Patented Aug. 4, 1953

2,647,815

UNITED STATES PATENT OFFICE

2,647,815

ALKYL DIFORMYL PHENYLENEDIAMINES

Saul R. Buc and Samuel A. Glickman, Easton, Pa., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

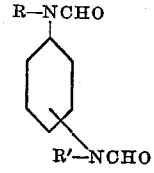
No Drawing. Application May 3, 1951, Serial No. 224,444

6 Claims. (Cl. 8—35)

1

This invention relates to a new group of compounds which are alkyl diformyl phenylenediamines and to a method for their preparation.

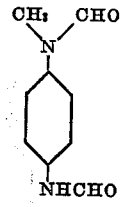
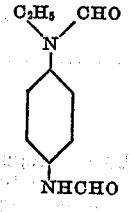
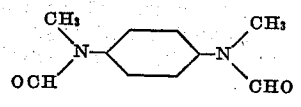
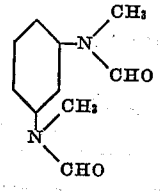
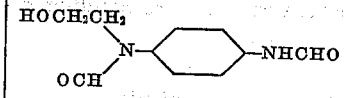
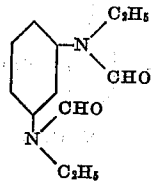
More particularly, it relates to compounds having the following general formula:

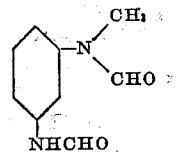
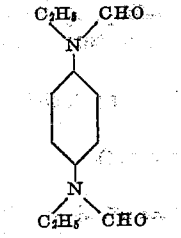
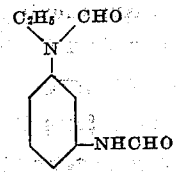
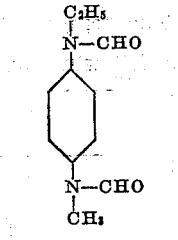
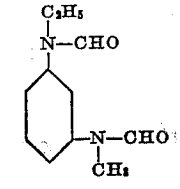


2

wherein R is selected from the group consisting of alkyl (methyl, ethyl, propyl, butyl) and hydroxy alkyl (hydroxy methyl, hydroxy ethyl, hydroxy propyl, hydroxy butyl), and wherein R' is selected from the group consisting of alkyl, hydroxy alkyl and hydrogen.

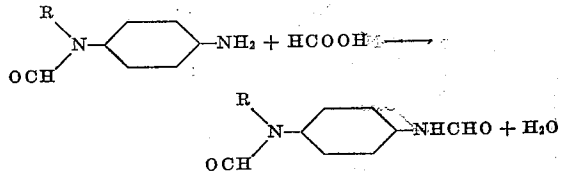
The compounds prepared are summarized in the following table:

Name	Formula	M. P. or Other Physical Property
N,N'-Diformyl-N-methyl-p-phenylenediamine.		138–141.
N,N'-Diformyl-N-ethyl-p-phenylenediamine.		79–81.
N,N'-p-Phenylenebis-N-methylformamide.		210–212.
N,N'-m-Phenylenebis-N-methylformamide.		148–150.
N,N'-Diformyl-N-2-hydroxyethyl-p-phenylenediamine.		oil.
N,N'-m-Phenylenebis-N-ethylformamide.		M. P.. 45–47. B. P .182–4/0.4 mm

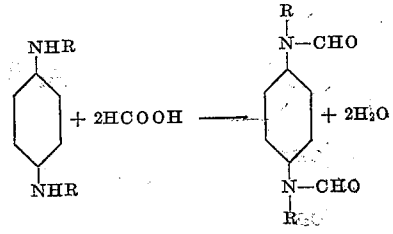
Name	Formula	M. P. or Other Physical Property
N,N'-Diformyl-N-methyl-m-phenylenediamine.		96–98.
N,N'-p-Phenylenebis-N-ethylformamide.		126–129.
N,N'-Diformyl-N-ethyl-m-phenylenediamine.		oil, not distillable.
N,N'-Diformyl, N-methyl N'-ethyl-p-phenylenediamine.		
N,N'-Diformyl, N-methyl N'-ethyl-m-phenylenediamine.		

Also, mixtures of the above, prepared either by mixing of the pure compounds or by synthesis from mixtures of intermediates. These compounds were prepared in two different ways:

(1) By formylation of the corresponding mono-formyl derivatives:



(2) By diformylation of the corresponding diamines:



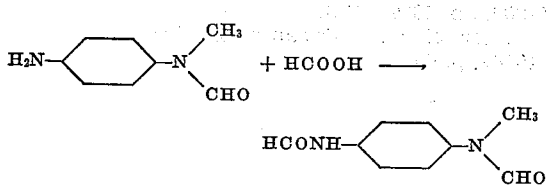
Formylation may be accomplished in either case by refluxing with formic acid alone or in the presence of an agent to remove the water formed azeotropically. Toluene, xylene or chlorobenzene are suitable agents. The latter is the preferred method.

The following examples illustrate preferred embodiments of the invention, but variations and substitutions may be made within the scope of the claims.

The new compounds are useful in solubilizing sulfuric esters of vat dyestuffs in aqueous mediums, particularly aqueous printing paste formulations. This property of the instant compounds is extremely valuable since one of the major problems one is faced with in vat dyeing is to produce a uniform, level, non-specky dyed product. To effect this it is necessary to have the dyestuff in as fine a state of sub-division as possible and preferably in solution. The new compounds of this invention enhance the solubility of the sulfuric acid esters of vat dyestuffs in aqueous mediums thereby leading to level, non-specky dyeings.

EXAMPLE 1

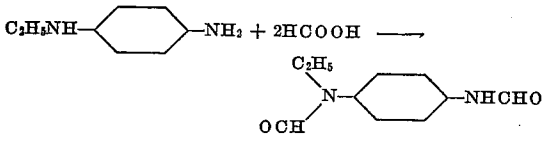
N,N'-diformyl-N-methyl-p-phenylenediamine



A crude sample of N-methyl, N-formyl-p-phenylenediamine, prepared by the catalytic reduction of 88 parts of the corresponding nitro-compound, was treated with 100 parts of 99% formic acid and refluxed three hours. The water and excess formic acid were removed in vacuo, and the product crystallized on scratching. M. P. 138–141° C.

EXAMPLE 2

N,N'-diformyl-N-ethyl-p-phenylenediamine



70.0 parts of p-ethyl nitroaniline is hydrogenated in 140 parts of 99% formic acid over a platinum catalyst. The catalyst is filtered and 500 parts toluene added to the mixture. Reflux through a fractionating column in such a manner that the toluene is continuously returned to the pot and the lower water formic acid layer is distilled. When the boiling point of toluene was reached the toluene was removed in vacuo and the residue crystallized. M. P. 79–81° C.

EXAMPLE 3

N,N'-dimethyl, N,N'-diformyl-m-phenylenediamine

A crude sample of N,N'-dimethyl-m-phenylenediamine, prepared by the Büchner reaction on 110 parts of resorcinol, was formylated with 200 parts, 90% formic acid and 500 parts toluene by the procedure described in Example 2. On removal of the solvents there was obtained 141 parts (73% yield based on resorcinol) of the desired product. M. P. 148–150° C.

EXAMPLE 4

N,N'-diethyl, N,N'-diformyl-p-phenylenediamine

A sample of N,N'-diethyl-p-phenylenediamine prepared by the Büchner reaction between hydroquinone and ethylamine was formylated as in Example 3. The product was isolated in the same way and melted at 126–129° C.

EXAMPLE 5

Mixture of (*a*) N,N'-dimethyl, N,N'-diformyl-p-phenylenediamine, (*b*) N,N'-diethyl, N,N'-diformyl-p-phenylenediamine and (*c*) N-methyl, N'-ethyl, N,N'-diformyl-p-phenylenediamine.

A mixture of N,N'-dimethyl-p-phenylenediamine, N,N'-diethyl-p-phenylenediamine and N-methyl, N'-ethyl-p-phenylenediamine containing methyl to ethyl groups in the ratio of one to three was formylated as in Example 3. The product melted at 96–150° C.

EXAMPLE 6

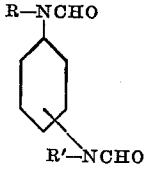
Identical with Example 5, but with methyl to ethyl groups in the ratio of one to nine. The product melted at 93–115° C.

EXAMPLE 7

Mixture of meta isomers prepared as in Example 5. Ratio of methyl to ethyl groups 9 to 1. M. P. of product 146–149.

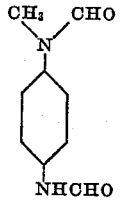
We claim:

1. A compound having the general formula:

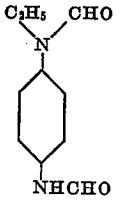


wherein the relative position of the two substituted amino groups is selected from the class consisting of m- and p-, R is selected from the group consisting of alkyl radicals of 1 to 4 carbon atoms and hydroxyalkyl radicals of 2 to 4 carbon atoms, and R' is selected from the group consisting of alkyl radicals of 1 to 4 carbon atoms and hydroxyalkyl radicals of 2 to 4 carbon atoms and hydrogen.

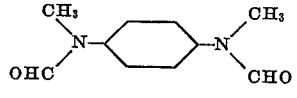
2. A compound having the formula:



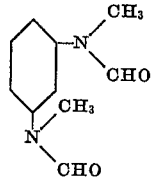
3. A compound having the formula:



4. A compound having the formula:



5. A compound having the formula:



6. A mixture of N,N'-dimethyl, N,N'-diformyl-p-phenylenediamine; N,N'-diethyl, N,N'-diformyl-p-phenylenediamine; and N-methyl, N'-ethyl, N,N'-diformyl-p-phenylenediamine; wherein the methyl and ethyl groups are in the ratio of 1:3.

SAUL R. BUC.
SAMUEL A. GLICKMAN.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,273,901	Morgan	July 30, 1918

OTHER REFERENCES

Major "J. Am. Chem. Society," vol. 53 (1931), pp. 4373 to 4378.

Brunck "Ber. Deut. Chem." vol. 25 (1892), p. 2722.

Grandmougin et al., "Ber. Deut. Chem." vol. 42 (1909), p. 4017 ANM.

Fieser et al., "Organic Syntheses," vol. 20 (1940), p. 66.