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PARTIAL REDUCTION OF POLYCYCLIC
AROMATIC HYDROCARBONSVirgil L. Hansley, Niagara Falls, N. Y., assignor to
E. I. du Pont de Nemours & Company, Wilmington,
Del., a corporation of DelawareNo Drawing. Application June 26, 1947,
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10 Claims. (Cl. 260-667)

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This invention relates to a method of partially reducing polycyclic aromatic hydrocarbons by reaction of such compounds with an alkali metal and a reducing alcohol.

The partial reduction of various polycyclic aromatic hydrocarbons, particularly naphthalene, by reaction with an alkali metal and a reducing alcohol has long been known. Thus, Bamberger and Lodter, Ann. 288, 75 (1895) added sodium to a boiling solution of naphthalene in ethyl alcohol to obtain 1,4-dihydronaphthalene. Although that method has remained as perhaps the most convenient way of making that compound, it is not well suited for the obtainment of 1,4-dihydronaphthalene when it is required in pure form. Product obtained by that method contains at best only 70-85%, 1,4-dihydronaphthalene due to unavoidable contamination with unconverted naphthalene and tetralin which are very difficult to separate. The tetralin impurity is probably formed by rearrangement of the 1,4-dihydro product to the 1,2-isomer which then undergoes further reduction. According to German Patent 306,724, the tetrahydro derivative is obtained if solvent naphtha is added to raise the boiling point of the reaction mixture.

Good yields of 1,4-dihydronaphthalene may be obtained by reacting naphthalene with sodium in certain special solvents at low temperatures and adding a compound which is a hydrogen donor gradually to the mixture as rapidly as the colored sodium-naphthalene intermediate addition compound is formed. (U. S. P. 2,171,867, 2,171,868 and 2,171,869.) This method is disadvantageous, however, in that it requires the exercise of considerable care and skill particularly in properly proportioning the reactants. Furthermore, it requires the use of relatively expensive reaction media and refrigeration.

Various catalytic methods for reducing polycyclic aromatic hydrocarbons have been proposed, but so far as I am aware all such methods, in the case of naphthalene, yield substantially only tetralin or decalin, rather than the 1,4-dihydro compound.

It is an object of the present invention to provide an improved method for hydrogenating naphthalene involving reaction with an alkali metal and a specific type of reducing alcohol whereby 1,4-dihydronaphthalene of high purity may be readily obtained in substantially quantitative yields. A further object is to provide an improved method of reducing polycyclic aromatic hydrocarbons of the type defined below to obtain various partially hydrogenated derivatives of

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such compounds. Still further objects will be apparent from the following description.

The above objects are accomplished in accordance with the invention by reacting a polycyclic aromatic hydrocarbon having at least two aromatic rings which are directly joined to each other, or a homologue thereof with an alkali metal and a secondary or tertiary alcohol, if desired, in an inert liquid solvent. After completion of the reaction the reaction mixture may be conveniently treated with water to hydrolyze the by-product alcoholate and then worked up in any desired manner to recover the partially hydrogenated product and the solvent and regenerated alcohol. I have discovered that this method is highly efficient and practical and may be carried out to obtain good yields of partially hydrogenated derivatives of such hydrocarbons.

In the case of several of such hydrocarbons the method effects hydrogenation so as to obtain but a single hydrogenation product. This is highly advantageous when mixed hydrogenation products are objectionable. Thus, with naphthalene, 2-methyl naphthalene and anthracene, the sole hydrogenation products are 1,4-dihydronaphthalene, 1,4-dihydro-2-methyl naphthalene and 9,10-dihydroanthracene, respectively. In some instances, however, more than one product results, but even in those cases the method is advantageous over prior methods in that it affords an easy and practical means for carrying out the hydrogenation to obtain partially hydrogenated products in high yields.

The method is especially well suited for the production of 1,4-dihydronaphthalene. That compound is obtained as substantially the only hydrogenation product and since the reaction is rapid and the yield based on naphthalene is substantially quantitative, the method may be practiced conveniently to obtain 1,4-dihydronaphthalene of high purity. No difficulty is generally experienced in obtaining that compound having a purity of at least 98% with but one simple distillation.

Another advantage of this method is that aromatic hydrocarbons containing sulfur compounds as impurities may be reduced without first removing the sulfur. In fact, the product from such a reduction of an impure starting material is recovered free of sulfur.

The hydrocarbons that may be partially reduced in accordance with the invention are those polycyclic aromatic hydrocarbons which have at least two aromatic rings directly joined to each other. They include polycyclic compounds of

the condensed ring type, such as naphthalene, wherein two carbon atoms are common to two rings. Also, included are those aromatic hydrocarbons such as diphenyl and fluorene wherein aromatic rings are joined directly. Homologues of both types of hydrocarbons are also included. Compounds such as diphenyl methane wherein the rings are separated by an aliphatic or other nucleus, instead of being directly joined, are excluded. Specific examples of compounds which may be used are: naphthalene, phenanthrene, fluorene, diphenyl, the diphenyl benzenes, ace-naphthene, retene, pyrene, picene, crysene and indene. Homologues of the above compounds such as 1- or 2-methyl naphthalene may be employed as may also certain derivatives of such compounds or their homologues wherein one or more of the hydrogens have been replaced by substituent groups such as the hydroxyl, the alkoxy and the amino groups. Among such compounds, the method is particularly well adapted to effect partial hydrogenation of naphthalene, anthracene and diphenyl.

Any secondary or tertiary aliphatic or cycloaliphatic alcohol may be used to practice the invention. Specific examples of such alcohols are: trimethylcarbinol, dimethylethylcarbinol, dimethylpropylcarbinol, dimethylisopropylcarbinol, diethylmethylcarbinol, triethylcarbinol, pentamethylethanol, dimethylcarbinol, diethylcarbinol, methylethylcarbinol, methylpropylcarbinol, methylisobutylcarbinol, cyclohexanol and the methyl cyclohexanols. The tertiary alcohols generally give somewhat better results than secondary alcohols although good results may be obtained with the latter. When considering all factors, including availability and cost, the three preferred compounds are trimethylcarbinol, dimethylethylcarbinol and methylisobutylcarbinol. Of these trimethylcarbinol is particularly preferred since it gives excellent results and has a boiling point much lower than the boiling points of the compounds to be reduced and their reduction products which facilitates separation and recovery of the alcohol for reuse. When using alcohols of the above type there is substantially no direct reaction between the alcohol and the alkali metal to liberate free hydrogen as long as any amount of the reducible hydrocarbon is present.

Trimethylcarbinol and toluene make almost an ideal reducing alcohol-solvent combination. The reaction may be carried out readily with this combination at what is generally the preferred temperature and recovery of the alcohol and solvent is relatively simple. Thus, the ternary azeotropic mixture of toluene, trimethylcarbinol and water boils at 76° C. and the anhydrous alcohol at 82° C. On the other hand, the atmospheric boiling point of 1,4-dihydronaphthalene is 210-212° C. Hence, the alcohol, and toluene, which boils at 111° C., may be effectively separated for reuse by a simple steam distillation. Since most polycyclic aromatic hydrocarbons and the partially hydrogenated products are less volatile than 1,4-dihydronaphthalene, the trimethylcarbinol-toluene combination is in general very well suited for use from the recovery standpoint regardless which hydrocarbon is being reduced.

The proportions of polycyclic aromatic hydrocarbon to alkali metal may be varied considerably, but in general theoretical quantities of the alkali metal, i. e., 2 atoms per mole of hydrogen to be introduced, is desirable. The preferred practice involves the use of a small excess of the

alkali metal, e. g., as much as a 10% excess. Still larger excesses may be used if desired, but such practice is wasteful and is not recommended.

The proportions of reducing alcohol to alkali metal may also be varied considerably. As a general rule at least one mole of alcohol will be used per atom of alkali metal and it is preferred to employ a 10-30% excess of alcohol over that amount. No particular harm results from the use of larger excesses, but likewise no particular advantages result therefrom. The manner of adding the alcohol is important and should be carried out by adding the alcohol, preferably diluted with substantial quantities of the inert solvent, to a mixture of the alkali metal dispersed in the solvent solution of the polycyclic aromatic hydrocarbon. Addition of the alcohol-solvent mixture should be at a rate which is equivalent to the rate at which the alcohol is consumed in the reaction. In other words, the buildup of an excess of alcohol in the reaction mixture while there is still free alkali metal therein should be avoided since such conditions result in the evolution of free hydrogen and thus reduces the efficiency of the operation. Of course, when an excess of alcohol is utilized there will eventually be present in the reaction mixture free alcohol even though addition under the conditions mentioned above have been adhered to. Too great an excess of reducing alcohol, however, thickens up the reaction mixture unnecessarily due to the formation of the insoluble alcoholate-alcohol complex (NaOR·HOR).

Any inert liquid of suitable boiling point which is a solvent for the hydrocarbon being reduced and the reduction product under the reaction conditions may be used. The term "inert" liquid is used to mean any liquid which does not react chemically with any of the reactants or the reaction products involved and does not cause the formation of an addition product between the alkali metal and the polycyclic aromatic hydrocarbon under the conditions of use. In certain cases the partially reduced hydrocarbon may serve as the reaction medium. Toluene and xylene and various petroleum fractions, particularly those high in paraffin hydrocarbons and boiling within the range 100-150° C. are especially well suited for the present purpose. The use of toluene or xylene, particularly the former, is preferred in most instances but the choice of the solvent and temperature depends to some extent upon the reaction being carried out. Certain ethers, such as dibutyl ether may also be used, but other more active ethers, i. e., the so-called "active" ethers as defined in Scott U. S. P. 2,027,000, are not suited for the present use. Such "active" ethers of which dimethyl glycol ether is typical, specifically promote the formation of addition compounds between the alkali metal and the aromatic hydrocarbon. They are not suited to the present use since they also promote reduction beyond the desired stage and polymerization of the sensitive partial reduction products desired. Inactive ethers such as dibutyl ether, as contrasted with the so-called "active" ethers, exert no such promoting effect and may be employed as solvent if desired. Use of an inert solvent is not necessary but is desirable. When used it is generally advantageous to employ sufficient solvent to dissolve completely the starting polycyclic aromatic hydrocarbon and the resulting partial reduction product and to dilute the reaction mixture so as to facilitate agitation thereof. While not necessary it is recommended

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that part of the solvent be added initially to the mixture containing the polycyclic aromatic hydrocarbon and the alkali metal and part be added along with the reducing alcohol. The preferred practice involves diluting the alcohol with about 2 to 3 volumes of the solvent such as toluene or xylene.

Reduction may be carried out at any temperature ranging from about 0 to 200° C. It is preferred that temperatures above the melting point of the alkali metal be used, but reaction at lower temperatures may be employed but special arrangements must be made to keep the sodium dispersed. The most preferred temperatures are within the range 80–150° C. although the choice of the particular temperature will depend to some extent upon the particular reactants involved. With most of the hydrocarbons, temperatures of 100–110° C. give excellent results and are preferred. With certain hydrocarbons somewhat higher temperatures give better results as in the case of diphenyl where a temperature of around 140° is recommended.

Generally, the present method will involve forming a solution of the hydrocarbon to be reduced in a suitable solvent such as toluene or xylene and then dispersing the alkali metal in that solution by means of heat and agitation. Agitation and maintenance of a temperature of, for example, 100–110° C. is then continued while a mixture of the reducing alcohol and the solvent is added. The rate of addition of the alcohol mixture is controlled so as to avoid the presence in the reaction mixture of an excess of alcohol until such time as practically all of the alkali metal has been consumed. The reaction is rapid at temperatures of about 100° C. and is generally complete within a matter of 2 hours or less. If an excess of metal is used such excess may be conveniently destroyed by addition of a lower alcohol such as methyl or ethyl alcohol, or the entire reaction may be drowned in water with due safety precautions. Separation of the regenerated alcohol and solvent is then accomplished by steam distillation and the separated materials may be dried or purified as required by known means for reuse. The reduction product remaining as a residue from the steam distillation step may then be washed and dried and, for most purposes, is sufficiently pure for use without further treatment. Simple fractional distillation of the residue under reduced pressure, will in most cases and particularly in the case of 1,4-dihydronaphthalene yield a product of high purity.

The reaction may be carried out by the controlled addition of the alkali metal to a solution which contains both the reducing alcohol and the compound to be hydrogenated. However, the reverse practice as described above gives much better results and is preferred. The invention is further illustrated by the following examples.

Example 1

Sodium, 50.6 g., was added in fairly large pieces to a boiling solution of 128 g. naphthalene in 500 cc. of absolute ethanol. The reaction time was 15 minutes. As soon as the reaction was completed, the reaction mixture was cooled and diluted with water to hydrolyze the alcoholates and separate the reduction product. After vacuum distillation, the recovered hydrocarbon analyzed 75.9% 1,4-dihydronaphthalene by bromine absorption at 0° C. in the dark and

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identification of the dibromo tetrahydronaphthalene.

The above example illustrates the use of a primary reducing alcohol in accordance with prior methods. The following examples illustrate similar reductions employing secondary and tertiary alcohols in accordance with my invention.

Example 2

A charge of 6 moles of naphthalene and 14.8 atoms of sodium was placed in a 2 gallon stainless steel reactor jacketed for circulation of a cooling or heating liquid as a means of regulating temperature. The charge was heated to 100–105° C. and agitation was started as soon as the sodium melted. After a few minutes to allow the sodium to become dispersed through the mixture, a mixture of 12.6 moles of trimethylcarbinol and 21.5 moles of toluene was added at a rate of 100 cc. per minute while maintaining the above temperature and while continuing agitation. During the reduction 20 liters of hydrogen were evolved. The by-product alcoholate was hydrolyzed by drowning the mixture in water and the toluene and regenerated alcohol were removed by steam distillation. The crude reaction product after separating from the aqueous layer was neutralized with dilute sulfuric acid and vacuum distilled. The 1,4-dihydronaphthalene obtained boiled at 100–102° C./25 mm. The material was 98.5% pure. The yield was practically quantitative.

Example 3

One mole of naphthalene, 2.09 atoms of sodium and 3.25 moles of toluene were charged into a 3-liter 3-neck glass reaction flask provided with an oil bath for heating, stirring means and inlet and outlet connections. After heating the charge to 100–105° C. 4 moles of trimethylcarbinol as a 30% solution in toluene was added slowly while continuing the stirring. Hydrogen evolution, representing loss by direct reaction of the sodium with trimethylcarbinol and moisture, amounted to 1.1 liter. The product isolated as described in Example 2 analyzed 98% 1,4-dihydronaphthalene. The yield was substantially quantitative.

Example 4

100 g. of 90% anthracene, 20 g. of sodium, and 170 cc. of toluene were charged into a 3-liter 3-neck flask in an oil bath, and heated to 114° C. Stirring was started to disperse the sodium. Then a mixture of 150 g. of methyl isobutyl carbinol in 302 g. toluene was fed into the stirred mixture over a period of 25 minutes. Upon recovery and vacuum distillation (165–170° C. at 8 mm.) of the reduced hydrocarbon, 90 g. of 9,10-dihydroanthracene was obtained, which is slightly less than the amount required by theory.

Example 5

One mole of 1-methyl naphthalene and 2.1 atoms of sodium were heated together to 100–105° C. and agitated to suspend the sodium as described in Example 2. A mixture of 6.5 moles of toluene and 2.7 moles of trimethylcarbinol was run into the resulting mixture over a period of 68 minutes while maintaining a temperature of 100–105° C. Reduction occurred to an extent equivalent to the introduction of 1.92 atoms of hydrogen per mole of methyl naphthalene, representing a yield of 96%. The reduction product was a water-white oil weighing 123 grams and

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boiling at 124–127° C./25 mm. It probably consisted of a mixture of the 1,4- and 5,8-dihydro isomers.

Example 6

The above example was repeated employing 1 mole of 2-methyl naphthalene and 2.1 atoms of sodium. A mixture of 6.8 moles of toluene and 3 moles of trimethylcarbinol was added during a period of 55 minutes. The reduction which took place was equal to the introduction of 1.96 atoms of hydrogen per mole of the methyl naphthalene, corresponding to 98% reduction. The product was a light, yellow oil boiling at 118.2° C./25 mm. It was believed to be pure 1,4-dihydro-2-methyl naphthalene.

Example 7

The method described in Example 2 was followed employing a charge of 1 mole of diphenyl, 4.25 atoms of sodium and 3 moles of xylene. The reaction temperature was 140–141° and the alcohol mixture consisted of 5.4 moles of trimethylcarbinol and 5.5 moles of xylene. The addition time was 70 minutes. The reduction effected was equivalent to 3.95 atoms of hydrogen per mole of diphenyl, corresponding to a yield of 98.7%. The product believed to be 1-phenyl-1,2-cyclohexene, was a water-white oil boiling at 103–104° C./8 mm. and melting at –12 to –18° C.

Example 8

0.7 mole of anthracene, 2.1 atoms of sodium and 2 moles of xylene were heated together and the sodium dispersed in the mixture at a temperature of 100–105° C. While maintaining that temperature and continuing agitation of the mixture, a mixture of 2.7 moles of trimethylcarbinol and 4.5 moles of toluene was introduced over a period of 60 minutes. An 85.5% yield of 9,10-dihydroanthracene, M. P. 108° C.; B. P. 165–170° C./8 mm., was obtained.

Example 9

0.7 mole of phenanthrene, 5 moles of toluene and 3.15 atoms of sodium were heated together to 102° C. While maintaining that temperature and continuing agitation of the resulting mixture, there was added during 65 minutes a mixture of 3.85 moles of trimethylcarbinol and 2 moles of toluene. The equivalent of somewhat more than 4 atoms of hydrogen were introduced per mole of phenanthrene. The product was a light, yellow oil, B. P. 160–165° C./8 mm.; M. P. 89° C.

Example 10

0.75 mole of acenaphthene, 2.25 atoms of sodium and 6 moles of toluene were heated together to 102° C. and a mixture of 4.5 moles of toluene and 6 moles of trimethylcarbinol was added during 80 minutes as in the previous example. The reduction corresponded to the introduction of 2.02 atoms of hydrogen per mole of acenaphthene. The product was a light, yellow to greenish viscous oil, B. P. 136–140° C./25 mm.; M. P. 20° C.

Example 11

A mixture of 0.7 mole p-diphenyl benzene, 7 moles of toluene and 3.6 atoms of sodium were heated to 101° C. and there was added thereto over a period of 110 minutes a mixture of 2.3 moles of toluene and 5 moles of trimethylcarbinol following the general procedure of the preceding examples. The reduction which resulted was equivalent to 2.7 atoms of hydrogen indicating

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that the main product was a tetrahydro diphenyl benzene. The product was semi-solid at room temperature and boiled at 190–200° C./7 mm.

The partially hydrogenated products obtainable by the present invention are useful for a variety of purposes. In some instances they are valuable for use in the preparation of various polymeric compositions. They are also useful, particularly when pure, as chemical intermediates, e. g., in the pharmaceutical field.

I claim:

1. A process for the production of 1,4-dihydronaphthalene comprising reacting naphthalene with an alkali metal and a tertiary aliphatic alcohol at a temperature not exceeding 110° C., employing at least 2 atoms of said metal per mole of naphthalene and at least 1 mole of said alcohol per atom of said metal.

2. The process of claim 1 wherein the alkali metal is sodium and the reaction is carried out at a temperature above the melting point of sodium but not exceeding 110° C.

3. The process of claim 2 wherein the reaction is carried out by adding the alcohol to an agitated mixture containing the naphthalene and the sodium at a rate substantially equal to the rate at which said alcohol is consumed by its reaction with said naphthalene and sodium to produce 1,4-dihydronaphthalene.

4. The process of claim 3 wherein the alcohol is trimethylcarbinol.

5. The process of claim 3 wherein the alcohol is dimethylethylcarbinol.

6. A process for the production of 1,4-dihydronaphthalene comprising adding a mixture of a tertiary aliphatic alcohol with an inert solvent to an agitated mixture of naphthalene and sodium maintained at a temperature above the melting point of sodium but not exceeding 110° C., said alcohol-solvent mixture being added at a rate substantially equal to the rate at which said alcohol is consumed by reaction with said naphthalene and sodium to produce 1,4-dihydronaphthalene, employing 2 to 2.2 atoms of sodium per mole of naphthalene and 1 to 1.3 moles of said alcohol per atom of sodium, continuing said addition until substantially all of said naphthalene has been converted to 1,4-dihydronaphthalene and recovering the latter from the resulting mixture.

7. The process of claim 6 wherein the alcohol is trimethylcarbinol.

8. The process of claim 6 wherein the alcohol is dimethylethylcarbinol.

9. The process of claim 6 wherein the inert solvent is toluene.

10. The process of claim 6 wherein the alcohol is trimethylcarbinol, the inert solvent is toluene, the temperature is maintained at 100 to 105° C. and the alcohol-solvent mixture consists of 2 to 3 volumes of toluene per volume of trimethylcarbinol.

VIRGIL L. HANSLEY.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Country	Date
306,724	Germany	July 10, 1918

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