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# SELECTIVE REDUCTION OF AROMATIC NITRO COMPOUNDS WITH STANNOUS CHLORIDE IN NON ACIDIC AND NON AQUEOUS MEDIUM

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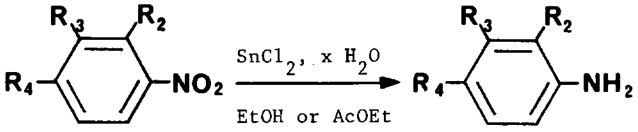
*Abstract : Aromatic nitro compounds are readily reduced by* $SnCl_2$*, 2* $H_2O$ *in alcohol or ethyl acetate or by anhydrous* $SnCl_2$ *in alcohol where other reducible or acid sensitive groups such as aldehyde, ketone, ester, cyano, halogen and O-benzyl remain unaffected.*

The reduction of nitro compounds to amines is a very useful synthetic transformation for which a vast array of reagents has been developped (1). The stannous chloride reduction which has been used from a very early period of chemistry is known to be acid catalysed (2). Thus, during almost one century, all reductions with stannous chloride have been carried out in the presence of acid and water.

However, Albert and Linnel reported in 1936 the preparation of anhydrous stannous chloride which they used in a mixture of acetic anhydride-acetic acid for the reduction of various nitroacridones (3). More recently, Satoh proposed the system sodium borohydride-stannous chloride for the selective reduction of aromatic nitro compounds in ethanol (4).

In our search for a mild, selective, inexpensive and general method for this transformation, we found that either $SnCl_2$, 2 $H_2O$ in alcohol or ethyl acetate, or anhydrous $SnCl_2$ in alcohol work very efficiently (5). A wide variety of substituted nitrobenzenes had been selectively reduced in almost quantitative yields using this simple procedure (see table). Under the conditions used, other reducible or acid sensitive groups are recovered unchanged. The table also shows that the yields of substituted anilines are not affected by the nature or the position of the aromatic substituents on the corresponding nitrobenzenes. The yields obtained in the presence of groups such al aldehyde, O-acetate and O-benzyl are particularly noteworthy.



| **R$_4$** | **R$_3$** | **R$_2$** | Yield[a] | Litt.[b] |
|---|---|---|---|---|
| Cl | H | H | 96 % | 9 |
| Cl | CN | H | 98 % | 10 |
| COOEt | H | H | 97 % | 9 |
| $OCH_3$ | H | H | 97 % | 9 |
| Cl | COOEt | H | 95 % | 11 |
| CHO | H | H | 96 % | 12 |
| COOH | H | H | 94 % | 9 |
| OH | H | H | 91 % | 9 |
| $OCOCH_3$ | H | H | 92 % | 13 |
| $OCH_3$ | H | CN | 99 % | 14 |
| H | $CH_3$ | COOH | 99 % | 15 |
| $PhCH_2O$ | H | H | 91 % | 1 b |

a) Yield of crude product, see experimental procedure

b) All compounds gave melting points, IR and NMR spectra that were in excellent agreement with litterature data.

A typical experimental procedure is illustrated below for the reduction of p-nitrobenzoic acid : a mixture (6) of 1.67 g (0.01 mole) of p-nitrobenzoic acid and

11.275 g (0.05 mole) of $SnCl_2$, 2 $H_2O$ (7) in 20 ml of absolute ethanol is heated at 70°C under nitrogen. After 30 mn the starting material has disappeared and the solution is allowed to cool down and then poured into ice. The pH is made slightly basic (pH 7-8) by addition of 5 % aqueous sodium bicarbonate (8) before being extracted with ethyl acetate. The organic phase is thorougly washed with brine, treated with charcoal and dried over sodium sulphate. Evaporation of the solvent leaves 1.5 g (94,5 %) of p-aminobenzoic acid, which gives one spot on tlc and melts over 300°C.

We feel that the mildness and the selectivity of this method which works in non-aqueous conditions together with the ease of the treatment and the purity of the products obtained should largely extend the scope of the use of stannous chloride which is a safe and inexpensive reagent.

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ethyl acetate as already noted by J.R. Sampey, J. Am. Chem. Soc., 52, 88 (1930).

7. $SnCl_2$, 2 $H_2O$ or anhydrous $SnCl_2$ can be used indifferently. When $SnCl_2$, 2 $H_2O$ may be utilized in ethanol (absolute or not) or in ethyl acetate or in a mixture of these solvents, the presence of ethanol is necessary for the reduction with anhydrous $SnCl_2$ to work.

8. 5 % aqueous sodium bicarbonate may be replaced by solid sodium bicarbonate, or aqueous or solid NaOH Without affecting the yield noticeably.

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