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Anodic Oxidation of Benzil Hydrazones in the Presence of Halide Ions

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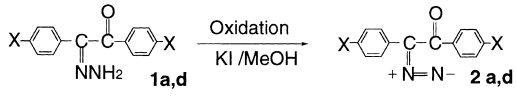
Benzil hydrazones were subjected to electrolytic oxidation in MeOH containing a halide ion source, such as KI and KBr. The results show that the reaction products were dependent on both the electrolytes and the substituents. In the presence of KI, benzoylphenyldiazomethanes were obtained, whereas in 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.[1] To date, the anodic oxidation of several hydrazones has been examined, including the direct electrolytic oxidation of benzophenone hydrazone to afford diphenyldiazomethane,[2] and the electrolytic oxidation of acylhydrazones of aliphatic ketones and aliphatic aldehydes to afford nitriles[3] and oxadiazoles,[4] 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**[5] and **2d**,[5] 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[6] and further oxidation of the corresponding diazo compounds occurred simultaneously.

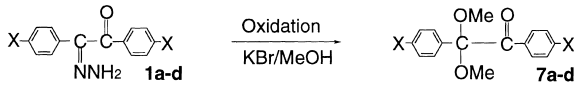
Table 1. Indirect Electrochemical Oxidation of Benzil Hydrazones in the Presence of KI



Hydrazone		Current passed	Product yield[a]	
	X	F mol^{-1}		%
1a	H	2.0	**2a**	76
1d	Cl	2.2	**2d**	90

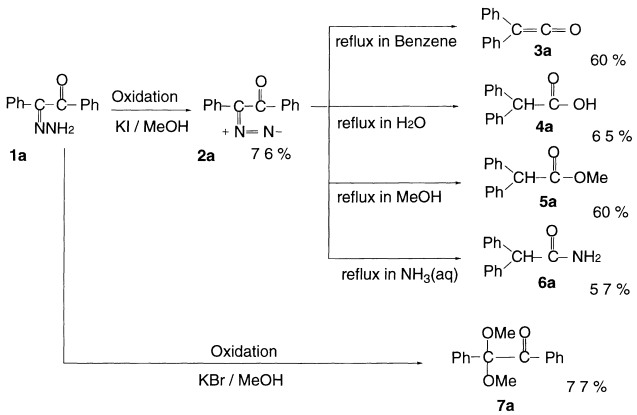
a) Isolated yields.

Table 2. Indirect Electrochemical Oxidation of Benzil Hydrazones in the Presence of KBr



Hydrazone		Current passed	Product yield[a]	
	X	F mol^{-1}		%
1a	H	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 two-fold 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.[8–9]

Experimental

Hydrazones were prepared from the corresponding benzils according to reported methods.[10] 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 an-

ode 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^{-1} 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_3 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.[11]

4,4′-Dimethylbenzil Dimethyl Acetal (7b): bp 175–176 °C/3 mmHg. IR (KBr): 1069, 1113, 1124, 1180, 1609, 1697 cm^{-1}. ^{1}H NMR($CDCl_3$) δ 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). ^{13}C NMR ($CDCl_3$) δ 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 $(M - OMe)^+$, 166, 165, 119, 91. HRMS *m*/*z* found: 253.1239 $(M - OMe)^+$, calcd for $C_{17}H_{17}O_2$: 253.1229.

4,4′-Dimethoxybenzil Dimethyl Acetal (7c): bp 194–196 °C/3 mmHg. IR (KBr): 1124, 1173, 1252, 1510, 1601, 1692 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 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). ^{13}C NMR ($CDCl_3$) δ 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 $(M - OMe)^+$, 182, 181, 135, 77. HRMS *m*/*z* found: 285.1109 $(M - OMe)^+$, calcd for $C_{17}H_{17}O_4$: 285.1127.

4,4′-Dichlorobenzil Dimethyl Acetal (7d): bp 175–176 °C/3 mmHg. IR (KBr): 1015, 1070, 1094, 1126, 1587, 1701 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 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). ^{13}C NMR ($CDCl_3$) δ 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 $(M - OMe)^+$, 187, 185, 139. HRMS *m*/*z* found: 293.0140 $(M - OMe)^+$, calcd for $C_{15}H_{11}Cl_2O_2$: 293.0136.

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