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Abstract

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ADDITION OF SILICON HYDRIDES TO DIMETHYLALLYLFERROCENYLSILANE IN THE PRESENCE OF H_2PtCl_6

Silicon-containing compounds of the ferrocene series have in recent years been synthesized in a number of studies. Schaaf ([1]) obtained siloxanylferrocenes—liquid substances with freezing points down to −60° and boiling points up to +460°. Guan Li, Sokolova, Leites, and Petrov ([2]) synthesized, from formyl-, acetyl-, and benzoylferrocene, silicon-free alcohols of the ferrocene series, and, by the action of γ-trimethylsilylpropylmagnesium chloride on the same carbonyl derivatives of ferrocene, silicon-containing alcohols with freezing points from −28 to −41°*.

Petrov, Sokolova, and Bakunchik ([3]), from methyl esters of mono- and dicarboxylic acids of ferrocene and α- and γ-magnesiohaloalkylsilanes, obtained anomalous synthesis products in the first case and normal ones in the second. All the compounds obtained—the ketone, keto ester, tertiary alcohol, and ditertiary glycol—proved to be solid substances with melting points from 60 to 108°, i.e., considerably lower than that of ferrocene itself (173°).

An attempt to carry out the addition of silicon hydrides to β-phenylvinylferrocene was unsuccessful ([2,4]). In this same latter investigation we for the first time obtained dimethylallylferrocenylsilane. The task of the present study was to investigate the addition of various silicon hydrides to this unsaturated compound with the aim of synthesizing both ferrocenyl-disilanes and their mono- and dichloro derivatives.

Dimethylallylferrocenylsilane was obtained in 43% yield by condensation of dimethylallylchlorosilane with ferrocenyl lithium. Dimethylallylchlorosilane was synthesized in 40% yield from dimethyldichlorosilane and allylmagnesium bromide. The properties of dimethylallylchlorosilane agreed with those reported in the literature ([5]). To n-butyllithium obtained under ordinary conditions in ether solution, taken in an amount of 0.25 mole, ferrocene was added in an amount of 46.5 g (0.25 mole). After heating the mixture for 10 hours at the boiling point of ether, 38 g (0.25 mole) of dimethylallylchlorosilane was added to it in an atmosphere of dry nitrogen. The mixture was heated again for 15 hours, after which it was poured onto ice. The ethereal solution was dried over Na_2SO_4; the unreacted ferrocene was filtered off and distilled off with superheated steam.

reaction scheme: ferrocene alcohol polymerization in the presence of BF3 with elimination of water; where R = H, CH3, C6H5, Si absent in the radical

Figure 1: reaction scheme: ferrocene alcohol polymerization in the presence of BF3 with elimination of water; where R = H, CH3, C6H5, Si absent in the radical

Dimethylallylferrocenylsilane: $n_D^{20} = 1.5570$; $d_4^{20} = 1.0889$; freezing point $-61°$.

Found, %: H 7.20; C 63.30
$C_{15}H_{20}FeSi$; calculated, %: H 7.10; C 63.37

Four silicon hydrides were synthesized: $(CH_3)(C_2H_5)_2SiH$ (^{6}), $(C_2H_5)_3SiH$ (^{7}), $(CH_3)(C_4H_9)_2 \cdot SiH$ (^{8}), and $(CH_3)(C_2H_5) \cdot SiHCl$ (^{9}), whose properties agreed with those given in the literature. The silicon hydride CH_3HSiCl_2 was obtained from the factory.

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* It has recently been shown that alcohols of the ferrocene series (α-alkoxyalkylferrocenes) are readily polymerized according to the scheme (^{11})

where $R = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_6H_5}$; Si is absent in the radical.

All syntheses of silicon-containing ferrocene derivatives were carried out according to the following procedure. A mixture of dimethylallylferrocenylsilane and a trialkylsilane (or alkylhalosilane) in a molar ratio of 1 : 3, as well as 0.3 ml of a 0.1 molar solution of H_2PtCl_6 in absolute isopropyl alcohol, was charged into a flask equipped with a reflux condenser, stirrer, and thermometer. On stirring such a mixture, its spontaneous heating by 5—50° was observed. After the temperature rise had ceased, the reaction mixture was heated at the boiling temperature of the trialkylsilane (or alkylhalosilane) for 15-20 min.

The excess trialkyl(or alkylhalogen)silanes were distilled off from the reaction products on a water bath. When $(CH_3)(C_2H_5)SiHCl$, $(CH_3)(C_2H_5)_2SiH$, and $(C_2H_5)_3SiH$ were used, distillation was carried out in a stream of dry nitrogen. $(CH_3)(C_4H_9)_2SiH$ was distilled off from the reaction products on a water bath and under vacuum.

The residue after distilling off the silicon hydrides was chromatographed on an Al_2O_3 column using petroleum ether, b.p. 40—60°. The reactions proceeded according to the equations below.

1. Dimethylferrocenyl-(γ-methyldiethylsilyl)-propylsilane

$$\text{dimethylallylferrocenylsilane} + (CH_3)(C_2H_5)_2SiH \xrightarrow{H_2PtCl_6} \text{dimethylferrocenyl-(-methyldiethylsilyl)-propylsila}$$

Taken for the reaction: 11.5 g (0.04 mole) of dimethylallylferrocenylsilane, 12.3 g (0.12 mole) of methyldiethylsilane, 0.3 ml of 0.1 M H_2PtCl_6. A red-brown liquid substance was obtained.

2. Dimethylferrocenyl-(γ-triethylsilyl)-propylsilane*. Taken: 7.7 g (0.027 mole) of dimethylallylferrocenylsilane, 9.6 g (0.081 mole) of triethylsilane, 0.3 ml of 0.1 M H_2PtCl_6. A dark-red liquid substance was obtained.

3. Dimethylferrocenyl-(γ-methyldibutylsilyl)-propylsilane. Taken: 8 g (0.028 mole) of dimethylallylferrocenylsilane, 13.3 g (0.084 mole) of methyldibutylsilane, 0.3 ml of 0.1 M H_2PtCl_6. A viscous dark-red liquid substance was obtained.

4. Dimethylferrocenyl-(γ-methylethylchlorosilyl)-propylsilane

dimethylallylferrocenylsilane+$(CH_3)(C_2H_5)HSiCl \xrightarrow{H_2PtCl_6}$ dimethylferrocenyl-(-methylethylchlorosilyl)-prop

Taken: 7.5 g (0.026 mole) of dimethylallylferrocenylsilane, 8 g (0.073 mole) of methylethylchlorosilane, 0.3 mole of 0.1 M H_2PtCl_6. Obtained: 9.6 g of a viscous dark-red-brown liquid substance.

5. Dimethylferrocenyl-(γ-methyldichlorosilyl)-propylsilane

dimethylallylferrocenylsilane+$CH_3HSiCl_2 \xrightarrow{H_2PtCl_6}$ dimethylferrocenyl-(-methyldichlorosilyl)-propylsilane

* Triethylsilane and methyldibutylsilane reacted with dimethylallylferrocenylsilane according to an analogous scheme.

Table 1

No.	Formula of compound, mol. wt.	Yield, %	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Found, % Fe_2O_3	Found, % $Fe_2O_3 + SiO_2$	Calculated, % C	Calculated, % H	Calculated, % Fe_2O_3	Calculated, % $Fe_2O_3 + SiO_2$	$T_{freez.}$, °C
1	$FcSi(CH_3)_2CH_2CH_2CH_2Si(CH_3)(C_2H_5)_2$ $C_{20}H_{34}FeSi_2$ [illegible]	56	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.8	—	[illegible]	[illegible]	20.7	—	−36
2	$FcSi(CH_3)_2CH_2CH_2CH_2Si(C_2H_5)_3$ $C_{21}H_{36}FeSi_2$ 400.55	57	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	—	19.95	—	−45
3	$FcSi(CH_3)_2CH_2CH_2CH_2Si(CH_3)(C_4H_9)_2$ $C_{24}H_{42}FeSi_2$ [illegible]	67	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	17.7	—	[illegible]	[illegible]	18.0	—	−39
4	$FcSi(CH_3)_2CH_2CH_2CH_2Si(CH_3)(C_2H_5)Cl$ $C_{18}H_{29}FeSi_2Cl$ 392.92	93	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	—	—	—	—	—	—
5	$FcSi(CH_3)_2CH_2CH_2CH_2Si(CH_3)Cl_2$ $C_{16}H_{24}FeSi_2Cl_2$ 399.31	98	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	—	—	—	—	—	—
6	$FcSi(CH_3)_2CH_2CH_2CH_2Si(CH_3)(C_2H_5)OSi(CH_3)(C_2H_5)CH_2CH_2CH_2Si(CH_3)_2Fc$ $C_{36}H_{58}Fe_2Si_4O$ 73	20	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Fig. 1

Figure 2: Fig. 1

4 g (0.014 mole) of dimethylallylferrocenylsilane, 5 g (0.043 mole) of methyldichlorosilane, and 0.3 ml of 0.1 M H_2PtCl_6 were taken. 5.7 g of a viscous dark substance was obtained.

The analytical data and properties of the newly obtained compounds are presented in Table 1. All ferrocenyl disilanes with a trimethylene bridge (as well as their halogen derivatives) are liquids with low solidification temperatures.

Hydrolysis of dimethylferrocenyl-(γ-methylethylchlorosilyl)-propylsilane was carried out according to the procedure of (10).

Fig. 1

The reaction products were extracted with ether and dried with Na_2SO_4. After the ether was distilled off, the residue was chromatographed on a column packed with Al_2O_3. In this process a crystalline product was eluted with petroleum ether; it proved to be ferrocene (m.p. 170°). A mixed sample of it with pure ferrocene had m.p. 172°. Yield 0.8 g (10.7%). Ferrocene evidently formed as a result of cleavage, under the action of HCl, of the ferrocene–Si bond; its formation can probably be eliminated by carrying out the hydrolysis in pyridine solution. After separation of the ferrocene, the reaction products were chromatographed using benzene. After the benzene was distilled off on a water bath and with the aid of dry nitrogen, 1.6 g (20%) of a very viscous, faintly colored substance was obtained. Its analytical data and properties are given in Table 1.

For compound No. 1 in Table 1 an IR spectrum was recorded, shown in Fig. 1; it revealed the presence of bands characteristic of ferrocene and of alkyl groups bonded to silicon. The spectral analysis was carried out at the Institute of Organic Chemistry of the Academy of Sciences of the USSR by L. A. Leites. The spectrum does not contradict the assigned formula*. There are bands characteristic of ferrocene: 3080, 1620, 1110, 1170, and of alkyl groups bonded to Si: 2910, 2950, 1250, 820.

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[[structural formula of a *ferrocenyl disilane shown]]

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

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