difference would probably not be observed in lithium salt solutions.

Summary

1. The influence of fluoride, chloride, borate and hydroxide ions on the glass electrode has been studied.

2. No negative ion as such appears to affect the alkaline errors of the glass electrode, but in certain cases these errors in solutions of high pH are greatly increased if the glass surface is exposed to one normal fluoride solutions having pH values lower than 7.0.

3. A new Beckman sodium-error free glass electrode has been investigated in one normal sodium solutions. In agreement with unpublished data of Dr. Beckman and his co-workers we find the sodium errors to be materially reduced by this new kind of glass.

The Preparation of Symmetrical Biaryls by the Action of Reducing Agents on Diazotized Amines. Reducing Agents

By Edward R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball and E. R. Read

In beginning our detailed study of the reaction outlined in an earlier paper,[1] we have selected as a standard diazotized amine that derived from anthranilic acid and have examined its conversion to diphenic acid by the action of a number of reducing agents. This paper reports our results using those containing cuprous copper. For each we have determined the necessary mole ratios and concentrations. Where reducing agents had been used in this reaction by previous workers, their stated procedures were in general followed at first, but desirable modifications were made in all cases and the procedures given in the experimental part of this paper represent those which we have found to be the optimum.

Experimental Part

General Experimental Procedure.—With the exception of the work using solutions of cuprous chloride in hydrochloric acid, the reactions were carried out by suspending or dissolving the reducing agent in the appropriate solvent (dilute ammonium hydroxide in most cases) and then adding the diazonium solution to the well-stirred reducing solu-tion by means of the addition tube already described.[1] If desirable, the reaction mixture was cooled by immersion in an ice-bath. At the conclusion of the reaction the solution was acidified with concentrated hydrochloric acid at a temperature specified for the individual case.

Hydrated Cuprous Oxide in Dilute Ammonium Hydroxide.—A mixture of hydrated cuprous and ferric oxides, prepared by the action of ferrous sulfate on ammoniacal solutions of cupric sulfate as described by Vorländer and Meyer,[2] was used in three experiments; the procedure and quantities of materials were as specified by these workers. Impure diphenic acid, m. p. 215–225°, was obtained in 57% yields.

When cuprous chloride was converted to the hydrated oxide by the action of aqueous sodium hydroxide as described by Huntress[3a] and the oxide so prepared used as described below, the results were essentially the same as those obtained by Huntress; a tarry by-product was often present and in one experiment we isolated o-chlorobenzoic acid from the lower melting by-products. Since acetic acid had been used in diazotization, the reducing agent was analyzed for chloride and was found to contain 80–90% unconverted chloride. This was the case even when freshly precipitated cuprous chloride had been used. By

(1) Atkinson and Lawler, This Journal, **62**, 1704 (1940).

(2) Vorländer and Meyer, Ann., **320**, 122–144 (1902).

(3) (a) Huntress, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, page 216; (b) This Journal, **55**, 2561 (1933); (c) **55**, 4268 and 4270 (1933).

the dropwise addition of an equivalent of 6 N sodium hydroxide to a well-stirred aqueous suspension of the chloride, we prepared the hydrated oxide essentially free of chloride. The method of Hodgson and Crook[4] and the slow addition of a solution of cuprous chloride in hydrochloric acid to an excess of base also gave chloride-free oxide but were unnecessarily complex. The use of a wetting agent had no detectable effect. The use of chloride-free hydrated oxide did not increase the yields of diphenic acid which were about 60% but did give a cleaner product.

Quantities of materials used were one-tenth those specified by Huntress.[3a] Hydrochloric acid was used for diazotization in many experiments without affecting the yield of diphenic acid. The treatment with saturated ammonium chloride solution was at the boil; the crude was also leached with 50 cc. of boiling water to remove lower melting by-products. Fifteen per cent. of the original crude was lost in this way. The leachings deposited a solid on cooling which consisted of 25% diphenic acid; this was not recovered. The leached crude had m. p. 215–225°. Final purification was as described by Huntress; during this step it was noticed that 10% of the leached crude was insoluble in the glacial acetic acid. This portion was a yellow solid, m. p. 303–304° decompn., and was identified as diphenylamine-2,2'-dicarboxylic acid by conversion[5] to acridone-4-carboxylic acid, m. p. 325–328°. Experiments carried out at a number of temperatures between 0 and 80° showed the lower temperatures to be preferable.

Hydrated Cupric Oxide in Dilute Ammonium Hydroxide.—To determine whether or not reducing agents were essential for this reaction the procedure used for the hydrated cuprous oxide was followed, using the material obtained by the action of sodium hydroxide on a solution of 33 g. of cupric chloride dihydrate. Because of the gelatinous nature of the material, it was suspended in 100 cc. of water and 60 cc. of concentrated ammonium hydroxide. Nitrogen was evolved as usual but acidification precipitated a much smaller quantity of solid. This was leached with boiling water. That portion insoluble in water proved to be diphenylamine-2,2'-dicarboxylic acid (0.7 g.). When the aqueous leaching cooled, 0.5 g. of benzoic acid crystallized out. The mother liquor gave an intense coloration with ferric chloride, indicating the presence of salicylic acid. No diphenic acid was detected.

Cupro-ammonia Ion in Dilute Ammonium Hydroxide.—These solutions were prepared by three essentially different methods; since they differed in composition the use of each in the biaryl synthesis was examined.

Method 1.—Five grams (0.036 mole) of anthranilic acid was diazotized in the usual way using 90 cc. of water, 18.5 cc. of concentrated hydrochloric acid and 2.63 g. (0.036 mole) of sodium nitrite dissolved in 53 cc. of water; the solution was filtered before use. Seven cc. of glacial acetic acid was sometimes used in place of the hydrochloric acid; no change in the yield of diphenic acid was noted.

A crystalline cupro-ammonia-sulfite complex was prepared by passing sulfur dioxide into an ammoniacal solution of cupric sulfate as described by Vorländer and

Meyer[2]; the decolorization of the solution was taken as the criterion of saturation. It was noticed that the amount of complex forming varied from one experiment to another, giving rise to erratic results. In contrast to the procedure of previous workers[2,3b,3c,6,7,8a] we chilled the solution, added a small amount of alcohol to facilitate precipitation and filtered off the complex. After washing with alcohol it was dried at room temperature. About 50–55 g. could thus be prepared from 25 g. of hydrated cupric sulfate. The complex was stable for four or five days if kept in a closed vessel. Samples of the solid from a number of preparations were dissolved in ammonium hydroxide solution and air passed in for two hours. The solutions were then analyzed for cupric copper by a colorimetric method,[9] using a photoelectric colorimeter. Values for cupric copper were between 13.2 and 14%. Results were reproducible for a given preparation. Similar analyses made on samples where oxidation was avoided showed approximately 2.7% cupric copper. For purposes of calculating mole ratios we assumed that the complex contained about 10.7% of cuprous copper.

Forty-three grams of the complex, containing 0.072 mole of cuprous copper, was dissolved in 65 cc. of concentrated ammonium hydroxide and 70 cc. of water. The diazonium solution was added during twenty minutes; temperature of the solution was 0–5°. No foaming occurred. The solution was acidified at room temperature and air passed through for two hours. The white or cream-colored diphenic acid was washed on the filter with water; it melted at 227–230° and was obtained in 80% yields.

If the value of the mole ratio Cu^+/RN_2X was less than unity the yield was greatly decreased. Similar results were obtained when 9.2 g. (0.073 mole) of anhydrous sodium sulfite was also dissolved in the reducing solution. Reducing solutions prepared by dissolving 10 g. of sodium sulfite and either 2 g. or 20 g. of hydrated cupric sulfate in the usual amount of water and ammonium hydroxide brought about the formation of no diphenic acid. Cupriammonia solutions were prepared by dissolving copper wire in nitric acid and then adding ammonium hydroxide. When sodium sulfite was added to these no decrease in the cupric copper content was observed by use of the colorimetric method. All of these results indicate the necessity for an adequate initial quantity of cuprous ion. Sulfite present in the complex does not regenerate the cuprous ion component after its destruction by the diazo compound, as alleged by Vorländer and Meyer.[2]

When the usual amount of complex was used but its concentration in the reducing solution doubled, yields fell to 60%. When 86 g. of complex was used, the volume of solution being the same or doubled, an 85% yield of diphenic acid was obtained. Lower yields were obtained as the temperature at which the reaction proceeded was raised.

Method 2.[2,7,8b]—Five grams (0.036 mole) of anthranilic acid was diazotized in the usual way using 9.2 cc. of concentrated hydrochloric acid, 15 cc. of water and a solution of 2.63 g. of sodium nitrite in 35 cc. of water.

(4) Hodgson and Crook, *J. Chem. Soc.*, 571 (1937).

(5) Ullmann, *Ann.*, **355**, 354 (1907).

(6) Hunn, THIS JOURNAL, **45**, 1028 (1923).

(7) German Patent 445,390, *Friedlander*, **15**, 300 (1928).

(8) (a) Cumming and Muir, *Chem. Abstr.*, **30**, 4491 (1936); (b) **31**, 4310 (1937).

(9) Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1936, Vol. I, p. 143.

Twelve and six-tenths grams (0.05 mole) of hydrated cupric sulfate was dissolved in 50 cc. of water and 21 cc. of concentrated ammonium hydroxide. To this solution there was added a solution of 3.55 g. (0.051 mole) of hydroxylamine hydrochloride (or an equivalent amount of commercial hydroxylammonium sulfate) in 8.5 cc. of 6 N sodium hydroxide and 12 cc. of water. This reduction was carried out just prior to use. The diazonium solution was added during fifteen minutes; temperature was about 10°. No foaming occurred. The solution was carefully acidified at the boil, and crystalline diphenic acid m. p. 226–230°, was precipitated in yields of 90%. When acidification was performed at room temperature the product was always stained yellow. The foregoing procedure has been carried out using as much as 50 g. of anthranilic acid. It is recommended for the preparation of diphenic acid.

When 5 g. of cupric sulfate (0.55 mole per mole RN₂X) and 2.8 g. of hydroxylamine hydrochloride (1 mole per mole RN₂X) was used the yield fell to 33%. When both the above ratios were slightly greater than unity, the yield was normal. When a four-fold excess of hydroxylamine was used the product melted at 217–227° and was obtained in yields of 75%. When the diazonium solution was diluted with 85 cc. of water, or when the reducing solution was diluted with 100 cc. of water the yield was normal and the product was lighter in color. This latter observation confirms a similar one of Vorländer and Meyer.[2]

Method 3.—Five grams of anthranilic acid was diazotized as described for Method 2, with the exception that an additional 85 cc. of water was present during diazotization. Ten and seven-tenths grams (0.11 mole) of purified cuprous chloride was partially dissolved in 25 cc. of concentrated ammonium hydroxide and 100 cc. of water. The diazonium solution was added during thirty minutes; temperature was about 5–10°. No foaming occurred. Acidification was at room temperature. Diphenic acid, m. p. 224–230°, was obtained in 82% yield. If acidification was at the boil the product was discolored.

When 60 cc. of concentrated ammonium hydroxide was used the product contained 10% of diphenylamine-2,2′-dicarboxylic acid. This product was also obtained, along with a small amount of diphenic acid, when the solvent for the cuprous chloride consisted exclusively of concentrated ammonium hydroxide. This is the first recorded use of cupro-ammonia solutions prepared by this method. Our study was prompted by the successful use of the "cuprous hydroxide" of Huntress[3a] which we found consisted of 90% cuprous chloride.

Cuprous Ion in Dilute Hydroxylamine.[2]—Five grams of anthranilic acid was diazotized as described in Method 3 of the preceding section. Thirteen and seven-tenths grams (0.055 mole) of hydrated cupric sulfate was dissolved in 50 cc. of water and to this solution there was added a solution of 16.7 g. (0.24 mole) of hydroxylamine hydrochloride in 40 cc. of 6 N sodium hydroxide and 40 cc. of water. The hydroxylamine used was so selected as to reduce the cupric ion and remain in reasonable excess. The diazonium solution was added during thirty minutes; temperature was about 10–15°. Troublesome foaming occurred. Acidification was at the boil. Pale yellow or white diphenic acid, m. p. 226–230°, was obtained in 70% yield.

If acidification was at room temperature the product was colored orange and had m. p. 180–220°. When 26 g. of cupric sulfate and 21 g. of hydroxylamine hydrochloride was used the product was contaminated with copper salts.

Cuprous Chloride in Hydrochloric Acid.—The procedure described by Ullmann[10a] for the treatment of diazotized o-nitroaniline was followed in every detail. Evolution of nitrogen stopped when but 10 cc. of the cuprous chloride solution had been added. Fourteen grams of o-chloronitrobenzene (89% yield) was obtained. The product not volatile with steam was recrystallized twice from benzene-ligroin, once from dioxane and was finally sublimed at 10 mm.; 0.5 g. of yellow crystals, m. p. 146–149°, was obtained, along with tars. The solid was not identified.

In each of four experiments the procedure of Ullmann[10b] for the treatment of diazotized m-nitroaniline was followed. As noted above the specified amount of cuprous chloride was not needed, although all was used in our work. Fourteen grams of m-chloronitrobenzene (40% yield) was obtained. In a fifth experiment the procedure as above for o-nitroaniline was used; m-chloronitrobenzene was obtained in 67% yield. In all this work the product not volatile with steam was a tar which on drying weighed 10–15 g. By a process of recrystallization from acetone and sublimation we were able to isolate 1 g. of cream-colored solid, m. p. 191–200°; recorded[11d] for 3,3′-dinitrobiphenyl, m. p. 200°.

The procedure used above with m-nitroaniline was employed with p-nitroaniline in three experiments. Forty per cent. yields of p-chloronitrobenzene were obtained, along with tars. The procedure used with o-nitroaniline as described above gave a 60% yield, with tars. No crystalline product could be isolated from the tars.

In each of five experiments 10 g. of anthranilic acid was diazotized in the usual way using 20 cc. of water, 38 cc. of 6 N hydrochloric acid and 5.4 g. of sodium nitrite in 20 cc. of water. Eight grams of cuprous chloride was dissolved in 35 cc. of concentrated hydrochloric acid and the solution added slowly with stirring to the cold diazonium solution. When 10 cc. had been added there was a vigorous evolution of nitrogen and a cream-colored solid, mixed with a red tar, appeared. In two experiments the solution was filtered at this point; addition of the balance of the cuprous chloride solution caused no further change and the products in all experiments were the same. The solids were washed with water, saturated ammonium chloride solution, and finally with water; the tar was removed mechanically. The crystalline portion weighed about 8 g., m. p. 136–138°; it was recrystallized from hot water and identified as o-chlorobenzoic acid, m. p. 140°. The tarry product weighed about 2 g. and when heated at 10 mm. and 50° about half sublimed and proved to be o-chlorobenzoic acid. The balance could not be crystallized; it was easily soluble in acetone.

Although it has been repeatedly claimed[11] that the procedure of Ullmann gives no biaryl, we nevertheless carried out the above study because some workers seem to have

(10) (a) Ullmann and Forgan, *Ber.*, **34**, 3803 (1901); (b) Ullmann and Frentzel, *ibid.*, **38**, 725 (1905).

(11) (a) Dennett and Turner, *J. Chem. Soc.*, 480 (1926); (b) Emde, *Apoth. Ztg.*, **30**, 293 (1915); (c) Wohlfart, *J. prakt. Chem.*, [2] **65**, 296 (1902); (d) Brydowna, *Chem. Abstr.*, **22**, 2372 (1928).

overlooked the fact that Ullmann's technique was the reverse of that used in the Sandmeyer reaction.

Summary

1. When suitable experimental techniques are employed, ammoniacal suspensions of hydrated cuprous oxide or solutions of cuproammonia ion are excellent reducing agents for the conversion of diazotized anthranilic acid to diphenic acid; yields as high as 90% are obtained.

2. The initial value of the ratio Cu^+/RN_2X should be unity or higher with all reducing agents. Concentration of cuprous ion in the reducing solution is not a critical factor.

3. The use of a solution of cuprous chloride in hydrochloric acid as recommended by Ullmann gives little or no biaryl but large yields of the Sandmeyer type product.

4. Cupri-ammonia solutions do not convert diazotized anthranilic acid to the biaryl.

The Introduction of Substituted Vinyl Groups. VII. ·Alkylidene and Substituted Vinyl Alkylmalononitriles

BY ARTHUR C. COPE AND KATHRYN E. HOYLE

The practicality with which a variety of substituted vinyl alkylmalonic and cyanoacetic esters can be prepared by the alkylation of alkylidene esters[1] has led us to investigate the application of this synthetic method in the malononitrile series.

Alkylidene Malononitriles.—Although a number of aromatic aldehydes have been condensed with malononitrile to form arylidene derivatives,[2] $ArCH=C(CN)_2$, the corresponding reaction of certain aliphatic aldehydes[3] and ketones[4] has been reported to produce alkylidene bismalononitriles, dimeric alkylidene malononitriles or other complex substances. Cyclohexanone,[2] acetone[5] and diethyl ketone[4] have been reported to form simple alkylidene malononitriles, $R_2C=C(CN)_2$, all of which were said to be crystalline solids melting between 165 and 175°.

We have condensed cyclohexanone with malononitrile in the presence of piperidine, acetic acid, piperidine acetate and ammonium acetate, and in each case obtained a liquid product, b. p. 137–138° (10 mm.). This product was proved to be cyclohexylidene malononitrile by ozonization, which produced cyclohexanone, and by its alkylation to 1-cyclohexenyl ethylmalononitrile, described below. The crystalline solid of m. p. 173.5–174.5° previously described as cyclohexylidene malononitrile[2] may have been a dimer or polymer of this substance.

Acetone, diethyl ketone and methyl propyl ketone were also condensed with malononitrile in the presence of piperidine acetate or ammonium acetate to give alkylidene derivatives, all of which are liquids. The liquid, monomeric isopropylidene malononitrile was obtained by condensing acetone with malononitrile in the presence of piperidine acetate and a large excess of acetic acid. It is very sensitive to traces of piperidine, in the presence of which it polymerizes to a crystalline dimer, m. p. 168–170°, which corresponds in properties to the product obtained by Schenck and Finken[5] from the reaction of acetone with malononitrile in the presence of potassium ethoxide. On the basis of molecular weight determinations in acetic acid, they concluded that their freshly prepared solid, m. p. 171.5°, was monomeric isopropylidene malononitrile, which on standing for two years changed into a dimer. Only very approximate molecular weight determinations supported this conclusion, however, for the solid is quite insoluble in acetic acid, and their observed freezing point depressions were small and variable. Cryoscopic molecular weight determinations on our solid product in dioxane and acetophenone solution proved it to be dimeric.

While monomeric alkylidene malononitriles were obtained from aliphatic ketones, the condensation of isovaleraldehyde with malononitrile gave a colorless liquid product which changed rapidly on standing into a red, viscous polymer, and was not investigated further.

(1) THIS JOURNAL, **62**, 314 (1940), and preceding papers.

(2) Cf. Corson and Stoughton, ibid., **50**, 2825 (1928).

(3) Diels, Gärtner and Kaack, Ber., **55**, 3439 (1922).

(4) Östling, Oeversikt Finska Vetenskaps-Soc. Forh., **57A**, No. 11 (1915); Chem. Abstr., **15**, 2829 (1921).

(5) Schenck and Finken, Ann., **462**, 267 (1928).