Regioselective Electroreduction of the Cationic Methoxycarbonylcobalticinium Complex $[Co(\eta-C_5H_4CO_2Me)(\eta-C_5H_5)]^+$

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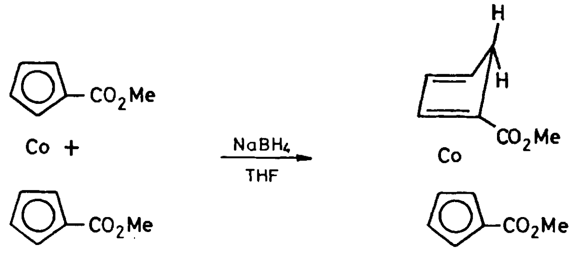
Summary Activation of the ester group in the title cationic cobalticinium complex makes its selective electrochemical reduction possible, providing a novel route to the new primary cationic alcohol in this series.

A few years ago, Khan and Watts[1] showed that the reduction of ketone derivatives of cyclopentadienyl(arene)-iron by $NaBH_4$ in 1,2-dimethoxyethane occurs simultaneously at the arene ring and the ketone. This led to alcoholic derivatives of η^5-cyclopentadienyl(η^5-cyclohexadienyl)iron. It is also well known that $NaBH_4$ in methanol,[2] and $LiAlH_4$ in ethers, may reduce both ester and acid groups into alcohols.[3] Ketones, aldehydes, or alcohols of the cobalticinium cation, isoelectronic with the cyclopentadienyl(arene)iron, are not yet known, while the esters and acids have been isolated.[4] It seemed to us to be possible to prepare at least the alcohol of the cobalticinium cation by reduction of the corresponding ester with the appropriate reagent. We report here the results of chemical ($NaBH_4$, $LiAlH_4$) and electrochemical reductions of cobalticinium carboxylate esters, and show that the corresponding alcohol is only obtained by electrochemical reduction in acidic aqueous medium.

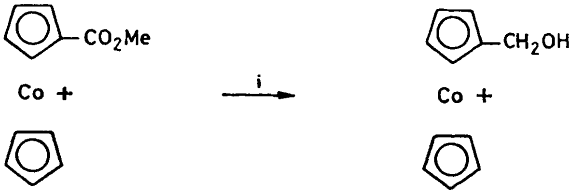
It is well established that the reduction of the cobalticinium cation using $NaBH_4$ or $LiAlH_4$ leads, after an *exo* nucleophilic attack, to the cyclopentadiene(cyclopentadienyl)cobalt.[5] When one or both rings are substituted by an electron-withdrawing carboxylate group, the nucleophile attacks the C atoms with the least electron density. Therefore, hydride addition occurs preferentially on the ring(s) with a carboxylate group, and at the β carbons.[6] Rosenblum and his co-workers showed that reduction of the 1,1′-bis(methoxycarbonyl)cobalticinium cation (**1**) with $NaBH_4$ in tetrahydrofuran (THF) gave (**2**) quantitatively; reduction of the ester groups did not take place.[7]



(1) (2)

When $LiAlH_4$ is used as the reducing reagent, neither compound (**2**) nor the alcohol of cyclopentadiene(cyclopentadienyl)cobalt is formed. The molecule decomposes, probably into cyclopentadienes and cobalt.

Electrochemical reduction of organic esters and acids into the corresponding alcohol is well established,[8] so we attempted to prepare the alcohol of the title cobalticinium cation by electrolytic reduction. In fact we found that, in aqueous alcoholic medium, esters or acids of the cobalticinium cation undergo two successive reductions; the first, reversible and mono-electronic, leads to the corresponding cobaltocene, while the second is not reversible and involves more than one electron, depending on the pH of the solution.† In basic buffered solutions, or in a non-aqueous medium, however, the two reduction steps are mono-electronic and reversible. In acidic solution (pH 3·4) the polarogram of the methoxycarbonylcobalticinium salt (**3**) shows a second reduction wave near that for discharge of the electrolyte support and its height corresponds to about five electrons. When electrolysis of (**3**) is performed in acidic solution at about −1·4 V *vs.* S.C.E. (standard calomel electrode), the number of Faradays transferred cannot be controlled owing to the proximity of the discharge of the electrolyte support. The current yield cannot then be evaluated. Despite this inconvenience we were able to isolate, after such an electrolysis, the alcohol (**4**) as the tetraphenylborate salt in good yield (60% based upon the conversion of the complex into product), m.p. (decomp.) 235 °C; ^1H n.m.r. (CD_3COCD_3) δ 7·6—6·7 (20H,m), 5·63 (5H,s), 5·52 (4H,m), 4·37 (2H,s), and 3·73 (1H,s); i.r. (Nujol) ν(OH) 3570 cm^{-1}.



(3) (4)

Conditions: i, Electrolysis (−1·4 V; pH 4, Prideaux–Ward buffer).

In contrast to the electrolysis of the unsubstituted cobalticinium salt,[10] we did not isolate any cyclopentadiene(cyclopentadienyl)cobalt derivative from the electrolysis of (**3**). This shows that the electroreduction is regioselective; the methoxycarbonyl group is reduced to the alcohol while the very easily reducible metallocene skeleton is not reduced.

(*Received*, 16*th December* 1980; *Com.* 1344.)

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† Classical Prideaux–Ward[9] buffered solutions containing Na$^+$ ions were used.

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