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SYNTHESIS OF PROPARGYL(ALLYL) ARYLOXYETHERS

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A convenient method for the synthesis of propargyl(allyl) aryloxyethers is proposed. It is notable that the synthesized compounds exhibit increased reactivity and are rich in nucleophilic centers. Experimental data have established that these compounds are stable and do not undergo hydrolysis. The yields of the target products in both cases are up to 89.2%. The reaction duration and the volume of substituents at the alkoxy group do not significantly affect the yield of the target products. The composition of the synthesized compounds includes groups of signals from protons of the allyl and propargyl groups. The reactions and purity of the obtained compounds were monitored by thin layer chromatography. The yields of allyl ethers are higher than those of propargyl ethers. Some physicochemical properties of the synthesized compounds are presented, and their composition and structure are confirmed by elemental analysis. All synthesized compounds have been identified by IR and NMR spectroscopy.

Keywords: propargyl(allyl) aryloxyethers, α -glycol monoethers, chloromethylpropargyl ether, chloromethylallyl ether, synthesis.

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Introduction

Propargyl(allyl)oxyethers, which have high synthetic potential due to the presence of two nonequivalent reactive centers in their composition (C=CH, HC=CH₂, C-OH), are widely used in the formation of C=C bonds, in particular, in the synthesis of heterocyclic compounds [1–7]. Structural analogues of such compounds are widely used in organic synthesis [8–11], including being valuable monomers for the preparation of macromolecules [12].

The proposed method for obtaining propargyl(allyl)oxyethers of the aromatic series is convenient in synthesis, as it allows the synthesis of compounds with high yields, especially for the ease of laboratory preparation, the availability of reagents, etc. Similar compounds having a propargyl(allyl) fragment are obtained mainly with the participation of inaccessible metal complex catalysts [13]. Such opportunities open up ways to synthesize previously unknown substances with beneficial properties.

Results and discussion

The purpose of this research is the synthesis of

chloromethyl(propargyl)allylic monoethers of α glycols. The latter were obtained by the interaction of 3-(1-chloroethoxy)prop-1-ene with benzaldehyde in anhydrous benzene and hexamethylphosphorotriamide (HMPTA) in an inert atmosphere of nitrogen on zinc ground in the form of fine chips in the presence of a catalytic amount of HgCl₂ (Scheme 1).

The proposed mechanism can be described by the equation given in Scheme 2, where $CuCl_2$ acts as a stabilizer for the resulting intermediate organoelement compound [14].

The structures of individually isolated pure substances 1-10 were confirmed by spectral methods. The IR spectra of the obtained products contain characteristic absorption bands of stretching vibrations of hydroxyl groups O–H at 3598–3603 cm⁻¹. In secondary alcohols 1-10, planar bending vibrations of O–H interact with fan vibrations of C–H, giving two bands at about 1420 cm⁻¹ and 1330 cm⁻¹ [15].

In the NMR spectra, hydroxyl protons appear in the region of 3.45-3.47 ppm. The geminal protons of the 2CH₂ groups of compounds **1–10**, also being

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diastereotopic due to the asymmetric carbon atom C, appear in the proton spectra and are present in the form of a doublet of doublets (AB system) in the area of 2.58–3.04 ppm.

Carrying out the reaction in a nitrogen atmosphere eliminates the hydrolysis of α -haloether, which easily decomposes in moist air.

The structure and composition of the obtained target compounds 1-10 were confirmed by IR and 1H and ¹³C NMR spectroscopies and elemental analysis.

Conclusions

Chloromethyl-(propargyl)allylic monoethers of α -glycols were synthesized. The latter were obtained by the interaction of 3-(1-chloroethoxy)prop-1-ene with benzaldehyde in anhydrous benzene and hexamethylphosphorotriamide in an inert atmosphere of nitrogen on zinc ground in the form of fine chips in the presence of a catalytic amount of HgCl₂.

Experimental part

IR spectra of compounds in a thin layer were recorded on a Specord 75 IR device. ¹H and ¹³C NMR spectra in CDCl₃-d₆ were recorded on a Bruker SF-300 instrument [300.13 (¹H), 75 (¹³C) MHz] (Germany), HMDS as an internal standard. Elemental analysis was performed on a «EURO EA 3000 (United Kingdom)» device EuroVector, manufactured in Italy.

The purity of the obtained compounds was monitored by thin layer chromatography on Silufol UV-254 plates, eluent acetone-hexane, 1:1.

All reaction products obtained were easily

separated from impurities and obtained with a purity of 99.95%. The synthesized compounds are clear, dark yellow liquids, highly soluble in organic solvents and insoluble in water, stable when stored at room temperature.

2 - [(Prop - 2 - yn - 1 - yl)oxy] - 1 - (2, 4, 6 - trimethylphenyl)ethan - 1 - ol (1)

In an inert atmosphere of nitrogen, 0.97 g (0.015 g-mol) of zinc ground in the form of fine chips, a catalytic amount of HgCl₂, 0.63 g (6 mmol) of 3-(1-chloromethyl)prop-1-ene, and 0.754 g (5 mmol) are added to a round-bottomed flask. Then 2,4,6-trimethylbenzaldehyde, 10 ml anhydrous benzene, 5 ml anhydrous ethyl acetate, 1 ml hexamethylphosphorotriamide (HMPTA) are added. The reaction mixture is boiled for 4 hours, cooled, drained and separated from excess zinc, hydrolyzed with a 5% hydrochloric acid solution. The organic layer is separated from the aqueous layer and the reaction products are extracted twice with ethyl acetate. After drying the extract with anhydrous sodium sulfate, the solvent is distilled off and the product is distilled in vacuum. Thus, 0.62 g (64.1%) of substance 1 was isolated at bp. 96–98°C (1 mm Hg). IR spectrum, v, cm⁻¹: 3601, 3303, 3080, 3012, 2200, 1640, 1420, 1333, 1270, 1100, 985, 840, 770, 702. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.24 s (3H, CH₃), 2.44 s (6H, 2CH₃), 2.50 t (1H, ≡CH, 4J 2.4 Hz), 2.56 d.d. (1H, CH₂, J 16.6, 2.3 Hz), 3.04 d.d. (1H, CH, CH₂, J 16.5, 10.7 Hz), 3.45 br.s. (1H, OH), 3.82 d.d (1H, ≡CCH₂O, ²J 16.2 Hz, ⁴J 2.4 Hz), 4.04 d.d (1H,

 $= CCH_2O, 2J 16.2 Hz, {}^4J 2.4 Hz), 4.49 d.d (1H, CH, J 10.4, 6.5 Hz), 7.32-7.82 m (2H, Ar). {}^{13}C NMR spectrum (CDCl_3), <math>\delta_C$, ppm: 20.5, 20.6, 40.0, 56.12 (=C-CH_2O), 60.7, 67.5, 68.34 (=CH), 79.45 (=C-CH_2O), 130.2, 134.5, 136.2, 136.7. Found, %: C 77.07; H 8.27.C₁₄H₁₈O₂. Calculated, %: C 77.03; H 8.31.

1-(4-Methoxy-2,3,6-trimethylphenyl)-2-[(prop-2yn-1-yl)oxy]ethan-1-ol (2)

Obtained as compounds (1), starting from chloromethylpropargyl ether and 4-methoxy-2,3,6trimethylbenzene. Yield 62.5%, bp. 101-102°C (2 mm Hg). IR spectrum, v, cm⁻¹: 3602, 3300, 3080, 3010, 2202, 1640, 1420, 1333, 1270, 1100, 985, 840, 770, 701. Spectrum ¹H NMR (CDCl₃), δ , ppm: 2.14 s (3H, CH₃), 2.42 d (6H, 2CH₃, J 13.6 Hz), 2.50 t (1H, =CH, ⁴J 2.4 Hz), 2.58 d.d. (1H, CH, J 16.6, 3.3 Hz,), 3.08 d.d. (1H, CH, J 16.6, 10.6 Hz), 3.41 br.s. (1H, OH), 3.78 s (3H, CH₃O), 3.81 d.d (1H, =CCH₂O, ${}^{2}J$ 16.2 Hz, ${}^{4}J$ 2.4 Hz), 4.05 d.d (1H, \equiv CCH₂O, ²J 16.2 Hz, ⁴J 2.4 Hz), 4.52 d.d (1H, CH, J 10.4, 6.5 Hz), 5.63 d (1H, CH, J 10.4 Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 14.1, 16.5, 21.2, 40.4, 55.4, 56.12 ($\equiv C - CH_2O$), 60.6, 67.4, 68.32 (≡CH), 79.23 (≡*C*−CH₂O), 110.7, 123.9, 129.6, 133.7, 136.6, 156.2. Found, %: C 77.51; H 8.64. C₁₅H₂₀O₂. Calculated, %: C 77.55; H 8.68.

1-(2,6-Dimethylphenyl)-2-[(prop-2-yn-1yl)oxy]ethan-1-ol (3)

Obtained as compounds (1), starting from chloromethylpropargyl ether 2,6and dimethylbenzene. Yield 63.9%, bp. 96-98°C (2 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3301, 3081, 3010, 2200, 1640, 1423, 1330, 1270, 1102, 985, 840, 770, 700. Spectrum ¹H NMR (CDCl₃), δ, ppm: 2.47 (3H, CH₃), 2.48 d.d. (1H, J 16.8, 2.58 Hz), 2.51 t (1H, ≡CH, 4 J 2.4 Hz), 2.98 s (1H, CH), 3.07 d.d., (1H, CH, J 16.5, 10.7 Hz), 3.45 br.s. (1H, OH), 3.84 d.d (1H, =CCH₂O, ²J 16.2 Hz, ⁴J 2.4 Hz), 4.06 d.d (1H, ≡CCH₂O, 2 J 16.2 Hz, ⁴J 2.4 Hz), 4.53 d.d (1H, CH, J 10.4, 6.5 Hz), 5.65 d (1H, CH, J 10.6 Hz), 7.01 d (2H, CH₂, J 7.3 Hz), 7.11-7.05 m (1H, Ar). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 20.6, 39.8, 56.12 (\equiv C-CH₂O), 60.7, 67.6, 68.31 (=CH), 79.47 (=C-CH₂O), 127.5, 129.4, 136.2, 137.5. Found, %: C 76.41; H 7.94. C₁₃H₁₆O₂. Calculated, %: C 76.44; H 7.90.

1-(2,4-Dimethylphenyl)-2-[(prop-2-yn-1-yl)oxy]ethan-1-ol (4)

Obtained as compounds (1), starting from chloromethylpropargyl ether and 2,4-dimethylbenzene. Yield 66.2%, bp. $96-98^{\circ}C$ (2 mm Hg). IR spectrum, v, cm⁻¹: 3601, 3302, 3080, 3010, 2202, 1640, 1420, 1330, 1270, 1100, 985, 842,

770, 700. ¹H NMR spectrum (CDCl₃), δ, ppm.: 2.34 d (6H, 2CH₃, J 4.5 Hz), 2.50 t (1H, \equiv CH, ⁴J 2.4 Hz), 2.75–2.61 m (2H, CH₂), 3.41 br.s. (1H, OH), 3.83 d.d. (1H, \equiv CCH₂O, ²J 16.1 Hz, ⁴J 2.4 Hz), 4.05 d.d. (1H, \equiv CCH₂O, ²J 16.1 Hz, ⁴J 2.4 Hz), 4.52 d.d. (1H, CH, J 10.4, 6.5 Hz), 5.38–5.30 m (1H, CH), 7.06–7.41 m (2H, Ar). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 18.7, 20.9, 42.1, 56.12 (C–CH₂O), 60.6, 66.7, 68.34 (\equiv CH), 79.46 (\equiv C–CH₂O), 125.2, 126.9, 131.2, 134. 1, 137.1, 137.3. Found, %: C 76.51; H 7.88. C₁₃H₁₆O₂. Calculated, %: C 76.44; H 7.90.

2 - [(Prop - 2 - yn - 1 - yl)oxy] - 1 - (2, 3, 4 - trimethylphenyl)ethan - 1 - ol(5)

Obtained as compounds (1), starting from chloromethylpropargyl ether and 2,3,6trimethylbenzene. Yield 69.3%, bp. 104-106°C (2 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3301, 3080, 3010, 2200, 1640, 1420, 1330, 1270, 1100, 985, 840, 770, 700. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.25 s (3H, CH₃), 2.32 s (3H, CH₃), 2.51 t (1H, ≡CH, ⁴J 2.4 Hz), 2.74–2.65 m (2H, CH₂), 3.47 br.s. (1H, OH), 3.84 d.d. (1H, \equiv CCH₂O, ²J 16.2 Hz, ${}^{4}J$ 2.4 Hz), 4.06 d.d. (1H, \equiv CCH₂O, ${}^{2}J$ 16.2 Hz, ⁴J 2.4 Hz), 4.51 d.d. (1H, CH, J 10.4, 6.5 Hz), 5.45 d.d. (1H, CH, J 8.2, 4.5 Hz), 7.18-7.39 m (2H, Ar). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 14.4, 20.4, 42.2, 56.12 (=C-CH₂O), 60.7, 67.2, 68.34 (CH), 79.46 (\equiv C–CH₂O), 122.9, 125.6, 129.1, 132.7, 136.7, 140.3. Found, %: C 76.42; H 7.84. C₁₃H₁₆O₂. Calculated, %: C 76.44; H 7.90.

2 - [(Prop - 2 - en - 1 - yl)oxy] - 1 - (2, 4, 6 - trimethylphenyl)ethan - 1 - ol(6)

Obtained as compounds (1), starting from chloromethylallyl ether and 2,4,6-trimethylbenzene. Yield 69.1%, bp. 108-110°C (1 mm Hg). IR spectrum, v, cm⁻¹: 3601, 3080, 3010, 1640, 1420, 1330, 1270, 1102, 985, 840, 770, 702. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.25 s (3H, 2CH₃), 2.42 s (6H, 2CH₃), 3.45 br.s. (1H, OH), 2.54 d.d. (1H, CH, J 16.6, 2.3 Hz), 4.16 d.d. (1H, OCH2, J 12.15, 1.61, 1.23 Hz), 4.51 d.d. (1H, CH, J 10.4, 6.5 Hz), 4.62 d.d.d. (1H, OCH₂, J 12.15, 5.34 Hz), 5.16 d.d.d. $(1H, H_2C=, J 9.15, 1.57, 1.23 Hz), 5.32 d.d.d. (1H, 1)$ H₂C=, J 17.21, 1.57, 1.61 Hz), 5.62 d.d. (1H, CH, J 10.6, 2.1 Hz), 5.84 d.d.d. (1H, OCH=, J 17.21, 9.15, 5.34 Hz), 7.12-7.46 m (2H, Ar). ¹³C NMR spectrum (CDCl₃), δ_c, ppm: 20.6, 40.0, 60.8, 67.4, 72.32 (=C-<u>C</u>H₂O), 117.63 (H₂C=), 134.63 (-HC=), 136.1, 136.8. Found, %: C 77.61; H 8.63. C₁₅H₂₀O₂. Calculated, %: C 77.55; H 8.68.

1-(4-Methoxy-2,3,6-trimethylphenyl)-2-[(prop-2-en-1-yl)oxy]ethan-1-ol (7)

Obtained as compounds (1), starting from

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chloromethylallyl ether and 2,3,6-trimethylbenzene. Yield 60.4%, bp. 112-114°C (1 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3081, 3010, 1641, 1420, 1330, 1270, 1100, 983, 840, 770, 702. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.12 s (3H, CH₃), 2.42 d (6H, 2CH₃, J 13.6 Hz), 2.57 d.d. (1H, CH, J 16.6, 3.3 Hz), 3.10 d.d. (1H, CH, J 16.6, 10.6 Hz), 3.44 br.s. (1H, OH), 4.18 d.d. (1H, OCH₂, J 12.15, 1.61, 1.23 Hz), 4.51 d.d. (1H, CH, J 10.4, 6.5 Hz), 4.62 d.d. (1H, OCH₂, J 12.15, 5.34 Hz), 5.16 d.d.d. $(1H, H_2C=, J 9.15, 1.57, 1.23 Hz), 5.32 d.d.d. (1H, 1)$ H₂C=, J 17.21, 1.57, 1.61 Hz), 5.64 d (1H, CH, J 10.4 Hz), 5.84 d.d.d. (1H, OCH=, J 17.21, 9.15, 5.34 Hz), 6.59 s (1H, Ar). ¹³C NMR spectrum $(CDCl_3), \delta_C, ppm: 14.1, 16.7, 21.1, 55.3, 60.7, 67.5,$ $72.33 (=C-\underline{CH}_{2}O), 117.64 (H_{2}C=), 134.63 (-HC=),$ 136.6, 156.2. Found, %: C 73.20; H 8.42. C₁₆H₂₂O₃. Calculated, %: C 73.25; H 8.45.

1-(2,6-Dimethylphenyl)-2-[(prop-2-en-1yl)oxy]ethan-1-ol (8)

Obtained as compounds (1), starting from chloromethylallyl ether and 2,6-dimethylbenzene. Yield 69.4%, bp. 113-115°C (1 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3081, 3010, 1640, 1420, 1330, 1270, 1100, 985, 840, 770, 702. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.46 s (6H, 2CH₃), 3.07 d.d. (1H, CH, J 16.5, 10.7 Hz), 3.41 us.s. (1H, OH), 4.16 d.d. (1H, OCH₂, J 12.15, 1.61, 1.23 Hz), 4.51 d.d. (1H, CH, J 10.4, 6.5 Hz), 4.63 d.d. (1H, OCH₂, J 12.15, 5.34 Hz), 5.16 d.d.d. (1H, H₂C=, J 9.15, 1.57, 1.23 Hz), 5.33 d.d.d. (1H, $H_2C=$, J 17.21, 1.57, 1.61 Hz), 5.65 d (1H, CH, J 10.6 Hz), 5.84 d.d.d. (1H, OCH=, J 17.21, 9.15, 5.34 Hz), 7.02 d (2H, Ar, J 7.3 Hz), 7.11-7.07 m (1H, Ar). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 20.7, 39.8, 60.8, 67.6, 67.6, 72.32 (=C-<u>C</u>H₂O), 117.67 (H₂C=), 134.63 (-HC=), 136.1, 137.4. Found, %: C 77.44; H 8.28. C₁₄H₁₈O₂. Calculated, %: C 77.03; H 8.31.

1-(2,4-Dimethylphenyl)-2-[(prop-2-en-1yl)oxy]ethan-1-ol (9)

Obtained as compounds (1), starting from chloromethylallyl ether and 2,4-dimethylbenzene. Yield 70.2%, bp. $114-116^{\circ}C$ (1 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3082, 3010, 1641, 1420, 1330, 1270, 1100, 985, 840, 770, 700. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.33 d (6H, 2CH₃, J 4.5 Hz), 2.76-2.62 m (2H, CH₂), 3.43 br.s. (1H, OH), 4.16 d.d. (1H, OCH₂, J 12.15, 1.61, 1.23 Hz), 4.51 d.d. (1H, CH, J 10.4, 6.5 Hz), 4.62 d.d. (1H, OCH₂, J 12.15, 5.34 Hz), 5.17 d.d.d. (1H, H₂C=, J 9.15, 1.57, 1.23 Hz), 5.31 d.d.d. (1H, H₂C=, J 17.21, 1.57, 1.61 Hz), 5.84 d.d.d. (1H, OCH=, J 17.21, 9.15, 5.34 Hz), 6.99 s (1H, Ar), 7.06 d (1H, Ar, J 7.9 Hz), 7.41 d (1H, Ar, J 7.8 Hz). ¹³C NMR

spectrum (CDCl₃), δ_{C} , ppm: 18.8, 20.8, 42.1, 60.6, 66.7, 72.33 (=C-<u>C</u>H₂O), 117.66 (H₂C=), 134.63 (-HC=), 134.9, 137.0, 137.4. Found, %: C 75.74; H 8.83. C₁₄H₁₈O₂. Calculated, %: C 75.69; H 8.80.

2 - [(Prop - 2 - en - 1 - yl)oxy] - 1 - (2, 3, 6 - trimethylphenyl)ethan - 1 - ol (10)

Obtained as compounds (1), starting from chloromethylallyl ether and 2,3,4-trimethylbenzene. Yield 89.2%, bp. 121-124°C (1 mm Hg). IR spectrum, v, cm⁻¹: 3603, 3080, 3010, 1640, 1420, 1330, 1270, 1100, 985, 840, 770, 700. Spectrum ¹H NMR (CDCl₃), δ, ppm: 2.26 s (3H, CH₃), 2.32 s (3H, CH₃), 2.65–2.75 m (2H, CH₂), 3.45 br.s. (1H, OH), 4.17 d.d. (1H, OCH₂, J 12.15, 1.61, 1.23 Hz), 4.53 d.d. (1H, CH, J 10.4, 6.5 Hz), 4.61 d.d. (1H, OCH₂, J 12.15, 5.34 Hz), 5.17 d.d.d. (1H, H₂C=, J 9.15, 1.57, 1.23 Hz), 5.31 d.d.d. (1H, H₂C= J 17.21, 1.57, 1.61 Hz), 5.44 d.d. (1H, CH, J 8.2, 4.5 Hz), 5.85 d.d.d. (1H, OCH=, J 17.21, 9.15, 5.34 Hz), 7.10–7.25 m (1H, Ar), 7.40 d (1H, Ar, J 7.5 Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 14.4, 20.5, 42.3, 60.8, 67.1, 72.32 (= $C-\underline{C}H_2O$), 117.67 (H₂C=), 122.9, 125.7, 129.2, 134.63 (-HC=), 132.8, 136.8, 140.2. Found, %: C 77.44; H 8.23. C₁₄H₁₈O₂. Calculated, %: C 77.03; H 8.31.

REFERENCES

1. Jiang B., Chen Z., Tang X. Highly enantioselective alkynylation of α -keto ester: an efficient method for constructing a chiral tertiary carbon center // Org. Lett. – 2002. – Vol.4. – No. 20. – P.3451-3453.

2. *Trost B., Weiss A.* The enantioselective addition of alkyne nucleophiles to carbonyl groups // Adv. Synth. Catal. – 2009. – Vol.351. – P.963-983.

3. *Anand N.K., Carreira E.M.* A simple, mild, catalytic, enantioselective addition of terminal acetylenes to aldehydes // J. Am. Chem. Soc. – 2001. – Vol.123. – No. 39. – P.9687-9688.

4. *A new* entry in catalytic alkynylation of aldehydes and ketones: dual activation of soft nucleophiles and hard electrophiles by an indium(III) catalyst / Takita R., Fukuta Y., Tsuji R., Ohshima T., Shibasaki M. // Org. Lett. - 2005. - Vol.7. - No. 7. - P.1363-1366.

5. *The gold(I)-catalyzed* cycloisomerization of 1,6-enynes to 1,4-dienes / Lee S.I., Kim S.M., Kim S.Y., Chung Y.K. // Synlett. - 2006. - Vol.14. - P.2256-2260.

6. *Gold(I)-catalyzed* alkoxyhalogenation of β-hydroxyα,α-difluoroynones / Schuler M., Silva F., Bobbio C., Tessier A., Gouverneur V. // Angew. Chem. Int. Ed. -2008. -Vol.47. - No. 41. - P.7927-7930. 7. *Talybov G.M.* Synthesis of alkyl 4-ethyn(en)yl-6methyl-1,3-dioxane-5-carboxylates // Russ. J. Org. Chem. – 2018. – Vol.54. – P.1739-1741.

8. *Propargyl* Claisen rearrangement: allene synthesis and beyond / Tejedor D., Mendez-Abt G., Cotos L., Garcia-Tellado F. // Chem. Soc. Rev. – 2013. – Vol.42. – P.458-471.

9. *Su C., Williard P.G.* Isomerization of allyl ethers initiated by lithium diisopropylamide // Org. Lett. – 2010. – Vol.12. – No. 23. – P.5378-5381.

10. Specific Z-selectivity in the oxidative isomerization of allyl ethers to generate geometrically defined Z-enol ethers using a cobalt(II)(salen) complex catalyst / Huang G., Ke M., Tao Y., Chen F. // J. Org. Chem. – 2020. – Vol.85. – No. 8. – P.5321-5329.

11. Asako S., Ilies L., Nakamura E. Iron-catalyzed orthoallylation of aromatic carboxamides with allyl ethers // J. Am. Chem. Soc. – 2013. – Vol.135. – No. 47. – P.17755-17757.

12. *Mechanism* of insertion polymerization of allyl ethers / Wimmer F.P., Caporaso L., Cavallo L., Mecking S., Falivene L. // Macromolecules. – 2018. – Vol.51. – No. 12. – P.4525-4531.

13. Nickel-catalyzed C-Br/C-H bis-phenylation of methyl 4-bromocrotonate: a stereoselective entry to methyl (E)-3,4diphenylbut-2-enoate / Funicello M., Chiummiento L., Lupattelli P., Tramutola F. // Synth. Commun. – 2015. – Vol.45. – P.1799-1806.

14. *Smith M.B., March J.* March's advanced organic chemistry: reactions, mechanisms, and structure. – John Wiley & Sons, Inc., 2007.

15. Silverstein R., Bassler G., Moril T. Spectroscopic identification of organic compounds. – M. Mir, 1977.

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СИНТЕЗ ПРОПАРГІЛ(АЛІЛ) АРИЛОКСИЕФІРІВ Г.М. Талибов

Запропоновано зручний метод синтезу пропаргіл (аліл) арилоксиефірів. Важливо зазначити, що синтезовані сполуки мають підвищену реакційну здатність і багаті на нуклеофільні центри. Експериментальні дані свідчать про те, що ці сполуки є стабільними і не піддаються гідролізу. Вихід цільових продуктів у обох випадках становить до 89,2%. Тривалість реакції та об'єм замісників в алкоксигрупі не мають суттєвого впливу на вихід цільових продуктів. Склад синтезованих сполук включає групи з сигналами від протонів алільної і пропаргільної груп. Реакції та чистота одержаних сполук контролювалися методом тонкошарової хроматографії. Вихід алільних ефірів вищий, ніж пропаргільних ефірів. Надано деякі фізикохімічні властивості синтезованих сполук. їх склад і структура підтверджені даними елементного аналізу. Всі синтезовані сполуки були ідентифіковані за допомогою ІЧ та ЯМР спектроскопії.

Ключові слова: пропаргіл(аліл) арилоксиефіри; α-глікольмоноефіри; хлорметилпропаргиловий ефір; хлорметилаліловий ефір, синтез.

SYNTHESIS OF PROPARGYL(ALLYL) ARYLOXYETHERS

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A convenient method for the synthesis of propargyl(allyl) aryloxyethers is proposed. It is notable that the synthesized compounds exhibit increased reactivity and are rich in nucleophilic centers. Experimental data have established that these compounds are stable and do not undergo hydrolysis. The yields of the target products in both cases are up to 89.2%. The reaction duration and the volume of substituents at the alkoxy group do not significantly affect the yield of the target products. The composition of the synthesized compounds includes groups of signals from protons of the allyl and propargyl groups. The reactions and purity of the obtained compounds were monitored by thin layer chromatography. The yields of allyl ethers are higher than those of propargyl ethers. Some physicochemical properties of the synthesized compounds are presented, and their composition and structure are confirmed by elemental analysis. All synthesized compounds have been identified by IR and NMR spectroscopy.

Keywords: propargyl(allyl) aryloxyethers; α -glycol monoethers; chloromethylpropargyl ether; chloromethylallyl ether; synthesis.

REFERENCES

1. Jiang B, Chen Z, Tang X. Highly enantioselective alkynylation of α -keto ester: an efficient method for constructing a chiral tertiary carbon center. *Org Lett.* 2002; 4(20): 3451-3453. doi: 10.1021/ol026544i.

2. Trost B, Weiss A. The enantioselective addition of alkyne nucleophiles to carbonyl groups. *Adv Synth Catal.* 2009; 351: 963-983. doi: 10.1002/adsc.200800776.

3. Anand NK, Carreira EM. A simple, mild, catalytic, enantioselective addition of terminal acetylenes to aldehydes. *J Am Chem Soc.* 2001; 123(39): 9687-9688. doi: 10.1021/ja016378u.

4. Takita R, Fukuta Y, Tsuji R, Ohshima T, Shibasaki M. A new entry in catalytic alkynylation of aldehydes and ketones: dual activation of soft nucleophiles and hard electrophiles by an indium(III) catalyst. *Org Lett.* 2005; 7(7): 1363-1366. doi: 10.1021/ol050069h.

5. Lee SI, Kim SM, Kim SY, Chung YK. The gold(I)catalyzed cycloisomerization of 1,6-enynes to 1,4-dienes. *Synlett.* 2006; 14: 2256-2260. doi: 10.1055/s-2006-949629.

6. Schuler M, Silva F, Bobbio C, Tessier A, Gouverneur V. Gold(I)-catalyzed alkoxyhalogenation of β -hydroxy- α , α -difluoroynones. *Angew Chem Int Ed.* 2008; 47(41): 7927-7930. doi: 10.1002/anie.200802162.

7. Talybov GM. Synthesis of alkyl 4-ethyn(en)yl-6methyl-1,3-dioxane-5-carboxylates. *Russ J Org Chem.* 2018; 54: 1739-1741. doi: 10.1134/S1070428018110210.

8. Tejedor D, Mendez-Abt G, Cotos L, Garcia-Tellado F. Propargyl Claisen rearrangement: allene synthesis and beyond. *Chem Soc Rev.* 2013; 42: 458-471. doi: 10.1039/C2CS35311C.

9. Su C, Williard PG. Isomerization of allyl ethers initiated by lithium diisopropylamide. *Org Lett.* 2010; 12(23): 5378-5381. doi: 10.1021/ol102029u.

10. Huang G, Ke M, Tao Y, Chen F. Specific Z-selectivity in the oxidative isomerization of allyl ethers to generate geometrically defined Z-enol ethers using a cobalt(II)(salen) complex catalyst. *J Org Chem.* 2020; 85(8): 5321-5329. doi: 10.1021/acs.joc.0c00004.

11. Asako S, Ilies L, Nakamura E. Iron-catalyzed orthoallylation of aromatic carboxamides with allyl ethers. *J Am Chem Soc.* 2013; 135(47): 17755-17757. doi: 10.1021/ja4106368.

12. Wimmer FP, Caporaso L, Cavallo L, Mecking S, Falivene L. Mechanism of insertion polymerization of allyl ethers. *Macromolecules*. 2018; 51(12): 4525-4531. doi: 10.1021/acs.macromol.8b00783.

13. Funicello M, Chiummiento L, Lupattelli P, Tramutola F. Nickel-catalyzed C-Br/C-H bis-phenylation of methyl 4-bromocrotonate: a stereoselective entry to methyl (E)-3,4-diphenylbut-2-enoate. *Synth Commun.* 2015; 45: 1799-1806. doi: 10.1080/00397911.2015.1049274.

14. Smith MB, March J. March's advanced organic chemistry: reactions, mechanisms, and structure. John Wiley & Sons, Inc.; 2007. doi: 10.1002/0470084960.

15. Silverstein R, Bassler G, Moril T. Spectroscopic identification of organic compounds. Moscow: Mir; 1977.