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HYDRAZO COMPOUNDS AND INVERSION THEREOF

William S. Calcott, Pennsgrove, and Frederick B. Downing and Norman C. Somers, Carneys Point, N. J., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

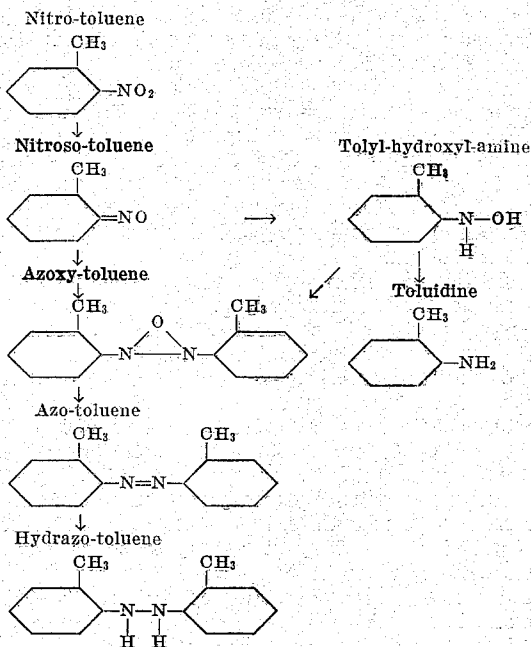
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This invention relates to hydrazo compounds and their production from nitro-benzenes. It also relates to the inversion of hydrazo-benzenes to benzidines. More particularly it deals with the formation of hydrazo-benzenes in a new form.

It is known that nitro-benzenes can be changed to hydrazo-benzenes by reduction with zinc and sodium hydroxide. It is also known that the products so obtained can be converted to benzidines by treatment with hydrochloric acid. (The Synthetic Dyestuff and Intermediate Products, Cain & Thorpe, 1918, page 22).

The general course of this reduction reaction is well understood, for example it has been pointed out that the alkaline reduction of nitro-toluene (a representative of this class) takes the following course (Zeit. Ang. Chem. 13, 435).



When the alkaline reduction of nitro-benzenes to hydrazo-benzenes by means of zinc and caustic is carried out in an aqueous medium, a very poor yield is obtained, 70% or more of the final product being toluidine.

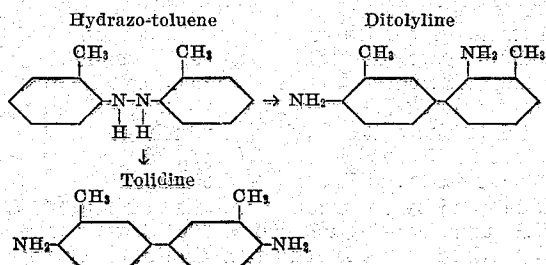
An early improvement in this process consisted in carrying out the reaction in an alcoholic medium. While this gave improved yields

of hydrazo-benzenes it involved the additional expense of alcohol recovery.

Izmailskii (U. S. S. Russia Patent 116 of Feb. 28, 1925) and Nelson and Prsial (U. S. Patent 1,644,434 of October 4, 1927) have recently suggested that this reduction be performed in the presence of a solvent, not miscible with water. This method gives better yields than are obtained in an aqueous medium but like the reaction in an alcoholic medium mentioned above involves the cost of solvent recovery.

As a third alternative, the reduction may be carried to the azo-benzene stage or somewhat further, without the use of any solvent or diluent whatever, other than the water introduced with the caustic solution used to activate the zinc; this water being less than 10% of the weight of the nitro-body. By the azo-benzene stage it is intended to refer to that portion of the reaction where the amount of the azo-benzene present is near the maximum; or where the melting point of the mixture begins to rapidly approach 115° C. After this stage is reached as the reduction continues, the freezing point of the charge rapidly rises, and it is therefore necessary to introduce some diluent with which the well agitated mass may be mixed to avoid its solidifying (at the reduction temperature desired), into a rigid cake and thus stopping the reduction. It has been customary, therefore, in this method, to add to the well agitated reduction mass, when its melting point begins to rise rapidly, an amount of hot water from once to twice the weight of the nitro-toluene charged. Thereafter the reduction has been completed by further addition of zinc and sodium hydroxide, yielding pellets of hydrazo-toluene together with zinc sludge. These pellets have the form of irregular granules averaging from 1 to 3 mm. in diameter.

When the inversion to benzidines is made by treatment with acid (for example, hydrazo-toluene to toluidine), the reactions chiefly occurring are:—



It has been found that the hydrazo-benzene pellets, produced according to the prior art, due to their density, smooth surface, and form, are entirely unsuited for economical inversion to benzidines by treatment with acid, the reaction being extremely slow.

For this reason, in the past it has been found advantageous to invert the hydrazo-benzene by one of two general methods. According to the first the difficultly reactive pellets have been dissolved in a solvent and by the second they have been disintegrated preparatory to treatment with acid. Both methods are inherently expensive and involve losses by oxidation of the hydrazo-benzene. In the solvent method the pellets have been dissolved in some substance such as alcohol, solvent naphtha or benzene and agitated with aqueous acid of suitable strength. This method involves the expense of solvent recovery and yields comparatively large portions of di-tolylene. In the pellet disintegration method an attempt to decrease the oxidation losses of hydrazo-benzene in grinding has been made by utilizing apparatus which excludes air. This is an additional cause for expense. Whether disintegrated in the presence or absence of air the treatment of the hydrazo compound with acid has usually followed as quickly as possible to further decrease the loss by oxidation.

It is obvious, therefore, that the prior art methods illustrated above, all possess undesirable and disadvantageous characteristics.

This invention has for an object the preparation of hydrazo-benzenes in a new physical form and improved methods for producing such compounds. Other objects are to devise new processes for the preparation of benzidines and to devise processes which will increase the yield and quality of hydrazo-benzenes and benzidines. Other objects will appear hereinafter.

The above objects are accomplished by the present invention whereby the reduction of nitro-benzenes to hydrazo-benzenes is carried out in the presence of a protective colloid and whereby the resultant hydrazo-benzene is inverted to a benzidine in the presence of a mineral acid.

It was shown above that in the production of hydrazo-benzenes, the reduction of nitro-benzene to the azo-benzene stage or further may be carried out without the addition of any solvent or diluent. It has now been discovered that if, at this stage, a quantity of water be added sufficient to carry the reduction products in suspension and containing an amount of protective colloid sufficient to form an emulsion of the reduction products in the water, the reduction may then be completed by further additions of zinc and caustic with numerous advantages.

The invention will be readily understood from the consideration of the following examples.

Example I

One hundred (100) g. of o-nitro-toluene were placed in a four-necked flask provided with means for rapidly agitating the contents thereof, a thermometer, a condenser and an inlet for zinc and sodium hydroxide. This flask was surrounded by a hot water bath. Small increments of zinc dust and of dilute aqueous sodium hydroxide were then fed into the agitated charge, which was maintained at 100 to 115° C. Upon reaching the azo-toluene stage, as judged by the amount of zinc added and by the color of the mass, 200 g. of a 0.2% aqueous soap solution at 100° C. were rapidly added and the reduction continued by the

addition of more zinc until the reduction mass was a light gray color, showing that the hydrazo stage had been reached.

The hydrazo-benzenes produced by the process set out above may be substantially freed from zinc-hydroxide by treatment with sulfuric acid. This will be clear from the following explanation. The slurry resulting from the above process was treated at ordinary temperatures with a 20% solution of sulfuric acid in an amount equal to 125% of the molecular quantity required to change all the zinc present to zinc sulfate. The mixture was agitated for 20 minutes and the hydrazo-toluene filtered off and washed with water.

The hydrazo-benzene produced as above set out may be treated directly with a mineral acid of suitable strength to invert it to the corresponding benzidine. This process will be readily understood from the following example.

Example II

Into a vessel provided with an agitator and cooling coils was charged 10% hydrochloric acid by weight, in about 100% excess of that theoretically required for the inversion. This acid was cooled to 0° C., and into it was shovelled, gradually with good agitation the moist, highly dispersed hydrazo-toluene, the temperature being kept under 10° C. until inversion was complete, as shown by chemical tests, after which the charge was heated to 70° C. and sufficient water added to dissolve the tolidine-hydrochloride. After this point the tolidine was freed from the tolidine by precipitation of tolidine sulfate and filtration. The base was then formed with sodium carbonate in the customary and well known way.

The protective colloid preferred is usually some water soluble salt of a fatty acid commonly termed a soap. Other protective colloids may be used however for example, a member or members of the group exemplified by Turkey red oil, glue, casein and the water soluble fraction of sludge acids (such as result from the treatment of petroleum oils or fractions thereof with sulfuric acid). The strength of the water solution of the protective colloid may vary but the solution need not ordinarily contain more than 5% of the colloid.

In the separation of the zinc from the hydrazo-benzenes the reactions may be carried out at ordinary or reduced temperatures. The preferred strength of sulfuric acid is from 10 to 20% although stronger or weaker acid may be used if desirable. The length of treatment with the sulfuric acid may be varied as desired although usually 20-30 minutes suffices for solution of the zinc. The minimum amount of sulfuric acid is that molecularly necessary to change the zinc present to zinc sulfate, but ordinarily an excess of acid is used. The excess should be as small as possible due to its effect on the hydrazo body and under usual operating conditions 25-50% excess is sufficient.

The quantity and identity of the mineral acid used for the inversion may vary, but it is preferred to use hydrochloric acid in concentrations of from 5 to 20% by weight. The use of nitric or other oxidizing acid is not permissible. It is to be understood that other concentrations and other mineral acids may be used. Preferably the temperatures used for inversion are below 10° C.

While this invention is not limited to any

specific nitro-benzene certain nitro bodies concerning which this invention has particular importance are: nitro-benzene, nitro-toluene, nitro-anisol, and their homologues.

The invention herein disclosed has numerous advantages among which are convenience of operation and substantially quantitative yields of benzidines.

The hydrazo-benzene produced by this process is in the form of extremely fine particles readily separable by filtration and capable of being inverted by an aqueous acid with great speed and with improved yields. This product may moreover be handled commercially with great freedom of oxidation probably due to the protecting action of the thin coat of colloid which adheres to the particles.

This invention avoids the necessity of disintegration of the solid hydrazo-benzenes and the recovery of solvents from the various stages of the reaction.

While certain theories have been set out to aid in understanding the invention it is not desired to limit it thereby.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. The process comprising adding to about 100 parts of ortho-nitro-toluene, small increments of zinc and a dilute solution of alkali-metal hydroxide while maintaining the temperature at about 100° C. to about 115° C., until the nitro-toluene has been reduced to the azo-toluene stage, adding about 200 parts of an aqueous approximately 2% soap solution which has a temperature of about 100° C., continuing the addition of zinc and alkali-metal hydroxide until the charge has been reduced to the hydrazo-toluene stage, washing the resultant product with about 10-20% sulfuric acid for from 20-30 minutes at not greater than ordinary temperatures, thereafter adding the said product in small increments to an approximately 10% hydrochloric acid solution held at about 0° C., the said hydrochloric acid being in an amount about twice that theoretically necessary to convert the hydrazo-toluene compound to tolidine, maintaining the temperature below about 10° C., until the inversion to tolidine is substantially complete and separating the tolidine.

2. The process comprising adding to about 100 parts of a nitro-benzene, small increments of zinc and a dilute solution of alkali-metal hydroxide while maintaining the temperature at about 100° C. to about 115° C., until the nitro-benzene has been reduced to the azo-benzene stage adding about 200 parts of an aqueous approximately 2% soap solution which has a temperature of about 100° C., continuing the addition of zinc and alkali-metal hydroxide until the charge has been reduced to the hydrazo-benzene stage, washing the resultant product with about 10-20% sulfuric acid for from 20-30 minutes at not greater than ordinary temperatures, thereafter adding the said product in small increments to an approximately 10% hydrochloric acid solution held at about 0° C., the said hydrochloric acid being in an amount about 200% of that theoretically necessary to convert the hydrazo-benzene compound to a benzidine, maintaining the temperature below about 10° C., until the inversion to the benzidine is sub-

stantially complete and separating the benzidine compound.

3. Hydrazo toluene in the form of fine particles having a coating of soap thereon and characterized by great freedom from oxidation.

4. Hydrazo-benzenes in the form of fine particles and having a coating of a protective colloid thereon.

5. Hydrazo-benzenes in the form of fine particles and having a coating of soap thereon.

6. In the process of inverting hydrazo-benzenes the steps of finely dividing the hydrazo-benzene and coating the surface of the particles with a protective colloid.

7. The process of producing hydrazo-toluene which comprises treating ortho-nitro-toluene with sufficient zinc and dilute alkali to convert it to the azo-toluene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction to hydrazo-toluene, and separating the hydrazo-toluene.

8. The process of producing hydrazo-benzenes which comprises treating nitro-benzenes with sufficient zinc and dilute alkali to convert them to the azo-benzene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction to hydrazo-benzenes, and separating the hydrazo-benzenes.

9. The hydrazo toluene body in the form of particles having a protective colloid on the surface thereof which is substantially identical with that resulting from the process of producing hydrazo-toluene which comprises treating ortho-nitro-toluene with sufficient zinc and dilute alkali to convert it to the azo-toluene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction to hydrazo-toluene, and separating the hydrazo-toluene body.

10. The hydrazo benzene body in the form of particles having a protective colloid on the surface thereof which is substantially identical with that resulting from the process of producing hydrazo-benzenes which comprises treating nitro-benzenes with sufficient zinc and dilute alkali to convert said nitro-benzene to the azo-benzene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction to hydrazo-benzenes, and separating the hydrazo-benzene body.

11. The process of obtaining high yields of hydrazo-benzenes from nitro-benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-benzene stage, adding a protective colloid in water and continuing the addition of zinc and hydroxide until a hydrazo-benzene is produced and then separating it.

12. The process of obtaining high yields of hydrazo-benzenes from nitro benzenes comprising treating a nitrobenzene with increments of zinc and dilute alkali metal hydroxide to reduce it to the azo-benzene stage, and adding water containing water soluble soap.

13. The process of obtaining high yields of hydrazo-benzenes from nitro benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-benzene stage, adding a soap solu-

tion and continuing the addition of zinc and hydroxide until a hydrazo-benzene is produced and then separating it.

14. The process of obtaining high yields of hydrazo-benzenes from nitro benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-benzene stage, and adding a soap solution of concentration less than 5% and continuing the treatment with zinc and hydroxide to form the hydrazo-benzene.

15. The process of obtaining high yields of hydrazo-benzenes from nitro benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-benzene stage, adding a dilute soap solution in an amount sufficient to cause the hydrazo benzene to be formed in small particles and continuing the treatment with zinc and hydroxide to form the hydrazo-benzene.

16. The product which is substantially identical with that resulting from the process of obtaining high yields of hydrazo-benzenes from nitro-benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-benzene stage, adding a dilute soap solution in an amount sufficient to cause the hydrazo-benzene to be formed in small particles.

17. The method of producing improved yields of finely divided, oxidation resistant hydrazo-toluene comprising treating nitro-toluene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-toluene stage, adding a dilute soap solution in an amount sufficient to cause the hydrazo-toluene to be formed in small particles and continuing the addition of zinc and hydroxide until a hydrazo-toluene is produced and then separating it.

18. The method of producing improved yields of finely divided, oxidation resistant hydrazo-benzenes comprising treating nitro-toluene with increments of zinc and dilute alkali-metal hydroxide to reduce it to the azo-toluene stage, adding a dilute soap solution in an amount sufficient to cause the hydrazo-toluene to be formed in small particles and continuing the addition of zinc and hydroxide until a hydrazo-toluene is produced and then separating it.

19. Hydrazo-benzenes in the form of fine particles having a coating of a protective colloid thereon and characterized by great freedom from oxidation.

20. The process of producing hydrazo-toluene which comprises treating ortho-nitro-toluene with sufficient zinc and dilute alkali to convert it to the azo-toluene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction with zinc and dilute alkali to hydrazo-toluene, and separating the hydrazo-toluene.

21. The process of producing hydrazo-benzenes which comprises treating a nitro-benzene with sufficient zinc and dilute alkali to convert it to the azo-benzene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction with zinc and dilute alkali to hydrazo-benzenes, and separating the hydrazo-benzenes.

22. The hydrazo-toluene body in the form of particles having a protective colloid on the surface thereof which is substantially identical with that resulting from the process of producing hydrazo-toluene which comprises treating ortho-nitro-toluene with sufficient zinc and dilute alkali to convert it to the azo-toluene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction with zinc and dilute alkali to hydrazo-toluene, and separating the hydrazo-toluene body.

23. The hydrazo-benzene body in the form of particles having a protective colloid on the surface thereof which is substantially identical with that resulting from the process of producing hydrazo-benzenes which comprises treating nitro-benzenes with sufficient zinc and dilute alkali to convert said nitro-benzene to the azo-benzene stage while maintaining the temperature at about 100° C. to about 115° C., thereafter adding an aqueous solution of a protective colloid, continuing the reduction with zinc and dilute alkali to hydrazo-benzenes, and separating the hydrazo-benzene body.

24. Hydrazo-benzenes in the form of fine particles having thereon a coating of a protective colloid from the group consisting of soap, Turkey-red oil, water soluble sludge acid fraction, glue and casein.

25. In the process of inverting hydrazo-benzenes by treatment with non-oxidizing mineral acids, the steps comprising finely dividing the hydrazo-benzene and coating the surface of the particles with Turkey red oil.

26. The process of obtaining high yields of hydrazo-benzenes from nitro benzenes comprising treating a nitro-benzene with increments of zinc and dilute alkali metal hydroxide to reduce it to the azo-benzene stage, adding water containing a member of the group consisting of soap, Turkey red oil, glue, water soluble sludge acid fraction and casein.

27. In the process of inverting hydrazo-benzenes by treatment with non-oxidizing mineral acids, the steps comprising finely dividing the hydrazo-benzene and coating the surface of the particles with water soluble sludge acid fraction.

WILLIAM S. CALCOTT.

FREDERICK B. DOWNING.

NORMAN C. SOMERS.