

Electroreductive Coupling of Aromatic Acyl Bromides to 1,2-Diketones

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The direct electroreduction of aromatic acyl bromides gave aromatic 1,2-diketones. The best result was obtained using a Pb cathode in acetonitrile containing Bu_4NClO_4 as a supporting electrolyte. Aromatic acyl bromides substituted by an electron-donating group afforded 1,2-diketones in moderate-to-good yields, whereas acylated endiols were formed exclusively from aromatic acyl bromides substituted by an electron-withdrawing group.

The reductive coupling of benzoyl chloride using metal reducing agents^{1–3} or by electroreduction^{4,5} has been reported to give α,α' -stilbenediol dibenzoate (Scheme 1). In this reaction, benzil initially formed by dimerization of a benzoyl radical is reduced to benzoin dianion, which reacts instantly with benzoyl chloride.² Therefore, half amounts of benzoyl chloride were wasted in the dimer formation. In order to obtain benzil from benzoyl chloride, reduction with activate lead,⁶ SmI_2 ,⁷ or Li under sonication⁸ has been reported. Other methods for the preparation of aromatic 1,2-diketones by the reductive coupling of aromatic acid derivatives include the reduction of aromatic acids with excess lithium,⁹ indirect electroreduction of aromatic esters using a consumable Mg anode in the presence¹⁰ or absence of SmCl_3 ,^{11,12} the reductive coupling of 2-aryl-2-oxazolinium salts with Zn or by electroreduction,¹³ and the reduction of aromatic acyl cyanides with SmI_2 or ZnI_2 .¹⁴ In this paper, we report that the direct electroreduction of aromatic acyl bromides afforded aromatic 1,2-diketones. This reaction provides an alternative method for the synthesis of aromatic 1,2-diketones without using metal reducing agents.

The results of the constant-current (0.1 A) electrolysis of benzoyl bromide using a divided cell are summarized in Table 1. The best yield of benzil (**1a**: 65%) was obtained using a Pb cathode in acetonitrile (AN) containing Bu_4NClO_4 as a sup-

Table 1. Constant Current Electrolysis of Benzoyl Bromide

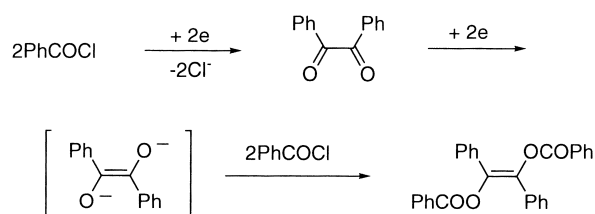
$\text{PhCOBr} \xrightarrow[0.1 \text{ A}]{+e} \text{Ph-C(=O)-C(=O)-Ph} \quad \textbf{1a} + \text{Ph-C(=O)-C(=O)-OCOPh} \quad \textbf{2a}$					
Run	Solvent	Cathode	Electrolyte	Yield ^{a)} of 1a /%	Yield ^{a)} of 2a /%
1	AN	Pb	Bu_4NClO_4	65	24
2	acetone	Pb	Bu_4NClO_4	43	36
3	THF	Pb	Bu_4NClO_4	3	10
4	DMF	Pb	Bu_4NClO_4	0	0
5	AN	Sn	Bu_4NClO_4	0	78
6	AN	Cd	Bu_4NClO_4	6	71
7	AN	Zn	Bu_4NClO_4	12	52
8	AN	Pt	Bu_4NClO_4	9	68
9	AN	C	Bu_4NClO_4	3	67
10	AN	Pb	Bu_4NBr	31	67
11	AN	Pb	Bu_4NBF_4	24	56
12	AN	Pb	LiClO_4	12	70

a) Isolated yields.

porting electrolyte (run 1). The yield of **1a** decreased in acetone (run 2). Using THF or DMF as a solvent, poor results were obtained due to the formation of complex mixtures (runs 3, 4). Only a Pb cathode gave good yields of **1a**. The other cathode materials (Sn, Cd, Zn, Pt, and graphite) yielded α,α' -stilbenediol dibenzoate (**2a**) as a main product (runs 5–9). As a supporting electrolyte, Bu_4NClO_4 afforded a better result than the other tetrabutylammonium salts (runs 10, 11). The use of LiClO_4 considerably increased the yield of **2a** (run 12).

It was predictable that the presence of oxygen influenced the result of the electrolysis, since it has been reported that benzil is decomposed to benzoic acid by electroreduction in the presence of oxygen.¹⁵ In fact, electrolysis without bubbling nitrogen gas lowered the yields of the products (**1a**: 49%, **2a**: 24%). Therefore, electrolysis needed to be carried out under a nitrogen atmosphere. The current density also affected the yield of the products. Good results were obtained over the range of 2 mA cm^{-2} (0.05 A, **1a**: 63%, **2a**: 25%) to 4 mA cm^{-2} (0.1 A). Electrolysis at 8 mA cm^{-2} (0.2 A) brought about a decrease in the yield of **1a** (32%) and an increase in that of **2a** (57%). Since we could not observe the reduction potential of benzoyl bromide, as previously reported,¹⁶ the cathode potential was measured during the constant-current electrolysis (0.1 A) of benzoyl bromide (Fig. 1). Initially, the cathode potential dropped rapidly, and then became stable at -0.85 V vs. SCE. After that, the potential gradually rose to -0.87 V vs. SCE at the end of electrolysis. The electrolysis of benzoyl bromide at a constant potential of -0.85 V vs. SCE gave a slightly better result (**1a**: 68%, **2a**: 14%) than did constant-current electrolysis (run 1 in Table 1), although a constant-current electrolysis is much more convenient than a constant-potential electrolysis.

Table 2 presents the results of electroreductive coupling of several aromatic acyl bromides and benzoyl halides under the same conditions as run 1 in Table 1. Aromatic acyl bromides substituted by an electron-donating group, such as a methoxy or methyl group, afforded 1,2-diketones **1b–d** in moderate-to-good yields (runs 2–4). On the other hand, it can be presumed that electron-withdrawing substituents lower the reduction potential of the 1,2-diketone and, therefore, facilitate the reduc-



Scheme 1.

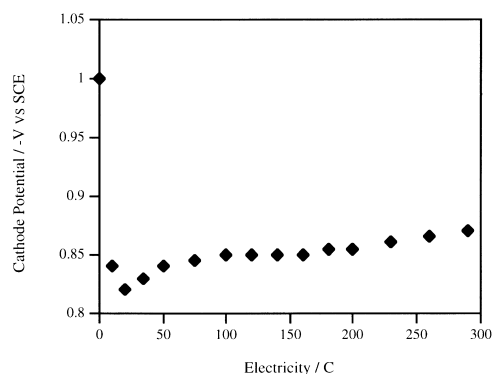


Fig. 1. Correlation between cathode potential and electricity in the electrolysis of benzoyl bromide (3 mmol) at 0.1 A using a Pb cathode in $0.3 \text{ mol dm}^{-3} \text{ Bu}_4\text{NClO}_4/\text{AN}$.

Table 2. Constant Current Electrolysis of Acyl Halides^{a)}

$\text{RCOX} \xrightarrow[0.1 \text{ A}]{+e} \begin{matrix} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{O} & & \text{O} \end{matrix} \quad \mathbf{1} + \begin{matrix} \text{R} & & \text{OCOR} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{RCOO} & & \text{R} \end{matrix} \quad \mathbf{2}$					
Run	R	X	Yield ^{b)} of 1 /%		Yield ^{b)} of 2 /%
1	Ph	Br	1a	65	2a 24
2	4-MeOC ₆ H ₄	Br	1b	52	2b 26
3	4-MeC ₆ H ₄	Br	1c	70	2c 12
4	2-MeC ₆ H ₄	Br	1d	40	2d 8
5	4-ClC ₆ H ₄	Br		0	2e 83
6	4-MeO ₂ CC ₆ H ₄	Br		0	2f 70
7	1-naphthyl	Br	1g	29	2g 32
8	PhCH=CH	Br	1h	14	2h 18
9	Ph	Cl	1a	6	2a 78
10	Ph	I	1a	30	2a 51
11	C ₂ H ₅	Br	1i	10	2i 42
12	C ₂ H ₅	Cl		0	2i 55

a) Electrolysis was carried out under the same conditions as run 1 in Table 1. b) Isolated yields.

tion of the 1,2-diketones to the benzoin dianion. Actually, the substitution of a chloro or methoxycarbonyl group brought about the exclusive formation of acylated endiols **2e**, **f** (runs 5, 6). The electroreduction of cinnamoyl chloride at a constant potential of -1.45 V vs. SCE with a mercury pool cathode in acetone containing LiClO_4 has been reported to give 2,4-dibenzyl-1,3-cyclobutanedione.¹⁷ Under our conditions, 1,2-diketone **1h** and acylated endiol **2h** were obtained from cinnamoyl bromide (run 8). The preferential formation of benzil (**1a**) is specific for benzoyl bromide; that is, the electrolysis of benzoyl chloride or iodide gave **2a** as a major product (run 9, 10). It has been reported that the reduction potential of benzoyl chloride is more negative than that of **1a**.⁴ Although the reduction potential of benzoyl iodide is unknown, this result shows that **1a** is more subject to reduction than benzoyl iodide under our conditions. Aliphatic acyl halides also yielded mainly acylated endiols (runs 11, 12).

Experimental

Starting Materials. Benzoyl bromide was commercially available. The other acyl bromides were prepared from aromatic acids by the reported methods.^{18,19} Benzoyl iodide was obtained by the treatment of benzoyl chloride with NaI.²⁰

General Procedure for Electroreduction. A solution of

Bu_4NClO_4 (4.1 g, 12 mmol) in dry acetonitrile (40 mL) was put into a divided cell of a 50 mL beaker (4.5 cm diameter, 6 cm height) equipped with an Pb cathode ($5 \times 10 \text{ cm}^2$), a Pt anode ($2 \times 2 \text{ cm}^2$), and a cylindrical ceramic diaphragm (2.5 cm diameter, 7 cm height). A stream of dry nitrogen gas was bubbled into the catholyte (outside the diaphragm) for 10 min. To the catholyte was added freshly distilled aromatic acyl bromide (3 mmol). Electrolysis was carried out at a constant current of 0.1 A under continuous bubbling of dry nitrogen gas until 290 C of electricity (1 F/mol) had passed. The electrolyte was poured into water and extracted with Et_2O . The products were isolated by column chromatography on silica gel (hexane–AcOEt).

Determination of Products. 1,2-Diketones **1b**, **1c**, **1d**, **1g**, and **1i** were confirmed by a comparison of their spectroscopic data with those of authentic samples prepared by reported methods.^{6,8} Acylated endiols **2** were determined by a comparison of their spectroscopic data with reported ones.^{1,2}

1h: R_f 0.5 (hexane–ethyl acetate, 5 : 1). IR (KBr) 1680, 1610, 1600, 1580, 1455, 760, 730, 695 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ 7.34–7.46 (m, 6 H), 7.46 (d, 2 H, $J = 15.0 \text{ Hz}$), 7.57–7.70 (m, 4 H), 7.85 (d, 2 H, $J = 15.0 \text{ Hz}$). ^{13}C NMR (50 MHz, CDCl_3) δ 120.08, 129.47, 129.54, 131.91, 134.91, 148.40, 189.75. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42; H, 5.38%. Found: C, 82.35; H, 5.41%.

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