Regio- and Stereo-specific Electroreduction of Cationic Acylcyclopentadienylareneiron Complexes

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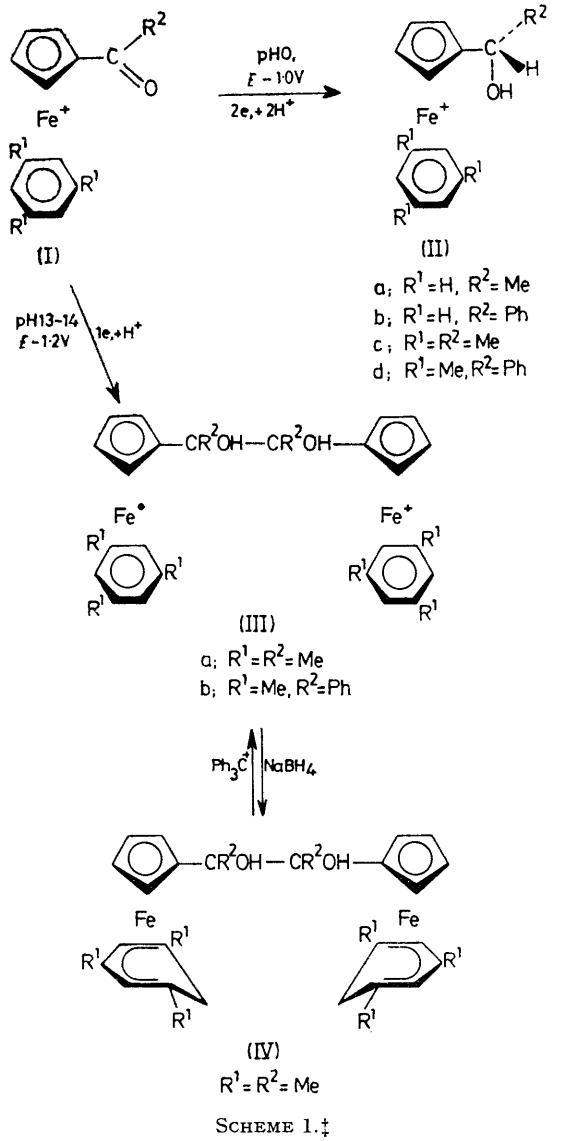
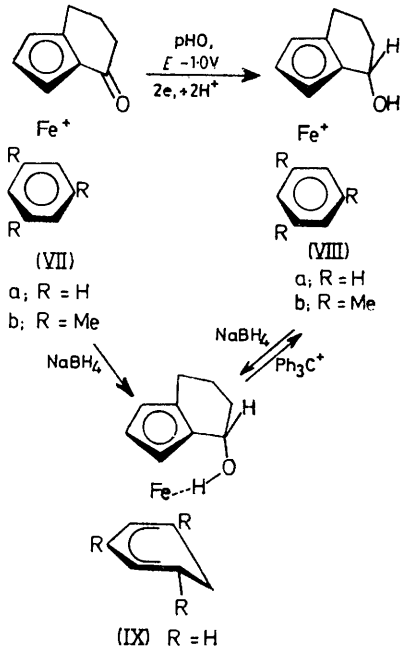
Summary Activation of a carbonyl group in cationic organometallic substrates such as the acylcyclopentadienylareneiron complexes (I), (V), and (VII) renders its electrochemical reduction easy and stereospecific, providing a route to the primary and secondary cationic alcohols (II) and (VI) or to the dinuclear dicationic pinacols (III).



SCHEME 1.‡

IN a recent communication, Khan and Watts[1] noted that the reduction of the ketones (I) by chemical reducing agents occurred simultaneously at both the carbonyl group and the benzene ring. We now report an easy and specific reduction



SCHEME 2.‡

of the carbonyl group in such cations, leaving the organometallic unit unchanged. This electrochemical method has proved to be so selective that, by varying the pH and the potential, either monocationic alcohols (II) or dicationic dinuclear pinacols (III) could be synthesized quantitatively (Scheme 1). Since it is difficult to carry out synthetically useful electroreduction of neutral organometallic ketones, activation by a cationic unit is necessary. The syntheses reported here are all so easily achieved that there is no need to isolate the ketones (I) obtained by ligand exchange between monoacylferrocenes and arenes.[2] The aqueous layers obtained from hydrolysis of these reaction mixtures can be submitted directly to controlled potential electrolysis on mercury.§

McGreer and Watts[3] have also reported that the reduction of the ester $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5CO_2R)]^+$ by $NaBH_4$ occurs on the benzene ring only to give the neutral cyclohexadienyl ester. In contrast, we have carried out the electrochemical reduction of the isomeric cationic acids (V) to the cationic primary alcohols (VI) [equation (1)] *via* aldehyde intermediates.

‡ All potentials refer to the saturated calomel electrode.

§ The structures of all new ketones, alcohols, and pinacols, which were isolated as their PF_6^- salts, were shown by elemental analyses, ^1H n.m.r., ^{13}C n.m.r., and i.r. spectroscopy, and $E_{\frac{1}{2}}$ and coulometry measurements.

$$(M\text{–}CO_2H)^+PF_6^- \xrightarrow[4e,\ +\ 4H^+]{pH=0} (M\text{–}CH_2OH)^+PF_6^- \quad (1)$$
$$-1{\cdot}2\ V\ddagger$$

(V) (VI)

M = $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5)$ or $(\eta^6\text{-}C_6H_6)Fe(\eta^5\text{-}C_5H_4)$

In order to see if there is any stereoselectivity in the reduction of related organometallic ketones, we synthesized the cyclohexenone complexes (VII) from the ferrocene analogues in a similar fashion to other ketones in this series.[2] Interestingly, the stereoselectivity of the electroreduction is as high (*ca.* 95%) as that observed using $NaBH_4$ as the reducing reagent (Scheme 2). Thus the *endo*-structure of the alcohols (VIII) resulting from attack *trans* to the metal is shown[3] by the position (*ca.* 3500 cm^{-1}) of the O–H stretching i.r. absorption of the neutral cyclohexadienyl derivative (IX) obtained by hydride addition to the cationic alcohol. The i.r. and ^{13}C n.m.r. spectra show only traces of the isomeric *exo*-derivative in both cathodic reduction and reduction with $NaBH_4$.

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[1] M. M. Khan and W. E. Watts, *J. Organometallic Chem.*, 1976, **108**, C11.
[2] D. Astruc and R. Dabard, *Tetrahedron*, 1976, **32**, 245.
[3] J. F. McGreer and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 103.