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ELECTROCHEMICAL SYNTHESIS OF 2-ARYL-2*H*-BENZOTRIAZOLES AND THEIR *N*-OXIDES BY CONTROLLED POTENTIAL CATHODIC ELECTROLYSIS

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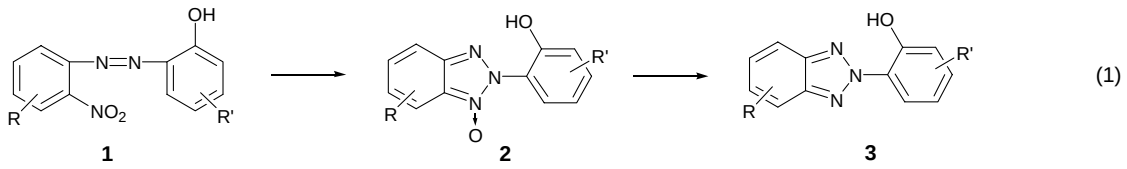
Abstract - Using a divided cell, reductive cyclizations of *o*-nitrophenylazo dyes (**1**) toward 2-aryl-2*H*-benzotriazole-1-oxides (**2**) or 2-aryl-2*H*-benzotriazoles (**3**) were successfully accomplished by the controlled potential cathodic electrolysis reactions. **1** was transformed to **2** under neutral conditions while **1** was transformed to **3** under basic conditions.

2-(2*H*-Benzotriazol-2-yl)phenols are widely used as ultraviolet absorbers for the protection of commercially important plastics against sunlight.[1] 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 also 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 accompany associated problems, *i.e.*



1 **2** **3** (1)

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). 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.[8] Except Lund's incomplete trial, the application of electrolysis reaction for the preparation of commercially useful benzotriazole was not extended for the synthetic utility. Herein we wish to report unique electrochemical reductive cyclizations of **1** toward **2**, or **3** directly in high yields depending on the electrolysis reaction conditions.

RESULTS AND DISCUSSION

Nitroarenes have been shown to have the ability to form radical anions in the presence of electron donors.[9] In fact, the LUMO energy level of nitro group lies in a relatively low, thus the formation of $ArNO_2^{-\bullet}$ can be explained by a single electron transfer (SET) process. 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.[10] In general, nitroso compounds, which are often postulated as intermediates, are too reactive to be isolated occasionally, even if indeed they are intermediate.

Based on electron accepting feasibility of nitroarenes, we have previously developed reductive cyclization of **1** with SmI_2 in THF, at room temperature to the corresponding benzotriazoles (**3**),[11] and we obtained high yielding reductive cyclizations of **1** without any of 2-aminophenols or benzotriazole-1-oxides. The driving force for such transformations is believed to come from the powerful reducing ability of Sm^{2+} [E^o (Sm^{3+}/ Sm^{2+}) = -1.55 V] which 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.[12]

If electron transfer ability controls the reaction, nitro group reduction initiated cyclization of *o*-nitrophenylazo dyes toward benzotriazoles should work electrochemically also under neutral conditions similar to the electrolysis of 2-nitroacylbenzenes.[13] Thus, we decided to try cathodic electrolysis reaction of **1** under neutral conditions.

Using a divided cell, various electrolysis reactions by applying controlled potential method were examined. Unfortunately, trial experiments with various solvents such as methanol, isopropyl alcohol, THF, CH_2Cl_2, DMF, and MeCN were not successful. Controls of reduction potential or variations of the amount of charge passed were not helpful either. In protic solvent system such as $LiClO_4$/MeOH, the reaction proceeded quite slowly because of solubility problem of substrates (**1**). In the case of aprotic

solvent system, the passage of electric current exhibited quite low efficiency probably due to the lack of solvating ability of intermediate ions. After the various reaction conditions examined, we could find the optimum condition for the reductive cyclization of *o*-nitrophenylazo dyes. By using co-solvent system, insolubility of substrate in protic solvent and the low efficiency of the current flow problem in aprotic solvent were solved both. Thus, the successful cathodic electrochemical cyclization reaction of **1** was obtained in co-solvent system such as CH_2Cl_2/MeOH (v/v = 1:1) or THF/H_2O (v/v = 1:1). To determine the proper reduction potential for the reductive cyclization of *o*-nitrophenylazo dyes, cyclic voltamogram (CV) of each compound was examined in a co-solvent system. A representative cyclic voltametric diagram is presented in Figure 1.

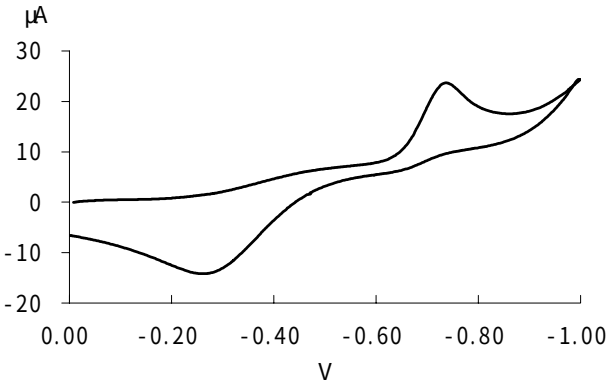


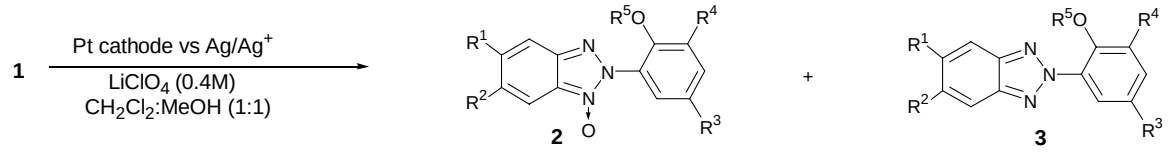
Figure 1. Cyclic voltamogram of 2,4-bis(1,1-dimethylethyl)-6-(2'-nitrophenylazo)phenol in CH_2Cl_2 /MeOH (v/v = 1:1, $LiClO_4$, 0.3 M) at a Pt cathode with a scan rate of $0.1Vs^{-1}$.

Based on this CV data, reductive cyclization of 2,4-bis(1,1-dimethylethyl)-6-(2'-nitrophenylazo)phenol was tested at –0.75 V in CH_2Cl_2/MeOH (v/v = 1:1) in the presence of $LiClO_4$ (0.4 M) electrolyte. As we expected, reductive cyclization indeed proceeded to provide the corresponding heterocyclic product in excellent yield (Table 1, entry 1). However, somewhat unexpectedly, the isolated product was benzotriazole-1-oxide (**2a**) rather than benzotriazole (**3a**).

It was very similar to SmI_2[11] or 2-bromo-2-nitropropane/Zn reaction system,[12] however, subsequent reaction to benzotriazole, *i.e.* deoxygenation of benzotriazole-1-oxide was not observed. Even at a more negative reduction potential applied, benzotriazole-1-oxide (**2c**) was not transformed to benzotriazole (**3c**) under the neutral conditions. Further investigations of the other 2-[(2'-nitrophenyl)azo]phenol derivatives gave the series of benzotriazole-1-oxides in excellent yields without any detectable benzotriazoles (Table 1, entries 1-5).

We tried reductive cyclization of 2-methoxy-2'-nitrophenylazobenzenes instead of 2-[(2- nitrophenyl)-

Table 1. Cathodic electrolysis reactions of various *o*-nitrophenylazo dyes under neutral conditions.



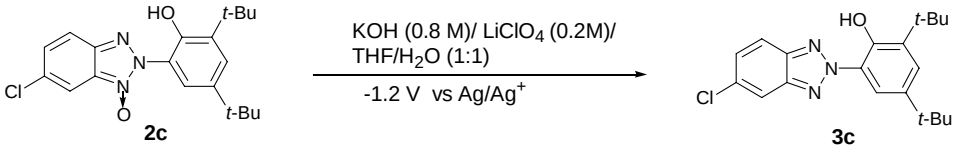
entry		substrate					charge passed (F mol^{-1})	potential (V)	yield (%)[a]	
		R^1	R^2	R^3	R^4	R^5			**2**	**3**
1	**1a** ;	H	H	*t*-Bu	*t*-Bu	H	6.7	-0.75	93 (**2a**)	-
2	**1b** ;	H	H	*t*-pentyl	*t*-pentyl	H	5.5	-0.95	95 (**2b**)	-
3	**1c** ;	H	Cl	*t*-Bu	*t*-Bu	H	6.6	-0.70	98 (**2c**)	-
4	**1d** ;	Cl	H	*t*-Bu	*t*-Bu	H	5.5	-0.80	85 (**2d**)	-
5	**1e** ;	H	H	Me	H	H	11	-0.80	88 (**2e**)	-
6	**1f** ;	H	H	*t*-Bu	*t*-Bu	Me	4.0	-0.90	65 (**2f**)	2 (**3f**)
7	**1g** ;	H	H	*t*-pentyl	*t*-pentyl	Me	9.9	-0.90	66 (**2g**)	1 (**3g**)
8	**1h** ;	H	Cl	*t*-Bu	*t*-Bu	Me	7.6	-0.95	60 (**2h**)	12 (**3h**)
9	**1i** ;	Cl	H	*t*-Bu	*t*-Bu	Me	8.3	-0.80	79 (**2i**)	1 (**3h**)
10	**1j** ;	H	H	Me	H	Me	13	-0.85	83 (**2j**)	-

[a]Isolated yield.

azo]phenol derivatives to see whether hydroxy functionality affected the reductive cyclization or not. Similar to 2-[(2-nitrophenyl)azo]phenols, cathodic electrolysis of 2-methoxy-2'-nitrophenylazobenzenes produced benzotriazole-1-oxides as a major product (Table 1, entries 6-10).

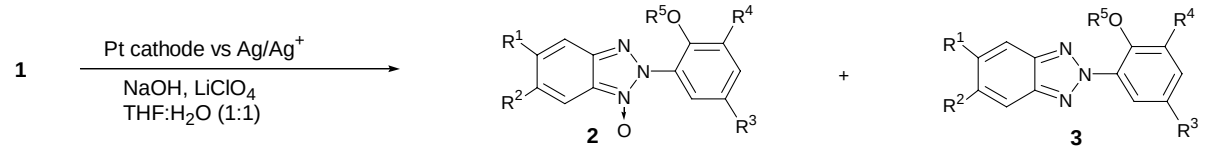
However, yields of benzotriazole-1-oxides were lowered and 1 – 12% of benzotriazole formation was observed. In addition, by-products coming from cleavage of the azo group such as 2-methoxyaniline and 1,2-diaminobenzene were obtained. It seemed that the azo group was getting easier to be reduced to produce by-products as the hydroxy group was substituted with the methoxy group probably because we had to apply higher reduction potential and/or pass more charges for the reductive cyclization of methoxy substituted *o*-nitrophenylazo dyes.

Even though we failed to transform benzotriazole-1-oxides to benzotriazoles under the neutral conditions, we could reduce benzotriazole-1-oxide (**2c**) to benzotriazole (**3c**) by applying a base in a proper co-solvent, THF/H_2O (v/v = 1:1) in 97% yield (eq. 2). Possibly, the adsorption of basic supporting electrolyte seems to create a special microenvironment in the reaction layer near the electrode that can induce effective conversion toward benzotriazole. It enlightens us on the possibility of direct transformation of **1** to **3**.



(2)

Table 2. Cathodic electrolysis reactions of various *o*-nitrophenylazo dyes under basic conditions.



entry		substrate					NaOH	$LiClO_4$(M)	charge passed (F mol^{-1})	potential (V)	yield (%)	
		R^1	R^2	R^3	R^4	R^5					**2**	**3**
1	**1a** ;	H	H	*t*-Bu	*t*-Bu	H	0.2	0	44	-1.40	-	89 (**3a**)[a]
2	**1b** ;	H	H	*t*-pentyl	*t*-pentyl	H	0.2	0	59	-1.60	-	92 (**3b**)[a]
3	**1c** ;	H	Cl	*t*-Bu	*t*-Bu	H	0.2	0	27	-1.30	-	92 (**3c**)[a]
4	**1d** ;	Cl	H	*t*-Bu	*t*-Bu	H	0.2	0	38	-1.45	-	98 (**3c**)[a]
5	**1e** ;	H	H	Me	H	H	0.2	0	39	-1.50	-	89 (**3e**)[a]
6	**1f** ;	H	H	*t*-Bu	*t*-Bu	Me	0.2	0.2	64	-1.40	24 (**2f**)[b]	40 (**3f**)[b]
7	**1g** ;	H	H	*t*-pentyl	*t*-pentyl	Me	0.1	0.2	24	-1.42	21 (**2g**)[b]	50 (**3g**)[b]
8	**1h** ;	H	Cl	*t*-Bu	*t*-Bu	Me	0.2	0.2	21	-1.40	28 (**2h**)[b]	45 (**3h**)[b]
9	**1i** ;	Cl	H	*t*-Bu	*t*-Bu	Me	0.1	0.2	49	-1.40	tr (**2i**)	63 (**3h**)[b]
10	**1j** ;	H	H	Me	H	Me	0.1	0.2	22	-1.35	tr (**2j**)	50 (**3j**)[b]

[a]GC yield with an internal standard (n-decane). [b]Isolated yield.

Scores of various basic electrolysis condition examinations led us to the optimum electrolysis conditions of direct transformation of **1** to **3** consequently. By applying the higher reduction potential in the presence of NaOH, 2-[(2'-nitrophenyl)azo]phenols were reduced to **3** [Pt cathode, 0.2 M NaOH/(THF : H_2O = 1 : 1, v/v), -1.3 ~ -1.5 V vs. Ag/AgCl] in good yields (Table 2, entries 1-5). All of the reactions produced **3** quite cleanly excluding **2**. For 2-methoxy-2'-nitrophenylazobenzenes [Pt cathode, 0.1 ~0.2 M NaOH/0.2 M $LiClO_4$ (THF:H_2O, v/v = 1:1), -1.35 ~ -1.42 V vs Ag/AgCl], we obtained a mixture of **2**, **3**, and 10 ~ 20% of 1-amino-2-methoxybenzenes and 1,2-diaminobenzenes (Table 2, entries 6-10). Compared to 2-[(2'-nitrophenyl)azo]phenol cases, by-product formation was increased and the yield of desired **3** was decreased.

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

EXPERIMENTAL

1. 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. Analytical gas chromatography (GC) was

performed on a Donam 6200 gas chromatograph equipped with a DB-1 column and Hitachi D-2500 integrator. ^{1}H NMR spectra were recorded on 300 or 500 MHz Bruker instrument and ^{13}C NMR spectra were recorded on 75 or 125 MHz Bruker instrument. Chemical shifts are in ppm from tetramethylsilane (TMS). High-resolution MS were recorded on a Jeol JMS-DX 303 mass spectrometer and GC/MS were recorded on a HP6890 mass spectrometer. IR spectra were recorded on a Nicolet 205 FT-IR. Analytical data were obtained with an EA-1110, CHNS-O CEinstruments. 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 predetermined response factors. Solid products were recrystallized from drops of dichloromethane/hexane co-solvent.

2. General procedure for the electrolysis reactions

An H type glass cell fitted with a glass frit disk diaphragm was used for the electrolysis. The catholyte, MeOH/CH_2Cl_2 or THF/H_2O (1:1, v/v) containing 0.3 mmol of substrate and a supporting electrolyte, $LiClO_4$ (0.4 M) and/or NaOH (0.1 - 0.2 M). Pt (25 x 25 mm, 0.05 mm thick) plate as a cathode and Pt (25 x 25 mm, 0.05 mm thick) plate as an anode were used respectively, and Ag/AgCl was used as a reference electrode. Controlled potential electrolysis was carried at rt in nitrogen atmosphere until the starting substrate was consumed completely (monitored by TLC and coulometer). After the evaporation of MeOH/CH_2Cl_2 or THF, the reaction mixture was quenched with 10% NH_4Cl and extracted with CH_2Cl_2 (40 ml x 3). The combined CH_2Cl_2 extracts were dried over $MgSO_4$ and the solvent was evaporated. The GC yield was determined by using an internal standard (*n*-decane) and, if necessary, the products were isolated by flash column chromatography with ethyl acetate-hexane co-solvent and/or recrystallized from drops of dichloromethane/hexane co-solvent. In case of benzotriazole-1-oxides, all products were reported with isolated yields since most of benzotriazole-1-oxides were decomposed to benzotriazoles during the GC analysis.

2,4-Bis(1,1-dimethylethyl)-6-(1-oxido-2*H*-benzotriazol-2-yl)phenol (2a) pale yellow solid, mp 181~183 ^{o}C (lit.,[5] mp 180~183 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 1.51 (s, 9H), 7.43-7.52 (m, 4H), 7.82-7.89 (m, 2H), 9.68 (1H, s); IR (KBr disc) 3500, 3060, 2950, 1435, 1395, 1150 cm^{-1}; GC-MS m/z (rel. intensity) 339 (100, M^{+}).

2,4-Bis(1,1-dimethylpropyl)-6-(1-oxido-2*H*-benzotriazol-2-yl)phenol (2b) pale yellow solid, mp 120~122 ^{o}C (lit.,[5] mp 118~120 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, 3H, *J* = 7.5 Hz), 0.80 (t, 3H, *J* = 7.5 Hz), 1.39 (s, 6H), 1.47 (s, 6H), 1.74 (q, 2H, *J* = 7.5 Hz), 2.05 (q, 2H, *J* = 7.5 Hz), 7.51-7.63 (m, 4H),

7.88-7.96 (m, 2H), 9.72 (s, 1H); IR (KBr disc) 3400, 3055, 2950, 1453, 1373, 1251 cm^{-1}; GC-MS m/z (rel. intensity) 367 (55, M^+).

2-(6-Chloro-1-oxido-2*H*-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (2c) pale yellow solid, mp 193~195 °C (lit.,[5] mp 191~193 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.57 (s, 9H), 7.54 (dd, 1H, *J* = 9.2, 1.8 Hz), 7.58 (d, 1H, *J* = 2.4 Hz), 7.65 (d, 1H, *J* = 2.4 Hz), 7.90 (d, 1H, *J* = 9.2 Hz), 7.92 (d, 1H, *J* = 1.8 Hz), 9.53 (s, 1H); IR (KBr disc) 3490, 3100, 2950, 1495, 1471, 1431, 1355, 1043 cm^{-1}; GC-MS m/z (rel. intensity) 375 (16, M^++2), 373 (44, M^+).

2-(5-Chloro-1-oxido-2*H*-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (2d) pale yellow solid, mp 137~139 °C (lit.,[14] mp 178~180 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 1.50 (s, 9H), 7.42 (dd, 1H, *J* = 9.0, 1.7 Hz), 7.51 (d, 1H, *J* = 2.5 Hz), 7.59 (d, 1H, *J* = 2.5 Hz), 7.79 (d, 1H, *J* = 9.0 Hz), 7.92 (d, 1H, *J* = 1.7 Hz), 9.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.12, 143.62, 142.02, 141.25, 135.18, 129.22, 127.53, 125.90, 124.03, 121.06, 118.14, 114.46, 35.71, 34.60, 31.36, 29.71; IR (KBr disc) 3490, 3100, 2950, 1495, 1471, 1431, 1355, 1043 cm^{-1}; HRMS(EI) calcd for $C_{20}H_{24}N_3O_2Cl$ 373.1557, found 373.1555. *Anal*. Calcd for $C_{20}H_{24}N_3O_2Cl$: C, 64.25; H, 6.47; N, 11.24. Found: C, 64.17; H, 6.50; N, 11.29.

4-Methyl-2-(1-oxido-2*H*-benzotriazol-2-yl)phenol (2e) pale yellow solid, mp 146~148 °C (lit.,[14] mp 138~140 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 7.09 (d, 1H, *J* = 8.5 Hz), 7.28 (dd, 1H, *J* = 8.5, 2.2 Hz), 7.40-7.52 (m, 3H), 7.56-7.81 (m, 2H), 9.73 (s, 1H); IR (KBr disc) 3475, 3095, 2960, 1594, 1507, 1219 cm^{-1}; GC-MS m/z (rel. intensity) 241 (100, M^+).

2-[2-Methoxy-3,5-bis(1,1-dimethylethyl)phenyl]-1-oxido-2*H*-benzotriazole (2f) white solid, mp 176~178 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 1.44 (s, 9H), 3.24 (s, 3H), 7.28 (d, 1H, *J* = 2.5 Hz), 7.37-7.41 (m, 1H), 7.48-7.51 (m, 1H), 7.63 (d, 1H, *J* = 2.5 Hz), 7.78-7.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.11, 146.34, 143.82, 142.25, 129.36, 127.94, 126.92, 126.50, 125.48, 124.40, 119.62, 114.25, 60.80, 35.89, 35.00, 31.37, 30.53; IR (KBr disc) 3079, 2964, 2912 cm^{-1}; HRMS(EI) calcd for $C_{21}H_{27}N_3O_2$ 353.2103, found 353.2106. *Anal*. Calcd for $C_{21}H_{27}N_3O_2$: C, 71.36; H, 7.70; N, 11.89. Found: C, 71.35; H, 7.71; N, 11.87.

2-[2-Methoxy-3,5-bis(1,1-dimethylpropyl)phenyl]-1-oxido-2*H*-benzotriazole (2g) white solid, mp 138~141 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 0.72 (t, 3H, *J* = 7.5 Hz), 0.74 (t, 3H, *J* = 7.5 Hz), 1.30 (s, 6H), 1.40 (s, 6H), 1.65 (q, 2H, *J* = 7.5 Hz), 1.83 (q, 2H, *J* = 7.5 Hz), 3.22 (s, 3H), 7.23 (d, 1H, *J* = 2.4 Hz), 7.37-7.40 (m, 1H), 7.47-7.51 (m, 2H), 7.77-7.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.01, 144.61, 142.22, 141.92, 129.74, 129.33, 126.95, 126.44, 125.49, 125.07, 119.61, 114.28, 60.71, 39.58, 38.20, 37.09, 34.62, 28.56, 28.41, 9.64, 9.23; IR ($CDCl_3$) 3084, 3061, 2933 cm^{-1}; HRMS(EI) calcd for $C_{23}H_{31}N_3O_2$ 381.2416, found 381.2422. *Anal*. Calcd for $C_{23}H_{31}N_3O_2$: C, 72.41; H, 8.19; N, 11.01. Found: C, 72.53; H, 8.21; N, 10.82.

6-Chloro-2-[2-methoxy-3,5-bis(1,1-dimethylethyl)phenyl]-1-oxido-2*H*-benzotriazole (2h) white solid, mp 186~189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 1.44 (s, 9H), 3.27 (s, 3H), 7.29 (s, 1H), 7.42 (d, 1H, *J* = 9.2 Hz), 7.61(s, 1H), 7.77 (d, 1H, *J* = 9.2 Hz), 7.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.57, 146.14, 143.62, 140.13, 132.43, 130.80, 127.83, 126.30, 125.27, 123.78, 120.67, 113.28, 60.67, 35.67, 34.76, 31.19, 30.42; IR ($CDCl_3$) 3107, 3084, 2972, 2901 cm^{-1}; HRMS(EI) calcd for $C_{21}H_{26}N_3O_2Cl$ 387.1714, found 387.1716. *Anal*. Calcd for $C_{21}H_{26}N_3O_2Cl$: C, 65.02; H, 6.76; N, 10.83. Found: C, 65.17; H, 6.76; N, 10.85.

5-Chloro-2-[6-methoxy-3,5-bis(1,1-dimethylethyl)phenyl]-1-oxido-2*H*-benzotriazole (2i) white solid, mp 135~137 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 9H), 1.39 (s, 9H), 3.18 (s, 3H), 7.22-7.28 (m, 2H), 7.56 (d, 1H, *J* = 2.4 Hz), 7.73-7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.69, 146.14, 143.59, 141.80, 135.01, 127.83, 127.72, 126.35, 123.81, 123.71, 118.18, 115.46, 60.69, 35.61, 34.74, 31.25, 30.46; IR ($CDCl_3$) 3102, 2961, 2933, 2869 cm^{-1}; HRMS(EI) calcd for $C_{21}H_{26}N_3O_2Cl$ 387.1714, found 387.1708. *Anal*. Calcd for $C_{21}H_{26}N_3O_2Cl$: C, 65.02; H, 6.76; N, 10.83. Found: C, 65.17; H, 6.79; N, 10.79.

2-[2-Methoxy-5-methylphenyl]-1-oxido-2*H*-benzotriazole (2j) white solid, mp 93~95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.80 (s, 3H), 7.02 (d, 1H, *J* = 8.7 Hz), 7.29 (d, 1H, *J* = 1.8 Hz), 7.31-7.44 (m, 3H), 7.75 (d, 1H, *J* = 8.7 Hz), 7.80 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.35, 141.67, 133.62, 130.57, 129.36, 128.72, 125.98, 125.37, 122.64, 119.26, 114.12, 112.46, 56.23, 20.21; IR ($CDCl_3$) 3074, 3017, 2964, 2934 cm^{-1}; HRMS(EI) calcd for $C_{14}H_{13}N_3O_2$ 255.1008, found 255.1007. *Anal*. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.43; H, 5.13; N, 16.46.

2-(2*H*-Benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (3a) pale yellowish white solid, mp 153 ~155 °C (lit.,[5] mp 154~156 °C). ^{1}H 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 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^+), 308 (100), 57 (5).

2-(2*H*-Benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)phenol (3b) white solid, mp 85~87 °C (lit.,[5] mp 86.5~88 °C). ^{1}H 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), 7.45 (m, 2H), 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^+), 322 (100).

2-(5-Chloro-2*H*-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)phenol (3c) white solid, mp 151~153 °C (lit.,[5] mp 152.5~154.5 °C). ^{1}H 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^++2), 357 (15, M^+), 342 (100), 149 (60), 57 (8).

2-(2*H*-Benzotriazol-2-yl)-4-methylphenol (3e) white solid, mp 129~130 °C (lit.,[5] mp 128~130 °C). ^{1}H 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), 7.46 (m, 2H), 7.92 (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^+), 168 (10), 93 (18).

2-[2-Methoxy-3,5-bis(1,1-dimethylethyl)phenyl]-2*H*-benzotriazole (3f) white solid, mp 129~132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.47 (s, 9H), 3.08 (s, 3H), 7.46-7.54 (m, 4H), 8.01-8.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 145.8, 145.0, 143.4, 133.7, 126.9, 125.6, 122.8, 118.5, 60.1, 35.6, 34.7, 31.3, 30.6; IR (KBr disc) 3062, 2990, 2867, 1489, 1424, 1280 cm^{-1}; GC-MS m/z (rel. intensity) 337 (34, M^+), 322 (100), 220 (30), 164 (20), 119 (70), 57 (15); HRMS(EI) calcd for $C_{21}H_{27}N_3O$ 337.2154, found 337.2157. *Anal*. Calcd for $C_{21}H_{27}N_3O$: C, 74.74; H, 8.06; N, 12.45. Found: C, 74.76; H, 8.09; N, 12.48.

2-[2-Methoxy-3,5-bis(1,1-dimethylpropyl)phenyl]-2*H*-benzotriazole (3g) white solid, mp 154~157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (t, 3H, *J* = 7.5 Hz), 0.70 (t, 3H, *J* = 7.5 Hz), 1.28 (s, 6H), 1.40 (s, 6H), 1.63 (q, 2H, *J* = 7.5 Hz), 1.83 (q, 2H, *J* = 7.5 Hz), 3.02 (s, 3H), 7.35 (d, 1H, *J* = 2.4 Hz), 7.40-7.47 (m, 3H), 7.97-8.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 145.0, 144.1, 141.5, 133.7, 127.6, 126.9, 123.5, 118.5, 60.0, 39.3, 37.9, 36.8, 34.4, 28.6, 28.4, 9.6, 9.2; IR (KBr disc) 3068, 2992, 2961, 2926, 2875, 1612, 1424, 1255 cm^{-1}; HRMS(EI) calcd for $C_{23}H_{31}N_3O$ 365.2467, found 365.2461. *Anal*. Calcd for $C_{23}H_{31}N_3O$: C, 75.58; H, 8.55; N, 11.50. Found: C, 75.77; H, 8.62; N, 11.47.

5-Chloro-2-[2-methoxy-3,5-bis(1,1-dimethylethyl)phenyl]-2*H*-benzotriazole (3h) white solid, mp 130-132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.43 (s, 9H), 3.05 (s, 3H), 7.38 (dd, 1H, *J* = 9.0, 1.5 Hz), 7.44 (d, 1H, *J* = 2.3 Hz), 7.50 (d, 1H, *J* = 2.3 Hz), 7.92-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 146.0, 145.3, 143.6, 143.5, 133.5, 132.8, 128.6, 125.9, 122.6, 119.7, 117.5, 60.3, 35.7, 34.7, 31.3, 30.6; IR (KBr disc) 3068, 2990, 2968, 2875, 1490, 1424, 1280, 1250, 1154, 1043 cm^{-1}; HRMS(EI) calcd for $C_{21}H_{26}N_3OCl$ 371.1764, found 371.1774. *Anal*. Calcd for $C_{21}H_{26}N_3OCl$: C, 67.82; H, 7.05; N, 11.30. Found: C, 67.89; H, 6.72; N, 11.28.

2-[2-Methoxy-5-methylphenyl]-2*H*-benzotriazole (3j) white solid, mp 130-132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.86 (s, 3H), 7.04 (d, 1H, *J* = 8.5 Hz), 7.30 (dd, 1H, *J* = 8.5, 2.1 Hz), 7.41-7.47 (m, 2H), 7.50 (d, 1H, *J* = 2.1 Hz), 7.95-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.25, 144.71, 131.47, 129.72, 127.90, 126.76, 118.36, 112.62, 56.40, 20.26; IR (KBr disc) 3070, 3013, 2974, 2938 cm^{-1} ; HRMS(EI) calcd for $C_{14}H_{13}N_3O$ 239.1059, found 239.1059. *Anal*. Calcd for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.28; H, 5.48; N, 17.59.

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