

2-Aryl-2*H*-benzotriazole Derivative Syntheses *via* Constant Current Cathodic Electrolysis Reaction

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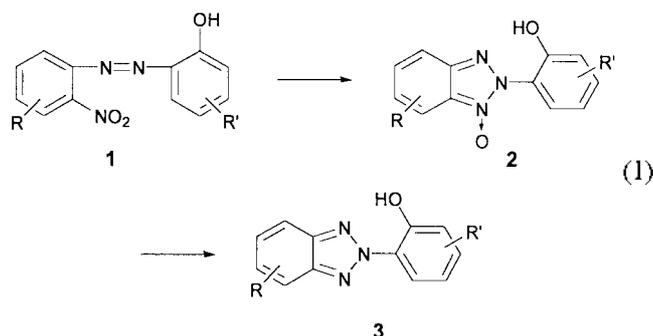
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Benzotriazoles, having an excellent effect of absorbing ultraviolet rays (200–400 nm), have been widely developed in view of the scope, the use and the process for the preparation as a very important industrial ingredient for absorbing UV. They have been used as a multipurpose ingredient in the field of plastics, polymers, oils and lubricants, and are demanded in a very large amount. In particular, since 1980's, benzotriazoles have been most widely used as a UV absorber for plastics.¹

For the synthetic utilization, a wide variety of reagents have been employed for the conversion of *o*-nitrophenylazo dyes (**1**) to 2-(2*H*-benzotriazol-2-yl)phenols (**3**), *i.e.* alkali sulfides,² zinc dust/sodium hydroxide,³ catalytic hydrogenation,⁴ and thiourea *S,S'*-dioxide and NaOH.⁵ In addition, we have reported the use of Bakers' yeast for the reductive cyclizations of **1** to **3** *via* 2-(1-oxido-2*H*-benzotriazol-2-yl)phenols (**2**), (eq. 1).⁶ However, most of the methods accompanies associated problems, *i.e.* benzotriazole-1-oxide formation,⁷ formation of 2-aminophenols which are hardly removed from the major products (**3**),⁴ dechlorination of chloro substituted *o*-nitrophenylazo dyes,⁷ work-up difficulties,⁶ and/or the requirement of drastic reaction conditions.



Alternatively, electrochemical approach could be a powerful methodology for the preparation of **3**. Lund examined electroreductive cyclization of 2-[(2'-nitrophenyl)azo]phenol in 0.1 N aqueous potassium hydroxide containing potassium chloride and he observed the formation of 2-(1-oxido-2*H*-benzotriazol-2-yl)phenol (82%, -0.60 V vs SCE).⁸ Even though he mentioned that isolated 2-(1-oxido-2*H*-benzotriazol-2-yl)phenol was transformed into 2-(2*H*-benzotriazol-2-yl)phenol by applying an increased the reduction potential

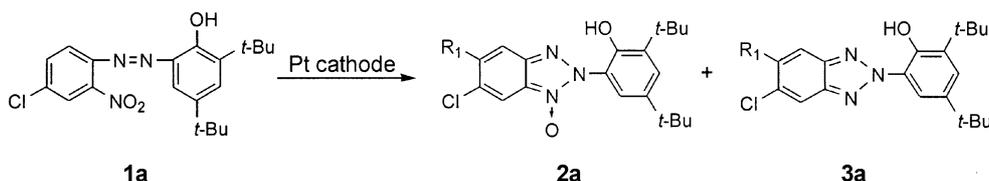
(-1.2 V vs SCE) under the same conditions, the yield was not reported. Except Lund's incomplete trial, the application of electrolysis reaction for the preparation of commercially useful benzotriazole was not extended much for the synthetic utility except our effort.⁹ Herein we wish to report unique electrochemical reductive cyclization of **1** toward **2** or **3** directly in high yields using constant current electrolysis reaction conditions which would be more useful for the mass production compared to any other chemical methods.

Results and Discussion

Based on electron accepting feasibility of nitroarenes, we have previously developed reductive cyclization of **1** with SmI₂ in THF, at room temperature to the corresponding benzotriazoles (**3**).¹⁰ The driving force for such transformations is believed to come from the powerful reducing ability of Sm²⁺ [$E^{\circ}(\text{Sm}^{3+}/\text{Sm}^{2+}) = -1.55$ V] that behaves as a one-electron donor. We have also investigated the reductive cyclization of 2-nitroarenes in the presence of zinc or indium as an electron donor and 2-bromo-2-nitropropane as an electron-accepting mediator. We have found that it also produced nitrogen-containing heterocyclic compounds such as 2,1-benzisoxazoles and benzotriazoles effectively.¹¹ If electron transfer ability controls the reaction, nitro group reduction initiated cyclization of *o*-nitrophenylazo dyes toward benzotriazoles should work electrochemically also and was proven by us recently.^{9,12} However, our effort for the electrolysis reaction was restricted to the controlled potential method that has somehow difficulty for the mass production because of reaction time control and reference electrode problem.

Thus, we decided to develop the controlled potential cathodic electrolysis reaction of **1**. Using a divided H cell and Pt electrode, electrolysis reactions by applying constant current method were examined. Since electrochemical reactions are affected by electrolyte, solvent ratio, and current (ampere) applied quite sensitively, we tried various control experiments to find the optimum condition by changing those reaction conditions. Some of selected control experiments are listed in Table 1.

Whenever we applied less than 20 mA to the reaction system, the reaction did not proceed well and starting substrate was recovered as a major one regardless of

Table 1. Representative optimization experiments of the constant current electrolysis of 2,4-bis(1,1-dimethylethyl)-6-(4-chloro-2-nitrophenylazo)phenol toward 2-aryl-2H-benzotriazole^a

Entry	Molarity (M)		Solvent (mL)		Charge passed (F mole ⁻¹)	Current (mA)	Yield (%) ^b	
	NaOH	LiClO ₄	THF	H ₂ O			2a	3a
1	0.1	0	20	20	30	30	12	56
2	0.1	0.2	20	20	53	30	2	64
3	0.2	0	20	30	41	30	tr	67
4	0.2	0	20	25	79	30	tr	76
5	0.2	0	20	20	86	30	7	74
6	0.3	0	20	20	77	25	7	68

^a0.3 mmol of substrate was used. ^bIsolated yield.

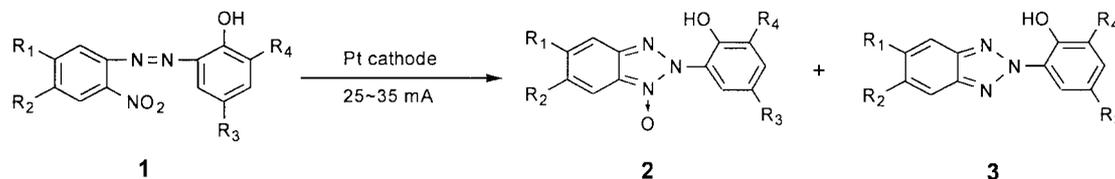
electrolyte and/or co-solvent. In addition, low concentration of NaOH electrolyte revealed ineffective charge pass resulting in the difficulty for the completion of the reaction (Table 1, entry 1). Electrolysis reaction was improved by using enlarged amount of electrolyte as well as properly controlled constant current (Table 1, entries 2-6). Thus 2,4-bis(1,1-dimethylethyl)-6-(4-chloro-2-nitrophenylazo)phenol was transformed into 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-(1,1-dimethylethyl)phenol in 76% yield after 79 Faraday/M passed with a proper condition [cathode and anode; Pt, electrolyte; 0.2 M NaOH, solvent; THF : H₂O = 4 : 5, room temperature, 30 mA, 30 hrs] as shown in Table 1, entry 4. As shown in Table 1, solvent ratio was also critical for the yield improvement; In THF : H₂O = 1 : 1 solvent system, benzotriazole N-oxide product was obtained as a minor product in any cases (Table 1, entries 1, 2, 5, 6).

Based on these control experiments, reductive cyclizations of various 6-(2'-nitrophenylazo)phenol derivatives were examined at 30 mA in THF/H₂O (v/v = 4/5) in the presence of NaOH (0.2 M) electrolyte. However, optimum condition obtained with 2,4-bis(1,1-dimethylethyl)-6-(4-chloro-2-

nitrophenylazo)phenol was not applicable for general uses. Thus we did the control experiments for each substrate varying the amount of electrolyte, solvent ratio, and current. Most of reductive cyclization proceeded well to provide the corresponding heterocyclic product in excellent yield (Table 2) if the proper condition applied.

While cathodic electrolysis of **1a-1c** produced **3** quite cleanly with good yield excluding **2**, electrolysis of **1d** and **1e** produced N-oxide as a by-product along with desired major product **3**. In the case of **1d** and **1e**, the overall yield was reduced if we use lower concentration of electrolyte or apply lower constant current. We are making an effort to transform benzotriazole N-oxides to the corresponding benzotriazoles (**3d** and **3e**) by changing reaction conditions.

Nitroarenes have been shown the ability to form radical anions, ArNO₂⁻ in the presence of electron donors.¹³ In addition, nitrosoarenes are also capable of accepting an electron. Russell reported that the SET process of nitrosobenzene in the presence of hydroxide ion occurs in < 0.5 sec to give nitrosobenzene radical anion.¹⁴ Thus nitro group in the substrate can accept the electron from the

Table 2. Electrochemical synthesis of 2-aryl-2H-benzotriazoles using constant current conditions^a

Entry	Substrate				NaOH (M)	Solvent (mL)		Current (mA)	Charge passed F mole ⁻¹ (time. h)	Yield (%) ^b		
	R ₁	R ₂	R ₃	R ₄		THF	H ₂ O			2	3	
1	1a :	H	Cl	<i>t</i> -Bu	<i>t</i> -Bu	0.2	20	25	30	79 (30)	tr	76 (3a)
2	1b :	Cl	H	<i>t</i> -Bu	<i>t</i> -Bu	0.2	20	30	35	177 (35)	tr	71 (3a)
3	1c :	H	H	<i>t</i> -Bu	<i>t</i> -Bu	0.2	20	30	30	41 (24)	tr	74 (3c)
4	1d :	H	H	<i>t</i> -pentyl	<i>t</i> -pentyl	0.3	20	20	35	127 (32)	20 (2d)	70 (3d)
5	1e :	H	H	Me	H	0.3	20	20	25	77 (25)	7 (2e)	68 (3e)

^a0.3 mmol of substrate was used. ^bIsolated yield.

cathode to form ArNO_2^- radical anion which can be transformed into nitrosoarenes accordingly *via* subsequent proton and electron transfers. We do believe ArNO^- radical anion forming by electron transfer from cathode to ArNO initiates the reductive cyclization towards *N*-oxide intermediate **2** that may convert into benzotriazoles by further cathodic reductive reaction.

In summary, we have established a novel constant current cathodic electroreductive cyclization of *o*-nitrophenylazo dyes toward benzotriazoles that could be a useful tool for the preparation of commercially important 2-(2*H*-benzotriazol-2-yl)phenol derivatives.

Experimental Section

General consideration. Most of chemical reagents were purchased from Aldrich and used without further purification in most cases. Solvents were purchased and dried by a standard method. Third distilled water was used as a co-solvent. For the electrolysis reaction, galvanostat method with an external resistance equipped Potentiostat model 410, 420A, and 640A of Electroynthesis Co. was applied. The reaction was monitored with TLC and Coulometer. Pt (foil, 1.0 mm, purity 99.9995%, 25 × 25 mm, Aldrich Co.) was used for working and counter electrode. LiClO_4 (purity 99.99%, Aldrich Co.) and NaOH (purity 93-100%, Ducksan Co.) were used for the electrolyte without further purification. Analytical gas chromatography (GC) was performed on a Donam 6200 gas chromatograph equipped with a DB-1 column and Hitachi D-2500 integrator. ^1H NMR spectra were recorded on 300 MHz Bruker instrument. Chemical shifts are in ppm from tetramethylsilane (TMS). High-resolution MS was recorded on a Jeol JMS-DX 303 mass spectrometer and GC/MS was recorded on a HP6890 mass spectrometer. IR spectra were recorded on a Nicolet 205 FT-IR. Melting points were determined on an Electrothermal apparatus and are uncorrected.

All the major products were isolated by flash column chromatography on silica gel (230-400 mesh ATSM, purchased from Merck) with eluents of mixed solvents (ethyl acetate and hexane). GC yields were determined by using an internal standard (*n*-decane) and were corrected with pre-determined response factors. Solid products were recrystallized from drops of dichloromethane/hexane co-solvent.

General procedure for the constant current electrolysis reactions. An H type glass cell fitted with a glass frit disk diaphragm was used for the electrolysis. The catholyte, THF/ H_2O (1:1 to 2:3, v/v) containing 0.3 mmol of substrate and a supporting electrolyte NaOH (0.2-0.3 M) with Pt (25 × 25 mm, 0.05 mm thick) plate as a cathode and Pt (25 × 25 mm, 0.05 mm thick) plate as an anode were used respectively. Constant current electrolysis reaction was carried out at room temperature in nitrogen atmosphere until the starting substrate was consumed completely (monitored by TLC and coulometer). After the evaporation of THF, the reaction mixture was quenched with 10% NH_4Cl and extracted with CH_2Cl_2 (40 mL × 3). The combined CH_2Cl_2

extracts were dried over MgSO_4 and the solvent was evaporated. The products were isolated by flash column chromatography with ethyl acetate-hexane co-solvent and/or recrystallized from drops of dichloromethane/hexane co-solvent.

2-(5-Chloro-2*H*-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (3a): White solid, mp 151-153 °C (lit.⁵ mp 152.5-154.5 °C). ^1H NMR (300 MHz, CDCl_3) δ 1.39 (s, 9H), 1.50 (s, 9H), 7.45 (d, 1H, $J = 2.0$ Hz), 7.47 (d, 1H, $J = 1.0$ Hz), 7.85-7.95 (m, 2H), 8.36 (d, 1H, $J = 2.0$ Hz), 11.52 (s, 1H); IR (KBr disc) 3490, 3100, 2950, 1495, 1471, 1431, 1355, 1043 cm^{-1} ; GC-MS m/z (rel. intensity) 359 (5, M^+), 357 (15, M^+).

2-(2*H*-Benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (3c): White solid, mp 153-155 °C (lit.⁵ mp 154-156 °C). ^1H NMR (300 MHz, CDCl_3) δ 1.39 (s, 9H), 1.51 (s, 9H), 7.40 (d, 1H, $J = 2.0$ Hz), 7.39-7.45 (m, 2H), 7.86-7.92 (m, 2H), 8.30 (d, 1H, $J = 2.0$ Hz), 11.76 (s, 1H); IR (CDCl_3) 3500, 3060, 2950, 1435, 1395, 1150 cm^{-1} ; GC-MS m/z (rel. intensity) 323 (35, M^+).

2-(2*H*-Benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)phenol (3d): White solid, mp 85-87 °C (lit.⁵ mp 86.5-88 °C). ^1H NMR (300 MHz, CDCl_3) δ 0.66 (t, 3H, $J = 7.5$ Hz), 0.70 (t, 3H, $J = 7.5$ Hz), 1.36 (s, 6H), 1.45 (s, 6H), 1.68 (q, 2H, $J = 7.5$ Hz), 2.00 (q, 2H, $J = 7.5$ Hz), 7.28 (d, 1H, $J = 2.0$ Hz), 7.42-7.49 (m, 2H), 7.88-7.95 (m, 2H), 8.23 (d, 1H, $J = 2.0$ Hz), 11.74 (s, 1H); IR (CDCl_3) 3400, 3055, 2950, 1453, 1373, 1251 cm^{-1} ; GC-MS m/z (rel. intensity) 351 (15, M^+).

2-(2*H*-Benzotriazol-2-yl)-4-methylphenol (3e): White solid, mp 129-130 °C (lit.⁵ mp 128-130 °C). ^1H NMR (300 MHz, CDCl_3) δ 2.38 (s, 3H), 7.08 (d, 1H, $J = 8.4$ Hz), 7.14 (dd, 1H, $J = 8.4, 1.8$ Hz), 7.43-7.50 (m, 2H), 7.88-7.95 (m, 2H), 8.18 (d, 1H, $J = 1.8$ Hz), 11.13 (s, 1H); IR (CDCl_3) 3475, 3095, 2960, 1594, 1507, 1219 cm^{-1} ; GC-MS m/z (rel. intensity) 225 (100, M^+).

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