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SELECTIVE REDUCTION OF NITRO COMPOUNDS
WITH TITANIUM(II) REAGENTS

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The reduction of nitro compounds to amines, an important synthetic reaction, is usually accomplished by means of catalytic hydrogenation,¹ metal and acids,^{2,3} reduction with hydride reagents^{4,5} and sulfurated sodium borohydride.⁶ A few attempts at the reduction of nitro groups using transition metal chlorides in the presence of sodium borohydride have also been reported.⁷

In general most of these methods have only limited applicability due to lack of selectivity subject to interference by other functional groups, low yields or unwanted side reactions.^{2,3} Quite a few of these reactions are performed under strongly acidic or basic, aqueous conditions and isolation of the amines from the reaction mixture poses a serious problem.

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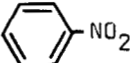
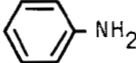
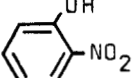
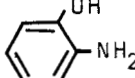
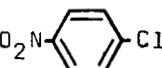
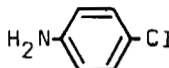
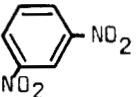
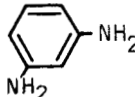
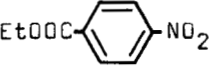
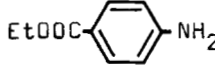
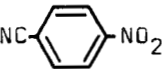

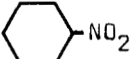
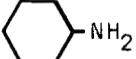
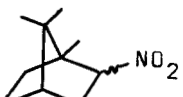

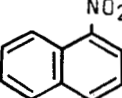
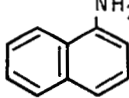
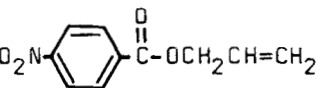
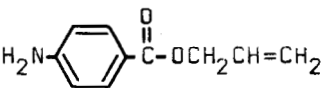
In our search for a mild, selective and general method for this transformation, we find that the Ti(II) species generated by the reduction of titanium tetrachloride with amalgamated magnesium offers a lot of advantages over the existing methods. Treatment of nitro compounds with amalgamated magnesium and titanium tetrachloride in THF/t-butanol at 0° for 0.5 - 1.0 hr yields amines in excellent yields. A wide variety of aromatic and aliphatic nitro compounds have been reduced selectively in the presence of other interfering functional groups (Table). Particularly noteworthy are the entries 3, 6 and 10 in the Table, containing easily reducible functional groups like chloro, cyano and allyl-carboxylate⁸ units respectively which are not affected under the reaction conditions.

From the data presented above it is evident that this methodology is mild, very selective and works efficiently under non-aqueous conditions.

General Procedure: To a solution of mercuric chloride (0.091 g, 0.33 mmol) in 4 ml of dry THF was added 36 mesh magnesium (0.144 g, 6 mmol) and the mixture was stirred at room temperature under nitrogen for 10 min.

The turbid supernatant liquid was withdrawn by syringe and the remaining amalgam was washed with three portions of THF. Dry THF (8 ml) was added and the mixture was cooled to -10° and treated with titanium tetrachloride (3 mmol) followed by the addition of nitrocompound (1 mmol) in THF (4 ml) and tertiary butanol (2 ml).

TABLE

Sl. No.	Nitro compound	Product ^a	% Yield ^b
1.			92
2.			94
3.			92
4.			94
5.			98
6.			94
7.			87
8.			89
9.			95
10.			96

a. Products were characterised by comparison with authentic samples (spectra, TLC and m.p.).

b. All yields refer to isolated products.

Stirring was continued at 0° for 0.5 - 1.0 hr and then water (5 ml) was added followed by dilution with ether (50 ml) and filtered through a short pad of celite and silica-gel and washed with ether (30 ml). The amine was isolated after evaporation of the solvent.

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8. Allyl and benzyl esters are converted to the parent carboxylic acids on treatment with Ti(II) reagent after 4-8 hrs at 0° (J. George and S. Chandrasekaran, Mss. submitted for publication).