

Preparation of 2-Methoxy-1,4-naphthoquinone from 2-Methoxynaphthalene

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In the course of our investigations on the ozonolysis of naphthoquinones, the need arose for 2-methoxy-1,4-naphthoquinone as an intermediate in the synthesis of certain 2,3-disubstituted naphthoquinones. The synthetic methods recorded in the literature¹⁻⁶ were rather cumbersome, whether the 2-methoxy derivative was formed directly or through methylation of the corresponding hydroxy compound. In principle, the most direct route would be oxidation of 2-methoxynaphthalene (nerolin), and preliminary experiments showed that the reaction was feasible.

Molho and Mentzer⁷ oxidised nerolin in glacial acetic acid with chromic acid and lead tetraacetate. Their statements about the yields of the reactions are somewhat vague, but it seems, at least for the oxidation with chromic acid, that they were in the neighbourhood of 2 or 3 %.

Fernholz⁸ oxidised nerolin with perbenzoic acid and obtained about 3 % yield of the quinone. Wessely *et al.*⁹ obtained through oxidation with lead tetraacetate a yield of 16 %.

The present method differs from that of Molho and Mentzer especially in the working-up of the reaction mixture. The following variables of the reaction have been systematically altered: a) amount of chromic acid, b) rate of addition of the oxidant, c) temperature in the first part of the reaction, and d) refluxing time of the reaction mixture. After the optimal conditions thus were found, also the amount and concentration of the acetic acid employed as a solvent were varied, but rather wide variations were without much influence on the reaction. The average yield of this procedure is 17 %. This is not a high yield, but in view of the easy availability and low cost of nerolin and the oxidant on one hand, and the time-consuming procedures when starting

with other materials on the other hand, this direct oxidation seems to have some merit.

Recommended procedure. 2-Methoxynaphthalene (25 g) in glacial acetic acid (250 ml) is heated to 70°C. To this solution is added during one hour chromic acid (100 g) in a mixture of water (75 ml) and glacial acetic acid (75 ml) while the reaction temperature is kept at 80°C. Thereafter the mixture is refluxed for 2 h and cooled to room temperature. Chloroform (100 ml) is added, followed by water until the mixture just separates into two phases. After shaking, the chloroform phase is separated, dried and evaporated to dryness in a stream of warm air (in larger batches the chloroform is preferably distilled off). The greenish residue is taken up in alcohol (100 ml), treated with charcoal and concentrated to a small volume. After some hours the crude product is collected on a suction filter. Yield 5.1 g (mean).

Identification of the reaction product. Recrystallised twice from water, m.p. 184–184.5°C, undepressed in mixture with an authentic sample. The infra-red spectrum was identical in all respects with that of authentic 2-methoxy-1,4-naphthoquinone.

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