

THE DISPLACEMENT OF THE HYDROXYL GROUP BY ANILINE IN FERROCENYLMETHANOLS

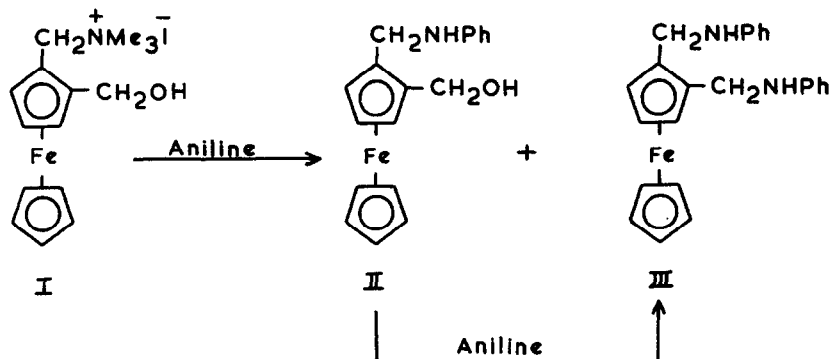
G. Marr, B. W. Rockett and A. Rushworth.

Department of Applied Science,
The Polytechnic,
Wolverhampton, England.

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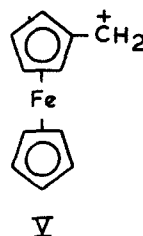
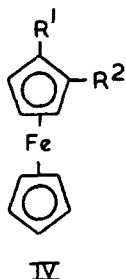
Recently the reactions of ferrocenylmethanols with malonic acid diethylesters (1) and N,N,N',N'-tetramethyldiaminomethane (2) have been reported in preliminary form. These reactions involved the replacement of the hydroxyl group by the dimethylamino and malonic ester groups respectively. We now report the first displacement of the hydroxyl group in ferrocenylmethanols by aniline.

The reaction of 1-dimethylaminomethyl-2-hydroxymethylferrocene methiodide (I) (3) with aniline gave a mixture of 1-N-phenylaminomethyl-



-2-hydroxymethylferrocene (II) and 1,2-di(N-phenylaminomethyl)ferrocene (III). A separate reaction of the hydroxymethyl-ferrocene (II) with aqueous aniline gave 1,2-di(N-phenylaminomethyl)ferrocene (III) in high yield (94%). When 1,2-di(hydroxymethyl)ferrocene (IV; $R^1 = R^2 = \text{CH}_2\text{OH}$) (3)

was heated in water with aniline for 16 hr. the diamine (III) was obtained and after only 2 hr. the amine (II) was obtained.



The iodo-ferrocene (IV; $R^1 = \text{I}$, $R^2 = \text{CH}_2\text{OH}$) (4) and ferrocenyl-methanol (5) (IV; $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{H}$) underwent reaction with aniline to give the amines (IV; $R^1 = \text{I}$, $R^2 = \text{CH}_2\text{NHPh}$) and (IV; $R^1 = \text{CH}_2\text{NHPh}$, $R^2 = \text{H}$) respectively. The ease of replacement of the hydroxyl group is attributed to the stability of the α -ferrocenylcarbonium ion (V) (6) and to the greater nucleophilic character of aniline as compared with hydroxyl in these reactions. Piperidine and benzylamine which are weaker bases than aniline did not displace the hydroxyl group from ferrocenylmethanol (IV; $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{H}$). When these amines reacted with the quaternary salt (I) only the ferrocenylmethyl-amines [IV; $R^1 = \text{CH}_2\text{N}(\text{CH}_2)_5$, $R^2 = \text{CH}_2\text{OH}$] and (IV; $R^1 = \text{CH}_2\text{NHCH}_2\text{Ph}$, $R^2 = \text{CH}_2\text{OH}$) were obtained respectively.

Structural assignments were made on the basis of satisfactory elemental analyses and absorption spectra.

References

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