

## Facile Cleavage Reactions of Styrylic Olefins using Electrochemical Methods

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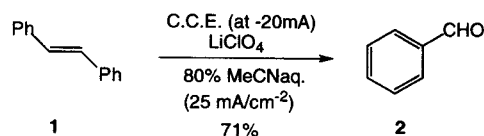
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**Abstract:** Negative constant current electrolysis of styrylic olefins in an aqueous solvent resulted in the oxidative cleavage of the double bonds, giving carbonyl compounds in good yields. The double bond conjugated with more than one aromatic ring was selectively cleaved.

Ozonolysis<sup>1</sup> and Lemieu-Johnson<sup>2</sup> reaction are very useful methods for cleaving olefins<sup>3</sup>. We are currently investigating electrochemical reaction of olefins<sup>4</sup>. In this paper, we wish to describe oxidative cleavage reactions of styrylic olefins into the corresponding carbonyl compounds<sup>5</sup> by means of electrochemical method. Although the oxidative cleavage of stilbene (**1**) have been reported<sup>6</sup>, our method is superior to the reported one in efficiency and selectivity.

*Trans*-stilbene (**1**) (0.3 mmol) in Ar-degassed 80% aqueous MeCN (20 ml) containing LiClO<sub>4</sub> (1.8 mmol) was subjected to constant current electrolysis with negative polarity (C.C.E. at -1.3~-1.4 vs. SCE, 25mA/cm<sup>2</sup>, 3.5h, room temperature) using platinum plate electrodes in an undivided cell, giving benzaldehyde (**2**)<sup>5</sup> in 71% yield (Scheme 1).



Scheme 1

The electrolysis of 1,1-diphenylethylene (**3**) under the same conditions gave benzophenone (**4**)<sup>5</sup> in 77% yield (Table 1, entry 2). Other results<sup>7</sup> are shown in Table 1. When stilbene oxide (**5**) and (*R,R*)-(+)-hydrobenzoin (**6**) were used as electrolytic substrates, the same oxidative cleavage reactions proceeded with consuming 5.0 and 4.0 F/mol to give **2** in 66% and 77% yields, respectively (entry 7, 8). The compound **5** or **6** was not detected during electrolytic oxidation of **1**. The intervention of the electrochemically formed H<sub>2</sub>O<sub>2</sub> was ruled out<sup>8</sup> because no oxidation occurred by the reaction with H<sub>2</sub>O<sub>2</sub> itself.

The positive C.C.E. of stilbene (**1**) resulted in the formation of **2** as similar to the negative C.C.E.

When stilbene (**1**) was subjected to electrolysis in a divided cell<sup>9</sup>, the oxidative cleavage reaction did not take place at all. The electrolysis of **1** in the anhydrous solvent in either divided or undivided cell resulted in the recovery of the starting material.

From the above results, these electrolytic oxidations were essentially required of both electrodes, an anode and a cathode, and aqueous conditions. The mechanism of this electrolytic oxidative cleavage reactions of olefins are currently under investigation.

It is noteworthy that the non conjugated double bond in **9**<sup>10</sup> and **10**<sup>10</sup> was unaffected during this electrolytic oxidation (Table 1, entry 9, 10)<sup>11</sup>.

### References and Notes

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Table 1. Cleavage of styryl compounds

entry	F/mol	product & yield <sup>a)</sup> (%)
1	7.0	PhCHO 71
2	7.0	Ph-C(=O)-Ph 77
3	7.0	Ph-C(=O)-Ph 79
4	7.0	PhCOMe 77
5	7.0	Ph-C(=O)-Ph 79
6	7.0	PhCHO 33
7 <sup>b)</sup>	5.0	PhCHO 66
8 <sup>b)</sup>	4.0	PhCHO 77
9	7.0	PhCHO 74
10	7.0	PhCHO 62
		PhCHO 72
		PhCHO 60

- a) All yields refer to the materials isolated by column chromatography.  
 b) When oxidations of **5** and **6** were conducted at the anode in a divided cell, we obtained benzaldehyde (**2**) from both compounds in good yields

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- (5) All of spectral data was identical with authentic sample.
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- (7) **7**: IR (neat) 3474, 1694, 1603  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05 (1 H, dq,  $J = 13.0, 4.9$  Hz), 2.54 (1 H, dddd,  $J = 13.0, 5, 4.5, 2.1$  Hz), 3.04 (1 H, ddd,  $J = 13.1, 4.9, 2.1$  Hz), 3.16 (1 H, ddd,  $J = 13.1, 13.0, 4.5$  Hz), 3.91 (1H, br. s, OH), 4.39 (1 H, dd,  $J = 13.0, 5.5$  Hz), 7.27 (1 H, d,  $J = 7.6$  Hz), 7.36 (1 H, t,  $J = 7.6$  Hz), 7.53 (1 H, dt,  $J = 7.6, 1.5$  Hz), 8.04 (1 H, dd,  $J = 7.6, 1.5$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  27.76 (t), 31.91 (t), 73.90 (d), 126.92 (d), 127.60 (d), 128.93 (d), 130.48 (s), 134.17 (d), 144.34 (s), 199.63 (s); HREIMS: found  $m/z$  162.0683 ( $\text{M}^+$ ); calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_2$  162.0680.
- 8**: IR (neat) 1721, 1696, 1601  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.79 (2 H, dt,  $J = 7.5, 1.2$  Hz), 3.35 (2 H, t,  $J = 7.5$  Hz), 7.33 (1 H, br. d,  $J = 7.5$  Hz), 7.44 (1 H, dt,  $J = 7.5, 1.2$  Hz), 7.53 (1H, dt,  $J = 7.5, 1.2$  Hz), 7.82 (1 H, dd,  $J = 7.5, 1.2$  Hz), 9.82 (1 H, t,  $J = 1.2$  Hz), 10.16 (1 H, br. s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  25.74 (t), 45.02 (t), 127.10 (d), 131.38 (d), 133.90 (d), 134.54 (d), 142.80 (s), 148.00 (s), 193.07 (s), 201.20 (s); HREIMS: found  $m/z$  162.0699 ( $\text{M}^+$ ); calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_2$  162.0680.
- (8) When we carried out of the electrolysis under  $\text{O}_2$  bubbling conditions, the reaction yields were decreased in all of substrates.
- (9) The cell was divided with a cation exchange membrane.
- (10) **9**: IR (neat) 1625, 1600  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.74 (3 H, s), 1.79 (3 H, s), 4.52 (2 H, d,  $J = 6.9$  Hz), 5.49 (1 H, br. t,  $J = 6.9$  Hz), 6.90 (2 H, d,  $J = 8.9$  Hz), 7.00 (1 H, d,  $J = 12.2$  Hz), 7.19 - 7.25 (1 H, m), 7.33 (2 H, dt,  $J = 7.5, 1.3$  Hz), 7.41 - 7.49 (4 H, complex), 7.43 (1 H, d,  $J = 12.2$  Hz); HREIMS: found  $m/z$  264.1510 ( $\text{M}^+$ ); calcd for  $\text{C}_{19}\text{H}_{20}\text{O}$  264.1513.
- 10**: IR (neat) 1630, 1595  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ) 1.72 (3 H,s), 1.78 (3 H, s), 4.47 (2 H, d,  $J = 6.9$  Hz), 5.47 (1 H, br. t,  $J = 6.9$  Hz), 6.50 (2 H, s), 6.75 (1 H, d,  $J = 8.9$  Hz), 6.76 (1 H, d,  $J = 6.9$  Hz), 7.14 - 7.29 (7 H, complex); HREIMS: found  $m/z$  264.1516 ( $\text{M}^+$ ); calcd for  $\text{C}_{19}\text{H}_{20}\text{O}$  264.1513.
- (11) **11**: IR (neat) 1700, 1600  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.76 (3 H,s), 1.81 (3H, s), 4.59 (2 H, d,  $J = 6.6$  Hz), 5.49 (1 H, br. t,  $J = 6.6$  Hz), 6.99 (2 H, d,  $J = 8.9$  Hz), 7.89 (2 H, d,  $J = 8.9$  Hz), 9.88 (1 H, s);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  18.26 (q), 25.82 (q), 65.17 (t), 114.95 (d), 118.78 (d), 129.82 (s), 131.96 (d), 139.12 (s), 163.98 (s), 190.79 (d); HREIMS: found  $m/z$  190.1015 ( $\text{M}^+$ ); calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2$  190.0994.