superior to the R-Mg-Br type. Further work is being planned to determine the relative merits of the iodides and bromides in reactions of the above type.

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[CONTRIBUTION NO. 61 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES IN THE DIPHENIC ACID AND PHTHALIC ACID SERIES. IV

BY H. W. UNDERWOOD, JR., AND G. E. BARKER[1]

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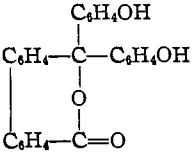
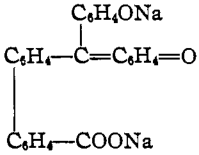
I. The Structure of Phenoldiphenein

Phenoldiphenein dissolves in sodium hydroxide solution with the development of a light yellow color.[2] The apparently anomalous behavior of this compound makes it desirable to obtain evidence regarding its structure. The arrangement of the groups in phenolphthalein has been established by the isolation of *p,p'*-dihydroxybenzophenone and benzoic acid from the melt obtained by the fusion of the phthalein with potassium hydroxide. The analysis of the potassium salt of phenolphthalein and the preparation of a dimethyl ether show the presence of two acidic hydrogen atoms and two hydroxyl groups. An account of the application of these procedures to phenoldiphenein is given in this paper. The results of our experiments show that phenoldiphenein and its sodium salt are represented by the formulas



$$\begin{array}{lcl} & C_6H_4OH & \\ & | & \\ C_6H_4- & C & -C_6H_4OH \\ | & | & \\ | & O & \\ | & | & \\ C_6H_4- & C & =O \end{array}$$

and



$$\begin{array}{lcl} & C_6H_4ONa & \\ & | & \\ C_6H_4- & C & =C_6H_4=O \\ | & & \\ | & & \\ C_6H_4- & COONa & \end{array}$$

Apparently the groups in diphenic anhydride give a light yellow instead of a red color to the sodium salt of the phenol condensation product.

Discussion of Experiments

All of the temperatures given are uncorrected.

Fusions of Phenolphthalein, Phenoldiphenein and the Fluorenone-phenol Condensation Product with Potassium Hydroxide.—A procedure which gave satisfactory results with phenolphthalein was first developed, and this was applied to phenoldiphenein and the fluorenone–phenol condensation product.

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[1] Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by G. E. Barker in partial fulfilment of the requirements for the degree of Bachelor of Science.

[2] Underwood and Kochmann, THIS JOURNAL, 45, 3071 (1923); 46, 2069 (1924).

An intimate mixture of 5 g. of powdered phenolphthalein (0.016 mole) and 20 g. of powdered potassium hydroxide (0.357 mole) was placed in a 60-cc. nickel crucible, and heated over a free flame until the solid melted. The crucible was allowed to cool while its contents were thoroughly stirred. The product was transferred to a mortar, ground to a fine powder and then placed in the crucible. After the mixture had been heated to its melting point, it was cooled, transferred to a mortar and reduced to a powder. The product was fused a third time. Since a solution of a sample of the mixture in water was not red, it was concluded that all of the phenolphthalein had been decomposed. The melt was extracted with four 50-cc. portions of boiling water and the solution was acidified with hydrochloric acid. The precipitate was collected on a filter, dried in the air and ground in a mortar with two 25-cc. portions of chloroform. Evaporation of the filtered chloroform extracts to dryness gave a colorless solid; this was crystallized from 15 cc. of boiling water. The product, which weighed 0.84 g. (43.8% yield) and melted at 119–120°, was identified as benzoic acid. The material which did not dissolve in chloroform was crystallized twice from 15 cc. of boiling water. About 1.1 g. (32.7% yield) of *p,p'*-dihydroxybenzophenone, m. p. 206–207°, was obtained.

The procedure described above was employed in the fusion of 3 g. of phenoldiphenein (0.0076 mole) with 9.6 g. of potassium hydroxide (0.1711 mole). During the fusion a white vapor which had an odor like that of biphenyl was evolved, and the mixture was black after a third fusion. Acidification of the filtered solution of the melt caused the evolution of considerable carbon dioxide and the formation of a dark colored gelatinous precipitate. The solid was collected on a filter, dried and extracted with four 10-cc. portions of boiling benzene. Evaporation of the benzene solutions to dryness gave a light gray solid which weighed 0.5 g. (33% yield) and melted at 110–111° after crystallization from a small amount of an alcohol–water mixture. The material dissolved in concd. sulfuric acid with the development of a wine-red color. The properties of this substance indicated that it was *o*-phenylbenzoic acid. Addition of an excess of bromine water to the filtrate from the gelatinous precipitate gave a colorless solid; this was filtered and dried in the air. The material, which weighed 1.22 g. and melted at 95°, was identified as *sym.*-tribromophenol; the product is equivalent to 0.347 g. of phenol (24.3% yield). Apparently phenoldiphenein is transformed into salts of phenol, *o*-phenylbenzoic acid and carbon dioxide by fusion with potassium hydroxide.

Similarly we secured 0.79 g. of *sym.*-tribromophenol (13.95% yield) and about 0.1 g. of *o*-phenylbenzoic acid (6% yield) from the melt obtained by fusing 3 g. of the fluorenone–phenol condensation product (0.0086 mole) with 7 g. of potassium hydroxide (0.1247 mole).

Analysis of the Potassium Salts of Phenolphthalein and Phenoldiphenein.—Procedures which gave satisfactory results with phenolphthalein were first developed, and these were applied to phenoldiphenein.

A solution of 0.5 g. of potassium hydroxide in 18 cc. of distilled water was thoroughly shaken with 1.49 g. of powdered phenolphthalein (calcd. amt. × 1.05) for twenty minutes and filtered. The filtrate was evaporated to dryness in a large dish; the dark red potassium salt was dried at 160° for four hours and cooled in a desiccator over concd. sulfuric acid.

Two-tenths gram of the dry potassium salt of phenolphthalein was placed in a weighed platinum crucible, and the latter was inclined on its side on a nichrome wire triangle. After three drops of pure, concd. sulfuric acid had been added to the salt, a platinum cover was placed on the crucible and the latter was carefully heated for about two and one-half hours at a temperature just below visible redness. At the end of this period the ash was practically colorless. A lump of pure ammonium carbonate about the size of a pea was introduced, and the mixture was heated to dull redness for half an hour.

The crucible was now allowed to cool to room temperature in a desiccator containing anhydrous calcium chloride, weighed, heated again and reweighed. This procedure was repeated until the weight of the crucible was constant. From the quantity of colorless potassium sulfate in the crucible the percentage of potassium in the salt was calculated.

Anal. Calcd. for $C_{20}H_{12}O_4K_2$: K, 19.83. Found: K, 19.88, 19.81.

The procedures described above were used for the preparation and analysis of the potassium salt of phenoldiphenein. This salt is an amorphous greenish-yellow powder; its color is between shade 1 of yellow and the normal tone of greenish-yellow in Mulliken's color charts.[3] A very dilute solution of the sodium salt of phenoldiphenein becomes practically colorless upon the addition of a large excess of concd. sodium hydroxide solution.

Anal. Calcd. for $C_{26}H_{16}O_4K_2$: K, 16.62. Found: K. 16.67, 16.61.

Lactone Dimethyl Ethers of Phenolphthalein and Phenoldiphenein.—Procedures which gave satisfactory results with phenolphthalein were first developed, and these were applied to phenoldiphenein.

A solution of 6 g. of phenolphthalein, 18 g. of methyl iodide (calcd. amt. × 3.36) and 0.6 g. of powdered potassium hydroxide in 40 cc. of methyl alcohol was maintained at 40–45° for twenty-four hours, and then 0.6 g. of powdered potassium hydroxide was added. At intervals of twenty-four hours another 0.6-g. and a 0.4-g. portion of powdered potassium hydroxide were introduced, and the mixture was kept at 40–45° during this period and for twenty hours after the last addition of alkali. The product was transferred to a beaker which was left in a vacuum desiccator over anhydrous calcium chloride until the solvent evaporated. The dry residue was placed in a beaker, stirred with 50 cc. of water, collected on a filter, washed with two 20-cc. portions of 5% potassium hydroxide solution and with 20 cc. of water and dried. The yield of phenolphthalein lactone dimethyl ether, m. p. 100–101°, was 5.68 g. (87%).

By use of the procedure described above, we secured 1.6 g. of crystalline lactone dimethyl ether of phenoldiphenein (50% yield) from 3 g. of phenoldiphenein, 7.26 g. of methyl iodide (calcd. amt. × 3.36) and 0.9 g. of powdered potassium hydroxide (calcd. amt. × 1.05), added in three portions of 0.25 g. and one of 0.15 g. Thirty-five cc. of methyl alcohol was used as a solvent. Phenoldiphenein lactone dimethyl ether was obtained in the form of colorless stout needles, m. p. 150–151°, by crystallization from a small amount of methyl alcohol. The compound is insoluble in 10% sodium hydroxide solution.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.59; H, 5.25. Found: C, 79.36, 79.56; H, 5.61, 5.58.

Forty grams of active, anhydrous aluminum chloride was added, with stirring, to 40 g. of dry phthalic anhydride and 50 g. of dry anisole (calcd. amt. × 0.855). After a reflux water condenser fitted with a drying tube containing anhydrous calcium chloride had been attached to the flask, the mixture was allowed to stand overnight at room temperature and then heated for three hours on a water-bath. The contents of the flask were diluted with 200 cc. of water and heated for an hour on a water-bath. The product was transferred to a beaker, and 50% sodium carbonate solution was added until the mixture was neutral. The solid was collected on a filter, ground in a mortar with two 50-cc. portions of 50% sodium carbonate solution and then with 50 cc. of 6 *N* potassium hydroxide solution. The material was collected on a filter again, washed with 50 cc. of water, dried and extracted with two 200-cc. portions of boiling methyl

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[3] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons. Inc., New York City, **1904**, Vol. I.

alcohol. The filtered methyl alcohol solution was concentrated and cooled in ice to facilitate the crystallization of the phenolphthalein lactone dimethyl ether. The product weighed 28 g. (35% yield) and melted at 100–101°.

By use of the procedure described above, we obtained 0.76 g. (11.1% yield) of crystalline lactone dimethyl ether of phenoldiphenein, m. p., 150–151°, from 5 g. of dry diphenic anhydride, 3.5 g. of dry anisole (calcd. amt. × 0.725) and 3.1 g. of active, anhydrous aluminum chloride. Fifty cc. of water was used to dilute the reaction mixture. The solid reaction product was washed successively with 15 cc. each of 50% sodium carbonate solution, 6 *N* potassium hydroxide solution and water. The dry material was extracted with two 50-cc. portions of boiling methyl alcohol.

II. Reactions of Derivatives of Diphenic Acid and Phthalic Acid with Acetic Anhydride

When the monomethyl, mono-ethyl, dimethyl and diethyl esters of diphenic acid were heated with acetic anhydride, each compound remained unchanged. Under similar conditions diphenamic acid was dehydrated in two different ways, giving diphenimide and 1-cyanobiphenyl-10-carboxylic acid; the diamide of diphenic acid was transformed into 2,2′-dicyanobiphenyl. These reactions are dehydrations and involve union of the side chains attached to the rings.[4] Since our investigations involve a comparison of the behavior of derivatives of diphenic acid and those of phthalic acid, we have studied the action of acetic anhydride upon the methyl and ethyl esters, the mono-amide and the diamide of phthalic acid.

Discussion of Experiments

Monomethyl Phthalate.—After a mixture of 25 g. of phthalic anhydride and 125 g. of absolute methyl alcohol (calcd. amt. × 23.1) had been refluxed on a water-bath for five hours, the excess methanol was distilled and the reaction product transferred to a beaker which was left in a desiccator over anhydrous calcium chloride for several hours. The yield of monomethyl phthalate, m. p. 82–82.5°, was 24.4 g. (80.2%).

Ten grams of the ester was heated with 20 g. of glacial acetic acid and 30 g. of acetic anhydride for sixteen hours at 145°. The mixture was cooled in ice and the solid which formed was collected on a filter and dried. The filtrate was concentrated by distillation at 145° and the residue was transferred to a beaker, cooled and dried. The solid reaction product, which weighed 8.1 g. (98.5% yield), was identified as phthalic anhydride. Two cc. of impure methyl acetate was obtained by several fractionations of the distillate. Three and nine-tenths grams of phthalic anhydride was secured by heating 10 g. of monomethyl phthalate for sixteen hours at 145°. Two 10-cc. portions of pure anhydrous ether were used to separate the unchanged ester from the phthalic anhydride.

Mono-ethyl Phthalate.—Twenty-five grams of phthalic anhydride was dissolved in 200 cc. of absolute ethyl alcohol (calcd. amt. × 20.4) by refluxing the mixture for two hours on a water-bath. Removal of the alcohol by distillation produced a sirupy liquid. In order to separate the mono-ethyl ester from diethyl phthalate, the product was dissolved in 100 cc. of water. The solution was maintained at its boiling point for an hour, and 25 g. of powdered barium carbonate was added during this period. The neutral mixture was cooled to room temperature and filtered; the filtrate was acidified with concd. hydrochloric acid and extracted with 100 cc. of ether. After the ether solution had been shaken with 10 cc. of water, it was dried overnight with 5 g. of an-

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[4] Underwood and Clough, This Journal, **51**, 583 (1929).

hydrous sodium sulfate and then filtered. The ether was removed by distillation on a water-bath. After drying in a vacuum desiccator over anhydrous calcium chloride, the product weighed 8 g. (24.4% yield).

By use of the procedure described above, we obtained 7.5 g. of phthalic anhydride (98.4% yield) by heating 10 g. of mono-ethyl phthalate with 20 g. of glacial acetic acid and 30 g. of acetic anhydride at 145° for sixteen hours. Two cc. of impure ethyl acetate was secured by several fractionations of the distillate. Ten grams of mono-ethyl phthalate yielded 4.7 g. of phthalic anhydride when heated at 145° for sixteen hours.

The results of our experiments show that the hydroxyl and alkoxyl groups in mono-methyl and mono-ethyl phthalates are loosely held.

Dimethyl and Diethyl Phthalates.—Ten g. of each of these compounds was heated with 20 g. of glacial acetic acid and 30 g. of acetic anhydride for sixteen hours at 145°, and the mixture was then fractionated. In each case, practically all of the ester was recovered unchanged.

Phthalamic Acid.—Acidification of a solution of 50 g. of phthalimide in 150 g. of 25% potassium hydroxide solution (calcd. amt. × 1.97) with concd. hydrochloric acid, gave a light brown precipitate. This was collected on a filter, ground with three 25-cc. portions of water in a mortar and dried. The yield of phthalamic acid, m. p. 147–148°, was 43.2 g. (77%).

After a mixture of 10 g. of phthalamic acid (the mono-amide of phthalic acid), 20 g. of glacial acetic acid and 30 g. of acetic anhydride had been refluxed for sixteen hours at 145°, practically all of the liquid was removed by distillation and the residue was stirred with 100 cc. of alcohol. The insoluble material was collected on a filter, washed and dried; this substance, which weighed 4.2 g., was identified as phthalimide. Evaporation of the filtrate to dryness gave 4.73 g. of phthalic anhydride. Ten grams of phthalamic acid was converted into 6.0 g. of phthalimide and 2.9 g. of phthalic anhydride by heating at 145° for sixteen hours. The products were separated by treatment with alcohol.

In "Beilstein" it is stated that phthalamic acid decomposes smoothly at 155° into phthalimide and water, and that treatment with glacial acetic acid transforms phthalamic acid into phthalic anhydride.

Phthalamide.—A mixture of 25 g. of phthalimide and 100 cc. of concd. ammonium hydroxide (*d* 0.9; calcd. amt. × 9.03) was maintained at its boiling point for twenty minutes, and then allowed to cool to room temperature. The precipitated phthalamide was collected on a filter, washed with 20 cc. of 5% ammonia solution and dried for half an hour at 100°. The product weighed 25.8 g. (92.5% yield) and melted at 219–220° with evolution of ammonia.

The solution obtained upon heating 10 g. of phthalamide, 20 g. of glacial acetic acid and 30 g. of acetic anhydride at 145° for an hour was cooled in ice. The precipitate which formed was collected on a filter and dried; it weighed 4.5 g. and melted at 170–172°. The properties of this substance indicated that it was *o*-cyanobenzamide. Practically all of the liquid in the filtrate was removed by distillation at 145°. When the residue was cooled in ice, it deposited a colorless solid which weighed 3.7 g. after drying. This product was identified as phthalimide. Ten g. of phthalimide was unchanged by heating for an hour at 145°.

In Beilstein it is stated that treatment with acetic anhydride (free from acetic acid) converts phthalamide into *o*-cyanobenzamide, phthalonitrile, phthalimide and acetylphthalimide.

Summary

Fusion with potassium hydroxide converts phenoldiphenein into the potassium salts of phenol and *o*-phenylbenzoic acid. The lactone di-

methyl ether of phenoldiphenein is formed by treatment of the latter with methyl iodide and potassium hydroxide and by the reaction of diphenic anhydride with anisole in the presence of anhydrous aluminum chloride. The presence of two acidic hydrogen atoms in phenoldiphenein is shown by analysis of the potassium salt. These transformations indicate that the structure of phenoldiphenein is similar to that of phenolphthalein and that the sodium salt of phenoldiphenein contains a quinoid ring. The groups in this salt give it a light yellow instead of a red color.

When dimethyl phthalate and diethyl phthalate are heated with acetic anhydride, each ester remains unchanged. Under similar conditions the monomethyl and mono-ethyl esters of phthalic acid yield phthalic anhydride. Phthalamic acid is converted into phthalimide and phthalic anhydride by treatment with acetic anhydride, and phthalamide gives *o*-cyanobenzamide and phthalimide.

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PREPARATION OF SOLID DERIVATIVES FOR THE IDENTIFICATION OF ETHERS

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Ethers are usually described as inert compounds; the carbon–oxygen bond is firmly held, and drastic treatments, such as heating with hydriodic acid or anhydrous aluminum chloride, are generally employed to split ethers. These methods are not suitable for the preparation of solid derivatives for the identification of small amounts of ethers. Recently it was shown that ethyl 3,5-dinitrobenzoate is formed by the treatment of the dinitrobenzoyl chloride with pure, dry ethyl ether in the presence of anhydrous zinc chloride.[2] This paper describes the preparation of crystalline 3,5-dinitrobenzoates from small amounts of representative, simple aliphatic ethers. Procedures for the conversion of typical aromatic ethers into crystalline bromo derivatives are also discussed.

Discussion of Experiments

All the temperatures given are uncorrected.

Purification of Ethers.—The aliphatic ethers were purified by the method described in a previous paper.[3] Experiments with samples of

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[1] Some of the experimental results described in this and a previous paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by G. C. Toone in partial fulfilment of the requirements for the degree of Master of Science. The bromo derivatives of the aromatic ethers were prepared by O. L. Baril.

[2] Underwood and Wakeman, THIS JOURNAL, **52**, 387 (1930).

[3] Underwood and Toone, *ibid.*, **52**, 391 (1930).