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## METHOD OF PRODUCING MONONITRODIPHENYLS

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Our invention relates to a method for producing mono nitrated diphenyls, and particularly 4- and 2- nitrodiphenyls, by nitrating diphenyl without the use of a solvent by the use of a mixture of nitric acid and sulfuric acid.

The object of our invention is to obtain substantially complete nitration of diphenyl, as 4- and 2- nitrodiphenyls. A further object is the use of mixed nitrating acids, in a manner whereby it is possible to obtain substantially complete nitration of the diphenyl without the formation of an objectionable quantity of dinitrodiphenyls.

In previous efforts at making nitrodiphenyls, according to such references as are to be found in the literature, efforts were directed principally toward producing dinitrodiphenyl and it was proposed to use nitric acid alone for this purpose. In carrying out the process, the rate of nitration was very slow, and moreover presented serious difficulties as a commercial operation. It was also proposed to subject the diphenyl directly to a mixture of concentrated nitric and sulfuric acids, but the difficulties with such a procedure are that a very large quantity of diphenyl remains as such and besides both mononitrodiphenyls and dinitrodiphenyls are formed in relatively large proportions. The presence of appreciable quantities of dinitrodiphenyls with mononitrodiphenyls is very objectionable because of the difficulty of separation of the dinitrodiphenyls from the mono nitro isomers. The most satisfactory method of mononitration heretofore proposed consisted, in the use of a solvent in nitrating, then separating the solvent.

We have discovered a method of carrying out the nitration, whereby mononitrodiphenyls may be produced without producing objectionable quantities of dinitrodiphenyls. In the preferred method for carrying out our invention we suspend powdered diphenyl in a mixture comprising sulfuric acid, nitric acid and water and then adding a mixture of concentrated nitric and sulfuric acids. The size of the diphenyl particles is not of special importance, though we prefer that the diphenyl pass a 20-mesh screen. The concentration of this acid mixture should be such that the diphenyl may remain in contact for a long period without appreciable nitration taking place. Spent or weak acid is suitable for use in suspending the diphenyl. By spent or weak acids, we mean acids which have been drained from the previous nitrations, or acids made up of proportions hereinafter stated.

We have found that while nitration may be carried out through a range of temperatures, in our preferred method we maintain the temperature of the nitrating mixture at from 35° to 40° C., during which time mixed nitrating acid is added. If higher temperatures are maintained, it is advisable to alter the concentration of the mixed acids used. The formation of dinitrodiphenyls seems to increase at higher temperatures of the nitrating mixture; and since the separation of dinitrodiphenyls from mononitrodiphenyls is very difficult, it is important to prevent the formation of the dinitrodiphenyls. Cooling coils or their equivalent are necessary to control the temperature of the nitrating mixture.

The reaction proceeds very smoothly and quietly as the mixed acid is added to the nitrator. By nitrating in the manner described with mixed acids, we find the reaction is not nearly so sensitive as when other methods are employed, for instance, when diphenyl is suspended in concentrated nitric acid, and sulfuric acid subsequently added thereto. Moreover, by our method there is less dinitrodiphenyl formed.

Another feature of commercial importance is that by our process we are able to use ordinary iron equipment for the construction of the nitrator, and are not confronted with

any serious corrosion difficulties from the acid handled. Control of the reaction in our process is by variation in the rate of addition of the mixed acid, and by varying the flow of the cooling water in the nitrator cooling coils.

Illustrative of the proportions of materials used and procedure, we give the following: Assuming 100 grams of diphenyl is suspended in spent acid or a mixture comprising

| | Per cent |
|---|---|
| Sulfuric acid | 45 |
| Nitric acid | 24 |
| Water | 30 |

Substantially no nitration occurs while the diphenyl is in the weak acid mixture. This mixture serves as a suspension medium and provides sufficient volume to permit even temperature control when nitration begins. Nitration is brought about by the addition of nitrating acid in the manner about to be described.

The suspension is constantly agitated and kept at a temperature of from 35° to 40° C., and the nitrating acid is added to the suspension. The mixed nitrating acid used per 100 grams of diphenyl comprises

| | Cubic centimeters |
|---|---|
| Sulfuric acid 66° Bé | 46 |
| Nitric acid 1.42 sp. gr. | 83.5 |

The rate of addition is regulated according to the heat generated and the ability of the cooling coils to remove the heat. Agitation is continued for a short time after all of the mixed acid is added. When nitration is carried out by this method, the resultant product is approximately 97% mononitrodiphenyls, and 3% dinitrodiphenyls.

After the nitrating acid mixture is all added and the mixture is agitated thereafter until the reaction is substantially complete and substantially no diphenyl remains in the mixture, the spent acid is drained off and separated from the mononitrodiphenyls, following which they are washed with water, which is then drained off. Water which contains a small quantity of alkali is then run into the nitrator and the mixture agitated to neutralize the remaining acid. This alkaline solution is drained off and washings with water are repeated in a similar manner, until all the salts resulting from the addition of the alkali are washed out of the nitrodiphenyls. When this washings have been completed, the water is carefully separated and the nitrodiphenyls are then heated to remove any remaining water which could not be separated otherwise.

After removing all the water, the mononitrodiphenyls are ready for separation of the isomers, and purification. We have found that separation of the isomers and purification can be accomplished by distillation and fractionation with the utmost efficiency. Separation may also be accomplished by fractional crystallization.

As an alternative method of carrying out our process, we may suspend 100 grams of diphenyl in a mixture comprised of 100 c. c. of water and 41 c. c. of nitric acid at 1.42 sp. gr. Substantially no nitration of the diphenyl occurs in this suspension, due to the presence of so large a proportion of water therein. We then add 118 c. c. of sulphuric acid in a manner already described for the mixed nitrating acids, meanwhile thoroughly agitating the suspension, and maintain the temperature of the mixture from between 70° to 75° C. When the sulphuric acid is added, it serves to combine with the water in the mixture and nitration of the diphenyl proceeds. The process of separation and washing is the same as that previously described.

While we have described our invention in but two forms, it will be obvious to those skilled in the art that it is not so limited but is susceptible of various changes and modifications, without departing from the spirit thereof, and we desire, therefore, that only such limitations shall be placed thereupon as are imposed by the prior art or as are specifically set forth in the appended claims.

What we claim is:

1. The process of producing mononitrodiphenyls which consists in providing a suspension of diphenyl in an acid solution containing nitric acid and of a strength below that at which substantial nitration of the diphenyl occurs, and adding to the suspension concentrated sulphuric acid to bring about a reaction between the nitric acid and the diphenyl.

2. The process of producing mononitrodiphenyls which consists in providing a suspension of diphenyl in an acid solution containing nitric acid and of a strength below that at which substantial nitration of the diphenyl occurs, adding to the suspension concentrated sulphuric acid to bring about a reaction between the nitric acid and the diphenyl, and maintaining the temperature during nitration below 75° C.

3. The process of producing mononitrodiphenyls which consists in providing a suspension of diphenyl in an acid solution containing nitric acid and of a strength below that at which substantial nitration of the diphenyl occurs, adding to the suspension concentrated sulphuric acid to bring about a reaction between the nitric acid and the diphenyl, maintaining the temperature during nitration between 70° and 75° C., and thoroughly agitating the mixture during the addition of the acid.

4. The process of producing mononitrodiphenyl which consists in providing a suspension of diphenyl in a solution of mixed nitric and sulphuric acids of a strength approximating that of spent acid from a previous nitration and below that at which substan-

tial nitration of the diphenyl occurs, agitating the mixture, and adding thereto a mixture of concentrated nitric and sulphuric acids, and maintaining the temperature between 35° and 40° C. during nitration.

5. The process of producing mononitrodiphenyl which consists in providing a suspension of diphenyl in a solution of mixed nitric and sulphuric acids of a strength approximating that of spent acid from a previous nitration and below that at which substantial nitration of the diphenyl occurs, agitating the mixture, adding thereto a nitrating mixture of concentrated nitric and sulphuric acids, and maintaining the temperature during nitration below that at which substantial quantities of dinitrodiphenyl is formed.

6. The process of producing mononitrodiphenyl which consists in providing a suspension of diphenyl in a solution of nitric and sulphuric acids comprising approximately 45% to sulphuric acid, 24% nitric acid and 30% water, agitating the mixture, adding thereto a mixture of concentrated nitric and sulphuric acids, maintaining the temperature during nitration below 40° C., and separating the mononitrodiphenyls from the mixture.

7. The process of producing mononitrodiphenyls which consists in forming a suspension of diphenyl in a solution of nitric and sulphuric acids of a concentration producing substantially no nitration, and adding thereto a mixture of concentrated nitric and sulphuric acids.

8. The process of producing mononitrodiphenyls which consists in forming a suspension of diphenyl in a solution of nitric and sulphuric acids of a concentration producing substantially no nitration, adding thereto a mixture of concentrated nitric and sulphuric acids, and controlling the temperature during nitration so that it does not exceed 40° C.

9. The herein described process of making mononitrodiphenyls substantially free from dinitrodiphenyl, which consists in suspending diphenyl in a spent solution of nitric and sulphuric acids, adding a mixed concentrated nitrating acid thereto, agitating said mixture during said addition, cooling said mixture to prevent overheating, separating spent acid following nitration, washing nitrated product to remove acid, and drying nitrated product to remove water therefrom.

10. The herein described process of making mononitrodiphenyls substantially free from dinitrodiphenyl, which consists in suspending powdered diphenyl in a mixture of nitric and sulphuric acids of such a concentration that substantially no nitration occurs, agitating said diphenyl acid mixture, adding a mixture of concentrated nitric and sulphuric acids to form mononitro compounds of diphenyl while exhausting said acids to approximately the concentration of the acid in which said diphenyl was suspended, maintaining a temperature of approximately 40° C., in the mixture during nitration, draining off spent acids following nitration, washing said mononitrodiphenyls with water containing a small quantity of an alkali, then washing said alkali from the mononitrodiphenyls and heating said mononitrodiphenyls to remove any water adhering thereto.

11. The process of producing mononitrodiphenyl which consists in suspending powdered diphenyl in a weak solution of nitric acid in water, and adding concentrated sulphuric acid to the solution.

12. The process of producing mononitrodiphenyl which consists in suspending powdered diphenyl in a weak solution of nitric acid in water, adding concentrated sulphuric acid to the solution, agitating the solution while adding the sulphuric acid, and maintaining the temperature below 75° C.

In witness whereof we affix our signatures.

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