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REACTIONS OF n-BUTYLLITHIUM WITH HALOFERROCENES AS ROUTES TO LITHIOFERROCENE

Frederick L. Hedberg and Harold Rosenberg
Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433

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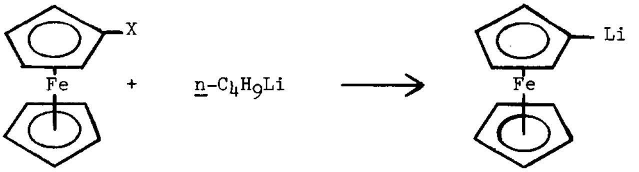
Lithioferrocene has proved to be a useful intermediate for the preparation of monosubstituted derivatives of ferrocene[1]. The only two routes to lithioferrocene previously reported are either the direct abstraction of a proton from ferrocene by an alkyllithium[2-5] (equation 1a) or an exchange reaction between chloromercuriferrocene and an alkyllithium[6-7] (equation 1b). The former reaction leads to either a mixture of lithioferrocene and 1,1'-dilithioferrocene[2-4] or a low yield of lithioferrocene[5]. The latter is complicated by the concurrent formation of a toxic and reactive dialkylmercury compound which, in this laboratory, has led to the formation of both alkylated and mercury-containing derivatives of ferrocene as undesirable side products[8].



(1a) X = H
(1b) X = HgCl
(1c) X = Br
(1d) X = I

We have found that the exchange reaction of stoichiometric amounts of n-butyllithium with bromoferrocene[9] and iodoferrocene[9] (equations 1c and 1d) affords high yields of lithioferrocene with no concurrent dilithiation. Optimum conditions involved the use of ether as solvent with addition of n-butyllithium at -70°. With iodoferrocene, complete reaction takes place at -70° over a 20-min. period, while with bromoferrocene it is necessary to allow the reaction mixture to warm to 0° over a 15-min. period to effect completion of the halogen-metal exchange.

From reaction 1c yields[10] ranged from 89-99%, while from reaction 1d yields were somewhat lower, ranging from 84-89%. The effect of higher reaction temperature upon yield was observed by carrying out both lithiations 1c and 1d at 0° for 15 min. The yield from 1c was lowered only slightly to 89-92%, while the yield from 1d was affected more, dropping to 70%. The previously reported[8] use of tetrahydrofuran (THF) as solvent in this reaction had a pronounced deleterious effect, affording yields of 40-75% for 1c either at 0° or -70°.

The high yields obtained from the above-described reactions, together with the absence of any reactive side products, appear to make halogen-metal exchange the preferred synthetic route to lithioferrocene.

The halogen-metal exchange reaction between bromoferrocene or iodoferrocene and n-butyllithium may be contrasted with the α-hydrogen abstraction which occurs upon reaction of chloroferrocene with n-butyllithium[11]. We have found no evidence of any metal-halogen exchange occurring in the latter reaction when run either in ether or in THF. (THF is the solvent of choice for the synthesis of 2-substituted chloroferrocenes via a 2-lithiochloroferrocene intermediate, since yields in excess of 85% can be obtained in 1.5 hrs. at 0° while much longer reaction times and higher temperatures are required to attain maximum yields in ether).

Initial results from a study involving extension of the halogen-metal exchange reaction to 1,1'-dibromoferrocene and 1,1'-diiodoferrocene indicate that yields of 1,1'-dilithioferrocene in excess of 70% may be obtained, but with some concurrent formation of lithioferrocene.

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