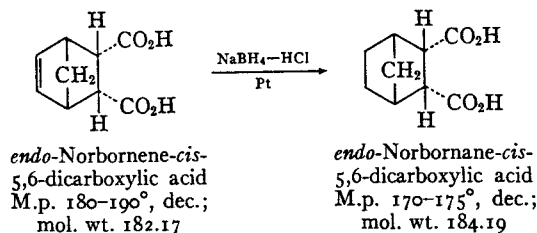


CHAPTER 16

Catalytic Hydrogenation



Conventional procedures for hydrogenation in the presence of a platinum catalyst employ hydrogen drawn from a cylinder of compressed gas and require elaborate equipment. H. C. Brown and C. A. Brown (1962) introduced the simple procedure of generating hydrogen internally from sodium borohydride and hydrochloric acid and prepared a highly active supported catalyst by reduction of platinum chloride with sodium borohydride in the presence of decolorizing carbon. The special apparatus described by these authors is here dispensed with in favor of the balloon technique employed for catalytic oxygenation (Chapter 14).

PROCEDURE

The reaction vessel is a 125-ml. filter flask with a white rubber bulb wired onto the side arm. Introduce 10 ml. of water, 1 ml. of platinum chloride solution,¹ and 0.5 g. of Norit and swirl during addition of 3 ml. of stabilized 1 *M* sodium borohydride solution.² While allowing 5 minutes for formation of the catalyst,

¹ A solution of 1 g. of PtCl₄ in 20 ml. of water.

² Dissolve 1.6 g. of sodium borohydride and 0.3 g. of sodium hydroxide (stabilizer) in 40 ml. of water. When not in use, the solution should be stored in a refrigerator. If left for some time at room temperature in a tightly stoppered container, gas pressure may develop sufficient to break the vessel.

dissolve 1 g. of *endo*-norbornene-*cis*-5,6-dicarboxylic acid in 10 ml. of water. Pour 4 ml. of concentrated hydrochloric acid into the reaction flask, followed by the hot solution of the unsaturated acid. Cap the flask with a large serum stopper, and wire it on. Draw 1.5 ml. of the stabilized sodium borohydride solution into the barrel of a plastic syringe, thrust the needle through the center of the stopper, and add the solution dropwise with swirling. The initial uptake of hydrogen is so rapid that the balloon may not inflate until you start injecting a second 1.5 ml. of borohydride solution through the rubber port. When the addition is complete and the reaction appears to be reaching an end point (about 5 min.), heat the flask on the steam bath with swirling and try to estimate the time at which the balloon is deflated to a constant size (about 5 min.). Heat and swirl for 5 minutes more and then release the pressure by injection of an open syringe.

Filter the hot solution by suction and place the catalyst in a jar marked for "catalyst recovery."³ Cool the filtrate and extract it with three portions of ether. Each extract is to be washed with saturated sodium chloride solution and filtered through sodium sulfate. Evaporation gives 0.8–0.9 g. of white solid.

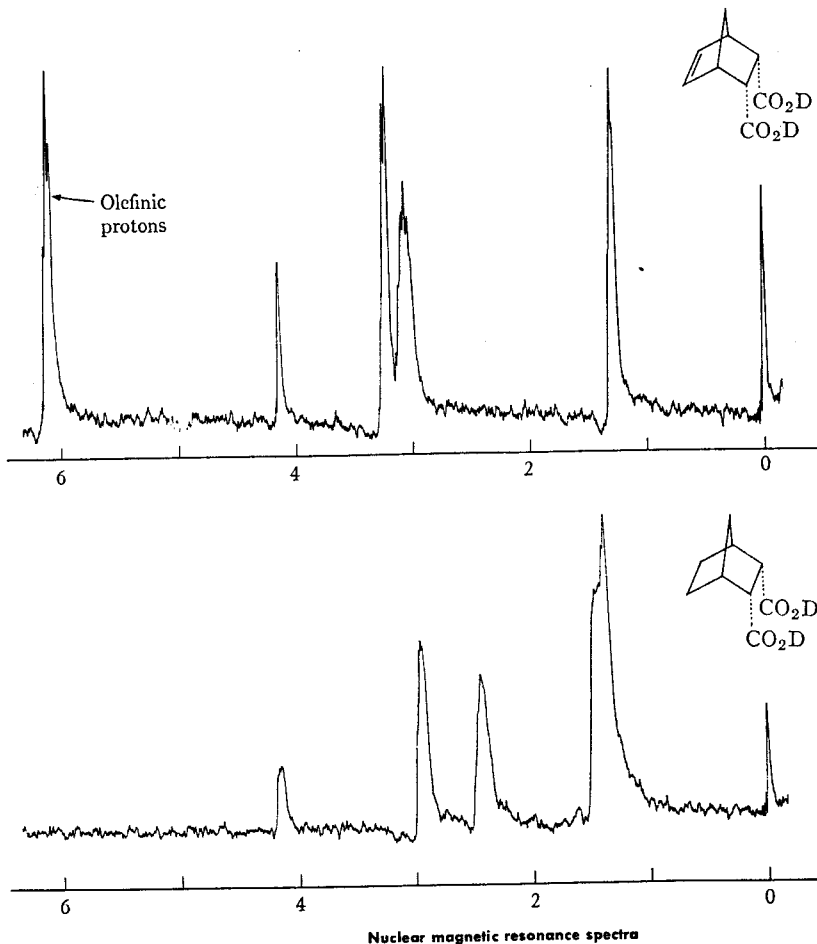
The only solvent of promise for crystallization of the saturated *cis*-diacid is water, and the diacid is very soluble in water and crystallizes extremely slowly and with poor recovery. However, the situation is materially improved by addition of a little hydrochloric acid to decrease the solubility of the diacid. Scrape out the bulk of the solid and transfer it to a 25-ml. Erlenmeyer flask. Add 1–2 ml. of water to the large flask, heat to boiling to dissolve residual solid, and pour the solution into the smaller flask. Bring the material into solution at the boiling point with use of a total of not more than 3 ml. of water (as a guide, measure 3 ml. of water into a second Erlenmeyer). With a capillary dropping tube add 3 microdrops of concentrated hydrochloric acid and let the solution stand for crystallization. Clusters of heavy prismatic needles soon separate; the recovery is about 90%. The product should give a negative test for unsaturation with acidified permanganate solution.

Observe what happens when a sample is heated in a melting point capillary to about 170° and see if you can account for the result. You may be able to confirm your inference by letting

³ Used catalyst can be sent for recovery to Engelhard Industries, 865 Ramsey St., Hillside, N. J.

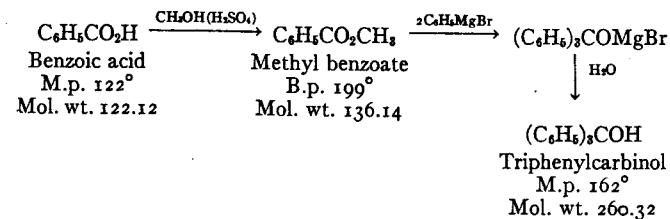
the bath cool until the sample solidifies and then noting the temperature and behavior on remelting.

The nuclear magnetic resonance spectra distinguish clearly between the unsaturated and saturated diacids. The spectra were taken in deuterium oxide in order to eliminate peaks due to protons of the carboxyl groups. The peak due to the two olefinic protons is completely eliminated on hydrogenation.⁴



⁴ Data by David H. Sachs, who made an additional observation of interest. If platinum chloride is treated with sodium borohydride and hydrochloric acid in an ethanol solution containing the unsaturated diacid (but no Norit), reduction to platinum metal does not occur. Evidently the unsaturated diacid combines with platinum chloride to form a stable π -complex.

Triphenylcarbinol



Benzoic acid is esterified by the Fischer method, and the methyl benzoate produced is used for the Grignard synthesis of triphenylcarbinol by interaction with two equivalents of phenylmagnesium bromide.

In Fischer esterification, methanol is used in excess both to shift the equilibrium in favor of the product and to serve as solvent for the solid acid component. Of the acid and Lewis acid catalysts commonly employed, sulfuric acid is preferred to hydrogen chloride because of greater convenience and to boron fluoride etherate because it is a more effective catalyst. In case either the alcohol or the acid involved in an esterification contains reactive double bonds or is sensitive to dehydration, boron fluoride etherate becomes the catalyst of choice.

In this two-step synthesis directions are given for the Grignard reaction of 5.0 g. (0.037 mole) of pure methyl benzoate and you are to adjust the quantities of reagents according to the amount of intermediate available. Satisfactory yield and quality of the final product require care in the preparation and purification of the intermediate ester as well as in the second step. The chief impurity in the Grignard reaction mixture is diphenyl, formed by the coupling reaction:

