

Electrooxidative Formation of 1,2-Diaroylcyclopropanes from 1,3-Diaroylpropanes in the Presence of KI

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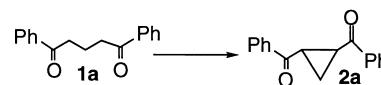
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Various 1,2-diaroylcyclopropanes were obtained in good yields by the indirect electrochemical oxidation of 1,3-diaroylpropanes in the presence of catalytic amounts of KI under very mild conditions.

Oxidations using molecular halogen as the oxidant have been extensively utilized in the syntheses of various organic compounds.^{1–8} Among these oxidation reactions, it is known that 1,2-dibenzoylcyclopropane can be formed by reacting equivalent amounts of iodine and 1,3-dibenzoylpropane.⁹ However, an alternative oxidation of the compound, without the use of molecular halogen, can be advantageous as a convenient synthetic method. Previously, Shono and co-workers reported on various indirect electrooxidations of organic compounds in a successive manner.^{10–13} We have also reported on the indirect electrooxidation of aromatic aldehydes,¹⁴ ketones,¹⁵ and benzil hydrazones¹⁶ to afford the corresponding methyl carboxylate, oxiranecarbonitrile, and diazomethanes, respectively, using halide ions as the mediator in MeOH. As a continuation in this series of studies, we carried out the indirect electrochemical oxidation of 1,3-diaroylpropanes (**1**) in the presence of catalytic amounts of KI to afford 1,2-diaroylcyclopropanes (**2**) in good yields.

Table 1 lists the reactions of 1,3-dibenzoylpropane (**1a**) involving various halide ion sources and electrolytes, and the resulting yields of 1,2-dibenzoylcyclopropanes (**2a**). According to the Table, the use of iodide ion sources in the presence of NaOMe was the most favorable reaction condition for obtaining high yields of **2a**. In the absence of a halide ion source, the formation of **2a** was not observed. In cases involving KBr or KCl instead of KI, the yields of **2a** were less than 10%, and most of the unreacted **1a** was recovered. In the case involving KI without a base, a lower yield was observed for **2a** (69%), along with the recovery of unreacted **1a** (22%). The addition of neutral or weakly basic electrolytes, such as (Et)₄NTs or NaOAc, respectively, resulted in decreasing the yield of **2a**. The required amount of KI was approximately one third or

Table 1. Influence of Halide Ions and Electrolytes for the Formation of 1,2-Dibenzoylcyclopropane **2a**^{a)}



Halide ion source (2 mmol)	Electrolyte (5 mmol)	Yield ^{b)} of 2a /%
KI	NaOMe	87
KI	NaOAc	41
KI	(Et) ₄ NTs	46
KI	None	69
NaI	NaOMe	85
KBr	NaOMe	7
KCl	NaOMe	8
None	NaOMe	0

a) **1a** (6 mmol) was oxidized by passing 2.6 F/mol of electricity. b) The yields were determined by GLC analysis.

less, based on the amount of **1a**.

Table 2 gives indirect electrochemical oxidation reactions using substituted **1** under conditions that are based on the results from Table 1. The oxidations of methyl, halo, and unsubstituted **1(a–c, i, j)** proceeded smoothly, using 2.4 F/mol of electricity at 15 °C, to afford the corresponding **2** in good yields. In those cases where the substitutions on the aromatic ring of **1(d–h)** involved electron-donating groups, such as alkoxy or aryloxy groups, relatively lower reactivities were observed for indirect oxidation; for example, 85% of **1d** remained unreacted after passing 2.6 F/mol of electricity at 15 °C, and 70% of **1f** was unreacted, even with an excess passing of 8.5 F/mol of electricity at 15 °C. However, raising the reaction temperature from 15 °C to 45 °C significantly increased both the current efficiency and the yield of the corresponding 1,2-diaroylcyclopropanes **2(d–h)**. These results appear to be based not only on the reactivity of the cationic iodide species formed on the anode, but also on the solubility of the substrates in MeOH.

In fact, most of the substrates dissolved in MeOH at a temperature of 45 °C to give a homogeneous solution in the initial stage of the oxidation. In conclusion, several 1,3-diaroylpropanes were cyclized in the presence of catalytic amounts of KI with the formation of a new carbon–carbon bond at the two α positions of the carbonyl groups to afford the corresponding 1,2-diaroylcyclopropanes in good to excellent yields under very mild conditions.

Experimental

The substrates were prepared via Friedel–Crafts acylation under typical conditions¹⁷ using 2 equivalents of the aromatic compounds, with glutaryl dichloride in CH₂Cl₂, and AlCl₃ as the catalyst. Other reagents were obtained from commercial suppliers, and were used without further purification. Preparative-scale electrooxidations were carried out in a tall beaker (50 mL) equipped with a fine frit cup as the cathode compartment, a cylindrical platinum net anode (diameter, 33 mm; height, 40 mm), and a nickel coil cathode. Compounds **1** were oxidized under the following conditions: a heterogeneous solution of **1** (6 mmol), KI (2 mmol),

Table 2. Indirect Electrochemical Oxidation of 1,3-Diaroylpropanes in the Presence of KI

$$\text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{R} \xrightarrow[\text{KI, NaOMe/MeOH}]{\text{Oxidation}} \text{R}-\text{C}(=\text{O})-\text{Cyclopropane}-\text{C}(=\text{O})-\text{R}$$

Compound	R	Current passed F mol ⁻¹	Reaction temp ^{a)} /°C	Yield ^{b)} of 2 %	mp/°C	
					1	2
1a	Ph-	2.4	15	85	70–71	105–107
1b	4-Me-C ₆ H ₄ -	2.4	15	83	112–114	108–110
1c	3,4-diMe-C ₆ H ₃ -	2.4	15	87	88–90	84–86
1d	4-MeO-C ₆ H ₄ -	2.8	45	84	99–101	100–102
1e	4- <i>n</i> -BuO-C ₆ H ₄ -	2.8	45	86	95–97	77–79
1f	4-PhO-C ₆ H ₄ -	2.8	45	87	99–101	89–91
1g	4-MeO-3-Me-C ₆ H ₃ -	2.8	45	82	135–137	106–107
1h	2-MeO-5-Me-C ₆ H ₃ -	2.8	45	89	68–70	124–126
1i	4-Cl-C ₆ H ₄ -	2.4	15	88	120–122	117–119
1j	4-Br-C ₆ H ₄ -	2.4	15	76	149–151	151–153

a) The temperature was maintained within ± 2 °C. b) Isolated yield.

and NaOMe (5 mmol) in MeOH (40 mL) was electrooxidized under a constant current (0.3 A). During electrooxidation, the anolyte was stirred using a magnetic stirring bar, and the temperature of the cell was maintained at approximately 15 °C or 45 °C (as indicated in Table 2). After completion of the electrolysis, a treatment of the reaction mixture was carried out as follows: the anolyte was cooled using an ice water bath; the resulting solids that precipitated were collected by filtration, washed with small portions of cold MeOH, and dried. In the case of **1a** and **1b**, the filtrate was concentrated in vacuo, followed by the addition of water to the residue. The organic substrates were extracted twice using ether, and dried over anhydrous sodium sulfate. The residue obtained after removal of the ether was recrystallized from small volumes of EtOH and added to the original precipitated solids.

trans-1,2-Di(4-methoxy-3-methylbenzoyl)cyclopropane (2g): mp 106–107 °C. IR (CCl₄) 1661, 1601, 1506, 1337, 1258, 1142, 1128 cm⁻¹. ¹H NMR (CDCl₃) δ 1.74 (t, 2H, *J* = 7 Hz), 2.24 (s, 6H), 3.35 (t, 2H, *J* = 7 Hz), 3.87 (s, 6H), 6.7–7.1 (m, 2H), 7.8–8.1 (m, 4H). ¹³C NMR (CDCl₃) δ 16.17 (CH₃), 19.63 (CH₂), 27.98 (CH), 55.50 (CH₃), 109.34 (CH), 126.97 (C), 128.56 (CH), 129.78 (C), 130.92 (CH), 162.07 (C), 196.23 (CO). MS *m/z* (rel intensity %) 338 (M⁺, 29), 189 (21), 149 (100), 106 (10), 91 (32). Found: C, 74.36; H, 6.56%. Calcd for C₂₁H₂₂O₄: C, 74.54; H, 6.55%.

trans-1,2-Di(2-methoxy-5-methylbenzoyl)cyclopropane (2h): mp 124–126 °C. IR (CCl₄) 1661, 1497, 1331, 1254, 1167, 1142, 1031 cm⁻¹. ¹H NMR (CDCl₃) δ 1.79 (t, 2H, *J* = 7 Hz), 2.27 (s, 6H), 3.37 (t, 2H, *J* = 7 Hz), 3.77 (s, 6H), 6.7–7.1 (m, 2H), 7.2–7.6 (m, 4H). ¹³C NMR (CDCl₃) δ 19.55 (CH₂), 20.24 (CH₃), 34.08 (CH), 55.71 (CH₃), 111.86 (CH), 128.51 (C), 129.81 (C), 130.39 (CH), 134.05 (CH), 156.98 (C), 200.02 (CO). MS *m/z* (rel intensity %) 338 (M⁺, 10), 189 (14), 149 (100), 106 (12), 91 (26). Found: C, 74.45; H, 6.65%. Calcd for C₂₁H₂₂O₄: C, 74.54; H, 6.55%.

trans-1,2-Di(4-chlorobenzoyl)cyclopropane (2i): mp 117–118 °C. IR (CCl₄) 1670, 1591, 1404, 1336, 1215, 1093, 1010 cm⁻¹. ¹H NMR (CDCl₃) δ 1.81 (t, 2H, *J* = 7 Hz), 3.37 (t, 2H, *J* = 7 Hz), 7.44, 7.98 (d, d, 8H, *J* = 9 Hz). ¹³C NMR (CDCl₃) δ 20.44 (CH₂), 28.34 (CH), 129.04 (CH), 129.74 (CH), 135.32 (C), 140.04 (C), 195.90 (CO). MS *m/z* (rel intensity %) 318 (M⁺, 11), 283 (9), 179 (25), 139 (100), 111 (52). Found: C, 63.73; H, 3.85; Cl, 22.17%. Calcd for C₁₇H₁₂Cl₂O₂: C, 63.97; H, 3.79; Cl, 22.21%.

trans-1,2-Di(4-bromobenzoyl)cyclopropane (2j): mp 151–153 °C. IR (CCl₄) 1670, 1587, 1398, 1337, 1215, 1072, 1008 cm⁻¹. ¹H NMR (CDCl₃) δ 1.86 (t, 2H, *J* = 7 Hz), 3.35 (t, 2H, *J* = 7 Hz), 7.60, 7.89 (d, d, 8H, *J* = 9 Hz). ¹³C NMR (CDCl₃) δ 20.44 (CH₂), 28.30 (CH), 128.76 (C), 129.82 (CH), 132.02 (CH), 135.68 (C), 196.15 (CO). MS *m/z* (rel intensity %) 408 (M⁺, 15), 327 (13), 223 (18), 183 (100), 144 (60). Found: C, 49.80; H, 2.94; Br, 39.13%. Calcd for C₁₇H₁₂Br₂O₂: C, 50.03; H, 2.96; Br, 39.16%.

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