

PATENT SPECIFICATION

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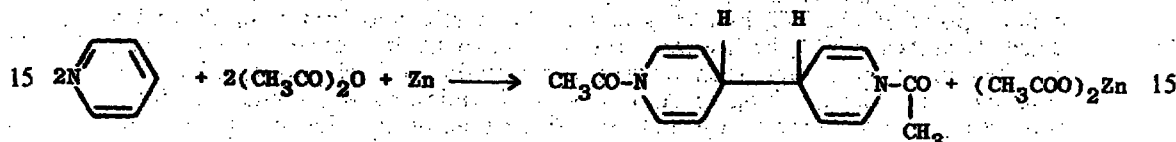
(54) QUATERNISATION OF DIPYRIDYL ACETATE TO N,N'-DIALKYL-1,4'-DIPYRIDILIUM DIHALIDE IN ACETIC ACID

(71) We, MONTEDISON S.p.A., an Italian body corporate of 31 Foro Buonoparte, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

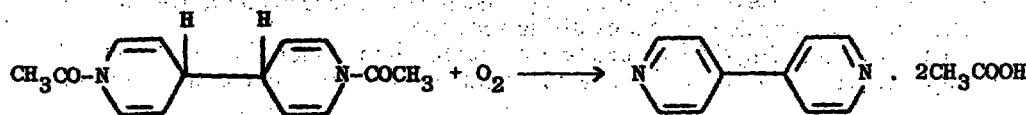
This invention relates to a process of quaternising dipyridyl diacetate to N,N' - dialkyl - 4,4' - dipyridylium dihalide. In particular the invention relates to the quaternisation of dipyridyl diacetate in acetic acid in a single step only, with high yields, excellent purity and with the possibility of using acetic acid for successive N-methylations of the same product.

The synthesis of 4,4'-dipyridyl diacetate has been disclosed by Dimroth in Berichte 54, 1921, page 2938; and Berichte 55, 1922, page 3695. The synthesis comprises the steps of:—

(1) reducing pyridine with zinc and acetic anhydride to form N,N' - diacetyl - tetrahydrodipyridyl:



(2) oxidizing diacetyl-tetrahydrodipyridyl with oxygen, in a solvent, to form dipyridyl diacetate:



The resulting dipyridyl diacetate is a colourless crystalline product having a melting point of 96°C. According to the disclosure when the dipyridyl diacetate is treated, in an aqueous medium, with ammonium hydrate, ammonium acetate forms and the base liberates as 4,4'-dipyridyl dihydrate that crystallizes to filiform needles having a melting point of 73°C.

In order to carry out the quaternisation of the latter substance it was then necessary to dehydrate 4,4'-dipyridyl dihydrate to 4,4'-dipyridyl (melting point=112°C) and to treat it with methyl halide in a suited solvent. Alternatively quaternisation can be conducted in water according to French Patent Specification No 1,390,773 of I.C.I.

It is an object of the present invention to provide an alternative method for the quaternisation of dipyridyl diacetate.

Therefore according to the invention there is provided a process for quaternising 4,4'-dipyridyl diacetate to form N,N' - dialkyl - 4,4' - dipyridylium

dihalide in which 4,4'-dipyridyl diacetate is reacted with an alkyl halide, in the presence of acetic acid at a temperature of from 60 to 150°C and at a pressure of from 2 to 10 kg/cm² (gauge).

The amount of acetic acid used as solvent for the dipyridyl diacetate is preferably at least equal to the amount of dipyridyl diacetate to be quaternised.

Under the above reaction conditions, when employing methylhalide, the yield of N,N'-dimethyl dipyridyl dihalide may be higher than 95% referred to the starting dipyridyl diacetate and the product may have a purity of 98 to 99%. The acetic acid employed may be repeatedly recycled at both the oxidation and the quaternisation stage (it has been ascertained that the acid can be recycled for more than 15 times without any decrease in the product purity or yields). The use of acid as solvent, as well as ensuring a proper adjustment of the temperature of the exothermic reaction and a uniform quaternisation degree of dipyridyl in every point of the reacting mass, avoids the problems of separation or recovery of the acetic acid that is liberated during the reaction (representing 43.5% of the product subjected to reaction).

The invention will now be illustrated with reference to the following Examples in which all pressures are gauge pressures.

Example 1

825 g (2.86 moles) of dipyridyl diacetate (96% pure) prepared according to the conventional Dimroth reaction, were introduced into an enamelled 3.5 litre autoclave, 1635 g of acetic acid (99%) were added and the mixture was heated to 114°C, and then methyl chloride was introduced at a pressure of 5.8 kg/cm². The reaction was completed during the first 2 hours, whereupon the introduction of methyl chloride was terminated, and heating was continued for a further 2 hours. After cooling the slurry obtained, was filtered to yield 1182 g of wet crystals, which were dried, while the acetic acid, separated by filtration, was utilized for further quaternisations.

660 g of N,N' - dimethyl - 4,4' - dipyridylum dichloride having a purity higher than 98% were obtained. The yield was 90% calculated on the dipyridyl introduced.

Example 2

865 g (3.54 moles) of diacetyl-tetrahydropyridyl (yellow crystals having a melting point of 132.5°C) in 1700 g of recycled acetic acid containing dipyridyl diacetate at its solubility limit were introduced into a 3.5 litre reactor. The mixture was heated to 40°C, and then oxygen was introduced finely dispersed in the reacting mass. The resulting reaction was exothermic and was moderated by a cooling liquid circulating in a jacket around the reactor in order to maintain the reaction temperature below 50°C.

The reaction was completed in 1 hour and the brown solution obtained was cooled, to precipitate crystals of dipyridyl diacetate which were recovered by filtration and dried.

800 to 820 g (2.86 moles) of dipyridyl diacetate, having a melting point of 96°C, were obtained, the yield being 76 to 80% calculated on diacetyl-tetrahydropyridyl. Acetic acid was recycled to the oxidizing reaction.

The resulting dipyridyl diacetate was quaternised under the conditions of Example 1, using as solvent, acetic acid coming from a preceding quaternisation.

Example 3

The acetic suspension of dipyridyl diacetate, obtained under the conditions of Example 2, was introduced at a temperature of 50°C and under stirring, into an enamelled autoclave, in which it was treated with methyl chloride at 114°C and 5.8 kg/cm² in accordance with Example 1. 720 g of N,N' - dimethyl - 4,4' - dipyridylum dichloride having a purity higher than 98% were obtained.

WHAT WE CLAIM IS:—

1. A process for quaternising 4,4'-dipyridyl diacetate to form N,N' - dialkyl - 4,4' - dipyridylum dihalide in which 4,4'-dipyridyl diacetate is reacted with an alkyl halide, in the presence of acetic acid at a temperature of from 60 to 150°C and at a pressure of from 2 to 10 kg/cm² (gauge).

2. A process as claimed in Claim 1 in which the alkyl halide is methyl halide.

3. A process as claimed in Claim 1 or Claim 2 in which the acetic acid is present in an amount at least equal to the weight of dipyridyl diacetate to be quaternised.



dihalide in which 4,4'-dipyridyl diacetate is reacted with an alkyl halide, in the presence of acetic acid at a temperature of from 60 to 150°C and at a pressure of from 2 to 10 kg/cm² (gauge).

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The invention will now be illustrated with reference to the following Examples in which all pressures are gauge pressures.

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1. A process for quaternising 4,4'-dipyridyl diacetate to form N,N' - dialkyl - 4,4' - dipyridylum dihalide in which 4,4'-dipyridyl diacetate is reacted with an alkyl halide, in the presence of acetic acid at a temperature of from 60 to 150°C and at a pressure of from 2 to 10 kg/cm² (gauge).

2. A process as claimed in Claim 1 in which the alkyl halide is methyl halide.

3. A process as claimed in Claim 1 or Claim 2 in which the acetic acid is present in an amount at least equal to the weight of dipyridyl diacetate to be quaternised.

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4. A process as claimed in any preceding claim in which the 4,4'-dipyridyl diacetate is obtained by oxidation of diacetyl-tetrahydropyridyl.

5. A process as claimed in Claim 4 in which the acetic acid is recycled after the quaternisation reaction and used as a solvent in the oxidation of diacetyl-tetrahydropyridyl.

6. A process as claimed in any of claims 1 to 4 in which the acetic acid is recycled after the quaternisation for use in further quaternisation of dipyridyl diacetate.

7. A process for quaternising 4,4'-dipyridyl diacetate to form N,N'-dialkyl dipyridylium dihalide substantially as herein described with reference to any one of the Examples.

8. N,N'-dialkyl dipyridylium dihalide when prepared by a method as claimed in any one of the preceding claims.

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