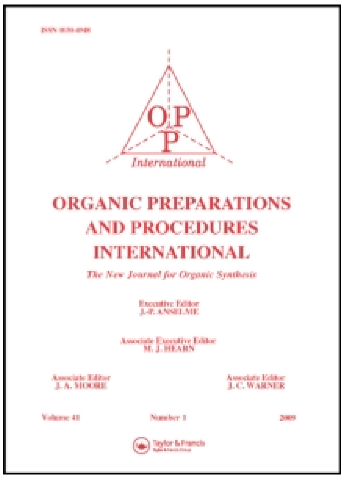

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PREPARATION OF SOME FERROCENYLSILANES[1]

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$$\mathrm{FcLi} + \mathrm{(CH_3)_3SiCl} \longrightarrow \mathrm{FcSi(CH_3)_3} \qquad \text{(I)}$$

$$\mathrm{FcLi} + \mathrm{(CH_3)_2SiCl_2} \longrightarrow \mathrm{FcSi(CH_3)_2Cl} \qquad \text{(II)}$$

$$\mathrm{FcLi} + \mathrm{(CH_3)_2Si(Cl)H} \longrightarrow \mathrm{FcSi(CH_3)_2H} \qquad \text{(III)}$$

$$\mathrm{FcSi(CH_3)_2Cl} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{FcSi(CH_3)_2H} \qquad \text{(III)}$$

$$\mathrm{FcSi(CH_3)_2Cl} \xrightarrow[\mathrm{PhNH_2}]{\mathrm{H_2O}} \mathrm{FcSi(CH_3)_2OH} \qquad \text{(IV)}$$

$$\mathrm{FcSi(CH_3)_2Cl} \xrightarrow[\mathrm{(C_2H_5)_3N}]{\mathrm{H_2O}} \mathrm{[FcSi(CH_3)_2]_2O} \qquad \text{(V)}$$

(Fc = ferrocenyl)

Organosilicon derivatives of ferrocene were originally prepared by reactions of lithio- and 1,1'-dilithioferrocene with triphenyl- and trimethylchlorosilanes.[2,3] In recent years, a sizeable number of ferrocenylsilanes have been described in the literature.[4] In this paper, we describe an improved route to ferrocenyltrimethylsilane (I) and extensions of the method for the synthesis of ferrocenyldimethylchlorosilane (II) and ferrocenyldimethylsilane (III). Also described are conversions of II to III, to ferrocenyldimethylsilanol (IV) and to 1,3-diferrocenyl-1,1,3,3-tetramethyldisiloxane(V).

EXPERIMENTAL

Ethyl ether and tetrahydrofuran were dried over sodium wire, and were subsequently distilled from sodium and from lithium aluminum hydride, respectively. Melting points are uncorrected.

Ferrocenyltrimethylsilane (I).--Into a three-necked, 1000-ml flask which had been flushed with nitrogen was added 50 g (0.27 mol) of ferrocene and 500 ml of 1:1 ethyl ether - tetrahydrofuran. Commercial *n*-butyllithium in hexane (0.28 mol) was added with stirring via a syringe, and the reaction mixture was allowed to stir at room temperature for 6 hr. Subsequently, 36.2 g (0.33 mol) of trimethylchlorosilane was slowly added via a syringe, and stirring was continued for an additional 10 hr at room temperature under nitrogen. The liquid portion was decanted from the lithium chloride which had formed, and was evaporated to produce an orange slurry. This residue was extracted with cold hexane in order to separate the product from most of the unreacted ferrocene. The hexane was evaporated and the process was repeated. The orange-red liquid was then distilled, and a small amount of ferrocene which had sublimed into the distillation head was removed. Ferrocenyltrimethylsilane, bp 111-114°/1.5 mm (lit.[3] 64-65°/0.045 mm), was obtained in 29% yield (19.9 g), together with a 6% yield (2.8 g) of 1,1'-bis(trimethylsilyl)-ferrocene, bp 131-134°/1.0 mm (lit.[3] 87-88°/0.06 mm).

Carbonation of a solution of lithiated ferrocenes prepared under analogous conditions produced a 35% yield of ferrocenoic acid and a 6% yield of ferrocene-1,1'-dicarboxylic acid.

Ferrocenyldimethylchlorosilane (II).--Ferrocenyllithium, prepared from 50 g (0.27 mol) of ferrocene and 0.28 mol of n-butyllithium as described above, was added with stirring and under nitrogen to a solution of 45.8 g (0.35 mol) of dimethyldichlorosilane in ethyl ether. The addition was conducted over a period of ca. 1 hr at room temperature. After an additional 10 hr, workup as described above produced 7.2 g (10% yield) of ferrocenyldimethylchlorosilane, bp 135-138°/1.5 mm. Nmr spectrum (CCl_4): τ 5.64 and 5.86 (m, 9, ferrocenyl protons), 9.39 (s, 6, methyl protons).

Anal.[5] Calcd. for $C_{12}H_{15}ClFeSi$: C, 51.72; H, 5.43; Cl, 12.72; Fe, 20.04. Found: C, 50.77; H, 5.68; Cl, 12.24: Fe, 19.38.

Ferrocenyldimethylsilane (III).--Ferrocenyllithium was prepared as previously described from 35 g (0.19 mol) of ferrocene, 0.19 mol of n-butyllithium and 250 ml of 1:1 ethyl ether - tetrahydrofuran. The resulting solution was slowly added to 23.6 g (0.25 mol) of dimethylchlorosilane in ethyl ether. The reaction mixture was allowed to stir for 1 hr, hydrolyzed, and the ether layer was separated, washed and dried. The orange slurry after evaporation of the ether was extracted several times with 25 ml portions of cold hexane to remove the product from unreacted ferrocene. The process was repeated several times, after which distillation produced 5.2 g (11% yield) of ferrocenyldimethylsilane, bp 160°/19 mm. Nmr spectrum ($CDCl_3$): τ 5.60 and 5.85 (m, 10, ferrocenyl protons and Si-H), 9.69 (d, 6, methyl protons, J = 3.5 Hz).

Ir spectrum (film): 3100, 1110, 1000 (s, π-C_5H_5), 2960, 1250 (s, $SiCH_3$), 2120 cm^{-1} (s, Si-H).

Anal. Calcd. for $C_{12}H_{16}FeSi$: C, 59.02; H, 6.60; Fe, 22.86. Found: C, 58.87; H, 6.74; Fe, 22.67.

Lithium Aluminum Hydride Reduction of Ferrocenyldimethylchlorosilane.--Into a three-necked, 500-ml flask which had been flushed with nitrogen was added 2.0 g (0.015 mol) of anhydrous aluminum chloride and 100 ml of ethyl ether. In a separate flask, 0.57 g (0.015 mol) of lithium aluminum hydride was dissolved in 50 ml of ethyl ether and the solution was slowly added to the reaction flask which was kept at 0° by means of an ice bath. The mixture was allowed to warm to room temperature while stirring, and 4.2 g (0.015 mol) of ferrocenyldimethylchlorosilane dissolved in 75 ml of ethyl ether was added slowly under nitrogen by means of an addition funnel. The mixture was allowed to stir for an additional hr and was hydrolyzed at 0°. The layers were separated, and the organic layer was washed with water, dilute sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and was evaporated. The remaining orange-red liquid was distilled, producing 3.4 g (93% yield) of ferrocenyldimethylsilane, bp 103°/0.6 mm. The nmr spectra of the product was identical to the spectra of III as described above.

Ferrocenyldimethylsilanol (IV).--A solution of 3.2 g (0.011 mol) of ferrocenyldimethylchlorosilane in 50 ml of ethyl ether was added over a 15 min period with stirring to a solution of 0.28 g (0.015 mol) of water and 1.24 g (0.013

mol) of aniline dissolved in 100 ml of ethyl ether. A white precipitate of aniline hydrochloride separated. After an additional 15 min, the mixture was filtered, dried over magnesium sulfate, and the solvent was evaporated. Chromatography of the resulting red oil on alumina and elution with hexane produced very small amounts of an unidentified orange solid, mp 73-74°, and a yellow-orange solid, mp 76-77°, which proved to be identical to V described below. Elution with ethyl ether produced 1.82 g (64% yield) of ferrocenyldimethylsilanol, which after recrystallization from hexane had a mp of 64-65°. Nmr spectrum ($CDCl_3$): τ 5.63 and 5.85 (m, 9, ferrocenyl protons), 8.17 (s, 1, Si<u>OH</u>), 9.62 (s, 6, methyl protons). Ir spectrum ($CHCl_3$): 3100, 1110, 1005 (s, π-C_5H_5), 2960, 1260 (s, $SiCH_3$), 3700-3300 (br, O-H), 1040 cm^{-1} (s, Si-OH).

Calcd. for $C_{12}H_{16}FeOSi$: C, 55.39; H, 6.20; Fe, 21.46. Found: C, 55.41; H, 6.41; Fe, 21.28.

<u>1,3-Diferrocenyl-1,1,3,3-tetramethyldisiloxane (V)</u>.--The above process was repeated, employing 0.226 g (0.013 mol) of water, 1.27 g (0.013 mol) of triethylamine, and 3.5 (0.013 mol) of ferrocenyldimethylchlorosilane. Chromatography of the mixture on alumina produced three bands. The first two bands, representing minor amounts of unidentified products, were eluted with hexane, and the last band was eluted with ethyl ether. The products were: 1st band, an orange solid, mp 86-87°; 2nd band, a yellow-orange solid, mp 74-75°; 3rd band, orange plates, which after recrystallization from

hexane produced 2.3 g (71% yield) of 1,3-diferrocenyl-1,1,3,3-tetramethyldisiloxane, mp 76-77°. Nmr spectrum ($CDCl_3$): τ 5.69 and 5.90 (m, 18, ferrocenyl protons), 9.71 (s, 12, methyl protons). Ir spectrum ($CHCl_3$): 3100, 1110, 1005 (s, π-C_5H_5), 2960, 1260 (s, $SiCH_3$), 1050 (br, Si-O-Si).

Anal. Calcd. for $C_{24}H_{30}Fe_2OSi_2$: C, 57.38; H, 6.02; Fe, 22.24. Found: C, 57.31; H, 5.75; Fe, 22.50.

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5. A satisfactory analytical sample could not be obtained, since II is very reactive on exposure to air.

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