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Electrosynthesis of 1,2 diketones by Reduction of Aromatic Esters at freshly Metal Coated electrodes : A Novel Coupling Reaction

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Abstract The one-step electrosynthesis of 1,2 aryldiketones has been achieved by constant current electrolysis of aromatic esters in an undivided cell fitted with a cadmium coated cathode and a sacrificial magnesium anode Evidence is given for a role of Mg^{2+} ions in the pathway of the reaction

Introduction

1,2 Diketones are useful synthetic intermediates They are generally prepared from esters via a multi-stage reaction, i e reductive acyloin condensation of an ester induced by alkali metals[1] followed by oxidation of the resulting α-hydroxyketone [2].

Direct electrochemical reduction of aromatic esters is a well known reaction yielding benzylic alcohols in protic media[3] and various products in other conditions[4] but the formation of diketones has so far not been reported

We have recently published that 1,2 aryldiketones can be obtained in fairly good yields when the electroreduction of an ester is effected in the presence of $SmCl_3$[5] We report here results on an improved electrochemical coupling of aromatic esters yielding 1,2 diketones under simple and mild conditions.

Experimental

As previously described[6], the electrochemical device is an undivided glass cell first fitted with a cadmium rod as anode surrounded by a nickel foam cathode (apparent area 20 cm^2). A solution of $CdBr_2$ ($5\ 10^{-2}$ mol l^{-1}) and Bu_4NBF_4 ($5\ 10^{-2}$ mol l^{-1}) in N,N dimethylformamide (DMF) was electrolysed (d.c 0 2 A during 20 mn) in order to make the cathode freshly coated with a slight deposit of cadmium.

The cadmium anode was then replaced by a magnesium rod (diameter 1 cm) and the solution was replaced by DMF 40 ml + Bu_4NBF_4 $3\ 10^{-2}$ mol.l^{-1} + aromatic ester 0 4 mol.l^{-1}. The constant current electrolysis (0 2 A, room temperature) was carried out until the consumption of ester (followed by G C analysis) reached at least 95% During the electrolysis the potential of the cathode remained in the range -2/-2 3 V *vs* a saturated calomel reference electrode.

After evaporation of DMF, acidification with dilute hydrochloric acid, extraction with diethyl ether and evaporation, a crude product was obtained which was purified by column chromatography on silica gel (5 % diethyl ether/pentane) Mass spectroscopic analyses were performed on a Finnigan GC-MS spectrometer and NMR spectra were recorded on a Varian (200 MHz) NMR spectrometer. All data are consistent with the structures listed in table 1

Results and discussion

Table 1 . Electrosynthesis of 1,2 Diketones at a Cadmium Coated Electrode

Ester	Diketone [R.N]	Isolated yield (%)
$\mathrm{Ph{-}CO_2Me}$	$\mathrm{Ph{-}CO{-}CO{-}Ph}$ [134-81-6]	81
$\mathrm{Ph{-}CO_2Et}$	$\mathrm{Ph{-}CO{-}CO{-}Ph}$ [134-81-6]	68
$\mathrm{Ph{-}CO_2Ph}$	$\mathrm{Ph{-}CO{-}CO{-}Ph}$ [134-81-6]	80
$\mathrm{4{-}CF_3{-}C_6H_4{-}CO_2Me}$	$\mathrm{(4{-}CF_3{-}C_6H_4{-}CO{-})_2}$ [73790-20-2]	30 (70[a])
$\mathrm{4{-}MeO{-}C_6H_4{-}CO_2Me}$	$\mathrm{(4{-}MeO{-}C_6H_4{-}CO{-})_2}$ [1226-42-2]	90
$\mathrm{4{-}\mathit{t}{-}Bu{-}C_6H_4{-}CO_2Me}$	$\mathrm{(4{-}\mathit{t}{-}Bu{-}C_6H_4{-}CO{-})_2}$ [76471-78-8]	75
$\mathrm{2{-}F{-}C_6H_4{-}CO_2Me}$	$\mathrm{(2{-}F{-}C_6H_4{-}CO{-})_2}$ [573-43-3]	60

[a] G C yield

The nature of both the anode and the cathode had a crucial influence on the reaction since yields of diketones were very low when aluminium was used instead of magnesium as sacrificial anode or when an uncoated cathode was employed. We also investigated the behaviour of various electrolytic metal deposits Lead, tin, or copper coating were made by electrolysis of $\mathrm{PbBr_2}$, $\mathrm{SnSO_4}$ or $\mathrm{CuSO_4}$ solutions in the presence of Pb-, Sn-, or Cu-anode respectively The electroreduction of methylbenzoate was then conducted in the same reaction conditions as those described for a cadmium coated electrode (table 2)

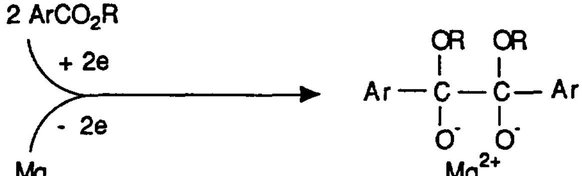
Table 2 Electroreductive synthesis of Benzil from Methylbenzoate at Various Coated Electrodes

Coating	Electric charge (Faraday mol.$^{-1}$)	Isolated yield (%)
Cadmium	1	85
Lead	1.5	68
Tin	2	85
Copper	2	20
No coating	0 25[a]	5

[a] a drastic passivation of the cathode prevents the exhaustive electrolysis.

Both chemical and faradaic yields were the highest with a cadmium coating, the reaction then requiring one Faraday per mole of ester. On the contrary very low yields of benzil, along many side products, were obtained with a copper-coating as well as in the absence of coating Further work is necessary to explain such an influence of the nature of the electrolytic deposit on the electroreduction of aromatic esters

Mg^{2+} ions issued from the sacrificial anode play a determinant role on the success of the synthesis. Since 1,2 aryldiketones are more easily reduced than the starting esters, they would therefore be further reduced in the electrolytic medium. We then assume that a key feature of this reaction is the protection of the diketone as a bis hemiketal stabilised as a Mg(II)-complex (scheme 1).



scheme 1

In order to obtain more informations on the reaction pathway, we have performed electroanalytical studies on aromatic esters (figure 1).

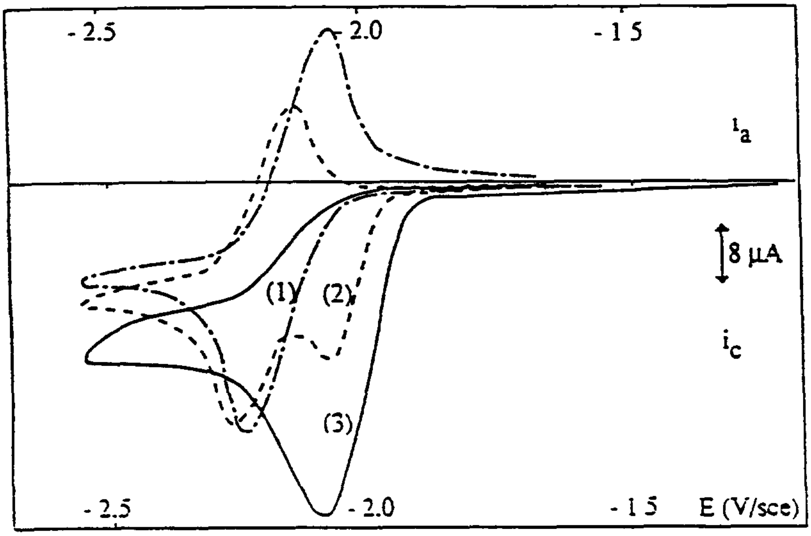


Figure 1 Cyclic voltammetry of methylbenzoate at a cadmium-coated gold microelectrode (scan rate = 0.1 V.s^{-1}.).

(1) .-.-.-.- DMF + Bu_4NBF_4 0.1 mol.l^{-1}.+ $PhCO_2Me$ 2.10^{-2} mol.l^{-1}

(2) ------ + $Mg(CF_3SO_3)_2$ 1.8 10^{-2} mol.l^{-1}.

(3) —— + $Mg(CF_3SO_3)_2$ 3.2 10^{-2} mol.l^{-1}.

Cyclic voltammogram of methylbenzoate at an uncoated or cadmium-coated gold microelectrode shows the classical one-electron system assigned to the reversible reduction of the ester into its radical anion[7]. When $Mg(CF_3SO_3)_2$ is added to the solution, the reduction signal of the ester is shifted to less negative potentials, the reverse anodic peak disappears and two electrons are now involved in this new reduction process as shown by chronocoulometric measurements.

These observations led us to assume that the electroreduction of an aromatic ester, in the presence of Mg^{2+} ions, gives the corresponding dianion and that the diketone is obtained by coupling of this dianion with the starting ester We cannot say if the dianion comes from a two-electrons cathodic reduction or from a fast disproportionation between two radical anions, as reported for the electroreduction of aromatic ketones[8].

The electron balance (two electrons per molecule of ester) observed in analytical conditions, where the concentration of the ester is low, can be explained either by a slow coupling reaction and/or by the protonation of the radical anion due to residual water.

To confirm the proposed mechanism, we carried out the electrolysis of methylbenzoate 0 4 mol l^{-1} in the presence of the non-electroreducible pivalaldehyde 0 8 mol l^{-1} We obtained equal amounts of benzil and the ketoalcohol Ph-CO-CH(OH)-*t*-Bu resulting from a coupling between the ester and the aldehyde.

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