Phosphinic Acid as a Bifunctional Reagent in the Catalytic Bamberger Rearrangement of Nitrobenzene to *para*-Aminophenol

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Phosphinic acid is proposed as a simultaneous hydrogen donor and proton source in the Pd/C catalysed transformation of nitrobenzene to *para*-aminophenol.

The Bamberger rearrangement is the most convenient and economical method for the synthesis of *para*-aminophenols directly from nitrobenzenes, particularly on an industrial scale.[1] The process is normally carried out by catalytic hydrogenation in the presence of precious metal catalysts under highly acidic conditions where the intermediate has been shown to be *N*-phenylhydroxylamine. An interesting recent development in catalytic transfer hydrogenation (CTH), an advantageous alternative to catalytic hydrogenation,[2] is the introduction of phosphinic acid and salts as hydrogen donors.[3] Typical unsaturated substrates are reduced, usually in the presence of Pd/C catalyst, according to the general equation (1),[4–6] where A is a hydrogen acceptor such as an olefin,[7] aryl halide[8,9] or nitroarene.[10]

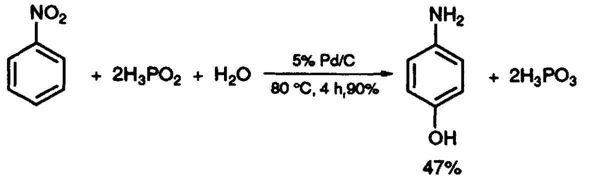
$$A + H_2PO_2^- + H_2O \rightarrow AH_2 + H_2PO_3^- \qquad (1)$$

We have now found that phosphinic acid can be applied as a dual-function reagent, both as a hydrogen donor and as a proton source, in the Bamberger reaction of nitrobenzene. The reaction proceeds according to Scheme 1.

In a typical procedure we mixed nitrobenzene (17.4 g, 140 mmol) with 25% aqueous phosphinic acid (74 g, 280 mmol) and 5% Pd/C (27 mg; 50% H_2O, 6.3 μmol) at 80 °C for 4 h. After cooling, the mixture was filtered and the (homogeneous) filtrate was neutralized by 50% aqueous sodium hydroxide to pH 7 (24 g of 50% NaOH). The precipitate was filtered *in vacuo* and washed twice with water (15 ml) and twice with methylene chloride (50 ml). After drying at 50 °C *in vacuo* we obtained 6.5 g of *para*-aminophenol (PAP, purity 99.3% by HPLC analysis), mp 189–190 °C (47% yield). The minor impurity was bis-(4-aminophenyl) ether. After analysis of the mother liquor we concluded that in view of the overall mass balance in the above procedure the conversion of nitrobenzene was 90% and the product distribution was 55% PAP, 42% aniline, 2% bis-(4-aminophenyl) ether and 1% *ortho*-aminophenol. Kinetic analysis of the system revealed that the process is zero order up to a conversion of 85%.

The selectivity of PAP was found to be strongly dependent on the extent of the reaction. Thus, using the above procedure, at a nitrobenzene conversion of 40%, PAP selectivity was higher than 85%, but this decreased at higher conversion. The selectivity to PAP was also sensitive to temperature and to the initial H_3PO_2 : nitrobenzene molar ratio. At 20 °C the selectivity fell to <15% and with H_3PO_2 as the limiting reactant a significant decrease in PAP selectivity was determined.

An unexpected relation was observed between the initial aqueous concentration of the phosphinic acid and the *para* : *ortho* ratio in the product. This ratio dropped from 70 : 1 with 10% aqueous H_3PO_2 to 10 : 1 for 50% (both experiments at comparable high conversions). The *para* : *ortho* ratio also depended on the conversion, being very high at low conversion (above 80 : 1 at 20% conversion). The overall reaction rate also increased with decreasing concentration of the phosphinic acid. This latter phenomenon can be attributed to the function of water which is an active substrate in this reaction which has to compete for an adsorption site on the catalyst surface.[11,12] The effect of polar solvents can also be attributed to the critical role of water in this system. Addition of either ethanol or THF, which formed a single liquid phase in the above mixture, resulted in a dramatic decrease in the reaction rate and selectivity. In addition, a remarkably low *para* : *ortho* ratio (<2 : 1) of aminophenol was obtained in THF. Addition of various surface-active quaternary ammonium salts to the original heterogeneous system, a common additive in various related patents,[13] did not improve the observed performance.



Scheme 1

The amount of the Pd/C catalyst did not affect the selectivity but had a significant effect on the rate. Use of 100 mg of 5% Pd/C in the above procedure resulted in a very strong exothermic reaction with the temperature rising to 160 °C in a few minutes and a buildup of pressure to 10^6 pascals, in a closed vessel. Under these conditions complete conversion was obtained in less than 10 minutes. Other catalysts, *e.g.* 5% Ru/C and 5% Pt/C, had approximately one half and one third of the activity of the Pd catalyst.

We have proved that the above reaction is a true hydrogen-transfer reaction rather than a dehydrogenation–hydrogenation process. No molecular hydrogen could be detected in these reactions either in the gas or the liquid phases. Essentially the same results were obtained in runs where open or sealed vessels were used. Hydroxylamine is clearly the intermediate in this hydrogen-transfer process. Interestingly, sodium phosphinate was proposed by Johnstone and co-workers[14] as the reagent of choice for the selective synthesis of hydroxylamines *via* catalytic hydrogen transfer.

We believe that the disclosed new procedure is a favourable and safe alternative for the Bamberger rearrangement using the traditional catalytic hydrogenation.

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