Heterogeneous Catalytic Transfer Hydrogenation of 4-Nitrodiphenylamine to *p*-Phenylenediamines

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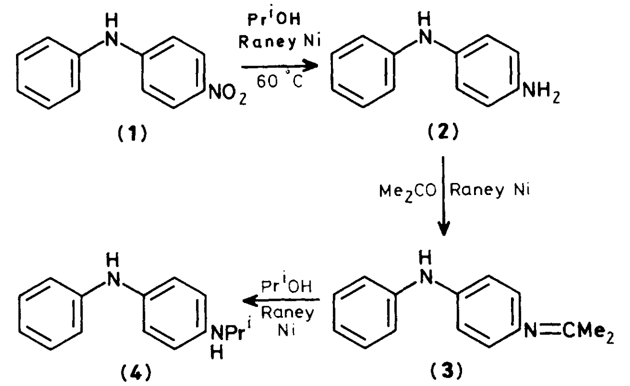
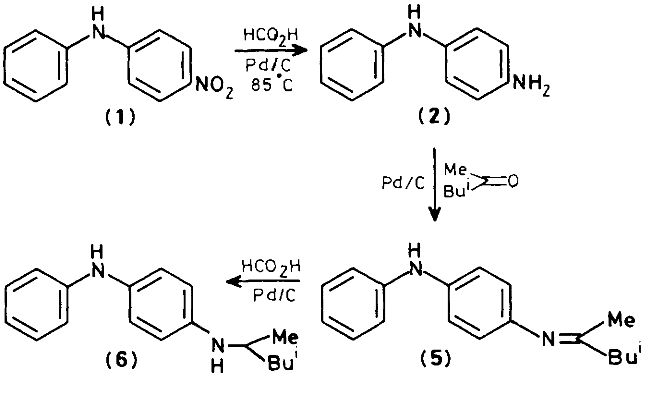
p-Phenylenediamine analogues have been prepared from 4-nitrodiphenylamine (**1**) by catalytic transfer hydrogenation in one stage; the process can be extended to the general condensation of a nitro compound with an alcohol (with Raney nickel as catalyst) or a ketone (with palladium as catalyst).

Transfer hydrogenation of aliphatic and aromatic nitro compounds to give the corresponding amines in the presence of a hydrogen donor solvent and a heterogeneous catalyst is well known.[1,2] Here we describe the preparation of amines of types (**4**) and (**6**) from 4-nitrodiphenylamine (**1**) in the presence of Raney nickel or palladium as catalyst. This process takes place in a single stage the intermediate 4-aminodiphenylamine need not be isolated. Amines of these types are generally used as antioxidants and antiozonants in the rubber industry and are manufactured at high temperature and pressure catalytically under an atmosphere of hydrogen. The present method, in contrast, uses very mild conditions and hence is cheap to operate and less hazardous.

The reaction consists of treating the nitro amine (**1**) with propan-2-ol and Raney nickel (100% wt/wt of reactant) (prepared as mentioned in ref. 3) in a flask fitted with a reflux condenser, for 4 h at 60 °C. The product (**4**) was found to be more than 98% pure by h.p.l.c. and m.p. [contaminant 2% of the diamine (**2**)]. The reaction takes place in three steps (Scheme 1): (1) formation of 4-aminodiphenylamine (**2**) by



Scheme 1



Scheme 2

Table 1. Yields of condensation products of 4-nitrodiphenylamine with various alcohols (Raney nickel catalyst, reflux temperature).

Alcohol	Yield (%)
Ethanol	70
Propan-2-ol	95
Butan-2-ol	26
4-Methylpentan-2-ol	3

transfer hydrogenation from propan-2-ol, which is converted into acetone; the catalyst abstracts hydrogen and forms a metal hydride species; (2) reversible condensation of (**2**) with acetone to yield the (unstable) imine (**3**); and (3) further hydrogenation, of the imine (**3**) to the amine (**4**), again with propan-2-ol as the hydrogen source. Steps (1) and (2) yield two and one mol. equiv. of water, respectively, for every mole of (**1**) reacted.

Step (3) is found to be rate-controlling; nitro-to-amino conversion takes place in about 30 min. If different hydrogen donor solvents are used, different condensation products are obtained; the yields of the amines depend on the solvent used (Table 1). The bulkier the solvent, the less the yield of the final product; the yield of the amine (**6**) is very low when 4-methylpentan-2-ol is used as solvent. However the product (**6**) can be obtained in 100% yield if 5% palladium-on-carbon (Johnson Matthey) is used (40% wt/wt of reactant) in place of Raney nickel at slightly higher temperature (85 °C), with formic acid as hydrogen donor solvent, and methyl isobutyl ketone and 4-nitrodiphenylamine as reactants (Scheme 2). Palladium abstracts hydrogen from the formic acid to form a metal hydride, liberating carbon dioxide. The other reaction steps remain the same as in the previous case.

If the amount of either catalyst or formic acid is increased, *N*-(*p*-anilinophenyl)formamide is produced as a side product, probably formed by direct condensation of 4-aminodiphenylamine (**2**) and formic acid. On exposure to u.v. radiation (254 nm) or treatment with aqueous sodium hydroxide this product reverts to 4-aminodiphenylamine (**2**), liberating gaseous carbon monoxide in the former case and sodium formate in the latter. Aqueous sodium formate is also a good hydrogen source and can be used in place of formic acid.

The transfer hydrogenation reaction reported here is preferable to the conventional hydrogenation process for the following reasons:

(a) Abstraction of hydrogen from the donor solvent by these catalysts is known to occur very readily, whereas the hydrogen gas used in conventional hydrogenation has to be dissociated by the catalyst in a higher energy process.

(b) The conventional hydrogenation is limited by mass transfer resistance; the hydrogen gas has to diffuse into the liquid before adsorption on the catalyst surface.

(c) The imine formed in step (2) is unstable, but the highly active metal hydride species formed by the abstraction of hydrogen from the donor solvent reacts immediately to form the stable amine.

(d) Amines are well known to poison catalysts. In the transfer hydrogenation process, since the hydrogen donor solvent is available in plenty, the high activity of the catalyst sites is maintained by continuous formation of metal hydride.

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