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REDUCTION OF ARYL NITRO-BODIES

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This invention relates to the manufacture of aryl azoxy, azo or hydrazobodies from aryl nitrobodies by the reduction of the latter with iron borings and caustic soda. In its more special aspects, this invention relates to the manufacture of hydrazobenzene, ortho-hydrazotoluene, and ortho-hydrazoanisole.

It is an object of this invention to provide a new and improved method of producing azoxy-, azo-, and hydrazobodies from aryl nitrobodies by the reduction of the latter with iron borings and caustic soda.

The reduction of aryl nitrobodies to produce azoxy, azo, or hydrazo bodies is an important commercial process and has been developed into numerous procedures and improvements. The reduction can be effected by the aid of zinc and caustic alkali, but most commercial processes prefer iron filings in view of its lower cost as compared to zinc, and in view of the low cost of the resulting organic compounds which necessitates the practice of extreme economy in their manufacture.

The use of iron and caustic alkali, however, introduces into the process several side problems, chief among which is the tendency of the iron borings to become coated with iron oxide formed during the reaction, which thereafter prevents the iron from coming in contact with and reducing further quantities of the nitrobody. Accordingly the art resorted to various methods to overcome this difficulty.

According to most processes the iron borings or filings would be subjected to special activation procedures, such as boiling in concentrated caustic soda prior to use. In some processes, the procedure was further modified by introducing the iron into the reaction mass in several steps whereby to stimulate the reaction after its initial spurts would be subsided. Practically all procedures required the use of concentrated caustic soda in large quantities, and the use of an organic solvent, such as toluene, xylene, or chlorobenzene. These features in turn, necessitated supplemental recovery steps, to recover the solvent and the excess alkali. The use of a solvent carries further with it the danger of over-reduction to the aniline stage, and requires therefore special precautions and means of control.

Now, according to our invention the above difficulties are neatly overcome and the reaction is made to proceed in the absence of a solvent and by the use of dilute caustic in moderate quantity, saving the necessity of alkali recovery. According to our invention, the nitroaryl compound for instance nitrobenzene, caustic soda, iron filings, and water are charged into a heated ball mill, and the charge is ground at an elevated temperature until the reduction of the nitrobenzene has been carried to the desired degree of completion. The end point is judged in the usual manner, for instance by taking samples which in the case of hydrazobenzene should be free of the red coloration of the azo body when extracted with xylene. The reduction products are then extracted from the iron sludge with xylene, and the product is recovered from the solvent, or treated further in solution, as desired.

The following example will serve to illustrate our preferred mode of operation, it being understood that it is not intended to limit this invention to any particular procedure. Parts mentioned are by weight.

380 parts of nitrobenzene, 360 parts of iron powder and 650 parts of aqueous caustic (35%) are charged into a ball mill containing steel balls and provided with means for heating and equipped with a reflux condenser. The mill is then rotated slowly for about 15 hours while maintaining its contents at a temperature 115 to 120° C. Samples are taken from time to time to determine the degree of reduction. To produce a hydrazo compound, a xylene extract of the test sample should be free of red color.

When the reduction to hydrazobenzene is complete the temperature of the mill is reduced to 100 to 105° C., 680 parts of xylene are added, and the mill rotated for 10 minutes. The xylene extract is decanted into a wooden tub provided with cooling coils, and the iron sludge in the mill is extracted with three additional portions of xylene of 340 parts each.

1400 parts of water are then added to the mill, the latter is rotated for 10 minutes, and the residual xylene is recovered by passing steam through the mass in the mill, and collecting the distillate.

On the inversion of the xylene extract by known methods (for instance, treatment with HCl), benzidine is obtained in very good yield.

Inasmuch as the hydrazobenzene is generally prepared for the sole purpose of producing benzidine, recovery of the hydrazobenzene as such is superfluous. However, where such a course is particularly desirable, it may be effected in the usual manner, for instance by steam-distilling the xylene extract.

In a similar manner other nitroaryl compounds may be reduced. This invention is particularly advantageous in the reduction of nitroaryl compounds of the benzene series, for instance nitrobenzene, o-nitrotoluene and o-nitroanisole. By the use of the proper quantity of iron, the reduction may be carried out to give the azoxy, the azo, or the hydrazo compound as desired.

The strength of the caustic soda employed may be varied within wide limits, for instance from 20 to 50%. It will be noted that most processes of the art are limited to the use of caustic soda stronger than 50%. The use of dilute caustic

has the advantages of initial low cost and that no recovery is necessary.

It is clear that although the apparatus is designated as a ball mill, other similar equipment, such as rod mills, are equally well adaptable to this operation.

The speed of rotation of the mill should be such that the grinding media do not cling to the sides due to the centrifugal force developed. This speed is best determined by experiment for each piece of equipment. The speed of rotation in turn governs the rate of reaction.

The quantity of iron may vary from 10 to 30% excess over theory (for the production of Fe_2O_3). While the quantity of caustic soda employed may vary within wide limits, excessive quantities should be avoided to prevent forming an emulsion with the xylene during the extraction step. On the other hand a sufficient quantity of caustic soda should be employed to give a fluid, workable mass. In actual practice, quantities of caustic soda from about 0.5 to 0.7 part (on NaOH basis) per part of nitrobenzene, have been found satisfactory.

The temperature of the reduction may be from 60° to 120° C. The lower temperatures are more desirable for the reduction of the homologues of nitrobenzene since it is well known that in such cases there is a greater tendency towards the formation of the corresponding substituted aniline. The temperature should preferably not be raised above 120° C. or else the water contained in the reaction mass will distill off resulting in thickening of the sludge.

It is an advantage of our process that the addition of the extracting medium can be deferred until the reduction is complete, as otherwise there is a tendency for excessive amounts of aniline to be formed (Amiantow et al.: Anilino. Prom. 2, 24 (1932)). It is clear that other organic solvents such as toluene and various solvent naphthas can be used in place of xylene. It is also clear that we are not limited in regard to the quantity of extracting medium used or the number of extracts made. The extraction is best made at 100° C. though it may be made at 60 to 110° C. The optimum time of an extraction is best determined for the particular piece of apparatus used; too short a time will result in inefficient extraction, while too long an extraction period will cause some of the hydrazobenzene to be reduced to aniline.

Many other variations and modifications will be apparent to those skilled in the art, without departing from the spirit of this invention.

As for the theory of this invention, it is our belief that the advantageous results are due to the attrition of the iron particles in the ball mill, constantly exposing to the reaction liquors fresh, active surfaces. However, it will be clear that our invention is not limited to any particular theory.

The present invention has the advantage of using a small excess of iron filings or borings and smaller amounts of weaker caustic soda. The excess of iron is about 10 to 30% over theory, as compared to 100 to 300% excesses used in most of the processes of the prior art.

The operation is much more simple than those which require the stepwise addition of the reagents. In the present invention the reagents are all added at once, and very little attention is required of the operator until the reduction is substantially complete.

The yield of reduction products obtained is better than those previously claimed.

In our process also the amount of caustic soda required is much less and is less concentrated than in some of the processes of the art (see for instance, German Patent No. 138,496); consequently, we can dispense with the step of caustic recovery.

The method of extracting the reduction products from the iron sludge is very efficient since excellent agitation and contact can be obtained by rotating the solvent with sludge and grinding media in the ball mill.

We claim:

1. In the process of reducing nitroaryl bodies by the aid of comminuted iron and aqueous alkali, the improvement which comprises subjecting the reaction mass to continuous attrition during the course of the reaction by working the mass in a ball mill.

2. The process of preparing a compound of the group consisting of azoxyaryl, azoaryl, and hydrazoaryl compounds of the benzene series, which comprises reacting with comminuted iron and aqueous alkali upon a nitroaryl compound of the benzene series while subjecting the entire mass to attrition in a mill, the aqueous alkali being of a strength less than 50%.

3. A process as in claim 2, the reaction being carried out in the absence of an organic solvent.

4. The process of preparing a compound of the group consisting of azoxyaryl, azoaryl, and hydrazoaryl compounds of the benzene series, which comprises reacting with comminuted iron and aqueous alkali of a strength less than 50% upon a nitroaryl compound of the benzene series in the absence of an organic solvent, while subjecting the entire mass to attrition in a ball mill, and then extracting the sludge thus formed with an organic solvent, to recover the organic reaction product.

5. The process of preparing a hydrazo compound of the benzene series, which comprises subjecting a nitro compound of the benzene series to the action of comminuted iron and aqueous caustic soda of 20 to 50% strength while milling the mass in a ball mill, extracting the resulting mass with an organic solvent, separating the bulk of the solvent by decantation, and then steaming the residual mass in the mill to extract therefrom the residual quantities of solvent.

6. A process as in claim 5, wherein the organic solvent is xylene.

7. The process of producing hydrazo benzene which comprises heating nitrobenzene with comminuted iron and aqueous sodium hydroxide at a temperature between 60° to 120° C., while subjecting the mass to attrition in a ball mill, the amount of iron being about 10 to 30% in excess of the theoretical quantity required for the given reduction, and the aqueous sodium hydroxide being of a strength between 20 and 50% NaOH by weight, and continuing the heating and attrition until a test sample shows no further the presence of azobenzene.

8. A process as in claim 7, being followed by the steps of extracting the reaction mass with xylene, to separate the organic reduction products from the inorganic ingredients of the mass.

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