

Electro Organic Synthesis Utilizing Mg Electrodes (II) – Novel Synthesis of Symmetric Azobenzenes from Nitrobenzenes –

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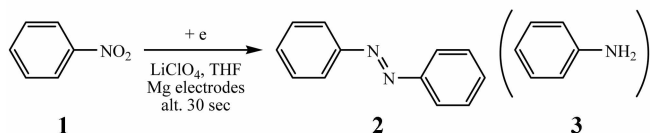
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On the way to study electro organic synthesis (EOS)^{1,2} utilizing alternating Mg electrodes, a novel synthetic route from the nitrobenzenes to symmetric azobenzenes was discovered in our laboratory.

The brief review about EOS was introduced by us.³ The EOS is expected to be an important organic synthetic tool in future because of its diverse application in industry in addition to compatibility with green chemistry.^{4,5} In the previous paper,³ we reported the optimized reaction conditions for the electro reductive coupling of aromatic halides: Mg rod for both of anode and cathode under a constant current,⁶ LiClO₄ as a electrolyte, THF or glyme⁷ as a solvent.

We have tried to extend EOS to other functional groups. Since nitrobenzenes were readily reduced under the various mild reaction conditions, we exposed several nitrobenzenes under EOS reaction conditions. Our reaction conditions were Mg for anode and cathode, LiClO₄, THF, room temperature under a constant current (current density – 42 mA/cm²). The currents of anode and cathode were alternated at an interval of 30 seconds in order to minimize the consumption of the metal. The reaction mixture was carefully monitored by TLC and then worked up when nitrobenzene **1** was completely disappeared. The new spot was isolated and characterized fully by TLC and spectroscopic methods with an authentic sample. To our surprise, it was azobenzene **2** instead of aniline **3** based on the previously reported paper.⁸ The optimized yield of **2** was 87.6 % with no trace of the desired aniline **3**. The amount of Mg consumed during the reaction was less than 5.0% for every attempt (eq. 1).



With the novel azo synthetic method in our hand, the various nitrotoluenes were submitted under our optimized reaction conditions (Table 1).^{9,10}

In general, the nitrotoluenes gave rise to the corresponding azo products in reasonable yields. It is noteworthy observation that *o*-nitrotoluene gave products in about 30% lower yield compared to others due to possible steric hinderance in these electro organic reaction. Since *p*-nitrotoluene provided

Table 1. Electro Reductive Coupling Reaction of Nitrobenzenes

Position	Entry	Alternating time (sec.)	Rx time (h)	Electricity (F/mol)	Yield (%)
Nitrobenzene 1	I	15	13.0	14.9	42.7
	II	30	10.0	11.5	87.6
	III	60	12.0	13.8	77.3
<i>o</i> -Nitrobenzene 4	IV	15	8.0	12.3	42.7
	V	30	7.0	9.0	31.4
	VI	60	12.5	19.2	22.5
<i>m</i> -Nitrobenzene 5	VII	15	6.0	9.3	50.5
	VIII	30	7.0	9.0	64.9
	IX	60	8.0	12.3	67.5
<i>p</i> -Nitrobenzene 6	X	15	8.0	10.2	56.0
	XI	30	7.0	7.2	71.8
	XII	60	12.5	12.8	58.6

*All reactions were performed at room temperature.

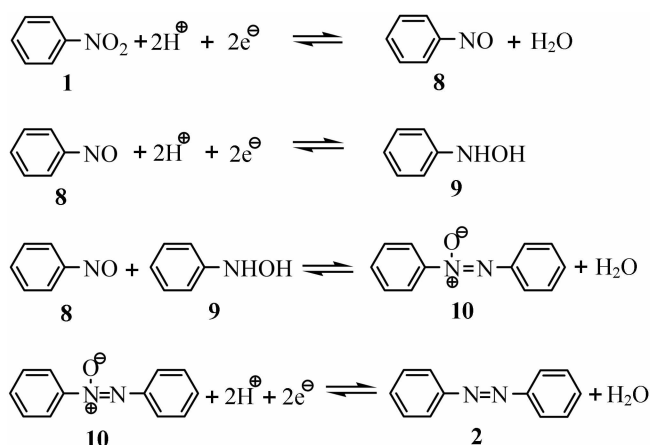
Table 2. Electro Reductive Coupling Reaction of *p*-Nitrotoluene

Entry	Amount of LiClO ₄ (eq.)	Rx time (h)	Electricity (F/mol)	Yield (%)
I	5	7	7.2	71.8
II	6	6	12.3	73.6
III	8.2	2.5	6.4	85.3

*All reactions were performed at room temperature.

the highest yield and the fastest reaction time (Entry XI), it was selected to further refining reaction condition about the amount of an electrolyte (Table 2).

The yield was progressively improved and the reaction time was significantly shortened as the amount of electrolyte was increased. The amount of electrolyte could not be increased more than 8.2 equivalent because of its limitation of solubility in THF. We assumed that the more electrolyte provided more electricity to improve the reaction yield



Scheme 1. The reduction mechanism of nitrobenzene.

and to shorten the reaction time.

Based on extensive literature search for electro reductive organic reaction of nitrobenzenes, our novel azo synthetic route can be rationalized by the following reaction mechanism (Scheme 1).

Nitrobenzene **1** was reduced to nitrosobenzene **8** by two-electron reduction. A part of nitrosobenzene **8** was reduced to phenylhydroxylamine **9** by two-electron reduction.^{11,12} Then azoxybenzene **10** was produced by coupling of **8** and **9** at the surface of the electrode. And reduction of the resulting **10** gave rise to the symmetrical azobenzene **2**.¹³ In order to confirm the proposed reaction mechanism, we are trying to isolate the reactive intermediates - **8**, **9**, **10** - in the course of our reaction and to use the commercially available **8** as a starting material.

The new synthetic route for the azo compounds is important since the azo compounds in addition to usage as classical dyes¹⁴ are reemphasized as optical recording materials and nonlinear optical materials.¹⁵ Azo compounds also are expected to be used photochromic dendrimers¹⁶ because molecular structure can be changed by light. The several unconventional methods for synthesis of the azo compounds - for example, nitrobenzene in carbonyl monoxide under 3000 atm at 250 °C by Kmiecik¹⁷ and catalytic transfer hydrogenation of nitrobenzene in methanol with lead as a catalyst by Gowda¹⁸ - were reported but their reaction conditions were too harsh to do in the laboratory.

Our novel single synthetic route will provide more convenient and efficient procedure than the traditional azo synthesis from nitrobenzene. Our procedure will be easily applied for industrial process with compatibility in environmental concern.

In summary, the symmetric azobenzenes were synthesized from the nitrobenzenes in a single step by utilizing electro organic synthesis (EOS). The Mg electrodes were recovered more than 95% at the end of reaction. Under the optimized reaction conditions we developed, various nitrobenzenes are currently examined in our laboratory with substituents on the ring including electron donating group as -CH₃, -NH₂,

-OH and electron withdrawing group as -NO₂, -CO₂R, -X. The further elucidation of reaction mechanism and its general application to other carbon skeletons are currently under investigation in our laboratory and will be discussed in due course.

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- Typical procedure is the following : LiClO₄ (3.90 g, 36.7 mmol, 4.51 eq.) and 40 mL of THF 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. Nitrobenzene **1** (1.00 g, 8.12 mmol, 1.00 eq.) in 20 mL of THF solution was added by syringe pump for 1 hour. 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 electro reduction, 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. After confirm that nitrobenzene **1** disappears in reaction mixture by TLC, ice cold 1.0 M HCl 30 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 : 40) as eluent gave rise to the azobenzene **2** (87.6%). 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 characterized fully by comparison TLC and by spectroscopic methods with authentic samples.
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