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Abstract

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FERROCENYLMETHYLLITHIUM

Earlier ([1]) we described the preparation of simple ethers of ferrocenylcarbinol from the iodomethylate of N,N-dimethylaminomethylferrocene. In the present work we have carried out the cleavage of the methyl ether of ferrocenylcarbinol with lithium and have used the ferrocenylmethyllithium thus obtained for the preparation of ferrocene derivatives. In addition, we found that simple ethers of ferrocenylcarbinol are readily obtained by heating ferrocenylcarbinol with the corresponding alcohols in the presence of acetic acid:

$$C_5H_5FeC_5H_4CH_2OH + ROH \xrightarrow{CH_3COOH} C_5H_5FeC_5H_4CH_2OR + H_2O.$$

In this way the methyl, ethyl, and benzyl ethers of ferrocenylcarbinol were obtained in yields of 73, 80, and 72%, respectively.

The ease of formation of simple ethers of ferrocenylcarbinol is explained by the stability of the ferrocenylmethylcarbonium ion ([2]).

The cleavage of the methyl ether of ferrocenylcarbinol by lithium was carried out by us in tetrahydrofuran. In this process ferrocenylmethyllithium is formed in high yield; we were unable to obtain it by other methods:

$$C_5H_5FeC_5H_4CH_2OCH_3 + 2\,Li \rightarrow C_5H_5FeC_5H_4CH_2Li + CH_3OLi.$$

The reaction conditions are analogous to those described by Gilman et al. ([3]) for the cleavage of simple benzyl ethers. The yield of ferrocenylmethyllithium is more than 80%, judging from the amount of methylferrocene formed on hydrolysis.

Ferrocenylmethyllithium reacts smoothly with trimethylchlorosilane, giving (ferrocenylmethyl)trimethylsilane in 68% yield:

$$C_5H_5FeC_5H_4CH_2Li + ClSi(CH_3)_3 \rightarrow C_5H_5FeC_5H_4CH_2Si(CH_3)_3 + LiCl.$$

When anhydrous ferric chloride acts on ferrocenylmethyllithium, radical coupling occurs and 1,2-diferrocenylethane is formed, identical with that obtained

in the condensation of ferrocene with formaldehyde in the presence of sulfuric acid ([4], [5]):

$$C_5H_5FeC_5H_4CH_2Li \xrightarrow{FeCl_3} C_5H_5FeC_5H_4CH_2CH_2C_5H_4FeC_5H_5.$$

Experimental Part

Methyl ether of ferrocenylcarbinol. To a solution of 3.24 g (0.015 mole) of ferrocenylcarbinol ([6]) in 90 ml of absolute methanol, 2.7 ml of glacial acetic acid was added. The solution was heated for 5 hours on a water bath, then cooled, and 100 ml of ether was added to it. The ether-alcohol solution was washed with water (2 portions of 300 ml), with 10% sodium carbonate solution, and again with water, and dried over $MgSO_4$. The solvent was distilled off, and the methyl ether of ferrocenylcarbinol was twice distilled in vacuo.

Yield 2.52 g (73% of theoretical). B.p. 106–107.5°/1.5 mm; n_D^{20} 1.6003. The constants agree with those described by us earlier [(1)].

Ethyl ether of ferrocenylcarbinol was obtained similarly to the methyl ether. The heating time was increased to 6 h. Yield 80% of theoretical. The constants agree with those described earlier [(1)]. B.p. 112–113.5°/2 mm; n_D^{20} 1.5855.

Benzyl ether of ferrocenylcarbinol was obtained analogously to the ethyl ether; purified chromatographically on Al_2O_3. Yield 73% of theoretical. Its m.p. and the m.p. of a mixed sample with the ether obtained earlier [(1)] were 88–89°.

Ferrocenylmethyllithium. *To a mixture of 0.7 g (0.1 g-atom) of lithium shavings* ***and 8 ml of absolute tetrahydrofuran, freshly distilled over Na,*** there was added, over the course of 45 min with stirring and cooling to −7, −5°, a solution of 1.15 g (0.005 mole) of the methyl ether of ferrocenylcarbinol in 7 ml of tetrahydrofuran. After approximately half of the ether solution had been added, the reaction mixture became slightly turbid and red dots appeared on the shiny surface of the lithium, indicating the start of the reaction. If the reaction did not begin upon addition of half of the ether, the temperature was raised for several minutes to 0°. After addition of all the ether, stirring was continued at −5° for 1 h. Then the dark-red solution of ferrocenylmethyllithium formed was, in some experiments, filtered under nitrogen from excess lithium.

Hydrolysis of ferrocenylmethyllithium. A solution of ferrocenylmethyllithium, obtained by the method described above from 2.3 g (0.01 mole) of the methyl ether of ferrocenylcarbinol and 1.4 g of lithium, was poured into a mixture of 10 g of ice and 3 g of NH_4Cl. Methylferrocene was extracted with ether. The ethereal solution was washed with water and dried with $CaCl_2$. After distillation of the solvent and recrystallization from methanol, 1.64 g of methylferrocene was obtained. Yield 82% of theoretical, calculated on the starting methyl ether of ferrocenylcarbinol. The m.p. of methylferrocene and the m.p. of a mixed sample of it with a sample obtained earlier [(7)] were 35–36°.

(Ferrocenylmethyl)trimethylsilane. To a solution of $C_5H_5FeC_5H_4CH_2Li$, obtained from 4.6 g (0.02 mole) of the methyl ether of ferrocenylcarbinol and 2.8 g of Li, there was added, with stirring over the course of 15 min, a solution of 4 ml (3.4 g; 0.03 mole) of trimethylchlorosilane in 8 ml of tetrahydrofuran; the temperature of the reaction mixture was −5—−3°. Stirring was continued for 10 min while cooling to 0°, 1 h at room temperature, and 1 h while heating to boiling. Then the reaction mixture was cooled and, after separation of excess lithium, poured into water (150 ml). (Ferrocenylmethyl)trimethylsilane was extracted with benzene. The benzene solution was washed several times with water and dried with anhydrous magnesium sulfate. After removal of the benzene, 4.4 g of a red-brown oily product was obtained, which was chromatographed on Al_2O_3. (Ferrocenylmethyl)trimethylsilane was eluted with petroleum ether and recrystallized twice from absolute CH_3OH. Yield 3.6 g (68.5% of theoretical). M.p. 46.5–47.5°.

	Found %:	C 61.79; 61.72;	H 7.35; 7.41
$C_{14}H_{20}FeSi$.	Calculated %:	C 61.76;	H 7.41.

Action of $FeCl_3$ on ferrocenylmethyllithium. To a solution of ferrocenylmethyllithium, obtained from 1.4 g (0.02 mole) of $C_5H_5FeC_5H_4 \cdot CH_2OCH_3$ and 1.4 g of lithium, while cooling to −30° and stirring, there was added over the course of 20 min a solution of 1.62 g (0.01 mole) of anhydrous $FeCl_3$ in 50 ml

* The preparation of ferrocenylmethyllithium and all reactions with it were carried out in an atmosphere of pure nitrogen.

** The quality of the lithium apparently plays a large role. Thus, with one of the lithium samples the reaction did not proceed.

*** Tetrahydrofuran was previously distilled over KOH and three times over metallic sodium.

abs. ether. The stirring was then continued for 1.5 hours at room temperature, and the mixture was poured through a fine copper mesh to separate pieces of lithium onto ice with NH_4Cl. The ether layer was separated. Conc. HCl and 2.5 g of $SnCl_2$ were added to the aqueous layer, after which it was extracted with benzene until the extracts were colorless. The ether and benzene solutions were combined, washed with water, with 10% sodium carbonate solution, and again with water, and dried over $CaCl_2$. The solvent was distilled off in vacuo, and 15 ml of petroleum ether was added to the residue. The precipitated 1,2-diferrocenylethane was filtered off, washed with petroleum ether, and recrystallized from ether. Weight 0.6 g. M.p. 196–197.5°. In a capillary sealed under vacuum, m.p. 200–200.5°.

Found, %: C 66.29; 66.40; H 5.62; 5.82; Fe 27.98; 27.88
$C_{22}H_{22}Fe$. Calculated, %: C 66.36; H 5.63; Fe 28.05

Literature data for 1,2-diferrocenylethane ([4]): m.p. 193–195°. After separation of the diferrocenylethane, the solution in petroleum ether was chromatographed on Al_2O_3. Petroleum ether eluted 0.7 g of methylferrocene; then a mixture of benzene with petroleum ether (2:1) eluted 0.08 g of diferrocenylethane, and benzene with ether eluted a small amount of ferrocenylcarbinol, m.p. 79–80°; a mixed sample with a specimen obtained from N,N-dimethylaminomethylferrocene methiodide ([6]) melted without depression. The total yield of 1,2-diferrocenylethane was 0.68 g (34% of theory).

The 1,2-diferrocenylethane obtained by us is identical with that formed in the condensation of ferrocene with formaldehyde ([4,5]) according to its IR spectrum; a mixed sample of the two specimens melts without depression (m.p. 196–197.5°).

New data on diferrocenylethanes obtained by the condensation of formaldehyde and benzaldehyde with ferrocene ([5]) and by the Friedel–Crafts reaction ([8]) are being submitted for publication simultaneously.

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named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.