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Reductive dechlorination of atrazine using sodium-borohydride catalysed by cobalt(II) phthalocyanines

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A series of functional metallophthalocyanines have been synthesized to study their role as a catalyst towards the reductive dechlorination of atrazine using sodium borohydride as a mild reducing agent. The cobalt(II) phthalocyanine bearing nitro groups at the peripheral position is the most efficient catalyst with exceptionally high catalytic activity in comparison to other functional cobalt(II) phthalocyanines.

Degradation of highly persistent pesticides into environmentally compatible products has been a worldwide environmental challenge. The widespread use of pesticides has led to public health concerns, increases the resistance of pests against various pesticides and results in the contamination of water, air and soil. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-triazine) is used as a selective herbicide to control the grassy and broadleaf weeds in corn, rangeland, sorghum and sugarcane crops.[1] Atrazine is a well recognized recalcitrant pollutant due to its slow degradation by physico-chemical or biological methods. The presence of atrazine even at very low concentrations is highly toxic for mammalian as well as aquatic organisms and is identified as a mammalian carcinogen and endocrine disrupter.[2]

In recent years, major efforts have been investigated in the development of effective methods to detoxify this contaminant present in the environment. The oxidative degradation of atrazine has been studied by Fenton's systems[3,4] UV, UV–H_2O_2,[5] UV–O_3,[6] UV–TiO_2,[7,8] metal-catalysed ozonation. Biodegradation of atrazine via microbial[9] and enzyme-catalysed[10,11] reactions are another way to detoxify it. Reductive degradation involving the use of zero-valent iron[12,13] is an additional approach for dechlorination of atrazine. Porphyrin and phthalocyanine complexes are also known to degrade atrazine by using titanium citrate as reducing agent,[14] and by photocatalytic[15] and electrocatalytic methods.[16] Although all the above methods transform atrazine into less toxic dechlorinated or dealkylated nonherbicidal products, similar transformations to detoxify these harmful chlorinated agrochemicals with mild reducing agents by metallophthalocyanines are still unexplored.

As far as environmental applications are concerned, metallophthalocyanines and metalloporphyrins have been used as a catalyst for a variety of eco-friendly reactions[17–20] which are effective in transforming harmful environmental pollutants into biodegradable moieties. The use of metallophthalocyanines as reduction promoting catalysts[20] under milder conditions stimulated us to investigate their activity towards the reductive dechlorination of atrazine in various conditions. Among the numerous available metallophthalocyanines, those bearing cobalt have been demonstrated to be effective catalysts for reductive mechanistic approach. Accordingly, the aims of the present study were to examine the catalytic reductive transformation of atrazine by different functional metallophthalocyanines, and to compare the use of mild, cheap and commercially available reducing agent sodium borohydride and metallophthalocyanines on the reaction rate and yield of the product.

The reaction of atrazine (**1**) with sodium borohydride in methanol catalysed by metallophthalocyanines (**3**) was performed at room temperature under different reaction conditions (Scheme 1). The functional metallophthalocyanines (MPcs) (**3a**–**3h**) were synthesized by the cyclocondensation of the corresponding phthalonitriles in the presence of metal salts under different reaction conditions in ionic liquids.[21] The reduction of atrazine (**1**) with $NaBH_4$ in the absence of MPcs (**3**) did not yield any product even after stirring the reaction mixture for 24 h at room temperature (Table 1, entry 1). However, the reaction of **1** (1 mmol) with $NaBH_4$ (4 mmol) catalysed by (**3a**) (0.1 mmol) in methanol gave the dechlorinated product, N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine (**2**) in a 98% yield

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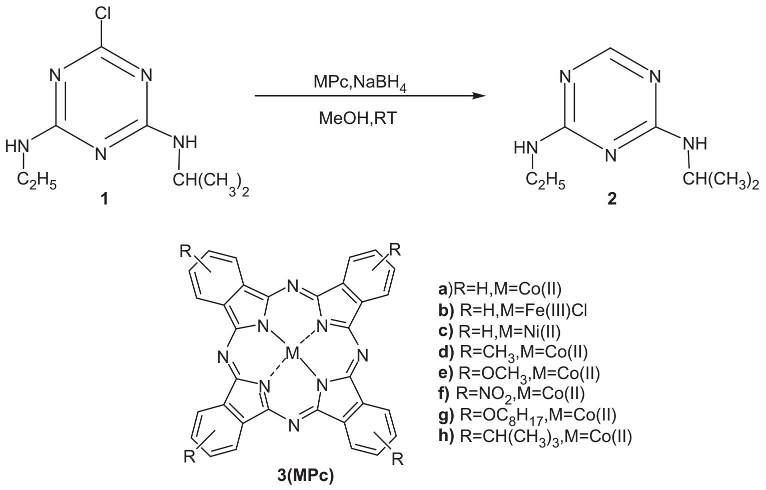


Scheme 1. Dechlorination reaction of atrazine catalysed by MPc using $NaBH_4$.

Table 1
Dechlorination of **1** to **2** with $NaBH_4$ catalysed by cobalt(II) phthalocyanine (**3a**) under different reaction conditions[a]

Entry	System	1: 3a: $NaBH_4$	Time (min)	Conversion (%)[b]	Yield[c] (%)
1	1/3a/$NaBH_4$	1:0:8	360	0	0
2	1/3a/$NaBH_4$	1:0.01:4	30	64	59
3	1/3a/$NaBH_4$	1:0.1:1	30	14	11
4	1/3a/$NaBH_4$	1:0.1:2	30	46	42
5	1/3a/$NaBH_4$	1:0.1:4	30	>99	95
6	1/3a/$NaBH_4$	1:0.1:8	30	100	96
7	1/3a/$NaBH_4$	1:0.1:4	10	34	28
8	1/3a/$NaBH_4$	1:0.1:4	60	100	98
9	1/3a/$NaBH_4$[d]	1:0.1:4	30	>98	95

[a] Reaction conditions: reactions were performed at room temperature in methanol.
[b] Based on substrate (**1**).
[c] Isolated yields.
[d] The reaction carried out in dark.

(Scheme 1) (Table 1, entry 8). The product was separated by column chromatography.

The melting point of **2** (181 °C) was compared with the melting point of *N*^{2}-ethyl-*N*^{4}-isopropyl-1,3,5-triazin-2,4-diamine (181–182 °C) reported in the literature.[22] In the ^1H NMR spectrum, the appearance of new peak as a singlet at δ 7.93 ppm corresponding to the aromatic proton and no major changes in the resonance for other protons confirmed the dechlorination of atrazine to aromatic C–H bond in **2**. In ^{13}C spectrum, the appearance of peaks for aromatic carbons in the region δ 164.89, 164.89, 165.54 and the peaks for ethyl and isopropyl group carbons attached to –NH in the aliphatic region at resonance δ 14.68, 22.58, 22.89, 35.35, 42.18 again confirmed no changes in the aliphatic region. The ESI–MS spectrum of **2** showed peak corresponding to its molecular mass *m*/*z* 181.1654 further confirmed the structure of the dechlorinated product (see Supplementary data).

To study the effect of concentration of sodium borohydride on the course of reaction, the reduction of **1** was carried out with different molar ratio of sodium borohydride using **3a** as catalyst in methanol at room temperature for 4 h, shown in Table 1. The increase in the amount of $NaBH_4$, that is, the substrate: catalyst: $NaBH_4$ ratio from 1:0.1:1 to 1:0.1:4, increases the yield of product from 11% to 95%. On further increasing the ratio up to 1:0.1:8, no major change in the yields was observed (Table 1, entries 3–6). The concentration of the catalyst also played a major role in the yield of the dechlorinated product, with the increase in molar ratio of substrate: catalyst: $NaBH_4$ from 1:0.01:4 to 1:0.1:4, a substantial increase in the yield from 59% to 95% was observed (Table 1, entries 2 and 5). The yields of the dechlorinated product also depend upon the reaction time. As the time duration of the reaction increased the yield of the product also increased. Only a 28% yield of **2** was obtained when reaction was carried out for 10 min, while the yield of the same increased to 95% and 98% when the time increased to 30 and 60 min, respectively (Table 1, entries 5, 7 and 8). The rate of the dechlorination reaction was observed to be same when the reaction was carried out in dark (Table 1, entry 9).

The effects of metal atom present at the core of the phthalocyanine ring also govern the yield of the reaction. The change of the central metal atom of phthalocyanine from Co to Ni and Fe showed decrease in the catalytic activities giving the 95%, 64% and 48% yields, respectively (Table 2, entries 1–3). This could be explained on the basis of difference in the redox potential of MPcs with the change in central metal atom.[23] The central metal changes the electronic state of the Pc ring, thereby causing a change in the oxidation potential of MPc. Further, the interaction with groups above and/or below the Pc plane produces significant changes in redox potentials and this may be responsible for the least catalytic activity of Fe(III)Cl-Pc (**3b**).[23b] The effect of nature of substituents attached to phthalocyanines ring on the course of reductive dechlorination process was also examined. The cobalt(II) phthalocyanines bearing electron-withdrawing nitro groups (**3f**) exhibited better catalytic potential than that bearing electron donating groups (**3d**) (Table 2, entries 4 and 6). However, the poor yield of **2** in the reduction reaction using **3g** as the catalyst could be attributed to self-aggregation tendencies of functionalized phthalocyanines in the solution phase[24] (Table 2, entry 7). Exceptionally

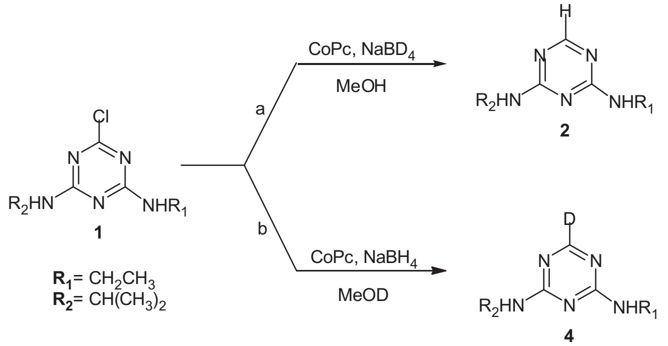
Table 2
Dechlorination of **1** to **2** with $NaBH_4$ catalysed by different functional metallophthalocyanines (**3**) and metal salts under different reaction conditions[a]

Entry	Catalyst	Time (min)	Conversion (%)[b]	Yield[c] (%)
1	**3a**	30	98	95
2	**3b**	30	55	48
3	**3c**	30	70	64
4	**3d**	30	84	77
5	**3e**	30	49	42
6	**3f**	30	>99	98
7	**3g**	30	39	32
8	**3h**	30	100	98
9	**3a**	30[d]	94	90
10	**$CoCl_2$**	60	58	54
11	**$NiCl_2$**	60	48	42
12	**$FeCl_3$**	60	33	26

[a] Reaction conditions: Reactions were performed at room temperature in methanol; substrate: catalyst: $NaBH_4$ = 1:0.1:4.
[b] Based on substrate (**1**).
[c] Isolated yields.
[d] Catalyst was reused.

high catalytic activity of cobalt(II) phthalocyanine bearing *t*-butyl group (**3h**) is primarily due to the nonaggregating property of **3h** in the solution phase[25] (Table 2, entry 8). After the reaction, the catalysts **MPc (3)** were quantitatively recovered and used again for reductions without any loss in catalytic activity (Table 2, entry 9), even though partial decomposition of **3g** was observed during the reduction and could not be reused. The catalyst **3h** could not be separated by direct filtration because of its good solubility in methanol, limiting its applicability in reductions. However, **3h** could be recovered quantitatively by column chromatography. The use of metal salts such as $CoCl_2$, $NiCl_2$ and $FeCl_3$ was sluggish giving the dechlorinated product **2** in 54%, 42% and 26% yields, respectively (Table 2, entries 10–12) even for a longer reaction time. Moreover, these catalysts decomposed after the reductions and could not be reused. According to the results obtained the reductions using MPc **3** as catalysts in the place of metal salts are more advantageous and apparently proceed through different pathway. The present study suggested the outstanding role of metallophthalocyanines as a catalyst and provides an opportunity to examine the mechanism for the reductive dechlorination reactions of cobalt(II) phthalocyanine.

In the reductive dechlorination of atrazine, the reaction of atrazine (**1**) using sodium borodeuteride ($NaBD_4$) in methanol (CH_3OH) gave **2** whereas, the reaction of atrazine (**1**) using sodium borohydride ($NaBH_4$) in deuterated methanol (CD_3OD) gave **4** (Scheme 2). The formation of **2** and **4** in the reactions justifies that the hydrogen which replaces the –Cl group present at the aromatic ring in dechlorinated product **2** came from methanol in the reaction. The structure of **4** was differentiated from the atrazine by the R_f difference in the TLC (thin layer chromatography) and confirmed by ^1H NMR spectroscopic and mass spectrometric analysis. In ^1H NMR spectrum, the absence of peak at δ 7.93 for aromatic proton clearly indicates the presence of deuterium at aromatic ring. The LC–MS spectrum of structure **4** showed the peak at molecular mass m/z 182.2 for $[M^+]$ which further confirmed the replacement of hydrogen by deuterium (Fig. 5 refer Supplementary data).



Scheme 2. Dechlorination of atrazine, (a) with $NaBD_4$ in MeOH, (b) with $NaBH_4$ in MeOD.

The reductive dehalogenation of atrazine was initiated by electron transfer from sodium borohydride to the central metal of the phthalocyanine, due to its ability to take electron reversibly in the D_z^2 orbitals, leading to the formation of [Co(I)Pc] which is characterized by UV–vis spectral studies of Co(II) Pc on addition of $NaBH_4$ in methanol. In UV–vis spectral analysis, on addition of methanolic solution of sodium borohydride to the solution of Co(II) Pc in methanol, the Q band of Co(II) Pc showed a red shift from 662 to 705 nm with the appearance of new band at 464 nm, specifying the formation of [Co(I)Pc] in the reaction.[20,26] The reaction of iron porphyrins with tetrabutylammonium borohydride has been known to generate covalently bound metal tetrahydroborate complexes in nonpolar solvents.[27] However, the polar solvents are not suitable for the generation of tetrahydroborate complexes. Thereby in polar organic solvents, alkylation of soluble [Co(I)Pc] with atrazine gives atrazine-Co(III)Pc as an intermediate by leaving chloride ion. This addition is in accordance with the alkylation of cobalt complexes with halogenated compounds[28–31] which was further supported by UV–vis spectroscopic titrations. The UV–vis titration of Co(II)Pc with sodium benzophenone ketyl as a reducing agent generates Co(I) species which on subsequent addition of methyl iodide reacts to give the bands corresponding to the formation of methyl-Co(III) Pc species[20b,30a] (Fig. 6 refer Supplementary data). The homolytic cleavage of labile Co–C bond[29,32] of alkyl-Co(III)Pc gives alkyl radical and Co(II) Pc.[28] Accordingly, Co–C bond of atrazine-Co(III) Pc moiety was homolytically cleaved to form atrazine radical and regenerates Co(II) Pc that can be reused several times without any loss in its catalytic activity. Deuterated studies indicate that the hydrogen replacing the –Cl group of atrazine comes from methanol, based on these results it has been proposed that the atrazine radical takes an electron from sodium borohydride and subsequently abstract a proton from methanol to give **2**.[33,34]

In summary, the reductive dechlorination of atrazine with sodium borohydride catalysed by metallophthalocyanines (**3**) gave the reduced product in excellent yields in shorter reaction time. The cobalt(II) phthalocyanines are catalytically more efficient than other metal phthalocyanines. The cobalt(II) phthalocyanine bearing electron withdrawing group at the peripheral position gave the reduced product in a 98% yield. Further, the present method offers various advantages such as the use of cheap and commercially available reducing agent, milder reaction conditions, easy work-up and the reusability of catalyst.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.10.080.

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33. *General procedure for the reductive dechlorination of atrazine* (**1**) *with sodium-borohydride catalysed by metal phthalocyanines* (**3**) *in methanol*: In a two-necked 50 ml round bottom flask, fitted with a nitrogen inlet tube and a condenser. Atrazine (**1**) (2.32 mmol) and cobalt(II) phthalocyanine (**3a**) (0.232 mmol) were added in methanol under nitrogen atmosphere. When the atrazine was completely dissolved, sodium borohydride (13.95 mmol) was added to the reaction mixture slowly within a period of 10 min. The reaction mixture was stirred at room temperature for 30–60 min. The progress of the reaction was examined by TLC. After completion of the reaction, reaction mixture was filtered to remove the catalyst **3a**, the filtrate was concentrated under reduced pressure. The dechlorinated product **2** was separated by column chromatography on silica gel (60–120 mesh), eluted with ethyl acetate/hexane (80:20). The same procedure was followed using different metal phthalocyanines and metal salts in reductive dechlorination of atrazine. Data for *N^2-ethyl-N^4-isopropyl-1,3,5-triazin-2,4-diamine* (**2**): mp: 181–182 °C (lit.[22] mp 182 °C**)**, IR (KBr, ν/cm^{-1}): 3488, 3342, 3178, 3116, 2925, 2851, 1684, 1638, 1588, 1527, 1300, 1180, 1085, 994, 916, 796, 638, 561, 455; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.93 (1H, s, Ar), 6.09 (1H (NH), m, (br), 5.09 (1H (NH), d (br)), 4.12 (1H, s, (br), CH), 3.38 (2H, s, (br), CH_2), 1.17 (9H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.68 (CH_3), 22.58 (CH_3), 22.89 (CH_3), 35.35 (CH_2), 42.18 (CH), 164.38, 164.89, 165.54 (Ar–C); ESI-MS: *m*/*z* calcd for $C_8H_{15}N_5$ 181.1327, observed: 181.1654 [M^+]. Data for (**4**): mp: 178–180 °C ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.72 (1H (NH), m (br), 5.01 (1H (NH), d (br)), 4.14 (1H, s, (br), CH), 3.41 (2H, s, (br), CH_2), 1.18 (9H, s, CH_3). LC–MS: *m*/*z* calcd for $C_8H_{14}DN_5$ 182.2, observed: 182.2 [M^+].
34. Spectral data for reduced compounds and UV–vis spectral studies are provided in Supplementary data.