of Health, and the yields have increased very greatly over those that were obtained prior to the institution of these changes.

Summary

By vigorous agitation of the reacting substances and partial removal of the water produced during the arsonation of phenol by arsenic acid, it is possible to secure a 33% yield of anhydrous sodium *p*-hydroxyphenylarsonate instead of the 20% yield obtained by previous methods.

It is suggested that a phenyl ester of arsenic acid may be an intermediate in the formation of hydroxyphenylarsonic acids by this reaction.

By distillation of aqueous solutions of *p*-hydroxyphenylarsonic acid, with steam, it is shown that at 100° this substance hydrolyzes scarcely at all into phenol and arsenic acid. This confirms Schmitz' results obtained by another method.

Boston 17, Massachusetts

[Contribution from the Department of Pharmacology, Harvard Medical School]

N-METHYL-PARA-AMINO-ORTHO-CHLOROPHENOL SULFATE, A NEW PHOTOGRAPHIC DEVELOPER

By Walter G. Christiansen

Received July 9, 1923

For a number of years N-methyl-*p*-aminophenol sulfate (Metol) has been the outstanding member of the aminophenol class of photographic developing agents, but analogous substances with additional groups attached to the benzene ring have not been investigated to determine the effect of these groups on the photographic developing properties of Metol. In this Laboratory the hydrochloride of *p*-amino-*o*-chlorophenol and the sulfate of its N-monomethyl derivative have been prepared. These compounds possess excellent developing properties when tested on both plates and paper but the methyl derivative is the superior; the finished plates and prints obtained by use of the latter substance are indistinguishable from those secured when Metol is used, but this material shows no marked advantages over Metol. Consequently, it may be concluded that the presence of a nuclear chlorine atom has little influence on the ability of Metol to function as a photographic developer. The amine is methylated by a well-known method, namely, condensation with formaldehyde and reduction of the condensation product.

Experimental Part

p-Nitro-*o*-chlorophenol.[1]—A mixture of 10 g. of c. p. *p*-nitrophenol with 200 cc. of concd. hydrochloric acid is heated in a tall, narrow beaker until solution is complete.

---

[1] The method herein described is a modification of that used by Kollrepp, *Ann.*, **234**, 3 (1886).

The solution is cooled to room temperature while it is stirred mechanically, and the nitrophenol partly separates again in very fine crystals. A special type of stirrer is used, because during the last part of the reaction, that is, after chlorination, the mass in the beaker is a thick paste. The stirrer is constructed from an ordinary T stirrer with long arms by bending the ends of the arms into vertical positions so that they are close to the walls of the beaker. Through a long-stem dropping funnel, the end of which is in the acid and just above the horizontal section of the stirrer, a solution of 3 g. of potassium chlorate in 60 cc. of water is run in slowly while the mixture is vigorously stirred with this device. The nitrophenol dissolves and then the chloro compound starts to separate. As the reaction proceeds, the paste becomes very thick, but the vigorous stirring prevents the end of the dropping funnel from becoming plugged and permits the chlorate solution to run into the mixture. The agitation is continued for 1/2 hour and the mixture is allowed to stand overnight. After filtration, washing with water and air drying, 11 g. of nearly white *p*-nitro-*o*-chlorophenol melting at 106–8° is obtained; the pure compound melts at 110°.[1]

The product can be purified by suspending it in hot water and adding glacial acetic acid gradually until the material dissolves completely. As the solution cools, pure *p*-nitro-*o*-chlorophenol separates.

***p*-Amino-*o*-chlorophenol.**—Sodium hydrosulfite (about 40 g.) is added gradually to a boiling solution of 10 g. of *p*-nitro-*o*-chlorophenol in 60 cc. of water containing 0.27 g. of sodium hydroxide, until the red color disappears. As the solution cools *p*-amino-*o*-chlorophenol precipitates. After this is separated, washed with water and air-dried, 5 g. of compound, m. p.,[2] 150–151°, is obtained as a white powder. By recrystallization from water, the substance can be secured in white needles.

Three g. of the amine is suspended in 25 cc. of water and treated with hydrochloric acid until it dissolves, and decolorizing carbon is added. The colorless solution obtained by filtering out the carbon is added to 35 cc. of concd. hydrochloric acid. After the liquid has been thoroughly cooled, the precipitated hydrochloride of *p*-amino-*o*-chlorophenol is separated, washed with hydrochloric acid and dried in a vacuum over sodium hydroxide. The white solid dissolves very readily in water to give a colorless solution that is acid to litmus but not to congo red. Ferric chloride oxidizes the material with the development of a deep blue color. When a solution of *p*-dimethylamino-benzaldehyde in dil. hydrochloric acid is added to an aqueous solution of the above hydrochloride, the solution becomes orange colored and an orange precipitate separates. In sodium hydroxide solution this amino chlorophenol oxidizes and becomes dark brown.

N-methyl-*p*-amino-*o*-chlorophenol.—A solution of 8.5 g. of *p*-nitro-*o*-chlorophenol in 200 cc. of water and 62.5 cc. of aqueous sodium hydroxide (d., 1.324) in a 500cc. round-bottom flask is heated to boiling. While it is being stirred mechanically, 20 g. of zinc dust is added during 10–15 minutes; this is sufficient to reduce the nitro group and produce a colorless solution. An additional 10 g. of zinc dust is added at once. A 3-hole stopper is inserted into the neck of the flask. Through 1 hole is a glass tube that dips below the liquid in the flask and serves as a sleeve for the stirrer, the second hole permits a reflux condenser to be attached and through the third hole a long-stem dropping funnel is introduced so that the end of the stem is below the surface of the liquid. The liquid is refluxed for 15 minutes and stirred vigorously, and then 5 cc. of formalin (37% formaldehyde) is added during 15 minutes. The refluxing is continued for 15 minutes longer and the solution is filtered through a hot funnel into a flask containing 10 g. of sodium bisulfite.[3] Concd. hydrochloric acid (about 70 cc.) is added until the precipitate that

---

[2] Kollrepp obtained this compound by another method of reduction and found the melting point of the pure substance to be 153°. Ref. 1, p. 6.

[3] The bisulfite prevents the hot alkaline solution from oxidizing and becoming black.

forms is redissolved, and then sodium carbonate is added until the solution no longer effervesces; this requires about 13 g. of sodium carbonate monohydrate. After the mixture has cooled it is extracted with three 50cc. portions of amyl acetate, and the extracts are filtered. By adding sulfuric acid dropwise to the amyl acetate, the amino compounds are precipitated as sulfates which are filtered out and extracted very thoroughly several times with alcohol to remove impurities. After it has dried, 7 g. of crude *N*-methyl-*p*-amino-*o*-chlorophenol sulfate is obtained.

By recrystallization from water, using decolorizing carbon, this substance separates as fine white needles that dissolve in water forming a colorless solution that is acid to litmus. The aqueous solution when treated (a) with ferric chloride becomes red and then very deep purple, (b) with sodium nitrite gives a white precipitate, (c) with sodium carbonate becomes brown.

Analyses. Calc. for $(C_7H_8ONCl)_2H_2SO_4.H_2O$: Cl, 16.45; S, 7.45. Found: Cl, 16.55, 16.25; S, 7.49, 7.45.

I wish to acknowledge the assistance of Mr. Arthur J. Norton in some of the experimental work.

Summary

The preparation of *p*-amino-*o*-chlorophenol hydrochloride and N-methyl-*p*-amino-*o*-chlorophenol sulfate is described. Both of these substances are good photographic developing agents but the methylated compound is the better. The latter compound appears to be equal to but no better than Metol, from which it differs only in having a chlorine atom attached to the benzene ring.

Boston 17, Massachusetts

[Contribution from the Chemical Laboratory, Harvard University]

REDUCTION POTENTIALS OF QUINONES. I. THE EFFECT OF THE SOLVENT ON THE POTENTIALS OF CERTAIN BENZOQUINONES

By James B. Conant and Louis F. Fieser

Received July 11, 1923

The measurement of reduction potentials affords a new method of studying quantitatively the free energy of an addition reaction which can be brought about with a series of related substances. By such quantitative studies the differences caused by substitution and by structural changes can be discovered and when sufficient data have been obtained it should be possible to make many interesting and important generalizations in regard to the driving force of a given organic reaction and the structure of the organic compound concerned.

The normal reduction potential of a quinone is a measure of the free energy of the reduction of that quinone in the solvent employed. It has been found that the normal potential for certain benzoquinones in aqueous solution is affected by the presence of salt[1] and that the potentials of a

---

[1] S. P. L. Sörensen, M. Sörensen and Linderström-Lang, *Ann. chim.*, **16**, 283 (1921).