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Bismuth(III) Chloride-Zinc Promoted Selective Reduction of Aromatic Nitro Compounds to Azoxy Compounds

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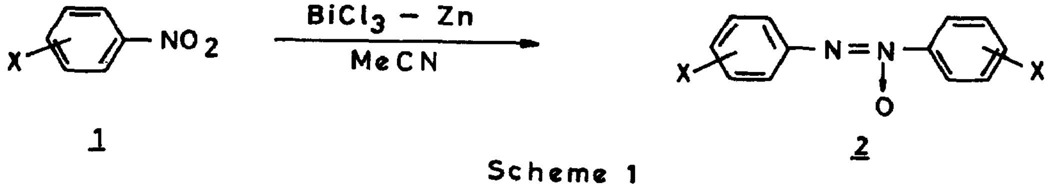
Abstract: In the presence of bismuth(III)chloride-metallic zinc aromatic nitro compounds have been found to be selectively reduced inter and intramolecularly to the corresponding N-oxides at ambient temperature in high yields.

Application of bismuth metal to organic synthesis has recently attracted much attention due to its potentiality as a reductant for various synthetic purposes[1]. Among group VA elements, bismuth is inexpensive, easy to handle and less toxic than arsenic and antimony and can be expected to play a crucial role in organic synthesis owing to its metallic character. However, to our knowledge synthetic methods using bismuth halides are scarcely studied[2]. Herein we wish to disclose the first example that bismuth(III)chloride-metallic zinc combination can be utilized for the selective reduction of aromatic nitro compounds both inter and intramolecularly to the corresponding azoxy compounds in high yields. There are many methods for the preparation of azoxy compounds by the reduction of nitro compounds[3], since side reactions (e.g. dehalogenation, polymerisation etc.) usually accompany the reductions, their use is limited.

In a typical reaction procedure (entry 1), to a suspension of metallic zinc powder (260mg, 4 mmol) in dry acetonitrile (15ml) was added bismuth trichloride (630mg, 2 mmol) followed by p-chloronitrobenzene (316mg, 2 mmol). The reaction mixture was stirred at ambient temperature for 1 h under nitrogen atmosphere, until most of p-chloronitrobenzene was consumed. Usual workup of the mixture followed by extraction with chloroform and purification by column chromatography on silica gel gave 4,4'-dichloro azoxybenzene in 85% yields exclusively and there was no evidence for the formation of N-phenylhydroxylamine or p,p'-dichloroazobenzene or p-chloroaniline. Typical results are summarized in the Table. In

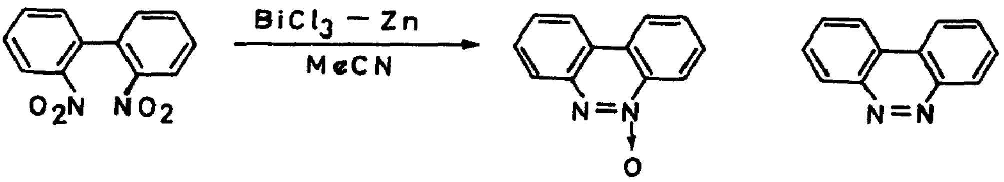


Scheme 1

the case of methyl 4-nitrocinnamate (entry 11, Table) the reaction occurred selectively at the nitro group and the carbon-carbon double bond in the substrate was not effected. High yields of azoxy compounds are obtained from nitro aromatics with ether or alkyl substituent, the positional relationship of the substituents in no way influencing the overall reaction. Both bromo and iodo-substituted nitro aromatics react smoothly with retention of the halogen, instead of its elimination[3a,4]. Therefore the reaction is general (Table) and can be employed for the synthesis of symmetrically substituted chloro, bromo, iodo, alkoxy and alkylazoxy compounds.

Interestingly it was also found that bismuthtrichloride-zinc system can be conveniently used to perform reductive intramolecular cyclisation of o,o'-dinitrobiphenyls to the corresponding benzo(c)cinnoline N-oxides 4 in good yields (Scheme 2). The reaction did not give any benzo(c)cinnoline 5. Reductants previously used include Na_2S in aqueous EtOH, Ph_3P in alkaline EtOH, hydrazine with Ra-Ni in EtOH, Na/Hg in MeOH, $LiAlH_4$, Zn in alkaline aqueous EtOH, H_2 with Ra-Ni in alkaline EtOH[5]. More recently $(PhTe)_2/NaBH_4$[6] and KOH/2-propanol[7] have also been used. But most of these methods leading to mixture of products.

In summary, the present new method employing bismuth(III)chloride-metallic zinc has some notable advantages compared with other methods. For example in the reduction of bromo or iodo nitrobenzene by Mg, Tl or Al reagents, the halogens were usually eliminated or complex products were formed[4] and in the reduction of alkyl substituted nitrobenzene by sodium alcoholate polymers were usually formed[8]. In contrast, in our examples none of these side reactions were observed. Therefore the present method because of its simplicity and high selectivity, constitutes a useful alternative to the commonly accepted procedure for the synthesis of various azoxybenzenes and benzo(c)cinnoline N-oxides.



3 4 5

Scheme 2

Table: Bismuth(III)chloride-Zinc mediated reduction of nitro compounds[9]

Entry	Nitro Aromatics	Azoxy Compounds[a]	Time[b] (h)	Yield[c] (%)	M.P. (°C)
1	4-Chloronitrobenzene	4,4'-Dichloro azoxybenzene	1	85	154 - 156[10a]
2	2-Chloronitrobenzene	2,2'-Dichloro azoxybenzene	1.5	70	53.5 - 55[10a]
3	3-Chloronitrobenzene	3,3'-Dichloro azoxybenzene	2	75	96 - 97[10a]
4	4-Nitrotoluene	4,4'-Dimethyl azoxybenzene	1.5	85	66 - 68[10a]
5	4-Ethylnitrobenzene	4,4'-Diethyl azoxybenzene	1	80	110 - 112[10b]
6	2-Nitrotoluene	2,2'-Dimethyl azoxybenzene	2	83	57 - 58[10a]
7	4-Nitroanisole	4,4'-Dimethoxy azoxybenzene	1	83	116.5-118.5[10c]
8	4-Iodonitrobenzene	4,4'-Diiodo azoxybenzene	1.5	70	208 - 210[10d]
9	4-Bromonitrobenzenes	4,4'Dibromo azoxybenzene	1	72	173 - 175[10e]
10	2-Nitrobiphenyl	2,2'-Diphenyl azoxybenzene	1.5	75	159 - 160[10h]
11	Methyl 4-nitro cinnamate	Dimethyl 4,4'-azoxycinnamate	2	83	57 - 85[10f]
12	o,o'-Dinitrobiphenyl	Benzo(c)cinnoline N-oxide	2	76	138 - 139[10g]

[a] Products were identified by the comparison of IR and NMR spectra and melting points with those of authentic samples.

[b] Increasing the time of reaction had no significant effect on the yield and resulted in minor amount of decomposition.

[c] Yields refers to the yield of pure isolated products.

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