' - diphenyl - N, N' - bis - (2-(2'-acyloxyethoxy)ethyl)ethylene diamines derived by the nucleophilic substitution of the chlorine atom in 2-(2'- acyloxyethoxy)ethyl chlorides with 1,2-diaryl amino ethanes (Alfred and Klaus-Gürgen, 1982; Korzhenevskaya *et al.*, 1991).

The next point for the study was the possibility of alkylating N-2-(2'-acyloxyethoxy)ethyl aryl amines with epichlorohydrine. N-2-(2'-Acetoxyethoxy)ethyl N-3-chlorine-2-hydroxypropyl aryl amines are formed with high outputs of 93 to 96 %. The structure of the synthesized compounds is confirmed by the data of element analysis and IR spectrum. IR spectra contain absorption bands in ranges of 1600-1605 (C=C-bond of an aromatic cycle) and 1740-1745 cm^{-1} ; these bands characterize the ester carbonyl group of 3200-3500 cm^{-1} for the hydroxyl group and 760 cm^{-1} for C-Cl bond (Zhanaliyeva, 1994; Zhanaliyeva *et al.*, 1994).

2. MATERIALS AND METHODS

2.1 Methods of producing diethylene glycol chlorohydrine derivatives

2.1.1 Acylation of diethylene glycol chlorohydrine with carbonic acids

2.1.1.1. Synthesizing 2- (2-formyloxyethoxy) ethylchloride.

A single-neck retort with Dean-Stark trap was taken and filled with 62.25 g of diethylene glycol chlorohydrine, 22.6 g of formylic acid, 200 ml of benzene, 2-3 drops of sulfuric acid. The solution was boiled until the water release stopped. Then the reaction mixture was flushed

with water to a neutral flush water medium. The organic layer was separated and then dried over magnesium sulfate. The solvent was distilled off in the water-jet pump vacuum, and the residue was fractionated in a vacuum. The product output was 64.6 g (85 %) with a boiling point of 85 °C at 1 mm Hg. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 3.85 (OCH_2 , 2H, m.), 3.50 (methylene groups, 6H, m.), and 8.1 (CHO, 1H, s.) ppm.

2.1.1.2. Synthesizing 2-(2'-acetoxyethoxy) ethyl chloride

This derivative was produced in a similar way from 62.25 g of diethylene glycol chlorohydrine, 36 g of acetic acid, 200 ml of benzene, 2-3 drops of sulfuric acid. The product output was 70 g (85%), the boiling point as 85 °C at 1 mm Hg; $d_4^{20} = 1.1527$; $n_D^{20} = 1.4381$. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 4.25 (COH_2 , 2H m.), 3.55 (methylene groups, 6H, m.), and 1.90 (CH_3 , 3H, s.) ppm.

2.1.1.3. Synthesizing 2-(2'-propionyloxyethoxy) ethyl chloride

This derivative was produced in a similar way from 62.25 g (0.5 g/w) of diethylene glycol chlorohydrine, 44.4 g (0.6 g/w) of propionic acid, 200 ml of benzene, and 2-3 drops of sulfuric acid. The reaction product output was 72 g (79 %) with a boiling point of 150 °C at 3 mm Hg. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 0.92 (CH_3 , 3H, t.), 1.45 (CH, 2H, m.), 2.30 (CH_2 , 2H, m.), 3.60 (methylene groups, 6H, m.), 4.25 (OCH_2 , 2H, m.) ppm.

2.1.1.4. Synthesizing 2-(2'-butyroyloxyethoxy) ethyl chloride

This derivative was produced in a similar way from 62.25 g (0.45 g/w) of diethylene glycol chlorohydrine, 58.8 g (0.6 g/w) of oily acid, 200 ml of benzene, and 2-3 drops of sulfuric acid. The reaction product output was 87 g (88 %) with a boiling point of 144 °C at 3 mm Hg. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 0.92 (CH_3 , 3H, t.), 1.40 (CH_2 , 4H, m.), 2.25 (CH_2 , 2H, m.), 3.65 (methylene groups, 6H, m.), 4.20 (OCH_2 , 2H, m.) ppm.

2.1.1.5. Synthesizing 2-(2'-chloracetoxyethoxy) ethyl chloride

This derivative was produced in a similar way from 12.4 g (0.15 g/w) of diethylene glycol chlorohydrine of monochloroacetic acid, 150 ml of toluene, and 2-3 drops of sulfuric acid. The reaction product output was 13 g (65 %) with a boiling point of 130 °C at 1 mm Hg. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 3.20 (ClCH_2 , 2H, s.), 3.45 (COH_2 , 2H, m.), 4.25 (methylene groups, 6H, m.) ppm.

2.1.1.6. Synthesizing 2-(2-benzoyloxy) ethyl chloride

This derivative was produced in a similar way from 62.5 g (0.5 g/w) of diethylene glycol chlorohydrine and 73.2 g (0.6/w) of benzoic acid. The reaction product output was 96 g (85 %) with a boiling point of 155 °C at 1 mm Hg. The IR spectrum is 1745 (ν COO) cm^{-1} . The PMR spectrum is 7.21 (3H, aromatic protons, m.), 7.83 (2H, aromatic protons, CH-COO, m.), 4.15 (OCH_2 -2H,m); 3.35 (methylene protons, 6H, m) ppm.

2.1.2 Nucleophilic substitution of chlorine atom of (2-(2'-acyloxyethoxy) ethyl chloride

2.1.2.1. N-2-(2'-Formyloxyethoxy) ethylaniline

A three-neck retort with a mechanical stirrer, a reverse fridge, and a thermometer was taken and filled with 9.3 g (0.1 g/w) of aniline, 16.7 g (0.11 g/w) of 2-(2'-formyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of sodium iodide, 6.89 g (0.0065 g/w) of sodium carbonate, and 50 ml of dry dimethyl formamide. The reaction mixture was heated for three to four hours at 110-120 °C. After the cooling, the precipitate was filtered and the solvent distilled off in the water-jet pump vacuum. The precipitate was extracted with benzene and flushed with water to pH=7. The organic layer was dried over magnesium sulfate. The residue was fractionated in the vacuum upon benzene stripping. The product output was 11.6 g (53 %) with a boiling point of 146 °C per mm Hg. The IR spectrum is 1760 (ν COO), 3280 (ν NH), 1600-1605 (ν C=C of the aromatic cycle), 1250 (ν COC) cm^{-1} .

2.1.2.2. N-2(2'-Formyloxyethoxyl) ethyl- o- toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of o- toluidine, 16.72 g (0.11 g/w) of 2-(2'- formyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of potassium iodide, 6.89 g (0.065 g/w) of sodium carbonate, and 70

ml of dry dimethyl formamide. The product output was 10.6 g (48 %) with a boiling point of 165 °C per mm Hg. The compound's IR spectrum is 1735-1745 (ν COO), 3380 (ν NH), 1600-1605 (ν C=C of the aromatic cycle) cm^{-1} . The PMR spectrum is 2.10 (Ar-CH₃, 3H, t.), 3.65 (methylene protons, 6H, m.), 3.90 (OCH₂, 2H, m.), 7.10 (aromatic protons, 4H, m.), 7.30 (CHO, 1H, s) ppm.

2.1.2.3. *N*-2-(2'-Formyloxyethoxy) ethyl - *m*-toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of *m*-toluidine, 16.72 g (0.11 g/w) of 2-(2'- formyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of potassium iodide, 65.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 12.9 g (56 %) with a boiling point of 180 °C/l mm Hg⁻¹. The PMR spectrum is 2.10 (Ar-CH₃, 3H, t.), 3.50 (methylene protons, 6H, m.), 4.25 (OCH₂, 2H, m.), 6.90 (aromatic protons, 4H, m.), 7.30 (CHO, 1H, s) ppm.

2.1.2.4. *N*-2-(2'-Formyloxyethoxy) ethyl-*p*-toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of *p*-toluidine, 16.72 g (0.11 g/w) of 2-(2'- formyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 14.7 g (60 %) with a boiling point of 179 °C/l mm Hg. The IR spectrum is 1735-1745 (ν COO), 3390 (ν NH), 1600-1605 (ν C=C of the aromatic cycle) cm^{-1} .

2.1.2.5. *N*-2-(2' Propionyloxyethoxy) ethylaniline

This derivative was produced in a similar way from 9.3 g (0.1 g/w) of aniline, 19.8 g (0.11 g/w) of 2-(2'- propionyloxyethoxy) ethyl chloride, 2.15 g (0.011 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 9.1 g (39 %) with a boiling point of 180 °C/l mm Hg. The IR spectrum is 1740-1750 (ν COO), 3380- 3420 (ν NH), 1605-1609 (ν C=C of aromatic cycle), and 1145-1280 (ν COC) cm^{-1} . The PMR spectrum is 1.00 (CH₃, 3H, t.), 2.15 (CH₃-CH₂, 2H, m.), 3.50 (methylene protons, 6H, m.), 4.05 (OCH₂, 2H, m.), 7.00 (aromatic protons, 5H, m.) ppm.

2.1.2.6. *N*-2-(2' - Propioniloxyethoxy) ethyl-*o*-toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of *o*-toluidine, 19.8 g (0.11 g/w) of 2-(2'- propionyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 12.8 g (51 %) with a boiling point of 139 °C/l mm Hg. The IR spectrum is 1745 (ν COO), 3400-3450 (ν NH), 1600-1610 (ν C=C of the aromatic cycle) cm^{-1} . The mass spectrum is m/z 251 (M^+ , 4%). 120 (H₃C-C₆H₄-NH-CH₂⁺), 237 (28%), 177 (32%), 134 (47%), 91 (27%).

2.1.2.7. *N*-2-(2' - Propionyloxyethoxy) ethyl-*m*-toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of *m*-toluidine, 19.8 g (0.11 g/w) of 2-(2'- propionyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 13.9 g (49 %) with a boiling point of 163 °C/l mm Hg. The IR spectrum is 1740-1745 (ν COO), 3380- 3400 (ν NH), 1600-1610 (ν C=C of aromatic cycle) cm^{-1} .

2.1.2.8. *N*-2-(2' - Propionyloxyethoxy) ethyl-*p*-toluidine

This derivative was produced in a similar way from 10.7 g (0.1 g/w) of *p*-toluidine, 19.8 g (0.11 g/w) of 2-(2'- propionyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 15 g (60 %) with a boiling point of 194 °C/l mm Hg. The IR spectrum is 1740 (ν COO), 3390- 3400 (ν NH), 1610-1610 (ν C=C of the aromatic cycle) cm^{-1} . The PMR spectrum is 1.00 (CH₃, 3H, t.), 2.15 (CH₃-CH₂, 2H, m.), 3.48 (methylene protons, 6H, m.), 4.15 (OCH₂, 2H, m.), 6.90 (aromatic protons, 4H, m.) ppm.

2.1.2.9. *N*-2-(2' - Chloroacetoxyethoxy) ethyl aniline

This derivative was produced in a similar way from 4.65 g (0.05 g/w) of aniline, 11 g (0.055 g/w) of 2-(2'- chloroacetoxyethoxy) ethyl chloride, 1.07 g (0.007 g/w) of KI, 3.45 g (0.0032 g/w) of sodium carbonate, and 50 ml of dry DMF. The product output was 6 g (44 %) with a boiling point of 135 °C/l mm Hg. The IR spectrum is 1750 (ν COO), 3420 (ν NH), 1630 (ν C=C of the aromatic cycle), and 740-755 (ν Cl) cm^{-1} .

2.1.2.10. *N*-2-(2' - Chloroacetoxyethoxy) ethyl-*o*-

toluidine

This compound was synthesized in a similar way from 11 g (0.055 g/w) of ethyl chloride, 1.07 g (0.007 g/w) of KI, 3.45 g (0.0032 g/w) of sodium carbonate, and 50 ml of dry DMF. The product output was 6.4 g (47 %) with a boiling point of 150 °C/I mm Hg. The IR spectrum is 1745 (ν COO), 3430 (ν NH), 1620 (ν C=C of the aromatic cycle), and 750-760 (ν Cl) cm^{-1} .

2.1.2.11. *N*-2-(2'-Chloroacetoxyethoxy) ethyl-*m*-toluidine.

This compound was synthesized similarly to the foregoing from 5.35 g (0.05 g/w) of *m*-toluidine, 11 g (0.055 g/w) of 2-(2'-chloroacetoxyethoxy) ethyl chloride, 1.07 g (0.007 g/w) of KI, 3.45 g (0.0032 g/w) of sodium carbonate, and 50 ml of dry DMF. The product output was 6.2 g (46 %) with a boiling point of 153 °C/I mm Hg. The IR spectrum is 1745 (ν COO), 3420-3450 (ν NH), 1620-1630 (ν C=C of the aromatic cycle), and 750-760 (ν C-Cl) cm^{-1} .

2.1.2.12. *N*-2-(2'-Chloroacetoxyethoxy) ethyl-*p*-toluidine.

This compound was synthesized similarly to the foregoing from 5.35 g (0.05 g/w) of *p*-toluidine, 11 g (0.11 g/w) of 2-(2'-chloroacetoxyethoxy) ethyl chloride, 1.07 g (0.007 g/w) of KI, 3.45 g (0.0032 g/w) of sodium carbonate, and 50 ml of dry DMF. The product output was 7.2 g (53 %) with a boiling point of 142 °C/I mm Hg. The IR spectrum is 1745 (ν COO), 3400-3430 (ν NH), 1610-1620 (ν C=C of aromatic cycle), 750-760 (ν C-Cl) cm^{-1} . The PMR spectrum is 3.55 (methylene protons, 6H, m.), 3.80 (OCH_2 , 2H, m.), 7.05 (aromatic protons, 4H, m.) ppm.

2.1.2.13. *N*-2-(2'-Benzoyloxyethoxy) ethyl aniline

In similar conditions this product was extracted from 9.3 g (0.1 g/w) of aniline, 25.1 g (0.11 g/w) of 2-(2'-benzoyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 13.7 g (48 %) with a boiling point of 190 °C/I mm Hg. The IR spectrum is 1730-1740 (ν COO), 3400-3410 (ν NH), 1600-1610 (ν C=C of the aromatic cycle), 2880-2930 (ν C-H), 1290 (ν COC) cm^{-1} . The PMR spectrum is 2.00 (CH_3 , 3H, c.), 3.60 (methylene protons, 6H,

m.), 4.15 (OCH_2 , 2H, m.), 6.60 (aromatic protons, 4H, m.) ppm. The mass spectrum is m/z 285(M^+), 163 (11%), 149 (19%), 122 (22%), 105 (100%).

2.1.2.14. *N*-2-(2'-Benzoyloxyethoxy) ethyl-*o*-toluidine

This compound was synthesized in a similar way from 10.7 g (0.1 g/w) of *o*-toluidine, 25.1 g (0.11 g/w) of 2-(2'-benzoyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 16.1 g (54 %) with a boiling point of 201 °C/I mm Hg. The IR spectrum is 1740-1745 (ν COO), 3420-3450 (ν NH), 1600-1610 (ν C=C of the aromatic cycle) cm^{-1} . The PMR spectrum is 2.05 (CH_3 , 3H, s.), 3.50 (methylene protons, 6H, m.), 4.20 (OCH_2 , 2H, m.), 6.60 (aromatic protons, 5H, m.) ppm.

2.1.2.15. *N*-2-(2'-Benzoyloxyethoxy) ethyl-*m*-toluidine

This compound was synthesized in a similar way from 10.7 g (0.1 g/w) of *m*-toluidine, 25.1 g (0.11 g/w) of 2-(2'-benzoyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 15.2 g (51 %) with a boiling point of 178 °C/I mm Hg. The IR spectrum is 1730 (ν COO), 3400 (ν NH), 1680 (ν C=C of the aromatic cycle) cm^{-1} . The PMR spectrum is 2.05 05 (CH_3 , 3H, s.), 3.60 (methylene protons, 5H, m.), 7.02 (aromatic protons, 4H, m.) ppm.

2.1.2.16. *N*-2-(2'-Benzoyloxyethoxy) ethyl-*p*-toluidine

This compound was obtained in a similar way from 10.7 g (0.1 g/w) of *p*-toluidine, 25.1 g (0.11 g/w) of 2-(2'-benzoyloxyethoxy) ethyl chloride, 2.15 g (0.013 g/w) of KI, 6.89 g (0.065 g/w) of sodium carbonate, and 70 ml of dry DMF. The product output was 16.9 g (57 %) with a melting point of 144 °C/I mm Hg. The IR spectrum is 170-1710 (ν COO), 3300-3320 (ν NH), 1680 (ν C=C of the aromatic cycle), 1130-1200 (ν COC) cm^{-1} .

2.1.3 Nucleophilic substitution of 2-(2'-acyloxyethoxy) ethyl chlorides with rhodanides

2.1.3.1. Synthesizing 2-(2'-formyloxyethoxy) ethylrhodane

A mixture of 3.81 g (0.25 g/w) of 2-(2'-formyloxyethoxy) ethyl chloride, 1.9 g (0.25 g/w)

of ammonium rhodanate, and 30 ml of methanol was boiled for five hours. The precipitate was vacuum-filtered. The product output was 2.3 g (68 %) with a boiling point of 168 °C per 1 mm Hg. The IR spectrum is 1735 (ν COO), 2150, 2180 (ν CN) cm^{-1} .

2.1.3.2. Synthesizing 2-(2'-propionyloxyethoxy) ethyl rhodane.

Similarly, this product was obtained from 405 g (0.25 g/w) of 2-(2'-formyloxyethoxy) ethyl chloride, 1.9 g (0.25 g/w) of ammonium rhodanate, and 30 ml of methanol. The product output was 2.6 g (65 %) with a boiling point of 170 °C per 1 mm Hg. The IR spectrum is 1740 (ν COO), 2150 (ν CN) cm^{-1} .

2.1.3.3. Synthesizing chloroacetoxyethyl ester of rhodane acetic acid.

A mixture of 40.2 g (0.2 g/w) of 2-(2'-chloroacetoxyethoxy) ethylchloride and 15.2 g (0.22 g/w) of ammonium rhodanate was boiled for five hours in 100 of methanol in a water bath. After the reaction mixture was cooled, the precipitate was filtered. The methanol was distilled off, and the residue extracted with benzene to neutral flush water medium. The organic layer was dried above magnesium sulfate. After the solvent was distilled off, the residue was vacuum-fractioned. The product output was 34.7 g (78 %) with a boiling point of 181-182 °C/3 mm Hg. The IR spectrum is 1740 (ν COO), 1130 (ν COC), 2160 (ν SCN) cm^{-1} . The calculated relative density are diffraction index are $d_4^{20} = 1.4962$ and $n_d^{20} = 1.2675$, respectively. The PMR spectrum is 4.3 (Cl-CH₂-CH₂, t.), 3.63 (CH₂-O-CH₂CH₂, t.), 3.83 (O=CCH₂, SCN) ppm.

3. RESULTS AND DISCUSSION

Acylation of alcohols with anhydrides and acid chlorides is often cited in the literature. The latter are derived from respective carbonic acids. We carried out reactions for acylating diethylene glycol chlorohydrine with carbonic acids proper. The hydroxyl group of diethylene glycol chlorohydrine was acylated using aliphatic and aromatic series carbonic acids. The compounds were synthesized by catalytic amounts of sulfuric acid, with the azeotropic distillation of released water, in benzene or toluene solution (Zhanaliyeva, 1994; Shriner *et al.*, 1980; Zhanaliyeva *et al.*, 2000). The reaction product

outputs are 85 to 88%. The reaction scheme is shown in Eq 3.

The synthesized compounds are easily distilled liquids. The IR spectra of these compounds contain ester carbonyl group absorption bands in a region of 1745 cm^{-1} and no absorption bands in a region of 3200 to 3500 cm^{-1} that are typical of the hydroxyl group. The PMR spectra of the synthesized compounds are characterized by signals of methylene group protons in a region of 3 to 3.45 ppm. For example, the chemical shift (CHSH) of OCH₂ protons for 2-(2'-acetoxyethoxy) ethyl chloride shows at 4.25 ppm (2H), signals of protons from other methylene groups are detected as a multiple with the center at 3.55 ppm (6H). The methyl group shows a chemical shift at 1.90 ppm, whereas the methenyl proton of 2-(2'-formyloxyethoxy) ethyl chloride shows this shift at 8.1 ppm.

The characteristic CHSH values for protons of the aromatic ring of 2-(2'-benzoyloxyethoxy) ethyl chloride and for methylene protons are 7.21 ppm (3H, aromatic protons, m.), 7.83 ppm (2H, aromatic protons, m.) and 3.35 ppm (6H, m.) and 4.25 ppm (OCH₂, 2H, m.), respectively (Zhanaliyeva *et al.*, 2000; Zhanaliyeva, 2016, 2017).

For some physical-chemical characteristics of the synthesized 2-(2'-acyloxyethoxy), ethyl chlorides, see table 1.

We studied reactions of 2-(2') ethyl chlorides with various nucleophilic reactive chemicals. Reaction products may be original substances for various kinds of organic synthesis, and 2-(2'-acyloxyethoxy) ethyl chloride may react with nucleophilic reactive chemicals in two ways:

1) nucleophilic substitution may occur on the chlorine atom;

2) nucleophilic particle may cause the bond breaking in the acyloxy group, which leads to the formation of diethylene glycol chlorohydrine and the respective amide when amines are used.

In the nucleophilic substitution of 2-(2' -acyloxyethoxy) ethyl chlorides with amines, it is the chlorine atom that is displaced. The reaction was carried out in dry dimethyl formamide. According to multiple tests, this reaction develops with difficulty without catalysts. Potassium iodide was used to activate the reaction, whereas sodium carbonate was used as the acceptor of haloid hydrogen (Zhanaliyeva, 1994, 2017). N-2-(2'-acyloxyethoxy) ethylarylamines are formed as showed in Eq. 4.

The need for using alkali metal iodides stems from the possibility of exchanging the chlorine atom for iodine under reaction. Since the C-I bond breaking energy is weaker than the C-Cl breaking energy, intermediate iodine derivatives are easily exposed to the nucleophilic substitution with the amino group.

2-(2'-Acyloxyethoxy) ethylchlorides interact with alkali metal rhodanides and form respective rhodanides. The reaction develops in relatively moderate conditions as compared with the nucleophilic substitution with amines (see Eq. 5).

The reaction product outputs are 65 to 68 %. The boiling point is 168°C/1-170°C per mm Hg, $n_D^{20}=1.4680-1.4760$; Rf is 0.70^x-0.83^x (x is the acetone/benzene system ratio =2:5).

The chlorine atom of the chlorine acetyl residue of 2-(2'-chloroacetoxyethoxy) ethyl chloride is easily exposed to the nucleophilic substitution with the rhodanide ion. In our case, ammonium thiocyanate was used as a reactive chemical. The reaction develops smoothly when the mixture of reactive chemicals is heated at a ratio of 1:1 and forms the β -chloroacetoxyethoxyethyl ester of rhodane acetic acid (see Eq. 6).

The IR spectrum of the synthesized ester contains characteristic absorption bands for the carbonyl group (ν COOP) at 1740 cm^{-1} , for the C-O-C group at 1130 cm^{-1} (variation in the C-O polar bond), and for the SCN group at 2160 cm^{-1} . Its PMR spectrum shows a paramagnetic shift of protons in the ClCH_2CH_2 -triplet methylene group at 4.30 ppm, in the $\text{O}=\text{C}-\text{CH}_2\text{C}$ singlet group at 3.83 ppm, and in the $\text{CH}_2\text{OCH}_2-\text{CH}_2$ triplet group at 3.63 ppm (Zhanaliyeva, 1994; Shriner *et al.*, 1980).

In the case of 2-(2'-chloroacetoxyethoxy) ethylchloride either one or both chlorine atoms may enter into the reaction. It appears that the reaction at a ratio of 1:1 between 2-(2'-chloroacetoxyethoxy) ethylchloride and the respective aromatic amine includes the substitution of the chlorine atom of the chloroacetyl residue. This behavior stems from its mobility as affected by the carbonyl group, which makes the breaking of the C-Cl bond easier (see Eq. 7).

It appeared impossible to exchange both chlorine atoms for the amino group; here, a complex mixture forms from which the reaction products cannot be extracted on an individual basis.

The interesting fact revealed by

comparing the results by the influence of the acyl group on substitution (see Table 2) is that the reaction product outputs drop with the transition from 2-(2'- formyloxyethoxy) ethyl chloride to the respective acetyl derivatives. For example, the target product outputs increase with the transition from aromatic to aliphatic and heterocyclic amines, i.e., these outputs increase with the increase in their basicity, which agrees with the literature data from (Zhanaliyeva, 1994, 2000; Alfred and Klaus-Gürgen, 1982).

4. CONCLUSION

The direction of the nucleophilic substitution of haloid alcohols and haloid esters with amines depends on the basicity of amines, existence and position of substituents in the aromatic ring in case of aryl amines, existence and absence of substituents in the α position relative to the halide atom, number of methylene groups between the halide and the hydroxyl (alcoyl) group, and also on the kind of halogen.

The chemistry of diethylene glycol chlorohydrine has been studied. It has been shown that diethylene glycol chlorohydrine can be used to produce compounds with various functional groups. It has been found out that the hydroxyl group of diethylene glycol chlorohydrine can react with carboxylic acids in the presence of catalysts, which causes the formation of esters. It has been found out that the nucleophilic substitution of the chlorine atom of 2-(2'-acyloxyethoxy) ethyl chlorides with the rhodanide ion goes smoothly in the presence of potassium iodide acting as an activator. It has been established that in this case, the acyloxy group remains unaffected. The acylation of N-2-(2'-acyloxyethoxy)ethyl arylamines develops for both, hydroxyl function group and amino function group; 1,2-diarylaminoethanes can react with 2-(2'-acyloxyethoxy)ethyl chloride as nucleophilic reactive chemicals. It has been found out that the target product outputs increase with the transition from aromatic to aliphatic and heterocyclic amines, i.e., these outputs increase with the increase in their basicity.

5. REFERENCES

1. Abraham, M.H., Grellier, P.L. Substitution at Saturated Carbon. Part.xx. The effect of the energy of Et_3N Etl and the Et_3N Transition State Comparison with Solvent effect on the Equilibria. *J. Chem. Soc.*, **1976**, 14, 1735–1741.

2. Alfred, G.B., Klaus-Gürgen, K.R. US Patent 4266071. Method of Obtaining N-(1'-alcoyloxycarbonyl)ethyl) – 2,6 dialkylanilines. *Bulletin of Inventions of Countries Worldwide*, **1982**, 57(3).
3. Arkhipov, A. Y., Cherkov, V. A., Litvinova, V. V., Anisimov, A. V. Nucleophilic substitution of the chlorine atoms in bis(2-chlorocyclohexyl) sulfide. *Vestnik Moskovskogo universiteta. Seriya 2: Khimiya*, **2000**, 41(2), 121–123.
4. Bennur, S.C. Jigajinni, V.B. Badger, V.V. 1-Substituted alkylamino 3- (4-guiazolyoxy) 2- pronanol trihudruchlorides and 1-substituted. *Rev.roum.chim.*, **1975**, 20(9), 1295–1299
5. Berezin, B. D. A Modern Course of Organic Chemistry [Kurs sovremennoy organicheskoy khimii]. Moscow: Vysshaya Shkola, **2003**.
6. Buhman, U., Puttnerr, R., Arnold, P. Chloracetanilide vertahren our Hers telling dieter verlindungen sowie diese enthalten de Herbizide Mittel. Application 28033662. Germany, **1980**.
7. Dustmukhamedov, T.T. Chemical Transformations of 2-(β -oxymethoxy) Alkyl Aryl Amines and Search for New Pesticides [Khimicheskiye prevrashcheniya 2-(β -oksimeoksi) alkilarilaminov i izyskaniye novykh pestitsidov], Thesis for a Doctor of Chemical Sciences, Academy of Sciences of UzSSR Institute of Chemistry of Plant Substances, Tashkent, **1973**.
8. Dustmukhamedov, T.T., Korzhenevskaya, N.G., Umarov, Kh.S., Mirzaev, M.S., Aripov, Kh.N., Karimov, R.K. Basic Properties of N- β -oxy-, N- β methoxy and N- β - ethoxy ethyl anilines [Osnovnyye svoystva N- β -oksi-, N- β metoksi i N- β - etoksietilanilinov]. *Uzbekskiy khimicheskii zhurnal (Uzbek Chemical Journal)*, **1989**, 6, 26–28.
9. Elderfield, R.L. Heterocyclic Compounds. Ch. 5. In R.C. Elderfield (Ed.). New-York: John Wiley and Sons; London: Chapman and Hall Limited, **1961**.
10. Gilmanov, R.Z., Falyakhov, I.F., Khairutdinov, F.G., Akhtyamova, Z.G., Nikitin, V.G., Gilmanova, T.B. Theoretical Aspects of Nucleophilic Substitution in 3-Halogennitropiridines [Teoreticheskiye aspekty reaktsii nukleofil'nogo zameshcheniya v 3-galogennitropiridinakh], *Vestnik Kazanskogo tekhnologicheskogo universiteta (Bulletin of Kazan Technological University)*, **2013**, 16, 17.
11. Gorodiov, V.P., Petrov, A.A. Products of Condensation of Ethylene Oxide with Acyl Derivatives of Glycerin, Mono- and Triethanolamine [Produkty kondensatsii okisi etilena s atsil'nymi proizvodnymi glitserina, mono- i trietanolamina]. *Zhurnal Prikladnoy Khimii (Journal of Applied Chemistry)*, **1966**, 39, 1808–1814.
12. Ivanov, V.G. Organic Chemistry [Organicheskaya khimiya]. Moscow: Akademiya, **2006**.
13. Katak, S. Procedure for Obtaining N-displaced Anilines. Application 60-13023 (Japan). *Bulletin of Inventions of Countries Worldwide*, **1985**, 20
14. Katsonovu, S., Ariro, M. (1976). Oxylhylyated amino anilines, Patent 76-80827 (Japan). **1976**, 85, 177094g.
15. Knoor, L. Synthesen in der Oxazinreiche. *Ber.*, **1989**, 22, 2081–2099.
16. Korzhenevskaya, N.G., Dustmukhamedov, T.T., Umarov, Kh.S., Chotiy, K.Yu., Mirzaev, M.S. Electronic Nature of Alkyl Radical in N-alkylaniline and Its Basicity [Elektronnaya priroda alkil'nogo radikala v N-alkilanilina i ikh osnovnost']. *Zhurnal obshchey khimii (Journal of General Chemistry)*, **1991**, 31(7), 1539–1542.
17. Korzhenevskaya, N.G., Kalmitskiy, N.R. On Basicity-Structure Relations in Series of Anidine and Its Derivatives [O korrelyatsiy osnovnost' – struktura v seriyakh anidina i ego proizvodnykh]. *Zhurnal obshchey khimii (Journal of General Chemistry)*, **1987**, 57, 1810–1813.
18. Korzhenevskaya, N.G., Titov, E.V. On Structure of the Substituent of NHCH_3 . *Ukrainskiy khimicheskii zhurnal (Ukrainian Chemical Journal)*, **1988**, 54, 184–185.
19. Lattes, A., Verdier, A. Reargues sur les reactions de la monochlorhydrine du glycol aves guelgues amines. *Bull Soc.Chim de France*, **1965**, 7, 2037–2049.
20. Mirzaev, M.S. Synthesis and Chemical Transformations of Alcoxyalkyl Aryl Amines and Search for New Pesticides [Sintez i khimicheskiye prevrashcheniya alkoksialkilarilaminov i poisk novykh pestitsidov], Thesis for a Doctor of Chemical Sciences, Tashkent, State University named after V.I. Lenin, **1987**.
21. Nenicesku, K.K. Organic Chemistry [Organicheskaya khimiya]. Ch. 1 and 2. Moscow: Inos. Lit. Publ, **1962**.
22. Petrov, K.D., Lagucheva, E.S., Mukhova, V.I. On Interaction of Ethylene Chlorohydrine with 2.5 Dichloroaniline [O

- vzaimodeystvii etilenkhlorgidrina s 2,5 dikhloranilinom], *Zhurnal obshchey khimii (Journal of General Chemistry)*, **1954**, 24, 1602.
23. Petrov, K.D., Lagucheva, E.S., Mukhova, V.I. Reactions of Halide Hydrines with Amines [Reaktsii galoidgidrinov s aminami], *Zhurnal obshchey khimii (Journal of General Chemistry)*, **1953**, 23, 403–405.
  24. Plyuchinskii, Ya.K., Lebedev, N.N., Smirnova, M.M. On Kinetics and Mechanism of Reactions of Amines with Ethylene Chlorohydrine and Ethylene Oxide in the Presence of Hydrogen Chloride [O kinetike i mekhanizme reaktsiy aminov s etilenkhlorgidrinom i okis'yu etilena v prisutstvii khloristogo vodoroda], *Zhurnal organicheskoy khimii (Journal of Organic Chemistry)*, **1966**, 2(12), 2108–2115.
  25. Pokonova, Yu.V. Chemistry and Technology of Halogen Esters [Khimiya i tekhnologiya galogen-efirov]. Leningrad: Leningrad State University Publishers, **1982**.
  26. Pokonova, Yu.V. Halide Esters: Production Methods, Properties, Applications [Galoid-efiry. Sposoby polucheniya, svoystva, primeneniya]. Moscow: Khimiya, **1966**.
  27. Shorygin, I.I., Beglov, V.N. On Trying to Close a Heterocycle in N (oxyethyl) aniline and its Benzoyl Derivatives [O popytke zamykaniya geterotsikla v N (oksietil) anilina i benzoil'nykh proizvodnykh ego]. *Zhurnal obshchey khimii (Journal of General Chemistry)*, **1936**, 5, 1707–1717.
  28. Shriner, R., Fuson, R.C., Curtin, D.Y., Morrill, T.C. Systematic Identification of Organic Compounds. New-York: John Wiley and Sons, **1980**.
  29. Temnikova, T.I. Theoretical Basics of Organic Chemistry, Ch. XI. [Teoreticheskiye osnovy organicheskoy khimii, gl. XI]. Moscow: Khimiya, **1968**.
  30. Traven, F.V. Organic Chemistry [Organicheskaya khimiya]. Moscow: Akademiya, **2008**.
  31. Tulyaganov, S.R. Synthesis and Some Transformations of Aryl-Embedded 2-Amino Alcohols [Sintez i nekotoryye prevrashcheniya arilavmeshchennykh 2-aminospirtov]. Thesis for a Doctor of Chemical Sciences, Tashkent, Academy of Sciences of UzSSR Joint Scientific Council on Chemistry and Chemical Technology, **1972**.
  32. Zhanaliyeva, R.N. Chemical Transformations of 2-(2'-gyroxyethoxy)-Ethyl and 3-(o-methoxy-phenoxy)-2-hydroxypropylchlorides [Khimicheskiye prevrashcheniya 2-(2'-giroksietoksi)-etil i 3-(o-metoksi-fenoksi)-2-gidroksipropilkhloridov]. Thesis for a Doctor of Chemical Sciences, Tashkent, Academy of Sciences of UzSSR Institute of Plant Chemistry, **1994**.
  33. Zhanaliyeva, R.N. Nucleophilic Substitution of Chlorine Atom of 2-(2'-acyloxy-ethoxy) Ethylchlorides. *Nauka i mir. Mezhdunarodnyy nauchnyy zhurnal (Science and world. International scientific journal)*, **2017**, 8, 20–22.
  34. Zhanaliyeva, R.N., Baktybaev, O.B., Shakhidoyatov, Kh.M., Kuandykova, R.K. Acylation of 3-(0-methoxyphenoxy)-2-Hydroxypropylchloride with Carbonic Acids [Reaktsii atsilirovaniya 3-(0-metoksifenoksi)-2-gidroksipropilkhlorida karbonovymi kislotami]. *Vestnik universiteta Yassavi (News of Yassavi University)*, **2000**, 6.
  35. Zhanaliyeva, R.N., Yakubov, A.V., Mukhitdinova, M.Kh., Shakhidoyatov, Kh.M. Studying the Nucleophilic Substitution of Chlorine Atom of β -(FORMULA -acyloxyethoxy) Ethylchlorides. *Proceedings of International Conference at the Tashkent Institute of Irrigation and Melioration*, **1994**, 55–56.
  36. Zhanaliyeva, R.N., Yakubov, A.V., Shakhidoyatov, Kh.M., Akhmetova, Sh.S. Interaction of β -(FORMULA acyloxyethoxy) Ethylchlorides with Nucleophilic Reactive Chemicals [Vzaimodeystviye β -(β -atsiloksietoksi) etilkhloridov s nukleofil'nyimi reagentami]. *Izvestiya Akademii Nauk Respubliki Kazakhstan (News of National Academy of Sciences of Republic of Kazakhstan)*, **1993**, 6, 165–169.
  37. Zhanaliyeva, N. Diethylene Glycol Chlorohydrine Acylation Reactions [Reaktsii atsilirovaniya khlorgidrina dietilenglikolya]. *Collection of Abstracts of Reports of XX Mendeleev Congress on General and Applied Chemistry*, Russia, **2016**.

EQUATIONS

TABLES

Table 1. Some physical-chemical characteristics of 2-(2'-acyloxyethoxy) ethyl chloride
R-COOCH₂CH₂OCH₂CH₂Cl

#	R	Out put, %	T Boil. point, °C /mm Hg s	n ²⁰ _d	Rf	Found, %		Empirical formula	Calculated, %	
						C	H		C	H
1	H	85	85/1	1.440	0.55	39.70	6.00	C ₅ H ₉ O ₃ Cl	39.34	5.90
2	CH ₃	85	85/1	1.440	0.80	43.18	6.80	C ₆ H ₁₁ O ₃ Cl	43.24	6.61
3	CH ₃ CH ₂	79	150/3	1.436	0.46	46.90	7.35	C ₇ H ₁₃ O ₃ Cl	46.53	7.20
4	CH ₃ (CH ₂) ₂	88	144/3	1.439	0.60	49.21	7.90	C ₈ H ₁₅ O ₃ Cl	49.35	7.11
5	ClCH ₂	65	135/1	1.465	0.66	36.70	4.59	C ₆ H ₁₀ O ₃ Cl ₂	35.82	4.97
6	C ₆ H ₅	85	155/1	1.515	0.78 ^x	57.53	5.50	C ₁₁ H ₁₃ O ₃ Cl	57.46	5.69

Reference: The individuality of the synthesized compounds was controlled by thin-layer chromatography, for example x) is the acetone/benzene system with a ratio of 1:5; in the rest of the cases this ratio = 1:9.

Table 2. *N*-2-(2^l-Acyloxyethoxy) ethyl amines and *N*-2-(2^l-acyloxyethoxy) ethyl rhodanes
 $R-COOCH_2CH_2OCH_2CH_2-R'$

#	R	R'	Output	Boil.pt.°C, mm Hg	n ²⁰ _d	Rf
1	2	3	4	5	6	7
1	H	C ₆ H ₅ -NH	53	145/1	1,5590	0,53
2	H	o-CH ₃ -C ₆ H ₄ -NH	48	165/1	1,4530	0,70
3	H	m-CH ₃ -C ₆ H ₄ -NH	56	180/1	1,4630	0,51
4	H	p-CH ₃ -C ₆ H ₄ -NH	60	179/1	1,4620	0,52
5	CH ₃	C ₆ H ₅ -NH	39	175/1	1,5234	0,46
6	CH ₃	o-CH ₃ -C ₆ H ₄ -NH	45	180/1	1,4589	0,45
7	CH ₃	m-CH ₃ -C ₆ H ₄ -NH	44	187/1	1,4587	0,59
8	CH ₃	p-CH ₃ -C ₆ H ₄ -NH	44	183/1	1,4640	0,60
9	CH ₃ CH ₂	C ₆ H ₅ -NH	39	180/1	1,4630	0,63
10	CH ₃ CH ₂	o-CH ₃ -C ₆ H ₄ -NH	51	179/1	1,4520	0,66
11	CH ₃ CH ₂	m-CH ₃ -C ₆ H ₄ -NH	49	163/1	1,4650	0,70
12	CH ₃ CH ₂	p-CH ₃ -C ₆ H ₄ -NH	60	194/1	1,4620	0,80
13	CH ₃ CH ₂ CH ₂	C ₆ H ₅ -NH	55	189/3	1,4631	0,80
14	CH ₃ CH ₂ CH ₂	o-CH ₃ -C ₆ H ₄ -NH	51	180/1	1,4537	0,66
15	CH ₃ CH ₂ CH ₂	m-CH ₃ -C ₆ H ₄ -NH	49	179/2	1,4820	0,61
16	C ₆ H ₅ -NH-CH ₂	p-CH ₃ -C ₆ H ₄ -NH	55	180/1	1,4620	0,62
17	o-CH ₃ -C ₆ H ₄ - NHCH ₂	Cl	44	135/1	1,4575	0,74*
18		Cl	47	150/1	1,5220	0,82*
19	m-CH ₃ -C ₆ H ₄ - NHCH ₂	Cl	46	153/2	1,4639	0,70*
20		Cl	53	142/1	1,4620	0,72*
21	C ₆ H ₅	C ₆ H ₅ -NH	48	190/1	1,5610	0,70
22	C ₆ H ₅	o-CH ₃ -C ₆ H ₄ -NH	54	201/1	1,4979	0,76
23	C ₆ H ₅	m-CH ₃ -C ₆ H ₄ -NH	51	178/1	1,5220	0,78
24	C ₆ H ₅	p-CH ₃ -C ₆ H ₄ -NH	57		-	0,56

Table 2. (continued to right side)

Found, %			Empirical formula	Calculated, %		
C	H	N		C	H	N
8	9	10	11	12	13	14
63,00	7,40	6,80	C ₁₁ H ₁₅ NO ₃	63,14	7,23	6,69
64,70	7,90	6,50	C ₁₂ H ₁₇ NO ₃	64,55	7,68	6,27
64,60	7,75	6,40	C ₁₂ H ₁₇ NO ₃	64,55	7,68	6,27
64,40	7,50	6,50	C ₁₂ H ₁₇ NO ₃	64,55	7,68	6,27
64,35	7,80	6,35	C ₁₂ H ₁₇ NO ₃	64,55	7,68	6,27
65,71	7,93	6,01	C ₁₃ H ₁₉ NO ₃	65,80	8,07	5,90
65,55	7,98	6,05	C ₁₃ H ₁₉ NO ₃	65,80	8,07	5,90
65,90	8,10	5,79	C ₁₃ H ₁₉ NO ₃	65,80	8,07	5,90
65,70	8,20	6,00	C ₁₃ H ₁₉ NO ₃	65,80	8,07	5,90
66,60	8,70	5,70	C ₁₄ H ₂₁ NO ₃	66,90	8,42	5,57
67,00	8,30	5,65	C ₁₄ H ₂₁ NO ₃	66,90	8,42	5,57
66,75	8,55	5,70	C ₁₄ H ₂₁ NO ₃	66,90	8,42	5,57
67,00	8,40	5,70	C ₁₄ H ₂₁ NO ₃	66,90	8,42	5,57
68,01	8,75	5,50	C ₁₅ H ₂₃ NO ₃	67,92	8,67	5,28
67,75	8,80	5,10	C ₁₅ H ₂₃ NO ₃	67,92	8,67	5,28
68,00	8,50	5,40	C ₁₅ H ₂₃ NO ₃	67,92	8,67	5,28
56,30	6,40	5,55	C ₁₂ H ₁₆ NOO ₃ Cl	55,48	6,21	5,43
57,30	6,80	5,25	C ₁₃ H ₁₈ NO ₃ Cl	57,46	6,63	5,15
57,70	6,50	5,00	C ₁₃ H ₁₈ NO ₃ Cl	57,46	6,63	5,15
57,32	6,45	5,05	C ₁₃ H ₁₈ NO ₃ Cl	57,46	6,63	5,15
71,65	6,80	4,80	C ₁₇ H ₁₉ NO ₃	71,37	6,66	4,91
72,40	6,98	4,80	C ₁₈ H ₂₁ NO ₃	72,24	7,02	4,68
72,35	7,12	4,75	C ₁₈ H ₂₁ NO ₃	72,24	7,02	4,68
72,45	7,15	4,73	C ₁₈ H ₂₁ NO ₃	72,24	7,02	4,68

Reference: The individuality of the synthesized compounds was controlled by thin-layer chromatography, for example:

^{x)} is the acetone/benzene system with a ratio of 2:5,

^{xx)} is the methanol system, in the rest of the cases, the solvent is the acetone/benzene system with a ratio of 1:5.