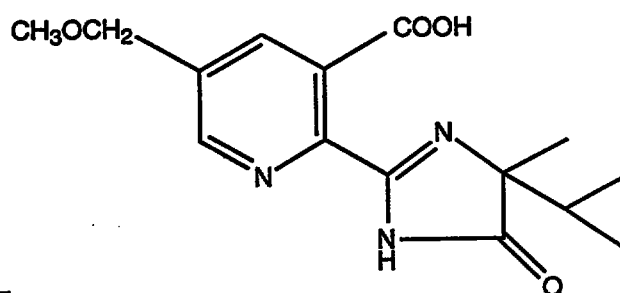


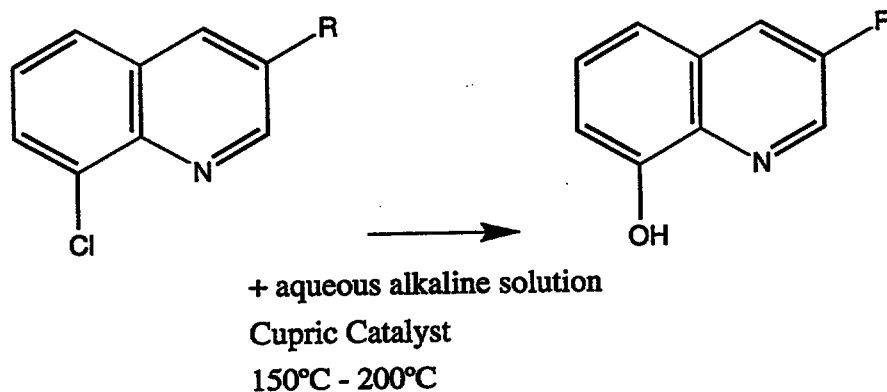
- 1 -

CONVERSION OF SUBSTITUTED 8-CHLOROQUINOLINES TO SUBSTITUTED 8-HYDROXYQUINOLINES

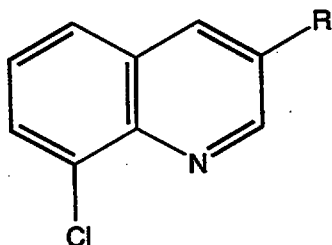
The invention relates to a process for the conversion of substituted 8-chloroquinolines to substituted 8-hydroxyquinolines in the presence of a cupric catalyst. The compound 8-hydroxy-3-methoxymethylquinoline, a product of the process, is a precursor to the imidazolinone herbicide of formula I.



More particularly the invention relates to a pressure reactor process for preparing substituted 8-hydroxyquinolines as follows:



Thus, according to the present invention there is provided a process for preparing substituted 8-hydroxyquinolines which comprises reacting substituted 8-chloroquinolines of the formula :



- 2 -

wherein R is C₁-C₄alkyl, hydroxy-C₁-C₄alkyl, C₁-C₄-alkoxy-C₁-C₄alkyl, C₁-C₄haloalkyl, or di-C₁-C₄alkylamino-C₁-C₄alkyl in a stirred pressure reactor with dilute alkaline solution in the presence of a cupric catalyst at a temperature within the range of 150°C - 200°C.

- 5 When R contains C₁-4alkyl it is preferably methyl or ethyl. When R is C₁-C₄alkoxy-C₁-C₄alkyl, it is preferably methoxymethyl. When R contains a halogen, the halogen is preferably fluorine or chlorine. When R is di-C₁-C₄alkylamino-C₁-C₄alkyl it is preferably dimethylaminoethyl or dimethylaminomethyl.

R is most preferably methoxymethyl.

- 10 The cupric catalyst is preferably a cupric salt or an organic cupric complex. A particularly preferred cupric salt is cupric sulfate, particularly cupric sulfate pentahydrate.

- When the cupric salt is a complex it is a complex with the 3-substituted-8-hydroxyquinoline and preferably a complex between cupric sulfate and the 3-substituted-8-hydroxyquinoline.
- 15

The alkaline solution is dilute i.e. aqueous, preferably in the range of up to 50% aqueous solution, more preferably from 2% to 50% aqueous solution, especially from 2% to 4% aqueous solution.

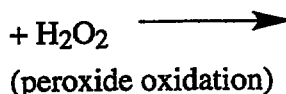
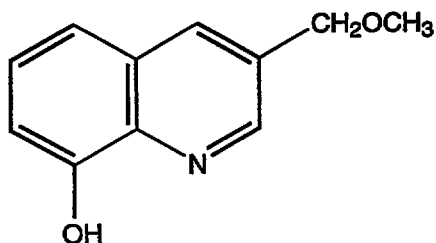
- The alkaline solution is preferably sodium hydroxide, particularly aqueous sodium hydroxide.
- 20

The reaction is carried out in the temperature range of 150°C to 200°C. The reaction is more preferably carried out in the temperature range of 160°C to 180°C and especially at 160°C or thereabouts.

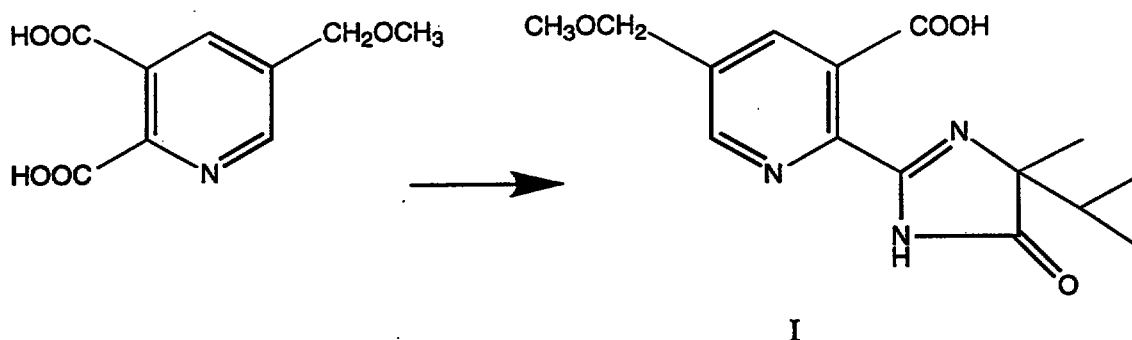
- The reaction is carried out in a sealed pressure reactor and is stirred. The reaction is preferably stirred for from 17 to 24 hours, especially 17 to 22 hours.
- 25

The compound 8-hydroxy-3-methoxymethylquinoline, which may be prepared according to the process of the present invention, is an intermediate in the synthesis of the imidazolinone herbicidal agent I as follows:

30



- 3 -



- 5 as taught in W.F. Reiker and W. A. Daniels, U.S. Patent No. 4,816,588 (1989) "Method for the Preparation of Pyridine -2,3-dicarboxylic Acids," and in Marinus Los U.S. Patent No. 4,798,619 (1989) "2-(2-Imidazolin-2-yl)pyridines and -quinolines and Use of Said Compounds as Herbicidal Agents."

10 The following examples illustrate the invention but are not to be construed as a limitation thereto.

Example 1

Into a tantalum liner in a 600ml stirred Parr pressure reactor is placed 4.15 g 8-chloro-3-methoxymethylquinoline (20 mmol), 8.0g 50% aqueous sodium hydroxide (100 mmol) and a solution of 250 mg cupric sulfate pentahydrate (1.0 mmol, 5 mole percent) in 95 ml of water. Sodium hydroxide concentration is 4%. The system is sealed, brought to 160°C and held for 21.5 hours. The cooled solution is filtered through Celite, extracted with two 20ml portions of toluene, then the aqueous layer is adjusted to pH 3-4 with sulfuric acid and finally to pH 7 with ammonium hydroxide. The mixture is extracted with two 50 ml portions of ethyl acetate. Rotary evaporation of the organic layer gives 2.39 g (63% yield) of crude 8-hydroxy-3-methoxymethylquinoline as a yellow green solid. The crude material is treated with two 500 ml portions of boiling water, leaving behind some insolubles. Long silky yellow needles of pure 8-hydroxy-3-methoxymethylquinoline separate out. After filtering and drying, 1.83 g (48% yield) is obtained.

25

Example 2

The Example 1 reaction is repeated in the same manner except 195 ml of water is used, thus the sodium hydroxide concentration is 2%. A similar workup affords 2.56 g (68% yield) of crude 8-hydroxy-3-methoxymethylquinoline. Recrystallization from hot water gives 1.92 g (51% yield) of pure material.



Example 3

The Example 1 reaction is repeated on a larger scale with modified workup. Into a one gallon #316 stainless steel stirred Parr pressure reactor is placed 31.1 g 8-chloro-3-methoxymethylquinoline (150 mmol), 60 g 50% aqueous sodium hydroxide (750 mmol), and a solution of 1.87 g cupric sulfate pentahydrate (7.5 mmol, 5 mole percent) in 1460 ml of water. The system is sealed, brought to 160°C and held for 17 hours. The cooled solution is filtered through Celite, then chilled thoroughly in an ice bath. The pH is adjusted to 4 with 50 ml concentrated hydrochloric acid, then to pH 8 with approximately 5 ml ammonium hydroxide. The resulting precipitate is filtered and washed with water. After drying overnight in a 60°C vacuum oven, 19.64 g of gray green powder, crude 8-hydroxy-3-methoxymethylquinoline (69% yield) is obtained. The filtrate is extracted with three 250 ml portions of ethyl acetate. Rotary evaporation of the organic layers gives 4.10 g of dark green oil, crude product (14% yield, thus total crude yield is 83%). Recrystallization of this oil from hot water affords 1.24 g of yellow-green needles of pure product.

Example 4

A cupric complex of 8-hydroxy-3-methoxymethylquinoline is prepared by reacting one equivalent of cupric sulfate pentahydrate with two equivalents 8-hydroxy-3-methoxymethylquinoline in excess aqueous sodium hydroxide. The precipitated green powder is filtered, washed with water, and dried to a constant weight. The Example 3 reaction is repeated, replacing the 1 mole percent cupric sulfate with 1.5 mole percent of the cupric complex of 8-hydroxy-3-methoxymethylquinoline. Similar work up gives an 80% yield of first crop product, and an additional 11% yield of second crop, thus overall crude yield is 91%.

Example 5

The Example 4 reaction is repeated using 1.0 mole percent of the cupric complex of 8-hydroxy-3-methoxymethylquinoline. The overall crude yield is 92%. The product is purified by precipitation of the hydrochloride salt by addition of concentrated hydrochloric acid to a solution of the crude product in acetone. Overall yield of the hydrochloride salt is 58%.

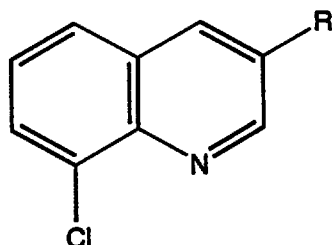
Example 6

The Example 5 reaction is repeated in an identical manner. The overall crude yield is 94%. Analyses of the product indicates a 78% real yield.



**CLAIMS**

1 A process for preparing substituted 8-hydroxyquinolines which comprises reacting substituted 8-chloroquinoline of the formula :



wherein R is C₁-C₄alkyl, hydroxy-C₁-C₄alkyl, C₁-C₄-alkoxy-C₁-C₄alkyl, C₁-C₄haloalkyl, or di-C₁-C₄alkylamino-C₁-C₄alkyl in a stirred pressure reactor with dilute alkaline solution in the presence of a cupric catalyst at a temperature within the range of 150°C - 200°C.

2 A process according to claim 1 wherein the cupric catalyst is a cupric salt or an organic cupric complex and the alkaline solution is sodium hydroxide.

3 A process according to claim 2 wherein 8-chloro-3-methoxymethylquinoline is converted to 8-hydroxy-3-methoxymethylquinoline.

4 A process according to claim 3 wherein the catalyst is 1 molar percent of the organic cupric complex prepared from the reaction of cupric sulfate and 8-hydroxy-3-methoxymethylquinoline, and the sodium hydroxide is 5 equivalents 2% aqueous sodium hydroxide wherein the reaction is stirred for 17 to 24 hours at a temperature of 160°C.

5 A process according to claim 3 wherein the catalyst is 5 molar percent cupric sulfate and the sodium hydroxide is 5 equivalents of 2% to 4% aqueous sodium hydroxide wherein the reaction is stirred for 17 to 22 hours at a temperature of 160°C.

6 A process according to claim 5 wherein the sodium hydroxide is 5 equivalents of 2% aqueous sodium hydroxide.

