Scientific article
UDC 547.514.721
DOI: 10.52957/2782-1900-2025-6-3-163-166

SYNTHESIS OF SIMPLE ETHERS BASED ON B-DIHYDROXY FERROCENE DERIVATIVES

N.V. Andrievskaya[1], B.V. Poliakov[1], E.S. Alekseeva[1], V.V. Vlasov[2]

Natalia Vladimirovna Andrievskaya, Candidate of Chemical Sciences, Associate Professor; **Boris Vladimirovich Polyakov**, Candidate of Chemical Sciences, Associate Professor**;** **Elizaveta Sergeevna Alekseeva**, Student; **Valery Vladimirovich Vlasov**, Candidate of Technical Sciences, Associate Professor
[1]Reshetnev Siberian State University of Science and Technology, 660037, Russia, Krasnoyarsk region, Krasnoyarsk, 31, Prosp. im. gazety "Krasnoyarskii rabochii"; *andriyevskayanv@sibsau.ru*
[2]Yaroslavl State Technical University, 150023, Russia, Yaroslavl, 88 Moskovsky pr.; *vlasovvv@ystu.ru*

Keywords: *ferrocene derivatives, 1-ferrocenyl-1,3-butanediol, aliphatic alcohols, sulfuric acid*

Abstract. *This paper demonstrates the feasibility of synthesizing simple ethers based on β-dihydroxy ferrocene derivatives. 1-Ferrocenyl-1,3-butanediol was used as the starting compound. The structures of the obtained compounds were confirmed by IR and ^{1}H NMR spectroscopy, as well as elemental analysis. The properties of the synthesized ferrocene derivatives were investigated.*

For citation:
Andrievskaya N. V., Poliakov B. V., Alekseeva E. S., Vlasov V. V. Synthesis of simple ethers based on β-dihydroxy ferrocene derivatives // From Chemistry towards Technology Step-by-Step. 2025. Vol. 6, Iss. 3. P. 163-166. URL: https://chemintech.ru/en/nauka/issue/6423/view

Introduction

Ferrocene and its derivatives have found widespread application as modifiers and stabilizers for polymers, initiators, and activators for the vulcanization of rubber compounds, absorbers of various types of radiation including cosmic radiation. They are also implemented as regulators of combustion processes, polymer composites, and highly effective non-toxic pharmaceutical substances. Ferrocene compounds are used to control the combustion of solid rocket propellants; liquid ferrocene derivatives also act as plasticizers.

The broad range of applications for ferrocene derivatives determines the development of compounds with multiple active functional groups. Therefore, the introduction of substituents containing ether groups into the side chain of ferroceryl derivatives is of particular interest. It gives a lot of opportunities for exploring practical uses of these compounds in various fields [1-9]. The most promising and debated areas of application for ferrocene derivatives with ether, alkyl, and complex substituents are polymer composites and solid propellant systems exhibiting good compatibility with each other [7, 9].

Main body

1-Ferrocenyl-1,3-butanediol was used as the starting compound. This compound can replace a hydrogen atom with metal atoms; its hydroxyl groups can be replaced with a wide range of alkyl and aryl substituents. Furthermore, it can form both simple and complex esters. It provides the opportunities for obtaining a multitude of new compounds and expands the scope of application for ferrocene derivatives. The synthesis of the new substances was conducted according to a methodology similar to presented in the literature [11]. Since ferrocene derivatives are tended to degradation of the organometallic core in the presence of weak acids and strong oxidizing agents, concentrated sulfuric acid was used as an agent to form a stable acidic environment and prevent a metallocene core from oxidizing.

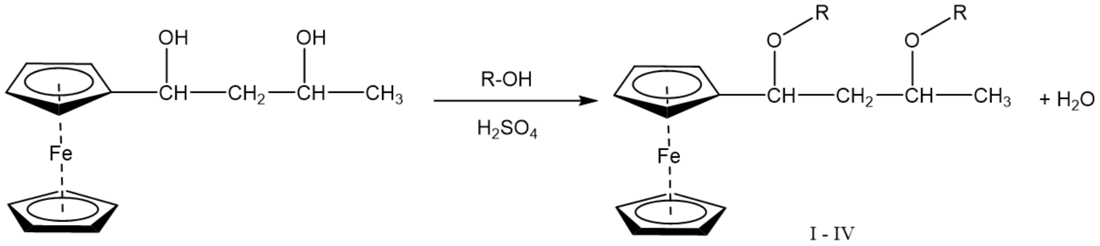
The presence of two hydroxyl groups in the side chain allows obtaining of ferrocene simple ethers via the reaction of 1-ferrocenyl-1,3-butanediol with aliphatic alcohols. The esters have a modifying effect on various oxidation-reduction processes and systems. The reaction between these compounds can proceed at both hydroxyl groups with the formation a mono-α- and γ-substituted product, and a di-α- and γ-substituted product.

To catalyze the process of simple ethers preparation, an acidic medium is required. Concentrated sulfuric acid was chosen as the catalyst.

Since the reaction can proceed at both hydroxyl groups, the formation of compounds at either the α- or γ-positions is possible. However, the hydroxyl group at the α-position of the ferrocenyl substituent is more sterically hindered compared to the γ-hydroxyl group. Therefore, the formation of 1-ferrocenyl-1-hydroxy-3-alkoxybutane becomes more probable. Furthermore, the γ-hydroxyl group exhibits greater reactivity due to the lesser inductive influence of the methyl substituent compared to the inductive effect exerted by the ferrocenyl moiety on the α-hydroxyl group.

Trace amounts of monosubstituted ferrocenyl alcohols, both α- and γ-substituted, were detected as byproducts of exhaustive substitution. Increasing the reaction time and temperature decreases the yield of the target product due to the cleavage of ether groups.

The reaction of 1-ferrocenyl-1,3-butanediol with aliphatic alcohols in the presence of sulfuric acid for 3 hours yields aliphatic ethers (I–IV), which are the products of the substitution of both hydroxyl groups, in quantitative yield (Scheme 1).



R = CH_3 (I), R = C_2H_5 (II), R = C_3H_9 (III), R = C_4H_9

Scheme 1. Synthesis of 1-ferrocenyl-1,3-butanediol esters

The reaction progress and purity of the obtained compounds were monitored by TLC on Silufol plates (Czechoslovakia) using toluene:ethyl acetate (1:1) as the eluent, with detection by exposure to metallic iodine vapors. For column chromatography, Silicagel L 100/200 (Chemapol) was used. IR spectra were recorded on a SPECORD 75IR spectrophotometer in the range of 4000–400 cm^{-1} as a film on KBr lenses. ^{1}H NMR spectra were acquired on a Bruker Avance III spectrometer (600 MHz) using TMS as an internal standard and $CDCl_3$ as the solvent. Elemental analysis was performed on a Vario EL III CHN analyzer. We determined melting temperatures in open capillaries on a PTP instrument (TU25-11-1144-76).

Conclusions

Aliphatic ethers of 1-ferrocenyl-1,3-alkoxybutanes have been synthesized. A series of simple ethers of 1-ferrocenyl-1,3-butanediol with linear aliphatic alcohols was obtained. The reaction with the aliphatic alcohol proceeds at both hydroxyl groups of 1-ferrocenyl-1,3-butanediol. The conditions for the reaction between 1-ferrocenyl-1,3-butanediol and aliphatic alcohols were determined. Increasing the size of the alkyl substituent in the aliphatic alcohol decreases its reactivity and the product yield.

Experimental part

1-Ferrocenyl-1,3-dimethoxybutane (I)

3.33 g (0.012 mol) of 1-ferrocenyl-1,3-butanediol was dissolved in 83.24 ml (2.6 mol) of methanol. With stirring, 21.44 ml (0.12 mol) of concentrated (96%) sulfuric acid was added. The reaction was conducted at 75 °C for 2 h. After the hold time, the mixture was poured into ice and neutralized with aqueous ammonia. The residue was extracted with toluene. The product was purified by column chromatography on silica gel using ethyl acetate as the eluent. Yield is 3 g (81.74 %). T_{melt} = 180 °C; black crystalline solid. IR-spectrum, cm^{-1} 2970, 1170, 1240, 1040, 1360, 1280, 1010, 870. Found, % C 62.9, H 6.9. Calculated, % C 63.6, H 7.3. NMR spectrum ^{1}H, δ, ppm: 4.10-4.30 m (9H, Fs), 3.30-3.48 m (8H, 2OCH, OCH_3), 2.50-3.86 m (8H, OCH_2), 1.80-1.86 m (2H, CH$\underline{CH_2}$CH), 1.18-1.24 m (3H, CH_3).

1-Ferrocenyl-1,3-diethoxybutane (II)

5 g (0.018 mol) of 1-ferrocenyl-1,3-butanediol was dissolved in 62.5 ml (1.36 mol) of ethanol. With stirring, 16.1 ml (0.089 mol) of concentrated (96%) sulfuric acid was added. The reaction was conducted at 85 °C for 3 h. After the hold time, the mixture was poured into ice and neutralized with aqueous ammonia. The residue was extracted with toluene. The product was purified by column chromatography on silica gel using ethyl acetate as the eluent. Yield is 4.1 g (68.3%). T_{melt} = 147 °C; black-brown crystalline solid. IR-spectrum, cm^{-1} 2900, 1080, 1140, 1290, 1330, 1285, 1100, 1020, 800. Found, % C 65.1, H 7.2. Calculated, % C 65.5, H 7.9. NMR spectrum ^{1}H, δ, ppm: 4.07-4.31 m (9H, Fc), 3.30-4.48 m (6H, 2OCH, OCH_2), 1.86 m (2H, CH$\underline{CH_2}$CH), 1.18-1.24 m (9H, CH_3).

1-ferrocenyl-1,3-dipropoxybutane (III)

5 g (0.018 mol) of 1-ferrocenyl-1,3-butanediol was dissolved in 62.5 ml (1.04 mol) of propyl alcohol. With stirring, 16.1 ml (0.089 mol) of concentrated (96%) sulfuric acid was added. The reaction was conducted at 85 °C for 3 h.

After the hold time, the mixture was poured into ice and neutralized with aqueous ammonia. The residue was extracted with toluene. The product was purified by column chromatography on silica gel using ethyl acetate as the eluent. Yield is 5.2 g (80%). T_{melt} = 154 °C;

black crystalline solid. IR-spectrum, cm^{-1} 2880, 1080, 1210, 1180, 1390, 1280, 1030, 1090, 780. Found, % C 66.4, H 8.1. Calculated, % C 67.04 H 8.38. NMR spectrum ^{1}H, δ, ppm: 4.10-4.30 m (9H, Fs), 3.30-4.48 m (6H, 2OCH, OCH_2), 1.86 m (2H, $CH\underline{CH_2}CH$), 0.99-1.50 m (13H, CH_2-CH_3, CH_3).

1-Ferrocenyl-1,3-dibutoxybutane (IV)

1.6 g (0.006 mol) of 1-ferrocenyl-1,3-butanediol was dissolved in 30 ml (0.4 mol) of n-butyl alcohol. With stirring and cooling, 7.2 ml (0.039 mol) of concentrated (96%) sulfuric acid was added. The reaction was conducted at 85 °C for 3 h. After the hold time, the mixture was poured into ice and neutralized with aqueous ammonia. The residue was extracted with *m*-xylene. The product was purified by column chromatography on silica gel using ethyl acetate as the eluent. Yield is 1.7 g (73.9%). T_{melt} = 125 °C; black crystalline solid. IR-spectrum, cm^{-1} 2940, 1070, 1150, 1290, 1390, 1200, 1100, 1000, 900. Found, % C 67.9, H 8.3. Calculated, % C 68.4 H 8.8. NMR spectrum ^{1}H, δ, ppm.: 4.05-4.31 m (9H, Fc), 3.30-3.48 m (6H, 2OCH, OCH_2), 0.96-1.44 m (17H, $2CH_2CH_2CH_3$, CH_3).

References

1. **Nesmeyanov A.N., Perevalova E.G., Tsiskaridze T.T.** *Izd. AN SSSR., Ser. khim.* 1966, 2209. (In Russian).
2. **Timker A.J., George M.H., Barrie J.A.** *J. Polym. Sci.: Polym. Chem. Ed.,* 1975, 13, 2005.
3. **Zhang H-y., Lei J., Chen Y-y., Lin L., Wu Q-a., Zang H-q.** Syntheses and characterization of the N,N'-bis(ferroceneylmethylene)etylenediamine Schiff base and its transition metal complexes. *Synth. React. Inorg. Met.-org. chem.* 2001, 31(6), 1053-1061. DOI: 10.1081/SIM-100105261.
4. **Denisov M.S., Pavlogradskaya L.V., Glushkov V.A.** Synthesis of biologically active substances with ferrocene and vanillin fragments (literature review). *Vestnik PGNIU. Khimiya,* 2017, 7(4), 429-457. DOI: 10.17072/2223-1838-2017-4-429-457 (In Russian).
5. **Potkin V.I., Dikusar E.A., Kletskov A.V., Petkevich S.K., Semenova E.A., Levkovskaya G.G., Zolotar R.M.** Synthesis of esters of metallocene alcohols and 4,5-dichloroisothiazole-3-carboxylic and 5-arylisoxazole-3-carboxylic acids. *ZhOKh*, 2016, 86(**2**), 310-316 (In Russian).
6. **Gurova D.A., Sorin E.S., Novikov G.F.** Photoinduced processes in the ferrocene+cyanate-ether system. *VMS. Seriya B*, 2022, 64(4), 304–310. DOI: 10.31857/S2308113922700115 (In Russian).
7. **Sinditsky V.P., Cherny A.N., Marchenkov D.A.** The mechanism of burnig catalysis by ferrocene derivatives. 2. Burning of fuels based on ammonium perchlorate with ferrocene derivatives. *FGV,* 2014, 50(2), 40-50 (In Russian).
8. **Zakharova O.V., Golounin A.V.** Iron-containing additives for automobile fuel. *Sovremennye naukoemkie tekhnologii*, 2010, (7), 172-174 (In Russian).
9. **Ushakov V.A., Nevzorov D.I., Kopytin A.V., Lalaian V.M.** Flammability and smoke-forming ability of polymer materials containing ferrocene derivatives. *Pozharovzryvoopasnost' veshchestv i materialov*, 2014, 23(7), 27-35 (In Russian).
10. **Minnahmetov T.Sh., Andrievskaya N.V., Polyakov B.V.** Production of glycidyl esters based on β-dihydroxyl derivatives of ferrocene. *ZhOKh*, 2015, 85(3), 525-526 (In Russian).
11. **Weigand K., Hilgetag G.** Experimental methods of organic chemistry. M.: Khimiya. 1968. 944 (In Russian).

Received 18.07.2025
Approved 21.08.2025
Accepted 16.09.2025