Patented Aug. 24, 1954

2,687,431

UNITED STATES PATENT OFFICE

2,687,431

PROCESS OF PREPARING NITRO PHENYLENEDIAMINES

Franz Marschall, Easton, Pa., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

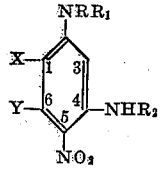
No Drawing. Application December 20, 1950, Serial No. 201,873

2 Claims. (Cl. 260—509)

1

This invention relates to an improved process for the preparation of certain nitro-phenylenediamines.

The process is more specifically concerned with the preparation of compounds of the following structural formula:

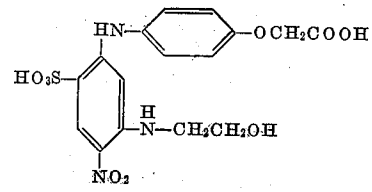


wherein R is hydrogen or alkyl, i. e., methyl, ethyl, propyl, butyl, amyl or the like and R_1 is an aliphatic radical such as alkyl as above, carboxy alkyl, such as carboxy methyl, carboxy ethyl, and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl, and the like, aryl, such as phenyl, toluyl and the like; carboxy alkyl aryl, such as carboxy methyl phenyl, carboxy ethyl phenyl, and the like, carboxy alkoxy aryl, such as carboxy methoxy phenyl, carboxy ethoxyphenyl; hydroxy alkyl aryl, such as hydroxy methyl phenyl, hydroxy ethyl phenyl, and the like; and hydroxy alkoxy aryl, such as hydroxy methoxy phenyl, hydroxy ethoxy phenyl and the like, R_2 is an alkyl group substituted by a hydrophilic group such as carboxy alkyl, such as carboxy methyl, carboxy ethyl and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl, and the like; sulfo alkyl such as, sulfomethyl, sulfoethyl, sulfopropyl, sulfobutyl and the like and X and Y are hydrogen, alkyl as above, sulfo or carboxy, or together represent the atoms necessary to complete a six-membered isocyclic ring system such as benzo and the like. It is to be observed that in the above compounds the substituent groups represented by R_1 and R_2 have a carbon atom thereof directly linked to the amino nitrogen atom. In other words, such compounds are true amines. Preferably the compounds which are utilized are the N-substituted 4,6-diamino-metanilic acids, in which case Y is hydrogen and X is sulfo.

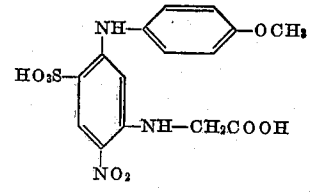
Examples of compounds illustrative of those within the general formula are the following:

2

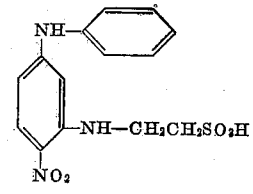
1.



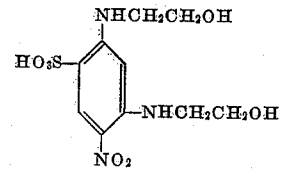
2.



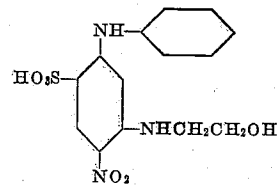
3.



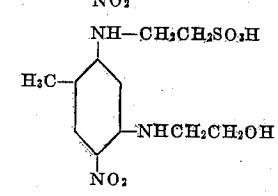
4.



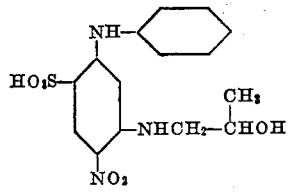
5.



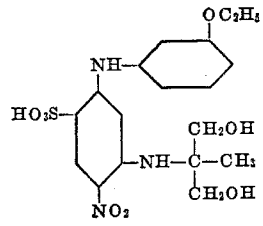
6.



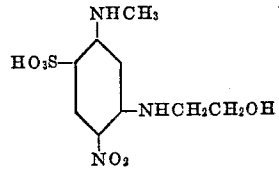
7.



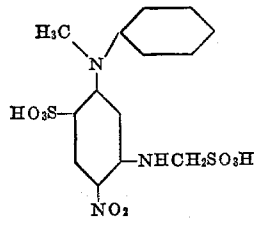
8.



9.



10.

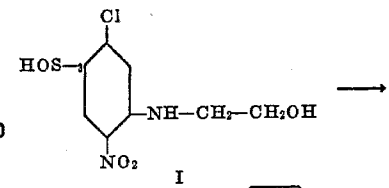


The aforementioned compounds are prepared by reacting in the proper sequence the sodium or potassium salt of 2,4-dichloro-5-nitro benzene sulfonic acid with the amines desired to be introduced into the 4-position and subsequently reacting that product with the amine desired to be introduced into the 2-position. The improved process is particularly concerned with the reaction of the 2-chloro compound with the desired amine in the presence of a weakly alkaline catalyst (i. e., having a pH below 12 in 1% concentrations) selected from the group consisting of oxides, carbonates and carboxylic acid salts of metals of group 2 of the periodic table and alkali metal and alkaline earth metal salts of organic carboxylic acids. The metals include beryllium, magnesium, calcium, zinc, strontium, cadmium and barium. Examples of the compounds include zinc oxide, cadmium oxide, calcium carbonate, barium carbonate, calcium bicarbonate, barium bicarbonate, strontium carbonate, calcium citrate, strontium tartrate, sodium acetate, potassium tartrate, etc.

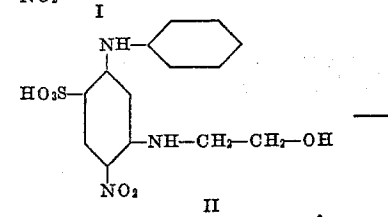
I have discovered that the yields are substantially increased when using the above described weakly alkaline compounds as compared with the use of stronger alkaline compounds such as sodium carbonate which is satisfactory in the reaction putting the amine in the 4-position.

The reaction temperatures may be varied quite widely. The reaction is preferably carried out in the range 140 to 160° C. Lower temperatures cause an increase in the time of reaction. At higher temperatures quality of the product deteriorates.

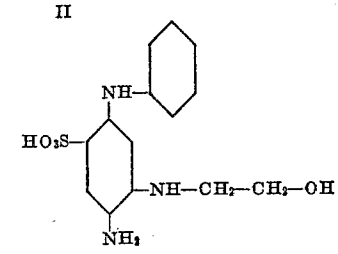
The compounds are useful in the preparation of new color developing substances such as illustrated in the following reaction:



I



II



III

The color developing substance III is described and claimed in co-pending application, Serial No. 101,913, filed June 28, 1949, by Robert C. Gunther and now U. S. Patent 2,570,116 dated October 2, 1951. The reduction of compound II to compound III may be accomplished by sodium hydrosulfite or the like and is not a part of the present invention.

The following example illustrates a preferred embodiment of the invention but substitutes and variations may be made within the scope of the claims.

Example

334.6 parts by weight 2-chloro-4-(2-hydroxyethylamino)-5-nitrobenzene potassium sulfonate are charged into an autoclave together with 30.4 parts of magnesium oxide, 111 parts of aniline and 1600 parts water. The autoclave is sealed and purged with nitrogen. The mixture is heated to about 150° C. over a period of 10–24 hours (pressure 60–80 lbs.). The excess aniline is then removed by steam distillation. After filtration the product is isolated as the potassium salt by salting out with potassium chloride in 97% yield. The free acid can also be isolated by evaporation of the acidified reaction mixture.

It will be understood that the process of the above example may be repeated using any of the other catalysts disclosed above and using amines other than aniline within the scope of the generic formula.

Additional examples of compounds which may be prepared by this process will be found in U. S. Patent 2,486,440.

I claim:

1. The process of producing an alkali metal salt of 2 - phenylamino - 4 - (2 - hydroxyethylamino) - 5-nitro benzene sulfonic acid which comprises heating in an autoclave to a temperature ranging from 140–160° C. an alkali metal salt of 2-chloro-4 - (2 - hydroxyethylamino) - 5 - nitro benzene sulfonic acid, aniline, water and magnesium oxide as the acid acceptor.

2. The process as defined in claim 1, wherein the alkali metal is potassium, and the temperature of heating it 150° C.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,836,295	Thiess et al.	Dec. 15, 1931
2,570,116	Gunther	Oct. 2, 1951

FOREIGN PATENTS

Number	Country	Date
285,877	Great Britain	Sept. 27, 1928
286,694	Great Britain	Oct. 11, 1928
134,097	Switzerland	July 30, 1929

OTHER REFERENCES

Joffe et al., Chemical Abstracts 31 668 (1937).