Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV, E. B. SOKOLOVA,

G. P. BAKUNCHIK

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Abstract

Full Text

Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV,
E. B. SOKOLOVA,
G. P. BAKUNCHIK

INTERACTION OF METHYL ESTERS OF FERROCENE MONO- AND DICARBOXYLIC ACIDS WITH α- AND γ-MAGNESIUM HALOALKYLSILANES

In the reaction of neopentylmagnesium chloride with trimethylacetic acid chloride, owing to steric difficulties, the reaction stops at an intermediate stage—the formation of neopentyl tert-butyl ketone (^{1}).

In the present study it was established that the structural analogue of neopentylmagnesium chloride—siliconeopentylmagnesium chloride—also reacts with the methyl ester of ferrocenemonocarboxylic acid according to an anomalous scheme; among the reaction products, siliconeopentyl ferrocenyl ketone was isolated.

$$(CH_3)_3SiCH_2MgCl + FcCOOCH_3 \longrightarrow FcCOCH_2Si(CH_3)_3$$

Likewise, siliconeopentylmagnesium chloride reacted according to the anomalous scheme with the dimethyl ester of ferrocenidicarboxylic acid. Here the reaction proceeded only at one ester group, and a keto-acid ester was formed.

$$(CH_3)_3SiCH_2MgCl{+}CH_3OOC{-}Fc{-}COOCH_3 \longrightarrow (CH_3)_3SiCH_2CO{-}Fc{-}COOCH_3$$

When magnesium chloropropyltrimethylsilane was allowed to react with the esters of ferrocene mono- and dicarboxylic acids, the reaction proceeded according to the normal scheme, with formation, respectively, of a tertiary alcohol and a glycol.

$$2\,CH_3Si(CH_3)CH_2CH_2CH_2MgCl{+}FcCOOCH_3 \longrightarrow FcC(OH)(CH_2CH_2CH_2Si(CH_3)_3)_2$$

$$4\,(CH_3)_3Si{-}CH_2{-}CH_2{-}CH_2{-}MgCl{+}\ \text{ferrocene derivative with two } COOCH_3 \text{ groups} \ \longrightarrow \begin{array}{c}\text{ferrocene de}\\ C(OH)(CH_2CH_2\end{array}$$

Experimental Part

1. Preparation of ferrocenedicarboxylic acids and their esters. Mono- and dicarboxylic acids of ferrocene were obtained by metalation of ferrocene with *n*-butyllithium in an ether medium, followed by carbonization by pouring the reaction mixture onto solid carbon dioxide. The salts of the acids formed were treated with water; the unreacted ferrocene was filtered off on a Büchner funnel. The free-

Table 1

Properties of the compounds obtained for the first time

No.	Name and structural formula	Yield, wt. %	m.p., °C	Found, % C	Found, % H	Found, % OH	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % OH
1	**(Trimethylsilyl)methyl ferrocenyl ketone**Structural formula: ferrocene-$COCH_2Si(CH_3)_3$	66	66	59.84	6.94	No	$C_{15}H_{20}OFeSi$	60.01	6.71	—
2	**Keto ester of ferrocenedicarboxylic acid**Structural formula: ferrocene bearing $COCH_2Si(CH_3)_3$ and $COOCH_3$	57	106–108	58.26	5.96	»	$C_{17}H_{22}OFeSi$	56.99	6.19	—

No.	Name and structural formula	Yield, wt. %	m.p., °C	Found, % C	Found, % H	Found, % OH	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % OH
3	**Di-γ-(trimethylsilylpropyl)ferrocenylcarbinol** Structural formula: ferrocene–$C(OH)[CH_2CH_2CH_2Si(CH_3)_3]_2$	90	60–62	61.70	9.33	3.91	$C_{23}H_{40}OFeSi_2$	62.14	9.07	3.83
4	**1,1′-bis-[4-oxa-1,7-di-(trimethylsilyl)-4-heptyl]-ferrocene** Structural formula: ferrocene bearing two $C(OH)[CH_2CH_2CH_2Si(CH_3)_3]_2$ groups	87	107–108			4.97	$C_{36}H_{70}O_2FeSi_4$	61.50	10.04	4.84

Free acids were isolated from the salt solution by treatment with concentrated HCl. Ferrocenemonocarboxylic acid was separated by extraction with ether in a Soxhlet apparatus. After evaporation of the ether, 17 g of ferrocenemonocarboxylic acid was isolated (yield 27%).

Ferrocenecarboxylic acid was obtained in the residue after extraction in an amount of 16 g (yield 22%). The dimethyl ester of ferrocenecarboxylic acid was obtained in an amount of 12 g, mp 114–115°. Literature value 114–115° (^{2}). The methyl ester of ferrocenemonocarboxylic acid was obtained in an amount of 4.7 g and had mp 69°. Literature value 70–71° (^{3}).

2. Trimethylchloromethylsilane and trimethyl-γ-chloropropylsilane. Trimethylchloromethylsilane was obtained by the reaction of methylmagnesium bromide with dimethylchloromethylchlorosilane in 50% yield. The product had the following properties: bp 95-97°, n_D^{20} 1.4179. Literature (4): bp 97.1°, n_D^{20} 1.4180. Trimethyl-γ-chloropropylsilane was obtained by addition of methyldichlorosilane to allyl chloride in the presence of H_2PtCl_6, followed by methylation of the two chlorine atoms on silicon with methylmagnesium bromide.

Trimethyl-γ-chloropropylsilane had the following properties: bp 66° at 43 mm, n_D^{20} 1.4300, d_4^{20} 0.8783, MR_D found: 44.33; calculated 44.38.

Methyldichloro-γ-chloropropylsilane was obtained in 43% yield. Its properties: bp 92° at 51 mm; n_D^{20} 1.4600. Literature (5) n_D^{20} 1.4600.

3. Reaction of methyl esters of ferrocenemonocarboxylic and ferrocenecarboxylic acids with Grignard reagents from trimethylchloromethylsilane and trimethyl-γ-chloropropylsilane. The Grignard reactions were carried out as usual in diethyl ether, first in the cold and then at the boiling point of the ether. The properties and yields of the compounds obtained for the first time are presented in Table 1.

For compound 1 the infrared spectrum showed the presence of an absorption band at 1712 cm^{-1}, characteristic of the C=O group. The same was observed for compound 2. For compound 3 the IR spectrum showed the presence of an absorption band at 3105 cm^{-1}, characteristic of the OH group. For compound 4 the spectrum showed absorption bands at 3105 and 3390 cm^{-1}, characteristic of the OH group; absorption bands typical of the C=O group were absent. The spectra were recorded on a UR-10 instrument in the regions 1650–1800 and 3000–3400 cm^{-1}.

Moscow Institute of Chemical Technology
named after D. I. Mendeleev

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