

QUINONE FORMATION IN THE THALLEIOQUIN REACTION.—A NEW PREPARATION OF QUINOLINE-*o*-QUINONE.\*BY GEORGE W. HARGREAVES.<sup>1</sup>

The mechanism of the well-known thalleioquin reaction for the detection of quinine has been the subject of many investigations (1, 2, 3, 4). Quinone formation in the quinoline nucleus has been quite generally recognized. This view is supported by the analogous color reactions of quinoline-*o*-quinone and 5,5-dichloro-6-ketoquinoline. Quinoline-*o*-quinone has previously been prepared by the oxidation of 5-amino-6-hydroxyquinoline (4, 5), and the dichloro-keto-compound by passing chlorine gas into a cold solution of 6-hydroxyquinoline. In neither case have these products been obtained under the same conditions that the thalleioquin reaction is undertaken. By the direct oxidation of 6-hydroxyquinoline with lead peroxide and dilute sulfuric acid, quinoline-*o*-quinone has been prepared under exactly the same conditions that the thalleioquin reaction can be produced according to the method of Pollaci (6). When a solution of the quinone sulfate is warmed with aniline, a red solution is produced. An oxidized solution of quinine reacts similarly. These facts are further evidence of quinone formation in the thalleioquin reaction. As the starting product in this investigation, 6-hydroxyquinoline has been prepared by a method which is less violent and gives better yields than the original Skraup (7) procedure.

## EXPERIMENTAL.

*6-Hydroxyquinoline*.—A mixture of 44 Gm. of *p*-nitrophenol, 100 Gm. of anhydrous glycerol, 60 cc. of glacial acetic acid and 55 cc. of concentrated sulfuric acid is refluxed in a two-liter flask for 24 hours. The reaction proceeds smoothly and the flame need not be removed when the reaction sets in. After refluxing, the mixture is cooled and 500 cc. of water added. The product is obtained by fractional precipitation using 40% NaOH at first in order to keep the volume low and the neutralization is completed with 10% NaOH. This fractional precipitation is carried out in a two-liter beaker surrounded by a bath of cold water and the mixture is stirred vigorously with a mechanical stirrer. This causes the tarry by-products to solidify and collect, for the most part, on the stirrer and on the sides of the beaker, greatly aiding the subsequent filtration. The alkali should be added slowly, for if added too rapidly there is danger of some of the hydroxyquinoline precipitating and being carried out with the tar. The first dark colored precipitates are filtered off and the lighter colored filtrate is neutralized with 10% NaOH whereupon the hydroxyquinoline separates as a yellowish to buff colored powder. It is best to carry out the fractional precipitation in stages, that is, the addition of alkali and filtration being repeated several times until the addition of alkali produces no more dark precipitation. A large plaited filter should be used as suction filtration is impossible due to the sticky nature of the precipitates. The final product, however, can be filtered with suction and should be washed with a small amount of water. Yield 35 Gm. The product is recrystallized from 10% acetone in water using a small amount of charcoal. It forms small white prisms, *m. p.* 193°.

The literature suggests recrystallization from water but the solubility of the product in hot water is very low and charcoal has practically no decolorizing action in this solvent. For most reactions, the precipitated hydroxyquinoline can be used without recrystallization. No detailed study has been made of the relation between yield and time of refluxing, however, the yield is less when boiling is less than 20 hours and there is no increase in yield when boiling is extended beyond 24

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