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A FACILE REDUCTION PROCEDURE FOR NITROARENES WITH Al-$NiCl_2$-THF SYSTEM

Parijat Sarmah and Nabin C Barua*

Division of Natural Products Chemistry
Regional Research Laboratory (CSIR)
Jorhat 785 006, Assam, India

Summary : *It has been demonstrated that aromatic nitro compounds could be reduced to the corresponding amines very efficiently using reagent system consisting of Al-$NiCl_2.6H_2O$-THF.*

In the recent years, reagents based on aluminium find wide application in organic synthesis[1] because of their ready availability, easy handling and low cost. In an earlier communication we demonstrated that the system consisting of metallic aluminium-nickel chloride hexahydrate in THF chemoselectively reduces the double bond of the α,β-unsaturated ketones without effecting other reducible functionalities like carbonyls, esters, isolated double bonds etc.[2] In this communication, we wish to report that this system very efficiently reduces the nitroarenes to the corresponding amines in an essentially neutral and mild conditions. Reduction of aromatic nitro compounds to the corresponding amines could be effected by a variety of reagents[3], viz., catalytic hydrogenation, $TiCl_3$, AlH_3-$AlCl_3$, formic acid and Pd-C, hydrazine and a catalyst and $NaBH_4$ with catalyst $NiCl_2$ (PPh_3) or $CoCl_2$. Some other procedures for the same purpose using $Et_3N^+HCO^-_2$/Pd[4], $Fe_3(CO)_{12}/Al_2O_3$[5] and $Ru_3(CO)_{12}$/CO[6] are also in use. Recently Han et al reported a montmorillonite catalysed reduction procedure for nitroarenes[7]. High cost of the reagents, poor yield and long reaction time are the main drawbacks of the most of these procedures. In our method the reaction time is very short and yield of the corresponding amines are excellent and work up procedure is very simple. Our results are summarised in Table I.

Although the mechanism of this reduction process is not clearly defined at this stage, the following experimental observations are noteworthy. Anhydrous $NiCl_2$ does not react with aluminium powder even after long exposure. But addition of few drops of water to this system initiates a vigorous exothermic reaction with evolution of H_2 and formation of a black precipitate which probably is Ni(O)[8]. The hydrogen might be produced by aluminium with HCl generated from hydrolysis of $NiCl_2$[9]. The reduction of nitro is probably due to electron transfer from Ni(O) to the former.

Table I : Reduction of Nitroarenes with Al-$NiCl_2.6H_2O$-THF

Entry	Nitro compound	Reaction time(min)	Product[a]	Yield (%)[b]
1.	C_6H_5-NO_2	10	$C_6H_5NH_2$	90
2.	p-$CH_3C_6H_4NO_2$	10	p-$CH_3C_6H_4NH_2$	95
3.	o-$CH_3C_6H_4NO_2$	10	o-$CH_3C_6H_4NH_2$	80
4.	p-$HOC_6H_4NO_2$	10	p-$HOC_6H_4NH_2$	85
5.	p-$HOOCC_6H_4NO_2$	10	p-$HOOCC_6H_4NH_2$	80
6.	p-$H_2NC_6H_4NO_2$	10	p-$H_2HC_6H_4NH_2$	90
7.	p-$ClC_6H_4NO_2$	10	p-$ClC_6H_4NH_2$	85
8.	m-$ClC_6H_4NO_2$	10	m-$ClC_6H_4NH_2$	90
9.	m-$O_2NC_6H_4NH_2$	10	m-$H_2NC_6H_4NH_2$	79
10.	6-Nitroquinoline	10	6-Aminoquinoline	80

a, Products are characterized by IR, NMR, MS and confirmed by direct comparison with authentic compounds.

b, Yield refers to the yields of isolated products of >95% purity.

General procedure: To a freshly mixed solid mixture of aluminium powder (10 mmol) and nickel chloride hexahydrate (15 mmol) is added a solution of the substrate (0.3 mmol) in freshly distilled THF. A vigorous exothermic reaction takes place immediately which subsides after few minutes. After about 5-10 minutes when TLC of the reaction mixture showed disappearance of the starting material the reaction mixture is diluted with THF (100 ml) and filtered. Evaporation of the filtrate gave the reduced products which are purified further by chromatography.

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