[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

CATALYTIC HYDROGENATION OF NITROBENZYL ALCOHOLS AND NITROBENZALDEHYDES

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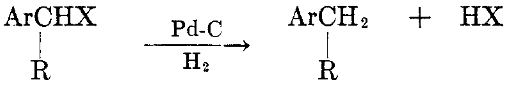
Debenzylation type hydrogenations such as those illustrated below are now well-established (1) using palladized charcoal. Hartung and Crossley (1b) stated that a platinum catalyst prepared in essentially the same fashion as their active palladium catalyst did not readily reduce propiophenone to propylbenzene. In these laboratories we have found (2) that whereas the rate of catalytic hydrogenation of benzyl alcohol to toluene can serve as a practical control for determining the activity of a batch of palladized charcoal catalyst, it cannot be used as a control for Adams' catalyst. Such reduction as occurs is slow and may involve other than debenzylating action.



$$\underset{R}{\underset{|}{ArCHX}} \xrightarrow[H_2]{Pd\text{-}C} \underset{R}{\underset{|}{ArCH_2}} + HX$$

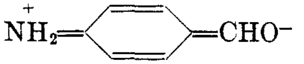
R = H, alkyl, or aryl
X = Halogen, OH, O-alkyl, OCOZ, NR'_2, or similar functions

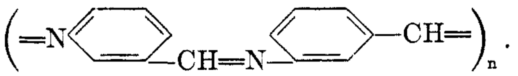
It became desirable to obtain *m*- and *p*-aminobenzyl alcohols for other work. These are described in the literature, prepared by laborious procedures. The rapid catalytic reduction of aromatic nitro to amino groups, the slower reduction of aldehydic carbonyl to alcohol, and the non-debenzylating character of Adams' catalyst made it seem reasonable that the products sought might be obtained in a single, smooth hydrogenation of the *m*- or *p*-nitrobenzyl alcohols or of the *m*- or *p*-nitrobenzaldehydes over this catalyst.

m-Nitrobenzyl alcohol over Adams' catalyst rapidly absorbed just the calculated amount of hydrogen (three moles) and gave a nearly quantitative yield of *m*-aminobenzyl alcohol. *p*-Nitrobenzyl alcohol likewise took up the same amount of hydrogen rapidly, but the clear and colorless methanol solution, obtained after removal of the platinum, on evaporation even at room temperature *in vacuo* gave only an insoluble polymer. This tendency of *p*-aminobenzyl alcohol to polymerize is well-known (3) and is catalyzed by acids, both acetic and hydrochloric acid having been used for this purpose. We have found no report of similar behavior for *m*-aminobenzyl alcohol, in fact it can be vacuum-distilled without appreciable decomposition, and forms a stable hydrochloride, m.p. 121° (4). The difference in reactivity (as for polymerization) between the *meta* and *para* isomers is explicable in terms of the activation or labilization of the methylol group by the strong mesomeric effect of a *para*, but not a *meta*, amino. This difference extends to the ability of the *para* isomer to condense readily with a variety of activated hydrogen compounds (such as undergo the Mannich reaction) in weakly acidic media to give *p*-aminobenzyl derivatives. With α-naphthol the product is 4-(*p*-aminobenzyl)-1-naphthol (5).

An authentic sample of *p*-aminobenzyl alcohol, prepared by lithium aluminum hydride reduction of *p*-aminobenzoic acid, when evaporated in methanol solution with a trace of acetic acid gave an insoluble yellow polymer.

Hydrogenations of the corresponding nitrobenzaldehydes were attempted because of their greater availability as compared with the nitro alcohols. *p*-Nitrobenzaldehyde took up the calculated volume of hydrogen (4 moles) quickly but *p*-aminobenzyl alcohol was isolated only as the polymer. In contrast, *m*-nitrobenzaldehyde reduced only slowly and uptake stopped after absorption of about one-half the calculated amount. At this point an insoluble, viscous polymer precipitated, coating thoroughly the catalyst and reduction bottle.

The difference in behavior of the two nitrobenzaldehydes can be explained in terms of the mesomeric effect. In each case the nitro group will undoubtedly be reduced preferentially leading to the corresponding aminobenzaldehydes as intermediates. That the *p*-isomer reduced smoothly with a hydrogen uptake corresponding to the formation of *p*-aminobenzyl alcohol we interpret as due to the resonance stabilization of the intermediate aminoaldehyde. Contributions of the type  should stabilize the molecule by diminishing the reactivity of both the amino and carbonyl functions for their characteristic condensations (in this case Schiff's base formation) as compared with the isolated, uncoordinated groups (aniline and benzaldehyde react rapidly to give a Schiff's base). With the *meta* isomer no such favorable resonance interaction can occur and the individual group reactivities will be closer to their normal values, presumably reacting to give a Schiff's base type polymer



Certainly *m*-aminobenzaldehyde is much less well characterized than its *o*- or *p*-isomers. Although several papers (6a, b, c, d) report the preparation and derivatives of this compound no well-defined identification of it by melting point or other properties has been made. Even *m*-acetylaminobenzaldehyde is reported by different authors as having the melting point 84° (6c) and 122° (6b) respectively.

EXPERIMENTAL

Reductions. Catalytic hydrogenations were carried out in a Burgess-Parr type apparatus in methanol solution, at room temperature, 2–3 atmospheres over-pressure of hydrogen, and with Adams' catalyst. When the hydrogn uptake was complete, the platinum-free solvent was evaporated on a steam-bath or in some cases at room temperature *in vacuo*.

m-Nitrobenzyl alcohol. m-Nitrobenzyl alcohol (15 g., 0.1 mole) absorbed just 0.3 mole of hydrogen in 40 minutes. The yield of *m*-aminobenzyl alcohol recrystallized from benzene was 12.4 g. (100%); m.p. 95–96°.

p-Nitrobenzyl alcohol. p-Nitrobenzyl alcohol (15 g., 0.1 mole) absorbed just 0.3 mole of hydrogen in 40 minutes. After removal of platinum the reduction mixture was a clear, colorless solution. Evaporation of methanol either on the steam-bath or at room temperature *in vacuo* gave only an insoluble yellow polymer which started to come out when about one-half the solvent had been removed; yield 10 g. (80%); m.p. > 250°. This polymer was practically insoluble in water, methanol, benzene, or mineral acids.

This hydrogenation was repeated a number of times and always took up the proper amount of hydrogen rapidly, but all attempts to isolate the desired *p*-aminobenzyl alcohol yielded only insoluble polymers of the type described.

p-Aminobenzyl alcohol. By the procedure of Nystrom and Brown (7) *p*-aminobenzyl alcohol; m.p. 63–64° (recrystallized five times from benzene), was prepared in 20% yield by reduction of *p*-aminobenzoic acid with lithium aluminum hydride. A small sample of this pure *p*-aminobenzyl alcohol on warming in methanol solution in the presence of a trace of acetic acid gave an insoluble high-melting yellow polymer; m.p. >250°.

m-Nitrobenzaldehyde. Hydrogenation of 7.6 g. (0.05 mole) of *m*-nitrobenzaldehyde proceeded at only a moderate rate, and stopped after about one-half the calculated hydrogen uptake (took 0.1 mole, calc'd 0.2 mole) during which time a very insoluble viscous polymer precipitated coating catalyst and bottle completely. This substance was insoluble in hot water, methanol, or hot glacial acetic acid.

p-Nitrobenzaldehyde. Several samples of *p*-nitrobenzaldehyde, 3.0 g. (0.02 mole), were reduced and always took up the calculated amount of hydrogen (0.08 mole) rapidly (within less than 45 minutes). All attempts to isolate *p*-aminobenzyl alcohol from the clear filtrate from platinum gave only insoluble yellow polymers (in good yields) of the type described under the reduction of *p*-nitrobenzyl alcohol.

SUMMARY

m- and *p*-Nitrobenzyl alcohols and *m*- and *p*-nitrobenzaldehydes have been reduced catalytically using Adams' catalyst. A reasonable theoretical explanation has been given for the different results obtained in the individual cases.

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