

The production of zinc oxide in the zinc condenser is due, then, to the oxidation of the zinc by carbon dioxide, or water vapor, both of which are present in considerable quantities in the gases issuing from the retort when reduction first starts. Additional carbon dioxide may be produced by the reaction $2\text{CO} = \text{CO}_2 + \text{C}$, which is catalyzed by the clay present in the condenser walls. Pure carbon monoxide is an excellent atmosphere in which to distil zinc, provided the walls of the apparatus are free of iron.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF DENVER]
A MODIFICATION OF THE SKRAUP SYNTHESIS OF QUINOLINE

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The Skraup synthesis of quinoline occupies a position of interest in organic chemistry because it offers a ready method of synthesis of the quinoline group of compounds.

Several modifications have been proposed since the method was inaugurated in 1880. The most important advance has been the enlargement of the yield. The ferrous sulfate modification is outstanding in this phase of the development.¹ The original Skraup method and all of the modifications to date possess one disadvantage in common. The reaction is usually vigorous and at times violent. Clarke and Davis writing in "Organic Syntheses" say, "In the Skraup synthesis of quinoline the principal difficulty has always been the violence with which the reaction generally takes place; it occasionally proceeds relatively smoothly, but in the majority of cases gets beyond control."¹ The occasional violence of the reaction renders the experiment objectionable as a routine laboratory experiment. The authors have succeeded in eliminating this danger by the addition of acetic acid to the reaction mixture, and have studied the effect of variations in the conditions upon the yield of quinoline obtained.

The safety attained by this modification is attested by the fact that the reaction has been carried out in our Laboratories by large classes of students observing no special precaution and the reaction has never become violent.

During the course of the investigation an unsuccessful attempt was made to render the reaction safe by dilution of the sulfuric acid. The method

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¹ H. T. Clarke and Anne W. Davis, "Organic Syntheses," John Wiley and Sons, New York, 2, 79 (1922).

used to obtain an equivalent dehydrating power of the sulfuric acid can be applied in many types of reactions and is therefore of interest. The method consists of the assumption that the dehydrating power of sulfuric acid is directly proportional to the heat of dilution. A curve very well adapted for the computation of the equivalent amount of the dilute sulfuric acid necessary may be found in a paper by Zeisberg.²

Acetic Acid Modification

The acetic acid modification of the original Skraup method is conducted as follows. The following reagents are weighed out and placed in a liter flask in the order given: aniline, 38 g.; nitrobenzene, 24 g.; glycerol, 100 g.; acetic acid (80%), 60 cc.; sulfuric acid (95%), 54 cc.

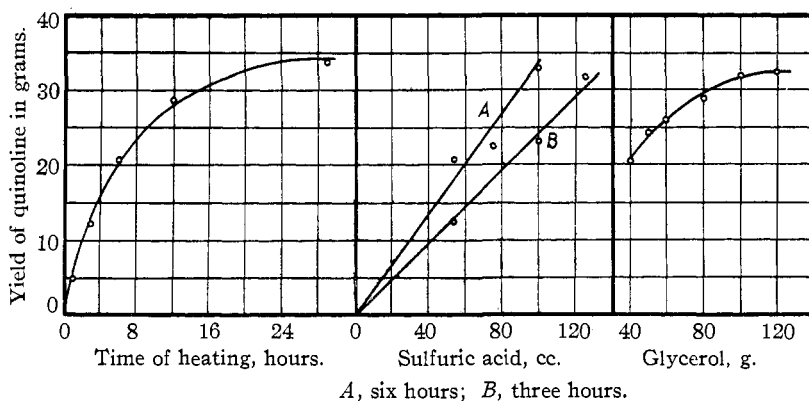


Fig. 1.

Fig. 2.

Fig. 3.

The flask is connected with a water reflux condenser and is heated with a Bunsen flame until the boiling point is reached. (In this modification it is not necessary to remove the flame while the reaction is taking place.) The contents of the flask are then kept simmering for a period of sixteen hours. The flame is removed, the contents are diluted with water and steam is passed through the contents of the flask until the distillate is clear, which shows that all of the nitrobenzene has been removed.

The contents of the flask are cooled, made alkaline with a concentrated solution of sodium hydroxide and again distilled with steam. When the distillate is clear, the current of steam is discontinued. The distillate is next dissolved in sulfuric acid, cooled and sodium nitrite solution is added until a drop of the solution causes a starch-potassium iodide spot to turn blue. The material is allowed to stand for about an hour and is then heated to about 100°, being kept at this temperature until thoroughly steamed out. This usually requires about an hour.

The contents of the flask are allowed to cool, are made alkaline with

² Zeisberg, *Chem. Met. Eng.*, 27, 23 (Fig. 4) (1922).

sodium hydroxide and again steam distilled. As in the preceding cases, the steam is passed in until the distillate comes over clear. The distillate is extracted with ether, the ether is evaporated and the resulting quinoline is weighed. Although in the various processes the material is usually further purified by distillation, in our work the results are based on comparisons of the yield at this stage.

Graphs.—The effect of the time of heating upon the yield of quinoline is shown in Fig. 1. The effect of varying the amount of sulfuric acid is shown in Fig. 2. The effect of the quantity of glycerol upon the yield of quinoline is shown in Fig. 3. The concentration of the acetic acid has no decided effect upon the yield of quinoline.

Theory of Modification

The authors believe and experiments indicate that the violence of the ordinary Skraup reaction is due to the sudden liberation of acrolein resulting from the action of sulfuric acid upon the glycerol. The acetic acid was introduced in an effort to form a glycerol mono or diacetate and thereby remove a large proportion of the glycerol from the reaction sphere. Acetic acid was used because it is quite stable and relatively cheap.

Summary

1. A modification of the Skraup process which may be conducted with safety has been developed.
2. The variation of the yield under different conditions has been studied.

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THE NITRATION OF PIPERONAL

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In a former paper² it was reported that commercial *o*-nitropiperonal yielded two benzylidene derivatives when treated with anthranilic acid in alcohol solution. The one was a yellow crystalline compound melting at 128° and the other yellowish-brown crystals melting at 185°. These two benzylidene products, in turn, reacted with acetic anhydride to form the corresponding nitropiperonylacet-keto-dihydrobenzmetoxazines melting at 206 and 165°, respectively. The conclusion was that Kahlbaum's

¹ Extract from a thesis by Margaret S. Klemme submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Ekeley, Rogers and Swisher, *THIS JOURNAL*, **44**, 1756 (1922). The *o*-nitropiperonal used was Kahlbaum's product. Material from the same lot was used in these experiments.