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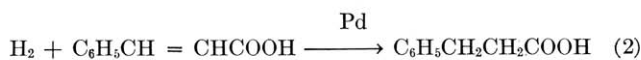
Hydrocinnamic Acid: Catalytic Hydrogenation

For the undergraduate organic
 chemistry laboratory

Catalytic hydrogenation is a type of chemical reaction of wide utility in industry and in the laboratory. Its use is recommended repeatedly in virtually all organic chemistry textbooks. On the other hand, seldom is it possible for undergraduate students to actually perform an experiment which involves catalytic hydrogenation. This is due mainly to the need to use gaseous hydrogen which is inconvenient and potentially hazardous. Also, special apparatus is ordinarily required even for hydrogenations carried out at atmospheric pressure.

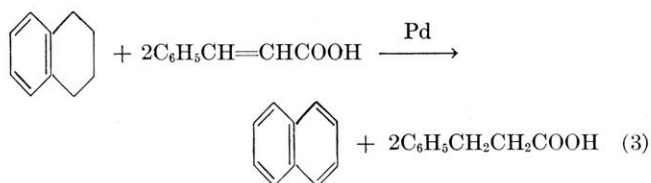
A type of reaction which circumvents these difficulties is catalytic hydrogen transfer. Hydrogen derived by catalytic dehydrogenation from an easily aromatized cyclic compound is transferred directly and in the same vessel to an unsaturated substance which is then catalytically hydrogenated. Such reactions are discussed in detail by Jackman (1).

We have adapted the reduction of cinnamic acid to hydrocinnamic acid with palladium in tetralin (2) for use in some of our undergraduate classes. Here, tetralin, present in excess of the amount needed, serves both as solvent and as the source of hydrogen.



Reactions (1) and (2) represent reactions which can be carried out independently of one another under conditions approximating those used in the experiment described below. Thus, tetralin is smoothly dehydrogenated to naphthalene under reflux in the presence of palladium (3). Catalytic hydrogenation of cinnamic acid takes place at atmospheric pressure and at room temperature, conditions milder than those used in this experiment (4).

Combination of the two reactions, as described below and summarized in reaction (3)



is efficient and further minimizes the evolution of hydrogen which theoretically may continue as long as unreacted tetralin is present. A satisfactory yield is obtained after refluxing the mixture of tetralin and cinnamic acid for 1-1.5 hours. Cyclohexene may also be used as the source of hydrogen but a 64-hour reflux period is required. In addition, the reaction is complicated by disproportionation of cyclohexene to benzene and cyclohexane (5).

It is thus possible to discuss and illustrate both hydrogenation and aromatization in conjunction with one simple preparation. The considerable difference in melting point between two structurally similar compounds, cinnamic and hydrocinnamic acids, mp 133° and 48.5°, respectively, may be pointed out and

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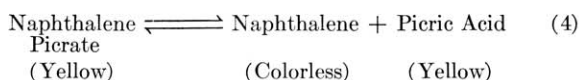
discussed. Also of interest are differences in solubility between these compounds and differences in chemical properties.

The catalyst utilized in the reaction is 30% palladium on activated carbon. Since it is relatively inexpensive, and only 0.1 g is used per student, the fact that it cannot be reused should not be a barrier to the experiment. Reactivation of the catalyst is probably not warranted.

Ordinarily, no effort is made to show the presence of naphthalene in the reaction mixture or to isolate it from the excess tetralin. Both the identification and isolation are, however, quite feasible; the processes are instructive in their own right, since they involve the selective formation and relative stabilities of arene picrates (molecular complexes of arenes and picric acid) (6).

Naphthalene picrate crystallizes when a mixture of tetralin and naphthalene is treated with ethanolic picric acid. The identification of this naphthalene derivative when compared with authentic naphthalene picrate serves to show the presence of the expected by-product.

In a slightly more elaborate but worthwhile procedure, naphthalene itself is recovered from its picrate. An instructive way of decomposing naphthalene picrate is to chromatograph it on an alumina column. This decomposition takes advantage of the equilibrium (4) which provides an opportunity either for introducing chromatography with a very simple system or for illustrating an unusual application thereof in which two substances of widely differing polarities are easily separated.



The preparation of hydrocinnamic acid has been successfully incorporated into a synthetic sequence starting from benzaldehyde and terminating in 1-indanone. Benzaldehyde is converted to cinnamic acid via Perkin condensation using potassium carbonate as the base. Cinnamic acid is catalytically reduced to hydrocinnamic acid by the method here described; and hydrocinnamic acid is cyclized to 1-indanone with polyphosphoric acid (7).

The Experiment¹

Hydrocinnamic Acid. To a solution of 5 g of cinnamic acid in 25 ml of tetralin (tetrahydronaphthalene) contained in a large test tube, 0.1 g of 30% palladium on activated carbon catalyst is added.² The solution is refluxed under an air condenser for 1.5 hours, is cooled, and is diluted with 25 ml of diethyl ether. The palladium catalyst is filtered off and hydrocinnamic acid is extracted from the filtrate with two 10-ml portions of 10% aqueous sodium hydroxide. The remaining organic liquid is dried over anhydrous calcium

¹ We wish to acknowledge the assistance of Miss Daiva Alyta and Mr. Robert Spector in working out and checking some of the experimental details of the synthesis.

² Engelhard Industries Inc., Chemical Division, Newark 2, N. J. Current cost: approximately \$12 per 30 g. Cost per student, \$0.04.

chloride and reserved for the identification and isolation of naphthalene.

The aqueous alkaline layer is acidified with concentrated hydrochloric acid until it is acid to Congo Red paper. It is then extracted with two 25-ml portions of diethyl ether, and the ether layer is dried over anhydrous calcium chloride.

The ether solution is distilled over the steam-bath, and the distillation residue is allowed to cool and stand until it crystallizes. Suction and ice cooling may be used to remove residual ether and to hasten crystallization. The crude acid should be weighed and a few small crystals set aside for use as seeds in subsequent crystallizations. The yield of crude acid is 2.5–3.0 g.

The hydrocinnamic acid is recrystallized from petroleum ether or from a mixture of water and ethanol. Approximately 250 ml of water and subsequently 10 ml of ethanol may be required to recrystallize approximately 2.5 g of hydrocinnamic acid. The reported melting point of hydrocinnamic acid is 48.5°.

Identification and Isolation of Naphthalene. One-half of the acid-free, dried, reaction mixture is distilled on the steam-bath until no further liquid (ether) distills and the warm residue is added to a solution of 2.5 g of picric acid in 25 ml of ethanol (warmed if necessary to effect solution). The solution is allowed to cool to room temperature, then chilled in ice-water. The crystals of naphthalene picrate are collected by suction filtration and allowed to air dry, and are then weighed. One gram of crude product is removed, its melting point is determined, and it is recrystallized from benzene or chloroform to constant melting point (reported mp 149.5°).

The major part of the picrate complex is dissolved in 25 ml of diethyl ether and is added to 20 g of chromatographic grade alumina made up into a column with petroleum ether as solvent. Elution of the adsorbed solid with diethyl ether is attended by its decomposition since the picric acid component of the complex is retained by the alumina and naphthalene is rapidly eluted. As the separation proceeds, the eluate is evaporated in portions until no further naphthalene appears. During this time, picric acid will have progressed very little down the column.

The crude naphthalene is weighed, its melting point is determined, and a portion of it is recrystallized from the minimum amount of methanol or ethanol. The melting point of the recrystallized naphthalene is determined as well as a mixed melting point with authentic naphthalene.

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