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SHORT COMMUNICATIONS

Synthesis of Glycidyl Propargyl Ether

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Abstract—Glycidyl propargyl ether was prepared in 80% yield from propargyl alcohol and epichlorohydrin in a superbasic suspension NaOH–DMSO.

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Glycidyl propargyl ether **1** {2-[(prop-2-ynyloxy)-methyl]oxirane} is a highly reactive bifunctional monomer, semiproduct, and building block for multipurpose organic synthesis, including synthesis of functional and biopolymers, new types of epoxy resins, and also innovation products of small-scale chemical industry [1–21].

Among its preparation procedures [1, 14–21] the most simple and available is the reaction of propargyl alcohol with epichlorohydrin in the presence of bases. However, the known examples of this reaction are characterized either by the moderate yields of the target product (51–63%), or by certain experimental difficulties (the reaction has been performed in one or two stages, varying solvents, bases, catalysts, reagents ratio, temperature, reaction time, and other parameters), or by both disadvantages [1, 18–21].

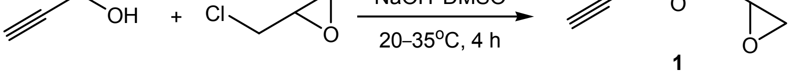
In extension of our systematic research on the application of superbasic systems in the organic synthesis [22–24] we developed conditions for preparation of ether **1** quickly and in a high yield.

The reaction of propargyl alcohol with epichlorohydrin in a superbasic suspension NaOH–DMSO (20–35°C, 4 h) led to the formation of glycidyl propargyl ether **1** in 80% yield at the molar ratio of the reagents 1.0 : 2.0 : 2.4. The decreased quantity of epichlorohydrin and NaOH results in a considerably decreased yield of ether **1** (Scheme 1).

The developed method makes more accessible this technically valuable polyfunctional monomer.

2-[(Prop-2-ynyloxy)methyl]oxirane (glycidyl propargyl ether) (1). To a mixture of 24.00 g (0.60 mol) NaOH and 100 mL of DMSO was added at stirring dropwise within 5 min 14.02 g (0.25 mol) of propargyl alcohol. The temperature of the mixture increased to 35°C. The reaction mixture was stirred for 30 min and within 20 min 46.26 g (0.50 mol) of epichlorohydrin was added dropwise maintaining the temperature at 25–30°C. After the end of epichlorohydrin addition, the reaction mixture was stirred for 3 h at room temperature, and afterwards 150 mL of water was added. The organic layer was separated, the water layer was extracted with ethyl ether (5 × 30 mL). The combined organic solutions were washed with water (4 × 30 mL) and dried with $MgSO_4$. The solvent was removed at a reduced pressure, the residue was distilled. Yield 22.4 g (80%), colorless mobile liquid, bp ~78°C (22 mmHg), n_D^{24} 1.4472. IR spectrum (thin film), ν, cm^{-1}: 3279, 3059, 3001, 2909, 2865, 2117, 1447, 1354, 1258, 1154, 1097, 1019, 978, 946, 918, 896, 851, 803, 760, 675, 593, 520, 464. ^1H NMR spectrum, δ, ppm: 2.44 t (1H, ≡CH, ^4J 2.4 Hz), 2.63 d.d (1H, OCH_2, cycle, ^2J 4.9, ^3J 2.6 Hz), 2.80 t (1H, OCH_2, cycle, $^2J = {}^3J =$

Scheme 1.



1

4.9 Hz), 3.16 d.d.d.d (1H, $\mathrm{OCH_2C\underline{H}}$, ^3J 5.9, ^3J 4.9, ^3J 3.1, ^3J 2.6 Hz), 3.48 d.d (1H, $\mathrm{OC\underline{H}_2CH}$, ^2J 11.4, ^3J 5.9 Hz), 3.81 d.d (1H, $\mathrm{OC\underline{H}_2CH}$, ^2J 11.4, ^3J 3.8 Hz), 4.19 d, 4.22 d (2H^{AB}, $\mathrm{OCH_2C{\equiv}}$, ^2J 15.6, ^4J 2.4 Hz). ^{13}C NMR spectrum, δ, ppm: 44.00 ($\mathrm{OCH_2}$, cycle), 50.24 ($\mathrm{OCH_2\underline{C}H}$), 58.20 ($\mathrm{O\underline{C}H_2C{\equiv}}$), 70.15 ($\mathrm{O\underline{C}H_2CH}$), 74.67 ($\mathrm{HC{\equiv}}$), 79.15 ($\mathrm{C{\equiv}}$). Signals assignment in the ^{13}C NMR spectrum was done with the help of 2D correlation HSQC. Found, %: C 64.41; H 7.10. $C_6H_8O_2$. Calculated, %: C 64.27; H 7.19.

NMR spectra were registered on a spectrometer Bruker DPX-400 [400.13 (^{1}H) and 100.62 (^{13}C) MHz]; heteronuclear correlation experiment ^{1}H–^{13}C HSQC was carried out on an instrument Bruker AV-400 in $CDCl_3$; internal references HMDS (δ_H 0.05 ppm), $CDCl_3$ (δ_C 77.00 ppm). IR spectrum was recorded on a spectrophotometer Varian 3100 FT-IR. All reagents and solvents used in the study were commercial products.

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