

Electro Organic Synthesis Utilizing Mg Electrodes (III) - E.O.S. Hydrogenation of Stilbene Equivalent to Catalytic Hydrogenation -

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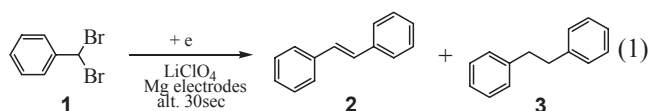
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Received September 25, 2008, Accepted November 26, 2008

Key Words : Electro organic synthesis, Mg electrode, E.O.S. hydrogenation

Because of its diverse application in industry and compatibility in green chemistry¹, the electro organic synthesis (E.O.S.)² is expected to provide the important organic synthetic tools in a near future. The brief review about the E.O.S. was introduced by us.³ Our continuing efforts to develop the E.O.S. utilizing alternated Mg electrodes, the synthetic routes from the nitro aromatic compounds to the azo compounds^{3a} and the reductive coupling of aromatic mono halides^{3b} were reported by our laboratory.

For further expansion of the our E.O.S. reaction, the benzal bromide **1** was exposed to our optimized aromatic mono halide coupling reaction.^{3b} The important reaction conditions were the following : Mg metal for both of anode and cathode and LiClO₄ as an electrolyte at the room temperature under a constant current⁴ (current density = 42 mA/cm²). The current of anode and cathode were altered at an interval of 30 second in order to minimize the consumption of metal. The two major spots were separated from the reaction residue in a low yield. They were characterized by TLC and by spectroscopic methods with the authentic samples. (Eq. 1)



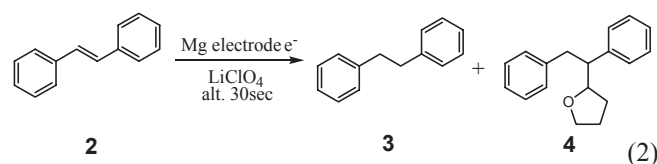
To our surprise, it gave rise to not only the desired *trans*-stilbene **2** but also the unexpected bibenzyl **3**⁶ under the various reaction conditions. (Table 1) The *cis*-stilbene **8** was not detected. The amount of the bibenzyl **3** was increased by the amount of electricity but the overall yields were still low. After applying various reaction condition, the low yield was drastically improved to 86% by changing the solvent from THF to diglyme. It could be explained that diglyme carried the better electric conductivity than THF. (diglyme: 3.45 F/h and THF : 0.9-1.8 F/h from Table 1) The formation of the *trans*-stilbene **2** was explained by the reductive coupling reaction of aromatic mono halide we reported.^{3b} However, the isolation of the unexpected bibenzyl **3** raised a challenging question about the course of the reaction.

With the interesting result in our hand, our attention was focused on the formation of the bibenzyl **3** under our E.O.S. reaction conditions. At first, we assumed that the unexpected bibenzyl was originated from the *trans*-stilbene since the ratio of them was varied by the reaction condition. Based on our as-

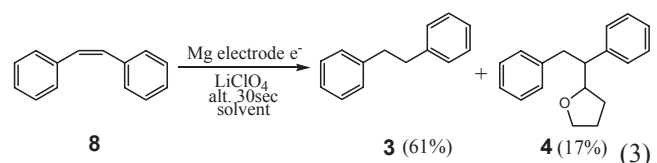
Table 1. Electroreductive coupling of aromatic dihalides

	Solvent	NaI (eq)	Rxtime (h)	Electricity (F/mol)	Yield(2+3) (%)	Ratio (2:3)
1	THF	0.0	4	4.9	24.0	1:0.6
2	THF	0.0	10	9.3	21.0	1:1.3
3	THF	0.1	4	7.3	21.0	1:1.6
4	Diglyme	0.0	2	6.9	86.0	1:4.7

sumption, the reactivity of the *trans*-stilbene **2** under the E.O.S. condition was carefully investigated. (Eq. 2)



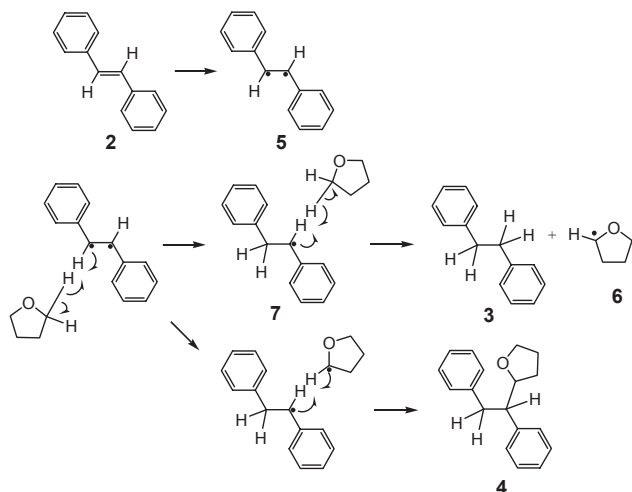
The *trans*-stilbene gave rise to the bibenzyl **3** and the 2-(1,2-diphenylethyl) tetrahydrofuran **4**,⁷ respectively. Meanwhile, the *cis*-stilbene **8** gave rise to the same result under our reaction condition. (Eq. 3)



The isolation of the compound **4** provided the crucial clue for the source of the hydrogen in our reaction. According to our previous experience and intensive literature search for mechanism of electro reductive organic reaction, our new hydrogenation route can be rationalized by the following reaction mechanism (Scheme 1). When the biradical **5** abstracted the α -hydrogen from THF successively, the bibenzyl **3** was obtained. And then the coupling reaction between the resulting THF radical **6** and the monoradical **7** produced the THF attached compound **4**. Participation of the THF radical under photolysis of ionic and radical pathways in bibenzyl derivatives was reported. It was noteworthy that the diglyme produce the bibenzyl **3** as a sole product. (Table 2) In case of the diglyme as the solvent, it was assumed that the reactive diglyme radical equivalent to **6** did not exit long enough in the

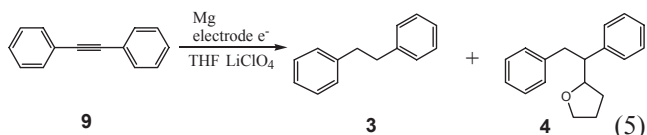
Table 2. Electroreduction of *trans*-Stilbene

	Solvent	Rxtime (h)	Electrolyte (eq)	Electricity (F/mol)	Voltage (V)	Yield(3+4) (%)	Ratio (3:4)
1	THF	2	13.2	8.97	50	94	70:24
2	THF	2	20.4	17.3	50	98	55:43
3	THF	4	13.2	17.8	25	89	78:11
4	Diglyme	2	11.3	8.99	50	79	79:0

**Scheme 1**

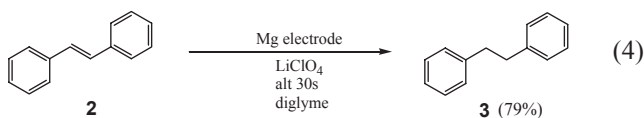
reaction medium to couple with the radical **7**. However, the significant different reactivity between of THF and diglyme is still under investigation.

In order to validate our observation, the diphenyl acetylene **9** were submitted under the our optimized E.O.S condition. It required more reaction time and the same tendency in reactivity (Eq. 5).



The *trans*-stilbene **2** was not isolated under our reaction condition. (Table 3) It suggested that the hydrogenation of the diphenyl acetylene **9** to the *trans*-stilbene **2** was significantly slower than hydrogenation of the *trans*-stilbene **2** to the bibenzyl **3**.

In conclusion, the hydrogenation reaction condition for the *trans*-stilbene utilizing Mg electrodes was established. (Eq. 4)



We named it as the **E.O.S. hydrogenation** of the stilbene. It was worthwhile to mention that our procedure require neither any exotic metal catalyst-for example: Ru(PPh₃)₄H₂, NaBH₄,⁸ Pd(OAc)₂, P(t-Bu)₃⁹ nor hydrogen gas¹⁰ compare to the conventional catalytic hydrogenation. The further elucidation of its reaction mechanism and general application to others carbon skeletons will be discussed in detail.

Table 3. Electroreduction of diphenyl acetylene

	Rxtime (h)	Temperature (°C)	Voltage (V)	Yield(3+4) (%)	Ratio (3:4)
1	4	r.t	50	80	60:20
2	4	0°C	50	70	47:23
3	8	r.t	25	72	67:5

Acknowledgments. This work was supported by the research program of Dongguk University. We are also grateful for generous financial support from KOSEF research project No. R 01-2001-000-00057-0.

References and Notes

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- Typical procedure is the following : LiClO₄ (2.04 g, 19.2 mmol, 11.5 eq.) and 25 mL of diglyme were added to three neck jacket reactor equipped with Mg electrodes (1×0.5×4 cm) for both cathode and anode fitted with condenser in argon atmosphere. The reaction mixture was continuously stirred till all LiClO₄ was dissolved. The *trans*-stilbene **2** (300 mg, 1.66 mmol, 1.00 eq.) in 10 mL of diglyme solution was added by syringe pump for 20 minute. The constant current was supplied with Takasako GPO 50-2 regulated DC power supply. (50 V, 350 mA, current density = 42 mA/cm²) During the electroreduction, the polarity of the electrode was altered with an interval of 30 second using a alternator. The progress of the reaction was monitored by TLC. When the *trans*-stilbene **2** was completely disappeared in the reaction mixture by TLC, ice cold 1.0 M HCl 50 mL was poured into the reaction mixture. The aqueous solution was extracted with diethyl ether (20 mL×2). The combined organic layers were washed with 30 mL of brine, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by silica gel column, as ethyl acetate : hexane (1 : 8) as eluent gave rise to the bibenzyl **3** (0.24 g, 79.1 %). After reaction finished, Mg was recovered more than 95.0 % by subsequent cleaning with H₂O and 1.0 M HCl.
- All compounds were isolated and fully characterized by comparison TLC and/or by spectroscopic methods with the authentic samples.
- (a) 2-(1,2-Diphenylethyl)tetrahydrofuran **4**. ¹H NMR (CDCl₃): δ 1.55-1.85 (m, 4H), 2.83-2.98, 3.02-3.14 (m, 2H), 3.36-3.41 (dt, 1H), 3.68-3.94 (m, 2H), 4.09-4.12 (m, 1H), 6.91-7.29 (m, 10H). (b) Berta, K.; Boris, S. *J. Org. Chem.* **2000**, *65*, 6890.
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