and a saturated aliphatic hydrocarbon, possibly butane. Diethyl succinate behaved like diethyl oxalate when heated with anhydrous zinc chloride.

Diethyl Malonate.—From one-fourth mole of diethyl malonate which had been refluxed with anhydrous zinc chloride for three hours we obtained 6 g. of ethyl acetate, 6 g. of unchanged ester and carbon dioxide; 0.2 g. of ethylene dibromide was secured. In a check run we isolated 8 cc. of a liquid which had the boiling point and other properties of *n*-pentane. Evidently two types of decomposition occurred—one involved the removal of both ethylene and carbon dioxide from one of the ester groups and the other involved the elimination of carbon dioxide from each ester group.

Summary

When ethyl formate, acetate, propionate and *n*-butyrate are heated with anhydrous zinc chloride each ester remains unchanged. Under similar conditions diethyl *o*-phthalate gives phthalic anhydride and ethylene, and ethyl benzoate yields benzoic acid, benzene and ethylene. Ethyl salicylate is transformed into phenol and *o*-ethylphenol through the loss of ethylene and carbon dioxide. From methyl benzoate we obtained benzoic acid and benzene, and from methyl salicylate we secured *o*-cresol and carbon dioxide. Anhydrous zinc chloride splits *iso*-amyl acetate, *n*-butyrate and benzoate into the corresponding acids and *iso*propylethylene, and polymerizes some of the latter. Ethyl cinnamate yields styrene, distyrene, metastyrene, carbon dioxide and ethylene. Diethyl malonate gives ethyl acetate, *n*-pentane, ethylene and carbon dioxide. Anhydrous zinc chloride reacts with diethyl oxalate forming ethyl chloride and a zinc salt; some of the ester is decomposed into carbon dioxide and a saturated aliphatic hydrocarbon. Diethyl succinate behaves like diethyl oxalate.

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SKRAUP'S REACTION APPLIED TO THE PHENYLENEDIAMINES. PREPARATION OF THE PHENANTHROLINES AND RELATED DIPYRIDYLS

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The Skraup reaction as applied to monoamines has proved to be a valuable synthetic method, but the double Skraup reaction, either in the original or in a modified form, applied to diamines, has generally given unsatisfactory results, especially with *p*- or *m*-phenylenediamine. It seems that either no attempts have been made to apply the reaction to *o*-phenylenediamine or, more probably, that no pure compounds were isolated from the resulting products and hence the results were not reported.

The writer has studied the production of phenanthrolines from the phenylenediamines and has found that results which compare favorably with the average monoamine as to yield and ease of purification can be obtained with the *m*- and *p*-diamine. *o*-Phenylenediamine, however, did not give *o*-phenanthroline but a compound, $C_{12}H_8N_2O$, crystallizing in deep, yellow colored needles. This compound was oxidized to a carboxylic acid which, on heating, loses carbon dioxide, forming a colorless base not identical with α,α-dipyridyl. *o*-Phenanthroline could not be separated from the Skraup reaction products, although it might have escaped detection, because of the large amount of amorphous products formed and the lack of information in regard to the properties of *o*-phenanthroline, which had not then been prepared.

According to Richter's "Organic Chemistry,"[1] *o*-phenanthroline is obtained from *o*-aminoquinoline, but no reference or description is given. α-Methyl-*o*-phenanthroline, however, has been prepared from 1-amidoquinaldine.

A. Kaufmann and Radoslav Radosevic[2] concluded that *p*-phenanthroline can be obtained only in small yield from *p*-phenylenediamine. They preferred to employ the corresponding aminoquinoline prepared from *p*-nitroaniline.

As the result of a study of the Skraup reaction, as applied to *m*- and *p*-phenylenediamines, with arsenic acid as the oxidizing agent, the conclusion has been reached that the important factors are water concentration and the method and time of heating. It is important to start the digestion with a high water concentration and to permit the gradual escape of water vapor as the reaction proceeds. There is a limited range of water concentration that is optimum; at a greater concentration the proper reaction will not take place at all and at a lower concentration the reaction is too vigorous for good results. This regulation of concentration is conveniently effected by using short air condensers; water condensers are used only toward the end of the reaction when the danger of tar formation is greatest.

A violent reaction is not permissible as with aniline and some other amines. The *m*- and *p*-diamines differ in behavior to such an extent that a method applicable to one is not suitable for the other. For example, in the case of *m*-phenylenediamine the reaction starts at a low water concentration and the temperature can be slowly elevated. Such treatment is not suitable for the *p*-diamine reaction. *o*-Phenylenediamine is a highly reactive substance, sensitive to oxidizing agents and subject to ring closure between the amino groups. Highly colored tarry products were always obtained from this compound, which yielded only a small amount of the yellow crystalline compound previously mentioned.

In following the directions of Skraup and Vortmann[3] in the preparation

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[1] Vol. III, p. 207, English translation of 11th German edition.

[2] A. Kaufmann and Radoslav Radosevic, *Ber.*, **42**, 2612 (1909).

[3] Skraup and Vortman, *Monatsh.*, **3**, 571 (1882).

of *m*-phenanthroline and the corresponding dicarboxylic acid and dipyridyl the writer obtained results similar to those of Blau.[4] The methods given below improve the yields and ease of manipulation of this phenanthroline as well as the *p*-phenanthroline and the corresponding derivatives.

The only sources of the α,β- and β,β-dipyridyls have been the corresponding phenanthrolines. If the *o*-phenylenediamine could be made to produce *o*-phenanthroline in good yield, it might prove to be a convenient method of preparing α,α-dipyridyl. The negative results so far obtained from the *o*-diamine and the poor yield obtained from the *o*-aminoquinoline do not offer much promise. The writer has prepared α,α-dipyridyl conveniently from the sodium and pyridine reaction.[5] It can also be formed in less than 15% yield by heating copper picolinate[6] or by heating pyridine in sealed tubes under pressure with ferric chloride.[7]

It has usually been assumed that acrolein is produced in the Skraup reaction and that this first condenses with the amino group and is then oxidized with ring closure. No instance has been recorded in which an intermediate product of acrolein with the amine has been isolated which can be further changed to the end-product.

Mann[8] attempted to prepare quinoline from the acrolein–aniline condensation product, with a negative result. The author, using the *m*-phenylenediamine condensation product, did not succeed in obtaining any phenanthroline. While the experiments with acrolein were conducted in an attempt to improve yields, they are of interest in considering the mechanism of the Skraup reaction.

The *p*-phenylenediamine gave better yields by the recommended procedure than the *m*-diamine, which is commonly regarded as the easier to manipulate. By the addition of alkali previous to oxidation with permanganate, the yield of dicarboxylic acid from either phenanthroline is more than doubled. A nearly quantitative yield of β,β-dipyridyl results when the dicarboxylic acid is heated in glycerine suspension. This method does not work well with α,β-dicarboxylic acid. In this case the elimination of one carboxyl group is effected by heating in an oil-bath at 200°, while the remaining one is removed by heating to a higher temperature. The yield of α,β-dipyridyl is nearly quantitative.

The writer prepared *o*-phenanthroline from *o*-aminoquinoline with some difficulty and found it to be similar to the isomeric phenanthrolines. This reaction might be considerably improved. The yellow compound $C_{12}H_8N_2O$ from *o*-phenylenediamine was obtained with such difficulty

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[4] Blau, *Monatsh.*, **13**, 330 (1892).

[5] C. R. Smith, This Journal, **46**, 414 (1924).

[6] Blau, *Monatsh*, **10**, 375 (1889).

[7] Hein and Retter, *Ber.*, **61**, 1790 (1929).

[8] Mann, *J. Chem. Soc.*, **121**, 2178 (1922).

and in such small yield that the carboxylic acid and the base produced on heating it were barely examined. A further study of these compounds would prove interesting.

Experimental

***p*-Phenanthroline.**—Fifty grams of *p*-phenylenediamine is mixed with 200 cc. of glycerine in a 2-liter Erlenmeyer flask. A mixture of 100 cc. of concentrated sulfuric acid and 100 cc. of arsenic acid (specific gravity of 1.80 and containing about 55% of As_2O_5) is slowly added while the mixture in the flask is agitated. Heat is applied carefully to produce and maintain a gentle ebullition, the flask being loosely covered with a small glass funnel to permit the escape of steam. After about one-half hour the contents should begin to turn brown. The funnel is then replaced by a short tube used as an air condenser. After heating is continued for about two hours, a test to determine the approximate amount of unaltered diamine is made by removing 1 cc. of the reaction mixture, diluting to 5 cc. with water and adding an excess of alcohol. *p*-Phenylenediamine sulfate separates on cooling if an appreciable quantity of the material is still unchanged, indicating that the heating should be continued with the air condenser until the test is essentially negative. The heating may now be continued under a water condenser for two hours, making the total time of digestion about five hours. The reaction mixture is now cooled and diluted with several portions of water, strong ammonia is added in excess, and the phenanthroline is extracted with several portions of benzol before the mixture has had time to cool. These extractions should be made as hot as is possible with the use of benzol by digesting solvent and mixture on the steam-bath preliminary to separation in the separatory funnel. The combined benzol extractions contain little tar, but nearly all of the phenanthroline with a little unaltered diamine. After evaporation of the benzol the residual *p*-phenanthroline is distilled without a thermometer, leaving the tar in the flask. The *p*-phennathroline while still liquid is poured in a thin steam into a large volume of water with continuous stirring and allowed to crystallize as the hydrate, which is filtered off and dried. To further purify and free it from unaltered diamine, it is liquefied with boiling water and poured again into a large volume of water. The product is then very satisfactory but can be further purified by being dissolved in alcohol or acetic acid and poured into water. The purification is not difficult when the Skraup reaction has been properly conducted. The yield is 65 g. of phenanthroline hydrate, representing about 60% of the theoretical.

β,β-Dipyridyl-dicarboxylic Acid.—The *p*-phenanthroline oxidizes best when it is finely divided and the reaction is conducted in alkaline solution. Twenty-five grams of *p*-phenanthroline hydrate is melted in about 500 cc. of hot water and poured into approximately 3 liters of cold water; 10 g. of potassium hydroxide is added and the cooled mixture is oxidized with 50 g. of potassium permanganate. The manganese dioxide is coagulated by heating to boiling and filtered off. The filtrate is evaporated to small volume, cooled and any phenanthroline which may separate is filtered off. The solution is now made just acid with acetic acid and digested on the steam-bath to remove the carbon dioxide present; the dicarboxylic acid is precipitated by the addition of copper acetate. The copper salt is decomposed by hydrogen sulfide from a suspension in boiling water. The dicarboxylic acid is obtained from the filtrate by evaporation and crystallization in the usual way.

β,β-Dipyridyl.—The decomposition of the dicarboxylic acid is best effected by heating it with sufficient glycerine to completely wet it. Gentle heating removes the carbon dioxide. The mixture is diluted with water, made alkaline with caustic soda and the dipyridyl extracted with ether. The dipyridyl distils over at 300 to 301° (corr.).

***m*-Phenanthroline.**—Fifty grams of *m*-phenylenediamine is mixed with 200 cc. of glycerine in a 2-liter flask. A mixture of 100 cc. of concentrated sulfuric acid and 100 cc. of arsenic acid (specific gravity of 1.80) is slowly added while the mixture is agitated in the flask. Heating is conducted as with *p*-phenylenediamine, but the loss of steam is permitted to take place more rapidly. A thermometer should be suspended in the mixture to insure that the temperature at ebullition is below 140° for about three hours of heating. The reaction has begun when a small test sample on dilution and the addition of ammonium hydroxide shows a flocculent precipitate. A short air condenser is employed during the 3-hour period. The temperature is permitted to rise gradually by alternating the air and water condensers until it reaches 150°, when a two-hour digestion with the water condenser completes the reaction. Caution should be increased at the last stage to avoid the formation of an excessive amount of tar.

The hot benzol extraction is made and the phenanthroline residue is distilled as with the *p*-diamine. The further purification is also conducted in the same way.

An extended series of experiments was conducted to study the effect of varying empirically the proportions of sulfuric acid, arsenic acid and glycerine, the same quantity (50 g.) of the diamine being used. While the results were not always uniform, because the conditions cannot be rigidly controlled, the proportions reported gave the best results. The best yield of benzol extract was 55 g., and the yield of pure dihydrate was 40 to 45 g.

The attempt to pass acrolein into the reacting mixture to facilitate and increase phenanthroline production resulted instead in loss. Acrolein was also passed into the diamine dissolved in glycerine until a heavy buff-colored precipitate was no longer produced. The sulfuric acid and arsenic acid were then added and the reaction was allowed to proceed as usual. Very little phenanthroline was formed.

A quantity of the condensation product of acrolein with the diamine was prepared by passing the gas into its solution in water. The product was amorphous and insoluble in acetone, alcohol and all other solvents tried. An experiment to subject this material to the Skraup reaction yielded no phenanthroline that could be separated.

Variations in the method of adding the reagents did not improve matters. In one experiment glycerine, *m*-diamine and arsenic acid were added slowly in one part to the sulfuric acid mixed with glycerine. An insoluble compound was formed which did not appear to be phenanthroline, but might possibly be the acrolein condensation product.

α,β-**Dipyridyl-dicarboxylic Acid.**—The yield of dicarboxylic acid is more than doubled by getting the phenanthroline in a finely divided condition and by the addition of alkali. The theoretical quantity of permanganate is used.

Melt twenty-five grams of dihydrate in 500 to 700 cc. of hot water and pour into 3 liters of cold water, agitating while the crystallization takes place to form it in a finely divided condition. Add ten grams of caustic potash, followed by 50 to 55 g. of potassium permanganate dissolved in water and added in small portions. Heat to boiling, filter off the manganese dioxide and evaporate the filtrate to low volume. Cool, filter off any separated unaltered phenanthroline, make acid with acetic acid and digest on the steam-bath. Instead of the silver salt, the writer uses advantageously the lead salt, which is formed by adding lead acetate and digesting until it becomes crystalline.

Suspend the lead compound in a large volume of hot water and pass in hydrogen sulfide. It is important to keep the mixture hot and pass in a large excess of gas to insure the complete precipitation of the lead. Add charcoal, filter off lead sulfide and charcoal and evaporate to dryness on the steam-bath. Take up with water, filter off the crystals, evaporate the filtrate for further crystals and combine all fractions. The yield of dicarboxylic acid is about 80 to 85% of the theoretical.

α,β-**Dipyridyl-monocarboxylic Acids.**—When the dicarboxylic acid is heated in an oil-bath to 190–200°, two different monocarboxylic acids are formed. The principal acid, described at length by Skraup, crystallizes in long woolly needles, but the second isocarboxylic acid crystallizes in prismatic needles, a small amount subliming up the sides of the vessel. A quantity of this was collected and analyzed.

Anal. Calcd.: C, 66.00; H, 4.00. Found: C, 65.78; H, 4.21.

The α,β-isomonocarboxylic acid melts at 152–154°. When the acid is heated to about 290°, carbon dioxide is evolved and α,β-dipyridyl is formed.

α,β-Dipyridyl.—It has been found that the yield of dipyridyl produced by directly heating the dicarboxylic acid, instead of using the calcium salt, is very good if each carboxyl group is removed at the lowest possible temperature. The dicarboxylic acid is placed in a small distilling bulb, which is immersed in an oil-bath. The bath is carefully heated to and maintained at 200° until all evolution of gas from the first carboxyl has ceased. The flask is removed and heated in a sand-bath until evolution of the second carboxyl is complete. The flask can now be heated over a direct flame until the α,β-dipyridyl is distilled off, and only a small amount of tarry residue is left. It distils completely at 298°.

Skraup Reaction with *o*-Phenylenediamine.—When the *o*-diamine is treated similarly to the *p*-diamine, the addition of ammonia brings down a dark colored precipitate. This is dissolved in acid and precipitated with ammonia several times to free it from coloring matter. The precipitate is finally washed with acetone and dried. A large volume of boiling benzol is used to extract a deep yellow compound crystallizing in silky needles. Final purification is effected by recrystallizing from benzol after filtering the hot solution previously digested with charcoal. The pure crystals melt at 253° (corr.).

Anal. Calcd. for $C_{12}H_8N_2O$: C, 73.50; H, 4.08; N, 14.3. Found: C, 73.70, 73.45; H, 3.96, 4.00; N (by Dumas), 15.0.

The substance is scarcely soluble in any of the usual solvents. It is slightly soluble in hot benzol or hot alcohol.

It is possible that some *o*-phenanthroline is formed, but the methods of separation were not adequate to separate it. The results were always variable, and sometimes even none of the yellow compound could be isolated.

Oxidation of $C_{12}H_8N_2O$.—When the compound was oxidized by means of alkaline permanganate, a carboxylic acid crystallizing in needles and melting at 167° was formed. When this acid was heated above the melting point, carbon dioxide was evolved and a residue formed which finally distilled undecomposed. When recrystallized from water this compound formed needles which melted at 113°. This substance was very soluble in hot water or cold dilute acids. On cooling the water solution, or neutralizing the acid solution with ammonia, the needles were again formed.

***o*-Phenanthroline.**—Ten grams of *o*-aminoquinoline was mixed with 25 cc. of glycerine, 12 cc. of sulfuric acid and 12 cc. of arsenic acid. The digestion was carried out similarly to that of *p*-phenylenediamine. After the reaction was considered ended, a large volume of water was added, followed by ammonia in slight excess. A black tarry precipitate was produced which was filtered off. A large excess of soda lye was added to the filtrate to precipitate the *o*-phenanthroline, which slowly crystallized in prismatic needles. The crystals were filtered off, washed with a little water, dissolved in acid and reprecipitated with soda lye. The precipitate was filtered, washed and dried. The dried product, weighing two grams, was extracted with boiling benzol, decolorized with charcoal, filtered and evaporated. The residue was crystallized from water after treatment with charcoal. Drying over sulfuric acid for several days resulted in 8.97% loss of water; calcd. for $1H_2O$, 9.09. The hydrate began to melt at 91° and finished at 95°. The anhydrous phenanthroline melted at 97°.

Anal. Calcd. for $C_{12}H_8N_2$: C, 80.00; H, 4.40. Found: C, 80.29; H, 4.73.

o-Phenanthroline distils undecomposed above 300°. It is soluble in alcohol, benzol and acetone, but insoluble in petroleum ether. It gives a red color with ferrous salts similar to the color obtained from *α,α*-dipyridyl. It was shown to be *o*-phenanthroline by oxidation with alkaline permanganate, forming a dicarboxylic acid crystallizing in needles. On heating, the dicarboxylic acid lost carbon dioxide and gave *α,α*-dipyridyl, as shown by its melting point (68°) and agreement with the known substance in odor, crystalline form and reaction with ferrous sulfate. The dicarboxylic acid was isolated by filtering off the manganese dioxide, making just acid with sulfuric acid, then alkaline with ammonia and evaporating to dryness. The residue was extracted with hot absolute alcohol. The acid left after evaporation of the alcohol crystallized from water in needles.

Summary

1. The double Skraup reaction can be satisfactorily applied to the *m*- and *p*-phenylenediamines with proper observance of water concentration, temperature and time of heating. The separation and purification of the respective phenanthrolines are described.

2. Oxidation of the phenanthrolines to their dicarboxylic acids by permanganate is best conducted at low temperatures with the addition of alkali.

3. *β,β*-Dipyridyl is satisfactorily prepared by heating its dicarboxylic acid in glycerine. *α,β*-Dipyridyl is prepared from its dicarboxylic acid by first eliminating one carboxyl at 200–210° and the other at 280–290°.

4. The double Skraup reaction when applied to *o*-phenylenediamine could not be made to yield *o*-phenanthroline but resulted only in a variable and small yield of a yellow crystalline substance, $C_{12}H_8N_2O$.

5. *o*-Phenanthroline was prepared from *o*-aminoquinoline. Its identity was established by oxidation to the dicarboxylic acid, which gave *α,α*-dipyridyl on heating.

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THE PREPARATION OF GAMMA-*d*-MANNONIC LACTONE

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Mannosaccharic lactone is a substance possessed of quite extraordinary properties.[1] The investigation of this lactone has been under way in this Laboratory for some time and has been especially time-consuming because of the difficulty of the preparation of the lactone in good yield. Fischer[2] reports only 2% on the basis of the weight of ivory nut meal hydrolyzed and oxidized and 7.5% from the oxidation of mannose.

The yield from the oxidation of pure mannonic lactone, however, is 30–35% according to Fischer[2] and even higher by the recently published method of Kiliani.[3]

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[1] *Cf.* Butler and Cretcher, THIS JOURNAL, **51**, 2167 (1929), for literature references.

[2] Fischer, *Ber.*, **24**, 539 (1891).

[3] Kiliani, *ibid.*, **54**, 456 (1921).