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Abstract

Full Text

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REDUCTION OF FERROCENECARBOXYLIC ACIDS

In our previous work ([1]) it was shown that ferrocene is metalated by butyllithium, giving a mixture of mono- and dilithium derivatives which, upon carboxylation, form a mixture of ferrocenemonocarboxylic and ferrocenedicarboxylic acids.

In the present work, ferrocenyl lithium and ferrocenecarboxylic acids have been used to obtain several other ferrocene derivatives, and it has been shown that ferrocene is readily metalated by phenylsodium ([2]), giving, after carboxylation, ferrocenedicarboxylic acid in 42% yield.

To phenylsodium, prepared in benzene from 10 g of sodium and 21 g of chlorobenzene ([3]), 18.6 g of ferrocene is added. The mixture is left overnight, then heated to boiling with stirring for 8 hours and poured onto solid carbon dioxide. Benzoic acid is removed by steam distillation. The air-dried ferrocenedicarboxylic acid is treated twice with hot benzene to remove the small amount of ferrocenemonocarboxylic acid formed. 55% of the ferrocene is recovered unchanged. The yield of ferrocenedicarboxylic acid is 42% of the theoretical amount and 94% based on the ferrocene that entered into the reaction.

The methyl ester of ferrocenedicarboxylic acid is readily reduced by $LiAlH_4$ not only to the corresponding alcohol, but also to dimethylferrocene. 1,1′-Di(hydroxymethyl)ferrocene was obtained by heating for two hours an ethereal solution of the methyl ester of ferrocenedicarboxylic acid (2 g) with an excess of lithium aluminum hydride $LiAlH_4$, prepared from 0.6 g of LiH and 5 g of $AlBr_3$. The yield of di(hydroxymethyl)ferrocene was 92% of theory, m.p. 85–86°; it crystallizes from alcohol and from a mixture of ether with petroleum ether.

Found, %:	C 58.66; 58.73; H 5.89; 5.81; Fe 22.39
$C_{12}H_{14}O_2Fe$. Calculated, %:	C 58.56; H 5.73; Fe 22.69

When the methyl ester of ferrocenedicarboxylic acid was heated for three hours with twice the above-indicated amount of $LiAlH_4$, 1,1′-dimethylferrocene was obtained (yield 89%, m.p. 29–30°); it dissolves very readily in organic solvents

and crystallizes on cooling to −10° from alcohol and from a mixture of petroleum ether with ether.

Found, %:	C 67.53;	67.70;	H 6.89;	6.81;	Fe 25.73;	25.36	
$C_{12}H_{14}Fe$. Calculated, %:	C 67.31;		H 6.59;		Fe 26.08		

Reduction of the methyl ester of ferrocenemonocarboxylic acid with lithium aluminum hydride gave ferrocenylcarbinol, yield 73%, m.p. 74-75°; it was purified by chromatographic adsorption on aluminum oxide and crystallizes from alcohol and from a mixture of ether with petroleum ether.

Found, %:	C 61.61;	61.66;	H 6.09;	5.83;	Fe 25.67;	25.46	
$C_{11}H_{12}OFe$. Calculated, %:	C 61.19;		H 5.60;		Fe 25.84		

Lithium aluminum hydride very readily reduces alcohols of the ferrocene series. Thus, upon reduction with $LiAlH_4$, 1,1′-di(diphenyloxymethyl)ferrocene gives 1,1′-dibenzhydrylferrocene in 87% yield, previously described by Pauson ([4]). Dibenzhydrylferrocene crystallizes well from benzene, m.p. 161-162°. Literature data ([4]): m.p. 162-163°.

Found, %:	C 83.43;	83.30;	H 6.01;	6.11;	Fe 11.17;	11.20	
$C_{36}H_{30}Fe$. Calculated, %:	C 83.39;		H 5.79;		Fe 10.81		

Di(diphenyloxymethyl)ferrocene was obtained by us in 51% yield upon the interaction of methyl ferrocenedicarboxylate with phenylmagnesium bromide, and also by the action of benzophenone on dilithioferrocene; in the latter case the yield was low; m.p. 179-180°. Both substances are identical with one another and with di(diphenyloxymethyl)ferrocene obtained by the interaction of dibenzoylferrocene with phenylmagnesium bromide, described by Riemschneider and Helm ([5]). Literature data ([5]): m.p. 179-181°.

Found, %:	C 78.53;	78.45;	H 5.66;	5.91;	Fe 10.30;	10.55	
$C_{36}H_{30}O_2Fe$. Calculated, %:	C 78.54;		H 5.45;		Fe 10.18		

Upon reduction with $LiAlH_4$ under the conditions in which alcohols are usually obtained, 1,1-dibenzoylferrocene gave dibenzylferrocene, previously described by one of us and N. A. Volkenau ([6]). Yield 87%.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.