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PREPARATION AND HYDROGENATION OF SCHIFF'S BASES

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This invention relates to the manufacture of N-aryl N'-alicyclic-p-phenylenediamines and to the manufacture of the Schiff's base intermediate. The invention particularly relates to the manufacture of N-phenyl-N'-cyclohexyl-p-phenylenediamine.

An object of the invention is to provide an economical process for the manufacture of N-aryl-N'-alicyclic-p-phenylenediamines. Another object is to provide a process for converting N-aryl-p-phenylenediamines to N-aryl-N' - alicyclic - p-phenylenediamines in high yields. Satisfactory methods for producing N-phenyl-p-phenylenediamine have been described and this intermediate is readily available. Particular objects are to provide a method for producing the Schiff's base from N-phenyl-p-phenylenediamine and cyclohexanone in high yield and to provide a method for reducing the Schiff's base without purifying it. Other and further objects will be apparent from the description following.

The reductive alkylation of p-phenylenediamine has been well documented. However, contrary to statements in the patent literature that reductive alkylation of N-phenyl-p-phenylenediamine with cyclohexanone is a simple matter, this reaction proceeds poorly. Yields have been too low to make the product economically attractive and competitive. This is surprising, especially since reductive alkylation of p-phenylenediamine and of N-cyclohexyl-p-phenylenediamine with cyclohexanone is indeed a simple matter under conditions heretofore described. Nevertheless, the reductive alkylation of N-phenyl-p-phenylenediamine has been singularly unsuccessful until discovery of the critical combination of reaction variables described herein.

The Schiff's base recation ultimately proved to be a crucial step but even after preparing the Schiff's base in a preliminary step, reduction gave low yields. It was discovered that the Schiff's base is extremely sensitive to moisture. This not only renders reductive alkylation infeasible, necessitating alkylation and reduction in separate steps, but requires formation of the Schiff's base in very high yield free from moisture and precursers thereof if its isolation and purification are to be avoided. Thus, formation of appreciable Schiff's base and water during hydrogenation, where heating is inevitable, must be avoided. However, it was further discovered that heating one mole of N-phenyl-p-phenylenediamine and at least three, preferably four, moles of cyclohexanone while removing water by azeotropic distillation gave essentially quantitative yields of the Schiff's base which product then reduced readily without the necessity of purifying it. Under these conditions the reactions can be effected with very high concentrations of reactants, thereby making the operation more economical. Moreover, hydrogenation of the Schiff's base succeeds without any diluent yielding a product only slighly inferior in assay and almost indistinguishable for its intended use from material hydrogenated in a solvent.

While a solvent, as for example benzene, can be added if desired, the excess of cyclohexanone is a satisfactory azeotroping agent. It is not necessary to form the Schiff's base at the atmospheric boiling point of cyclohexanone. Mild heating is sufficient to effect condensation so that azeotroping under pressures less than atmospheric is feasible and is preferred because it reduces side reactions

and reduces opportunity for thermal decomposition. The optimum temperature for conducting the reaction is about 90° C., the pressure being adjusted so as to maintain azeotroping at about this temperature. Although not distillable, the Schiff's base is stable over a wide temperature range but there is evidence that small quantities of by-products which accompany its formation at temperatures above 90° C. poison the catalyst in the hydrogenation step. The yields of hydrogenated product tended to decrease slowly but significantly as the temperature at which the Schiff's base was formed increased from 90° to 160° C.

After forming an essentially quantitative yield of the dry Schiff's base, the reduction is straightforward. It is preferred to distill off the bulk of the excess cyclohexanone and to add another solvent, as for example, isopropanol, benzene or methyl alcohol, although neither step is essential. All of the cyclohexanone may be removed by reduced pressure distillation. If desired a solution may be prepared for transporting, pumping and storage. The Schiff's base may be reduced using formic acid in the Leukart reaction but more economically by catalytic reduction over nickel. The examples below will illustrate the invention in greater detail.

N-phenyl-p-phenylenediamine, M.P. 75° C., B.P. 179–181° C./1 mm., 50 parts by weight (0.27 molecular proportion) and 200 parts by weight of benzene are added to a glass or glass-lined reactor fitted with thermometer, stirrer, water trap, condenser and outlet to vacuum pump. To the benzene solution 82 parts by weight (0.83 molecular proportion) of cyclohexanone are added and the mixture heated to refluxing temperature. Water begins to collect in the trap when the pot temperature reaches 84° C. Heating and stirring are continued for 2.8 hours at 88–89° C. during which time approximately 90% of the water expected from a quantitative conversion collects in the trap. There is probably some holdup of water in the equipment because it was demonstrated by adding water to dry Schiff's base and then hydrogenating that 5% and 10% of a mole of water per mole of base reduced the yield of hydrogenated product approximately 8% and 18% respectively.

The reaction mixture is then transferred to an autoclave, 4.1 parts by weight nickel catalyst prepared from nickel formate added and the vessel purged several times with hydrogen at 100 lbs./in.^{2}. Hydrogen pressure is then increased to 300 lbs./in.^{2} and the reaction mixture stirred and heated to 130° C. The reaction continues at 130–150° C. over about 1.5 hours. The contents of the autoclave are then filtered while hot to remove catalyst. Upon cooling the bulk of the product crystallizes from solution and is separated by filtration. The benzene is removed from the filtrate by distillation and the residue subjected to steam to remove further volatile constituents by steam distillation. The solid product remaining is recrystallized from heptane. A 96% yield of N-cyclohexyl-N'-phenyl-p-phenylenediamine, M.P. 115–117° C. is obtained.

The reaction rate in the first step increases significantly upon increasing the cyclohexanone ratio to four moles per mole of amine but further increase has no beneficial result. According to a preferred modification, 73 parts by weight (0.40 mole) of N-phenyl-p-phenylenediamine and 155 parts by weight (1.58 moles) of cyclohexanone are charged into a glass or glass-lined reactor fitted as described above. Additional cyclohexanone, 13 parts by weight (5.13 mole) is added to the outlet side of the water trap. The line to the pump leads through a dry ice-acetone trap.

The reaction mixture is heated to 85° C. and the pressure of the system reduced to 135 mm. where refluxing starts. Water forms rapidly at first, then more slowly

until after 60 minutes the theoretical quantity has been collected, no additional water being observed in the reflux. The pressure is gradually reduced to 48 mm. while the temperature is maintained at 80–85° C. Cyclohexanone, 81 parts (70% of the excess charged) is then distilled from the reaction mixture at 78–80° C. under 40–50 mm. pressure.

The 75% (by weight) solution of the Schiff's base in cyclohexanone obtained by the above procedure is charged into an autoclave, diluted with 70 parts by weight of benzene to produce a 50% solution of the Schiff's base in the mixed solvent and 5.0 parts moisture-free Raney nickel added. The autoclave is purged twice with hydrogen under 100 lbs./in.^{2} hydrogen and the contents heated to 135° C. Absorption of hydrogen takes place at 135–150° C. for 45 minutes.

The reactor is cooled to 40–50° C., then opened and the solution filtered to remove catalyst. Benzene is removed by distillation and high boiling volatile constituents removed by steam distillation. The dark solid which remains dispersed in the water is collected on a filter and dried at 70° C. The yield of N-cyclohexyl-N'-phenyl-p-phenylenediamine is 95%.

A particular advantage of the process is that use of distilled N-phenyl-p-phenylenediamine is unnecessary. The crude reaction product resulting from catalytic reduction of 4-nitrosodiphenylamine reacts satisfactorily. After separating the catalyst by filtration and removing solvent, water of reaction and any other distillable constituents from the filtrate, the crude residue may be converted directly to the anil. For example, to 72.9 parts by weight of crude N-phenyl-p-phenylenediamine obtained as described, 156 parts by weight of cyclohexanone are added. The stirred mixture is heated (or cooled) to a pot temperature of about 50–60° C. The pressure is then reduced to approximately 200 mm. Hg and heat applied until refluxing sets in (approximately 80° pot, 62° head temperature). The heat is then cut back and refluxing maintained by slowly reducing the pressure. The condensate consists of the azeotrope mixture of cyclohexanone and water. The lower water layer is collected while the ketone layer is recycled. The pressure is brought down to 50 mm. Hg during the stripping of the water.

When all the water of reaction has been collected as evidenced by constant pot and head temperatures, and a very slow or absent rate of water formation (reaction time about 50–60 min. from beginning of water removal) the excess cyclohexanone is stripped to a final condition of 150° pot temperature at 20 mm. Hg. The recovered ketone, 100% of the excess used, is saved for reuse in the next batch.

The crude anil weighs about 105 parts by weight. An equal weight of 2-propanol or 1-butanol is then added and the solution charged to an autoclave along with Raney nickel which has been washed free of water with 2-propanol. The catalyst charge is 4% based on the weight of Schiff's base, 4.2 parts dry basis.

The clave is purged, brought up to 850 lbs./in.^{2} hydrogen pressure, agitation started and heat applied. A slow uptake of hydrogen occurs at about 100° C. but the major portion of reaction occurs at about 140° C. The reaction mixture is maintained between 140–150° C. until the absorption of hydrogen ceases. It is then held at 150° C. until the absorption of hydrogen ceases. It is then held at 150° C. to insure complete reaction. The autoclave contents are then cooled to about 90° C., the clave is vented and the contents filtered to remove the catalyst. The filter cake is washed with 2-propanol and kept moist until transferred back to the clave or temporarily stored under 2-propanol. The autoclave contents should be filtered hot to prevent precipitation of the product.

The filtered product is distilled to remove solvent and small amounts of higher boiling material. The main portion of 2-propanol is removed at atmospheric pressure. When the pot temperature rises to about 125° the gradual application of vacuum to about 200 mm. Hg pressure will remove the majority of the remaining alcohol. The distillation is continued to 150° C. pot temperature at 20 mm. Hg. The pot residue is 100 parts by weight of N-cyclohexyl-N'-phenyl-p-phenylenediamine, melting about 105° C.

Other alicyclic ketones may be employed in the process, as for example cyclopentanone and lower alkyl cyclohexanones providing at least one ortho position is unsubstituted. Examples of suitable alkyl cyclohexanones comprise o - methylcyclohexanone, p - methylcyclohexanone, m - methylcyclohexanone, 2,4 - dimethylcyclohexanone, 3,5 - dimethylcyclohexanone and 2,4,5 - trimethylcyclohexanone. Other N - aryl - p-phenylenediamines may be used, as for example N-naphthyl-p-phenylenediamine. Cyclopentanone is much more sluggish in reaction than cyclohexanone but by the herein described process it is possible to prepare the heretofore unknown N-cyclopentyl-N'-phenyl-p-phenylenediamine.

N-phenyl-p-phenylenediamine, M.P. 75° C., B.P. 179–181° C./1 mm., 46 parts by weight, and 84 parts by weight of cyclopentanone are added to a glass or glass-lined reactor fitted with a thermometer, stirrer, water trap, condenser and outlet to vacuum pump. The reaction mixture is heated to about 95–100° C. and the pressure of the system reduced to induce refluxing at this temperature. The condensate consists of an azeotrope mixture of cyclopentanone and water. The reaction is continued until the theoretical quantity of water has been collected in the trap. The excess cyclopentanone is then distilled from tthe reaction mixture under reduced pressure, an equal weight of 2-propanol added and the solution transferred to an autoclave together with 5.0 parts of dry Raney nickel catalyst. The autoclave is purged twice with hydrogen and the contents heated to 135° C. under hydrogen pressure of about 500 lbs./in.^{2}. Absorption of hydrogen takes place at 135–155° C. for about 50 minutes. The reaction is cooled and the contents filtered to remove catalyst and the product allowed to crystallize from solution. The product, N-cyclopentyl-N'-phenyl-p-phenylenediamine, is a solid, M.P. 76–77° C. analyzing 5.54% nitrogen as compared to 5.52% calculated for $C_{17}H_{20}N_2$. This compound is a more effective antioxidant for rubber than N-cyclohexyl-N'-phenyl-p-phenylenediamine.

It is intended to cover all changes and modifications of the examples of the invention herein chosen for purposes of disclosure which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. In the method of preparing N-phenyl and N-naphthyl N'-cycloalkyl-p-phenylenediamines by reacting the corresponding N-substituted p-phenylenediamine with a cycloalkanone and catalytically reducing the resulting Schiff's base, the combination of steps which comprises heating a reaction mixture consisting of one molecular proportion of a member of the group consisting of N-phenyl-p-phenylenediamine and N-naphthyl-p-phenylenediamine, at least three molecular proportions of a cycloalkanone selected from the group consisting of cyclohexanone, cyclopentanone, methylcyclohexanone, 2,4-dimethylcyclohexanone, 3,5-dimethylcyclohexanone and 2,4,5-trimethylcyclohexanone and azeotroping agent selected from the group consisting of the aforesaid cycloalkanones in excess of the one molecular proportion required for reaction and benzene, while azeotropically distilling water from the reaction mixture below 150° C., said azeotropic distillation being continued until substantially the theoretical amount of water produced in the formation of the Schiff's base has been removed, then subjecting the dry undistilled composite Schiff's base to the action of molecular hydrogen in the presence of a nickel hydrogenation catalyst and hydrogenating the carbon-nitrogen double bond of the Schiff's base.

2. In the method of preparing N-phenyl-N'-cyclohexyl-p-phenylenediamines by reacting N-phenyl-p-phenylenediamine with cyclohexanone and catalytically reducing the resulting Schiff's base, the combination of steps which comprises heating a reaction mixture consisting of one molecular proportion of N-phenyl-p-phenylenediamine and at least four molecular proportions of cyclohexanone while azeotropically distilling water from the reaction mixture under less than atmospheric pressure at 80–100° C. as a cyclohexanone azeotrope, said azeotropic distillation being continued until the theoretical amount of water produced in the formation of the Schiff's base has been removed, then subjecting the dry undistilled composite Schiff's base to the action of molecular hydrogen in the presence of a nickel hydrogenation catalyst and hydrogenating to N-cyclohexyl-N'-phenyl-p-phenylenediamine.

3. In the method of preparing N-phenyl-N'-cyclohexyl-p-phenylenediamines by reacting N-phenyl-p-phenylenediamine with cyclohexanone and catalytically reducing the resulting Schiff's base, the combination of steps which comprises heating a reaction mixture consisting of one molecular proportion of N-phenyl-p-phenylenediamine and at least four molecular proportions of cyclohexanone while distilling below 150° C. under less than atmospheric pressure said distillation being continued until the theoretical amount of water produced in the formation of the Schiff's base has been removed as cyclohexanone azeotrope and the bulk of the cyclohexanone has been removed, adding solvent selected from the group consisting of lower alkanols and benzene in amount sufficient to form a solution then subjecting the solution of the dry undistilled composite Schiff's base to the action of molecular hydrogen in the presence of a nickel hydrogenation catalyst and hydrogenating to N-cyclohexyl-N'-phenyl-p-phenylenediamine.

4. In the method of preparing N-phenyl-N'-cyclo-

pentyl-p-phenylenediamines by reacting N-phenyl-p-phenylenediamine with cyclopentanone and catalytically reducing the resulting Schiff's base, the combination of steps which comprises heating a reaction mixture consisting of one molecular proportion of N-phenyl-p-phenylenediamine and at least four molecular proportions of cyclopentanone while distilling below 150° C. under less than atmospheric pressure said distillation being continued until the theoretical amount of water produced in the formation of the Schiff's base has been removed as cyclopentanone azeotrope and the bulk of the cyclopentanone has been removed, adding solvent selected from the group consisting of lower alkanols and benzene in amount sufficient to form a solution then subjecting the solution of the dry undistilled composite Schiff's base to the action of molecular hydrogen in the presence of a nickel hydrogenation catalyst and hydrogenating to N-cyclopentyl-N'-phenyl-p-phenylenediamine.

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