parts of water at 25°. It crystallizes from water in colorless needles which under the microscope appear as six-sided prisms having roof-like ends. When a solution of mercuric acetate is added to a solution of the salt the resulting solution assumes an intense purple coloration. This color comes gradually, about three minutes elapsing before the full color is developed. In solutions of "Metol" stronger than 1–1000 the production of the color is accompanied by the precipitation of beautiful scales which were found to be mercurous acetate, and the color in this concentration is best described as being very similar to that of ordinary grape juice. The formation of mercurous acetate would indicate that the color is an oxidation product. The color observed by Clark[1] upon treating "Metol" with a solution of ferric chloride, is no doubt also produced by oxidation of the amine, but the color caused by mercuric acetate is many times more intense.

Hydroquinone and the salts of *p*-amidophenol give no color at all when treated with mercuric acetate, and since the color is developed by a very small quantity of "Metol" (a solution 1–100000 giving a very good intensity) this reaction might be used to estimate the compound colorimetrically, and some experiments with the Schreiner colorimeter gave promising results.[2]

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ORGANIC CHEMICAL REAGENTS.[3] III. β-PHENYLHYDROXYLAMINE AND CUPFERRON.

BY C. S. MARVEL AND OLIVER KAMM.

Received December 3, 1918.

The use of organic reagents as precipitants for metals and acids in inorganic analysis is coming more and more to the fore. Among the special reagents of this class that have been introduced recently into analytical chemistry and which have found an ever-increasing application are dimethylglyoxime, cupferron, nitroso-β-naphthol, and nitron. During the past two years the shortage in the supply of the most important reagent of the above group, dimethylglyoxime, has been met by the preparation of several hundred pounds of this product by the Department of Organic Manufacturers of the University of Illinois. Improved directions for this preparation have recently been published[4] for the aid of anyone wishing to undertake the manufacture of this reagent.

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[1] *Loc. cit.*

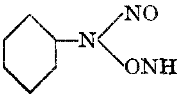
[2] Amidol (C_6H_3-OH-$(NH_2)_2$ 1, 2, 4) gives a somewhat similar color but this is changed to pink on the addition of acetic acid while the purple color produced with "Metol" remains unchanged under similar treatment.

[3] For previous papers in this field see: THIS JOURNAL, 40, 1281, 1950 (1918).

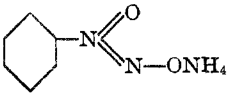
[4] THIS JOURNAL, 40, 1281 (1918).

Cupferron[1] is the next most important reagent to dimethylglyoxime. Its use has not yet been very extensive in laboratories, owing partly to its high price and to the difficulty with which it is made and partly to the fact it is not well known. This communication contains directions for its manufacture which are not only easily carried out in the laboratory but may also be adapted to its technical production. Moreover, the process is so simple that cupferron should be available on the market at a very low figure.

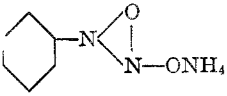
Cupferron is the ammonium salt of *n*-nitroso-β-phenylhydroxylamine,



The formula may be, however,



or



It is prepared from β-phenylhydroxylamine, ammonia, and amyl nitrite according to the method of Baudisch.[2] In previous publications the actual yield of product obtained was not mentioned. Following the procedure of Baudisch, we have obtained in 20 experiments a variable yield of from 60 to 100 g. of cupferron from 240 g. of nitrobenzene. The color of the product varied from white to brown. According to the modified directions given below, a uniform yield of 150 g. of light cream-colored product may be obtained from 240 g. of nitrobenzene.

β-Phenylhydroxylamine.

The preparation of β-phenylhydroxylamine by the zinc-dust reduction of nitrobenzene will be found described in most of the laboratory manuals of organic chemistry. Unusual claims as to yields are made, however, by various authors. Gattermann[3] states that it is almost quantitative; Bernthsen[4] is content with the statement "Yield, practically theoretical;" but in Cohen's "*Practical Organic Chemistry*," on the other hand, is recorded a yield more in accord with actual experimental results.

It may easily be demonstrated that quantitative yields cannot be

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[1] The following articles have already appeared on the uses of cupferron in analytical chemistry: *Chem. Ztg.*, **33**, 1298 (1909); *Z. anorg. Chem.*, **66**, 426 (1910); **68**, 52 (1910); **72**, 94 (1911); *Z. angew. Chem.*, **23**, 969 (1910); *Z. anal. Chem.*, **50**, 35 (1911); *Atti accad. Lincei* **22**, I, 30; *C. A.*, **7**, 1688 (1913); *Gazz. chim. ital.*, **43**, I, 570 (1913); *Am. J. Sci.*, **37**, 173 (1911); **38**, 137 (1912); **42**, 151 (1916); *Anales soc. espan. fis. quim.*, **12**, 379 (1914); *C. A.*, **9**, 2202 (1915); *Chem. News*, **114**, 13 (1916); THIS JOURNAL, **39**, 2358 (1917).

[2] *Chem. Ztg.*, **35**, 913 (1911); *J. Ind. Eng. Chem.*, **3**, 629 (1911).

[3] Translation of 11th German edition (1914).

[4] J. J. Sudborough Translation (1912).

obtained in the usual preparation of β-phenylhydroxylamine by this method. The product is soluble in cold water to the extent of one part in fifty; in a saturated sodium chloride solution its solubility is considerably decreased. Twenty g. of phenylhydroxylamine was dissolved in a liter of water at room temperature, after which the solution was saturated with sodium chloride and cooled to 0°. Eleven g. of product was recovered, thus demonstrating a loss of 9 g. This value agrees with that obtained when phenylhydroxylamine is extracted by means of ether from the mother liquors obtained in the usual preparation. In the method described by Gattermann, the actual yield of *dry* β-phenylhydroxylamine therefore cannot exceed 64% provided no losses occur in manipulation. If, however, ice is added as directed, the volume of the liquors will be larger and the yield correspondingly decreased. The statement that the yield is almost quantitative is therefore incorrect.

It is possible that the inaccuracies concerning the yield of β-phenylhydroxylamine may be traced to the fact that the product obtained in the usual manner retains considerable moisture. A portion of material was filtered with suction, pressed down firmly, and the suction maintained for an hour. A sample which appeared to be fairly dry was then dried to constant weight in a vacuum desiccator over sulfuric acid. The loss of moisture corresponded to 20% of its weight. All of the yields of phenylhydroxylamine recorded in the present work are based upon *dry* weight. Accordingly the yields may appear low, but they can be duplicated.

Effect of Temperature on the Yield of β-Phenylhydroxylamine.—In the reference by Baudisch and King already given, the following statement is made: "Continuous vigorous stirring and the keeping of the temperature within the prescribed limits (15 to 18°) are the essentials which determine a good yield." Other writers recommend that the temperature be maintained below 13 to 15°, and in several instances a temperature below 11° is suggested. Bamberger,[1] however, originally prepared β-phenylhydroxylamine at the temperature of boiling water. A series of experiments was conducted therefore in order to study the effect of variation in temperature upon the yield obtained. The results of experiments made at 7 different temperatures ranging from 10 to 80° C. using 60 g. of nitrobenzene, indicate that the low temperatures usually recommended are unnecessary; they were, no doubt, based upon erroneous ideas traceable to the German patent literature.[2] The best yield of β-phenylhydroxylamine was obtained at a temperature of from 50 to 60°, the actual weight of dry product isolated amounting to 65%, or correcting for the phenylhydroxylamine in the filtrate, 85% of the theoretical amount.

[1] *Ber.*, **27**, 1347, 1549 (1894).

[2] D. R. P. No. 89,978; *Friedlaender*, **4**, 47 (1894–1897).

TABLE I.—YIELDS OF β-PHENYLHYDROXYLAMINE. 60 G. NITROBENZENE USED.

Expt. No.	Temperature.	Volume of filtrate and washings. Cc.	Yield of *dry* product. G.
1	10°	2000	23
2	20	1400	27
3	30	1450	29
4	40–50	1250	32
5	50–60	1250	36
6	60–70	1400	32
7	80	1300	33

The relatively large volume of the filtrate in Expt. 1 is due to the addition of ice in order to maintain the temperature at 10°. Solubility corrections, however, fail to bring the yield up to that obtained at a temperature of from 50° to 60°. Temperatures above 60° produce a slightly decreased yield of product, due no doubt to the formation of appreciable quantities of aniline. Products obtained at temperatures above 60° possess a brownish color, so that a temperature of from 40 to 60° is to be recommended.

The advantages of reducing nitrobenzene at a temperature higher than that ordinarily given in laboratory directions are: (*a*) the time required for the reduction is considerably reduced; (*b*) less attention is required during the reduction; (*c*) less wash water is required since the product is more soluble in the warm solution, and therefore less is held in the zinc oxide; (*d*) the yield of product isolated is increased.

Directions for the Preparation of β-Phenylhydroxylamine.—The following directions have been found convenient for the preparation of β-phenylhydroxylamine by the reduction of nitrobenzene in $^1/_2$ kg. portions.

Eight liters of water, 500 g. of nitrobenzene, and 250 g. of ammonium chloride are placed in a 4-gallon earthenware jar. The mixture is stirred vigorously by means of an efficient mechanical stirrer, and 670 g. of zinc dust (75–80%) is sifted into the reaction mixture during the course of 15 to 20 minutes. As the reduction proceeds, the temperature gradually rises to 50 or 60°. In order to obtain a light-colored product it is advisable to maintain the temperature below 60°, and this may be done best by the addition of small portions of cracked ice. Usually less than one kilo of ice is required.

After the zinc dust has been added the stirring is continued for 15 minutes longer. The end of the reaction is indicated by the fact that the temperature of the reaction mixture no longer rises. Stirring is continued for 5 minutes longer, after which the phenylhydroxylamine solution is filtered from the zinc oxide by means of suction and the residue washed with about one liter of warm water.

The filtrate, which should measure not more than 10 liters, is placed in an enamelled pan, saturated with common salt, and cooled to 0°.

The phenylhydroxylamine begins to crystallize out even at 30°. The yield of product after filtration by suction amounts to from 330 to 390 g. The average yield of *dry* product is 290 g., which corresponds to 64% of the theory. For the preparation of cupferron, it is, however, unnecessary to use dry phenylhydroxylamine.

Notes.—The method as given above is no doubt adaptable to the preparation of larger quantities of β-phenylhydroxylamine than indicated in the above run, in which case it may be advantageous to lower the proportion of water used. No doubt an appreciable loss of phenylhydroxylamine occurs, due to absorption in the zinc oxide mass, a loss which could be partly obviated by the use of pressure filtration.

Reduction of 500 g. of nitrobenzene may be effected even in 15 minutes, a result that cannot be attained by reduction at lower temperatures.

Cupferron.

Cupferron may be prepared from β-phenylhydroxylamine by dissolving the latter in ether, saturating the solution at 0° with ammonia gas, and adding the theoretical quantity of amyl nitrite. This method was presented by Baudisch,[1] who suggested that ammonia gas be passed into the ether solution during 10 minutes. Variable yields and colored products result when these directions are followed literally. When the ether solution is actually *saturated* with ammonia gas, good yields of a light cream-colored product are invariably obtained. An additional modification of the Baudisch method in order to adapt the method to production on a larger scale is recorded below under the heading "Preparation of Cupferron."

Several attempts have been made to produce cupferron without the use of ether as a solvent, without the isolation of phenylhydroxylamine, and by substitution of sodium nitrite for amyl nitrite. In a few instances fair yields were obtained in these experiments, but the quality of the product was always inferior in color and this color could not be removed. This method therefore is not recommended, although further development particularly in attempting to get the product white might give valuable results. Brief mention of some of these experiments is made here for the benefit of anyone who may wish to study further the possibilities involved.

Expt. 1.—Nitrobenzene was reduced to β-phenylhydroxylamine in the manner already described. The filtrate from the zinc oxide was cooled to 0°, the theoretical amount of hydrochloric acid added, and the *n*-nitroso-β-phenylhydroxylamine precipitated[2] by the addition of the theoretical amount of sodium nitrite solution. Without filtering, the precipitate of "cupferron acid" was redissolved by the addition of a slight

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[1] *Loc. cit.*

[2] Wohl, *Ber.*, 27, 1435 (1894).

excess of ammonium hydroxide and the cupferron precipitated by saturating the solution with ammonium chloride. The product, although crystalline, was poor in color and the yield was low.

Expt. 2.—The preceding experiment was repeated with a sample of β-phenylhydroxylamine which had been salted out and redissolved in distilled water. Results were as in Expt. 1.

Expt. 3.—Expt. 1 was repeated but the "cupferron acid" (*n*-nitroso-β-phenylhydroxylamine) was immediately filtered off with suction, dissolved in ether, and cupferron precipitated by passing ammonia gas into the ether solution. From 480 g. of nitrobenzene 285 g. of cupferron were obtained, but the product possessed a yellow color.

Expt. 4.—*n*-Nitroso-β-phenylhydroxylamine, when first precipitated, possesses a light color but soon becomes reddish brown. In order to avoid exposure to air during filtration which occurred in Expt. 3, the product was extracted by means of ether, and then the cupferron precipitated with ammonia gas. The color of the product was again unsatisfactory, although the yield was almost 300 g. from 480 g. of nitrobenzene.

Preparation of Cupferron.

The moist β-phenylhydroxylamine obtained from 725 g. of nitrobenzene by the method already described is weighed and dissolved in 3 liters of ordinary ether. The ether-insoluble material (sodium chloride) is also weighed, the difference between the two weighings being a fairly accurate measure of the amount of β-phenylhydroxylamine in solution.

The ether solution is filtered through a dry filter paper into a 5-liter, round-bottom flask. The flask is fitted with an efficient mechanical stirrer, and is immersed in an ice-salt bath. When the temperature of the solution has fallen to 0°, a rapid stream of dry ammonia gas (from a cylinder of compressed gas) is passed into the solution. After about 15 minutes, the theoretical quantity of freshly distilled amyl nitrite (107 g. for every 100 g. of β-phenylhydroxylamine) is added slowly through a dropping funnel. The addition of amyl nitrite usually requires about $^1/_2$ hour, during which time the stream of ammonia gas is continued in order that ammonia will always be in excess. If this precaution is not observed a colored product will result. The temperature of the reaction mixture should be maintained below 10° and this temperature may be maintained best by controlling the rate at which the amyl nitrite is added. An appreciable rise in temperature will cause the volatilization of considerable quantities of ether and of ammonia.

After the amyl nitrite has been added the reaction mixture is stirred for about 10 minutes longer in order to insure completion of the reaction, after which the cupferron is filtered off and washed several times with small portions of fresh ether. The product is spread on sheets of paper until all traces of ether have been lost and is then stored in bottles where it is exposed to the vapors of ammonium carbonate. This may be done by protecting each cork with a double sheet of filter paper and placing a lump of ammonium carbonate between the cork and the filter paper.

The yield of cupferron from a given weight of β-phenylhydroxylamine averaged 80 to 90% of that theoretically possible. Since the yield of β-phenylhydroxylamine from nitrobenzene is about 65%, the yield of cupferron from nitrobenzene is about 50% of the theoretical.

Notes.—In the preparation of cupferron, Baudisch and King have recommended that the amyl nitrite be added all at one time. This procedure is satisfactory only when the amount of phenylhydroxylamine used is less than 200 g., otherwise the reaction becomes extremely vigorous and an excessive proportion of ether is lost. The directions given above, on the other hand, should prove adaptable for the preparation of large quantities of cupferron. For the rapid preparation of small quantities of material the amyl nitrite may be added all at one time, provided sufficient excess of ammonia is present. The solvent ether may be replaced by benzene, but this modification offers no advantages for the preparation of cupferron on a laboratory scale.

In the experiments described above, it is found that 75% of the ether and 95% of the amyl alcohol used may be recovered and one man working 6 to 7 hours is able to prepare 800 g. of cupferron. It is found that, even with the present high cost of chemicals and labor, cupferron may be prepared at considerably less than the pre-war price. The present price, moreover, is based on the production in the laboratory where the labor charge is fully 30% of the total cost. It is, therefore, evident that when prepared on a technical scale with normal prices for raw materials, cupferron should be very cheap and may become not only a very common laboratory reagent but also find technical application other than as a precipitant in analytical chemistry.

URBANA, ILL.

[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE TRANSLOCATION OF THE MINERAL CONSTITUENTS OF THE JACK BEAN.[1]

BY G. DAVIS BUCKNER.

Received December 5, 1918.

Introduction.

In a previous communication[2] from this laboratory, experiments were described concerning the translocation of the mineral constituents dur-

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[1] Published by permission of the Director of the Kentucky Agricultural Experiment Station.

[2] G. Davis Buckner, "Translocation of Mineral Constituents of Seeds and Tubers of Certain Plants during Growth," *J. Agri. Res.*, **5**, 449 (1915).