PHOTOSTIMULATED REDUCTIVE CYCLIZATION OF *o*-NITROPHENYLAZO DYES USING SODIUM HYDROXIDE IN ISOPROPYL ALCOHOL. A NEW SYNTHESIS OF 2-ARYL-2*H*-BENZOTRIAZOLES

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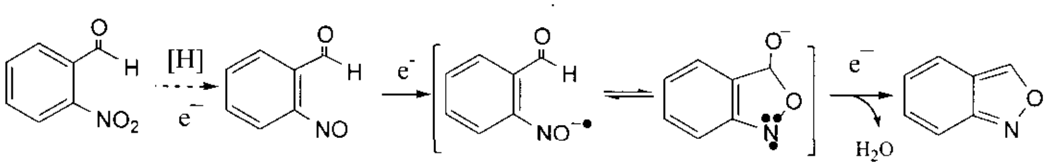
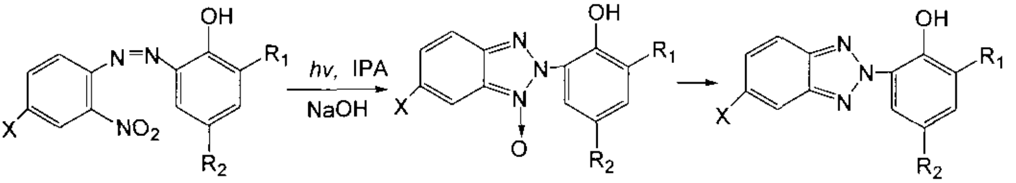
Abstract - *o*-Nitrophenylazo dyes with NaOH were irradiated in isopropyl alcohol to give the corresponding benzotriazoles. The photostimulated reductive cyclization proceeds through the formation of *N*-oxides as an intermediate.

Nitroarenes have been shown the ability to spontaneously form radical anions in the presence of electron donor.[1] In fact, the LUMO energy level of nitro group lies in a relatively low, thus it is capable of explaining the formation of $ArNO_2^{-\cdot}$ by a single electron transfer (SET) process.[1] In addition, nitrosoarenes are also capable of accepting an electron. The LUMO energy for nitrosobenzene (-5.35 eV) is lower than nitrobenzene by 1.87 eV on Hückel method.[2] Russell reported that the ET process of nitrosobenzene in the presence of hydroxide ion in DMSO-*tert*-BuOH occurs in < 0.5 sec to give nitrosobenzene radical anion.[3] In the presence of oxygen these solution yields nitrobenzene while in the absence of oxygen azoxybenzene is very rapidly produced.[3] The solution of nitrosobenzene radical anion persists only for minutes.[3] In general, nitroso compounds, which are often postulated as intermediates, are too reactive to be isolated, if indeed they are intermediate.[4] Even though nitrosoarenes have been proved to be a good candidate for an electron acceptor, the reactions for the use of nitrosoarene radical anion are rare. It would be predictable that the highly reactive nitrosoarene radical anion can be trapped by a proper *ortho* substituent in the cyclization fashion. Thus, we have investigated the reductive cyclization of *o*-nitrobenzaldehydes ($o\text{-}O_2NC_6H_4CHO$) in the presence of an electron donor and have found that the reaction to produce 2,1-benzisoxazole is efficient (Eq 1).[5a] It appears to be formed by initially reduction of nitroarenes to nitrosoarenes, followed by reductive cyclization of nitrosoacylbenzene radical anion.



As a part of our continuing study on the reductive cyclization *via* ET processes, we have also found an efficient cyclization reaction of *o*-nitrophenylazo dyes (**1**) to benzotriazoles (**3**) by using 2-bromo-2-nitropropane and Zn dust.[5b] The products, 2-(2'-hydroxyphenyl)-2*H*-benzotrizaoles (**3**), are widely used as UV absorbers for the protection of commercially important plastics against sunlight.[6] A wide variety of chemical reagents have been employed for the conversion of **1** to **3**.[5b,7] Herein we report a new synthetic method for the preparation of plastic additives (**3**) by the photostimulated reductive cyclization of *o*-nitrophenylazo dyes (**1**) in NaOH solution.

A mixture of *o*-nitrophenylazo dye (**1a**) (20 mmol) and NaOH (8 g) in isopropyl alcohol (150 mL) was irradiated through a Pyrex filter at 85 °C for 24 h, and the benzotriazole [8] (**3a**) was isolated in a good yield.



1 (**1a**: R_1, R_2= *t*-Bu, X=H) **2**, *N*-Oxide **3**, Benzotriazole

In this case, the reduction of nitro compound (**1a**) to benzotriazoles (**3a**) proceeded through an intermediate stage involving *N*-oxide (**2a**) as we expected. We tried to monitor the formation of *N*-oxide

(**2a**) during the transformation of **1a** to **3a** by HPLC. The decrease of **1a** is counterbalanced by a favorable trend with the sum of **2a** and **3a** (Table 1, entries 1-3). In order to control the reduction of **1a** the amount of NaOH and the reaction period were changed, however, it was failed to stop the reduction at the stage of *N*-oxide (**2a**).

Table 1. Reductive cyclization of *o*-nitrophenylazo dyes (**1a**) under various conditions.[a]

entry	1a	Condition			Additive	Time	Product, %[c]	
		Base(equiv)	*hν*[b]	solvent		(h)	**3a**	**2a**
1	**1a**	NaOH, 10	Pyrex	IPA	none	24	78	4 (8)
2	**1a**	NaOH, 10	Pyrex	IPA	none	10	56	14 (21)
3	**1a**	NaOH, 10	Pyrex	IPA	none	2	35	20 (41)
4	**1a**	NaOH, 10	Quartz	IPA	none	24	81	3 (9)
5	**1a**	NaOH, 10	dark	IPA	none	24	31	14 (39)
6	**1a**	NaOH, 10	Pyrex	IPA	DBN[d]	24	42	6 (32)
7	**1a**	NaOH, 10	Pyrex	IPA	DNB[e]	24	59	9 (9)
8	**1a**	KOH, 10	Pyrex	IPA	none	24	62	11 (12)
9	**1a**	NaOH, 10	Pyrex	EtOH	none	24	46	4 (38)

[a] All reactions were carried out with 20 mmol of reactant at 85 °C. [b] 250 W Hanovia lamp was used with Pyrex filter, otherwise as indicated. [c] *Product yields were measured by* HPLC *and yields in parentheses were the recovered starting material.* [d] 10 mol% of DBN (=di-*tert*-butyl nitroxide) was employed. [e] 10 mol% of DNB (=*p*-dinitrobenzene) was employed.

As a control experiment, the reaction mixture was irradiated under different photochemical conditions. The change of wavelength did not influence on the product yield (entry 4). The benzotriazole (**3a**) can be isolated upon sunlamp photolysis in 74% yield, and the reaction proceeds slowly under this condition. However, when the same reaction was performed in the dark, benzotriazole (**3a**) was obtained in 31% yield along with 14% of *N*-oxide (**2a**) (entry 5). In order to determine whether radicals and radical anions were involved in the reaction, some trapping experiments were carried out (entries 6 and 7).[1, 9] The photostimulated processes are inhibited and retarded in the presence of 10 mol% of ($tert$-Bu)$_2$NO$^{\bullet}$.[9a-c] The inhibition period is around 10 min and the yield of **3a** is decreased nearly in half. Also, it was found that in the presence of 10 mol% of *p*-dinitrobenzene (a good radical anion scavenger[9d]), the total amounts of **3a** and **2a** were decreased.

Other *o*-nitrophenylazo compounds with NaOH were also irradiated in isopropyl alcohol; all of the reductive cyclizations were successful under the similar conditions and provide benzotriazoles in reasonable yields (Table 2). In the case of chloro-substituted *o*-nitrophenylazo dye (**1b**), the corresponding benzotriazole (**3b**) was obtained in high yield without giving any dechlorinated product (entry 2).

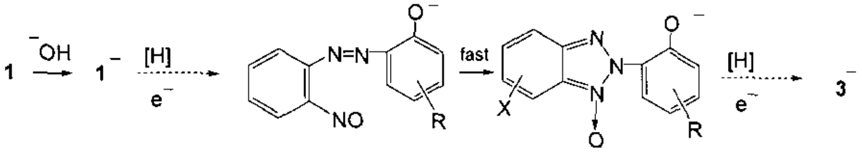
Table 2. Photostimulated reduction of *o*-nitrophenylazo dyes using NaOH in isopropyl alcohol.[a]

entry	1				NaOH	Time	Product, %[b]
		R_1	R_2	X	(equiv)	(h)	**3**
1	**1a**	*tert*-Bu	*tert*-Bu	H	10	24	78
2	**1b**	*tert*-Bu	*tert*-Bu	Cl	10	24	83
3	**1c**	H	Me	H	10	24	89
4	**1d**	H	Et	H	10	24	87
5	**1e**	Me	Me	H	10	24	89
6	**1f**	*tert*-Pentyl	*tert*-Pentyl	H	10	24	67

[a] A mixture of **1a** (7.75 g, 20 mmol) with NaOH (8 g) in isopropyl alcohol (150 mL) was irradiated at 85 °C for 24 h. Then the resulting mixture was poured into 10 % hydrochloric acid and CH_2Cl_2. The organic layer was washed, dried, concentrated, and purified by recrystallization from ethanol. [b] Isolated yields.

The results indicate that **3a** is formed *via* radical and radical anion pathway shown in Scheme. The intramolecular electron transfer of phenoxide ion to nitro moiety occurs easily because of the relative stability of the phenoxy radical and the low-lying antibonding π-orbital of nitro moiety. And the following reduction process takes place to the formation of nitroso stage intermediate likewise Eq 1. Even though we did not monitored nitroso compound, the cyclyzed *N*-oxide (**2**) was observed (the structure (**2a**) was confirmed by comparison with authentic samples prepared independently[8]). The next deoxygenation step of *N*-oxide is similar to the first reduction step. In fact, under the only thermal condition, the reduction of **1a** was slowly proceeded to give **3a** in ~30% yield in the dark at 85 °C (entry 5). However, the reduction under the thermal condition was not completed even through a prolonged reaction time of 48 h, thus the solution must be irradiated and heated to occur with ease.

Scheme



In summary, the photostimulated reductive cyclization of *o*-nitrophenylazo dyes using NaOH in isopropyl alcohol provides an efficient method for the synthesis of benzotrizoles. In fact, the use of a nonmetallic reducing agent has a crucial advantage as far as the environmental problem is concerned. Work is now in progress to apply this reductive cyclization for the construction of other heterocyclic ring systems.

ACKNOWLEDGMENT

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