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Abstract

Full Text

Chemistry

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SYNTHESIS OF METHYLFERROCENE

Recently, various mono- and dialkylferrocenes have been described, obtained by direct alkylation of ferrocene in the presence of aluminum chloride ($^{1—4}$) or by reduction of the corresponding ketones (^{5}) and acids (^{6}).

In the present work we have carried out the synthesis of methylferrocene by two routes: by reduction of the methyl ester of ferrocenecarboxylic acid with lithium aluminum hydride (yield 83%) and by reduction of the iodide of N,N-dimethylaminomethylferrocene with sodium amalgam (yield 94%). In the latter case, as a by-product of the reaction, a small amount of the simple ether of ferrocenylcarbinol is formed: $(C_5H_5FeC_5H_4CH_2)_2O$.

Experimental Part

Preparation of methylferrocene from the iodide of N,N-dimethylaminomethylferrocene*

A filtered solution of 1.2 g (0.0032 mole) of the iodide of N,N-dimethylaminomethylferrocene (^{7,8}) in 60 ml of water was added to a sodium amalgam cooled with ice water, prepared from 12 g of sodium and 12 ml of mercury. The reaction mixture was heated on a water bath for 8 hr at 90-100°. The dark-orange crystalline precipitate of methylferrocene that formed was filtered off and washed with water. Yield 0.6 g (94% of theoretical). The methylferrocene was recrystallized from petroleum ether (separates on cooling to −10°), m.p. 35.5-36.5°.

Found, %: C 66.26; 66.46; H 6.09; 6.11; Fe 27.80; 27.59
$C_{11}H_{12}Fe$. Calculated, %: C 66.03; H 6.04; Fe 27.91

From the mother liquors collected from several experiments, the simple ether of ferrocenylcarbinol $(C_5H_5FeC_5H_4CH_2)_2O$ was isolated chromatographically (on Al_2O_3) together with methylferrocene. Methylferrocene was eluted with petroleum ether, and the ferrocenylcarbinol ether with sulfuric ether or with a mixture of ether and benzene 1:4. M.p. 128-129.5° (from petroleum ether).

Found, %: C 64.21; 64.04; H 5.49; 5.45; Fe 26.92; 26.91
$C_{22}H_{22}OFe$. Calculated, %: C 63.81; H 5.35; Fe 26.98

Literature data (^{9}): m.p. 129-130°.

Decreasing the excess of sodium amalgam, although it lowers the yield of methylferrocene, makes it possible to reduce larger amounts of the iodide at once.

Thus, 16 g of the iodide of N,N-dimethylaminomethylferrocene were reduced with amalgam prepared from 46 g of sodium and 30 ml of mercury (heating for 12 hr). The methylferrocene was extracted with petroleum ether (twice, 80-100 ml each). After partial distillation of the solvent, the crystallized methylferrocene had m.p. 33-34°. Yield 6.1 g (75% of theoretical).

* Carried out jointly with Yu. A. Ustynyuk.

The residue after extraction of methylferrocene was dissolved in hot petroleum ether, from which methylferrocene (0.2 g), ferrocenylcarbinol simple ether (0.13 g), and ferrocenylcarbinol (0.15 g) were isolated chromatographically (on Al_2O_3).

The amount of ferrocenylcarbinol ether increases if the methyl iodide solution is added to warm amalgam.

Preparation of methylferrocene from the methyl ester of ferrocenecarboxylic acid. To an ethereal solution of lithium aluminum hydride, prepared from 1 g of lithium hydride and 8 g of aluminum bromide, 1.75 g (0.072 mole) of the methyl ester of ferrocenecarboxylic acid was added. The reaction mixture was vigorously stirred for 4 hours while being heated to boiling, and then decomposed with water and dilute hydrochloric acid. The aqueous layer contains ionic iron. The ethereal solution was washed with soda solution and water and dried over magnesium sulfate. The residue after distilling off the ether was dissolved in petroleum ether, and methylferrocene was isolated by chromatographic adsorption on alumina. Methylferrocene is readily eluted with petroleum ether. 1.2 g of methylferrocene was obtained. Yield 83%. M.p. 35.5-36.5°. A mixed sample with methylferrocene obtained from N_1N-dimethylaminomethylferrocene melted without depression (35.5-36.5°).

Found, %: C 66.28; 66.42; H 6.20; 6.22; Fe 27.46; 27.31
$C_{11}H_{12}Fe$. Calculated, %: C 66.03; H 6.04; Fe 27.91.

The infrared and ultraviolet spectra of methylferrocene obtained by the different methods are, respectively, identical*.

IR spectrum (in Vaseline oil): 810-820, 924, 1004, 1037, 1106, 1227, 1378, 1468, 1655 cm^{-1}. UV spectrum (in octane): λ_max (lg ϵ_max): 324 (1.716), 435 (1.921).

In another experiment, the reaction mixture described above was stirred for 1 hour at room temperature and gently boiled for 3 hours. Ferrocenylcarbinol was obtained in a yield of 77% of theory, and its simple ether, identical with that formed from N_1N-dimethylaminomethylferrocene, in a yield of 8%.

From ferrocenecarboxylic acid itself, methylferrocene was obtained in a yield of 20% of theory (the reduction conditions were the same as for the methyl ester of the acid).

In work devoted to the alkylation of ferrocene under Friedel-Crafts reaction conditions, one of us and N. S. Kochetkova (2) described methylferrocene with m.p.

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118–119°. The methylferrocene obtained in the present work by the two above-mentioned routes has m.p. 35.5–36.5°, and the data relating to this methylferrocene leave no doubt. The reasons for this contradiction will be clarified additionally.

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* The spectra were taken in the molecular spectroscopy laboratory of the Department of Organic Chemistry of Moscow State University.

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

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