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SYNTHESIS AND INTRAMOLECULAR CYCLIZATION OF PROPARGYL ETHERS DERIVED FROM 1-BROMO(IODO)-3-ORGANYLOXY-2-PROPANOL

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The interaction of bromine (iodine)-releasing reagents, such as N-bromosuccinimide (NBS) or a mixture of iodine and clinoptilolite ($(NaK)_4CaAl_6Si_{30}O_{72}$), with an equimolar mixture of 3-organyloxy-1-propene and propynol results in the formation of propargyl ethers of 1-bromo(iodo)-3-organyloxy-2-propanol. The outcome of the catalytic hydration reaction of these ethers depends on the halogen atom present. Bromo derivatives are converted into the expected keto-bromo ethers, whereas iodo derivatives undergo simultaneous hydrolysis of the C—I bond and intermolecular ketalization, forming hydroxy derivatives of 1,4-dioxane. The hydration products of propargyl ethers derived from 1-bromo-3-organyloxy-2-propanol serve as key compounds for the synthesis of 2,2,5-trisubstituted 1,4-dioxanes through intermediate hydroxy diethers formed via reactions with organomagnesium reagents. The reactions and purity of the synthesized compounds were monitored using thin-layer chromatography. The yields of allyl ethers were higher than those of propargyl ethers. Some physicochemical properties of the synthesized compounds were measured, their composition and structure were confirmed by elemental analysis, and their identities were verified using IR and NMR spectroscopy.

Keywords: heterocyclization, 1-bromo(iodo)-3-organyloxy-2-propanol, haloalkoxylation, propargyl ethers, catalytic hydration, 1,4-dioxane derivatives.

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Introduction

Acetylene halide ethers, possessing a variety of practically useful properties, are widely used in organic synthesis [1—3], including the production of biologically active compounds [4,5].

A one-step method for synthesizing β-bromo(iodo) ethers of acetylene alcohols involves the haloalkoxylation of substrates with double bonds [5]. This study focuses on the synthesis of propargyl ethers derived from 1-bromo(iodo)-3-organyloxy-2-propanol and their subsequent conversion into 1,4-dioxane derivatives. These derivatives, in addition to their high synthetic potential, are effective inhibitors of acid-induced metal corrosion [6].

Results and discussion

We have determined that a convenient one-step method (yield up to 62%) for the preparation of propargyl ethers of 1-bromo(iodo)-3-organyloxy-2-propanol **1—6** involves the use of bromine (iodine)-releasing reagents such as NBS or a mixture of I_2 and CPT. These reagents are applied to an equimolar mixture of 3-organyloxy-1-propene and propynol.

The presence of ^{1}H NMR signals in the regions 3.48 d.d (1H, J=10.3, 5.8 Hz, CH_2Br), 3.38 d.d (1H, J=10.2, 5.7 Hz, CH_2Br), and 4.41 d.d (1H, J=5.7 Hz, CH) for bromo derivatives and 3.28 d.d (1H, J=10.2, 5.7 Hz, CH_2I), 3.41 d.d (1H, J=10.2, 5.7 Hz, CH_2I), and 4.43 d.d (1H, J=5.7 Hz, CH) for iodo derivatives confirms the regioselectivity of the haloalkoxylation reaction.

The resulting unsaturated bromoethers (compounds **1—3**), under the conditions of the Kucherov reaction, undergo transformation into keto ethers (compounds **7—9**). These keto ethers are readily

converted into the corresponding halohydroxy diethers (compounds **10–15**) upon treatment with Grignard reagents. Subsequent alkaline treatment of the halohydroxy diethers leads to heterocyclic products resulting from the intramolecular elimination of hydrogen halide, 2,2,5-trisubstituted 1,4-dioxanes (compounds **16–21**).

The formation of compounds **16–21** in good yields is also achieved through the direct reaction of ketobromo(iodo) diethers (compounds **7–9**) with the corresponding organylmagnesium bromides in a diglyme medium. This approach eliminates the need for isolating intermediate compounds **10–15**.

Meanwhile, the hydration of iodoethers **4–6** proceeds with the simultaneous hydrolysis of the C–I bond and the closure of a six-membered ring. As a result, hydroxyl-containing derivatives of 1,4-dioxane (compounds **22–24**) are formed (Scheme).

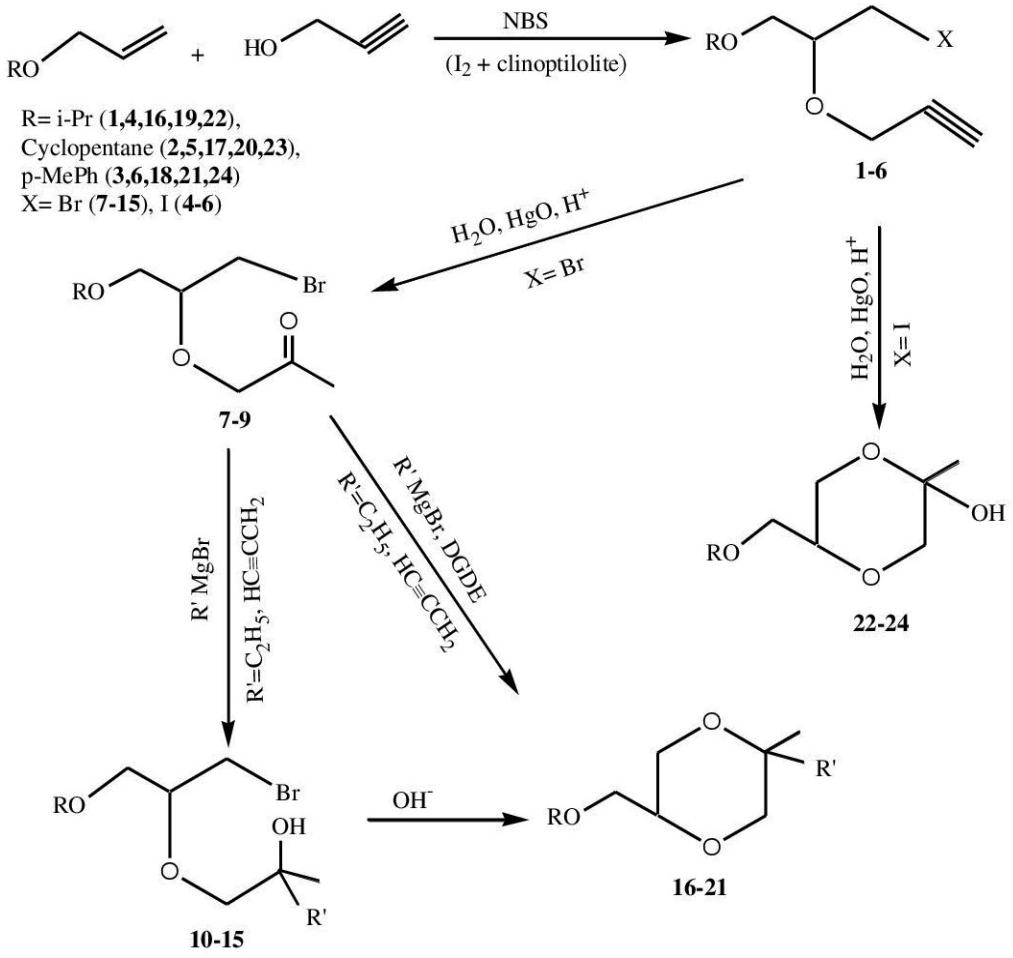
The composition and structure of the obtained compounds were confirmed by elemental analysis, as well as by IR and ^{1}H NMR spectroscopy.

Conclusions

Bromine(iodine)-alkoxylation of 3-organyloxy-1-propene with propynol in the presence of CPT and crystalline iodine or NBS results in propargyl ethers of 1-bromine(iodine)-3-organyloxy-2-propanol in high yield. These compounds, under the conditions of the Kucherov reaction, undergo transformation into heterocyclic compounds. The formation of heterocyclic compounds is attributed to the intramolecular cyclization of the resulting intermediate keto-hydroxy ether, i.e., the tandem hydrolysis of the C–I bond and hydration of the C≡C bond in the reaction products.

Experimental

The starting 3-organyloxy-1-propenes were synthesized according to the described procedure. IR spectra of the compounds in the microlayer and in tablets with KBr were recorded using a Specord-75 instrument. ^{1}H NMR spectra of the substances in $CDCl_3$ solution were recorded on a Bruker SF-300



Scheme

instrument (300.134 MHz), with HMDS as the internal standard.

Propargyl ether of 1-bromo-3-i-propoxy-2-propanol (**1**) *(general method)*

To a cooled (−5^{0}C) and stirred equimolar mixture of 25 g (0.25 mol) allyl-propyl ether and 14 g (0.25 mol) propynol, 44 g (0.25 mol) NBS was gradually added, ensuring that the temperature of the reaction mixture did not exceed 0^{0}C. The stirring was continued at room temperature for 5 hours, after which the resulting succinimide was filtered off. The mixture was made alkaline by adding a solution of 15 g of sodium hydroxide in 100 mL of water, then extracted with ether and dried over $CaCl_2$. After the ether was removed, the residue was distilled under vacuum. Compound **1** was isolated in a yield of 41.15 g (70%) at a boiling point of 65−66^{0}C (2 mm Hg). IR spectrum (ν, cm^{-1}): 620 (C−Br), 1100 (C−O−C), 2100 and 3300 (C≡CH). №H NMR spectrum (δ, ppm, $CDCl_3$): 0.81 d (6H, $2CH_3$, J=7.1 Hz), 1.21 t (2H, CH_2, J=7.5 Hz), 2.46 t (1H, CH, J=2.3 Hz), 3.23 m (4H, CH_2OCH_2), 3.37 d.d (1H, CH_2Br, J=10.5, 5.7 Hz), 3.41 d.d (1H, CH_2Br, J=10.5, 5.7 Hz), 3.87 m (1H, CH), 4.02 d (2H, $\equiv CCH_2O$, J=2.3 Hz). Found, %: C 45.95, H 6.46, Br 33.96. $C_9H_{15}BrO_2$. Calculated, %: C 45.98, H 6.43, Br 33.98.

Likewise, based on:

− allyl ether of cyclopentane, propynol, and NBS, *propargyl ether of 1-bromo-3-cyclopentoxy-2-propanol* (**2**) was obtained (yield 65%) with a boiling point of 80−82^{0}C (2 mm Hg). IR spectrum (ν, cm^{-1}): 628 (C−Br), 1040 (C−O−C), 2201 and 3331 (C≡CH). ^{1}H NMR spectrum (δ, ppm, $CDCl_3$): 0.77−1.25 m (11H, ring protons), 2.46 t (1H, CH, J=2 Hz), 4.04 d (2H, CCH_2O, J=2 Hz), 3.41 d.d (1H, CH_2Br, J=10.5, 5.7 Hz), 3.41 d.d (1H, CH_2Br, J=10.5, 5.7 Hz), 3.87 d (2H, CH_2O), 3.84 m (1H, CH). Found, %: C 52.36, H 6.99, Br 28.90. $C_{12}H_{19}BrO_2$. Calculated, %: C 52.38, H 6.96, Br 29.04.

− allyl ether of phenol, propynol, and NBS, *propargyl ether of 1-bromo-3-phenoxy-2-propanol* (**3**) was obtained (yield 68.5%) with a boiling point of 99−100^{0}C (2 mm Hg). IR spectrum (ν, cm^{-1}): 635 (C−Br), 1101 (C−O−C), 2201 and 3331 (C≡CH), 680, 757, 991, 1121, 1503, 1596, 2233, 2926, 3060 (C_6H_5). Found, %: C 53.52, H 4.90, Br 29.64. $C_{12}H_{13}BrO_2$. Calculated, %: C 53.55, H 4.87, Br 29.69.

Propargyl ether of 1-iodo-3-i-propoxy-2-propanol (**4**) *(general method)*

To a cooled (−5 to 0^{0}C) and vigorously stirred mixture of 14 g (0.25 mol) propargyl alcohol and 25 g (0.25 mol) allyl i-propyl ether, 0.26 g of CPT was added, followed by 63.45 g (0.25 mol) of finely ground crystalline iodine. Stirring was continued at room temperature for 3−4 hours. The resulting mixture was filtered, and the filtrate was washed with a $Na_2S_2O_3$ solution and extracted with ether. The extract was dried over $CaCl_2$, the ether was removed, and the residue was recrystallized. A yield of 47.9 g (68%) of compound (4) was obtained, with a melting point of 52−53^{0}C (from heptane). IR Spectrum (ν, cm^{-1}): 552 (C−I), 1107 (C−O−C), 2100 and 3331 (C≡CH). ^{1}H NMR spectrum (δ, ppm, $CDCl_3$): 0.73 t (3H, CH_3), 1.24 m (2H, CH_2), 2.42 t (1H, ≡CH), 3.23 m (4H, CH_2OCH_2), 3.27 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 3.43 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 3.84 m (1H, CH), 4.02 d (2H, $OCH_2C\equiv$). Found (%): C 38.28, H 5.32, I 44.92. $C_9H_{15}IO_2$. Calculated (%): C 38.32, H 5.36, I 44.98.

Likewise, based on:

− allyl ether of cyclopetnanol, propynol and crystalline iodine, *propargyl ether of 1-iodo-3-cyclopentoxy-2-propanol* (**5**) was obtained with a yield of 57.6%); mp. 60−61^{0}C (from heptane). IR spectrum (ν, cm^{-1}): 561 (C−I), 1100 (C−O−C), 2102 and 3330 (C≡CH). ^{1}H NMR spectrum (δ, ppm, $CDCl_3$): 0.73−1.24 m (8H, C_5H_8), 2.44 t (1H, ≡CH), 3.29 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 3.41 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 3.45 d (2H, 2CHO), 3.65 m (2H, 2CHO), 4.11 d (2H, $OCH_2C\equiv$). Found, %; C 44.72, H 5.96, I 39.38. $C_{10}H_{17}IO_2$. Calculated, %: C 44.74, H 5.94, I 39.39.

− allyl ether of p-Me-phenol, propynol and crystalline iodine, *propargyl ether of 1-iodo-3-4-Me-phenoxy-2-propanol* (**6**) was obtained with a yield of 67.2%; bp. 115^{0}C (2 mm Hg). IR spectrum (ν, cm^{-1}): 560 (C−I), 1100 (C−O−C), 2100 and 3330 (C≡CH), 1515, 1620, 3060, 3080 (C_6H_5). ^{1}H NMR spectrum (δ, ppm, $CDCl_3$): 2.5 t (1H, ≡CH, J=2.4 Hz) 3.41 d (2H, $2CH_2O$), 3.28 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 3.41 d.d (1H, CH_2I, J=10.5, 5.7 Hz), 4.09 d (2H, $OCH_2C\equiv$, J=2.5Hz), 7.15 m (5H, C_6H_5). Found, %: C 45.55, H 4.18, I 40.08. $C_{13}H_{15}IO_2$. Calculated, %; C 45.59, H 4.14, I 40.14.

5-Bromomethyl-4,7-dioxa-2-decanone (**7**) *(general method)*

To a mixture of 0.65 g (0.003 mol) of mercury oxide, 1 ml of H_2SO_4, and 24 ml of water, heated to 60^{0}C and stirred, 11.75 g (0.05 mol) of compound (**I**) was gradually added. The reaction mixture was maintained at 60−65^{0}C for 6 hours under reflux. After cooling, the mixture was extracted with ether, and the aqueous layer was saturated with sodium chloride and extracted again with ether. The combined organic phases were dried over Na_2SO_4. The solvent was removed, and the residue was distilled under

vacuum. Yield: 8.6 g (68%) of compound **7**, with a boiling point of 62–63°C (4 mm Hg). IR spectrum (ν, cm^{-1}): 651 (C–Br), 1101 (C–O–C), 1721 (C=O). Found (%): C 42.67, H 6.80, Br 31.50. $C_{10}H_{19}BrO_3$. Calculated (%): C 42.70, H 6.77, Br 31.57.

Compounds (**8** and **9**) were obtained in a similar way:

– *5-Bromomethyl-6-cyclopentyloxy-2-hexanone* (**8**). Yield 65%, bp. 78–79°C (4 mm Hg). IR spectrum (ν, cm^{-1}): 645 (C–Br), 1102 (C–O–C), 1725 (C=O). Found, %: C 49.13, H 7.24, Br 27.14. $C_{12}H_{21}BrO_3$. Calculated, %: C 49.16, H 7.22, Br 27.25.

– *5-Bromomethyl-6-phenoxy-2-hexanone* (**9**). IR spectrum (ν, cm^{-1}): 642 (C–Br), 1101 (C–O–C), 1724 (C=O), 684, 756, 992, 1120, 1501, 1594, 2233, 2924, 3062 (C_6H_5). Yield 63%, bp. 95–96°C (4 mm Hg). Found, %: C 50.16, H 5.30, Br 27.79. $C_{12}H_{15}BrO_3$. Calculated, %: C 50.19, H 5.26, Br 27.83.

3-Methyl-6-bromomethyl-5,8-dioxa-3-undecanol (**10**) *(general method)*

To the cooled (0–5°C) and stirred Grignard reagent, prepared from 2.4 g (0.1 g-atom) of magnesium and 10.9 g (0.1 mol) of ethyl bromide in 300 ml of absolute ether, 20.24 g (0.08 mol) of compound (**VII**) was added. The mixture was boiled for 8 hours and then decomposed with acidified water (HCl). The organic layer was separated, neutralized with a 2% $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was removed, and the residue was distilled under reduced pressure. Yield: 14.7 g (65%) of compound **10**, with a boiling point of 135–136°C (2 mm Hg). IR spectrum (ν, cm^{-1}): 642 (C–Br), 1101 (C–O–C), 1723 (C=O), 3601 (O–H). Found (%): C 46.62, H 8.23, Br 28.16. $C_{11}H_{23}BrO_3$. Calculated (%): C 46.65, H 8.19, Br 28.21.

Compounds **11–15** were obtained in a similar way:

– *3-Methyl-6-bromomethyl-5-oxa-7-cyclopentyloxy-3-heptanol* (**11**). Yield 56%, bp. 150–151°C (2 mm Hg). IR spectrum (ν, cm^{-1}): 637 (C–Br), 1102 (C–O–C), 1725 (C=O), 3603 (O–H). Found, %: C 52.00, H 8.45, Br 24.68. $C_{14}H_{27}BrO_3$. Calculated, %: C 52.02, H 8.42, Br 24.72.

– *3-Methyl-6-bromomethyl-5-oxa-7-phenoxy-3-heptanol* (**12**). Yield 50%, bp. 180–181°C (1 mm Hg). IR spectrum (ν, cm^{-1}): 632 (C–Br), 1102 (C–O–C), 1723 (C=O), 3600 (O–H). Found, %: C 52.98, H 6.70, Br 25.15. $C_{14}H_{21}BrO_3$. Calculated, %: C 53.01, H 6.67, Br 25.19.

– *4-Methyl-7-bromomethyl-6,9-dioxa-1-dodecin-4-ol* (**13**). Yield 67%, bp. 148–150°C (2 mm Hg). IR spectrum (ν, cm^{-1}): 637 (C–Br), 1102 (C–O–C), 1723 (C=O), 3601 (O–H). Found, %: C 49.13, H 7.16, Br 27.18. $C_{12}H_{21}BrO_3$. Calculated, %: C 49.16, H 7.2, Br 27.25.

– *4-Methyl-7-bromomethyl-6-oxa-8-cyclopentyloxy-1-octin-4-ol* (**14**). Yield 67%, bp. 162–163°C (2 mm Hg). IR spectrum (ν, cm^{-1}): 631 (C–Br), 1102 (C–O–C), 1724 (C=O), 3600 (O–H). Found, %: C 54.04, H 7.53, Br 23.89. $C_{15}H_{25}BrO_3$. Calculated, %: C 54.06, H 7.56, Br 23.96.

– *4-Methyl-7-bromomethyl-6-oxa-8-phenoxy-1-octin-4-ol* (**15**). IR spectrum (ν, cm^{-1}): 637 (C–Br), 1102 (C–O–C), 2201 and 3331 (C≡CH), 686, 757, 992, 1121, 1501, 1596, 2233, 2926, 3061 (C_6H_5). Yield 62%, bp. 190–191°C (1 mm Hg). Found, %: C 55.02, H 5.82, Br 24.40. $C_{15}H_{19}BrO_3$. Calculated, %: C 55.06, H 5.85, Br 24.42.

2-Methyl-2-ethyl-5-i-propyloxymethyl-1,4-dioxane (**16**)

8.5 g (0.03 mol) of compound **10** was added to a stirred suspension of 4.44 g of KOH in 80 ml of diethyl ether. The mixture was boiled for 4 hours and decomposed by adding water. The ether layer was separated and dried with Na_2SO_4. After removing the ether, the residue was distilled under reduced pressure. Yield 4.7 g (78%), bp. 55–56°C (1 mm Hg). IR spectrum (ν, cm^{-1}): 637 (C–Br), 1102 (C–O–C), 2201 and 3331 (C≡CH). Found, %: C 65.29, H 11.00. $C_{11}H_{22}O_3$. Calculated, %: C 65.31, H 10.96.

Compounds (**17–21**) were obtained in a similar way:

– *2-Methyl-2-ethyl-5-cyclopentyloxymethyl-1,4-dioxane* (**17**). Yield 69%, bp. 72–74°C (1 mm Hg). IR spectrum (ν, cm^{-1}): 632 (C–Br), 1102 (C–O–C), 2201 and 3331 (C≡CH). Found, %: C 69.35, H 10.83. $C_{14}H_{26}O_3$. Calculated, %: C 69.38, H 10.81.

– *2-Methyl-2-ethyl-5-Me-phenyloxymethyl-1,4-dioxane* (**18**). IR spectrum (ν, cm^{-1}): 637 (C–Br), 1101 (C–O–C), 2201 and 3301 (C≡CH). Yield 63%, bp. 92–93°C (1 mm Hg). Found, %: C 71.12, H 8.60. $C_{14}H_{20}O_3$. Calculated, %: C 71.16, H 8.53.

– *2-Methyl-2-propargyl-5-i-propyloxymethyl-1,4-dioxane* (**19**). IR spectrum (ν, cm^{-1}): 632 (C–Br), 1100 (C–O–C), 2201 and 3330 (C≡CH). Yield 77%, bp. 68–69°C (1 mm Hg). Found, %: C 67.92, H 9.48. $C_{12}H_{20}O_3$. Calculated, %: C 67.89, H 9.50.

– *2-Methyl-2-propargyl-5-cyclopentyloxymethyl-1,4-dioxane* (**20**). IR spectrum (ν, cm^{-1}): 634 (C–Br), 1101 (C–O–C), 2201 and 3331 (C≡CH).Yield 60%, bp. 82–84°C (1 mm Hg). Found, %: C 71.37, H 9.63. $C_{15}H_{24}O_3$. Calculated, %: C 71.39, H 9.59.

– *2-Methyl-2-propargyl-5-Me-phenyloxymethyl-1,4-dioxane* (**21**). IR spectrum (ν, cm^{-1}):

637 (C−Br), 1100 (C−O−C), 2201 and 3330 (C≡CH), 683, 757, 991, 1120, 1501, 1594, 2213, 2929, 3060 (C_6H_5). Yield 63%, bp. 104−105^{0}C (1 mm Hg). Found, %: C 73.11, N 7.40. $C_{15}H_{18}O_3$. Calculated, %: C 73.15, H 7.37.

*Compounds **16−21** (general method)*

A cooled (0єC) and stirred Grignard reagent, prepared from 5.9 g of organylmagnesium bromide in «anhydrous» diglyme, was gradually combined with ketobromoethers **7−9**. The mixture was heated to 75−80^{0}C with continuous stirring for 4 hours, then allowed to cool to room temperature. It was decomposed by the addition of water and treated with diethyl ether. The organic phase was separated, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residues were purified to isolate compounds **16−21**.

2-Methyl-2-hydroxy-5-propoxymethyl-1,4-dioxane (**22**)

To a mixture of 0.65 g (0.003 mol) of mercury oxide, 1 ml of H_2SO_4 and 24 ml of water, heated to 60^{0}C and stirred, 14.1 g (0.05 mol) of compound **4** was gradually added. The mixture was boiled at 60−65^{0}C for 6 hours, extracted with ether. The aqueous layer was saturated with sodium chloride and extracted again with ether. The combined organic phases were dried using Na_2SO_4. After removing the ether, the residue was distilled under reduced pressure. 6.5 g (68%) of compound **22** was isolated, bp. 95−96^{0}C (1 mm Hg). IR spectrum (ν, cm^{-1}): 1101 (C−O−C), 3602 (O−H). Found, %: C 56.85, H 9.57. $C_9H_{18}O_4$. Calculated, %: C 56.82, H 9.54.

Compounds **23** and **24** were obtained in a similar way:

− *2-Methyl-2-hydroxy-5-cyclopentyloxymethyl-1,4-dioxane* (**23**). Yield 77%, bp. 117−119^{0}C (1 mm Hg). IR spectrum (ν, cm^{-1}): 1102 (C−O−C), 3603 (O−H). Found, %: C 62.60, H 9.66. $C_{12}H_{22}O_4$. Calculated % C 62.58, H 9.63.

− *2-Methyl-2-hydroxy-5-phenoxymethyl-1,4-dioxane* (**24**). Yield 63%, bp. 152−153^{0}C (1 mm Hg). IR spectrum (ν, cm^{-1}): 1105 (C−O−C), 3602 (O−H), 686, 757, 992, 1121, 1501, 1596, 2233, 2926, 3061 (C_6H_5). Found, %: C 64.24, H 7.20. $C_{12}H_{16}O_4$. Calculated, %: C 64.27, H 7.19.

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СИНТЕЗ І ВНУТРІШНЬОМОЛЕКУЛЯРНА ЦИКЛІЗАЦІЯ ПРОПАРГІЛОВИХ ЕФІРІВ, ПОХІДНИХ ВІД 1-БРОМО(ЙОДО)-3-ОРГАНІЛОКСИ-2-ПРОПАНОЛУ

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Взаємодія реагентів, що виділяють бром (йод), таких як N-бромсукцинімід (NBS) або суміш йоду та клиноптилоліту ($(NaK)_4CaAl_6Si_{30}O_{72}$), з еквімолярною сумішшю 3-органілокси-1-пропену та пропінолу призводить до утворення пропаргілових ефірів 1-бромо(йодо)-3-органілокси-2-пропанолу. Результат реакції каталітичної гідратації цих ефірів залежить від присутнього галогену. Бромо-похідні перетворюються на очікувані кето-бромо ефіри, тоді як йодо-похідні одночасно зазнають гідролізу за зв'язком C—I і міжмолекулярної кеталізації, утворюючи гідроксипохідні 1,4-діоксану. Продукти гідратації пропаргілових ефірів, похідних від 1-бромо-3-органілокси-2-пропанолу, є ключовими сполуками для синтезу 2,2,5-тризаміщених 1,4-діоксанів через проміжні гідрокси-діефіри, які утворюються в реакціях з органомагнієвими реагентами. Реакції та чистоту синтезованих сполук контролювали за допомогою тонкошарової хроматографії. Вихід аллільних ефірів був вищим, ніж пропаргілових ефірів. Було визначено деякі фізико-хімічні властивості синтезованих сполук, їхній склад і структуру підтверджено методом елементного аналізу, а ідентифікацію проведено за допомогою ІЧ- і ЯМР-спектроскопії.

Ключові слова: гетероциклізація; 1-бромо(йодо)-3-органілокси-2-пропанол; галоалкоксиляція; пропаргілові ефіри; каталітична гідратація; похідні 1,4-діоксану.

SYNTHESIS AND INTRAMOLECULAR CYCLIZATION OF PROPARGYL ETHERS DERIVED FROM 1-BROMO(IODO)-3-ORGANYLOXY-2-PROPANOL

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The interaction of bromine (iodine)-releasing reagents, such as N-bromosuccinimide (NBS) or a mixture of iodine and clinoptilolite ($(NaK)_4CaAl_6Si_{30}O_{72}$), with an equimolar mixture of 3-organyloxy-1-propene and propynol results in the formation of propargyl ethers of 1-bromo(iodo)-3-organyloxy-2-propanol. The outcome of the catalytic hydration reaction of these ethers depends on the halogen atom present. Bromo derivatives are converted into the expected keto-bromo ethers, whereas iodo derivatives undergo simultaneous hydrolysis of the C—I bond and intermolecular ketalization, forming hydroxy derivatives of 1,4-dioxane. The hydration products of propargyl ethers derived from 1-bromo-3-organyloxy-2-propanol serve as key compounds for the synthesis of 2,2,5-trisubstituted 1,4-dioxanes through intermediate hydroxy diethers formed via reactions with organomagnesium reagents. The reactions and purity of the synthesized compounds were monitored using thin-layer chromatography. The yields of allyl ethers were higher than those of propargyl ethers. Some physicochemical properties of the synthesized compounds were measured, their composition and structure were confirmed by elemental analysis, and their identities were verified using IR and NMR spectroscopy.

Keywords: heterocyclization; 1-bromo(iodo)-3-organyloxy-2-propanol; haloalkoxylation; propargyl ethers; catalytic hydration; 1,4-dioxane derivatives.

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