An Abnormal Grignard Product. The Reaction of Benzoylferrocene with Methylmagnesium Halides

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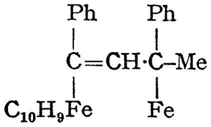
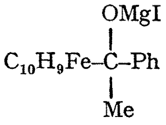
RECENT work on reductive reactions of metallocenyl ketones has uncovered a surprising array of molecules.[1] In particular, Horspool and Sutherland reported[2] that acylmetallocenes react with alkylmagnesium iodides to yield ferrocenylethylenes.

We required 1-ferrocenyl-1-phenylethylene in connection with other studies, and Horspool and Sutherland's work suggested that it might be conveniently synthesized by the reaction of methylmagnesium iodide with benzoylferrocene. Accordingly, we heated a benzene–ether solution of MeMgI (0·013 mole) and benzoylferrocene (0·0034 mole) under reflux for 1 hr., worked-up the reaction with aqueous ammonium chloride, and then analysed the reaction mixture by t.l.c.[3] No alcohol was evident, only a compound with R_F 0·9. Crystallization of the reaction mixture from *n*-hexane afforded compound (I) (320 mg.) as a yellow-orange crystalline solid, m.p. 139·0—142·5°. The analysis and mass spectrum, of (I) indicated the formula $C_{36}H_{32}Fe_2$. The n.m.r. spectrum (CCl_4) showed one methyl group as a singlet at τ 8·6. Upon catalytic micro-hydrogenation, compound (I) absorbed 1 mole of hydrogen; ozonization of (I) led to benzoylferrocene. These results indicate that (I) is an unusual olefinic dimer—presumably formed *via* addition to the olefin by the intermediate carbonium ion postulated by Horspool and Sutherland.[2]



$\underset{\mathrm{C_{10}H_9Fe}}{\overset{\mathrm{Ph}}{\mathrm{C}}}{=}\mathrm{CH}{\cdot}\underset{\mathrm{Fe}}{\overset{\mathrm{Ph}}{\mathrm{C}}}{-}\mathrm{Me}$

(I)



$\mathrm{C_{10}H_9Fe}{-}\underset{\mathrm{Me}}{\overset{\mathrm{OMgI}}{\mathrm{C}}}{-}\mathrm{Ph}$

(II)

While at present a more detailed mechanism for the formation of (I) is unclear, the importance of the intermediate alkoxymagnesium iodide (II) would seem assured, since (I) was also obtained by treating ferrocenylmethylphenylmethanol with methylmagnesium iodide. In our hands, when methylmagnesium bromide and benzoylferrocene reacted under the conditions described above for methylmagnesium iodide and benzoylferrocene, the main product was 1-ferrocenyl-1-phenylethylene.

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[2] W. M. Horspool and R. G. Sutherland, *Tetrahedron Letters*, 1967, 4165.

[3] R. E. Bozak and J. H. Fukuda, *J. Chromatog.*, 1967, **26**, 501.