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PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOHN EDWARD DOWNES and JANET ELISABETH JAMESON

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COMPLETE SPECIFICATION

Process for Preparing Bipyridylium Compounds

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, 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 for the production of alkyl quaternary salts of 4,4'-bipyridyls.

Previously proposed methods for the production of N-alkyl-4,4'-bipyridylium diquaternary salts require the use of alkyl halides or alkyl sulphates as quaternising agents. These quaternising agents, however, suffer from various disadvantages. For example, dimethylsulphate is a toxic substance which is dangerous to handle, while methyl chloride requires the use of pressures above atmospheric pressure to obtain a satisfactory yield of product. We have now discovered that N-alkyl-4,4'-dipyridylium diquaternary salts can be prepared by an alternative reaction process.

According to the present invention, we provide a process for the production of N-alkyl diquaternary salts of 4,4'bipyridyls which comprises heating a 4,4'-bipyridyl for a period of at least three minutes with an aliphatic carboxylic acid containing 2 to 5 carbon atoms substituted in the alpha position with a radical capable of conversion into a stable negative ion and recovering an N-alkyl-4,4'-diquaternary dipyridylium salt.

The process may if desired be carried out in the presence of an inert diluent.

Suitable 4,4'-bipyridyls for use in the process include 4,4'-bipyridyls substituted in one or both rings with one or more alkyl groups, especially one or more alkyl groups having from one to four carbon atoms. Examples are 2,2'-dimethyl-4,4'bipyridyl and 2,6-dimethyl-4,4'-bipyridyl. 4,4'-Bipyridyl is particularly suitable.

The process may conveniently be carried out by heating an admixture of the reactants to a temperature of from 80° to 150°C. A particularly suitable temperature is 120°C. The reaction mixture is maintained at this temperature for at least three minutes and conveniently about ten minutes. While generally no practical advantage is gained from very extensive reaction times e.g. longer than two hours, there is no actual upper limit to the length of time which may be taken if desired. Recovery of the product from the reaction mixture may be carried out by any of a variety of known techniques, e.g. solvent recrystallisation.

The reaction may also be carried out by heating the reactants in the presence of an inert diluent, preferably a solvent having a boiling point of at least 100°C. The temperature of reaction when using a diluent is generally between 80° and 250°C. and preferably 150° to 200°C. The time necessary for reaction varies according to the temperature and the reactants from a few minutes upward; generally one or two hours are sufficient.

In general, any inert organic diluent or water can be used, but particularly preferred diluents are polar, for example ethoxyethanol and N,N'-dimethylformamide. The solvent can be used alone or together with a wetting agent, or a substance may be used which possesses wetting properties and at the same time is capable of acting as a diluent, for example a condensate of nonyl phenol and ethylene oxide sold under the Trade Mark "Lissapol".

Another particularly useful class of substances capable of acting both as a wetting

[*Price 4s. 6d.*]

agent and a diluent is the amine oxide type of wetting agent, more particularly those wherein the nitrogen atom of the amine oxide bears at least one long chain group having from five to twenty-five carbon atoms.

The alpha substituent in the aliphatic carboxylic acid used in the process is preferably a halogen atom, for example Cl or Br. The aliphatic carboxylic acid is preferably a halogenoacetic acid. A particularly suitable halogenoacetic acid is chloracetic acid.

Equivalent amounts of the reactants can conveniently be used but a slight excess of the quaternising agent is preferred in order to ensure that all the 4,4'-bipyridyl undergoes reaction.

The invention is illustrated by the following Examples.

EXAMPLE 1.

This Example illustrates the preparation of 1,1' - dimethyl - 4,4' - bipyridylium dichloride. 19.2 parts of 4,4' - bipyridyl dihydrate were warmed with 20 parts of chloracetic acid in an oil bath to 105°C.

The reaction was exothermic and the temperature rose to 132°C.; the green liquid reaction mixture changed to a buff solid in 4 minutes. The solid was recrystallised from a methanol/ethanol mixture; the yield was 76.3% determined by reduction to the radical and measurement of the optical density at 600 mμ, according to the method described by Yuen, Bagness and Miles, Analyst, 1967, 92, 375.

EXAMPLE 2.

This Example illustrates the preparation of 1,1' - dimethyl - 4,4' - bipyridylium dichloride.

One part of 4,4' - bipyridyl was warmed with 2 parts of chloroacetic acid and 2 parts of ethoxyethanol in an oil bath to 123°C.; the reaction mixture reached 110°C. before solidifying. The mixture was then heated at 200°C. for 90 minutes. Yield—92.5%, determined as in Example 1.

EXAMPLE 3.

This Example illustrates the preparation of 1,1' - dimethyl - 4,4' - bipyridylium dichloride. The process of Example 2 was repeated except that in place of ethoxyethanol, an equal volume of dimethylformamide was used as the solvent. The maximum temperature reached was 114°C. and the mixture was heated at 160°C. for 90 minutes. Yield—73%, determined as in Example 1.

EXAMPLE 4.

This Example illustrates the preparation of 1,1' - dimethyl - 4,4' - bipyridylium dichloride. The process of Example 2 was repeated, except that instead of ethoxyethanol an equal volume of a condensate of nonyl phenyl and ethylene oxide was used as a solvent. The maximum temperature reached was 112°C. and the mixture was heated at 160°C. for 90 minutes. Yield—76.5%, determined as in Example 1.

WHAT WE CLAIM IS:—

(1) A process for the production of N-alkyl diquaternary salts of 4,4'-bipyridyls which comprises heating a 4,4'-bipyridyl for a period of at least three minutes with an aliphatic carboxylic acid containing two to five carbon atoms substituted in the alpha position with a radical capable of conversion into a stable negative ion, and recovering an N-alkyl 4,4'diquaternary bipyridylium salt.

(2) A process claimed in Claim 1 wherein the reaction is carried out in the presence of an inert diluent.

(3) A process claimed in Claim 2 wherein the diluent comprises a wetting agent.

(4) A process claimed in Claim 1 wherein the reaction is carried out in the absence of a diluent at a temperature in the range 80—150°C.

(5) A process claimed in Claim 2 wherein the bipyridyl is a substituted 4,4'-bipyridyl.

(6) A process claimed in Claim 4 wherein the bipyridyl is a substituted 4,4'-bipyridyl.

(7) A process claimed in Claim 2 wherein the alpha substituent of the aliphatic carboxylic acid is a halogen atom.

(8) A process claimed in Claim 4 wherein the alpha substituent of the aliphatic carboxylic acid is a halogen atom.

(9) A process claimed in Claim 7 wherein the halogen-aliphatic carboxylic acid is chloracetic acid.

(10) A process claimed in Claim 8 wherein the halogeno-aliphatic carboxylic acid is chloracetic acid.

(11) Alkyl diquaternary salts of 4,4'-bipyridyls prepared by the process claimed in any of Claims 2, 5, 7 and 9.

(12) Alkyl diquaternary salts of 4,4'-bipyridyls prepared by the process claimed in any of Claims 4, 6, 8 and 10.

(13) A process claimed in Claim 2 substantially as described particularly with reference to Examples 2, 3 and 4.

(14) A process claimed in Claim 4 substantially as described, particularly with reference to Example 1.

T. W. ROBERTS,
Agent for the Applicants.

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