

2, 7- AND 2, 10-DISUBSTITUTED BIFERROCENYLS (1)

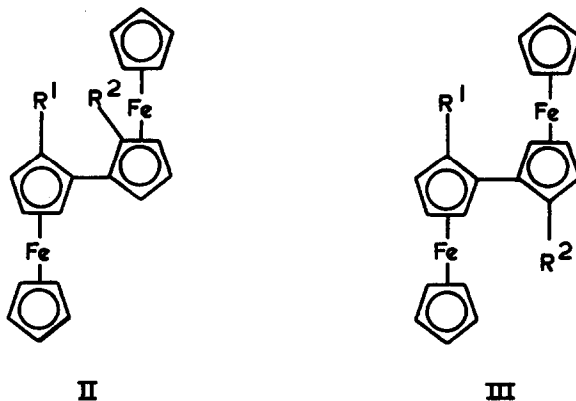
G. Marr, R. E. Moore and B. W. Rockett

Department of Applied Science,
Wolverhampton College of Technology,
Wolverhampton, England.

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As part of an investigation of the chemistry of 1, 2-disubstituted ferrocenes (2) we wished to have available the title compounds for comparison with the corresponding 2, 2'-disubstituted biphenyls. Hitherto these compounds have not been accessible by electrophilic substitution of biferrocenyl since this reaction afforded complex product mixtures (3) that contained only traces of the 2-substituted compounds and none of the 2, 7- or 2, 10-disubstituted derivatives.

Recently, we have reported the synthesis of 2-(NN-dimethylaminomethyl) ferroceneboronic acid (I) (2b, 4) and we considered that the coupling reactions of this intermediate might provide a convenient route to the required biferrocenyl derivatives. Thus the amino-acid (I) was converted smoothly by aqueous cupric acetate at 50° to a mixture of the two isomeric diamino-biferrocenyls. These products were conveniently separated by chromatography on alumina, and the diamine first eluted, m.p. 203-205.5° (41%) showed an AB quartet for the two methylene groups in the proton magnetic resonance spectrum. This diamine gave only a mono-methiodide under mild conditions and it is tentatively assigned the unsymmetrical structure (II; $R^1 = R^2 = CH_2NMe_2$). The more strongly adsorbed diamine, m.p. 103-105.5° (54%) showed a singlet for the methylene protons in the p.m.r. spectrum and afforded the corresponding di-methiodide. This product is presumably the centrosymmetric diamine (III; $R^1 = R^2 = CH_2NMe_2$). It is significant that 2-(dimethylaminomethyl)ferrocenylacetate was not isolated from the products



of this reaction since ferrocenylboronic acid gave predominantly ferrocenylacetate (5) under similar conditions. Similar mixtures of the 2,7- and 2,10-disubstituted biferrocenyls were obtained from the coupling of 2-lithio (NN-dimethylaminomethyl)ferrocene (6) in diethyl ether by anhydrous cobalt chloride (7), titanium tetrachloride (8) and copper acetate although the yields were low.

The mono-methiodide (II; $R^1 = \text{CH}_2\text{N}^+\text{Me}_3\text{I}^-$, $R^2 = \text{CH}_2\text{NMe}_2$), m.p. decomp. from 140° , was reduced smoothly by sodium amalgam to the methyl-amine (II; $R^1 = \text{CH}_3$, $R^2 = \text{CH}_2\text{NMe}_2$), m.p. $126-128.5^\circ$ (82%). This amine was quaternised under mild conditions and the methiodide (II; $R^1 = \text{CH}_3$, $R^2 = \text{CH}_2\text{N}^+\text{Me}_3\text{I}^-$), m.p. decomp. from 165° , underwent a variety of nucleophilic displacement reactions. The products from these reactions together with their yields and melting points are summarised in the Table. The displacements were usually complete within a few minutes at the reflux temperature. Since the analogous reactions with 1,2-disubstituted ferrocenes required extended reaction times these displacements demonstrate the ease of formation of the 2-(ferrocenyl)ferrocenyl carbonium ion.

TABLE

Nucleophilic substitutions of 2-methyl-7-(dimethylaminomethyl)biferrocenyl methiodide
in aqueous solution

Reagent	Product R ²	M.p.	Yield (%)
	(II; R ¹ = Me)		
NaOH	CH ₂ OH	184 - 185 ^o	82
NaOH/MeOH	CH ₂ OMe	123.5-125.5	49
	CH ₂ OH		35
Na/Hg	Me	158-159	22
	CH ₂ OH		59
KCN	CH ₂ CN	149-151 (decomp.)	48
PhNH ₂	CH ₂ NHPh	122.5-124	92
(CH ₂) ₅ NH	CH ₂ N(CH ₂) ₅	142.5-144	89

Structural assignments were made on the basis of satisfactory elemental analyses and absorption spectra. We thank the Wolverhampton College of Technology for a research assistantship to R. E. M.

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