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UNITED STATES PATENT OFFICE

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PROCESS FOR THE HYDROGENATION OF NAPHTHALENE COMPOUNDS

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5 Claims. (Cl. 260—590)

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Our invention relates to a process for the hydrogenation of naphthalene compounds and more particularly to a process for the hydrogenation of these compounds with the aid of a Raney metal alloy.

The reduction of naphthalene and its derivatives has been carried out by various catalytic processes, as well as by reduction with sodium and alcohol, sodium amalgam, and metals with acids. For the most part, catalytic hydrogenations involve the use of relatively high temperatures and pressures, and no generalization can be made as to the course of the hydrogenation. On reducing with certain agents, such as sodium and alcohol and sodium amalgam, hydrogenation usually occurs in only one ring, and the various tetralin derivatives can be obtained. However, substituted naphthalene derivatives do not always give the desired tetrahydro derivative, since hydrogenation occurs indiscriminately in either the substituted or unsubstituted ring, depending upon the type and position of substituents present.

The use of an alkali solution together with a Raney alloy for effecting reduction of organic compounds is now well known. However, such alloy and alkali combination is unable to effect hydrogenation of benzene or of substituted benzene-like phenol and other phenol compounds. In fact, so far as we are aware, Raney alloys have never successfully been employed for the hydrogenation of aromatic double bonds; compounds containing aromatic double bonds have usually required much more vigorous hydrogenating conditions than are available by the use of a Raney alloy, despite the fact that such alloy provides both a metal which produces hydrogen in statu nascendi in the aqueous alkali solution, as well as the resulting catalytic Raney metal, usually nickel, or similar metal which is inactive toward the alkali solution.

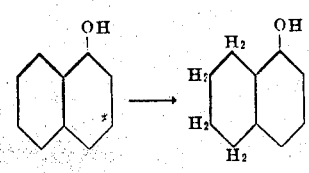
We have now found that by the use of a Raney alloy and aqueous alkali, it is possible to hydrogenate, under extremely mild conditions, the naphthalene ring system to the corresponding tetrahydro derivatives. Not only was such hydrogenation unexpected in view of the relative inertness of benzene and phenol compounds under the same conditions, but a selective type of hydrogenation can be accomplished in contradistinction to the random hydrogenation that is obtained with the agents referred to hereinabove. Of particular interest in the process of the invention is the ease with which naphthalene derivatives substituted in one ring can be hydrogenated to the tetrahydro derivative, the unsubstituted ring being the one that is reduced. This circumstance presents a most valuable advantage for the production of many tetrahydro derivatives, since most of the known methods for reducing substituted naphthalenes do not always give the desired product.

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In accordance with the present invention, therefore, various naphthalene derivatives, substituted on only one or on both rings, are subjected to the reducing action of a Raney alloy in an aqueous alkali solution or suspension. Where the naphthalene is substituted on only one ring, usually only the unsubstituted ring will be hydrogenated to the tetrahydro derivative; however, in certain cases, as with β-naphthol, some reduction of the substituted ring will take place. The same degree of reduction will generally be obtained also with naphthalene compounds substituted on both rings. The reaction may take place at the boiling point of the mixture, although lower temperatures can be employed with correspondingly longer periods of reaction to insure good yield. A temperature of 65–75° C. will usually be satisfactory.

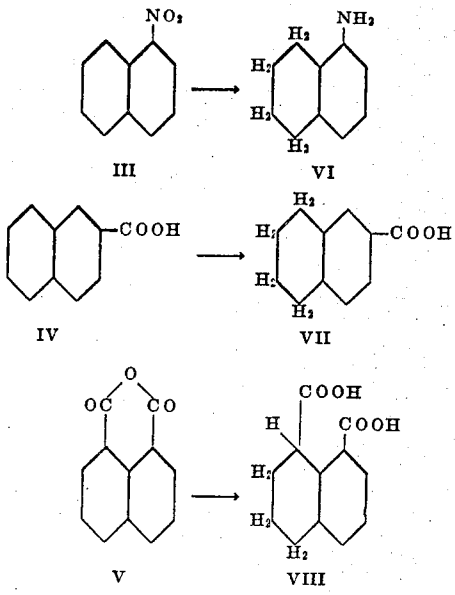
In the course of the reduction process of the present invention, other groups susceptible to reduction will be simultaneously reduced. Thus, nitro groups will be reduced to amino groups, keto groups to methylene, and a double bond will be saturated.

The selective character of the hydrogenation will be recognized from a few typical examples. Thus, α-naphthol (I) gives the ar-tetrahydro derivative (II):



I II

Similarly, α-nitrophthalene (III), β-naphthoic acid (IV), and naphthalic anhydride (V), undergo, on reduction with Raney's alloy, hydrogenation of the unsubstituted benzene ring (VI, VII) or of only one of the rings if both are substituted (VIII):



III VI

IV VII

V VIII

Satisfactory procedures for carrying out the present invention are illustrated by the following examples which are, however, not intended to indicate the scope of the invention.

EXAMPLE 1

Preparation of 1-hydroxy-5,6,7,8-tetrahydro-β-naphthoic acid

Ten grams of 1-hydroxy-β-naphthoic acid are dissolved in 300 cc. of 10% sodium hydroxide and, with stirring and heating, 30 gm. of Raney's nickel-aluminum alloy is added in the course of 1–2 hours. At the end of the addition of the alloy, the solution is heated for an additional hour or two and filtered from the nickel residue. The alkaline filtrate is then acidified to Congo red paper with concentrated HCl and cooled. The precipitated acid is dissolved in sodium carbonate, filtered, and acidified. The tetrahydro acid is obtained from dilute alcohol in the form of fine, white needles melting at 156–158° C.

EXAMPLE 2

Preparation of ar-tetrahydro-α-naphthol

Ten grams of α-naphthol are reduced as described under Example 1, and after acidification of the alkaline solution, extraction with chloroform, and recrystallization of the chloroform residue from petroleum ether, there is obtained the ar-tetrahydro-α-naphthol melting at 70–71° C.

EXAMPLE 3

Preparation of 3-hydroxy-5,6,7,8-tetrahydro-β-naphthoic acid

Ten grams of 3-hydroxy-β-naphthoic acid are reduced, isolated, and purified as described under Example 1. After recrystallization from dilute methyl alcohol, the ar-tetrahydro-3-hydroxy-β-naphthoic acid is obtained as white crystalline material melting at 178–180°. The acetate, which may be prepared in the usual manner, gives on recrystallization from benzene-petroleum ether small, fine, white needles melting at 141–142°.

EXAMPLE 4

Preparation of ar-tetrahydro-β-naphthoic acid

Ten grams of β-naphthoic acid are reduced as described under Example 1. The crude reduction product, after recrystallization from aqueous methyl alcohol, melts at 153–154°.

EXAMPLE 5

Preparation of ar-tetrahydro-α-naphthylamine

Ten grams of α-nitro-naphthalene are mixed with 350 cc. of 10% sodium hydroxide. To the aqueous solution is added 50 cc. of ethyl alcohol, and then 30 gm. of Raney's alloy in the course of 1–2 hours. This reduction is run in a flask provided with an adapter carrying an efficient water-cooled condenser. After the reduction is completed, the mixture is steam distilled. The steam distillate is extracted with ether, dried, and after evaporation of the ether, the residue is distilled. It boils at 261–263° at atmospheric pressure. The compound, on diazotization with sodium nitrite, couples with β-naphthol, and gives a hydrochloride melting at 258–260°. The acetyl derivative, prepared in the usual manner, melts at 156–157°, which is in agreement with the literature.

EXAMPLE 6

Preparation of 1,8-dicarboxytetralin

Ten grams of naphthalic anhydride are dissolved in 300 cc. of 10% sodium hydroxide and treated with 35 gm. of Raney's alloy as described under Example 1. The crude acid, after recrystallization from aqueous alcohol, separates as small, shining plates melting at 185–186°.

EXAMPLE 7

Preparation of 2-methyl-5,6,7,8-tetrahydronaphthalene

Ten grams of β-methylnaphthalene are reduced as described under Example 5. The reduction product, after isolating in the usual manner, can be identified as the 2-methyl-5,6,7,8-tetrahydronaphthalene by permanganate oxidation.

EXAMPLE 8

Preparation of ar-tetrahydro-β-naphthol

Ten grams of β-naphthol are reduced as described under Example 1. In this reduction some ac-β-tetrahydronaphthol is formed which is lost by volatilization with steam. The reduction product is worked up in the usual manner, and after recrystallization from petroleum ether is obtained in the form of long, fine, white needles melting at 61–62°.

EXAMPLE 9

Preparation of 2-ethyl-5,6,7,8-tetrahydronaphthalene

Ten grams of methyl-β-naphthyl ketone is reduced as described under Example 5, using 40–45 gm. of Raney's alloy. It is necessary to use approximately 50 cc. of alcohol to keep some of the ketone in solution. The ethyl tetralin which is obtained boils at 243–245° and can be identified by oxidation with potassium permanganate.

EXAMPLE 10

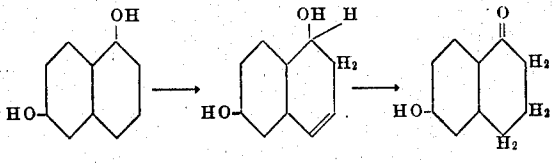
Preparation of 6-hydroxy-α-tetralone

Ten grams of 1,6-dihydroxy naphthalene are dissolved in 400 cc. 10% sodium hydroxide and heated to approximately 50°. In the course of about one hour, 35 g. of Raney nickel-aluminum

alloy are slowly added. The reaction mixture is worked up as described in the previous examples and the hydroxy tetralone obtained is recrystallized from water and melted at 150–152°.

Somewhat better yields of the tetralone are obtained when the reaction is carried out in an inert atmosphere such as nitrogen, using the apparatus described for reduction of alkali insoluble compounds as illustrated under Example 5. After the reduction is completed, the solution is filtered directly into a mixture of ice under HCl, the semi-solid extracted with ether and the ether dried and evaporated. Recrystallization of the residue from water gives the pure 6-hydroxy-α-tetralone.

The 6-hydroxy-α-tetralone is a valuable intermediate in the synthesis of the female sex hormone, estrone. The production of tetralone may be represented by the following equation:



It is, however, also possible that a simultaneous reduction of the ring containing the 1—OH group and oxidation of such group occur without actual production of the dihydroxy intermediate indicated above.

EXAMPLE 11

5,6,7,8-tetrahydro-1-naphthaleneacetic acid

10 g. α-naphthaleneacetic acid is reduced in 250 cc. of 10% sodium hydroxide with 25 g. of Raney alloy. The reduction product is worked up in the usual manner and after recrystallization from benzene-petroleum ether, the tetrahydro derivative is obtained as white, crystalline needles melting at 132–133°.

EXAMPLE 12

2,7-dihydroxy-tetrahydronaphthalene

10 g. of 2,7-dihydroxynaphthalene is reduced in aqueous alkali with Raney alloy as described in the previous example. The crude product is a yellowish-green solid which after recrystallization from water separates as a white, crystalline material melting at 146–147°.

In the above examples, the Raney alloy has in all cases been a nickel-aluminum alloy. However, other alloys containing a metal capable of reacting with sodium or potassium hydroxides in aqueous solution to yield hydrogen, and also a metal which is relatively non-reactive to alkali and which will act to catalyze the hydrogenation, such metal being in the form of a skeleton catalyst after solution of the reactive metal, may be employed. Thus, the alloys may contain magnesium, calcium, or zinc in place of the aluminum, while the nickel may be replaced in whole or in part by copper or the like. The hydrogen-generating metal and the catalytic metal may be used together but in non-alloyed condition, especially where the catalytic metal is in skeleton form. Thus, powdered aluminum or aluminum turnings may be used together with a skeleton nickel catalyst prepared by dissolving out the aluminum from a Raney nickel aluminum alloy of any suitable percentage composition by reaction with an alkali solution.

With many naphthalene compounds, such as various naphthalenes, naphthoic acids, and hydroxy-naphthoic acids, the aqueous alkali solution will act as a satisfactory solvent; however, where the starting compound is of low solubility in the aqueous alkali, alcohol or other organic solvent miscible with water may be added to dissolve the same, as in the above Example 10. The production of 6-hydroxy-α-tetralone is more particularly described and claimed in our application Serial No. 96,135, filed May 28, 1949.

We claim:

1. Process for the hydrogenation of naphthalene compounds which comprises subjecting such compounds to the action of an aqueous alkali solution in the presence of an alloy of a metal capable of reacting with the alkali solution to yield hydrogen and a catalytic metal which is relatively inert toward the alkali solution.

2. Process for the hydrogenation of naphthalene compounds which comprises subjecting such compounds to the action of an aqueous alkali solution in the presence of a Raney nickel-aluminum alloy.

3. Process for the hydrogenation of naphthalene compounds which comprises subjecting a naphthalene compound substituted in only one of its rings to the action of an aqueous alkali solution in the presence of an alloy of a metal capable of reacting with the alkali solution to yield hydrogen and a catalytic metal which is relatively inert toward the alkali solution.

4. Process for the manufacture of tetrahydro naphthalene derivatives which comprises subjecting a substituted naphthalene compound to the action of aqueous alkali in the presence of an alloy of a metal capable of reacting with the alkali solution to yield hydrogen and a catalytic metal which is relatively inert toward the alkali solution, and continuing the reaction until four atoms of hydrogen have been added to the naphthalene compound.

5. 2,7-dihydroxy-tetrahydronaphthalene.

DOMENICK PAPA.
ERWIN SCHWENK.

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Certificate of Correction

Patent No. 2,475,718. July 12, 1949.

DOMENICK PAPA ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 18, claim 1, line 25, claim 2, line 31, claim 3, after the word "solution" insert *at a temperature not exceeding the boiling point of the solution*; line 38, claim 4, before "aqueous" insert *an*; same line, after "alkali" insert *solution at a temperature not exceeding the boiling point of the solution*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of November, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.