

ORGANOMETALLIC DERIVATIVES

II*. THE PREPARATION OF 1-LITHIO-1'-(TRIMETHYLSILYL)FERROCENE AND ITS USE IN THE SYNTHESIS OF SOME HETERO-ANNULARLY SUBSTITUTED (TRIMETHYLSILYL)FERROCENES

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SUMMARY

The reaction of 1-(chloromercuri)-1'-(trimethylsilyl)ferrocene with *n*-butyllithium gave 1-lithio-1'-(trimethylsilyl)ferrocene. This lithio derivative was condensed with paraformaldehyde, dimethylformamide, anthraquinone, benzophenone, phenyl cyanide, methyl cyanide, carbon dioxide, pyridine and quinoline to give a series of heteroannularly substituted (trimethylsilyl)ferrocenes. The hydroxyl group of 1-(hydroxymethyl)-1'-(trimethylsilyl)ferrocene was displaced by the anilino group in aqueous solution of aniline.

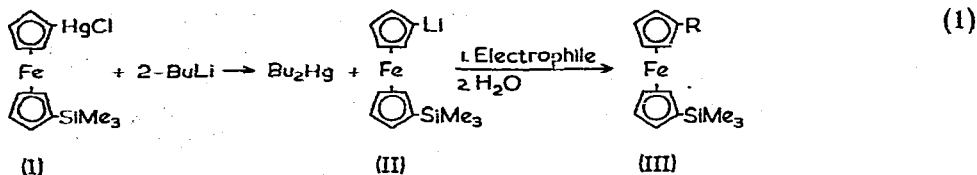
INTRODUCTION

Recently we described the preparation of some heteroannularly substituted (trimethylsilyl)ferrocenes from 1-(chloromercuri)-1'-(trimethylsilyl)ferrocene (I). The treatment of the mercuri-ferrocene (I) with the copper salts CuX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{SCN}$ and $\text{SO}_2\text{C}_6\text{H}_5$) gave the corresponding heteroannularly substituted ferrocenes (III; $\text{R} = \text{Cl}, \text{Br}, \text{SCN}$ and $\text{SO}_2\text{C}_6\text{H}_5$) and on treatment with iodine it gave 1-iodo-1'-(trimethylsilyl)ferrocene. This was the first report of the preparation of these heteroannularly substituted derivatives in good yields. Previously those that had been prepared were made by the metallation of an alkylferrocene and the condensation of the metallated derivative with a chlorosilane. This method gave a mixture of products from which the heteroannularly substituted derivative was isolated only in low yield².

RESULTS AND DISCUSSION

We now report the preparation of some heteroannularly substituted (trimethylsilyl)ferrocenes in good yields from 1-lithio-1'-(trimethylsilyl)ferrocene. The mercuriferrocene (I) was treated with two moles of *n*-butyllithium to give the lithioferrocene (II) and di-*n*-butylmercury³.

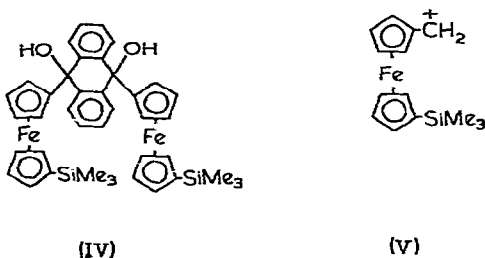
* For Part I see ref. 1.



Scheme A

The lithioferrocene (II) was condensed with the aldehydes paraformaldehyde and dimethylformamide⁴ to give the alcohol (III; R=CH₂OH) and the aldehyde (III; R=CHO) respectively. The aldehyde (III; R=CHO) was characterized as its semicarbazone.

Addition of a three fold excess of anthraquinone to the lithioferrocene (II) afforded two carbonyl addition products, the monoferrocenyl derivative (III; R=C₁₄H₉O₂) and the diferrocenyl derivative (IV). The isolation of (IV) due to the addition of two molecules of the lithioferrocene to anthraquinone was unexpected because on addition of 1-lithio-2-[(dimethylamino)methyl]ferrocene under similar conditions only one of the carbonyl groups underwent reaction⁵.



Condensation of the lithioferrocene (II) with benzophenone gave the ferrocenyl alcohol (III; R=Ph₂COH). The lithioferrocene (II) reacted smoothly with phenyl cyanide and methyl cyanide to give the ferrocenyl ketones (III; R=COPh) and (III; R=COMe) respectively. A reaction of the lithioferrocene (II) with solid carbon dioxide gave the heteroannularly substituted carboxylic acid (III; R=COOH) in good yield. The lithioferrocene (II) added across the C-N bond of the nitrogen bases pyridine and quinoline to give the heteroannularly substituted pyridyl- (III; R=C₅H₄N) and quinolyl- (III; R=C₉H₆N) ferrocenes respectively⁶.

1-(Hydroxymethyl)-1'-(trimethylsilyl)ferrocene was heated with aniline in aqueous solution and displacement of the hydroxyl group occurred to give the ferrocenyl amine (III; R=CH₂NHPh) in 82% yield⁷. The ease of replacement of the hydroxyl group can be attributed to the stability of the α -ferrocenyl carbonium ion (V)⁸.

EXPERIMENTAL

Light petroleum had b.p. 40–60° and n-butyllithium was used as a solution in hexane. All the reactions were carried out under an atmosphere of dry oxygen free nitrogen.

1-Lithio-1'-(trimethylsilyl)ferrocene (II)

n-Butyllithium (0.003 mole) was added to a solution of 1-(chloromercuri)-1'-(trimethylsilyl)ferrocene (0.74 g, 0.0015 mole) in ether. The mixture was stirred at room temperature for 1 h when exchange was assumed to be complete.

Hydrolysis of 1-lithio-1'-(trimethylsilyl)ferrocene (II)

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (1.0 g, 0.002 mole) as described above. The reaction mixture was hydrolysed, extracted with ether and the dried (MgSO_4) ether extracts were evaporated to leave a red oil (1.21 g). The oil was analysed by gas-liquid chromatography with a Pye series 104 chromatograph using a 0.04×1.5 m column packed with 10% Apiezon L on Kieselguhr. The composition of the oil was: trimethylsilylferrocene (53%) di-n-butylmercury (47%). The retention times of these products were identical with those of authentic samples.

1-(Hydroxymethyl)-1'-(trimethylsilyl)ferrocene (III; R = CH₂OH)

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (2.0 g, 0.004 mole) as described above. A suspension of paraformaldehyde (1.8 g, 0.06 mole) in dry ether (20 ml) was added slowly to the lithioferrocene (II). The mixture was stirred for 30 min at room temperature and heated under reflux for $1\frac{1}{2}$ h. The mixture was hydrolysed, extracted with ether and the dried (MgSO_4) ether extracts were evaporated (on a rotary evaporator) to leave a red oil. The oil was chromatographed on alumina, light petroleum eluted trimethylsilylferrocene (0.45 g) and ether eluted the ferrocenyl alcohol (III; R = CH_2OH) (0.60 g, 51%), which crystallised from light petroleum as pale yellow needles, m.p. 50–51°. (Found: C, 58.3; H, 6.9. $\text{C}_{14}\text{H}_{20}\text{FeOSi}$ calcd.: C, 58.3; H, 7.0%.)

1-Formyl-1'-(trimethylsilyl)ferrocene (III; R = CHO)

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (2.0 g, 0.004 mole). Dimethylformamide (1.09 g, 0.015 mole) in ether (10 ml) was added, the mixture was heated under reflux for 15 h and the work-up was carried out as described above. Light petroleum eluted (trimethylsilyl)ferrocene (0.125 g) and bis[1'-(trimethylsilyl)ferrocenyl]mercury (0.08 g)¹. Benzene/light petroleum mixtures eluted the aldehyde (III; R = CHO) (0.50 g, 43%) which was characterised as its semicarbazone. The semicarbazone was prepared in the usual manner and it was crystallized from ethanol water as a red solid, m.p. 142–143°. (Found: C, 52.5; H, 6.4. $\text{C}_{15}\text{H}_{21}\text{FeN}_3$ calcd.: C, 52.5; H, 6.20%.)

Condensation of lithioferrocene (II) with anthraquinone

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (2.0 g, 0.004 mole) as described above. A suspension of anthraquinone (3.12 g, 0.0015 mole) in dry benzene (100 ml) was added slowly to the lithioferrocene (II) and the mixture was stirred at room temperature for 20 h. The work up was as described above. Light petroleum eluted (trimethylsilyl)ferrocene (0.31 g) and bis[1'-(trimethylsilyl)ferrocenyl]mercury (0.14 g). Benzene/light ether mixtures eluted the diferrocenyl derivative (IV) (0.36 g, 25%) which crystallised from ether/light petroleum as yellow granules, m.p. 165.5–167°. (Found: C, 66.55; H, 6.3; Fe, 15.5. $\text{C}_{40}\text{H}_{44}\text{Fe}_2\text{O}_2\text{Si}_2$ calcd.: C, 66.55; H, 6.3; Fe, 15.5.)

C, 66.3; H, 6.1; Fe, 15.4%) Ether eluted the ferrocenyl ketone (III; $R=C_{14}H_9O_2$) which crystallised from light petroleum as red granules, m.p. 141–142°. (Found: C, 69.6; H, 5.7. $C_{27}H_{26}FeSiO_2$ calcd.: C, 69.5; H, 5.6%.)

1-(Hydroxydiphenylmethyl)-1'-(trimethylsilyl)ferrocene (III; $R=Ph_2COH$)

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (0.74 g, 0.0015 mole). A solution of benzophenone (1.82 g, 0.01 mole) in ether (75 ml) was added and the mixture was stirred at room temperature for 3 h. The work up was as described above. Light petroleum eluted (trimethylsilyl)ferrocene (0.10 g) and benzene eluted the ferrocenylalcohol (III; $R=Ph_2COH$) (0.43 g, 64%) which crystallised from light petroleum as pale yellow needles, m.p. 77–78°. (Found: C, 70.9; H, 6.4. $C_{26}H_{28}FeOSi$ calcd.: C, 71.0; H, 6.1%.)

1-Benzoyl-1'-(trimethylsilyl)ferrocene (III; $R=COPh$)

A solution of the lithioferrocene (II) was prepared from the mercuriferrocene (I) (2.0 g, 0.004 mole). A solution of benzonitrile (1.03 g, 0.01 mole) in ether (10 ml) was added and the mixture was heated under reflux for 2 h. The work-up was as described above. Light petroleum eluted (trimethylsilyl)ferrocene (0.23 g) and bis[1'-(trimethylsilyl)ferrocenyl]mercury (0.13 g). Benzene/light petroleum eluted an unidentified product (0.175 g) which crystallised from light petroleum as yellow needles, m.p. 167–169°. (Found: C, 71.7; H, 5.8; N, 7.4%.) Ether eluted the ferrocenyl ketone (III; $R=COPh$) (0.975 g, 66%) which crystallised from light petroleum as dark red needles, m.p. 75–76°. (Found: C, 66.15; H, 6.10. $C_{20}H_{22}FeOSi$ calcd.: C, 66.3; H, 6.1%.)

1-Acetyl-1'-(trimethylsilyl)ferrocene (III; $R=COMe$)

The above experiment was repeated but acetonitrile (0.41 g) was added to the lithioferrocene (II) (0.002 mole). Ether eluted the ferrocenyl ketone (III; $R=COMe$) (0.167 g, 27%) which crystallised from ether/light petroleum as light brown crystals, m.p. 41–42°. (Found: C, 60.05; H, 6.6; Fe, 18.4. $C_{15}H_{20}FeOSi$ calcd.: C, 60.0; H, 6.7; Fe, 18.6%.)

1-Carboxy-1'-(trimethylsilyl)ferrocene (III; $R=CO_2H$)

A solution of the lithioferrocene (II) (0.002 mole) was prepared as described above and poured onto a slush of solid carbon dioxide in ether. The ether solution was extracted with aqueous 2 M sodium hydroxide and the extracts were acidified with hydrochloric acid when the carboxyferrocene (III; $R=CO_2H$) (0.26 g, 78%) separated as a red oil. The oil crystallised from light petroleum as pale yellow needles, m.p. 98–99°. (Found: C, 56.2; H, 5.9; Fe, 18.4. $C_{14}H_{18}FeO_2Si$ calcd.: C, 55.6; H, 6.0; Fe, 18.5%.)

1-(2-Pyridyl)-1'-(trimethylsilyl)ferrocene (III; $R=C_5H_4N$)

A solution of the lithioferrocene (II) (0.002 mole) was prepared as described above. A solution of pyridine (1.0 g, 0.0125 mole) in ether (150 ml) was added, the mixture was heated under reflux for 20 h. The work up was as described above. Light petroleum eluted (trimethylsilyl)ferrocene (0.40 g) and ether eluted the pyridylferrocene (III; $R=C_5H_4N$) (0.14 g, 21%) which was characterised as its picrate. The picrate

was deposited from ethanol as a deep purple solid, m.p. 138–140°. (Found: C, 51.3; H, 4.5; Fe, 9.8. $C_{24}H_{24}FeN_4O_7Si$ calcd.: C, 51.1; H, 4.3; Fe, 9.9%.)

1-(2-Quinoly)-1'-(trimethylsilyl)ferrocene (III; $R = C_9H_6N$)

The above experiment was repeated but quinoline (1.29 g, 0.01 mole) was added to the lithioferrocene (II) (0.004 mole). Benzene/light petroleum eluted the quinolyferrocene (III; $R = C_9H_6N$) (0.43 g, 28%) which was characterised as its picrate. The picrate crystallised from ethanol as purple-black crystals, m.p. 172–174°. (Found: C, 54.55; H, 4.15; Fe, 9.15. $C_{28}H_{25}FeN_4O_7Si$ calcd.: C, 54.8; H, 4.1; Fe, 9.1%.)

1-[(Phenylamino)methyl]-1'-(trimethylsilyl)ferrocene (III; $R = CH_2NHPh$)

The hydroxymethylferrocene (III; $R = CH_2OH$) (1.0 g, 0.0038 mole) and aniline (4.65 g, 0.05 mole) in water (150 ml) were heated under reflux for 60 h. The mixture was extracted with ether and the dried ($MgSO_4$) ether extracts were evaporated to leave a red oil which was chromatographed on alumina. Ether/light petroleum mixtures eluted the aminoferrocene (III; $R = CH_2NHPh$) (0.70 g, 82%)* which crystallised from ethanol/water as yellow needles, m.p. 58–59°. (Found: C, 66.2; H, 6.9; Fe, 15.3. $C_{20}H_{25}FeNSi$ calcd.: C, 66.1; H, 6.9; Fe, 15.4%.) Ether eluted unreacted starting material (III; $R = CH_2OH$) (0.32 g).

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* Yield is based on unrecovered starting material.