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# METALLATION OF FERROCENE WITH n-BUTYLPOTASSIUM

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## Summary

The metallation of ferrocene with n-butylpotassium, prepared in situ from potassium (—)(1*R*)-menthoxide and n-butyllithium, has been studied. The reaction is a convenient method of producing 1,1'-dimetallated ferrocene in good yield. Using a large excess of n-butylpotassium, mixtures are obtained containing up to 8 metal atoms in the ferrocene rings.

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## Introduction

Many studies have been made of the metallation of ferrocene, particularly using organolithium compounds as metallating agents, and the combination of n-butyllithium and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMED) is a very convenient reagent for the preparation of 1,1'-dilithioferrocene [1]. As part of our studies [2,3] on [1]ferrocenophanes we needed a source of 1,1'-dimetallated ferrocene formed in the absence of a tertiary amine. Thus it was decided to investigate the metallation of ferrocene using organopotassium reagents. Some studies have been reported of the metallation of ferrocene with organosodium compounds, but even after long reaction times, the yields of dimetallated species were quite low [4—6]. There do not appear to be any reports of the use of organopotassium compounds to metallate ferrocene.

## Results

We have found that ferrocene is rapidly metallated by a suspension of n-butylpotassium in hexane and that the predominant product is the 1,1'-dimetallated ferrocene. The n-butylpotassium was prepared in situ from potassium (—)(1*R*)-menthoxide and n-butyllithium [7]. When potassium (—)(1*R*)-menthoxide was suspended in a solution of ferrocene in hexane and n-butyllithium was added to the mixture, a red precipitate formed immediately. After 30 min stirring, either the precipitate was washed with hexane and then treated with an excess of deuterium oxide, or in some cases the total reaction mixture was treated with an

TABLE 1

DEGREE OF METALLATION ($C_{10}H_{10-x}FeK_x$)

| | n-BuK/$C_{10}H_{10}Fe$ (mol. ratio) | $x$ | Washed precipitate | | Total product | |
|---|---|---|---|---|---|---|
| | | | Composition (%) | Yield (%) | Composition (%) | Yield (%) |
| A | 2.0/1 [a] | 0 | 0.4 | | 5.3 | |
| | | 1 | 18.1 | | 17.2 | |
| | | 2 | 66.0 | 92.8 | 62.8 | 97.6 |
| | | 3 | 12.2 | | 11.6 | |
| | | 4 | 3.4 | | 3.2 | |
| B | 2.5/1 [a] | 0 | — | | 0.4 | |
| | | 1 | 10.7 | | 10.7 | |
| | | 2 | 74.3 | 97.6 | 73.9 | 98.1 |
| | | 3 | 10.8 | | 10.7 | |
| | | 4 | 4.3 | | 4.3 | |
| C | 20/1 [b] | 1 | | | 0.5 | 79.0 |
| | | 2 | | | 2.0 | |
| | | 3 | | | 9.4 | |
| | | 4 | | | 29.1 | |
| | | 5 | | | 22.8 | |
| | | 6 | | | 18.1 | |
| | | 7 | | | 9.8 | |
| | | 8 | | | 5.5 | |
| | | 9 | | | 2.2 | |
| | | 10 | | | 0.6 | |

[a] Reaction time 30 min at 20°C. [b] Reaction time 22 h at 20°C.

excess of deuterium oxide. The deuterated ferrocene was then recovered by column chromatography on alumina.

The relative amount of each deuterated species present in the deuterated ferrocene was determined from mass spectral measurements of the molecular ions. It has been shown that exchange of hydrogen for deuterium in the mass spectrometer does not occur readily and is of low significance in studies on ferrocene [8]. The results of the metallation studies are shown in Table 1 (A and B).

## Discussion

Using a molar ratio of n-butylpotassium to ferrocene of 2.5/1, ferrocene is rapidly converted in high yield to a solid which is predominantly the dimetallated species, but significant amounts of mono- and tri-metallated species are also formed. From a study of the mass spectral measurements of the intensities of peaks at *m/e* 121, 122, 123 and 124, due to the fragments $C_5H_5Fe^+$, $C_5H_4DFe^+$, $C_5H_3D_2Fe^+$, $C_5H_2D_3Fe^+$ respectively, it can be concluded that 1,1′-rather than 1,2-disubstitution and 1,2,1′- rather than 1,2,3-trisubstitution had taken place. Compared with the use of n-butyllithium/TMED as a metallating agent for ferrocene, n-butylpotassium is less selective in the formation of the 1,1′-dimetallated species.

In view of the rapid reaction of n-butylpotassium with ferrocene and the formation of some tri- and tetra-metallated species it was decided to investigate the metallation reaction using a large excess of n-butylpotassium, (Table 1, C). The results show that significant amounts of hepta- and octa-metallated species were produced. This compares with the use of a large excess of n-butyllithium/TMED where the hepta-metallated species was the highest metallated species produced in significant amounts.

Ferrocene can therefore be metallated cleanly and rapidly by n-butylpotassium in hexane, to give in good yield a product containing predominantly the 1,1'-dimetallated species. This has already been of use in the preparation of [1]ferrocenophanes and further work is in progress.

## Experimental

The preparations of all metallated ferrocenes were carried out under an atmosphere of oxygen-free, dry nitrogen, using dried, degassed solvents.

Potassium (—)(1*R*)-menthoxide was prepared from (—)(1*R*)-menthol (3.91 g, 25 mmol) and potassium (2.0 g, 51 mmol) by stirring and heating under reflux in hexane for 48 h. After cooling, the white suspension of potassium (—)(1*R*)-menthoxide was decanted from excess potassium.

### *General procedure for metallating ferrocene (Table 1, B)*

Ferrocene (1.86 g, 10 mmol) was added to a stirred suspension of potassium (—)(1*R*)-menthoxide (25 mmol) in hexane (100 $cm^3$). After the ferrocene had dissolved, n-butyllithium (25 mmol) was added and a red precipitate formed immediately. The mixture was stirred for 30 min and then the solid allowed to settle. After removing the supernatant liquid by syringe the solid was washed with hexane (100 $cm^3$). The hexane was removed by syringe and combined with the supernatant liquid. After the addition of further hexane (100 $cm^3$) to the solid, it was treated with deuterium oxide (1.5 $cm^3$, 38 mmol) and stirred for 10 min. The orange solution was dried over magnesium sulphate, filtered and the hexane removed under reduced pressure. The solid was dissolved in the minimum volume of a 1/1 (v/v) mixture of toluene/petroleum ether (b.p. 60—80°C) and chromatographed on a column of Grade I neutral alumina using the same solvent mixture as eluent. The deuterated ferrocene recovered from the column contained traces of an unidentified involatile oil, and final purification of the ferrocene was effected by sublimation under reduced pressure.

Mass spectra were recorded on a Hitachi—Perkin—Elmer RMU-6.

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