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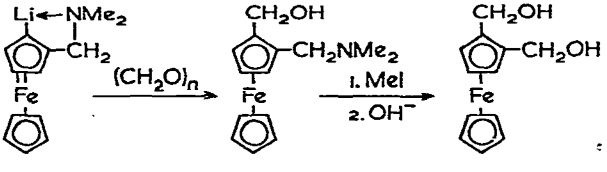
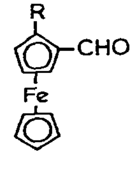
The synthesis of some 2-substituted ferrocene-carbinols and -carboxaldehydes through lithiation

The recent publication by Tirouflet and Moïse[1] on the synthesis of 1,2-diformylferrocene prompts us to report our preparation of some 2-substituted ferrocene-carbinols and -carboxaldehydes through 2-lithio-1-[(dimethylamino)methyl]-ferrocene (I)[2]. We have used this intermediate previously in the synthesis of 1,2-disubstituted ferrocenes[2,3].

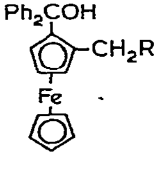
The lithioamine (I) was condensed with paraformaldehyde[4] to give the amino-alcohol (II) m.p. 45–46° in 75% yield (lit.[1] oil b.p. 125–130°/0.5 mm) which was quaternised by methyl iodide. This methiodide was smoothly converted to the diol (III) m.p. 118° (lit.[1] 116°) in 69% yield on boiling with aqueous sodium hydroxide. Oxidation of the diol (III) with "active" manganese dioxide[5] in chloroform over 12 h gave a mixture of 2-(hydroxymethyl)formylferrocene (IV) m.p. 88° in 50% yield (lit.[1] oil) and 1,2-diformylferrocene (V) m.p. 171° in 50% yield (lit.[1] 190°), and these products were separated by chromatography on alumina. After reaction for 24 h the predominant component (87%) of the product was the dialdehyde (V), whereas after 3 h 76% of the hydroxyaldehyde (IV) was obtained.



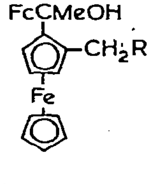
(I) (II) (III)



(IV, $R = CH_2OH$)
(V, $R = CHO$)
(VII, $R = CPh_2OH$)



(VI, $R = OH$)
(VIII, $R = NMe_3I$)



(IX, $R = NMe_2$)
(X, $R = OH$)

$Fc = C_{10}H_9Fe$

2-(Diphenylhydroxymethyl)formylferrocene (VII) m.p. 235–236° was prepared similarly in 88% yield by the oxidation of 2-[(diphenylhydroxymethyl)ferrocene]methanol (VI)[2] and by the Sommelet reaction of the methiodide of 2-[(diphenylhydroxymethyl)dimethylaminomethyl]ferrocene (VIII), the aldehyde (VII) was also characterised as its oxime m.p. 206.5–208°.

The lithioamine (I) was also condensed with acetylferrocene to give the diferrocenylcarbinol (IX) m.p. 162° in 30% yield which was converted to the diol (X) m.p. 78° in 48% yield through the reaction of the corresponding methiodide with boiling aqueous sodium hydroxide.

All new compounds gave satisfactory analyses for three or more elements and exhibited the expected infrared absorption spectra.

Further transformations of the lithioamine (I) and the derived alcohols and carbonyl compounds are under investigation.

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