# 2-BROMO-2-NITROPROPANE/Zn PROMOTED REDUCTIVE CYCLIZATIONS OF ORTHO-CARBONYL, IMINO, OR AZO SUBSTITUTED NITROBENZENES

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**Abstract** - Under the mild conditions, reductive cyclizations of 2-nitrobenzaldehydes, 2'-nitroacetophenone, and *N*-(2-nitrobenzylidene)anilines were accomplished in the presence of 2-bromo-2-nitropropane/Zn in methanolic solution. Under the similar conditions in MeOH/$CH_2Cl_2$, *o*-nitro-substituted phenylazobenzenes have been converted into 2-aryl-2*H*-benzotriazoles *via* reductive cyclizations that are widely used as UV absorbers. Synthesis and mechanistic details are discussed.

## INTRODUCTION

The *N*-containing 5-membered heterocyclic compounds are of great importance in organic synthesis, medicinal chemistry, and industry. 2,1-Benzisoxazole (anthranil) has been known for a long time, and a modest number of 2,1-benzisoxazole derivatives have a patented usage, *i.e.* anti-inflammatory, antituberculotic, lipodemia, and analogs of psilocene and muscomal.[1a] Some of 2,1-benzisoxazole derivatives are also useful key intermediates in the synthesis of biologically active molecules such as quinazolinones and 1,4-benzodiazepines.[2] The methods of preparation of 2,1-benzisoxazoles include nitro and acyl group side chain interaction in *o*-nitroacylbenzene derivatives,[1-8] *i.e.* catalytic hydrogenation,[1] thionyl chloride,[2b] reductive transformations by zinc/acetic acid,[3] triethyl phosphite,[4] and *electrolysis reaction*.[9] However, useful synthetic methods of 2,1-benzisoxazoles have not been well established.

2-(2'-Hydroxyphenyl)-2*H*-benzotriazoles are widely used as UV absorbers for the protection of commercially important plastics against sunlight.[10] A wide variety of reagents have been employed for

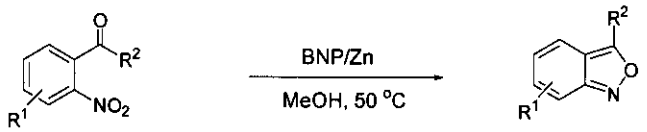
the conversion of *o*-nitrophenylazobenzenes to 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles, *i.e.* alkali sulfides,[11] zinc dust/sodium hydroxide,[12] catalytic hydrogenation,[13] and thiourea *S,S'*-dioxide and NaOH.[14] We also reported the use of Bakers' yeast for the reductive cyclizations of *o*-nitrophenylazobenzenes to 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles *via* 2-(2'-hydroxyphenyl)-2*H*-benzotriazole *N*-oxides.[15] However, most of the methods accompany problems, *i.e.* benzotriazole *N*-oxide formation,[16] formation of *o*-aminoazophenols which are hard to remove from the desired product,[13] dechlorination of chloro substituted *o*-nitrophenylazobenzenes,[16] work-up difficulties,[15] and/or drastic reaction conditions.

In the course of our study on reductive cyclization reaction of 2-nitroarenes,[17] we found an efficient synthetic method of 2,1-benzisoxazoles by using 2-bromo-2-nitropropane (BNP) and Zn dust which was the first example of BNP/Zn.[18] Based on the result, we extend our novel method for the preparation of 2,1-benzisoxazoles and 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles as well as mechanistic consideration. Herein we wish to report synthetic and mechanistic study of unique reductive cyclizations of 2-nitrobenzaldehydes, 2'-nitroacetophenone, and *N*-(2-nitrobenzylidene)anilines toward 2,1-benzisoxazoles, and *o*-nitrophenylazobenzenes toward 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles which were accomplished in the presence of BNP/Zn.

## RESULTS AND DISCUSSION

*Synthetic Consideration of 2,1-benzisoxazoles*

On the reductive reaction of 2-nitrobenzaldehyde under acidic conditions (aq. HCl/Zn/MeOH) which are similar to known procedure,[3] the yield of cyclized product 2,1-benzisoxazole (**2a**) was relatively low and some by-products including 2-aminobenzaldehyde were observed. Even with an optimum condition [aq. HCl (5 equiv.)/Zn (5 equiv.)/MeOH], only 74% of cyclized product (**2a**) was obtained along with more than 23% of 2-aminobenzaldehyde by-product which was not easy to separate from the desired product. In the case of 2'-nitroacetophenone in acidic conditions [aq. HCl (5 equiv.)/Zn (5 equiv.)/MeOH], it produced about 1:1 mixture of cyclized product and 2'-aminoacetophenone.




(1)

**1** $R^1$ = H, Cl, OMe, $OCH_2O$; $R^2$ = H, Me **2**

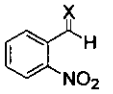
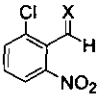
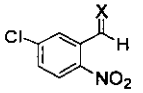
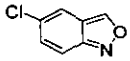
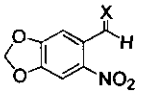
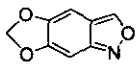
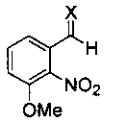
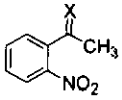
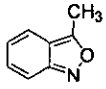
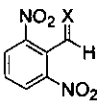
However, by using BNP/Zn in neutral conditions, by-product formation was decreased marvelously. The optimized reaction of 2-nitrobenzaldehydes or 2'-nitroacetophenone (**1**) with BNP (1.2 equiv.) and Zn

(5 equiv.) in methanol at 50 °C produced 2,1-benzisoxazoles (**2**) in excellent yields (eq 1, Table 1).

Both BNP and zinc dust were essential for the reductive cyclization of 2-nitrobenzaldehyde under the neutral conditions since it produced **2** in a trace amount with most of the reactant retained without BNP. The role of BNP is likely to be an electron acceptor due to its low lying antibonding π-orbital which has been employed in $S_{RN}1$ process, and the utility of BNP has been observed in elsewhere.[19]

For the extension of synthetic utility, we examined the reductive cyclizations of various substituted *N*-(2-nitrobenzylidene)anilines by using BNP and Zn dust under the optimized conditions that were obtained from the reactions of acylnitrobenzenes, and we found that it worked well for *N*-(2-nitrobenzylidene)anilines toward 2,1-benzisoxazoles as well as acylnitrobenzenes (Table 1).

**Table 1.** The reactions of substituted 2-nitrobenzaldehydes, 2'-nitroacetophenone, or *N*-(2-nitrobenzylidene)anilines in the presence of BNP (1.2 equiv.)/Zn (5 equiv.) in MeOH.

| entry | substrate | X | | time (h) | temp (°C) | product | | yield (%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 |  | O | **1a** | 5 | 50 |  | **2a** | 98 |
| 2 | | NPh | **3a** | 4 | rt | | | 96 |
| 3 |  | O | **1b** | 7 | 50 |  | **2b** | 95 |
| 4 | | NPh | **3b** | 4 | rt | | | 96 |
| 5 |  | O | **1c** | 8 | 50 |  | **2c** | 80 |
| 6 | | NPh | **3c** | 4 | rt | | | 83 |
| 7 |  | O | **1d** | 5 | 50 |  | **2d** | 91 |
| 8 | | NPh | **3d** | 4 | rt | | | 91 |
| 9 |  | O | **1e** | 5 | 50 |  | **2e** | 78 |
| 10 | | NPh | **3e** | 4 | rt | | | 73 |
| 11 |  | O | **1f** | 5 | 50 |  | **2f** | 90 |
| 12 |  | O | **1g** | 48 | 50 |  | **2g** | 38[b] |
| 13 | | NPh | **3g** | 18 | rt | | | 4[b] |

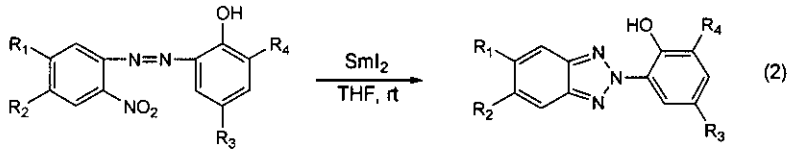
[a]GC yield with an internal standard. [b]Starting material was recovered.

In most cases, cyclization was successful with excellent yields independent of the position and the character of the substituent. Compared to 2-nitrobenzaldehydes, the reaction of *N*-(2-nitrobenzylidene)anilines proceeded faster at lower reaction temperature. The reaction of *N*-(2-nitrobenzylidene)aniline (**3a**) with BNP (1.2 equiv.) and Zn (5 equiv.) in methanol at room temperature produced 2,1-benzisoxazole (**2a**) in 96% yield within 4 h accompanied by 60~70% of aniline as a co-product which would be a leaving group from the substrate. Again, both BNP and Zn dust were essential for the reductive cyclization of *N*-(2-nitrobenzylidene)aniline (**3**) under the neutral conditions since no effective reaction was observed without BNP or Zn.

The reductive cyclization of chloro-substituted 2-nitrobenzaldehydes or *N*-(2-nitrobenzylidene)anilines produced desired chloro-substituted 2,1-benzisoxazoles in high yields without giving any dechlorinated products (Table 1, entries 3-6). It also provides an efficient and selective synthesis of 2,1-benzisoxazole derivatives that are substituted with acid labile alkoxy functional groups using our BNP/Zn condition (Table 1, entries 7-10). The reductive cyclization of 2,6-dinitrobenzaldehyde or *N*-(2,6-dinitrobenzylidene)aniline was strongly retarded because of dinitro functionality (Table 1, entries 12, 13).

*Synthetic Consideration of 2-Aryl-2*H*-benzotriazoles*

We have previously reported reductive cyclization of nitroarenes that have -N=N- functionality on the ortho position, *i.e.* *o*-nitrophenylazobenzenes (**4**) with $SmI_2$ in THF, at room temperature to the corresponding 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles (**5**).[20] We obtained high yielding reductive cyclizations of **4** without any of *o*-aminoazophenols or benzotriazole *N*-oxides formed (eq 2). The driving force for such transformations is believed to come from the powerful reducing ability of $Sm^{2+}$ [$E^{\circ}$ ($Sm^{3+}$/ $Sm^{2+}$) = -1.55 V] which behaves as a one-electron donor. Since the electron transfer ability controls the reaction, we do believe those nitroarenes should work with BNP/Zn in neutral conditions also.




(2)

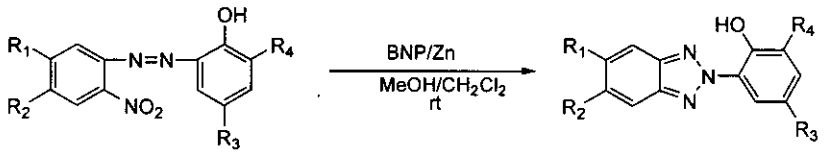
**4** $R_1$, $R_2$ = H, Cl, $R_3$ = Me, *t*-Bu, *t*-pentyl; $R_4$ = H, *t*-Bu, *t*-pentyl **5**

Thus, another type of compound, *o*-nitrophenylazobenzene was tried with BNP/Zn in MeOH similar to 2,1-benzisoxazole formation reaction conditions. Unfortunately, the reductive cyclizations toward 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles with BNP/Zn in MeOH failed to react because of low solubility of starting substrate (**4**). However, using a proper co-solvent, the reaction worked properly as we expected.

The reaction of 2,4-bis(1,1-dimethylethyl)-6-(2'-nitrophenylazo)phenol (**4a**) (1 equiv.) with BNP (1.2 equiv.)/Zn (12 equiv.) in MeOH/$CH_2Cl_2$ (v/v, 5:1) at room temperature produced 2-(2'-hydroxyphenyl)-2*H*-benzotriazole (**5a**) in 72% yield within 4 h. The rest were identified as 2-amino-4,6-bis(1,1-dimethylethyl)phenol and 1,2-diaminobenzene which came from the simple reduction of azo and nitro groups easily removable from the major product (**5a**).

In order to test the synthetic utility of the BNP/Zn conditions for this type of compound, we examined the reductive cyclizations of various substituted *o*-nitrophenylazobenzenes toward 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles which are widely used as ultraviolet absorbers for the protection of commercially important plastics against sunlight. Our work concerning the reductive cyclization of **4** using BNP/Zn was summarized in the Table 2. Similar to the reactions of ortho-carbonyl or imino substituted nitrobenzenes, chloro-substituted *o*-nitrophenylazobenzenes transformed to benzotriazoles without giving any of dechlorinated products.

**Table 2.** Reductive cyclization of *o*-nitrophenylazobenzenes (**4**) using BNP (1.2 equiv.)/ Zn (12 equiv.) in MeOH/$CH_2Cl_2$ (v/v, 5:1) at room temperature.




| entry | substrate | time (h) | product | yield (%)[a] |
|---|---|---|---|---|
| 1 | **4a**, $R_1$ = H, $R_2$ = H, $R_3$ = *t*-Bu, $R_4$ = *t*-Bu | 4 | **5a** | 72 |
| 2 | **4b**; $R_1$ = H, $R_2$ = H, $R_3$ = *t*-pentyl, $R_4$ = *t*-pentyl | 3 5 | **5b** | 71 |
| 3 | **4c**; $R_1$ = H, $R_2$ = Cl, $R_3$ = *t*-Bu, $R_4$ = *t*-Bu | 4 | **5c** | 88 |
| 4 | **4d**; $R_1$ = Cl, $R_2$ = H, $R_3$ = *t*-Bu, $R_4$ = *t*-Bu | 3.5 | **5c** | 79 |
| 5 | **4e**; $R_1$ = H, $R_2$ = H, $R_3$ = Me, $R_4$ = H | 21 | **5e** | 83 |

[a]GC yield with an internal standard, 2-amino-4,6-bis(1,1-dimethylethyl)phenol and 1,2-diamino-benzene were obtained as by-products.

*Mechanistic Consideration*

As mentioned before, BNP (-0.13 V, Hg cathode, 0.1 M $LiClO_4$/MeOH, Ag/AgCl, 20 mV/s) could act as an electron acceptor due to its low lying antibonding π-orbital.[19] It is also well known that the carbon-halogen bond in α-halogenated nitroalkanes is usually reduced at a less negative potential than the nitro group, and 2-nitropropan-2-yl radical formation in electrolysis reaction was described by Simonet[21] and

Barba.[22]

In our BNP/Zn mediated reaction, intermediate radical anion of the type $[(Me)_2C(NO_2)Br]^{\cdot-}Zn^{+\cdot}$, formed by a one-electron transfer mechanism, is thought to be involved. The radical anion arising from the first electron transfer can undergo fragmentation to give a 2-nitropropan-2-yl radical (eq 3) that may react with nitroarene substrate.

$$Me_2C(NO_2)Br \overset{ET}{\rightleftharpoons} Me_2C(NO_2)Br^{-\bullet} \longrightarrow Me_2\dot{C}NO_2 + Br^- \qquad (3)$$

Formation of 2-nitropropan-2-yl radical was evidenced from the observation of a trace amount of 2,3-dimethyl-2,3-dinitrobutane, coupling product from 2-nitropropan-2-yl radical, and easily removable 2-nitropropane (probably one of the disproportionation product) during the reductive cyclization of 2-nitroacylbenzenes or *N*-(2-nitrobenzylidene)anilines toward 2,1-benzisoxazoles.

For mechanistic purposes, several inhibition experiments were carried out. Under the $O_2$ atmosphere, the reactions of 2-nitrobenzaldehyde with BNP/Zn/$O_2$ at 50 °C for 5 h were retarded completely and only the reactant was recovered. In the presence of 10 mol% of *m*-dinitrobenzene or di-*tert*-butyl nitroxide, BNP assisted reductive cyclization reaction was retarded effectively.[18] Detailed measurements of kinetic chain length with 5 mol% of di-*tert*-butyl nitroxide exhibited about 1 (inhibition time; 10 ~ 15 min.). Apparently electron transfer processes are involved during the reductive cyclization reaction resulting in 2,1-benzisoxazole even though it is not a chain reaction. Results of inhibition experiments are shown in Figure 1 and Figure 2.

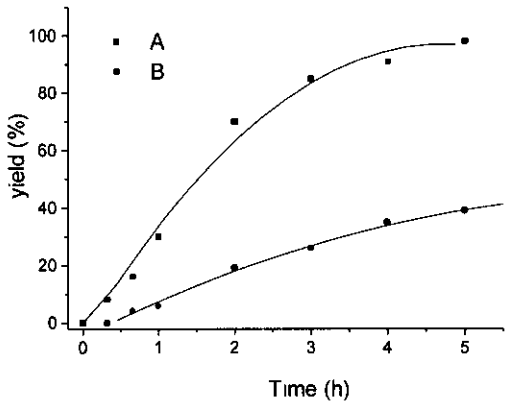



**Figure 1**. Reactions of 2-nitrobenzaldehyde (0.17 M) with BNP (0.20 M) and Zn in MeOH at 50 °C; A, in the absence of *m*-dinitrobenzene (*m*-DNB); B, in the presence of *m*-DNB (10 mol %)

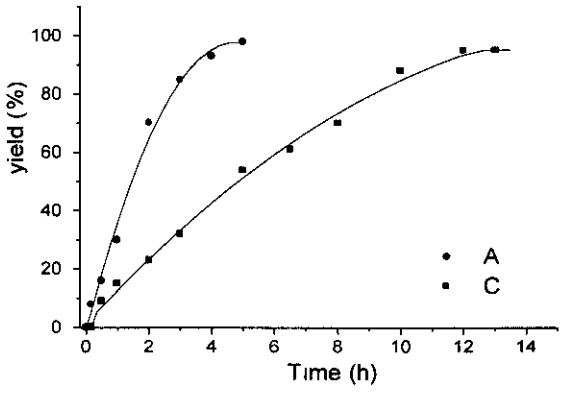
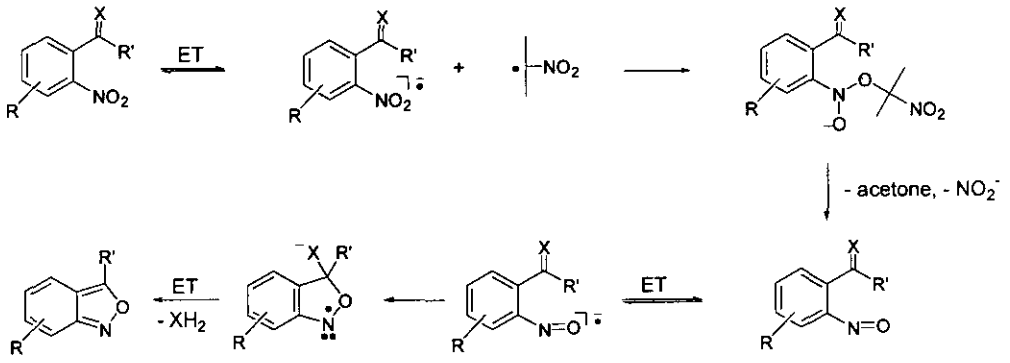



**Figure 2**. Reactions of 2-nitrobenzaldehyde (0.17 M) with BNP (0.20 M) and Zn in MeOH at 50 °C; A, in the absence of di-*tert*-butyl nitroxide (DBN); C, in the presence of DBN (5 mol %), inhibition time, ~10 min

Thus, 2-nitropropan-2-yl radical intermediate (eq 3) generated from BNP and zinc could couples with 2-nitrobenzaldehyde or *N*-(2,6-dinitrobenzylidene)aniline radical anion which was also formed by electron transfer from zinc to the substrate (2-nitrobenzaldehyde, -0.59 V, -0.84 V (Hg cathode); *N*-(2-nitrobenzylidene)aniline, -0.79 V (Pt cathode), 0.1 M $LiClO_4$/ MeOH, Ag/AgCl, 20 mV/s).[23] The loss of acetone and nitrite anion from the coupled intermediate would drive the formation of nitroso intermediate which was observed by GC-MS analysis of on-going reaction mixture. Plausible mechanism is presented in Scheme 1.

**Scheme 1**



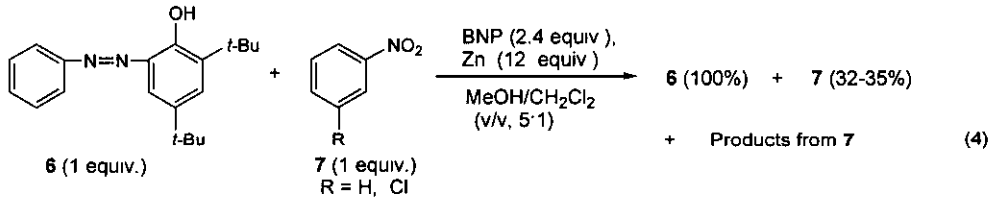

Similar trend was observed for the reductive cyclization of *o*-nitrophenylazobenzenes with BNP/Zn in $MeOH/CH_2Cl_2$. In control experiments, without BNP and/or Zn transformation of **4** to **5** was not possible while retaining most of the reactant. Under $O_2$ atmosphere, the reactions of **4a** with BNP/Zn at room temperature for 8 h gave nothing but full recovery of the reactant (Table 3, entry 2). In the presence of 10 mol% of *m*-dinitrobenzene or di-*tert*-butyl nitroxide, the reductive cyclization reactions resulted in effective inhibition (Table 3, entries 3, 4).

To confirm functional group selectivity of the reductive reaction, some experiments were done. From the cyclic voltammetric data, **4a** (-0.73 V, Pt cathode, 0.4 M $LiClO_4/MeOH/CH_2Cl_2$ (v/v, 5:1), Ag/AgCl, 100 mV/s) is easily reducible compared to 2,4-*bis*(1,1-dimethylethyl)-6-phenylazophenol (-1.2 V, Pt cathode, 0.4 M $LiClO_4/MeOH/CH_2Cl_2$ (v/v, 5:1), Ag/AgCl, 100 mV/s). In addition, competition reaction between nitro and azo group of selected model compounds resulted in the reduction of nitro group only leaving azo functionality intact (eq 4). Products of the competition reaction were derivatives of aniline, azobenzene, and azoxybenzene which came from nitroarene (**7**).

**Table 3.** The reactions of 2,4-bis(1,1-dimethylethyl)-6-(4'-chloro-2'-nitrophenylazo)phenol (**4c**) (1 equiv.) with BNP (1.2 equiv.)/ Zn (12 equiv.) in MeOH/$CH_2Cl_2$ (v/v, 5:1) in the presence of inhibitors at 0 °C (entries 1, 3, 4) or at room temperature (entry 2).

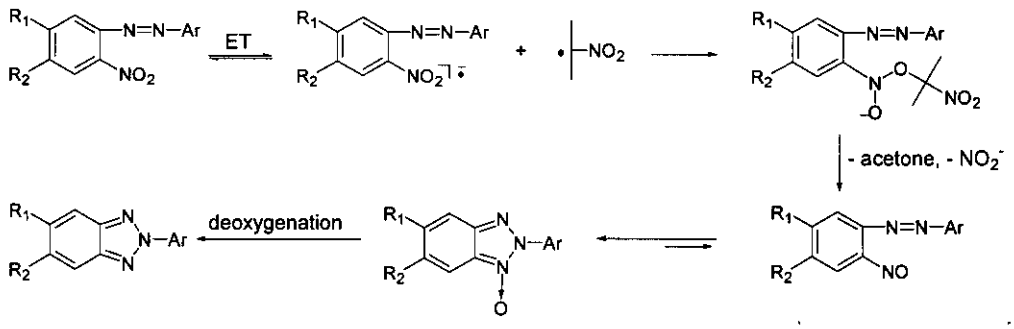
| entry | Inhibitor | Time (h) | **4c** (yield%)[a] | Products (yield%)[a] |
|---|---|---|---|---|
| 1 | none | 0.75 | - | 18 (**5c**) + 68 (*N*-oxide) |
| 2 | $O_2$ | 8 | 100 | - |
| 3 | 10 mol% *m*-dinitrobenzene | 0.75 | 50 | 10 (**5c**) + 36 (*N*-oxide) |
| 4 | 10 mol% di-*tert*-butyl nitroxide | 0.75 | 10 | 14 (**5c**) + 63 (*N*-oxide) |

[a]Isolated yield.




Thus, similar to 2,1-benzisoxazole formation reaction, we do believe 2-nitropropan-2-yl radical formed from BNP and zinc (eq 3) reacts with nitro group first rather than azo group to form the nitroso intermediate. Plausible mechanism is shown in Scheme 2.

**Scheme 2**




In conclusion, we have now established a mild and novel reaction route for 2,1-benzisoxazoles and benzotriazoles by using 2-bromo-2-nitropropane and Zn dust that would be a new synthetic methodology.

## EXPERIMENTAL

### 1. General consideration

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 Jeol or 500 MHz Bruker instrument and $^{13}$C NMR spectra were recorded on 75 MHz Bruker instrument. Chemical shifts are in ppm from tetramethylsilane (TMS). High-resolution MS were recorded on a Jeol JMS-DX 303 mass spectrometer. IR spectra were recorded on a Nicolet 205 FT-IR. Analytical data were obtained with an EA-1110, CHNS-O CE instruments. Cyclic voltammetric data were recorded on EG & G instrument. Melting points were determined on an Electrothermal apparatus and are uncorrected.

Products were isolated by flash column chromatography on silica gel (70 - 230 mesh ATSM, purchased from Merck) with eluents of mixed solvents (hexane and ethyl acetate). GC yields were determined by using an internal standard (toluene or decane) and were corrected with predetermined response factors.

## 2. General procedure for the reductive cyclizations

2-Bromo-2-nitropropane (0.403 g, 2.4 mmol) at 50 °C (acylbenzenes) or at rt (imines and azobenzenes) was added to a stirred solution of 2-nitroarene derivative (2 mmol) and zinc dust (0.654 g, 10 mmol for acylbenzenes and imines, 1.570 g, 24 mmol for azobenzenes) in deoxygenated MeOH (6 mL, for acylbenzenes and imines), or in MeOH/$CH_2Cl_2$ (v/v, 33/6.6 mL, for azobenzenes). Stirring was continued until the reaction was completed under Ar atmosphere. The reaction was filtered through a pad of Celite and the filtrate concentrated *in vacuo*. The residue was taken up in $CH_2Cl_2$/10% aqueous $NH_4Cl$ solution and extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic layer was dried over $MgSO_4$ and concentrated. The GC yield was determined with an internal standard and, if necessary, the products were isolated by flash column chromatography with ethyl acetate-hexane (5/95 ~ 1/99) co-solvent and were fully characterized. For the full spectral data of the products, see our previous reports (ref 9 for 2,1-benzisoxazoles and ref 15 for benzotriazoles).

**2,1-Benzisoxazole (2a)**[9,24] Liquid, Yield; 98% (from **1a**), 96% (from **3a**). TLC (30% ethyl acetate/hexane) $R_f$ 0.52; $^1$H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.64-7.56 (m, 2H), 7.36-7.27 (m, 1H), 7.04-6.99 (m, 1H).

**4-Chloro-2,1-benzisoxazole (2b)**[9] White solid, mp 51 - 53 °C, Yield; 95% (from **1b**), 96% (from **3b**). TLC (30% ethyl acetate/hexane) $R_f$ 0.73; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, 1H, $J$ = 0.9 Hz), 7.54 (dd, 1H, $J$ = 0.9, 9.0 Hz), 7.22 (dd, 1H, $J$ = 6.9, 9.0 Hz), 7.00 (d, 1H, $J$ = 6.9 Hz).

**5-Chloro-2,1-benzisoxazole (2c)**[9] Pale yellowish white solid, mp 80 - 82 °C (lit.,[3] mp 78 °C), Yield; 80% (from **1c**), 83% (from **3c**). TLC (30% ethyl acetate/ hexane) $R_f$ 0.63; $^1$H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.61-7.56 (m, 2H), 7.28-7.21 (m, 1H,).

**2,5,7-Trioxa-1-aza-*s*-indacene (2d)**[9] White solid, mp 115 - 117 ℃, Yield; 91% (from **1d**), 91% (from **3d**). TLC (30% ethyl acetate/hexane) $R_f$ 0.46; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, 1H, $J$ = 0.7 Hz), 6.80 (d, 1H, $J$ = 0.7 Hz), 6.68 (s, 1H), 5.99 (s, 2H).

**7-Methoxy-2,1-benzisoxazole (2e)**[9] Liquid, Yield; 78% (from **1e**), 73% (from **3e**). TLC (30% ethyl acetate/hexane) $R_f$ 0.44; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.11 (d, 1H, $J$ = 8.7 Hz), 6.93 (dd, 1H, $J$ = 7.2, 8.7 Hz), 6.48 (d, 1H, $J$ = 7.2 Hz), 4.01 (s, 3H).

**3-Methyl-2,1-benzisoxazole (2f)**[9,25] Liquid, Yield; 90% (from **1f**). TLC (30% ethyl acetate/ hexane) $R_f$ 0.38; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, 1H, $J$ = 8.8 Hz), 7.43 (d, 1H, $J$ = 8.8 Hz), 7.28-7.24 (m, 1H), 6.91 (dd, 1H, $J$ = 6.4, 8.8 Hz), 2.79 (s, 3H).

**2-(2'*H*-Benzotriazol-2'-yl)-4,6-di-*tert*-butylphenol (5a)**[15] Pale yellowish white solid, mp 153 ~155℃ (lit.,[14] 154~156℃), yield; 72%. TLC (5% ethyl acetate/hexane) $R_f$ 0.41; $^1$H NMR (300 MHz, $CDCl_3$) δ 11,76 (s, 1H), 8.24 (d, 1H, $J$ = 2.4 Hz), 7.84-7.91 (m, 2H), 7.37-7.44 (m, 2H), 7.36 (d, 1H, $J$ = 2.4 Hz), 1.45 (s, 9H), 1.33 (s, 9H).

**2-(2'*H*-Benzotriazol-2'-yl)-4,6-bis(1",1"-dimethylpropyl)phenol (5b)**[15] White solid, mp 85~87℃(lit.,[14] 86.5~88℃), yield; 71%. TLC (5% ethyl acetate/hexane) $R_f$ 0.44; $^1$H NMR (300 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.23 (d, 1H, $J$ = 2.4 Hz ), 7.88-7.95 (m, 2H ), 7.42-7.49 (m, 2H), 7.26 (d, 1H, $J$ = 2.4 Hz), 1.98 (q, 2H, $J$ = 7.5 Hz), 1.67 (q, 2H, $J$ = 7.5 Hz), 1.44 (s, 6H), 1.34 (s, 6H), 0.63-0.74 (m, 6H).

**2-(5'-Chloro-2'*H*-benzotriazol-2'-yl)-4,6-di-*tert*-butylphenol (5c)**[15] White solid, mp 151~153℃(lit.[14] 152.5~154.5℃), yield; 88% (from **4c**), 79% (from **4d**). TLC (5% ethyl acetate/hexane) $R_f$ 0.52; $^1$H NMR (300 MHz, $CDCl_3$) δ 11.52 (s, 1H), 8.26 (d, 1H, $J$ = 2.4 Hz), 7.80-7.93 (m, 2H), 7.43 (d, 1H, $J$ = 1.0 Hz), 7.40 (d, 1H, $J$ = 1.8 Hz), 1.51 (s, 9H), 1.39 (s, 9H).

**2-(2'*H*-Benzotriazole-2'-yl)-4-methylphenol (5e)**[15] White solid, mp 129~130℃ (lit.,[14] 128~130 ℃), Yield; 83%. TLC (5% ethyl acetate/hexane) $R_f$ 0.29; $^1$H NMR (300 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.18 (d, 1H, $J$ = 1.5 Hz), 7.88-7.95 (m, 2H), 7.43-7.50 (m, 2H), 7.06-7.16 (m, 2H), 2.38 (s, 3H).

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