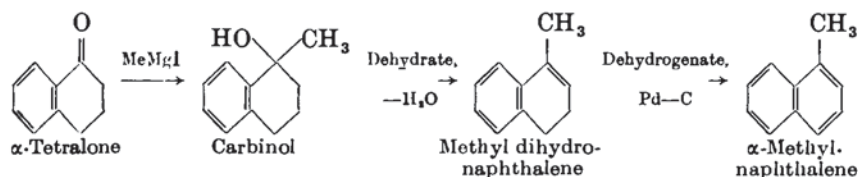


bath. Whilst stirring gently, add a solution of 15 g. of potassium hydroxide in 50 ml. of 50 per cent. aqueous ethanol dropwise very slowly from the dropping funnel; after 0.5–1 ml. of the solution has been added, a vigorous evolution of nitrogen commences and the temperature rises. Adjust the rate of addition so that the temperature is maintained at 10–20°; the duration of the addition of alkali is about 2 hours and the nitroso compound ultimately disappears. Stir the orange-yellow solution for a further 30 minutes, and then add 2*N*-hydrochloric acid until the solution is acidic to litmus paper (*ca.* 50 ml.).

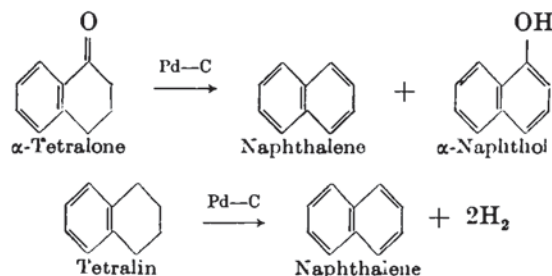
Introduce a solution of 100 g. of sodium bisulphite in 200 ml. of water and continue the stirring, preferably for 10 hours with exclusion of air. A thick precipitate separates after a few minutes. Collect the bisulphite compound by suction filtration, wash it with ether until colourless, and then decompose it in a flask with a lukewarm solution of 125 g. of sodium carbonate in 150 ml. of water. Separate the ketone layer, extract the aqueous layer with four 30 ml. portions of ether, dry the combined organic layers over anhydrous magnesium sulphate, remove the ether at atmospheric pressure, and distil the residual oil under reduced pressure from a Claisen flask with fractionating side arm (Fig. II, 2*A*, 5). Collect the *cycloheptanone* at 64–65°/12 mm.; the yield is 23 g.

VI,35. DEHYDROGENATION OF HYDROAROMATIC COMPOUNDS

Dehydrogenation (the conversion of alicyclic or hydroaromatic compounds into their aromatic counterparts by removal of hydrogen and also, in some cases, of other atoms or groups) finds wide application in the determination of structure of natural products of complex hydroaromatic structure. Dehydrogenation is employed also for the synthesis of polycyclic hydrocarbons and their derivatives from the readily accessible synthetic hydroaromatic compounds. A very simple example is the formation of β -methyl-naphthalene from α -tetralone (which is itself prepared from benzene—see Section IV,143):

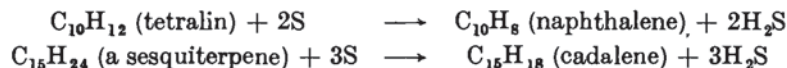


α -Tetralone may also be directly dehydrogenated to a mixture of naphthalene and α -naphthol, whilst tetralin yields naphthalene under similar conditions.



The principal dehydrogenating agents are (i) sulphur, (ii) selenium, and (iii) catalytic metals.

Sulphur. The general method is to heat the compound at 200–260° with the theoretical amount of sulphur required to bring it to the aromatic state :



Selenium. The substance is heated with a large excess of selenium at 280–350° for 36–48 hours. Better yields (and less side reactions) are usually obtained than with sulphur, but, owing to the higher temperature, rearrangements are more likely. Oxygen-containing groups are particularly prone to elimination.

Palladium and platinum catalysts. These catalysts are generally employed with a charcoal or asbestos carrier. The dehydrogenation can be conducted in the vapour phase by distilling the compound through a tube containing the catalyst heated to 300–350°, but the liquid phase method is generally more convenient. Charcoals or asbestos are employed containing 10–30 per cent. of the metal. It has been established that the best results are obtained by conducting the process in an actively boiling medium (*e.g.*, mesitylene, b.p. 165°; *p*-cymene, b.p. 177°; naphthalene, b.p. 218°; and α -methyl-naphthalene, b.p. 242°) and to provide for the elimination of the hydrogen as it is formed (*e.g.*, by sweeping the system with a stream of carbon dioxide).

Preparation of 30 per cent. palladium or platinum catalysts (charcoal or asbestos carrier).

Purification of charcoal. Heat "Norit" charcoal on a water bath for 6 hours with 10 per cent. nitric acid, filter, wash free from acid, and dry at 100°. If the acid-washed form of "Norit" charcoal is available, it may be used directly without further purification.

Purification of asbestos. Boil Gooch asbestos (tremolite, not chrysolite variety) with concentrated nitric acid, filter, wash free from acid, and dry at 100°.

Method A. Cool a solution of the nitrate-free dichloride, prepared from or equivalent to 5.0 g. of palladium or platinum, in 50 ml. of water and 5 ml. of concentrated hydrochloric acid in a freezing mixture, and treat it with 50 ml. of formalin (40 per cent. formaldehyde) and 11 g. of the carrier (charcoal or asbestos). Stir the mixture mechanically and add a solution of 50 g. of potassium hydroxide in 50 ml. of water, keeping the temperature below 5°. When the addition is complete, raise the temperature to 60° for 15 minutes. Wash the catalyst thoroughly by decantation with water and finally with dilute acetic acid, collect on a suction filter, and wash with hot water until free from chloride or alkali. Dry at 100° and store in a desiccator.

Method B. For some purposes a slightly more active catalyst is obtained when it is prepared in more concentrated solutions. The procedure is the same as above, but the volumes of solution for 5 g. of metal are: dilute acid, 25 ml.; formaldehyde, 35 ml.; potassium hydroxide, 32 g. in 32 ml. of water.

The above catalysts contain about 30 per cent. of metal: catalyst with 10 per cent. of metal may be readily prepared by reducing the quantity of platinum or palladium chloride used.

Broadly speaking, the differences in effectiveness of palladium and platinum catalysts are very small; the choice will generally be made on the basis of availability and current price of the two metals. Charcoal is a somewhat more efficient carrier than asbestos.

DEHYDROGENATION OF TETRALIN

For small scale dehydrogenations, the apparatus shown in Fig. VI, 35, 1 may be used. Place 2.5 g. of purified tetralin (1) and 0.25 g. of palladised charcoal in the apparatus and heat to boiling for 4 hours in a slow current of dry carbon dioxide. Naphthalene, m.p. 81°, collects on the condenser in almost quantitative yield. If it is desired to follow the progress of the dehydrogenation, attach the side tube through a "sofnolite" (or soda lime) U-tube to a nitrometer filled with potassium hydroxide solution: almost the theoretical quantity of hydrogen will be collected.

If the current of inert gas is omitted, the reaction is complete after about 22 hours.

Note.

(1) Commercial tetralin may be purified as follows. Wash the technical product repeatedly with 10 per cent. of its volume of concentrated sulphuric acid, then with 10 per cent. sodium carbonate solution, followed by water, dry with anhydrous calcium sulphate, filter from the desiccant, reflux over sodium, and finally distil from sodium. Collect the pure tetralin at 206-207°.

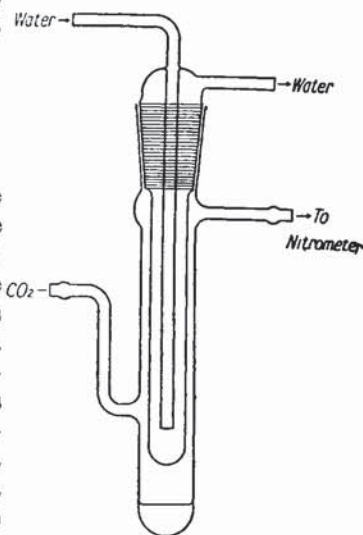


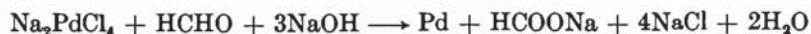
Fig. VI, 35, 1.

VI,36. PREPARATION OF PALLADIUM CATALYSTS FOR HYDROGENATION

Palladium catalysts are useful alternatives to Adams' platinum oxide catalyst described in Section III,150. The nearest equivalent to the latter is palladium chloride upon carbon and it can be stored indefinitely; the palladium salt is reduced to the metal as required:



The catalyst is also employed in the form of the finely-divided metal deposited upon activated carbon (usually containing 5 or 10 per cent. Pd); two methods of preparation are described, in one reduction is effected with alkaline formaldehyde solution and in the other with hydrogen:



Catalysts reduced with formaldehyde contain no adsorbed hydrogen and are less pyrophoric.

Barium sulphate is frequently used as a support for the palladium (compare the Rosenmund reduction of acid chlorides, Section IV,120); barium carbonate

may also be employed when it is required to maintain the neutrality of the hydrogenation mixture. At times these are to be preferred to carbon which may, in some instances, so strongly adsorb the hydrogenation product that recovery is incomplete or difficult.

A. Palladium chloride on carbon. Prepare a solution of 4.2 g. of anhydrous palladium chloride (1) in 10 ml. of concentrated hydrochloric acid and 25 ml. of water by heating on a boiling water bath for 2 hours or until solution is complete. Add 70 ml. of water and pour all the resulting solution over 46 g. of nitric acid - washed activated carbon (2) contained in an evaporating dish or Pyrex crystallising dish. Mix the palladium chloride solution thoroughly with the carbon, and dry the mixture first on a water bath and then in an oven at 100° : stir occasionally. Powder the mass (49 g.) and store in a tightly-stoppered bottle.

This palladium chloride catalyst does not deteriorate during storage. When required for use, place the required quantity in a hydrogenation bottle (compare Fig. III, 150, 1) and reduce it with hydrogen in the solvent to be used for the hydrogenation ; a neutral solvent is to be preferred for the reduction of the palladium chloride. When no more hydrogen is absorbed by the catalyst, collect it on a sintered glass funnel, wash it with more of the solvent to remove the hydrogen chloride and then return it, with the aid of a little fresh solvent, to the reduction bottle : it is essential to keep the catalyst moist with the solvent during the washing process as it is pyrophoric. The presence of hydrogen chloride during the hydrogenation of many organic compounds is desirable (see introductory paragraph to Section III, 150) or is without effect ; in such cases, the palladium chloride on carbon is added to the solvent and hydrogen acceptor before reduction.

B. Palladium on carbon catalyst (10 per cent. Pd). Add a solution of 2.1 g. of palladium chloride (1) in 1.5 ml. of concentrated hydrochloric acid and 10 ml. of water (prepared as in A) to a solution of 44 g. of A.R. crystallised sodium acetate in 125 ml. of water contained in a 250-500 ml. reduction bottle, introduce 11.5 g. of nitric acid - washed activated carbon (2) and hydrogenate the mixture at 1.1 atmospheres until absorption ceases (2-5 hours). Collect the catalyst on a Buchner funnel, wash it with five 100 ml. portions of water, and suck as dry as possible. Dry the catalyst at room temperature (3) and then over potassium hydroxide pellets or anhydrous calcium chloride in a vacuum desiccator. Powder the catalyst (12-12.5 g.) and store it in a tightly-stoppered bottle.

C. Palladium on carbon catalyst (5 per cent. Pd). Suspend 41.5 g. of nitric acid - washed activated carbon in 600 ml. of water in a 2-litre beaker and heat to 80°. Add a solution of 4.1 g. of anhydrous palladium chloride (1) in 10 ml. of concentrated hydrochloric acid and 25 ml. of water (prepared as in A), followed by 4 ml. of 37 per cent. formaldehyde solution. Stir the suspension mechanically, render it alkaline to litmus with 30 per cent. sodium hydroxide solution and continue the stirring for a further 5 minutes. Filter off the catalyst on a Buchner funnel, wash it ten times with 125 ml. portions of water, and dry and store as in B. The yield is 46 g.

D. Palladium on barium sulphate catalyst (5 per cent. Pd). (4) Prepare a solution of 4.1 g. of anhydrous palladium chloride (1) in 10 ml. of concentrated hydrochloric acid and 25 ml. of water (as in A). Add all at once 60 ml. of 6*N*-sulphuric acid to a rapidly stirred, hot (80°) solution of 63.1 g. of A.R. crystallised barium hydroxide in 600 ml. of water contained in a 2-litre beaker. Add more 6*N*-sulphuric acid to render the suspension just acid to litmus (5). Introduce the palladium chloride solution and 4 ml. of 37 per cent. formaldehyde solution into the hot mechanically-stirred suspension of barium sulphate. Render the suspension slightly alkaline with 30 per cent. sodium hydroxide solution, continue the stirring for 5 minutes longer, and allow the catalyst to settle. Decant the clear supernatant liquid, replace it by water and resuspend the catalyst. Wash the catalyst by decantation 8–10 times and then collect it on a medium - porosity sintered glass funnel, wash it with five 25 ml. portions of water and suck as dry as possible. Dry the funnel and contents at 80°, powder the catalyst (48 g.), and store it in a tightly-stoppered bottle.

Notes.

(1) Alternatively, the equivalent quantity of palladium chloride dihydrate may be used.

(2) Any of the commercial forms of activated carbon (Norit, Darco, etc.) may be employed; the carbon should be heated on a steam bath with 10 per cent. nitric acid for 2–3 hours, washed free from acid with water, and dried at 100–110° before use.

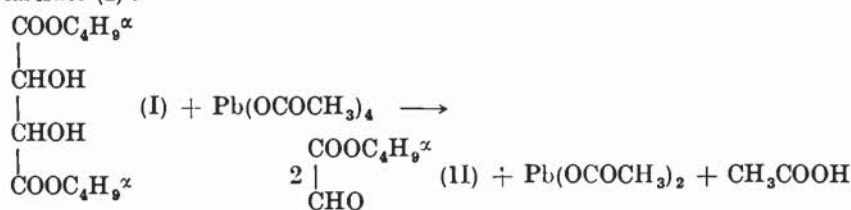
(3) Heating may cause ignition of the carbon.

(4) This is an improvement on the procedure described in Section IV,120, Note 3.

(5) Where it is advantageous to maintain the neutrality of the hydrogenation mixture, palladium upon barium carbonate catalyst is recommended: the barium hydroxide and sulphuric acid are then replaced by 46.5 g. of precipitated barium carbonate and the volume of hydrochloric acid is reduced to 4.1 ml.

**VI,37. OXIDATION WITH LEAD TETRA-ACETATE
n-BUTYL GLYOXYLATE**

An interesting application of lead tetra-acetate is to the preparation of the otherwise difficulty-accessible *n*-butyl glyoxylate (II) by oxidation of di-*n*-butyl *d*-tartrate (I):



Place a mixture of 125 ml. of A.R. benzene and 32.5 g. of di-*n*-butyl *d*-tartrate (I) in a 500 ml. three-necked flask, equipped with a Hershberg stirrer (Section II,7) and a thermometer. Stir the mixture rapidly and add 58 g. of lead tetra-acetate (Section II,50,15) in small portions over a period of 20 minutes whilst maintaining the temperature below 30° by occasional cooling with cold water. Continue the stirring for a further 60 minutes. Separate the salts by suction filtration and wash with two