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# UNSYMMETRICALLY DISUBSTITUTED FERROCENES
# VI*. THE SYNTHESIS AND REACTIVITY OF SOME 2-SUBSTITUTED FERROCENEMETHANOLS AND -CARBOXALDEHYDES**

G. MARR, B. W. ROCKETT AND A. RUSHWORTH
*Department of Applied Science, Wolverhampton College of Technology, Wolverhampton (Great Britain)*

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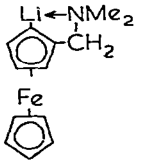
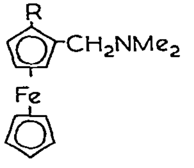
## SUMMARY

The reaction of lithiated [(dimethylamino)methyl]ferrocene with paraformaldehyde and dimethylformamide has given 2-[(dimethylamino)methyl]ferrocenemethanol and 2-[(dimethylamino)methyl]ferrocenecarboxaldehyde, respectively. These aminoferrocenes have been converted into a variety of 1,2-disubstituted ferrocenes. 2-[(Dimethylamino)methyl](methoxymethyl)ferrocene has been reacted with lithium to yield the corresponding (lithiomethyl)ferrocene which was condensed with benzophenone.

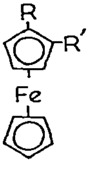
The preparation of several 1,2-disubstituted ferrocenes has been achieved recently[3-9] by the condensation of electrophilic reagents with 2-lithio[(dimethylamino)methyl]ferrocene (I). We now wish to report the use of the lithio-amine (I) in the preparation of some 2-substituted ferrocenemethanols and -carboxaldehydes.



(I)



(II)



(III)

The lithio-amine (I) was condensed with paraformaldehyde[10] to give the amino-alcohol (II; $R=CH_2OH$) which was converted to its methyl ether (II; $R=CH_2OMe$) by treatment with aqueous acetic acid/methanol mixtures. This ether was cleaved by stirring it with lithium in tetrahydrofuran and on condensation of the lithiated intermediate with benzophenone 2-(2-hydroxy-2,2-diphenylethyl)[(dimethylamino)methyl]ferrocene [II; $R=CH_2C(OH)Ph_2$] was obtained.

The amino-alcohol (II; $R=CH_2OH$) was quaternised by methyl iodide, and this methiodide was converted to the diol (III; $R=R'=CH_2OH$) by boiling with

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* For Part V see ref. 1.

** Some of these results have been presented in a preliminary form[2].

aqueous alkali. When this diol was treated with dilute acetic acid a low molecular weight polymer was obtained which corresponded to the self condensation of six molecules of the diol[11,12]. Oxidation of the diol (III; $R=R'=CH_2OH$) with "active" manganese dioxide[13,14] gave a mixture of 2-(hydroxymethyl)ferrocenecarboxaldehyde (III; $R=CH_2OH$, $R'=CHO$) and ferrocene-1,2-dicarboxaldehyde (III; $R=R'=CHO$) and the variation in the yields of these two products with time has been previously recorded[2]. Tirouflet and Moise[15] have also prepared the ferrocene-alcohols (II; $R=CH_2OH$; III; $R=R'=CH_2OH$ and the ferrocenealdehydes (III; $R=CH_2OH$, $R'=CHO$; and $R=R'=CHO$) using similar preparative methods. The monoaldehyde (III; $R=CH_2OH$, $R'=CHO$) was transformed easily to the dialdehyde (III; $R=R'=CHO$) by further treatment with manganese dioxide. The dialdehyde readily formed the disemicarbazone and dioxime, and the oximes of the aldehydes (III: $R=CH_2OH$, $R'=CHNOH$; and $R=R'CHNOH$) were dehydrated to the corresponding cyanides (III; $R=CH_2OH$, $R'=CN$ and $R=R'=CN$) with dicyclohexylcarbodiimide[16].

The lithio-amine (I) was condensed with dimethylformamide[17] to give 2-[(dimethylamino)methyl]ferrocenecarboxaldehyde (II; $R=CHO$) and this aldehyde was also prepared by the oxidation of the amino-alcohol (II; $R=CH_2OH$) with manganese dioxide. The aldehyde (II; $R=CHO$) was unstable in air and it was characterised as its oxime. When the amino-alcohol (II; $R=CH_2OH$) was treated with manganese dioxide some of the dialdehyde (III; $R=R'=CHO$) was isolated which indicated that oxidative degradation of the (dimethylamino)methyl group had occurred[18]. This proposal was supported by the oxidation of [(dimethylamino)-methyl]ferrocene with manganese dioxide to give ferrocenecarboxaldehyde in low yield. 2-[(Dimethylamino)methyl]ferrocenecarboxaldehyde oxime was dehydrated easily to give the cyanide (II; $R=CN$) which was identical with the cyanide obtained from the reaction between cuprous cyanide and 2-bromo[(dimethylamino)methyl]-ferrocene[19].

All of the 1,2-disubstituted ferrocenes prepared in this study contained an unsubstituted cyclopentadienyl ring and as expected[20] absorbed in the IR near to 1100 and 1000 $cm^{-1}$. The region around 900 $cm^{-1}$ has been used by Rosenblum *et al.*[21,22] and Benkeser *et al.*[23] to distinguish between 1,2- and 1,3-disubstitution in ferrocene and all the 2-substituted ferrocenes prepared in this study exhibited absorptions in this region but as we have previously reported[3,4,6] they did not all conform to any simple rule.

## EXPERIMENTAL

For general directions see Part I[5].

### 2-*Lithio*[*(dimethylamino)methyl*]*ferrocene* (*I*)

This compound was prepared in ether from [(dimethylamino)methyl]-ferrocene and a 22% solution of n-butyllithium (10% excess) in hexane at room temperature[7].

### 2-[*(Dimethylamino)methyl*]*ferrocene methanol* (*II*; $R = CH_2OH$)

A suspension of paraformaldehyde (1.45 g, 0.048 mole) in dry ether (50 ml) was added dropwise to a stirred solution of the lithio-amine (I) (0.04 mole) when boiling occurred. The mixture was stirred for 1 h at room temperature, hydrolysed and extracted with ether. The dried ($MgSO_4$) ethereal extracts were evaporated (on a rotary evaporator) to afford a red oil. The oil was chromatographed on alumina, benzene eluted [(dimethylamino)methyl]ferrocene (3.0 g) and methanol ether mixtures eluted 2-[(dimethylamino)methyl]ferrocenemethanol which crystallised from light petroleum as yellow plates (6.51 g, 60%), m.p. 45–46° (lit.[15] oil, b.p. 125–130°/0.5 mm). (Found: C, 61.55; H, 7.2; Fe, 20.4. $C_{14}H_{19}FeNO$ calcd.: C, 61.55; H, 7.4; Fe 20.4%.) The PMR spectrum ($CDCl_3$) showed a broad peak at $\tau$ 4.41 (1 H; hydroxyl proton), a singlet at $\tau$ 5.99 overlapping a multiplet centred at $\tau$ 6.07 (10 protons), doublets centred at $\tau$ 5.28 and $\tau$ 7.30 ($J = 12$ Hz) (2 H; methylene protons)[24,25] and a singlet at $\tau$ 7.89 (6 H; *N*-methyl protons).

The methiodide was obtained by the reaction of the ferrocenemethanol (II; $R = CH_2OH$) with an excess of methyl iodide in methyl cyanide, and crystallised on the addition of dry ether as a light yellow crystalline solid which did not melt, but darkened and decomposed from 203°. (Found: C, 43.5; H, 5.3; Fe, 13.25. $C_{15}H_{22}FeINO$ calcd.: C, 43.4; H, 5.3; Fe, 13.5%.)

### 2-[(*Dimethylamino*)*methyl*](*methoxymethyl*)*ferrocene* (*II*; $R = CH_2OMe$)

2-[(Dimethylamino)methyl]ferrocenemethanol (22 g, 0.081 mole) was dissolved in a mixture of methanol (150 ml) and aqueous 4% acetic acid (150 ml), and this mixture was heated under reflux with stirring for 44 h. The reaction mixture was poured into a slurry of sodium bicarbonate and water. This mixture was extracted with ether and the dried ($MgSO_4$) extracts were evaporated leaving a red oil which was chromatographed on alumina. Ether/methanol mixtures eluted the methyl ether (II; $R = CH_2OMe$) (7.2 g, 44%) as a red oil and it was characterised as its methiodide (see below). Further elution with ether methanol mixtures gave the amino-alcohol (II; $R = CH_2OH$) (6.6 g).

The methiodide of (II; $R = CH_2OMe$) was prepared as described above and was precipitated from methyl cyanide on addition of dry ether as yellow granules, m.p. 201–202°. (Found: C, 44.9; H, 5.6; Fe, 12.9. $C_{16}H_{24}FeINO$ calcd.: C, 44.8; H, 5.6; Fe, 13.0%.)

### 2-(2-*Hydroxy*-2,2-*diphenylethyl*)[(*dimethylamino*)*methyl*]*ferrocene* [*II*; $R = CH_2C(OH)Ph_2$]

The methyl ether (II; $R = CH_2OMe$) (1 g, 0.003 mole) and lithium (0.35 g, 0.05 mole) in tetrahydrofuran (15 ml) were stirred rapidly for 18 h at room temperature. The excess lithium was removed by filtration and the filtrate was added to a stirred solution of benzophenone (3.6 g, 0.02 mole) in dry ether (50 ml). This mixture was left at room temperature for 4 h, hydrolysed and extracted with ether. The dried ($MgSO_4$) ethereal extracts were evaporated to afford a red oil. The oil was chromatographed on alumina, ether eluted the amino-ferrocene [II; $R = CH_2C(OH)Ph_2$] which crystallised from light petroleum as orange-yellow granules (0.4 g, 26%), m.p. 109–110°. (Found: C, 73.8; H, 6.7; Fe, 12.6. $C_{27}H_{29}FeNO$ calcd: C, 73.8, H, 6.65; Fe, 12.7%.) The PMR spectrum ($CCl_4$) showed a singlet at $\tau$ 7.82 (6 H; *N*-methyl protons), a singlet at $\tau$ 6.11 which overlapped with multiplets centred at $\tau$ 6.30 and $\tau$ 6.70 together with singlets at $\tau$ 7.03, 7.23 and 7.43 (12 H; eight cyclopentadienyl ring protons and four methylene protons) and a multiplet centred at τ 2.71 (11 H; ten phenyl protons and one hydroxyl proton). This reaction was repeated several times and the product yields were very variable and sometimes no cleavage of the ether (II; $R = CH_2OMe$) by lithium occurred.

*Ferrocene*-1,2-*dimethanol* (*III*; $R = R' = CH_2OH$)

2-[(Dimethylamino)methyl]ferrocenemethanol methiodide (3.32 g, 0.008 mole) was added to aqueous sodium hydroxide (100 ml, 1 *M*) and the mixture was heated under reflux with stirring for 15 h. The reaction mixture was cooled and extracted with ether and the dried ($MgSO_4$) ethereal extracts were evaporated to give the diol (III; $R = R' = CH_2OH$) (1.35 g, 69%) which crystallised from benzene as yellow plates, m.p. 117–118° (lit.[15] m.p. 116°). (Found: C, 58.7; H, 5.8; Fe, 22.6. $C_{12}H_{14}FeO_2$ calcd.: C, 58.6; H, 5.7; Fe, 22.7%.) The PMR spectrum ($CDCl_3$) showed a broad peak at τ 6.88 (2 H; hydroxyl protons) and a singlet at τ 5.94 partly overlapping a multiplet centred at τ 5.78 (12 H; four methylene protons and eight cyclopentadienyl ring protons).

*Ferrocene*-1,2-*dicarboxaldehyde* (*III*; $R = R' = CHO$) *and* 2-(*hydroxymethylferrocenecarboxaldehyde* (*III*; $R = CH_2OH$, $R' = CHO$)

"Active" manganese dioxide (10 g) was added to a solution of ferrocene-1,2-dimethanol (0.83 g, 0.0034 mole) in chloroform (50 ml) and the mixture was stirred at room temperature for 24 h. The mixture was filtered and the resultant red solution was evaporated to give a dark red oil which was chromatographed on alumina. Benzene/ether mixtures eluted ferrocene-1,2-dicarboxaldehyde (0.72 g, 88%) which crystallised from light petroleum as red needles, m.p. 171° (lit.[15] m.p. 190°). (Found: C, 59.3; H, 4.21; Fe, 23.0. $C_{12}H_{10}FeO_2$ calcd.: C, 59.5; H, 4.2; Fe, 23.1%.) The PMR spectrum ($CDCl_3$) showed singlets at τ −0.35 (2 H; aldehyde protons) and at τ 5.64 (5 H; protons in unsubstituted ring), and an unsymmetrical triplet centred at τ 5.10 overlapping with an unsymmetrical doublet centred at τ 4.81 (3 H; protons in substituted ring). Ether/methanol mixtures eluted 2-(hydroxymethyl)ferrocenecarboxaldehyde (III; $R = CH_2OH$, $R' = CHO$) (0.10 g, 12%) as a red oil which crystallised from light petroleum as orange-red crystals, m.p. 87–88° (lit.[15] oil). (Found: C, 59.0; H, 5.0; Fe, 22.6. $C_{12}H_{12}FeO_2$ calcd.: C, 59.1; H, 5.0; Fe, 22.9%.) The PMR spectrum ($CDCl_3$) showed a singlet at τ 0.04 (1 H; aldehyde proton) and a singlet at τ 5.71 which overlapped with complex multiplets centred at τ 5.37 and τ 6.09 (11 H; eight cyclopentadienyl ring protons, two methylene protons and one hydroxyl proton).

*Reaction of* 2-(*hydroxymethyl*)*ferrocenecarboxaldehyde* (*III*; $R = CH_2OH$, $R' = CHO$) *with manganese dioxide*

A reaction of 2-(hydroxymethyl)ferrocenecarboxaldehyde (0.45 g, 0.0018 mole) with manganese dioxide was carried out as in the preceding experiment to give ferrocene-1,2-dicarboxaldehyde (0.35 g, 82%) which was identical (m.p. and IR spectrum) with a sample of the dialdehyde (II; $R = R' = CHO$) prepared in the previous experiment.

2-(*Hydroxymethyl*)*ferrocenecarboxaldehyde oxime* (*III*; $R = CH_2OH$, $R' = CHNOH$)

Hydroxylamine hydrochloride (0.27 g, 0.004 mole) in water (2 ml) was added to the aldehyde (III; R = $CH_2OH$, R' = CHO) (0.24 g, 0.001 mole) in ethanol (15 ml) and sodium hydroxide (0.4 g, 0.01 mole) was added. The mixture was heated under reflux for 1 h, cooled and poured into water where it was neutralised with solid carbon dioxide. The mixture was extracted with ether and the dried ($MgSO_4$) ethereal extracts were evaporated and the residue was chromatographed on alumina. Elution with methanol/ether mixtures afforded the product (0.18 g, 71%) which crystallised from benzene/light petroleum as light brown plates, m.p. 112–113°. (Found: C, 55.8; H, 5.0; Fe, 21.4. $C_{12}H_{13}FeNO_2$ calcd.: C, 55.6; H, 5.1; Fe, 21.6%.)

*Ferrocene-*1,2*-dicarboxaldehyde dioxime (III; R = R' = CHNOH)*

The reaction of the dialdehyde (III; R = R' = CHO) (0.24 g, 0.001 mole) and hydroxylamine hydrochloride (0.54 g, 0.008 mole) was carried out as in the preceding experiment and afforded a red oil which on chromatography gave the dioxime (III; R = R' = CHNOH) (0.21 g, 78%) which crystallised from benzene/light petroleum as light brown plates, m.p. 105–106°. The elemental analysis of this compound was consistent with two molecules of the dioxime retaining one molecule of benzene. (Found: C, 58.2; H, 4.95; Fe, 17.8; N, 9.1. $C_{30}H_{30}Fe_2N_4O_4$ calcd.: C, 57.9; H, 4.9; Fe, 17.95; N, 9.0%.) The dioxime was deposited from ether/light petroleum as a light brown powder, m.p. 55–60°, and the elemental analysis indicated that no solvent molecules had been retained. (Found: C, 53.1; H, 5.0. $C_{12}H_{12}FeN_2O_2$ calcd.: C, 53.0; H, 4.45%.) When this compound (m.p. 55–60°) was recrystallised from benzene/light petroleum the crystals (m.p. 105–106°) were obtained which were identical with those originally crystallised from a mixture of benzene and light petroleum.

The disemicarbazone of ferrocene-1,2-dicarboxaldehyde was prepared in the usual manner, and it was an orange powder which did not melt below 300° and was deposited from a large quantity of methanol. (Found: C, 47.5; H, 4.65; Fe, 15.7. $C_{14}H_{16}FeO_2N_4$ calcd.: C, 47.2; H, 4.5; Fe, 15.7%.)

2-*(Hydroxymethyl)cyanoferrocene (III; R = $CH_2OH$, R' = CN)*

The oxime (III; R = $CH_2OH$, R' = CHNOH) (0.60 g, 0.002 mole) was added to dicyclohexylcarbodiimide (0.50 g, 0.002 mole) in dry benzene (25 ml) and the mixture was heated under reflux for 20 h. On cooling, dicyclohexylurea was collected by filtration and the mother liquor was concentrated, and the residue was chromatographed on alumina. Methanol/ether mixture eluted 2-(hydroxymethyl)cyanoferrocene (0.38 g, 69%) which crystallised from benzene/light petroleum as yellow needles, m.p. 99–100°. (Found: C, 59.8; H, 4.6; Fe, 23.2. $C_{12}H_{11}FeNO$ calcd.: C, 59.8; H, 4.6; Fe, 23.2%.)

1,2*-Dicyanoferrocene (III; R = R' = CN)*

The reaction of the dioxime (III; R = R' = CHNOH) (0.58 g, 0.002 mole) and dicyclohexylcarbodiimide (1.00 g, 0.004 mole) in benzene was carried out as in the preceding experiment. 1,2-Dicyanoferrocene (III; R = R' = CN) (0.26 g, 60%) was eluted from alumina with benzene and it crystallised from benzene/light petroleum as yellow needles, m.p. 143–144°. (Found: C, 61.0; H, 3.5; Fe; 23.5. $C_{12}H_8FeN_2$ calcd.: C, 61.1; H, 3.4; Fe, 23.7%.)

*Reaction of dilute acetic acid with ferrocene-*1,2*-dimethanol*

The diol (III; R = R' = $CH_2OH$) and 2% acetic acid (100 ml) were heated under reflux for 20 h. On cooling, a pale yellow solid was collected by filtration, and it was crystallised from benzene. It did not melt below 300° but darkened from 230°. (Found: C. 63.4; H, 5.4; Fe, 24.25; mol. wt., 1388. $C_{12}H_{12}FeO$ calcd.: C, 63.2; H, 5.3; Fe, 24.5%; mol. wt., 228 × 6 = 1368.)

### 2-[*(Dimethylamino)methyl*]*ferrocenecarboxaldehyde* (*II*; *R=CHO*)

(*a*) *From dimethylformamide and lithio-amine* (*I*). Dimethylformamide (7.31 g, 0.1 mole) in ether (10 ml) was added dropwise to a solution of the lithio-amine (I) (0.05 mole) which was cooled in ice. The resultant deep red solution was allowed to warm to room temperature and was stirred for 17 h hydrolysed and extracted with ether until the extracts were almost colourless. The dried ($MgSO_4$) ether extracts were evaporated to leave a dark red oil. This oil was dissolved in absolute ethanol (75 ml) and hydroxylamine hydrochloride (10 g) was added. The mixture was heated under reflux for 2.5 h, cooled and poured into a slurry of sodium bicarbonate and water. This mixture was extracted with ether and the dried ($MgSO_4$) extracts were evaporated to leave a dark red oil which was chromatographed on alumina. Ether/benzene mixtures eluted [(dimethylamino)methyl]ferrocene (2.86 g) and elution with methanol/ether mixtures gave 2-[(dimethylamino)methyl]ferrocenecarboxaldehyde oxime (II; R=CHNOH) (6.8 g, 47%) which was deposited from light petroleum as an orange powder, m.p. 103–104°. (Found: C, 58.6; H, 6.35; Fe, 19.3. $C_{14}H_{18}FeN_2$ calcd.: C, 58.8; H, 6.35; Fe, 19.5%.)

(*b*) *Oxidation of* 2-[*(dimethylamino)methyl*]*ferrocenemethanol with manganese dioxide*. The amino-alcohol (II; R=$CH_2OH$) (1.0 g, 0.0036 mole) and "active" manganese dioxide (5 g) were stirred in chloroform (10 ml) for 20 h and the experiment was carried out as described above. Ferrocene-1,2-dimethanol (0.21 g, 24%) (m.p. and IR spectrum identical with those of an authentic sample) was eluted with benzene/ether mixtures, and methanol/ether mixtures eluted the ferrocenecarboxaldehyde (II; R=CHO) (0.64 g, 64%), the oxime of which was identical (m.p. and infrared spectrum) with the oxime (II; R=CHNOH) prepared in the preceding experiment.

The methiodide of (II; R=CHNOH) was prepared as described above and crystallised from methyl cyanide on addition of dry ether as an orange micro-crystalline solid which did not melt but darkened and decomposed from 160°. (Found: C, 42.3; H, 5.1; Fe, 12.95. $C_{15}H_{21}FeIN_2O$ calcd.: C, 42.1; H, 4.95; Fe, 13.05%.)

### 2-*Cyano*[*(dimethylamino)methyl*]*ferrocene* (*II*; *R=CN*)

The oxime (II: R′ = CHNOH) (0.52 g, 0.0018 mole) and dicyclohexylcarbodiimide (0.637 g, 0.0034 mole) were heated under reflux in dry benzene (40 ml) for 6 h as described above. The cyanoferrocene (II; R=CN) was eluted from alumina as a red oil (0.30 g, 49%) which crystallised from light petroleum as red-orange plates (m.p. 71–72° and IR spectrum identical with those of an authentic sample[19]).

### *Oxidation of* [*(dimethylamino)methyl*]*ferrocene with manganese dioxide*

[(Dimethylamino)methyl]ferrocene (1.33 g, 0.0055 mole) and "active" manganese dioxide (5 g) were stirred together in chloroform (10 ml) for 17 h, as previously described. Ferrocenecarboxaldehyde (III; R=CHO, R′=H) (0.15 g, 13%) (m.p. and IR spectrum identical with those of an authentic sample) was eluted from alumina with benzene, and benzene/ether mixtures eluted [(dimethylamino)-methyl]ferrocene (0.823 g).

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