BIS-(2-PYRIDYL-1-OXIDE) DISULFIDE

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Int. Cl 6... (2-PYRIDYL-1-OXIDE) DISULFIDE
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References Cited

UNITED STATES PATENTS
2,686,786 8/1954 Shaw et al. ................. 260/294.8 G


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ABSTRACT
An improved integrated route to bis-(2-pyridyl-1-oxide) disulfide is provided by oxidizing 2-chloropyridine with permaleic acid to form 2-chloropyridine-1-oxide followed by mercaptization with a selected alkali metal sulfide to form the alkali metal salt of 2-mercaptopyridine-1-oxide and then oxidation with hydrogen peroxide under selected pH conditions.

8 Claims, No Drawings
**BIS-(2-PYRIDYL-1-OXIDE) DISULFIDE**

This invention relates to an improved, integrated method for preparing bis-(2-pyridyl-1-oxide) disulfide in high purity and high yield. More particularly, this invention involves the preparation of the aforesaid disulfide compound in an integrated, in-situ method by oxidizing the alkali metal salt of 2-mercaptoypyridine, which is obtained by oxidation of 2-chloropyridine with maleic acid followed by mercaptization with a selected sulfide, with hydrogen peroxide using selected pH conditions.

The preparation of bis-(2-pyridyl-1-oxide) disulfide (also referred to as 2,2'-dithiodipyrindine-1,1'-dioxide) hereinafter referred to as the disulfide, has been previously broadly disclosed in U.S. Pat. No. 2,742,476 wherein mercaptoypyridine-1-oxide is reacted with an oxidizing agent. U.S. Pat. No. 3,759,932 also generally discloses the preparation of a disulfide compound using an in-situ preparation technique wherein mercaptoypyridine is not isolated. While these references broadly disclose the preparation of the disulfide, problems have arisen when using the alkali metal salt of 2-mercaptoypyridine-1-oxide in an in-situ technique wherein the alkali metal salt was obtained by oxidizing 2-chloropyridine with maleic acid to form the N-oxide followed by mercaptization to form the salt. When using this system, oxidation by the known techniques as shown for example in U.S. Pat. No. 2,742,476 resulted in the formation of undesired by-products such as the alkali metal maleate and alkali metal fumarate. This contaminated the desired disulfide product and lowered the yield.

It has now been found that when using maleic acid in the preparation of 2-chloropyridine-1-oxide during the integrated preparation of the disulfide, the above noted by-product formation can be avoided and surprisingly high yields obtained by operating the final oxidation in the presence of hydrogen peroxide at selected pH conditions. More particularly the oxidation of the alkali metal salt of 2-mercaptoypyridine-1-oxide is carried out at a pH of about 4 to about 5 and preferably from about 4.5 to about 5. The overall reaction scheme of this invention is illustrated by the following equation:

\[
\text{NaSH} \quad \text{H}_2\text{O}_2 \quad \text{pH 4-5}
\]

In the reaction of this invention as illustrated above, 2-chloropyridine is oxidized to the N-oxide using maleic acid in accordance with known procedures as disclosed for example in U.S. Pat. No. 2,951,844. The mercaptization of the 2-chloropyridine N-oxide is carried out using an alkali metal sulfide or alkali metal hydro-

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**EXAMPLE I**

A 2-liter, 3-neck flask fitted with a stirrer, thermometer and addition funnel was charged with 1,866 g of a reaction mixture containing the sodium salt of 2-mercaptoypyridine-1-oxide. This reaction mixture had
an assay of 7.2 percent (135 g) of the sodium salt of 2-mercaptoypyridine-1-oxide, 7 percent sodium chloride and 13–14 percent total of sodium maleate and sodium fumarate. This mixture was obtained by oxidizing 2-chloropyridine with permaleic acid and then mercaptizing with NaSH. The pH was then adjusted to 4.5 with concentrated hydrochloric acid and the resulting warm solution was cooled to 25°C and 52 ml of 30 percent hydrogen peroxide (12 percent excess over stoichiometry) in 160 ml water added dropwise over a 30 minute period with stirring. The reaction was slightly exothermic with the temperature rising to approximately 30°C. at the end of the peroxide addition. Stirring of the now precipitated bis-(2-pyridyl-1-oxide) disulfide product was continued for 2 more hours to assure completeness of the reaction. The disulfide product formed was collected by filtration and the filter cake washed with 50 ml water follower by 50 ml of methanol. After air drying, a total of 112 g (98 percent yield based on starting sodium salt of 2-mercaptoypyridine-1-oxide) of bis-(2-pyridyl-1-oxide) disulfide was obtained with a melting point of 200°–201°C: and an assay of 98 percent.

EXAMPLE II

Using the same procedure as Example I with a reaction mixture containing 25.6 g of the sodium salt of 2-mercaptoypyridine-1-oxide, 14 g of 10 percent hydrogen peroxide, a pH of 4.0 and a reaction time of 18 hours, 17.0 g of the disulfide product was obtained (79.8 percent yield based on sodium salt) having as assay of 97.8 percent.

EXAMPLE III

Using the same procedure as Example I with a reaction mixture containing 25.6 g of the sodium salt of 2-mercaptoypyridine-1-oxide, 14 g of 10 percent hydrogen peroxide, a pH of 5.0, a reaction temperature of 20° to 23°C, and a reaction time of 18 hours, 19.0 g of the disulfide product was obtained (89.3 percent yield based on sodium salt) and an assay of 97.7 percent.