## Anodic Oxidation of Benzil Hydrazones in the Presence of Halide Ions

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Benzil hydrazones were subjected to electrolytic oxidation in MeOH containing a halide ion source, such as KI and KBr. The results show that the reaction products were dependent on both the electrolytes and the substituents. In the presence of KI, benzoylphenyldiazomethanes were obtained, whereas in the presence of KBr, benzil dimethyl acetals were obtained.

The anodic oxidation of nitrogen-containing organic compounds, such as hydrazones, can be widely used as a clean synthetic method.<sup>1</sup> To date, the anodic oxidation of several hydrazones has been examined, including the direct electrolytic oxidation of benzophenone hydrazone to afford diphenyldiazomethane,<sup>2</sup> and the electrolytic oxidation of acylhydrazones of aliphatic ketones and aliphatic aldehydes to afford nitriles<sup>3</sup> and oxadiazoles,<sup>4</sup> respectively. In the present work, we found that the indirect electrochemical oxidation of benzil hydrazone 1a and 4,4'-dichlorobenzil hydrazone 1d using KI as a halide ion source afforded corresponding diazo compounds, 2a<sup>5</sup> and 2d,<sup>5</sup> in good yield, respectively (Table 1). However, we were not able to isolate the corresponding diazo compounds from 4,4'dimethylbenzil hydrazone 1b and 4,4'-dimethoxybenzil hydrazone 1c using KI under the same electrolytic conditions. In these cases, mixtures of the corresponding 5 and 7 were formed. Since continual evolution of nitrogen gas from the anolyte was observed during these electrolyses, it can be reasoned that both Wolff rearrangement<sup>6</sup> and further oxidation of the corresponding diazo compounds occurred simultaneously.

Table 1.Indirect Electrochemical Oxidation of BenzilHydrazones in the Presence of KI

Hydrazone		Current passed	Product yield <sup>a)</sup>	
	Х	$F mol^{-1}$		%
1a	Н	2.0	2a	76
1d	Cl	2.2	2d	90

a) Isolated yields.

Table 2.Indirect Electrochemical Oxidation of BenzilHydrazones in the Presence of KBr

0	<b>-</b>	OMe O
x ~ c c ~ v	Oxidation	
~Y	KBr/MeOH	x- <xx< th=""></xx<>
NNH2 <b>1a-d</b>		ÓMe 7a-d

Hydrazone		Current passed	Product	Product yield <sup>a)</sup>	
	Х	$F mol^{-1}$		%	
1a	Н	4.2	7a	77	
1b	Me	3.8	7b	81	
1c	OMe	4.0	7c	83	
1d	Cl	4.2	7d	75	

a) Isolated yields.



Scheme 1.

In contrast, benzil dimethyl acetals 7a-d were obtained as the result of replacing the electrolyte from KI to KBr under the same electrolytic conditions (Table 2). Electrolysis in the presence of KBr, differing from KI, required approximately a twofold increase in the amount of electricity for the reactions to go to completion. Interestingly,  $7a^7$  was obtained in 80% yield through an alternate route by means of the anodic oxidation of 2a using KBr. It can be suggested that 7a-d were additionally oxidized products of the corresponding diazo compounds. Also, when using NaI or NaBr instead of KI or KBr as the halide ion source 2a, 2d, and 7a-b were obtained in comparable yields, respectively. However, direct oxidation in the absence of a halide ion source resulted in an almost complete recovery of the starting material 1a-d. Moreover, as shown in Scheme 1, attempted to one-pot conversions of 1a to diphenylketene 3a, diphenylacetic acid 4a, methyl diphenylacetate 5a, and diphenylacetamide 6a were carried out. In conclusion, we carried out the electrochemical preparation of diazo compounds and benzil dimethyl acetals from benzil hydrazones using KI and KBr as electrolytes under mild conditions, respectively, without the use of a metal oxidant.<sup>8–9</sup>

## **Experimental**

Hydrazones were prepared from the corresponding benzils according to reported methods.<sup>10</sup> The electrolyses were carried out at a constant current of 0.3A in a 50 mL beaker cell, which was separated from the cathode compartment by a glass filter. The anode was a cylindrical platinum gauge (diameter, 33 mm; height, 40 mm) and the cathode was a nickel wire coil. The cell was cooled to 15 °C, and the anolyte solution was magnetically stirred. Typical procedures were as follows. Procedure A (Table 1): A mixture of 1a (1.79 g, 8 mmol), KI (0.66 g, 4 mmol), and NaOAc (0.33 g, 4 mmol) was placed in the cell, and MeOH (40 mL) was added. 2.0 F/mol of electricity (0.3 A, 1.43 h) was passed through the reaction mixture. After concentration of the anolytes in vacuo at room temperature, the resulting precipitates were collected by filtration, washed with cold MeOH, and dried to afford 2a (1.35 g, 76%). Procedure B (Table 2): A mixture of 1a (1.79 g, 8 mmol), KBr (0.48 g, 4 mmol), and NaOAc (0.33 g, 4 mmol) was placed in the cell, and MeOH (40 mL) was added. 4.2 F mol<sup>-1</sup> of electricity (0.3 A, 3.0 h) was passed through the reaction mixture. After evaporation of MeOH, the residue was treated with water (30 mL), and an oily layer was extracted with ether and dried. The residue obtained after the removal of ether was purified by distillation (169-170 °C/7 Torr) to afford 7a (1.58 g, 77%). One-pot conversions of 1a into 3a-6a were achieved using a five-fold increase in the amount of anolyte obtained by Procedure A as follows (Scheme 1). 3a: After removing MeOH in vacuo at room temperature, benzene (50 mL) was added, and the reaction mixture was refluxed for 0.5 h. After removal of benzene, distillation in vacuo afford 3a (4.66 g, 60%). 4a: After removing MeOH in vacuo at room temperature, a mixture of NaOH (5 g) and water (40 mL) was added, and the reaction mixture was refluxed for 0.5 h. The reaction mixture was washed with ether, then acidified with conc. HCl. The resulting precipitates were collected by filtration, washed with water, and dried to afford 4a (5.15 g, 65%). 5a: After concentrating the anolyte to one-fifth of its original volume, the residual solution was refluxed for 2 h. To the solution, water (30 mL) was added, followed by extraction with ether. The residue obtained after the removal of ether was recrystallized from MeOH to afford 5a (5.42 g, 60%). 6a: After removing MeOH in vacuo at room temperature, conc. NH<sub>3</sub> solution (80 mL) was added, then refluxed for 2 h. The precipitates were collected by filtration, then washed with a small amount of water and ether to afford **6a** (4.81 g, 57%). The melting and boiling points of the product were in agreement with those reported in the literature.<sup>11</sup>

**4,4'-Dimethylbenzil Dimethyl Acetal (7b):** bp 175–176 °C/3 mmHg. IR (KBr): 1069, 1113, 1124, 1180, 1609, 1697 cm<sup>-1</sup>. <sup>1</sup>H NMR(CDCl<sub>3</sub>)  $\delta$  2.27 (6H, s, Me × 2), 3.20 (6H, s, MeO × 2), 7.0–7.3 (4H, m, Ar), 7.50, 8.00 (4H, d, d, J = 8 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.13 (Me), 21.54 (Me), 49.92 (MeO), 103.72 (C), 126.89 (CH), 128.84 (CH), 129.21 (CH), 130.18 (CH), 131.85

(C), 134.18 (C), 138.65 (C), 143.54 (C), 194.73 (CO). MS m/z 253 (M - OMe)<sup>+</sup>, 166, 165, 119, 91. HRMS m/z found: 253.1239 (M - OMe)<sup>+</sup>, calcd for C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>: 253.1229.

**4,4'-Dimethoxybenzil Dimethyl Acetal (7c):** bp 194–196 °C/3 mmHg. IR (KBr): 1124, 1173, 1252, 1510, 1601, 1692 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.20 (6H, s, MeO × 2), 3.72 (6H, s, MeO × 2), 6.7–7.0 (4H, m, Ar), 7.53, 8.18 (4H, dd, J = 9 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  49.84 (MeO), 55.10 (MeO), 55.22 (MeO), 103.59 (C), 113.37 (CH), 113.86 (CH), 127.21 (C), 128.23 (CH), 129.33 (C), 132.42 (CH), 159.95 (C), 163.21 (C), 193.51 (CO). MS *m/z* 285 (M – OMe)<sup>+</sup>, 182, 181, 135, 77. HRMS *m/z* found: 285.1109 (M – OMe)<sup>+</sup>, calcd for C<sub>17</sub>H<sub>17</sub>O<sub>4</sub>: 285.1127.

**4,4'-Dichlorobenzil Dimethyl Acetal (7d):** bp 175–176 °C/3 mmHg. IR (KBr): 1015, 1070, 1094, 1126, 1587, 1701 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.22 (6H, s, MeO × 2), 7.29, 8.00 (4H, dd, J = 9 Hz, Ar), 7.32, 7.54 (4H, dd, J = 9 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  50.21 (OMe), 103.35 (C), 121.00 (C), 128.43 (CH), 128.68 (CH), 129.00 (CH), 131.49 (CH), 132.46 (C), 135.36 (C), 139.67 (C), 190.67 (CO). MS *m*/*z* 293 (M – OMe)<sup>+</sup>, 187, 185, 139. HRMS *m*/*z* found: 293.0140 (M – OMe)<sup>+</sup>, calcd for C<sub>15</sub>H<sub>11</sub>Cl<sub>2</sub>O<sub>2</sub>: 293.0136.

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