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SHORT COMMUNICATIONS

New Synthesis of 1,2-Diol Monopropargyl Ethers

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Abstract—1,2-Diol monopropargyl ethers have been synthesized by reactions of chloromethyl propargyl ether with benzaldehyde, acetophenone, and cyclopentanone in the presence of zinc and mercury(II) chloride.

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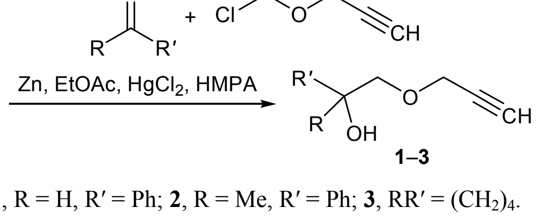
Condensation of carbonyl compounds with α-halocarboxylic acid esters in the presence of zinc with formation of β-hydroxy esters is known as Reformatsky reaction [1]. For more than 120 years, these reactions have been used to synthesize various organic compounds containing a hydroxy group [2–5]. Herein, I report for the first time Reformatsky reaction with α-halo ethers. Acetylenic alcohols possess a high synthetic potential due to the presence in their molecules of reactive terminal triple bond (C≡CH) and hydroxy group and are widely used for building up carbon–carbon bonds, in particular in the synthesis of heterocyclic compounds [6–12].

Improvement of methods for the synthesis of propargyl ethers, especially of their derivatives containing a hydroxy group, study of their chemical properties, and extension of their application scope have now become an important part of research in organic synthesis. Structural analogs of such compounds are used as antimicrobial additives [13, 14], metal corrosion inhibitors [15], modifiers for phenol–formaldehyde oligomers, components of adhesives, and protective polymer coatings [16, 17]. Thus, introduction of additional reactive groups (such as OH) into propargyl ether molecules extends their synthetic potential and improves their practically useful properties.



1–3

1, R = H, R′ = Ph; **2**, R = Me, R′ = Ph; **3**, RR′ = $(CH_2)_4$.

The structure of alcohols **1**–**3** was confirmed by spectral data. In the ^{1}H NMR spectra of **1**–**3**, the OH proton resonated at δ 3.45–3.47 ppm, and their IR spectra contained absorption bands in the region 3598–3603 cm^{-1}, which are typical of O–H stretching vibrations [18–20]. The reactions were carried out in a nitrogen atmosphere to avoid hydrolysis of the initial α-halo ether.

2-[(Prop-2-yn-1-yl)oxy]-1-phenylethan-1-ol (1). A mixture of 1.0 g (15 mmol) of fine zinc turnings, a catalytic amount of mercury(II) chloride, 0.6 g (6 mmol) of chloromethyl propargyl ether, 0.5 g (5 mmol) of benzaldehyde, 10 mL of anhydrous benzene, 5 mL of anhydrous ethyl acetate, and 1 mL of HMPA was refluxed for 4 h under nitrogen. The mixture was cooled, the solution was separated by decanting and treated with 15 mL of 5% aqueous HCl, and the mixture was stirred for 1 h at room temperature. The organic phase was separated, the aqueous phase was extracted with ethyl acetate (2×25 mL), the extracts were combined with the organic phase and dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was distilled under reduced pressure. Yield 1.19 g (68%), bp 89–90°C (1 mm), d_4^{20} = 1.0304, n_D^{20} = 1.5326, MR_D 53.04, calcd. 53.66. IR spectrum, ν, cm^{-1}: 3603 (O–H), 3287, 3085, 3065, 3030, 2110 (C≡C), 1600, 1490, 1100 (C–O–C), 985, 770 (Ph), 700. ^{1}H NMR spectrum, δ, ppm: 2.55 t (1H, ≡CH, ^4J = 2 Hz), 3.45 br.s (1H, OH), 3.96 d.d (2H, CH_2O, J = 14.2, 7.2 Hz), 4.11 d (2H, OCH_2C≡, ^4J = 2 Hz), 4.84 d (1H, CHO, J = 14.2 Hz), 7.15–7.55 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 57 (≡CCH_2O), 68 (≡CH), 73 (≡**C**CH_2O), 94.2 (COH), 124.0 (C_{arom}), 126.8 (2C, C_{arom}), 126.9 (2C, C_{arom}), 131.9 (C_{arom}). Found, %: C 75.94; H 5.39. $C_{11}H_{12}O_2$. Calculated, %: C 74.98; H 6.86.

Compounds **2** and **3** were synthesized in a similar way.

1-[(Prop-2-yn-1-yl)oxy]-2-phenylpropan-2-ol (2). Yield 62%, bp 101–102°C (2 mm), d_4^{20} = 1.0251, n_D^{20} = 1.5384, MR_D = 58.04, calcd. 53.31. IR spectrum, ν, cm^{-1}: 3598 (O–H), 3287, 2110 (C≡C), 3085, 3065, 3030, 1600, 1490, 1100 (C–O–C), 985, 700, 770 (Ph). ^{1}H NMR spectrum, δ, ppm: 1.02 s (3H, CH_3), 2.65 t (1H, ≡CH, ^4J = 2 Hz), 3.46 br.s (1H, OH), 3.65 s (2H, CH_2O), 4.25 d (2H, $OCH_2C\equiv$, ^4J = 2 Hz), 7.25–7.75 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 23.1 (CH_3), 56 ($\equiv C\mathbf{C}H_2O$), 69 (≡CH), 75 ($\equiv\mathbf{C}CH_2O$), 80 (OCH_2), 93.2 (COH), 126.0 (C_{arom}), 126.8 (2C, C_{arom}), 126.9 (2C, C_{arom}), 129.9 (C_{arom}). Found, %: C 75.94; H 7.39. $C_{12}H_{14}O_2$. Calculated, %: C 75.76; H 7.42.

1-{[(Prop-2-yn-1-yl)oxy]methyl}cyclopentan-1-ol (3). Yield 67%, bp 101–102°C (2 mm), d_4^{20} = 1.0621, n_D^{20} = 1.4965, MR_D = 42.42, calcd. 42.96. IR spectrum, ν, cm^{-1}: 3605 (O–H), 3289, 3082, 3065, 3031, 2100 (C≡C), 1604, 1490, 1100 (C–O–C), 985, 700, 770 (Ph). ^{1}H NMR spectrum, δ, ppm: 1.15–1.23 m [8H, $(CH_2)_4$], 2.65 t (1H, ≡CH, ^4J = 2 Hz), 3.44 s (2H, CH_2O), 3.47 br.s (1H, OH), 4.15 d (2H, $OCH_2C\equiv$, ^4J = 2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24 (2C, CH_2), 32 (2C, CH_2), 56 ($\equiv CCH_2O$), 69 (≡CH), 75 ($\equiv\mathbf{C}CH_2O$), 80 (OCH_2), 96.2 (COH). Found, %: C 70.24; H 9.49. $C_9H_{14}O_2$. Calculated, %: C 70.1; H 9.15.

The IR spectra of **1**–**3** were recorded on a Specord 75 IR spectrometer from solutions in carbon tetrachloride. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker SF-300 instrument at 300.13 and 75 MHz, respectively, using $CDCl_3$ as solvent and hexamethyldisiloxane as internal standard.

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