United States Patent [19]

Nelson et al.

[11] **3,720,702**

[45] **March 13, 1973**

[54] **PARTIAL REDUCTION OF PHTHALONITRILES**

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[73] Assignee: **Ciba Corporation**, Summit, N.J.

[22] Filed: **Dec. 29, 1969**

[21] Appl. No.: **888,825**

[52] **U.S. Cl.**.....**260/465 D**, 260/340.3, 260/340.5, 260/464, 260/465 E, 260/465.4, 260/465.5, 260/561 R, 260/562 R, 260/562 A, 260/563 R, 260/570.9, 260/583 R, 260/583 P

[51] **Int. Cl.**.....**C07c 121/78**

[58] **Field of Search** .....260/465 D, 465 E

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

814,631 6/1959 Great Britain

OTHER PUBLICATIONS

Wagner–Zook, Synthetic Org. Chem., John Wiley & Sons, Inc., London, pp. 567–568 (1953).

Primary Examiner—Lewis Gotts
Assistant Examiner—Dolph A. Torrence
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[57] **ABSTRACT**

Dinitriles of organic acids, containing both cyano groups attached to vicinal carbon atoms, can be reduced without undue ring-formation and loss of nitrogen, by hydrogenating them in a liquid carboxylic acid anhydride, first over a palladium and then over a platinum catalyst, to yield the correspondingly acylated bis-aminomethyl compounds.

9 Claims, No Drawings

PARTIAL REDUCTION OF PHTHALONITRILES

BACKGROUND OF THE INVENTION

According to L. Kh. Freidlin et al. (Chem. Abstr. 54, 8836*a*) and U.S. Pat. No. 2,773,902 it is known, that either succinic or phthalic acid dinitriles cannot be reduced satisfactorily in various media to yield the corresponding tetramethylene- or o-xylylenediamine. Instead, ring-formation and loss of nitrogen occurs, to yield predominantly or exclusively the tetramethylen- or o-xylylenimine (pyrrolidine or isoindoline) respectively.

Surprisingly it was found that normal reduction to the diamine does occur in a stepwise reduction process by choosing (a) a liquid carboxylic acid anhydride as the reaction medium, (b) a palladium catalyst in the first hydrogenation step yielding the acylated aminomethyl-mononitrile and (c) a platinum catalyst in the second hydrogenation step, yielding the acylated diamine. If desired, said acylated amino compounds (amides) can be hydrolyzed in the usual manner, to yield the free mono- or diamine or acid addition salts thereof.

SUMMARY OF THE INVENTION

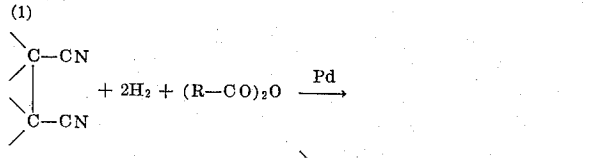
The present invention concerns and has for its object the provision of a new process for the:

1. partial reduction of an organic acid dinitrile containing both cyano groups attached to vicinal carbon atoms, by subjecting it to hydrogenation in a liquid carboxylic acid anhydride over a palladium catalyst, to yield the corresponding acylated aminomethyl-mononitrile which, if desired, can be hydrolyzed to yield the free amine or acid addition salts thereof and/or
2. further reduction of said free or acylated aminomethyl-mononitrile according to known methods, preferably in a liquid carboxylic acid anhydride over a platinum catalyst, to yield the correspondingly acylated bis-aminomethyl compound which, if desired, can be hydrolyzed to yield the free diamine or acid addition salts thereof.

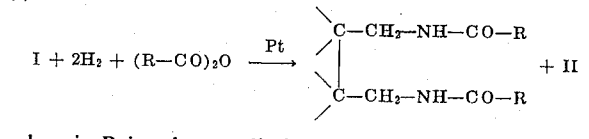
DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred process of the invention can be depicted as follows:

(1)



(2)

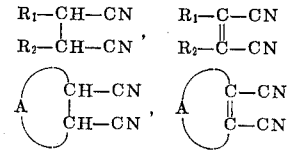


wherein R is a lower alkyl, preferably such with up to four carbon atoms.

The organic dinitrile can be derived from an aliphatic or preferably an aromatic dicarboxylic acid,

such as an α,β-lower (alkanoic, alkenoic or alkynoic)-acid, as well as a three to seven ring-membered cyclo-(alkane, alkene or alkadiene)-1,2-dicarboxylic acid or an isocyclic or heterocyclic, mono- or polycyclic aromatic o-dicarboxylic acid.

Preferred aliphatic starting materials are those of the formulae



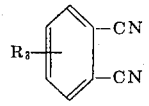
wherein each of R_1 and R_2 is hydrogen or lower alkyl and A is lower alkylene or alkenylene.

Most preferred are monocyclic, isocyclic aromatic ortho-dinitriles, e.g., those of the formula

NC—Ph—CN

in which Ph is a 1,2-phenylene radical, which advantageously is unsubstituted, but can also be substituted by one or more than one of the same or different substituents attached to any of the positions available for substitution. Such substituents are, for example, lower alkyl, such as methyl, ethyl, n- or i-propyl or -butyl, free, etherified or esterified hydroxy or mercapto, for example, lower alkoxy, alkylenedioxy or alkylmercapto, such as methoxy, ethoxy, n- or i-propoxy or -butoxy, methylenedioxy, 1,1- or 1,2-ethylenedioxy, methyl- or ethylmercapto, or halogen, such as fluoro, chloro or bromo, trifluoromethyl, nitro or amino, such as di-lower alkylamino, e.g., dimethylamino or diethylamino. The term "lower," referred to above and hereinafter in connection with organic radicals or compounds respectively, defines such with up to seven, preferably up to four, carbon atoms. Preferred radicals Ph are 1,2-phenylene, (lower alkyl)-1,2-phenylene, (lower alkoxy)-1,2-phenylene, (lower alkylmercapto)-1,2-phenylene, (halogeno)-1,2-phenylene, (trifluoromethyl)-1,2-phenylene, (nitro)-1,2-phenylene, (amino)-1,2-phenylene or (di-lower alkylamino)-1,2-phenylene.

Especially valuable starting materials are those of the formula

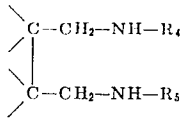


in which R_3 is hydrogen, methyl, methoxy, chloro, trifluoromethyl or nitro.

The liquid carboxylic acid anhydride, used as reaction medium and reactant as well, is preferably a lower alkanoic acid anhydride, e.g. acetic or propionic anhydride. It can be used in the presence or advantageously the absence of other diluents, preferably such as are inert to the reagents and are solvents thereof. In the former instance it can be used in equivalent amounts, otherwise a suitable excess thereof has to be applied, in order to facilitate the stirring or shaking of the reaction mixture.

The palladium and platinum catalysts used in the process of the invention are either the finely divided metals themselves, for example, obtained from suitable compounds thereof, e.g., platinum oxide, or advantageously said metals precipitated on suitable carriers, such as charcoal, e.g., 5 to 10 percent palladium on charcoal.

Other conventional reducing agents of the free or acylated aminomethyl-mononitrile, e.g., that corresponding to Formula I are, for example, nascent hydrogen, advantageously generated from alcohols, e.g., lower alkanols, and alkali metals, e.g., sodium, or complex light metal hydrides, such as alkali metal aluminum hydrides, e.g., lithium aluminum hydride, which reduction agents may yield compounds of the type



wherein each of R_4 and R_5 is hydrogen or lower alkyl, preferably such with up to five carbon atoms.

The hydrolysis of any resulting amide can be performed with the use of acidic or basic hydrolyzing agents, advantageously aqueous mineral acids such as hydrohalic acids, e.g., concentrated hydrochloric acid, to yield the corresponding acid addition salts.

The process of the invention is carried out according to otherwise standard conditions, e.g., in the presence or absence of diluents, for example, hydrocarbons, such as alkanes, cycloalkanes or benzenes, e.g., n-heptane, cyclohexane or toluene and/or inert atmospheres, e.g., nitrogen, at low, normal or advantageously elevated temperature and/or pressure, for example hydrogenating between about room temperature and about 100°, preferably between about 40° and 60° and between atmospheric pressure and about 10 at., preferably between about 3 and 4 at. In case nitro or other reducible groups are present in the starting material, these will be hydrogenated simultaneously in the usual manner.

The invention further includes any variant of the present process, in which an intermediate product obtainable at any stage of the process is used as starting material and any remaining steps are carried out, or the process is discontinued at any stage thereof, or in which the starting materials are formed under the reaction conditions, or in which the reaction components are used in the form of their salts. Mainly, those starting materials should be used in the above reactions that lead to the formation of those compounds indicated as being specially valuable.

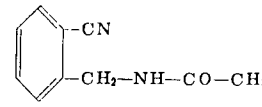
Starting materials are known or, if new, can be prepared according to the methods used for the preparation of the known products.

The products of the invention are also known or, if new, can be used in the manner described for the known products, for example those described in the above-cited art or in J. Org. Chem. 33, 670 (1968), Austral. J. Chem. 21, 256 (1968) or Belg. Pat. No. 713,698.

The following examples illustrate the invention and are not to be construed as being limitations thereon. Temperatures are given in Centigrade, pressures in atmospheres and all parts given are parts by weight.

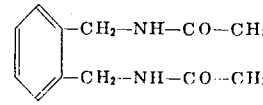
EXAMPLE 1

A 500 ml hydrogenation vessel is flushed with nitrogen and charged with 1 g 10 percent palladium on charcoal, 100 ml acetic anhydride and 12.8 g phthalonitrile and again flushed with nitrogen. Hereupon hydrogen is introduced while shaking, the pressure set to 3.4 at. and the temperature raised to 50°. After shaking overnight, the mixture is filtered and the filtrate evaporated in vacuo. The residue is taken up in ice water, the mixture filtered and the residue washed with water. It is suspended in 100 ml toluene, the mixture concentrated, the concentrate cooled and the precipitate formed filtered off, to yield the 2-acetylaminomethylbenzonitrile of the formula



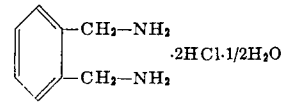
melting at 125°–126°.

8.7 g thereof are added to the suspension of 0.5 g platinum oxide and 150 ml acetic anhydride in the same vessel flushed with nitrogen. Hydrogen is applied at 3.4 at., the temperature raised to 45° and the mixture shaken until no more hydrogen is absorbed. The mixture is diluted with 50 ml acetic acid, filtered, the filtrate evaporated in vacuo and the residue recrystallized from about 50 ml toluene, to yield the α,α'-diacetamido-o-xylene of the formula



melting at 162°–164°.

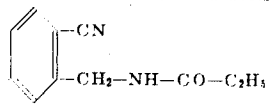
The mixture of 2 g thereof, 10 ml 37 percent hydrochloric acid and 10 ml water is heated to 90° for 48 hours. It is cooled, filtered and the residue dried at 50° in vacuo, to yield the α,α'-diamino-o-xylene dihydrochloride hemihydrate of the formula



melting over 300°.

EXAMPLE 2

A 500 ml hydrogenation vessel is flushed with nitrogen and charged with 2 g 5 percent palladium on charcoal, moistened with 10 ml propionic anhydride. Hereupon 25.6 g phthalonitrile and 190 ml propionic acid are introduced, the vessel flushed with hydrogen, the pressure set to 3.4 at and the temperature to about 50°–56. After the hydrogen uptake slowed to a nearly complete stop, the vessel is flushed with nitrogen and the contents filtered. The filtrate is evaporated in vacuo, the residue quenched in 150 ml water and the oily solid dissolved in 150 ml hot 2-propanol. After cooling, the precipitated starting material is filtered off and washed with 10 ml of 2-propanol. The filtrate is evaporated in vacuo, the residue taken up in 125 ml hot toluene, the solution cooled, the precipitate formed filtered off, washed with 15 ml cold toluene and recrystallized from 100 ml toluene, to yield the 2-propionylaminomethyl benzonitrile of the formula

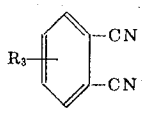


melting at 89°–91°.

We claim:

1. A process for the partial reduction of the dinitrile having the formula NC-Ph-CN, wherein Ph is 1,2-phenylene, (lower alkyl)-1,2-phenylene, (lower alkoxy)-1,2-phenylene, (lower alkylmercapto)-1,2-phenylene, (halogeno)-1,2-phenylene, (trifluoromethyl)-1,2-phenylene, (nitro)-1,2-phenylene, (amino)-1,2-phenylene or (di-lower alkylamino)-1,2-phenylene, which consists in subjecting one mol equivalent of said dinitrile to hydrogenation with 2 mol equivalents of hydrogen in at least one mol equivalent of a liquid lower alkanoic acid anhydride over finely divided palladium, to yield the corresponding acylated aminomethyl-mono-nitrile.

2. Process as claimed in claim 1, wherein dinitriles of the formula



are used as starting material, in which R_3 is hydrogen, methyl, methoxy, chloro, trifluoromethyl or nitro.

3. Process as claimed in claim 1, wherein phthalonitrile is used as starting material.

4. Process as claimed in claim 1, wherein acetic anhydride is used as lower alkanoic acid anhydride.

5. Process as claimed in claim 1, wherein the finely divided palladium is precipitated on charcoal.

6. Process as claimed in claim 5, wherein about 5–10 percent palladium is precipitated on charcoal.

7. Process as claimed in claim 1, wherein the hydrogenation is carried out between about room temperature and about 100° and between atmospheric pressure and about 10 at.

8. Process as claimed in claim 1, wherein the hydrogenation is carried out between about 40° and 60° and about 3 and 4 at.

9. A process for the partial reduction of phthalonitrile, which consists in subjecting one mol equivalent of said dinitrile to hydrogenation with two mol equivalents of hydrogen in at least one mol equivalent of a liquid lower alkanoic acid anhydride over finely divided palladium, to yield the corresponding acylated aminomethyl-mononitrile.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,720,702 Dated March 13, 1973

Inventor(s) John Archibald Nelson et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, after "[73] Assignee:" delete "Ciba Corporation, Summit, N. J." and substitute --- CIBA-GEIGY Corporation, Ardsley, N. Y. ---.

Signed and sealed this 23rd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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