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Preparation of 2-Aryl-2*H*-benzotriazoles by Zinc-Mediated Reductive Cyclization of *o*-Nitrophenylazophenols in Aqueous Media without the Use of Organic Solvents

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Abstract: Zinc powder-mediated reductive cyclization of *o*-nitrophenylazophenols in alkaline solution affords the corresponding 2-aryl-2*H*-benzotriazoles in high yields under mild reaction conditions. *No organic solvents* are used in the reaction and only minimal amounts in the work-up.

Keywords: 2-aryl-2*H*-benzotriazoles; *o*-nitrophenylazophenols; reaction in water; reductive cyclization; zinc powder

Benzotriazoles, having an excellent efficacy of absorbing ultraviolet rays (200–400 nm), have been utilized extensively as archetypical photostabilizer additives in the field of plastics, polymers, oils and lubricants, and are required in very large amounts. In particular, as ultraviolet absorbing agents, 2-(2′-hydroxyphenyl)benzotriazole (TIN-P) and 2-(2′-hydroxy-5-methylphenyl)benzotriazole (Tinuvin-P) have been most widely employed in polyols and polyurethane foam for more than 40 years.[1a–f] They are especially useful for the protection of organic polymeric substances, such as thermoplastics, coating materials, recording materials and even wool, against deterioration due to synthetic ultraviolet irradiation and/or sunlight. Without ultraviolet absorbers, extended exposure of the polymer backbone to solar radiation often leads to photodegradation and oxidation of the surface of the polymeric materials. These photostabilizer additives protect polymeric substances as well as organic pigments from UV radiation or sunlight, thus helping to preserve the original appearance and physical integrity of the polymeric system during outdoor weathering. A distinguishing, although not unique, feature of these substances is the presence of an intramolecular hydrogen bond, which is believed to be a key component in the mechanism for the dissipation of light energy.[1g–i] Therefore, a great deal of attention has been focused on the development of simple, practical and economic methods for the preparation of benzotriazoles. A number of methods has been reported for the conversion of *o*-nitrophenylazophenols to benzotriazoles with various reducing agents such as zinc powder in aqueous methanol in the presence of alkali hydroxide,[2a,b] glucose and zinc dust in aqueous ethanol in the presence of sodium hydroxide,[2c] hydrazine hydrate in the presence of alkali hydroxide,[3] hydroxylamine,[4] hydrogenation under pressure over palladium on carbon,[5] platinum sulfide on carbon,[6] or Raney Ni[7] in an appropriate solvent in the presence of sodium hydroxide or diethylamine, and paraformadehyde suspended in isopropyl alcohol containing sodium hydroxide and a small amount of 2,3-dichloro-1,4-benzoquinone or naphthoquinone,[8] samarium diiodide,[9] thiourea *S*,*S*-dioxide in sodium hydroxide,[10] baker's yeast,[11] or with saccharides in the presence of fluorenol.[12] Furthermore, a synthesis of 2-aryl-2*H*-benzotriazoles by controlled-potential cathodic electrolysis has been reported.[13] $Ru_3(CO)_{12}$ has been found to catalyze the reductive carbonylation of *o*-nitrophenylazo compounds in the presence of triethylamine.[14] Some limitations and shortcomings have been noted in most of these reported methods. The reductants such as hydrazine, hydroxylamine, saccharide, samarium diiodide, thiourea *S*,*S*-dioxide and noble metals such as Pd, Pt, Ru, Rh are expensive, especially in view of establishing an industrially viable process. Undesired benzotriazole *N*-oxides and *o*-aminoazophenols are formed unavoidably as by-products, where it is troublesome to separate these from the desired benzotriazoles. Dehalogenation occurs in the case of the reductive cyclization of halogen-substituted *o*-nitrophenylazobenzenes (over-reduction), when metals such as Pd, Pt, Ru, Rh or Raney Ni-catalyzed hydrogenation methods are employed, where again, it is difficult to separate the products from the unwanted dehalogenated triazoles.[15] In some cases, harsh reaction conditions such as high pressure and high reaction temperature are required.[5–7] The zinc powder-mediated reduction of azo compounds reported usually requires an excess amount of zinc as reductant (6–83 equivs).[2a,c] Here, the reductive cyclization reactions of azo compounds are carried out by adding the zinc powder directly to a solution of sodium hydroxide, and it should be noted that this type of operation can be dangerous as vigorous reactions can occur. Hydrogen gas is rapidly evolved when zinc powder is added in portions directly to the reaction mixture. From an experimental standpoint in the laboratory and due to operational reasons in the industry, adding a liquid alkaline solution to the vessel is much more convenient and much safer than adding zinc powder in portions to the reactor. It must also be noted that almost all of the reactions reported have been carried out in *organic solvents*, such as MeOH, EtOH, *n*-BuOH, *i*-PrOH, THF, toluene or xylene, many of which have considerable toxicity. Therefore, based on both economical and practical reasons, the authors deemed it important to develop an effective method for the reductive cyclization of *o*-nitrophenylazophenols using only water as solvent.

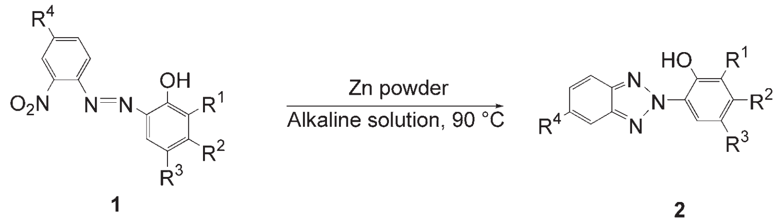
In this communication, we report that *o*-nitrophenylazobenzenes are efficiently cyclized reductively by adding an aqueous alkaline solution to a mixture of substrate and zinc powder in water to give the corresponding benzotriazoles in high yields without the formation of any by-products, such as over-reduced products and/or benzotriazole *N*-oxides, where the reaction proceeds *in the absence of organic solvents*. The results are summarized in Table 1 and Scheme 1.

Thus, a 25 wt% aqueous NaOH solution was added to a mixture of azo compound and zinc powder in water and the resulting suspension was heated at 90°C for up to 1 h, as indicated in Table 1 (monitored by HPLC). In order to optimize the reaction conditions, the zinc powder-mediated reductive cyclization of *o*-nitrophenylazobenzene **1a** was carried out in various alkaline solutions. Surprisingly, the reductive cyclization was found to be finished immediately after addition of the 25 wt% aqueous alkaline solution at 90°C to afford the corresponding triazole **2a** in yields of 92% (NaOH, Run 1) and 91% (KOH, Run 2). The cyclization became slow, when the reaction was carried out at 70°C, 50°C or room temperature, where still some starting material **1a** was detected after 12 h (12% at 70°C), (34% at 50°C) and (59% at room temperature, all determined by HPLC). The reductive cyclization of **1a** was not complete when the concentration of NaOH (9.6 g →5.0 g) was decreased. Here, **2a** was formed in only 42% (HPLC ratio), even after 10 h at 90°C. No significant difference was observed between using NaOH and KOH aqueous solutions. Similarly, azo compounds **1b–h** were cyclized efficiently to the corresponding triazoles **2b–h** in good to excellent yields, all in the absence of organic sol-

Table 1. Zn-mediated reductive cyclization of *o*-nitrophenylazophenols.[a]

Run	Azo	Time [h]	Product	Yield [%][d]	mp of **2** [°C]	Reported mp [°C]
1	**1a**	f[c]	**2a**	92	124.2 – 125.4	124.5 – 126.5[10a]
2[b]	**1a**	f[c]	**2a**	91	124.0 – 125.0	124.5 – 126.5[10a]
3	**1b**	f[c]	**2b**	93	92.4 – 93.6	92.5 – 94.5[10a]
4	**1c**	f[c]	**2c**	90	104.0 – 105.2	103 – 105[2b]
5	**1d**	f[c]	**2d**	88	92.4 – 93.6	124 – 126[10b]
6	**1e**	f[c]	**2e**	90	128.2 – 129.4	129 – 130.5[10b]
7	**1f**	0.5	**2f**	87	80.4 – 81.6	80 – 82[11]
8	**1g**	1	**2g**	86	148.5 – 149.6	147 – 149[10a]
9	**1h**	0.5	**2h**	89	139.2 – 140.6	139.7 – 140.3[16]
10	**1i**	0.5	**2i**	91	120.6 – 121.8	121 – 122.5[10a]
11	**1j**	1	**2j**	90	147.6 – 148.8	147 – 149[10a]
12	**1k**	0.5	**2k**	92	136.2 – 137.6	136 – 138[10a]

[a] 25 wt% aqueous NaOH (9.6 g) was added dropwise to a mixture of azo compounds (10 mmol) and zinc (20 mmol) in water (150 mL) unless otherwise stated.
[b] 25 wt% KOH was used.
[c] The reaction was complete after the addition process.
[d] Isolated yield.



a: $R^1 = R^2 = R^4 = H, R^3 = Me$; **b:** $R^1 = R^2 = R^4 = H, R^3 =$ *t*-Bu; **c:** $R^1 = R^2 = R^4 = H, R^3 =$ *t*-octyl;
d: $R^1 = R^2 = R^4 = H, R^3 = OMe$; **e:** $R^1 = R^3 = R^4 = H, R^2 = MeO$; **f:** $R^2 = R^4 = H, R^1 = R^3 =$ *t*-amyl;
g: $R^2 = R^4 = H, R^1 = R^3 =$ *t*-Bu; **h:** $R^1 =$ *t*-Bu, $R^3 = Me, R^2 = R^4 = H$; **i:** $R^1 = R^2 = H, R^3 =$ *t*-Bu, $R^4 = Cl$;
j: $R^1 = R^3 =$ *t*-Bu, $R^2 = H, R^4 = Cl$; **k:** $R^1 =$ *t*-Bu, $R^3 = Me, R^2 = H, R^4 = Cl$

Scheme 1.

vents. In these procedures, benzotriazole *N*-oxides were not detected. In the case of using chloro-substituted azo compounds **1i--k** as substrates, no dechlorinated products (over-reduced products) could be detected. Here, it is of benefit to employ zinc as reductant compared to the reported methods.

In conclusion, we have demonstrated that zinc powder is an efficient reductant for the cyclization of *o*-nitrophenylbenzenes in aqueous alkaline solutions. The protocol is characterized by easy manipulation and product separation, high selectivity and mild reaction conditions. This procedure offers the practical convenience of obviating the need of handling inflammable and toxic organic solvents. From an environmental point of view, this process also shows a potential advantage in reducing the adverse impact of solvent disposal. Further work on the reductive cyclization of *o*-nitrophenylbenzenes with other metals in aqueous alkaline solutions is currently in progress in our laboratory and the results will be published in due course.

Experimental Section

Typical Procedure

To a mixture of 2-nitro-2′-hydroxy-5′-methylazobenzene (**1a**; 2.57 g, 10 mmol) and zinc dust (1.32 g, 20 mmol, 2.0 equivs.) in water (140 mL) was added dropwise a 25 wt % aqueous NaOH solution (9.6 g, 60 mmol, 6.0 equivs.) within 0.5 h at 90 °C (Run 1). The reaction mixture was stirred at 90 °C for 1 h (monitored by HPLC). After the reaction was complete, the reaction mixture was neutralized with concentrated HCl to pH 2–3 to consume unreacted zinc and filtered. The solid was recrystallized from MeOH, affording 2-(2-hydroxy-5-methylphenyl)benzotriazole (**2a**); mp 124.2–125.8 °C (Lit.: 124.5–126.5 °C);[3] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.34$ (3H, s, CH_3), 6.92–7.18 (2H, m), 7.28–7.54 (2H, m), 7.82–8.06 (2H, m), 8.22 (1H, d, $J = 2.0$ Hz), 11.21(1H, s); GC-MS: $m/z = 225$ (M^+), 210 (M^+-15), 196, 182, 168, 154, 141, 93, 78, 66, 51.[11]

All of the *o*-nitrophenylazophenols and triazoles are known compounds and were identified on the basis of their melting points, ^{1}H NMR and GC-MS data.

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