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AN ABNORMAL GRIGNARD REACTION OF ALKYL MAGNESIUM IODIDES - A CONVENIENT SYNTHESIS OF FERROCENYLETHYLENES.[1]

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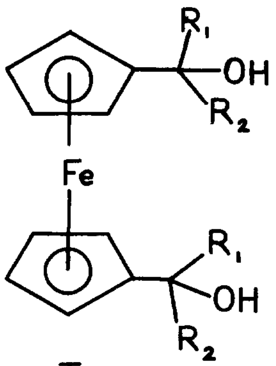
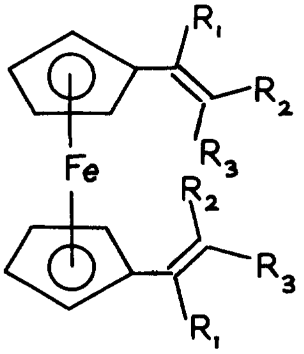
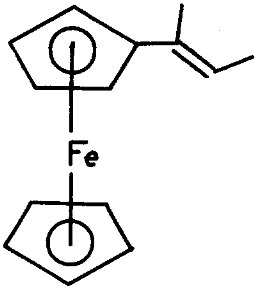
In an extension of our work on the synthesis of ferrocenophanes[1a] we required diols of the general structure (I). Several of these diols are described in the literature, and in particular, Ia(R_1=R_2=CH_3) has been synthesised in 56% yield by the reaction of 1,1 -diacetylferrocene and methyl magnesium iodide.[2] Reinvestigation of this reaction showed that the low yield of diol was attributable to concomitant formation of the bis olefin (IIa, R_1=CH_3, R_2=R_3=H) in 32% yield. This is a very convenient synthesis of 1,1 -bis-isopropenylferrocene since the other routes to this compound involve the prior formation of dimethylfulvene[3] or methylenetriphenyl phosphorane.[1] Another attempt at its preparation led to the formation of polymeric material.[2]



I



II



III

Since previous workers[2,4,5] have shown that attempts to prepare bis olefins of the general structure (II) lead either to cyclic ethers or polymers we have attempted to explore the generality of this reaction. In the cases we have examined the use of alkyl magnesium iodides leads to the formation of the most highly substituted olefin while the corresponding bromides give excellent yields of the diols without any trace of olefin. The reaction is not confined to bis olefin since the mono olefin, 2-ferrocenylbut-2-ene(III) can be obtained in 68% yield from the reaction of acetylferrocene with ethyl magnesium iodide.

Typically a solution of the acyl ferrocene in benzene is added to an excess of the alkyl magnesium iodide in dry ether. The reaction mixture is left at room temperature overnight before quenching with ice-water. T.L.C. examination shows the presence of olefin at this stage - neither ammonium chloride nor acid work-up conditions are necessary for olefin formation. It is also important that the corresponding diols are obtained from these reactions are stable under these conditions. The olefin can conveniently be separated from all other products by chromatography on alumina. The diols were also purified by chromatography and are stable under the conditions used. Our results are shown in the table.

TABLE

ACYL FERROCENE		CH_3MgI	C_2H_5MgI	C_2H_5MgBr
1,1 -diacetyl	Olefin%	32 (IIa. $R_1=CH_3$) $R_2=R_3=H$	41% (IIb. $R_1=R_2=CH_3$) $R_3=H$	NIL
	Diol.%	56 (Ia. $R_1=R_2=CH_3$)	56% (Ib. $R_1=CH_3$) $R_2=C_2H_5$	88% (Ib. $R_1=CH$) $R_2=C_2H_5$
1,1 -dipropionyl	Olefin%	49 (IIb. $R_1=R_2=CH_3$) $R_3=H$	26% (IIc. $R_1=C_2H_5$) $R_2=CH_3$ $R_3=H$	- - -
	Diol.%	47 (Ib. $R_1=CH_3$) $R_2=C_2H_5$	62% (Ic. $R_1=R_2=C_2H_5$)	- - -
Acetyl	Olefin%	- - -	68% (III)	NIL
	Diol.%	- - -	20% (IV)	50%[6]

Elimination of HOMgX from a Grignard reagent is not without precedent,[7] but the reaction conditions employed are usually severe involving the use of acid and/or refluxing solvents. It is tempting to postulate that this facile reaction involves ionisation of the magnesium alcoholate to give an intermediate ferrocenyl carbinyl carbonium ion which have been shown to be remarkably stable.[8] The specificity of iodide in this reaction still requires clarification.

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