

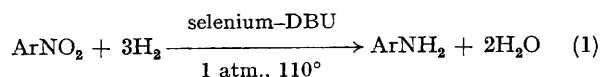
## Selenium-1,8-Diazabicyclo[5,4,0]undec-7-ene Catalysed Reduction of Nitrobenzenes with Hydrogen

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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,<sup>1</sup> and with carbon monoxide<sup>2</sup> 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)<sup>3</sup> catalysed reduction of nitrobenzenes with hydrogen under atmospheric pressure at 110 °C to yield anilines [equation (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.<sup>4</sup> When this reaction was carried out in the presence of nitrobenzene at 25 °C, only trace amounts of aniline were formed.<sup>‡</sup>

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<sup>-1</sup>. 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.

‡ 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<sub>2</sub> (1 ml min<sup>-1</sup>) 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<sub>2</sub> (50 kg cm<sup>-2</sup>) 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.

<sup>1</sup> C. Grundmann and W. Ruske, *Chem. Ber.*, 1953, **86**, 939; 'Organic Syntheses' col. vol., **3**, ed. E. C. Horning, Wiley, New York, 1962, p. 59.

<sup>2</sup> A. F. M. Iqbal, *Tetrahedron Letters*, 1971, 3385; T. Kajimoto and J. Tsuji, *Bull. Chem. Soc. Japan*, 1969, **42**, 827.

<sup>3</sup> E. Haruki, M. Arakawa, N. Matsumara, Y. Otsuji, and E. Imoto, *Chem. Letters*, 1974, 427; H. Oediger and Fr. Möller, *Angew. Chem.*, 1967, **79**, 53.

<sup>4</sup> K. Kondo, N. Sonoda, and H. Sakurai, *J.C.S. Chem. Comm.*, 1974, 160; *Tetrahedron Letters*, 1974, 803; *Bull. Chem. Soc. Japan*, in the press; K. Kondo, N. Sonoda, and S. Tsutsumi, *J.C.S. Chem. Comm.*, 1972, 308; *Chem. Letters* 1972, 373, 401; *Tetrahedron Letters*, 1971, 4885.

<sup>5</sup> M. Hojo, Y. Takagi, and Y. Ogata, *J. Amer. Chem. Soc.*, 1960, **82**, 2459; O. J. Cope and R. K. Brown, *Canad. J. Chem.*, 1961, **39**, 1965; *ibid.*, 1962, **40**, 2317.

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

TABLE. Relative reactivity<sup>a</sup> of nitrobenzenes in the selenium-DBU catalysed reduction

X-C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> X	X-C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> k <sub>X</sub> /k <sub>H</sub> <sup>b</sup>
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

<sup>a</sup> PhNO<sub>2</sub> (10 mmol), X-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (10 mmol), DBU (10 mmol), metallic selenium (1 mg atom) and 1 atmosphere of H<sub>2</sub> in 10 ml toluene at 110 °C for 20 h. <sup>b</sup> From g.l.p.c.

obtained from several nitrobenzenes are summarized in the Table. Nitrobenzenes with electron withdrawing groups were reduced faster than those with electron donating groups.<sup>5</sup>

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

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