

РЕАКЦІЇ ТРЕТ-БУТИЛГІДРОПЕРОКСИДУ З ТРИ-, ЧОТИРИ- ТА П'ЯТИЧЛЕННИМИ КИСНЕВМІСНИМИ ГЕТЕРОЦИКЛАМИ

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Проведено реакції трет-бутилгідропероксиду зі сполуками, що містять три-, чотири- та п'ятичленні дизаміщені кисневмісні гетероцикли. Встановлено, що основними продуктами взаємодії є відповідні β -, γ - та δ -гідроксиперокси. Вивчено вплив умов проведення процесу на вихід та склад продуктів взаємодії. Будову отриманих сполук підтверджено даними елементного, функціонального аналізу та ІЧ- і ЯМР-спектрів. Одержані пероксидні сполуки можуть становити інтерес як перспективних ініціаторів для отримання олігомерів з гідроксильними або пероксидними групами, а також як напівпродукти для синтезу інших класів органічних функціональних пероксидів.

Ключові слова: дизаміщений оксиран, дизаміщений оксетан, дизаміщений діоксолан, трет-бутилгідропероксид.

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DECOMPOSITION OF THREE-, FOUR-, AND FIVE-MEMBERED OXYGEN HETEROCYCLES BY TERT-BUTYL HYDROPEROXIDE.

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The reactions of tert-butyl hydroperoxide with compounds containing three-, four-, and five-membered disubstituted oxygen-containing heterocycles were carried out. It was established that the main products of the interaction are the corresponding β -, γ - and δ -hydroxyperoxides. The influence of conditions for conducting the process on the output and the composition of the products of interaction was studied. The structure of the compounds obtained is confirmed by the data of elemental, functional analysis and infrared and NMR spectra. The resulting peroxide compounds may be of interest as promising initiators for the production of oligomers with hydroxyl or peroxide groups, as well as intermediates for the synthesis of other classes of organic functional peroxides.

Key words: disubstituted oxirane, disubstituted oxetane, disubstituted dioxolane, tert-butylhydroperoxide.

Problem statement and its relation to important scientific tasks. Organic peroxides play an important role in solving many theoretical and applied problems of chemistry, biology and medicine at the moment [1]. These compounds are widely used as oxidants, disinfectants, bleachers, etc. A number of hydroperoxides are formed as intermediates in the production of many organic oxygen-containing compounds by oxidation reactions with molecular oxygen. However, the most important use of functional peroxides is their use as initiators of free radical reactions in the processes of obtaining and processing polymers in both industry and in scientific research., The interest in functional peroxides is due to the possibility of their use as intermediates for obtaining surface-active initiators and initiator monomers, as

well as activators of surfaces of different nature in recent years [2, 3]. This is due to the fact that in recent years intensively developed chemistry of surface-active polymers that contain reactive functional groups at the ends or lateral branches of the macromolecular chain, including peroxide. Such substances are used as active modifiers of the interphase surface of colloidal systems, intermediates for the synthesis of block and branched copolymers, nanoreactors for obtaining nanoparticles of metals of a given size. Of particular importance is the use of such polymers as carriers for the targeted delivery of synthetic medicinal substances and biomolecules in living cells of organisms [4–6].

It is well known that compounds that contain small heterocycles in the molecule, especially oxygen-containing heterocycles, are capable of attaching C-, N-, O- and S-nucleophiles as a result of the opening of the cycle under relatively mild conditions. [7]. Due to this, the compounds can be successfully used as building blocks for the production of various ω -functional compounds, in particular, functional peroxides [8]. For α -substituted heterocycles, the direction of attachment depends on the conditions of the reaction, in particular the nature of the used catalyst [9]. Therefore, the reactions of hydroperoxides and functional peroxides with oxygen-containing heterocyclic compounds can be an important method for obtaining new types of functional peroxide initiators.

Analysis of recent searches and publications. Compounds containing small carbocyclic and heterocycles in the molecule are unique reagents which, due to their high reactivity under mild conditions, react with the decomposition of the intense cycle, as well as the transformation with its expansion and regrouping [10]. It is also known that for such heterocycles there is a complex dependence of the stress energy of a molecule on the size of the cycle, namely, the maximum stress and, accordingly, the greatest reactivity is observed in three- and four-membered cycles, and in five-membered cycles, there is a decrease in the voltage of the molecule [10]. Among the cyclic compounds, particular attention is required to the oxygen-containing heterocycles whose reactions with nucleophilic reagents, in particular with hydroperoxides, allow the addition of hydroxyalkyl fragments in these compounds [11, 12]. The mutual placement of the introduced hydroxyl group and the nucleophilic center is determined by the size of the oxygen-containing heterocycle, and the direction of discovery of the cycle – depends on the type of catalysis (acidic, basic). Therefore, this reaction when using as starting compounds of oxygen-containing heterocycles of various types can be a convenient method of synthesis of hydroxyl-containing peroxides with different mutual placement of hydroxyl and peroxide groups. Such peroxides that contain a primary OH group or a reactive halogen atom in the molecule can be valuable reagents for obtaining new types of peroxide monomers, peroxide-containing surfactants, polymer modifiers, and the like. [2, 8]. Previously, we have already reported the production of surfactants based on disubstituted oxiranes [13] and oxetane [14].

Aim of the work. The synthesis of new hydroxyl-containing peroxides by the reaction of tert-butyl hydroperoxide with three-, four-, and five-membered oxygen-containing 2,2-disubstituted heterocycles, the study of the features of this reaction and the properties of the resulting compounds.

Presentation of the main material and discussion of the results. The reactions of tert-butyl hydroperoxide with oxides of alkenes, oxetane and dioxolane were carried out.

Interaction of tert-butylhydroperoxide with 2,2-disubstituted oxiranes

The interaction of t-butylhydroperoxide (TBHP) with 2,2-dimethyl- (1a) and 2,2-diphenyloxiran (1b) was performed for the production of di-tertiary β -hydroxyperoxides.

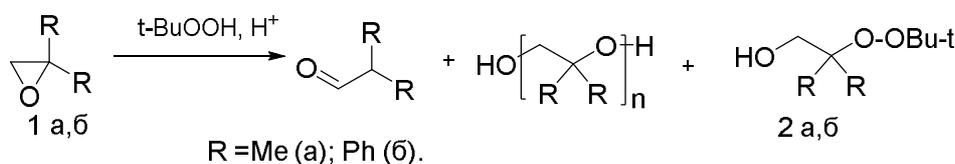


Fig. 1. Scheme of interaction of oxiranes with tert-butylhydroperoxide.

H. Kropf was shown [15] that the addition of hydroperoxides to asymmetric oxiranes at an alkaline catalyst takes place under a less substituted atom of Carbon and leads to the formation of the β -hydroxy peroxide as the primary product of the interaction. Hydroxyperoxide, in the presence of alkali, undergoes a partial degradation by binding O-O with the formation of carbonyl compounds. Increasing the number of substituents, especially aryls, in the oxiran cycle contributes to this process. We have found that β -hydroxyhydroperoxides are quantitatively decomposed in these conditions. In conditions of acid catalysis, the addition of hydroperoxide occurs to a more substituted Carbon atom [11, 12]. Therefore, we used as a catalyst sulfate acid. Initially, as an environment for the reaction, aprotic solvents (dioxane, diethyl ether, dichloromethane or excess hydroperoxide) were used, and the reaction was carried out at a temperature of $-10 \dots 20$ °C. It has been established that in these conditions, irrespective of the ratio of the reactants, there are three main primary reactions: the rearrangement of oxirane to aldehyde (the prevailing reaction), the polymerization of oxirane and the addition of hydroperoxide. When reacting in a protic solvent, 2-methylpropan-2-ol, which does not react with oxiranes, the addition of hydroperoxide becomes the main direction of interaction. When conducting the reaction in an aqueous medium, the consumption of oxirane for hydrolysis is significantly increased. Taking into account the above, the interaction of TBHP with oxiranes 1a, b was carried out at a molar ratio of TBHP: Oxirane, 2: 1, at a temperature of $-10 \dots -8$ °C in an anhydrous environment of tert-butyl alcohol. Under these conditions, the yield of hydroxyperoxides (2a, b) 7 hours after the start of the reaction was 67...72 %, which significantly exceeds the yield on known methods to this time.

Interaction of tert-butylhydroperoxide with substituted oxetane.

To obtain γ -hydroxyperoxides containing other functional groups, the interaction of tert-butylhydroperoxide (TBHP) with the disubstituted functional oxetane [3- (3-bromomethyl) oxetan-3-yl] methanol was performed. Oxetanes are similar to oxirane by chemical properties. However, the lower energy of the four-membered cycle voltage in comparison with the oxiran ring contributes to the reduction of the reactivity of these compounds in the adherence reactions. Therefore, we hoped that with a suitable type of catalyst, it would be possible to selectively conduct a nucleophilic substitution over the halogen atom or to join the oxetanic cycle. It has been established that in the presence of zinc chloride, at different temperatures of reactants up to 80 °C TBHP with oxetane 3 in the interaction practically does not enter. At the same time, under the conditions of basic catalysis (alkaline aluminum oxide), the reaction is not marked by regressivelectivity. In this case, the interaction of oxetane 3 with TBHP was carried out in a medium of tetrahydrofuran at 20 °C. for 75–90 hours. in an atmosphere of argon .. Control of the course of the reaction was carried out iodometrically and using thin-layer chromatography. In these conditions simultaneously there is substitution of the halogen atom in the endocyclic bromomethyl group with the formation of peroxide 3a, the breakdown of the oxetanic cycle with the formation of peroxide 3b, and a product of a consistent reaction at both reaction centers is formed – peroxide 3c (Fig. 2).

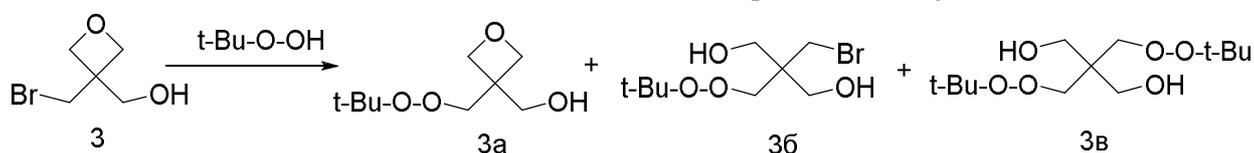
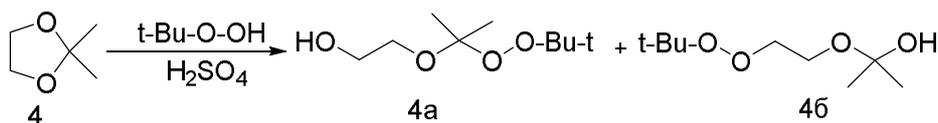


Fig. 2. Scheme of the reaction of distilled oxetane with tert-butyl hydroperoxide.

The maximum yield of hydroxyperoxide (3a) was achieved 80 hours after the reaction began. An increase in the time of synthesis leads to an increase in the reaction products of the proportion of diperoxide (3c). Thus, the interaction during 230 hours leads to 73 % of the output of diperoxide 3c. An increase in the amount of catalyst (alkaline aluminum oxide) and a slight increase in temperature (up to 35 °C) had no significant effect on the yield and the ratio of target peroxides.

Interaction of tert-butylhydroperoxide with 2,2-dimethyl-1,3-dioxolane.

We previously carried out the reaction of 1,3-dioxanes with hydrogen peroxide and hydroperoxides and on the example of 4,4-dimethyl-1,3-dioxane, it was shown that the attack of hydroperoxide nucleophile in the presence of mineral acid occurs at the position of 6 heterocycles [8] at the Carbon atom. As a result of this reaction, hydroxyl-containing peroxides and hydroperoxides can be produced. At the same time, we did not find information about analogous reactions of 1,3-dioxolanes. Therefore, the interaction of 2,2-dimethyl-1,3-dioxolane 4 with TBHP was performed (Fig. 2). The ratio of the reactants - dioxolane 4 and TBHP was 1: 2, as the catalyst used sulfate acid in equivalence to dioxolane. The interaction was carried out at 5 °C for 4-5 hours. without the use of solvent.



Puc.3. Sheme of the reaction of disubstituted dioxolane with tert-butyl hydroperoxide.

As a result of the reaction two products were formed: peroxy-ketal 4 (45 % yield) and semi-ketal 4b (10% yield). With a decrease in the temperature of the process, the yield of compound 4b slightly increased.

Experimental part. Solvents (2-methylpropan-2-ol, tetrahydrofuran, dichloromethane) used the qualification of “puriss.,” immediately distilled before use. Tetrahydrofuran was used in the catalogs “Aldrich” and “Fluka” without preliminary purification. Sulfate acid was used for the qualification of “puriss.,” the content of the basic substance was 95.5 %.

The identity of the synthesized compounds was checked by thin layer chromatography on Silica gel 60 F254 (Merck) plates in a cuvette, running through the solvent front of 100 mm. ¹H NMR spectra were recorded on the “Bruker 150” device with a working frequency of 300 MHz in deuteriochloroform at a concentration of substances of 5...10 %, and the internal standard is hexamethyldisiloxane. The purity of synthesized compounds (volatiles) was controlled by gas-liquid chromatography on a Selmichrom-1 chromatograph; column with a length of 1 m and a diameter of 3 mm, a carrier “Chromaton N-super” (granularity 0.12...0.16 mm); liquid phase silicone elastomer SE-30 or Carbowax 40M (5 % mass); detector - cathometer; gas carrier - helium. Gas-carrier consumption – 2 l / h. Evaporator temperature 125 °C. The molecular mass of the compounds obtained was determined cryoscopically in benzene according to the methods given in the papers [9, 10]. The content of active oxygen in hydroperoxides was determined iodometrically in acetic acid solution by the method [17]. Primary hydroxyl groups in the synthesized compounds were determined by the method of [18] acylation with acetic anhydride in pyridinium followed by titration of 0.1 N aqueous sodium hydroxide solution.

2,2-dimethyloxirane (1a) was prepared by interaction 15.3 g (0.1 mole) of 1-bromo-2-methyl-2-propanol and 11.0 g (0.27 mole) of sodium hydroxide powder in 75 ml of xylene at 20...30 °C for 8 hours. After distillation, the yield of the substance was 5.2 g (72.6 %), b.p. 51°C (lit. b.p.50,0...51,5 °C, d₄²⁰ 0.8311 [19]).

1,1-Diphenyloxirane (1b) was prepared from benzophenone according to the procedure [19]. Oxirane was b.p. 140 °C (lit. b.p. 140,0...142,0 °C / 0,6 kPa, [19]).

2-tert-Butylperoxy-2-methylpropan-1-ol (2a). To a solution of 4.0 g (0.044 mole) of tert-butylhydroperoxide and 1.4 g (0.02 moles) of 1,1-dimethyloxirane in 6 ml of 2-methyl-2-propanol at a temperature of -10 ... -8 °C under intense stirring was added dropwise by 3 ml of 1 N. solution of sulfate acid in 2-methyl-2-propanol. The reaction mixture was maintained at this temperature for 5 hours, neutralized with sodium carbonate and distilled off in vacuo. A fraction was selected from the b.p.. 40,0 °C / 0,4 kPa. 2.4 g (73 % yield) of peroxide was obtained. Mol. mass is 156 (cryoscopically in benzene), calculated 162.22. Found, % C 58.97; H 10.37. C₈H₁₈O₃. Calculated, %: C, 59.23; H 11.18. ¹H NMR (CDCl₃), δ ppm: 1.19 s (9H, - (CH₃)₃); 1.24 s. (2 * 3H, 2 * CH₃); 2.6 s (1 H, -CH₂-OH); 3.43 s. (2H, -CH₂-OH).

2-tert-Butyl-peroxy-2,2-diphenylethanol (2b) was synthesized analogously from 4.0 g (0.044 mole) of tert-butyl hydroperoxide and 3.9 g (0.02 mole) of 2,2-diphenyloxirane in 6.0 ml of 2-methyl-2-propanol. The product obtained was chromatographed on aluminum oxide of the second activity level, eluent is hexane-diethyl ether as 1:1. 3.8 g of target hydroxyperoxide was obtained, yield 68 %. Mol. mass 219 (cryoscopically in benzene), calculated 224.22. Found %: C 68.01; H 8.02. C₁₃H₂₀O₃. Calculated, %: C, 69.61; H 8.99. ¹H NMR (CDCl₃), δ ppm: 1.19 s (9H, - (CH₃)₃); 7.40 m. (5H, Ph-H); 2.6 s (1 H, -CH₂-OH); 3.78 s (2H, -CH₂-OH).

3-Bromomethyl-3-hydroxymethyloxetane (3). A solution of 7.2 g (0.31 mole) Sodium carbonate in 350 ml of absolute ethanol was slowly added to a solution of 80 g (0.31 mole) of 2,2-bis (bromomethyl) propane-1,3-diol in 150 ml of ethanol. The mixture was refluxed and stirred for 2.5 hours, cooled, sodium bromide was filtered off and concentrated in vacuo to a viscous state. Fractionally distilled from the Vigre's column. 37.3 g (68 % yield) of the target product were obtained. b.p. 141...142 °C (1-2 mm Hg). Found, % C: 33.12; H 5.0, Br 43.94. C₅H₉O₂Br. Calculated, %: C, 33.17; H 5.01, Br 44.14. ¹H NMR (CDCl₃), δ, ppm: 2.85 t (1H, -O.N), 3.89 d (2H, -CH₂-OH), 3.83 s (2H, -CH₂-Br), 4.29 d. (2H, oxetane), 4.34 d (2H, oxetane).

[3- (tert-Butylperoxymethyl) oxetane-3-yl] methanol (3a). A mixture of 2 g of aluminum oxide, 9 ml of tetrahydrofuran and 0.202 g (0.0025 mole) of tert-butyl hydroperoxide was stirred for 2 min. in an argon atmosphere, and 0.135 g (0.0075 mole) of 3-bromomethyl-3-hydroxymethyloxetane in 10 ml of chloroform was added. The reaction mixture was kept stirring at 20 °C. for 80 hours, after which 250 ml of ethanol was added and placed in a refrigerator for 12 hours, filtered through a layer of silica gel. We are distillation of solvents. Purified by chromatography on silica gel (eluent, dichloromethane-tert-butyl methyl ether (5: 1), yield of substances was 0.64 g (45 %), m.p. 16-17.5 °C. Mol. mass 190 (cryoscopic in benzene), calculated 201.5 Found, %: C, 56.88; H, 9.51, C₉H₁₈O₄, Calculated, %: C, 56.82; H, 9.54. ¹H NMR (CDCl₃), δ, ppm: 3.59 t (2H, -CH₂-OH), 3.75 (1H, OH), 4.29-4.33d, (2H, oxetane), 4.34 and 4.57d (2H, oxetane).

2- (Bromomethyl) -2- (tert-butylperoxymethyl) propane-1,3-diol (3b) was prepared analogously to compound 3a from 0.135 g (0.0075 mole) oxetane (3), 0.202 g (0.0025 mole) of t-butyl hydroperoxide in the presence of 2 g of aluminum oxide in 9 ml of tetrahydrofuran. Purified by chromatography on silica gel (eluent dichloromethane-tert-butyl methyl ether (5: 1) yield of the product was 0.25 g (35 %). Mol. mass 285 (cryoscopic in benzene), calculated 287.14 Found, %: C, 37.71 H, 6.60, Br, 27.77, C₉H₁₉O₆ Calculated, %: C, 37.64; H 6.67; Br 27.83. ¹H NMR (CDCl₃), δ, ppm. 1.28 s (9H, -(CH₃)₃); 2.61 t (1H, -OH); 4.05 s (2H, -CH₂-OH); 3.86 s (2H, -CH₂-Br); 4.81 s (4H, -C-CH₂-O).

2,2-Bis (tert-butylperoxymethyl) propane-1,3-diol (3c). A mixture of 2 g of aluminum oxide, 0.404 g (0.005 mole) of t-butyl hydroperoxide and 9 ml of tetrahydrofuran was stirred for 2 min. in an atmosphere of argon. A solution of 0.135 g (0.0075 mole) oxetane (3) in 10 ml of chloroform was added. The mixture was maintained at stirring at 20 °C. for 230 h., 250 ml of ethanol was added and placed in a refrigerator for 12 h. Filtered through a pad of silica gel and washed with ethanol. We are distilled of solvents. The target product was purified by column chromatography on silica gel. The eluent mixture is dichloromethane-tert-butyl methyl ester (5: 1). Yield of the target product was 1.53 g (73 %). B.p. 29–30 °C. Mol. mass 283 (cryoscopic in benzene), calculated 280.36. Found, %: C 55.83 H 10.11. C₁₃H₂₈O₆. Calculated, %: C 55.69; H 10.07. ¹H NMR (CDCl₃), δ, ppm.: 1.28 s (18H, -(CH₃)₃); 2.61 t (1H, -OH); 4.05 s (4H, -CH₂-OH); 4.82 s (4H, -C-CH₂-O).

2,2-Dimethyl-1,3-dioxolane (4). A solution of 10 g (0.16 mole) of ethylene glycol, 16.6 g (0.16 mole) of 2,2-dimethoxypropane and (0.016 mole) of p-toluenesulphonic acid at a temperature of 20 °C. for 70 hours, after which the sodium carbonate was neutralized and filtered through a layer aluminum oxide. After distillation, of the target product were obtained 8.5 g (85 % yield). B.p. 92–93 °C. Found, %: C 58.90; H, 9.90; O 31.20. Calculated, %: From 58.80; H, 9.87; O 31.33.

2- [1- (tert-Butylperoxy) ethoxy] ethanol (4a). To a mixture of 6.12 g (0.06 mole) of 2,2-dimethyl-1,3-dioxolane and 10.8 g (0.12 mole) of TBGP, 0.1 mole of 80 % sulfate acid solution was added dropwise at 5 °C. The reaction mixture was kept stirring for 5 hours, the sulphate acid was neutralized with

magnesium oxide, the reaction product was extracted with dichloromethane and dried over magnesium sulfate. After distillation in vacuo, the yield of peroxide was 2.75 g (45 %). B.p. 60 °C at 15 mm Hg. Found, %: C 54.03; H, 10.15; O 35.47. Calculated, %: C 53.91; H, 10.18; O 35.91.

2- (tert-Butylperoxy) ethoxy] propan-2-ol (4b) was prepared analogously to the substance (4a) from 6.12 g (0.06 mmol) of 2,2-dimethyl-1,3-dioxolane and 10.8 g (0.12 mol) TBGP at 5 °C for 4-5 hours in the presence of 0.1 mol of 80 % sulfuric acid. The yield of peroxide was obtained 0.61 g (10 %). B.p. 45 °C (0.1 mm Hg). Found, %: C 51.36; H, 9.34; O 39.30. Calculated, %: C 51.52; H, 9.26; O 39.22.

Conclusions. The reactions of tert-butyl hydroperoxide with three-, four-, and five-membered oxygen-containing heterocycles (2,2-dimethyloxirane, 3-bromomethyl-3-hydroxymethyloxetane and 2,2-dimethyl-1,3-dioxolane) were carried out. It is shown that the disclosure of the oxirane's cycle occurs regionally and allows high yielding of ditertiary peroxides with the primary OH group. The reaction of oxetane and oxolane, although it allows the production of functional tertiary-primary peroxides, however, does not show regiospecificity and leads to the formation of a mixture of peroxide compounds.

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