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Preliminary communication

METALATION OF FERROCENE WITH n-PENTYLSODIUM. EXAMINATION OF THE REACTION IN THE PRESENCE AND ABSENCE OF *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE (TMEDA)*

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Summary

The metalation of ferrocene with n-pentylsodium in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) for 1 h at room temperature gave approximately 90% 1,1'-disodioferrocene and 10% sodioferrocene in near quantitative yields. In the absence of TMEDA, metalation proceeded in a much lower overall yield (20—25%) giving, in addition to the above products, compounds resulting from polymetalation of ferrocene. Overall yields and product distributions were obtained, in all cases, by gas chromatographic analysis of the trimethylsilylferrocene derivatives obtained by treating the reaction with trimethylchlorosilane.

Several laboratories have recently reported that n-pentylsodium is strongly activated as a metalating agent by *N,N,N',N'*-tetramethylethylenediamine (TMEDA). For instance, Trimitsis and co-workers [1] found that both 1,3-dimethylnaphthalene and *m*-xylene were quantitatively dimetalated by n-pentylsodium in the presence of TMEDA. In the absence of TMEDA, monometalation occurred in low yield. Additionally, this laboratory [2] has shown that both ethylbenzene and cumene were metalated by the n-pentylsodium/TMEDA reagent to give, with time, α-methylbenzylsodium or α-cumylsodium. In the cumene system the overall yields were ∿65% and, in the ethylbenzene reaction, the overall yields were nearly quantitative. In the absence of TMEDA, the overall yields were much lower and considerable amounts of ring-metalated products in addition to the side-chain products were observed, even after extended reaction times [3].

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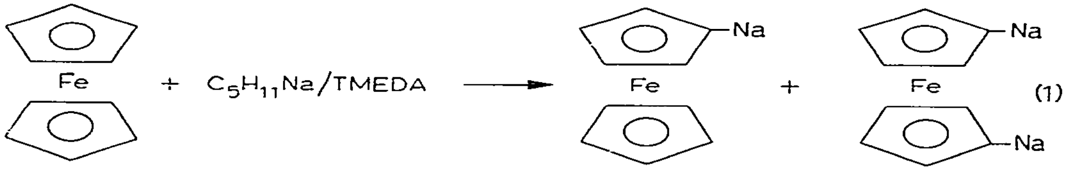
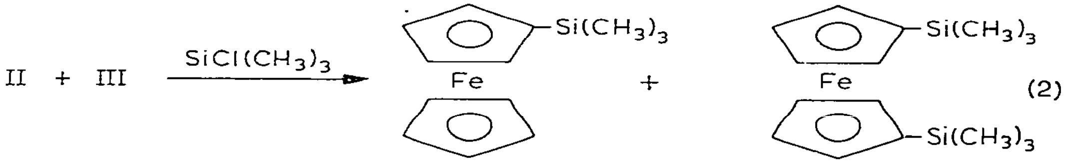
We now wish to report that the reaction* of ferrocene(I) (0.05 mol) with n-pentylsodium (∿0.07 mol) in the presence of TMEDA (0.15 mol) for 1 h at room temperature gave a mixture of 10—15% of sodioferrocene(II) and 85—90% of 1,1′-disodioferrocene(III) in nearly quantitative overall yields** (90—100%). Increasing the ferrocene concentration to 0.2 mol while holding the n-pentylsodium and TMEDA concentrations constant did not change the overall yields or product distribution significantly. Additionally, when the reaction was studied as a function of time from 1 min to 24 h, the product distribution was found to be essentially invariant. We also observed in this experiment that the concentration of unreacted ferrocene remained approximately constant after 1 min, indicating that reaction 1 is essentially complete within this time period.



(I) (II) (III)

The metalation mixtures were analyzed by adding trimethylchlorosilane, thus converting the sodioferrocenes to their corresponding trimethylsilyl derivatives. These compounds then were analyzed for product composition and overall yield by gas chromatography (GC). The analysis of an authentic mixture of IV and V established the validity of this analytical procedure.



(IV) (V)

When 0.05 mol of ferrocene was metalated with ∿0.07 mol of n-pentylsodium in the absence of TMEDA at room temperature for 1 h, an overall yield of only ∿20—25% was realized consisting of approximately 20% II, 60% III and 20% polysodioferrocenes of the type $C_{10}H_{10-n}FeNa_n$ (n = 3 to 6). As in the experiments using TMEDA, changing the ferrocene concentration did not significantly alter the product distribution or yield.

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*In a typical experiment, the n-pentylsodium was prepared in a Morton flask (high speed stirring apparatus) by the dropwise addition of 10.7 g (0.1 mol) of 1-chloropentane in 25 ml of octane to a 5.75 g (0.25 mol) sodium dispersion in 100 ml of octane at −10 to −20°C over 1.5 h. The mixture was stirred for an additional 0.5 h at −10 to −20°C before 9.3 g (0.05 mol) of sublimed ferrocene and 17.4 g (0.15 mol) of freshly distilled TMEDA were added to the mixture. After the resulting mixture was stirred for 1 h at room temperature, 27.2 g (0.25 mol) of distilled trimethylchlorosilane was added to the flask in a rapid dropwise fashion. The reaction mixture was stirred for at least 1 h at room temperature before 50 ml of methanol and 50 ml of water were added to the flask to destroy unreacted sodium and trimethylchlorosilane. This mixture was then worked up using standard extraction techniques and analyzed employing gas chromatography.

**Percentage yields were based on an assumed 70% production of n-pentylsodium.

The identity of the polysodioferrocenes was determined by isolating their corresponding trimethylsilyl derivatives by vacuum distillation and preparative GC. Mass spectral analysis of these GC fractions showed signals at *m/e* values 402, 474, 546 and 618 which were assigned to the parent ions of the tris-, tetrakis-, pentakis-, and hexakis-(trimethylsilyl)ferrocene derivatives, respectively. These compounds presumably arose from the reaction of trimethylchlorosilane with the corresponding polysodioferrocenes formed in the metalation reaction in the absence of TMEDA. These findings parallel those of Halasa and Tate [4] who reported that ferrocene was polylithiated by n-butyllithium in the presence of TMEDA at 70°C for 5 h.

Previous work involving the metalation of ferrocene with organosodium reagents was largely non-quantitative in nature and was carried out in the absence of TMEDA. Nesmeyanov [5] reported that ferrocene was dimetalated with either n-pentylsodium or phenylsodium giving only insignificant quantities of monometalation. However, Seyferth [6] later reported that significant quantities of monosodioferrocene were also observed in addition to the disodio compound. In both cases, yields were poor and no polymetalated products were reported. When Benkeser and co-workers [7] examined the metalation of ferrocene with n-pentylsodium, they found evidence for trimetalation in addition to mono- and di-metalation. In a related experiment, Rausch and Ciappenelli [8] reported that the metalation of ferrocene with n-butyllithium in the presence of TMEDA in hexane for 6 h gave 98% 1,1′-dilithioferrocene and only 1.8% lithioferrocene as adjudged by carbonating the reaction and isolating the resulting carboxylic acids.

Work is currently underway in our laboratory to examine the kinetic and/or thermodynamic factors in the ferrocene metalation reaction. Additionally, the structures of the polytrimethylsilylferrocenes are being studied to determine the orientation of these substituents on the ferrocene rings.

Acknowledgements

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