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MONTMORILLONITE CATALYZED REDUCTION OF NITROARENES WITH HYDRAZINE

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Abstract. Aromatic nitro compounds were readily reduced to the corresponding amino compounds in good yields with montmorillonite(K-10) and hydrazine.

There is a growing list of successful applications of montmorillonite clay(K-10)-based reagents to organic synthesis such as acetal formation from alcohols and organic gem-dihalides[1], porphyrin synthesis by condensation of pyrrole with aldehydes[2], nitration of phenols[3], conversion of alcohols to nitrites[4], oxidation of alcohols to aldehydes or ketones[5], benzoins to benzils[6] and selective reduction of nitroarenes[7]. The above examples are all promoted by either clay supported iron(III) nitrate or copper(II) nitrate[8]. Some of these are phase transfer process with clay supported catalysts[1]. In this paper, we wish to communicate this striking effect of montmorillonite on the reduction of aromatic nitro compounds in the presence of hydrazine. Results are presented in the Table.
The obvious advantages over conventional methods are elimination of use of expensive catalysts[7] and improvements on reaction conditions. Perhaps more important,however, is the elimination of the need to prepare catalyst.
Typical procedure for this reduction is as follows. To a stirred suspension of montmorillonite(3g)[9] and nitroarene(10 mmol) in dry ethanol(10 ml), anhydrous hydrazine(62.5 mmol) was added in a single portion.
The resulting reaction mixture(slightly exothermic and effervescent) was refluxed for 2-14 hr under nitrogen. The contents was filtered and washed with ethanol or benzene to remove clay. Removal of solvents by flash evaporation gave the amino compounds. Hydrazine alone did not effect a reduction nor did montmorillonite alone in the case of nitrobenzene. Attemped reduction of nitropropane, phenylnitromethane or benzonitrile under same conditions resulted in recovery of the starting materials. Dry montmorillonite did not improve the yields significantly. However, absolute ethanol was critical to use as a reaction solvent.
When nitrobenzene was reduced under standard conditions with 99% of ethanol(10 ml, 9.9 ml of absolute ethanol-0.1 ml of water) as a solvent,

Table. Montmorillonite Catalyzed Reduction of Nitroarenes with Hydrazine[a]

Nitro Compounds	Products	Time(hr)	Yield(%)[b]
C_6H_5-NO_2	C_6H_5-NH_2	3	85,50[c]
o,m,p-$CH_3C_6H_4$-NO_2	o,m,p-$CH_3C_6H_4$-NH_2	6	85,85,90
o,p-HOC_6H_4-NO_2	o,p-HOC_6H_4-NH_2	4	90,29[d]
o,m,p-ClC_6H_4-NO_2	o,m,p-ClC_6H_4-NH_2	4	90,95,93
p-$HOCH_2C_6H_4$-NO_2	p-$HOCH_2C_6H_4$-NH_2	8	90[d]
o,m,p -$CH_3OC_6H_4$-NO_2	o,m,p-$CH_3OC_6H_4$-NH_2	8	85,90,92
p-BrC_6H_4-NO_2	p-BrC_6H_4-NH_2	6	95
p-$NH_2C_6H_4$-NO_2	p-$NH_2C_6H_4$-NH_2	14	89[d]
p-$ClCH_2C_6H_4$-NO_2	p-$ClCH_2C_6H_4$-NH_2	2	95
1-Nitronaphthalene	1-Aminonaphthalene	2	96
6-Nitroquinoline	6-Aminoquinoline	2	96
8-Nitroquinoline	8-Aminoquinoline	2	94

a. All reaction were refluxed in dry ethanol. b. Isolated
c. Hydrazine monohydrate was emplyed. d. HPLC yield

only 62% of aniline along with unchanged nitrobenzene was obtained by GC. Using dry ethanol, nitrobenzene was readily reduced to aniline in good yield as shown in Table. We are presently investigating the scope and limitation of the applications of clay to other catalyzed transformations.

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9.Purchased from Aldrich Chemie(W.Germany) and applied directly without any treatment.

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