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LETTERS TO THE EDITOR

Synthesis of Glycidyl Ethers on the Basis of β-Dihydroxy Derivatives of Ferrocene

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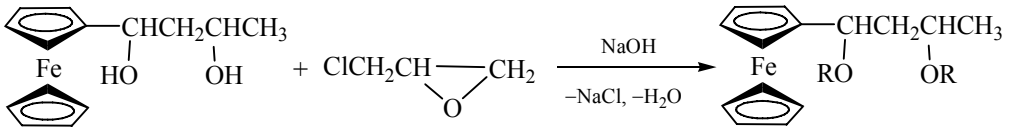
Successful application of the ferrocene derivatives as polymer modifiers as well as initiators and rubber cure activators call for a search for new compounds with several active functional groups. Introduction of substituents containing the epoxy group in the side chain of the ferrocene derivatives, which should expand the range of their practical use, is of great interest [1].

In this work, we have shown the possibility of preparation of the glycidyl ethers on the basis of β-dihydroxy derivatives of ferrocene. As starting ferrocene compounds we have used 1-ferrocenylbutane-1,3-diol and 1,1'-ferrocenediylbutane-1,3-diol. The synthesis was performed by the known procedure [2, 3]. The reaction of 1-ferrocenylbutane-1,3-diol with epichlorohydrin in the presence of NaOH at 60–70ºC for 3 h affords diglycidyl ether (**I**), the product of substitution of the two hydroxy groups, in quantitative yield (Scheme 1).

The reaction of 1-ferrocenylbutane-1,3-diol with epichlorohydrin in the presence of NaOH at 60–70ºC for 6 h affords tetraglycidyl ether (**II**), the product of etherification of the four hydroxy groups (Scheme 2).

1-[1,3-Di(glycidyloxy)butyl]ferrocene (I). 2 g (7 mmol) of 1-ferrocenylbutane-1,3-diol was dissolved in 20 mL (0.25 mol) of epichlorohydrin, 4 mL

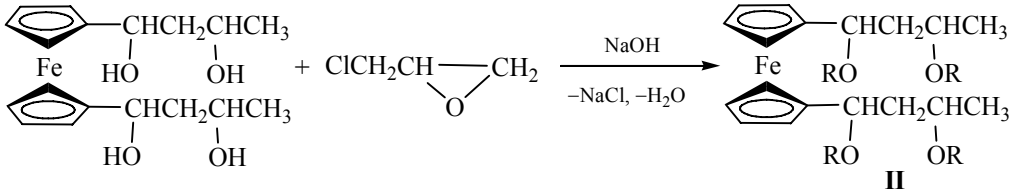
Scheme 1.



I

R = $CH_2CH(O)CH_2$.

Scheme 2.



II

R = $CH_2CH(O)CH_2$.

(0.05 mol) of 50% aqueous NaOH was added, and the mixture was heated for 3 h at 60°C. After completion of the reaction the mixture was evaporated, the residue was extracted with acetone. The product was purified by column chromatography on silica gel, eluent hexane. Yield 1.51 g (54%), yellow-orange oil. IR spectrum, ν, cm^{-1}: 3047, 2920, 1353, 1230, 1120, 1013, 890, 830, 760. ^1H NMR spectrum, δ, ppm: 4.10–4.40 m (9H, Fc), 3.30–3.80 m (4H, 2OCH, OCH_2), 2.50–3.10 m (8H, OCH_2 + $CHCH_2^{epoxy}$), 1.50–1.70 m (2H, $C\underline{CH_2}C$), 1.15–1.40 m (3H, CH_3). Found, %: C, 61.50; H, 6.64. Calculated, %: C, 62.18; H, 6.74.

1,1'-Di[1-(1,3-diglycidyloxybutyl)]ferrocene (II) was prepared similarly from 2 g (6 mmol) of 1,1'-ferrocenediyldibutane-1,3-diol, 20 mL of epichlorohydrin (0.25 mol), and 8 mL (0.1 mol) of 50% aqueous NaOH. Reaction time 6 h. Yield 1.42 g (44%), dark-red oil. IR spectrum, ν, cm^{-1}: 3080, 2900, 1450, 1370, 1270, 1240, 940, 830, 740. ^1H NMR spectrum, δ, ppm: 4.10–4.40 m (8H, Fc), 3.60–3.80 m (4H, OCH), 3.30–3.60 m (4H, OCH_2), 2.70–3.25 m (8H, OCH_2, CH^{epoxy}), 2.30–2.60 m (8H, CH_2^{epoxy}), 1.35–1.65 m (4H, $CH\underline{CH_2}CH$), 1.10–1.25 m (6H, CH_3). Found, %: C, 61.03; H, 7.31. Calculated, %: C 61.43; H, 7.16.

The reaction progress was monitored and the purity of the products was checked by TLC on the Silufol plates, eluent acetone–hexane, 1 : 1, development in iodine vapor. For column chromatography, Silicagel L 100/200 (Chemapol) was used. IR spectra were recorded on a Specord 75IR spectrophotometer in the IR range 4000–400 cm^{-1} as films on KBr plates. ^1H NMR spectra were registered on a Bruker Avance III instrument (600 MHz), in $CDCl_3$, internal reference TMS. Elemental analysis was performed on a Vario EL III CHN analyzer.

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