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Abstract

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Synthesis of Alkylferrocenes by the Friedel-Crafts Reaction

We ([1]) were the first to describe the reaction of alkylation of ferrocene with alkyl halides in the presence of anhydrous aluminum chloride. An excess of the alkyl halide was used as the solvent.

In the present work we succeeded in carrying out the same reaction without resorting to an excess of alkyl halide, and thereby in increasing the yield of mono- and dialkyl derivatives of ferrocene. As solvent we used *n*-heptane or absolute petroleum ether (b.p. 60-80°).

By direct alkylation of ferrocene with alkyl halides (methyl chloride, isopropyl chloride) or with unsaturated hydrocarbons (ethylene), we obtained previously unknown alkylferrocenes: methylferrocene, dimethylferrocenes, isopropylferrocene, diisopropylferrocenes, and isomeric diethylferrocenes, both alkyl groups of which are located in one cyclopentadiene ring.

The isomeric alkylferrocenes were separated chromatographically on anhydrous alumina. In doing this we used an automatic flow refractometer PRA-25 of the system of I. V. Obreimov, V. I. Dianov-Klokov, and E. A. Shibalov ([2]).

Comparison of the IR spectra of the isomeric diethylferrocenes obtained by us (I and II) and of the diethylferrocene obtained by one of us and Vol' kenau by reduction of diacetylferrocene III ([4]) gave the following results. Diethylferrocene III, containing ethyl groups in different cyclopentadiene rings ([4]), has no characteristic frequencies in the region 1000-1200 cm^{-1}. Diethylferrocenes I and II have frequencies 998 and 1107 cm^{-1}; in addition, substance II also has a frequency 1277 cm^{-1} of high intensity (the latter is completely absent in substances I and III); consequently, I and II are isomers of III, i.e., they contain both ethyl groups in one cyclopentadiene ring. Methyl- and dimethylferrocenes, isopropyl- and diisopropylferrocenes also have characteristic frequencies in the region 1000 cm^{-1} and 1107 cm^{-1} (characteristic of ferrocene itself and of its monosubstituted derivatives)*.

Thus, introduction of the first alkyl group into the cyclopentadiene ring, just as occurs in the aromatic series, facilitates entry of the second alkyl into the same cyclopentadiene ring; in this case a mixture of dialkylferrocenes with substituents in one ring is obtained.

Experimental Part

Methylferrocene. A stream of gaseous methyl chloride, prepared by the method described in ([3]), from 820 g of anhydrous zinc chloride, 525 ml of conc. HCl, and 105 ml of methyl alcohol, was passed into a solution of 40 g of ferrocene in 325 ml of *n*-heptane. Gradually, while heating to 55-60°, 30 g of aluminum chloride was introduced. Heating was continued for 5 h. After decomposition in the usual manner, 20.4 g of liquid products was isolated

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* The measurement of the IR spectra was carried out by L. A. Kozitsina and B. V. Lokshin, to whom the authors express their gratitude.

reaction and 10 g of unreacted ferrocene was recovered. From the liquid products, by fractional distillation followed by recrystallization from absolute ethyl alcohol, 1.5 g of methylferrocene was obtained. M.p. 118-119°.

Found, %:	C 65.77; 65.80; H 5.87; 5.91; Fe 28.30; 28.26
$C_{11}H_{12}Fe$. Calculated, %:	C 65.95; H 6.15; Fe 27.95

Methylferrocene consists of yellow fluffy plates, almost odorless; soluble in all ordinary organic solvents, insoluble in water. In alcohol it is appreciably more soluble than ferrocene. A 3.2 g mixture of dimethylferrocene isomers was obtained, b.p. 127-128°/13 mm, $n_D^{20} = 1.6001$, $d_4^{20} = 1.2646$.

Found, %:	C 67.33; 67.48; H 6.56; 6.51; Fe 25.95; 25.91
$C_{12}H_{14}Fe$. Calculated, %:	C 67.32; H 6.55; Fe 26.13

Dimethylferrocene is a dark-red liquid with a camphor odor, readily soluble in ordinary organic solvents, insoluble in water.

In addition, 4.3 g of a mixture of other liquid products of methylation of ferrocene, b.p. 130-150°/13 mm, was obtained; these were not subjected to detailed study.

Diethylferrocene isomers. Similarly, from 40 g of ferrocene dissolved in 300 ml of petroleum ether, 20 ml of ethyl bromide, and 10 g of aluminum chloride, under the same conditions at a temperature of 50-60° and an experiment duration of 5-6 hr, the following was obtained: 8.8 g of liquid products; 22.6 g of unreacted ferrocene was recovered (the average yield of alkylation products, calculated on the initial ferrocene (17.4 g) and the diethylferrocene obtained, was 39%). From these, 4.2 g of monoethylferrocene was obtained, i.e., 18.5% of theory.

Separation of the reaction products was carried out by successive chromatography of fractions boiling in the ranges: 106-108°/5 mm, 118-123°/15 mm, and

125–140°/15 mm on anhydrous aluminum oxide by the method described above. The following were obtained:

Ethylferrocene
$n_D^{20} = 1.6010$; $d_4^{20} = 1.2628$ ([1,4]). $MR_{\text{found}} = 58.06$.

Diethylferrocene I
$n_D^{20} = 1.5822$; $d_4^{20} = 1.2002$. $MR_{\text{found}} = 67.35$.

Found, %: C 69.16; 69.24; H 7.39; 7.21; Fe 22.94; 22.73

Diethylferrocene II
$n_D^{20} = 1.5850$; $d_4^{20} = 1.2041$. $MR_{\text{found}} = 67.35$.

Found, %:	C 69.35; 69.37; H 7.28; 7.25; Fe 22.85; 22.91
$C_{14}H_{18}Fe$. Calculated, %:	C 69.51; H 7.40; Fe 23.09

Isopropylferrocene. Similarly, from 40 g of ferrocene dissolved in 300 ml of absolute petroleum ether, 20 ml of isopropyl chloride, and 7.5 g of anhydrous aluminum chloride, after workup by the usual method, 7.33 g of liquid products was obtained. 26.7 g of unreacted ferrocene was recovered. Separation of the liquid reaction products was carried out by successive chromatography of fractions boiling in the ranges: 106–107°/3 mm; 115–120°/3 mm; 120–140°/3 mm on anhydrous aluminum oxide (weight 50 g, layer height 40 cm, solvent *n*-heptane) using an automatic flow refractometer PRA-25 ([2]). This gave 2.3 g of isopropylferrocene, $n_D^{20} = 1.5897$; $d_4^{20} = 1.2230$. $MR_{\text{found}} = 62.92$.

Found, %:	C 68.58; 68.49; H 7.09; 7.07; Fe 23.49; 24.37
$C_{12}H_{16}Fe$. Calculated, %:	C 68.50; H 7.06; Fe 24.44

Isopropylferrocene is a dark-red liquid with a characteristic camphor odor, readily soluble in ordinary organic solvents and insoluble in water.

Also obtained was 3.3 g of diisopropylferrocene, $n_D^{20} = 1.5815$; $d_4^{20} = 1.2160$.

Found, %: C 70.80; 71.01; H 7.84; 7.76; Fe 21.29; 21.31
$C_{16}H_{22}Fe$. Calculated, %: C 71.15; H 8.16; Fe 20.56

A dark-red liquid with a characteristic camphor odor, readily soluble in ordinary organic solvents and insoluble in water.

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