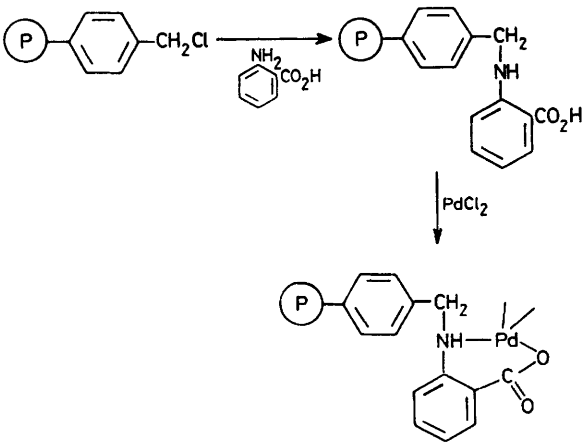
Ready Hydrogenation of Nitrobenzene and Benzonitrile with a Polymer-bound Palladium Catalyst

By NORMAN L. HOLY
(*Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky* 42101)

Summary A polymer-bound catalyst has been discovered which provides the first example of hydrogenation of nitro and nitrile functional groups with a Pd^{II} catalyst.

WE report the first examples of hydrogenation of a nitro and a nitrile group using a Pd^{II} catalyst. These hydrogenations are unusual in that Pd^{II} hithertofore has shown only a very narrow range of hydrogenation activity;[1] thus, the catalyst we have utilized represents a significant departure from previous palladium chemistry.

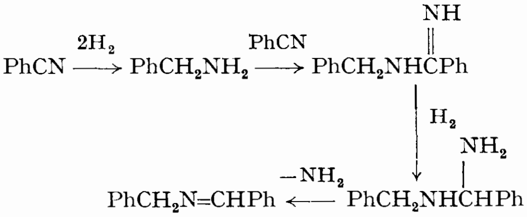
The catalyst was prepared by treating chloromethylated polystyrene beads (Rohm and Haas XAD-4, 2·82 mequiv. Cl per g) with 50% molar excess of anthranilic acid in diethyl ether and stirring for 12—24 h. After filtering and washing thoroughly with ethanol, 10 g of the beads were suspended in 500 ml of acetone and 0·60 g (3·39 mmol) of $PdCl_2$ and 5 ml of acetonitrile were added. The suspension was refluxed for 48 h, filtered, and washed with acetone, and vacuum-dried (Scheme 1), analysis (3·01% Pd, 0·39% N) indicated a 1·01 : 1·00 relationship between palladium and anthranilic acid.



SCHEME 1

Hydrogenation of 500 mmol of nitrobenzene with 0·132 mmol (based on Rh) of the catalyst at 1000 lb in^{-2} and 80 °C for 3·5 h resulted in a 97% conversion into aniline; no other products were detected. The filtered and washed catalyst was also active, establishing that the palladium did not elute from the beads and serve as a homogeneous catalyst. The catalyst was active even at room temperature, making it comparable in activity to the most active homogeneous catalysts.[2]

A nitrile is one of the most difficult functional groups to hydrogenate and there are exceptionally few soluble complexes or metal clusters capable of demonstrating activity.[3] Yet, with 0·300 mmol of the catalyst and 200 mmol of benzonitrile, hydrogenation at 100 °C and 700 lb in^{-2} (24 h) effected a 60% conversion and yields of 66 and 33%, respectively, of *N*-benzylbenzamidine and α-(benzylideneamino)toluene (Scheme 2). The course of the reaction is similar to that effected by other heterogeneous catalysts.[4]



$$PhCN \xrightarrow{2H_2} PhCH_2NH_2 \xrightarrow{PhCN} PhCH_2NH\overset{NH}{\overset{\|}{C}}Ph \xrightarrow{H_2} PhCH_2NH\overset{NH_2}{\overset{|}{C}}HPh$$

$$PhCH_2N{=}CHPh \xleftarrow{-NH_2} PhCH_2NH\overset{NH_2}{\overset{|}{C}}HPh$$

Scheme 2

ESCA studies are particularly vital in establishing the oxidation state of the metal. The $3d_{3/2}$ and $3d_{5/2}$ levels of palladium metal are reported to be at 340·9 and 335·7 eV, respectively.[5] Several Pd^{II} complexes (no amine complexes were included in the study) have binding energies of 342—344 and 336·6—339·6 eV, respectively, for these levels.[5a] In a sample of once-used catalyst (for nitrobenzene hydrogenation) peaks occur at 343·0 and 337·6 eV. The energies are compatible with a 2+ oxidation state. Further evidence for Pd^{II} was gained by treating the used catalyst sample with ethanolic cyanide: 90% of the palladium was removed (comparable to the amount removed by Bailar[6]) and the catalyst retained only 1% of its original activity.

The author is indebted to Western Kentucky University for financial support and Dr. Richard Shalvoy for ESCA data.

(*Received*, 24*th July* 1978; *Com.* 792.)

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