The Formation of the αα-Ferrocenyldicarbanion: a Novel Displacement of Cyanide by n-Butyl-lithium

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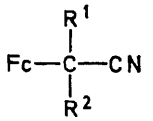
Summary The αα-ferrocenyldicarbanion was prepared by the action of n-butyl-lithium on ferrocenylacetonitrile: when ferrocenyl-αα-dibenzylmethylcyanide was treated with n-butyl-lithium displacement of the cyanide group occurred.

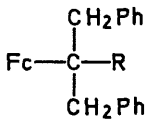
THE α-ferrocenylcarbonium ions are unusually stable[1] and they have received considerable attention but the corresponding α-ferrocenylcarbanions have not been well investigated.

We have now prepared the αα-ferrocenyldicarbanion by treatment of ferrocenylmethylcyanide (I; R^1 and $R^2 = H$)[2] with n-butyl-lithium at room temperature for fifteen minutes. The ready formation of this dicarbanion indicates that the protons on the α-carbon atom are quite acidic and presumably here the ferrocenyl group behaves as a typical

aromatic nucleus and helps to stabilize the carbanion by enhancing charge delocalization.[3] The dilithio-derivative (I; $R^1 = R^2 = Li$) was condensed with benzyl chloride and methyl iodide to give the ferrocenyl-cyanides (I; $R^1 = R^2 = CH_2Ph$) and (I; $R^1 = R^2 = Me$) in 70 and 60% yields respectively. The ^1H n.m.r. spectrum of the benzyl derivative (I; $R^1 = R^2 = CH_2Ph$) exhibited signals at τ (CCl_4) 2·73 (10H, m, 2Ph), 5·83 (5H, s, unsubstituted cyclopentadienyl ring protons), 5·95 (2H, m, substituted ring protons), 6·14 (2H, m, substituted ring protons) and 6·96 (4H, s, methylene protons): principal i.r. absorption frequencies (KBr) 704vs, 760vs, 830vs, 1005s, 1105s, 1430vs, 1500s, and 2230w cm^{-1}.



(I)



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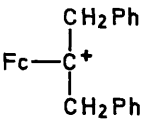
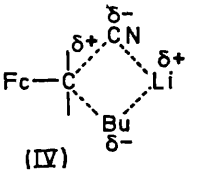
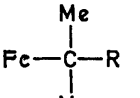


(III)

When the cyanide (I; $R^1 = R^2 = CH_2Ph$) was treated with n-butyl-lithium the expected ketone (II; R = COBu) was not isolated, but displacement of the cyanide occurred and on hydrolysis the monosubstituted ferrocene (II; R = H) was isolated. This indicated that the α-ferrocenylcarbonium ion (III) was formed readily by nucleophilic attack of the n-butyl-lithium on the α-carbon atom. When the reaction mixture was treated with deuterium oxide the presence of the deuteriated derivative (II; R = D) in the product could not be detected (mass spectrum and ^1H n.m.r.) and the protonated compound (II; R = H) was isolated. This suggested that the displacement of cyanide by n-butyl-lithium proceeded *via* a four-centred transition state (IV) and that the α-ferrocenylcarbonium ion abstracted a proton from the butyl moiety to give the protonated derivative (II; R = H) before hydrolysis occurred. When the ferrocenyl-cyanide (I; $R^1 = R^2 = Me$) was treated with n-butyl-lithium under similar reaction conditions C–CN bond cleavage did not occur but the lithium reagent added to the cyanide group



(IV)



(V)

in the conventional manner to give the expected butyl ketone (V; R = COBu).

All new compounds exhibited the requisite analytical and spectral properties.

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[1] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.
[2] J. M. Osgerby and P. L. Paulson, *J. Chem. Soc.*, 1958, 656.
[3] D. C. Ayres, 'Carbanions in Synthesis," Oldbourne Press, London 1966, pp. 1—2.