Selenium–1,8-Diazabicyclo[5,4,0]undec-7-ene Catalysed Reduction of Nitrobenzenes with Hydrogen

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Summary Selenium–DBU catalysed reduction of nitrobenzenes with hydrogen under atmospheric pressure at 110° has been carried out successfully.

THERE have been several reports on catalytic reduction of nitrobenzene with hydrogen,[1] and with carbon monoxide[2] in the presence of some hydrogen sources such as water and acetic acid. We now report the novel selenium–DBU (1,8-diazabicyclo-[5,4,0]undec-7-ene)[3] catalysed reduction of nitrobenzenes with hydrogen under atmospheric pressure at 110 °C to yield anilines [equation (1)].

$$ArNO_2 + 3H_2 \xrightarrow[1\text{ atm., }110°]{\text{selenium–DBU}} ArNH_2 + 2H_2O \quad (1)$$

Metallic selenium readily oxidised hydrogen under atmospheric pressure at 25 °C in the presence of DBU to give a hydrogen selenide species, which forms a salt with DBU.[4] When this reaction was carried out in the presence of nitrobenzene at 25 °C, only trace amounts of aniline were formed.‡

In a typical catalytic reaction, a mixture of 10 mmol of nitrobenzene, 10 mmol of DBU and 1 mg atom of metallic selenium in 10 ml toluene was stirred vigorously at 110 °C and hydrogen bubbled into the mixture at a rate of 1 ml min^{-1}. G.l.p.c. analysis of the reaction mixture after 25 h showed a 12% yield of aniline, which corresponds to 3·6 times the equimolar amount of selenium as catalyst. Higher concentrations of catalyst gave higher yields of aniline.§ Longer reaction time, higher hydrogen pressure and higher temperature¶ also increased the yield. In the absence of catalyst aniline was not formed. The results obtained from several nitrobenzenes are summarized in the Table. Nitrobenzenes with electron withdrawing groups were reduced faster than those with electron donating groups.[5]

TABLE. Relative reactivity[a] of nitrobenzenes in the selenium–DBU catalysed reduction

$X\text{-}C_6H_4NO_2$ X	$X\text{-}C_6H_4NH_2$ k_X/k_H[b]
H	1·0
m-Cl	18
p-Cl	5·2
m-Me	0·91
o-Me	0·60
p-Me	0·28
p-MeO	0·11

[a] $PhNO_2$ (10 mmol), $X\text{-}C_6H_4NO_2$ (10 mmol), DBU (10 mmol), metallic selenium (1 mg atom) and 1 atmosphere of H_2 in 10 ml toluene at 110 °C for 20 h. [b] From g.l.p.c.

Nitrosobenzene and phenylhydroxylamine were also reduced to aniline under the same reduction conditions as above.

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‡ The reducing species seemed to be a DBU salt of hydrogen selenide and the reduction of nitrobenzene at room temperature was slow.

§ Reduction of nitrobenzene (3 mmol) with 1 atmosphere of H_2 (1 ml min^{-1}) by Se (10 mg atom), DBU (10 mmol) in toluene (10 ml) at 110° for 25 h gave 93% yield of aniline.

¶ Nitrobenzene (10 mmol), DBU (10 mmol), Se (1 mg atom) and H_2 (50 kg cm^{-2}) in toluene (10 ml) were reacted at 150° in an autoclave for 25 h to give aniline in 80% yield, which corresponds to 24 times the equimolar amount of selenium as catalyst.

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