odor and was apparently an isomeric compound or a mixture of isomers. The recovered "menthol" had the following constants: $(\alpha)_D$ $-17°$, d_{20}^{25} 0.927, and n_D^{25} 1.4610. A hydrocarbon fraction boiling lower than sec-butylbenzene was obtained in the hydrogenation of the esters of α-phenylbutyric acid. This appeared to be isopropylbenzene but the amount available was too small to be identified with certainty. The 2-phenylpropanol-1 was present in the reaction mixture from ethyl α-phenylpropionate as 2-phenylpropyl-α-phenylpropionate (186–188° (13 mm.)). The rotation of the alcohol (100°, 13 mm.) was determined in pyridine and it was characterized as the

benzoate (201–202° (20 mm.)). The (α) of the latter was $+0.50°$. The yields recorded in Table I for ethyl β-methylvalerate, ethyl α-ethylpelargonate and ethyl δ-phenylvalerate are calculated on the basis of the weight of material obtained after filtration of the catalyst.

Summary

The preparation of various optically active alcohols by the hydrogenation of optically active esters, alcohols and ketones over copper–chromium oxide and nickel has been described.

MADISON, WIS.   RECEIVED DECEMBER 11, 1933

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# The Action of Alkali on Dianilinodibromobenzoquinone

BY MURRAY M. SPRUNG[1]

During a study of the reactions of tetrabromomethylquinol and bromanil, dianilinodibromoquinone was obtained. This substance was prepared as early as 1872 by Stenhouse,[2] who analyzed it, but gave no melting point or further description. In order to establish that the bromines had been replaced symmetrically, as in similar reactions of this type, two reactions were carried out: 2,5-diphenoxy-3,6-dibromoquinone was treated with aniline, in the hope that the dianilinodibromoquinone would be formed; and the dianilinodibromoquinone, itself, was treated with alkali, in the expectation that bromoanilic acid (2,5-dihydroxy-3,6-dibromoquinone) would be obtained.

The first reaction went quantitatively as expected,[3] and therefore established the symmetrical nature of the compound; it is 2,5-dianilino-3,6-dibromo-p-benzoquinone. The second reaction, however, gave no trace of bromoanilic acid. Instead, two new quinone derivatives were obtained. The first, a pale yellow substance, was identified as 2,5-dianilino-3,6-dihydroxybenzoquinone, formed by replacement of the second pair of bromine atoms by hydroxyl groups. The second, a chocolate brown substance, proved to be the mono-anil of the dianilinodihydroxyquinone. The structure of the anil was established by its synthesis from the latter compound and aniline in alkaline solution, and by its hydrolysis to dianilinodihydroxyquinone and aniline in acid solution.

(1) The work to be described was done while the author was a National Research Council Fellow.

(2) Stenhouse, Ann., Sup., **8**, 22 (1872).

(3) Cf. Jackson and Grindley, Am. Chem. J., **17**, 597 (1895), who studied the reaction between dichlorodiphenoxy quinone and aniline.
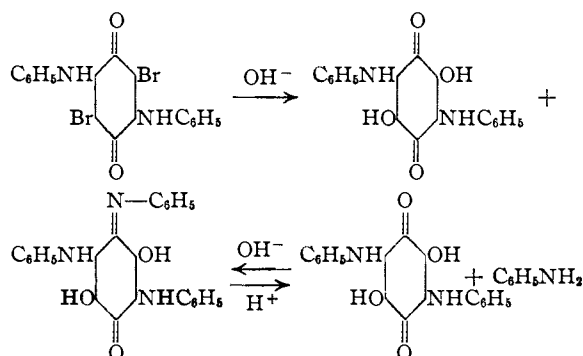
By-products of the reaction between dianilinodibromoquinone and alkali are hydrogen bromide, aniline and small amounts of impure materials formed by replacement of both bromine and anilino groups. It is from the latter type of replacement that the aniline necessary for the formation of the anil comes. However, no pure compound containing less than two nitrogen atoms could be isolated.

Both dianilinodihydroxyquinone and its mono-anil are acidic substances, but the former is a considerably stronger acid than the latter. Advantage was taken of this fact in effecting a separation of the two.

It was observed that bromoanilic acid was unaffected when heated with aniline or when boiled with excess alkali. This is of interest in view of the fact that alkali readily replaces the bromine atoms of dianilinodibromoquinone, and that the phenoxy groups in dibromodiphenoxyquinone are easily replaced either by hydroxyl or by anilino groups. Hydroxyl groups thus markedly decrease the ease of replacement of other substituents in such symmetrically substituted quinones. The ease of replacement under compara-

ble conditions is roughly in the order $C_6H_5O >$ $Br > NHC_6H_5 > OH$.[4]

Experimental

Preparation of 2,5-Dianilino-3,6-dibromo-p-benzoquinone.—Fifteen and seven-tenths grams (1.3% excess) of aniline, dissolved in 350 cc. of 95% alcohol, was added rapidly to 18.0 g. of bromanil, suspended in 1000 cc. of boiling 95% alcohol. The mixture was boiled until all the yellow flakes of bromanil were replaced by the brown flakes of the product (about thirty minutes). The yield was quantitative, *i. e.*, 19.0 g. The crude product melted at 260–260.5° (dec.) and was pure enough for most purposes. After crystallization from toluene, it melted at 261° (dec.). It forms dark, lustrous, permanganate brown needles, which are insoluble in all low boiling solvents, but appreciably soluble in pyridine, toluene or bromobenzene.

Preparation from 2,5-Diphenoxy-3,6-dibromoquinone and Aniline.—Two grams of pure diphenoxydibromoquinone was suspended in 100 cc. of boiling 95% alcohol and 1.00 g. (25% excess) of aniline, dissolved in 25 cc. of 95% alcohol, was added. The mixture was heated in the steam-bath for ten hours, when all the diphenoxydibromoquinone had disappeared. The cooled mixture was filtered from the brown flakes of dianilinodibromoquinone; these were washed with cold alcohol and dried. The yield, 1.9 g., is practically quantitative. No depression in melting point was observed when this material was mixed with a sample of dianilinodibromoquinone, obtained as above.

Reaction of Dianilinodibromoquinone with Sodium Hydroxide.—Ten grams of dibromodianilinoquinone was covered with 40 cc. of 95% alcohol and 250 cc. of a warm 12.5% solution of sodium hydroxide added. The mixture, heated on the steam-bath for three minutes, gave a deep red solution, which became clear yellow after two more minutes. The solution was then rapidly cooled in ice and salt, and 2 N hydrochloric acid added (*ca.* 400 cc.) until a red precipitate began to form, then in small amounts until the red substance was all precipitated (*ca.* 50 cc. more). The red material, after settling, was filtered, washed thoroughly with cold water and then repeatedly (on the filter) with ether. It was dried in a vacuum desiccator. The average yield of the mono-anil in a number of experiments was 3.2 g. The dried substance was chocolate brown in color.

To the filtrate and washings was added 50 cc. more 2 N hydrochloric acid, which precipitated the dianilinodihydroxyquinone. After standing in the ice box for 2 hours, this was filtered, and washed with ice-cold water. The average yield was 2.4 g. By extracting the filtrate and washings several times with ether, 0.7 g. more (average) was obtained.

The reaction mixture was tested (at various stages of the reaction) for bromide ion and for aniline. Both were present, the first in large amounts, the second in appreciable quantities.

Unless the above procedure was followed carefully, the yields were very considerably reduced, and intractable products were obtained.

(4) *Cf.* Jackson and Holton, THIS JOURNAL, **36**, 551 (1914), and earlier papers.

2,5-Dianilino-3,6-dibromo-p-benzoquinone crystallizes from the ordinary organic solvents in lemon-yellow, microscopic needles. It was very difficult to separate this substance completely from small amounts of the red anil which invariably contaminated it. A sample used for analysis was crystallized as follows: from dilute ethyl alcohol, twice from a mixture of ethyl alcohol and benzene, from benzene, from alcohol and chloroform, from benzene and chloroform, and finally from absolute alcohol. The pure material melted at 206–207° (dec.).

Anal. Calcd. for $C_{18}H_{14}O_4N_2$: C, 67.0; H, 4.4; mol. wt., 324. Found: C, 67.0, 66.4; H, 4.9, 5.0; mol. wt. (in ethylene dibromide), 326.

The substance is distinctly acidic. It may be titrated in the presence of phenolphthalein, despite the yellowish color of the alkaline solution.

Neut. equiv. Subs., 0.0450 g.; 0.1097 N NaOH, 2.50 cc. Calcd. for $C_{18}H_{14}O_4N_2$ (dibasic): 2.54 cc.

2,5-Dianilino-3,6-dibromobenzoquinone Monoanil.—The crude anil was amorphous-looking, and varied somewhat in color. The pure substance (after being crystallized several times from benzene) melted consistently at 139°, with marked decomposition. It is inappreciably soluble in all low-boiling solvents except alcohol and benzene; more readily soluble in high-boiling solvents, such as xylene, nitrobenzene, bromobenzene and chlorobenzene, but is partially decomposed at the boiling points of such solvents. It is slowly soluble in dilute alkali, more rapidly on warming, giving a deep red solution, from which dilute acids reprecipitate the original material. Boiling dilute or concentrated hydrochloric acid hydrolyzes it readily, giving dianilinodihydroxyquinone and aniline. It is slowly hydrolyzed by cold, dilute or concentrated acids, and even on long standing in the air, it slowly goes over into the yellow parent compound.

Hydrolysis of the Anil with Dilute Hydrochloric Acid.—Five hundred and fifteen thousandths of a gram of the purified anil and 20 cc. of 2 N hydrochloric acid were heated on the steam-bath in a small flask until the anil was completely dissolved (*ca.* thirty minutes). The cooled solution was filtered from a small amount of carbonized material, neutralized with alkali and extracted repeatedly with ether. The ether was evaporated at room temperature. The yield of dianilinodibromoquinone was 0.409 g. (calculated, 0.417 g.). It was identified by melting point and mixed melting point (with a sample prepared as above). The aqueous layer was made distinctly alkaline and boiled with a few drops of chloroform. A strong odor of phenyl isocyanide indicated the presence of aniline.

Preparation of the Anil from 2,5-Dianilino-3,6-dihydroxybenzoquinone and Aniline.—Seventy-five hundredths of a gram of dianilinodihydroxyquinone was dissolved in 20 cc. of 12.5% sodium hydroxide, 1.0 cc. of aniline was added and the mixture boiled for eight minutes. The deep red solution which resulted was cooled, filtered from tarry matter and acidified with 25 cc. of 2 N hydrochloric acid. The flocculent precipitate which then resulted was filtered, washed thoroughly with water, then with ether, dried and crystallized twice from benzene. The product melted at 139–141° (dec.), and at 139–140° (dec.) when mixed with a pure sample of the anil.

Summary

2,5 - Dianilino -3,6 - dihydroxy - *p* - benzoquinone and its mono-anil are described. They are obtained by the action of aqueous alkali on 2,5-dianilino-3,6-dibromo-*p*-benzoquinone.

SCHENECTADY, N. Y.   RECEIVED NOVEMBER 20, 1933

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK]

Reactions of Carbohydrates in Liquid Ammonia: Preliminary Paper

BY IRVING E. MUSKAT[1]

The recent advances in the chemistry of carbohydrates are due in a large measure to the introduction of the method of preparation of their methyl ethers. Two methods of methylation are in general use; one introduced by Purdie and his collaborators[2] consists of treating the sugar with silver oxide and methyl iodide, while the other, introduced by Haworth,[3] uses methyl sulfate as the methylating reagent. Either method is time consuming, and it is usually necessary to repeat the process a number of times to ensure complete methylation. It is presumably not possible to control either method so as to methylate a specified number of hydroxyl groups; all free hydroxyl groups are attacked. Neither method is well suited to the use of small quantities of material. In addition, the Purdie method is rather expensive, since it is customary to use five times the theoretical quantity of silver oxide and seven to ten times the theoretical quantity of methyl iodide for each methylation.

It has been known for some time that some alcohols will react with sodium or potassium in liquid ammonia solution to form salts. Kraus, White and their collaborators[4] have treated these salts in liquid ammonia with alkyl halides and thus formed the corresponding ethers. It was therefore considered possible that this general reaction might be introduced into sugar chemistry with considerable advantage. Thus, for example, if methylglucoside were soluble in liquid ammonia, it could be treated with sodium or potassium to form the salt which, in turn, could be made to react with methyl iodide, for instance, to give the methylated derivative.

(1) National Research Fellow in Chemistry.

(2) Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903); Purdie and Bridgett, *ibid.*, **83**, 1037 (1903); *et seq.*

(3) Haworth, *ibid.*, **107**, 8 (1915).

(4) Kraus and White, THIS JOURNAL, **45**, 768 (1923); White, *ibid.*, **45**, 779 (1923); White and Knight, *ibid.*, **45**, 1780 (1923); Kraus and Kawamura, *ibid.*, **45**, 2756 (1923); White, Morrison and Anderson, *ibid.*, **46**, 961 (1924).
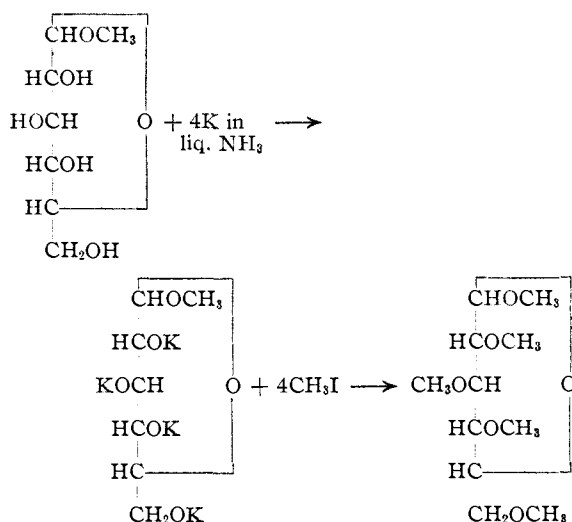
A preliminary investigation has shown that such salts of carbohydrates are formed, and the behavior of these salts opens a new field for the study of the mechanism of carbohydrate reactions and the synthesis of derivatives hitherto difficult to prepare, or unobtainable. Some of the possibilities and limitations of the method as revealed in this preliminary study are presented here.

Apparatus and Procedure

The apparatus and experimental method employed in this work are essentially those described by Johnson and Fernelius[5] in their recent review on the chemistry of liquid ammonia. Complete detailed directions are given in this review for obtaining the liquid ammonia from the commercial supply tanks and purifying it, as well as the description of the apparatus and technique for working with ammonia both at its boiling point ($-33.4°$) and at room temperature under pressure (the vapor pressure of liquid ammonia at ordinary temperature is about 8.5 atm.). The method described by Johnson and Fernelius is used for those reactions where the alkali metal salt must be freed from ammonia before coupling with any other reagent which would react with the ammonia. However, in those cases, such as alkylations, where the entire re-

(5) Johnson and Fernelius, *J. Chem. Ed.*, **6**, 441 (1929).