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An improved synthesis of ferrocene-1,1'-dicarbaldehyde

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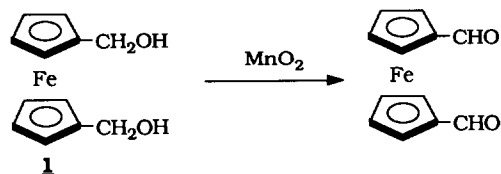
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Abstract

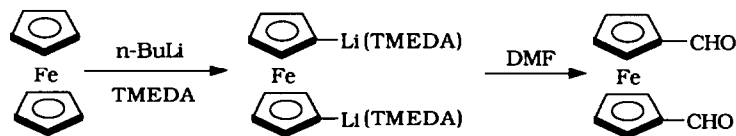
Ferrocene-1,1'-dicarbaldehyde has been prepared in 70% yield in a one-pot procedure from dilithioferrocene-TMEDA complex and dimethylformamide.

Introduction

Derivatives of ferrocene have been widely studied because of their value as starting materials in both organic and organometallic chemistry. In 1961 Osgerby and Pauson [1] reported the preparation of ferrocene-1,1'-dicarbaldehyde in modest yield by oxidation of 1,1'-bishydroxymethylferrocene, **1**, with MnO_2 [2]. Compound **1** was in turn prepared in a three-step procedure starting from ferrocene [3].



Recently, compound **1** was prepared [4] in 54% yield from 1,1'-dilithioferrocene-TMEDA [5,6] and paraformaldehyde. We report a much simpler and efficient synthesis of ferrocene-1,1'-dicarbaldehyde directly from ferrocene in good yield by treating the dilithioferrocene-TMEDA complex with dimethylformamide (DMF) [7].



Experimental

The reaction was carried out in a Schlenk-type apparatus under argon. Ferrocene (5 g, 26 mmol) in 60 ml of dry ether was treated with 35.3 ml of 1.6 M

n-butyllithium (56 mmol) in hexane, and subsequent addition of 8.5 ml of tetramethylethylenediamine (TMEDA) (56 mmol) [4,5]. The reaction mixture was stirred for 20 h, then 6.5 ml of DMF (previously dried over CaH_2 and distilled) was added dropwise at -78°C . After 2 h stirring, the mixture was hydrolysed at -78°C . The organic phase was extracted with CH_2Cl_2 and dried over MgSO_4 , and the solvent then removed. Two crystallisations from cyclohexane gave ferrocene-1,1'-dicarbaldehyde (4.55 g, 18.8 mmol) as shiny red crystals in 70% yield. [NMR in (CDCl_3) 200 MHz (δ): 4.65 ppm (s, 4H); 4.9 ppm (s, 4H); 10 ppm (s, 2H). Analysis: Found: C, 59.76; H, 4.17. Calc.: C, 59.54; H, 4.16%.

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