Organic Syntheses

A Publication
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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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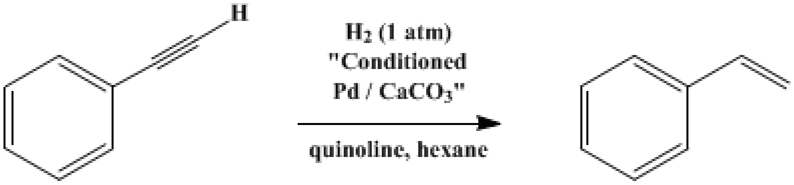
PALLADIUM CATALYST FOR PARTIAL REDUCTION OF ACETYLENES[1]

$$H_2PdCl_4 + H_2O + CaCO_3 \longrightarrow PdO/CaCO_3$$

$$PdO/CaCO_3 + HCO_2H \longrightarrow Pd/CaCO_3$$

$$Pd/CaCO_3 \xrightarrow{Pb(OCOCH_3)_2} \text{conditioned } Pd/CaCO_3$$



Submitted by H. Lindlar and R. Dubuis[2].
Checked by F. N. Jones and B. C. McKusick.

1. Procedure

Palladous chloride (1.48 g., 0.0083 mole) (Note 1) is placed in a 10-ml. Erlenmeyer flask, and 3.6 ml. (0.043 mole) of 37% hydrochloric acid is added. The flask is shaken at about 30° until the palladous chloride is dissolved. The chloropalladous acid solution is transferred to a 150-ml. beaker with 45 ml. of distilled water (Note 2). The beaker is equipped with a pH meter and a magnetic or mechanical stirrer. The pH of the stirred solution is brought to 4.0–4.5 by slow addition of aqueous 3*N* sodium hydroxide from a buret. A precipitate may form at high local concentrations of sodium hydroxide, but it dissolves on further stirring. The solution is diluted to approximately 100 ml. in a graduated cylinder and placed in a 200-ml. or 250-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer and a thermometer and partly immersed in a bath of oil or water. Precipitated calcium carbonate (18 g.) (Note 3) is added. The well-stirred suspension is heated to 75–85° and held at this temperature until all the palladium has precipitated, as indicated by loss of color from the solution; this takes about 15 minutes. With the mixture still at 75–85°, 6.0 ml. of sodium formate solution (about 0.7*N*) (Note 4) is added. During the addition CO_2 escapes and the catalyst turns from brown to gray; rapid stirring is essential to keep the mixture from foaming over. An additional 4.5 ml. of the sodium formate solution is added, and the reduction is completed by stirring the mixture at 75–85° for 40 minutes. The catalyst, which is now black, is separated on a 10-cm. Büchner funnel (Note 5) and washed with eight 65-ml. portions of water.

The moist catalyst is placed in a 200-ml. or 250-ml. round-bottomed flask equipped as described above. Water (60 ml.) and 18 ml. of a 7.7% solution of lead acetate (Note 6) are added. The slurry is stirred and heated at 75–85° for 45 minutes. The catalyst is separated on a 10-cm. Büchner funnel, washed with four 50-ml. portions of water, sucked as dry as possible, and dried in an oven at 60–70° (Note 7). The dried catalyst, a dark gray powder, weighs 19–19.5 g. (Note 8).

To establish that the catalyst is active and selective, it is convenient to test it by quantitative hydrogenation of phenylacetylene to styrene. The reaction flask of a low-pressure hydrogenation apparatus (Note 9) is charged with 2.04 g. (0.0200 mole) of phenylacetylene, 0.10 g. of the palladium catalyst, 1.0 ml. of quinoline (Note 10), and 15 ml. of olefin-free petroleum ether (b.p. 80–105°) or hexane (Note 11). The apparatus is evacuated, and hydrogen is admitted to a pressure slightly above 1 atm. Stirring or shaking is started, causing rapid absorption of hydrogen. The hydrogen pressure is kept close to 1 atm. Absorption of the first 0.0200 mole of hydrogen requires 10–90 minutes, depending on the activity of the catalyst. Hydrogen absorption then abruptly slows but does not stop. In synthetic work it is desirable to stop the reaction soon after the required amount of hydrogen has been absorbed.

2. Notes

1. Palladium chloride, Engelhard, 60% Pd, was obtained from Engelhard Industries, 113 Astor Street, Newark 14, New Jersey.
2. All water used in the procedure should be distilled or deionized water or chlorine-free tap water.
3. A commercial grade of "precipitated" (not "powdered" or "prepared") calcium carbonate is satisfactory, if it can be filtered easily. The checkers used Fisher Catalog No. C-62 Calcium Carbonate, U.S.P. (Precipitated Chalk).
4. To prepare the sodium formate solution, a filtered solution of 15 g. (0.14 mole) of anhydrous sodium carbonate in 80 ml. of water is diluted to 120 ml. Approximately 4 ml. (4.9 g., 0.10 mole) of 99% formic acid (a commercial grade) is then added dropwise until the solution is weakly alkaline to phenolphthalein.
5. The checkers found a funnel with a fritted disk convenient. Thorough washing is essential.
6. The solution is prepared by dissolving 9.0 g. (0.024 mole) of a commercial grade of lead acetate, $Pb(OCOCH_3)_2 \cdot 3H_2O$, in 100 ml. of water.
7. The checkers dried the catalyst for 2 hours in a vacuum oven at 60° (1 mm.).
8. The catalyst has been stored for more than 3 years with no loss in activity.
9. The hydrogen pressure and the design of the apparatus are not critical; any apparatus in common use is satisfactory. The checkers used an apparatus having a magnetically stirred reaction flask as described by Wiberg.[3]
10. Less quinoline (as little as 5% of the weight of the catalyst) often suffices for hydrogenations of this type. The submitters report that 2,2'-(ethylenedithio) diethanol (available from Fluka AG., Chemische Fabrik, CH-9470 Buchs, Switzerland) has proved to be more effective than quinoline in most selective hydrogenations. Between 1 and 10 parts per thousand calculated on the weight of the catalyst is usually sufficient (private communication from H. Lindlar and P. P. Gutmann).
11. Benzene, toluene, or acetone may be used as solvent for substances insoluble in paraffins. Alcohols are usually unsatisfactory media.

3. Discussion

The preparation of the catalyst is a slight modification of the original procedure.[4]

4. Merits of the Preparation

This form of palladium can be used for the hydrogenation of almost any triple bond to the double bond. Reduction of doubly substituted acetylenes gives *cis* olefins.

References and Notes

1. Checkers' note: Among organic chemists this catalyst is commonly called "Lindlar catalyst."
2. Chemical Research Department, F. Hoffmann-LaRoche & Co. Ltd., Basel, Switzerland.
3. K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, New York, 1960, pp. 228–230.
4. H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

olefin-free petroleum ether

chloropalladous acid

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

formic acid (64-18-6)

CO_2 (124-38-9)

calcium carbonate (471-34-1)

acetone (67-64-1)

toluene (108-88-3)

lead acetate

palladium (7440-05-3)

Quinoline (91-22-5)

sodium formate

phenolphthalein (77-09-8)

styrene (100-42-5)

Phenylacetylene (536-74-3)

palladous chloride,
palladium chloride (7647-10-1)

hexane (110-54-3)

2,2'-(ethylenedithio) diethanol