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1964

SovietRxiv

Abstract

Full Text

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ALKYLATION OF FERROCENE

The reaction, first carried out by us (^{1}), of the alkylation of ferrocene with alkyl halides or olefins in the presence of $AlCl_3$ according to Friedel–Crafts leads to a mixture of alkylferrocenes in an overall yield of 20–30% (65% in the case of isobutylene (see (^{2})).

It was observed that, in the presence of the alkylating mixture, along with alkylation there also occurs oxidation of ferrocene and its homologs to the corresponding ferricinium salts, which, as is known (^{6}), are not further alkylated. Thus, from the reaction mixture it was always possible, by reduction with Na_2SO_3, to recover about 40–50% of ferrocene. The ability of the central metal atom to be oxidized under the action of strong acids and the carbonium ion was discussed in the works of Sorokin and Domrachev (^{3}), and also of Rosenblum and co-workers (^{4}). In this connection it seemed of interest to study the alkylation of ferrocene in the presence of a reducing agent.

In the present work the alkylation of ferrocene with ethyl bromide and tert-butyl chloride in the presence of an equimolecular mixture of $AlCl_3$ and $LiAlH_4$ is described. In this way the overall yield of alkylation products was raised to 80–90%.

In the alkylation products there is contained a mixture of a large number of different alkyl homologs of ferrocene (for example, in the case of exhaustive ethylation of ferrocene one may theoretically expect 35 homologs of different degrees of alkylation, from mono- to decaethyl-substituted, inclusive). The purpose of the present work was the selection of such alkylation conditions under which mainly the first or the last members of this series should be obtained. Under the action of ethyl bromide, up to 50% of the previously described mono- and diethylferrocenes were obtained, with an overall yield of 85%.

Table 1

Gas-chromatographic analysis of standard mixtures

	$C_{10}H_{10}Fe$, taken	$C_{10}H_{10}Fe$, found	$C_{10}H_9FeC_2H_5$, taken	$C_{10}H_9FeC_2H_5$, found	$C_{10}H_8Fe(C_2H_5)_2$, taken	$C_{10}H_8Fe(C_2H_5)_2$, found
I	53.5	55.0	46.5	45.0	–	–
I		52.6		47.0		
II	30.25	34.0	69.7	66.0	–	–

	$C_{10}H_{10}Fe$, taken	$C_{10}H_{10}Fe$, found	$C_{10}H_9FeC_2H_5$, taken	$C_{10}H_9FeC_2H_5$, found	$C_{10}H_8Fe(C_2H_5)_2$, taken	$C_{10}H_8Fe(C_2H_5)_2$, found
III	63.5	65.7	36.5	34.3	–	–
III		66.35		33.65		
IV	28.9	30.3	33.3	32.5	37.8	37.2
IV		28.5		31.1		38.4

For analysis of the mixture of ethylation products, the method of gas-liquid capillary chromatography was used. It was shown on standard mixtures of ferrocene, ethylferrocene, and 1,1′-diethylferrocene that these mixtures are analyzed with an accuracy of 3–3.5% when the concentration is calculated from the peak areas (see Table 1). Consideration of the data of gas-liquid chromatographic analysis (see Table 2) shows that, with an unchanged amount of $LiAlH_4$, the yield and composition of the ethylation products depend only on the ferrocene/ethyl bromide ratio.

Under the action of tert-butyl chloride, the principal reaction products under certain conditions are tri-tert-butylferrocene (m.p. 86–87°) and tetratertiary butylferrocene (m.p. 196°). The last two substances were studied by us in detail for the first time. The IR spectra of these substances do not contain-

frequencies appear in the region of 1000 and 1100 cm^{-1}, which indicates that the third tert-butyl group is already directed to the second ferrocene nucleus. Apparently, the tetra-derivative (m.p. 196°) is 1,3,1′,3′-tetra-tert-butylferrocene.

Table 2

	Molar ratio ferrocene : ethyl bromide : aluminum	Recovery of ferrocene, g	Total yield of alkylation products, g	Yield, % ethylferrocene	Yield, % diethylferrocenes	Ratio ethylferrocene : diethylferrocene
1	1 : 2 : 1	0.42	3.3	21.3	22.1	1 : 1.01
2	1 : 1 : 1	1.17	2	27.3	13.1	1 : 0.48
3	1 : 1 : 2	1.01	2.5	29.9	15.7	1 : 0.52

The NMR spectra* of tri- and tetra-butylferrocene are consistent with this assumption and show that the tert-alkyl radical does not undergo isomerization during the reaction. For tri-tert-butylferrocene in CCl_4 solution, the chemical shifts from tetramethylsilane are $\tau_1 = 6.02 \cdot 10^{-6}$, $\tau_2 = 5.93 \cdot 10^{-6}$ (ring H) (^{8}), $\tau_3 = 8.77 \cdot 10^{-6}$ (H_{CH_3}, singlet).

For tetra-tert-butylferrocene under the same conditions: $\tau_1 = 6.10 \cdot 10^{-6}$ (ring H, singlet) (^{8}), $\tau_3 = 8.77 \cdot 10^{-6}$ (H_{CH_3}, singlet).

A final conclusion about the structure of this substance can be made on the basis of X-ray structural analysis, which is currently being carried out.

No higher alkylation products than tetra-tert-butylferrocene were detected in the reaction products.

Experimental part

1. Gas-chromatographic separation of alkylferrocenes was carried out on a silver capillary column with an internal diameter of 0.3 mm and a length of 12 m. The stationary phase was Apiezon L; the separation temperature was 130°, inlet pressure 0.83 atm gauge. Detection was by flame ionization. The relative retention time (α) of diethylferrocene was 1.76, of ethylferrocene 1.28, and of ferrocene 1.00.

The results of analysis of a standard mixture of ferrocene, ethylferrocene, and diethylferrocene are given in Table 1.

It should be noted that, when calculating component concentrations from peak areas, we encountered no difficulties due to the different iron contents in the components analyzed (see Fig. 1).

Our conclusion that iron atoms do not contribute an additional component to the ion current was confirmed using $Fe(CO)_5$, which gave no peak under flame-ionization detection.

Details concerning the chromatographic apparatus were described by us earlier. The purity of the ferrocene, solvents, and ethyl bromide used was checked by gas chromatography.

2. Synthesis of standard samples was carried out according to known procedures (^{9,10}). The constants had the following values:

$$C_{10}H_9FeC_2H_5, \qquad n_D^{20}\ 1.6010\ (^{9,10}), \qquad d_4^{20}\ 1.263\ (11)$$

$$C_{10}H_8Fe(C_2H_5)_2, \qquad n_D^{20}\ 1.5803\ (^{9,10}), \qquad d_4^{20}\ 1.184\ (11)$$

3. Alkylation of ferrocene with ethyl bromide. To a solution of 3.00 g (0.0161 mol) of ferrocene in 60 ml of dry *n*-heptane were added 0.61 g (0.0161 mol) of lithium aluminum hydride and various amounts of aluminum chloride (see Table 2). To the resulting mixture, with stirring–

over 1.5 h at a temperature of 60°, a solution of ethyl bromide in 10 ml of dry heptane was added. Stirring at this temperature was continued for 1.5 h. The reaction mixture was cooled to 0° and carefully decomposed with 70 g of a water–ice mixture. The organic layer was separated, and the aqueous layer was washed with ether (4 times with 20 ml). The organic extracts were combined, washed with water (2 times with 20 ml), and dried over magnesium sulfate; the solvent was removed in vacuo. The residue was treated with petroleum ether (b.p. 40–60°) and filtered through a layer of chromatographic alumina. From the filtrate, unreacted ferrocene was separated by low-temperature crystallization at −40, −60°. The total yield of alkylation products was 3.3 g, corresponding, calculated as diethylferrocene, to 84.5%; calculated as triethylferrocene, to 76%. After distillation in vacuo the liquid products were divided into two fractions:

Fraction I: 100–130°/1 mm. 2.32 g, n_D^{20} 1.5800, contains a mixture of ferrocene, ethylferrocene, and isomeric diethylferrocenes (the content of the products in this mixture was determined by gas chromatography, see Table 2). The amount of ferrocene obtained from low-temperature crystallization and from the gas-chromatographic analysis data was summed (see Table 2).

Fraction II: 130–150°/1 mm. 0.83 g, contains a mixture of isomeric triethylferrocenes, n_D^{20} 1.5700. Gas-chromatographic analysis of this fraction shows the absence in it of ferrocene, ethylferrocene, and a mixture of isomeric diethylferrocenes. No fractions boiling above 150° were found. Resinous residue 0.15 g.

4. **Alkylation of ferrocene with tert-butyl chloride.** Under the conditions of the preceding experiment, the following were used: 2.5 g of ferrocene, 0.52 g of lithium aluminum hydride, 1.8 g of anhydrous aluminum chloride, 5 g of tert-butyl chloride. The work-up was carried out in the same manner. After removal of the solvent, 3.5 g of oily crystals were obtained. Upon repeated chromatography on Al_2O_3 from *n*-hexane, there were obtained 0.01 g of ferrocene, 0.5 g of mono- and di-tert-butylferrocenes, 0.77 g of tri-tert-butylferrocene, m.p. 85°.

Found %:	C 74.36, 74.67;	H 9.66, 9.77;	Fe 15.88, 15.79
$C_{22}H_{34}Fe$. Calculated %:	C 74.61;	H 9.64;	Fe 15.75

and 0.68 g of tetra-tert-butylferrocene. After recrystallization from absolute alcohol, m.p. 195–196°.

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* The NMR spectra were measured on a TsLA-5535 NMR spectrograph at a frequency of 40 MHz by E. I. Fedin and P. V. Petrovskii, to whom the authors express their deep gratitude.

Found %:	C 76.18, 76.04;	H 10.40, 10.25;	Fe 13.42, 13.61
$C_{26}H_{42}Fe$. Calculated %:	C 76.25;	H 10.10;	Fe 13.65

The purity of individual fractions during chromatography was checked by thin-layer chromatography on Al_2O_3 from hexane on a 12.5 × 26 cm plate. Layer thickness 1 mm. Development with iodine.

For ferrocene $R_f = 0.61$; mono-tert-butylferrocene $R_{f_1} = 0.64$; di-tert-butylferrocenes $R_{f_2} = 0.67$; tri-tert-butylferrocene $R_{f_3} = 0.72$; tetra-tert-butylferrocene $R_{f_4} = 0.78$.

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Received
3 II 1964

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