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Ferrocene Compounds. V. Indirect Electrochemical Reduction of Acetylferrocene

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2,3-Diferrocenyl-2,3-butanediol (II) has been obtained by the indirect electrochemical reduction of acetylferrocene (I) using an electrochemically generated sodium amalgam. The approximative value of the half-wave reduction potential of acetylferrocene (I) and the stereochemistry of (II) has been determined. Pinacol (II) was rearranged to 2,3-diferrocenylbutane-3-ol (III), dehydrated to 2,3-diferrocenyl-1,3-butadiene (IV) and anhydride of 4,5-diferrocenyl-4-cyclohexene-1,2-dicarboxylic acid (V) was formed by the Diels-Alder reaction of (IV).

It has been reported that attempts to convert acetylferrocene to the corresponding pinacol (II) by treatment with magnesium amalgam or by a Clemmensen reduction give mainly ethylferrocene (87%) and very little (3%) of the desired pinacol (II)^{1,2}. In view of the electron-donating properties of ferrocene and its aromatic character, we considered it worthwhile to investigate the electrochemical behaviour of acetylferrocene (I).

In addition, we considered it of interest to find the optimal conditions for the preparative electropinacolisation of acetylferrocene.

RESULTS AND DISCUSSION

The polarographic behaviour of aromatic carbonyl compounds in aqueous electrolytes indicates that a one-electron reduction in an acid medium corresponds to the reduction of the protonated ketone forming the free radical. In an alkaline media a one-electron reduction occurs without protonation of the ketone, corresponding to the formation of the radical anion. Constant current electrolysis at the plateau of the first polarographic wave, both in an acid and an alkaline media, gives the pinacol³. The *d,l/meso* ratio for benzenoid pinacols, prepared by electrochemical reduction of acetophenone and substituted acetophenone is about 1 for an acidic medium, where the two radicals dimerize. In a basic medium, the radical anion is electrochemically generated and the *d,l/meso* ratio for the pinacol is increased to 2—3^{4,5}.

We have found that acetylferrocene was polarographically inactive over the whole pH range of aqueous-ethanolic Britton-Robinson buffer*. On the other hand it was reduced nearly quantitatively by constant current electrolysis in

* E. Laviron *et al.* indicate polarographic reduction of acetylferrocene in aqueous-ethanolic Prideaux-Ward buffers in the pH range between 3—5. Furthermore, they noticed its decomposition under influence of light⁷.

aqueous-ethanolic sodium hydroxide at the decomposition potential of sodium amalgam at -2.1 V *vs.* S.C.E.* to 2,3-diferrocenyl-2,3-butanediol (II).

In order to explain the reduction of acetylferrocene in aqueous-ethanolic solution of sodium hydroxide**, we would have liked to predict an approximate value of its half-wave potential, correlating half-wave potentials of some benzenoid ketones with some structural data of corresponding aromatic nuclei given in Table I. We have plotted literature values of the half-wave potentials of the benzenoid arylmethyl ketones with the lowest unoccupied HMO orbital energies — LUMO (HMO)¹², p-bands¹³, the resonance energies per π electron — REPE (HMO)¹⁴, and the aromatic stabilities per electron As/e (HMO)¹⁵ of the corresponding aromatic nuclei (Table I.). Unfortunately, we could not find relevant data for ferrocene in available literature. Moreover, there are some differences for the values of the lowest unoccupied molecular orbital energy of ferrocene between several authors¹⁶. So far we had correlated, there are good linear relationships between the data of LUMO, p-bands, REPE, and As/e of the corresponding aromatic nuclei and the first spectroscopic $\pi \rightarrow \pi^*$ bands of arylmethyl ketones, so that we extended the correlation to the half-wave potentials and the first spectroscopic $\pi \rightarrow \pi^*$ bands of arylmethyl ketones.

TABLE I

Polarographic Half-Wave Reduction Potentials and Energies of the First Spectroscopic $\pi \rightarrow \pi^$ Band of the Arylmethyl Ketones; the Lowest Unoccupied HMO Orbital Energies, p-Bands, the Resonance Energies per π Electron and Aromatic Stabilities of the Corresponding Aromatic Nuclei*

Molecule	Ar—CO—CH ₃		Ar—H			
	$E_{1/2} - E$ (S.C.E.) V	$\pi \rightarrow \pi^*$ band $\Delta E/eV$	LUMO ¹² (HMO) — m_{n+1}	p-band ¹³ $\Delta E/eV$ β	REPE ¹⁴ (HMO) β	As/e ¹⁵ (HMO) β
9-acetylanthracene	— 1.52	3.2 ⁸	0.41	3.3	0.047	0.045
2-acetylnaphthalene	— 1.65	4.2 ⁹	0.62	4.4	0.055	0.056
4-acetylbiphenyl	— 1.71	4.3 ¹⁰	0.71	5.0	0.060	0.062
acetophenone	— 1.86	5.2 ¹⁰	1.00	6.1	0.065	0.073
acetylferrocene	—	5.6 ¹¹	—	—	—	—

U. v.-spectra are recorded in ethanol. $\pi \rightarrow \pi^*$ bands are determined according to the reported data⁸⁻¹¹.

Fig. 1. shows the plot between $E_{1/2}$ *vs.* the first spectroscopic $\pi \rightarrow \pi^*$ band of the arylmethyl ketones. A good linear relationship is apparent, the graphically determined value of the reduction potential of acetylferrocene is about -1.93 V *vs.* S. C. E. *i. e.* 20 mV more negative than the cathodic limit of the solvent-supporting electrolyte, which is -1.91 V *vs.* S. C. E. From this analysis it can be seen that the reduction potential of acetylferrocene in

* The same product was obtained by reduction of (I) with sodium amalgam in aqueous-ethanolic solution of sodium hydroxide.

** Although in an alkaline medium, the height of the first polarographic wave of arylmethyl ketones could be slightly dependent on the kind and concentration of the cations present in supporting electrolyte, the half-wave potential of the first polarographic wave is not affected by it³.

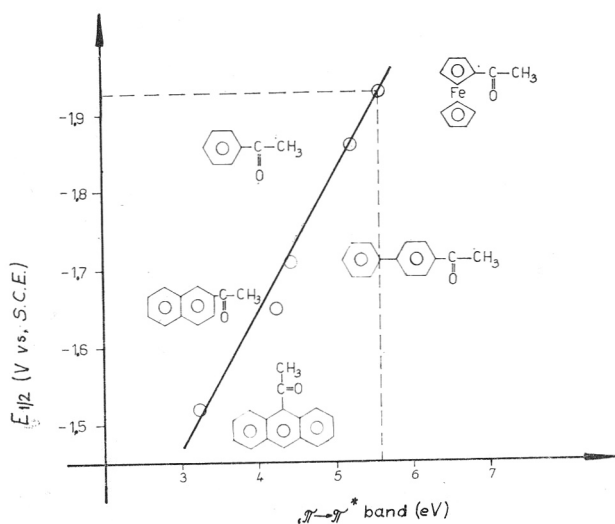
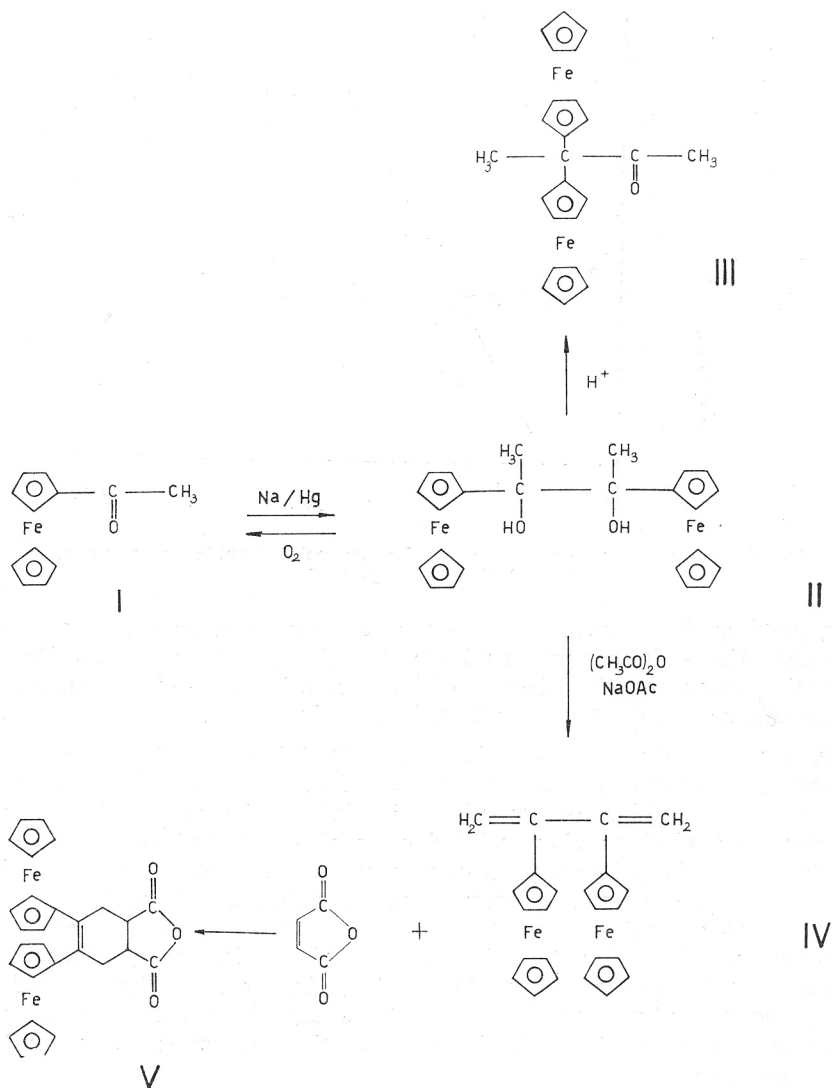


Fig. 1. Plot of the first spectroscopic $\pi \rightarrow \pi^*$ bands vs. polarographic half-wave potentials $E_{1/2}$ of some arylmethyl ketones.

investigated media is quite near to the equilibrium potential of the sodium amalgam¹⁷. Hence it is understandable that the reduction of acetylferrocene can easily occur at the decomposition potential of sodium amalgam in aqueous-ethanolic solution of sodium hydroxide.

By n. m. r. analysis of crude 2,3-diferrocenyl-2,3-butanediol (II), (as earlier described for benzenoid pinacols¹⁸) it was found that the *d, l/meso* ratio in the pinacol is 2.25. This corresponds to the data for benzenoid pinacols, which were prepared by electrochemical reduction of arylmethyl ketones in a basic medium, where the primary product of a one electron reduction is the radical anion^{4,5,18}. The resulting ferrocenyl radical anion could readily form the contact ion pair with sodium cation^{3,19}, and hence it favours coupling to the *d, l* isomer, which can explain the stability of the ferrocenyl pinacol (II) in aqueous-ethanolic sodium hydroxide. All these data indicate that the reduction of acetylferrocene proceeds by electron transfer from sodium amalgam to the ketone, forming the radical anion at the decomposition potential of sodium amalgam.

2,3-Diferrocenyl-2,3-butanediol (II) dissolved in organic solvents is easily oxidized to the parent ketone (I). By the action of mineral acids (II) is quantitatively rearranged with extraordinary ease to give 2,2-diferrocenylbutane-3-one (III). When heated in acetic anhydride (II) is dehydrated completely to 2,3-diferrocenyl-1,3-butadiene (IV). The high reactivity of 2,3-diferrocenyl-2,3-butanediol (II) is believed to be a consequence of easy formation of α -ferrocenyl carbonium ions as intermediates^{2,21}. In contrast to the reported²² 2-ferrocenyl-1,3-butadiene, 2,3-diferrocenyl-1,3-butadiene (IV) hardly reacts with maleic anhydride to form the Diels-Alder adduct (V). The decrease in rate is probably caused by unfavourable electronic interactions of the ferrocenyl substituents with a dienic moiety.



Spectral evidence from i. r. and n. m. r.-spectra support the assigned structures.

EXPERIMENTAL

Polarography

All polarograms were obtained with Polarimeter PO4, Radiometer, Copenhagen in a standard polarographic H cell, at the dropping mercury electrode at 25°C. The polarograms of 1×10^{-3} M solutions of the arylmethyl ketones (given in Table I) were recorded in aqueous-ethanolic sodium hydroxide (ethanol — 1 M aqueous solution of NaOH) 2:1 against a standard calomel electrode K 401, Radiometer, Copenhagen, as the reference. Reagents were of *p. a.* purity and the ketones were recrystallized to the relevant melting points. IR drop has not been compen-

sated, but all the measurements have been done at the same conditions and in the same polarographic cell. 1×10^{-3} M acetylferrocene was investigated over the whole pH range of 50% aqueous-ethanolic Britton-Robinson buffers⁶. Electrolysis was performed in a 170 ml cell with a ceramic diaphragm \varnothing 40 mm for separating cathodic from anodic chambers, mercury cathode of area 50 cm², reference — saturated calomel electrode and platinum wire as anode. Catholyte was stirred by magnetic stirrer, and cooled by circulating water around the outer part of the electrolytic cell. Cathodic potential was measured by a vacuum-tube voltmeter Model URV-2, and as a source of current DC generator »Iskra« Kranj was used.

Analytical Instrumentation

The melting points were determined on a Kofler microscope and are uncorrected. The i.r.-spectra were recorded using KBr pellets with a Perkin-Elmer Infra-Red Model 137. The u.v. spectra were measured on a Perkin Elmer UV/VIS Model 124 spectrophotometer. The n.m.r spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as the internal standard.

2,3-Diferrocenyl-2,3-butanediol (II)

In the cathodic chamber of an electrolytic cell 1.5 g (6.3 mmol) acetylferrocene (I) dissolved in 80 ml 96% ethanol and 80 ml aqueous solution of NaOH were added. The anodic chamber contained 40 ml of 10% aqueous solution of NaOH. Electrolysis was carried out at a constant current density of 4 A/dm². After 3 hours, a crude yellow produkt of (II) appeared in the cathodic chamber, and the cathodic potential arose to the value of -2.1 V vs. S. C. E. Catholyte was removed and a following reduction of (I) in the fresh portion of a electrolyte at cathode that contained sufficient quantity of sodium amalgam was run about 2—3 min. Crude product was filtered off, washed with water and dried. Yield is 90%. M.p. 140—3°C. N.m.r. (CDCl₃) were recorded for crude and dry product. Two singlets $\delta = 1.34$ ppm, $\delta = 1.52$ ppm (*d,l* and *meso*-CH₃) two singlets $\delta = 2.54$ ppm, $\delta = 2.47$ ppm (*d,l* and *meso*-OH) singlet $\delta = 4.11$ ppm (unsubstituted ferrocenes rings) two multiplets $\delta = 3.70$ —3.94 ppm $\delta = 3.94$ —4.33 ppm (substituted ferrocenes rings). It was found that the *d,l/meso* ratio in the pinacol was 2.25. Singlet $\delta = 2.38$ ppm (CH₃CO—) and two triplets $\delta = 4.47$ ppm and $\delta = 4.74$ ppm (substituted ferrocenes rings) of very low intensities were due to the unreacted acetylferrocene. I.r. spectrum 3650—3300 (cm)⁻¹ (OH groups). It was purified for elemental analysis by dissolving in cold ethanol and precipitating with water. N.m.r. (CCl₄) of purified product showed no signals of (I). Two singlets $\delta = 1.32$ ppm, $\delta = 1.48$ ppm (*d,l* and *meso* CH₃—6 H) $\delta = 2.30$ ppm (*d,l* and *meso* —OH —2 H) singlet $\delta = 4.07$ ppm two multiplets $\delta = 3.54$ —3.74 ppm and $\delta = 3.74$ —4.25 ppm (ferrocenes protons — 18 H).

Anal. C₂₄H₂₆Fe₂O₂ (458.172) calc'd.: C 62.91; H 5.72%
found: C 62.81; H 5.42%

2,3-Diferrocenyl-2,3-butanediol (II) dissolved in organic solvent spontaneously goes back to the parent ketone. Attempts to recrystallise (II) from hot heptane or ethanol gave the mixture of the ketone (I) and the pinacol (II).

2,3-Diferrocenylbutane-3-on (III)

1 g (2.18 mmol) of 2,3-diferrocenyl-2,3-butanediol (II) was dissolved in 47 ml acetone. The reaction mixture was cooled in an ice-salt bath and 4 ml conc. HClO₄ was added. After the addition of ice, solution was allowed to stand for 2 hours, the precipitated crystals were filtered off, washed with water and dried. Yield was 87%. The sublimate at 180/0.02 mm is a pale yellow powder with m.p. 122—3°C. I.r. (CCl₄) ν (C=O) = 1709 cm⁻¹ that agrees with ref. 2. N.m.r. (CDCl₃) singlet $\delta = 1.88$ ppm (CH₃, C-4, 3 H) singlet $\delta = 2.05$ ppm (—CH₃, C-1, 3 H) singlet $\delta = 4.04$ ppm (unsubstituted ferrocene rings) multiplet $\delta = 4.00$ —4.16 ppm (substituted ferrocene rings— 18 H).

2,3-Diferrocenyl-1,3-butadiene (IV)

A mixture of 4 g (8.7 mmol) of 2,3-diferrocenyl-2,3-butanediol (II) and 2 g (24.4 mmol) of anhydrous sodium acetate and 100 ml of acetic anhydride was heated 2.5 hours in an inert atmosphere at 134 °C. The reaction mixture was cooled to room temperature and poured with stirring on ice in a 500 ml Erlenmeyer flask. After standing overnight in the refrigerator crystals precipitated, were filtered off, washed with water till neutral and dried. The yield was 50%. Recrystallised from ethanol the crystal had a m.p. 112–13 °C. I.r. (CCl₄) 1620 cm⁻¹ (olefinic absorption). N.m.r. (CCl₄) δ = 3.95 ppm (singlet — unsubstituted ferrocene rings) and two triplets δ = 4.02–4.14 ppm and δ = 4.18–4.28 ppm — substituted ferrocene rings in positions 3,4 and 2,5-totally 18H. Two groups of two pairs signals δ = 5.14–5.21 ppm and δ = 5.37–5.44 ppm is due to CH₂=C (4H) J = 2.1 Hz.

Anal. C₂₄H₂₂Fe₂ (424.140) calc'd.: C 68.38; H 5.25%
found: C 68.31; H 5.10%

Anhydride of 4,5-diferrocenyl-4-cyclohexene-1,2-dicarboxylic acid (V)

1 g (2.37 mmol) of 2,3-diferrocenyl-1,3-butadiene (IV) was mixed with 1 g (10.2 mmol) maleic anhydride in 70 ml xylene. The reaction mixture was refluxed for 4 hours. After cooling to room temperature the solution was evaporated *in vacuo* to 1/4 volume. Upon cooling orange crystalline material precipitated. It was filtered off, washed with 96% ethanol and dried. Yield is 80%. Recrystallised from ethanol it gave a m.p. 199–202 °C. I.r. (ν-CO—O—CO—) 1867, 1845 (m) (doublet) and 1775 (s) cm⁻¹. N.m.r. (CDCl₃) δ = 4.08 ppm singlet, two triplets δ = 3.85 ppm and δ = 4.00 ppm (ferrocenes protons, 18H) δ = 3.5 ppm multiplet (methylene protons, 2H) 3.0 ppm multiplet (methylene protons, 4H).

Anal. C₂₈H₂₄Fe₂O₃ (520.172) calc'd.: C 64.65; H 4.65%
found: C 64.38; H 4.59%

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SAŽETAK

Feroceni V. Indirektna elektrokemijska redukcija acetilferocena

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Indirektnom elektrokemijskom redukcijom acetilferocena (I) djelovanjem elektrokemijski generiranog natrijevog amalgama sintetiziran je 2,3-diferocenil-2,3-butandiol (II). Određena je približna vrijednost redukcijskog poluvalnog potencijala acetilferocena (I) i stereokemija (II). Pinakol-pinakolinskom pregradnjom (II) sintetiziran je 2,2-diferocenilbutan-3-on (III), a dehidratacijom 2,3-diferocenil-1,3-butadien (IV). Diels-Alderovom reakcijom (IV), pripremljen je anhidrid 4,5-diferocenil-4-cikloheksen-1,2-dikarbonske kiseline.

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