chain of the ketone, since the 3,5-dibromo-2,4-dihydroxy-1-ethylbenzene was prepared by reduction of 3,5-dibromo-2,4-dihydroxyacetophenone.

Summary

1. Improvements in methods of preparation and purification of acyl and alkyl resorcinols are reported.
2. Six new halogen derivatives of acyl and alkyl resorcinols were prepared and their properties described.
3. Evidence was presented to establish the position of the bromine atoms in dibromo-ethylresorcinol and tetrabromoresacetophenone.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

NAPHTHOL STUDIES. I. THE BROMINATION OF 1,5-DIHYDROXYNAPHTHALENE

BY ALVIN S. WHEELER AND DAVID R. ERGLE[1]

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The halogenation of juglone was first investigated by Wheeler and Scott.[2] Two atoms of chlorine entered the quinone nucleus when chlorination took place in warm glacial acetic acid. However, under like conditions three atoms of bromine were substituted in the molecule. Only a dichloro and a tribromo derivative could be obtained by direct action of the halogens. Attention has now been turned to the halogenation of the dihydric naphthol, 1,5-dihydroxynaphthalene, from which by oxidation with chromic acid, juglone is obtained. By varying the conditions we have introduced into the nuclei two, three and four atoms of bromine, whereas in another study now in progress in this Laboratory only two and three atoms of chlorine have been introduced into the rings. These halogenated naphthols have been oxidized to halogenated naphthoquinones, but none of them corresponds to the halogenated juglones.

The commercial raw material, the dihydroxynaphthalene, was purified by recrystallization from hot water. For bromination glacial acetic acid solutions were used for preparing the dibromo and tribromo derivatives. Iodine was used as a catalyst and a temperature of 80° was necessary in order to obtain the best yields. In order to introduce four atoms of bromine, a chloroform solution of the diacetate was necessary, a catalyst such as iodine and six moles of bromine.

We believe that the structures indicated in the charts are the correct ones

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[1] This paper is a portion of a thesis presented by David R. Ergle to the Faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy in 1930.

[2] Wheeler and Scott, THIS JOURNAL, 41, 833 (1919).

for these new compounds. The bromine atoms in the dibromo compound B are placed in the beta positions since we are dealing with naphthols. The naphthoquinone C is undoubtedly a para quinone since this isomer forms so readily in general. The tribromo naphthoquinone has been proved to be such (see below). In the dibromo compound it is clear that one bromine atom is in the quinone ring since one is readily replaced by the aniline radical. As for the tribromo compound K, the third bromine atom enters para to the hydroxyl group. In this compound positions 4 and 8 are identical. The bromine atoms in the tetrabromo compound S are placed in positions 2,4,6,8, making this a symmetrical molecule. Its oxidation by chromic acid yields a naphthoquinone which is a para quinone, the bromine atom in position 4 being lost in the process. For final proof of its structure the naphthoquinone was found to yield a pyroboracetate ester, a reaction which ties an hydroxyl group to a carbonyl group only when these are ortho to each other, as shown by Dimroth and Faust[3] and later by Dimroth.[4]

When five moles of bromine were used and the reaction mixture was kept at room temperature, the dibromo compound was first formed and much later the tetrabromo derivative. However, one of the two acetyl groups in R was hydrolyzed, as proved by the formation of a monobenzoate, V.

The dibromohydroxynaphthoquinone C is not identical with but is isomeric with the 2,3-dibromojuglone (m. p. 167°) of Wheeler and Naiman.[5] The tribromohydroxynaphthoquinone L likewise is an isomer of the tribromojuglone (m. p. 170°) of Wheeler and Scott.[6]

Experimental

Dibromodihydroxynaphthalene

Purification of 1,5-Dihydroxynaphthalene.—Thirty grams of the commercial product was made into a thick paste with water, suspended in 3 liters of water containing 200 cc. of methyl alcohol and boiled under a reflux for three hours. After cooling to 80° it was saturated with sulfur dioxide and then digested below the boiling point for an hour. It was filtered on a large fast filtering paper in a hot water funnel, the filtrate falling on crushed ice; nearly colorless needles, m. p. 258°; yield, 15–20 g.

2,6-Dibromo-1,5-dihydroxynaphthalene, $C_{10}H_4(OH)_2Br_2$(B).—This compound was first made at room temperature but the yield was greatly increased when the temperature was elevated; 10 g. of dihydroxynaphthalene was dissolved in 350 cc. of glacial acetic acid, a few small crystals of iodine were added and, while the solution was stirred and kept at 80°, 6.5 cc. of bromine (2 moles) dissolved in 25 cc. of glacial acetic acid was added dropwise during the course of thirty minutes. On cooling the solution, the product crystallized out in pale olive green needles. It was washed on the filter with petroleum ether; weight, 14.5 g. or 76% of the theoretical yield; colorless needles on

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[3] Dimroth and Faust, *Ber.*, **54**, 3021 (1921).

[4] Dimroth, *Ann.*, **446**, 108 (1926).

[5] Wheeler and Naiman, THIS JOURNAL, **44**, 2333 (1922).

[6] Wheeler and Scott, *ibid.*, **41**, 838 (1919).

recrystallizing from glacial acetic acid. The substance darkens at 200° and does not melt at 300°. It is soluble in ether and dilute sodium hydroxide, difficultly soluble in chloroform and insoluble in carbon tetrachloride.

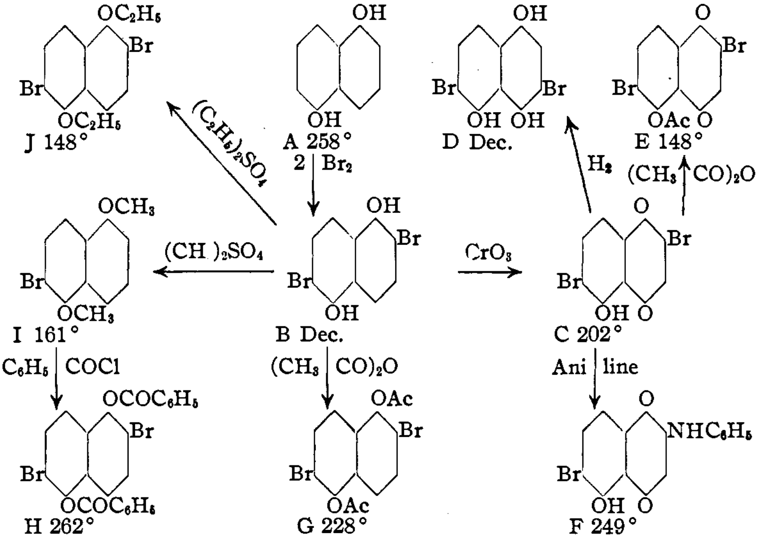
Anal. Calcd. for $C_{10}H_6O_2Br_2$: Br, 50.31. Found: Br, 50.52.

Diacetate, $C_{10}H_4(OCOCH_3)_2Br_2$**(G).**—Compound B was heated with an excess of acetic anhydride for an hour at 100°, giving straw yellow needles, colorless on recrystallizing from alcohol; product m. p. 228°; soluble in ether, benzene and acetic acid; insoluble in petroleum ether.

Anal. Calcd. for $C_{14}H_{10}O_4Br_2$: Br, 39.80. Found: Br, 39.68.

Dimethyl Ester, $C_{10}H_4(OCH_3)_2Br_2$**(I).**—Compound B was dissolved in 2 moles of dilute sodium hydroxide. To this solution at 60° an excess of dimethyl sulfate was added in small amounts until an acid reaction was obtained. More alkali was added and more sulfate but not enough to give an acid reaction. Reddish-purple crystals formed. These were washed on the filter with water. An alcoholic solution with charcoal was boiled until colorless. The filtered solution was concentrated and gave a small amout of colorless microscopic plates which melted at 161°. The dimethyl ether is soluble in ether, benzene and chloroform; slightly soluble in cold alcohol and in petroleum ether.

Anal. Calcd. for $C_{12}H_{10}O_2Br_2$: Br, 46.24. Found: Br, 45.90.



Diethyl Ether, $C_{10}H_4(OC_2H_5)_2Br_2$**(J).**—The crude product was a dull red solid. This was dissolved in benzene and boiled. After filtration the solvent was distilled off and the pink residue was recrystallized from hot alcohol as nearly colorless needles, m. p. 148°; soluble in benzene, slightly soluble in cold acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{14}H_{14}O_2Br_2$: Br, 42.89. Found: Br, 42.77.

Dibenzoate, $C_{10}H_4(OCOC_6H_5)_2Br_2$**(H).**—The dibenzoate was prepared by treating a pyridine solution of B with an excess of benzoyl chloride. Much heat was evolved and the whole quickly became a solid mass of yellow crystals. Addition of water gave a heavy yellow oil which was washed with sodium hydroxide and finally with water. Addition of alcohol changed the oil to a solid. This was recrystallized from warm pyridine as colorless needles, m. p. 262°; slightly soluble in hot acetic acid; insoluble in ether and in alcohol.

Anal. Calcd. for $C_{24}H_{14}O_4Br_2$: Br, 30.41. Found: Br, 29.94.

2,6-Dibromo-5-hydroxy-1,4-naphthoquinone, $C_{10}H_3O_2OHBr_2$(C).—To a suspension of 10 g. of B in 200 cc. of glacial acetic acid was added at one time 20 g. of chromic acid dissolved in the smallest amount of water. The mixture turned red, effervesced and the temperature rose to 85°. During the vigorous effervescence, which continued for about fifteen minutes, the material went into solution with a brownish-yellow color. Sometimes it was necessary to start the evolution of gas by warming the mixture. The oxidation was complete when a drop of the solution showed red needles under the microscope, about fifteen minutes in time. After cooling the solution the crystals were filtered off and washed with water; weight, 2.8 g. On recrystallizing from hot acetic acid, the product was obtained in rich red needles, sharply pointed and in clusters; m. p. 202°; soluble in benzene and in chloroform; difficultly soluble in ether and alcohol. It dissolves in alcoholic sodium hydroxide with a purple color which quickly changes to red.

Anal. Calcd. for $C_{10}H_4O_3Br_2$: Br, 48.19. Found: Br, 48.11.

Acetate, $C_{10}H_3O_2(OCOCH_3)Br_2$(E).—The quinone was boiled in acetic anhydride for fifteen hours and the product recrystallized from hot alcohol as golden-yellow needles, m. p. 148°; soluble in acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{12}H_6O_4Br_2$: Br, 42.78. Found: Br, 42.95.

2,6-Dibromo-1,4,5-trihydroxynaphthalene, $C_{16}H_3(OH)_3Br_2$(D).—One gram of C was dissolved in 35 cc. of warm acetic acid. The solution was shaken with additions of zinc dust until the red solution became pale yellow. The filtered solution was dropped upon crushed ice. The crystals so obtained were recrystallized from alcohol by adding water until separation began; colorless needles, darkening at 110° and decomposing at 157°; very soluble in acetic acid, less soluble in carbon tetrachloride and insoluble in petroleum ether; dissolves in dilute sodium hydroxide with a violet coloration, quickly turning to a reddish-brown; readily oxidized back to the quinone with ferric chloride.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: Br, 47.90. Found: Br, 47.74.

6-Bromo-5-hydroxy-2-anilino-1,4-naphthoquinone, $C_{10}H_3O_2OHBrNHC_6H_5$(F).—One-half gram of C was dissolved in 70 cc. of hot alcohol, 1.5 g. of aniline was added and the solution boiled for five minutes. Needles of gun metal luster and red by transmitted light resulted. When heated a red vapor was evolved at 190°. After recrystallization from hot benzene the melting point was 249°.

Anal. Calcd. for $C_{16}H_{10}O_3NBr$: Br, 23.25. Found: Br, 23.27.

Further Notes on Compound C.—An attempt was made to prepare the pyroboroacetate ester. A reddish-purple color was obtained and a product which was too unstable to be isolated.

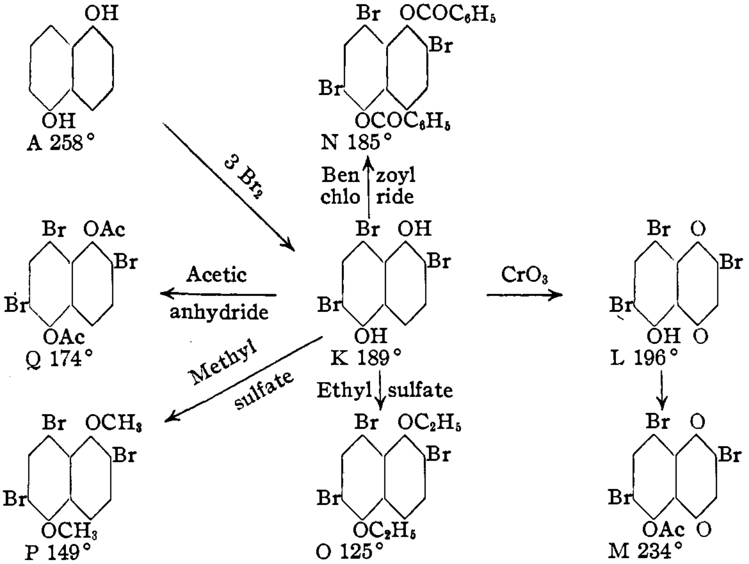
If a glacial acetic acid solution of C is treated with a little concd. nitric acid, short yellow needles crystallize out. This product explodes at 243°. It dissolves in dilute sodium hydroxide, giving a red solution which stains the skin. It contains nitrogen but no bromine.

Tribromodihydroxynaphthalene

2,6,8-Tribromo-1,5-dihydroxynaphthalene, $C_{10}H_3(OH)_2Br_3$(K).—Twenty grams of dihydroxynaphthalene was dissolved in 700 cc. of hot glacial acetic acid and a few crystals of iodine added. While the temperature was maintained at 80° a solution of 19.5 cc. of bromine dissolved in 50 cc. of glacial acetic acid was added as follows: 46 cc. was allowed to drop in slowly. Much hydrogen bromide was evolved. One-half of the remainder was added in one portion and after ten minutes the last portion was added slowly. The solution was removed from the water-bath, allowed to stand for fifteen minutes and then cooled. The pale greenish-yellow crystals which formed were filtered and washed with petroleum ether; weight, 35 g. or 70.5% of the theoretical. Purification was effected by dissolving the product in glacial acetic acid at 100° (decomposes at higher temperatures), shaking with charcoal and filtering. An abundant mass of colorless cotton-like crystals appeared on cooling. The substance melts with decomposition at 189°, is soluble in acetone and in ether, slightly in cold acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{10}H_5O_2Br_3$: Br, 60.45. Found: Br, 60.08.

It is converted by concd. nitric acid into a compound containing nitrogen but no bromine. It consists of yellow needles which explode at 249° and dissolve in dilute sodium hydroxide with a blood red color.



Diacetate, $C_{10}H_3(OCOCH_3)_2Br_3$(Q).—Compound K was boiled for four hours with acetic anhydride, giving yellow needles which became colorless on boiling an alcoholic solution with charcoal; m. p. 174°; soluble in benzene; insoluble in ether.

Anal. Calcd. for $C_{14}H_9O_4Br_3$: Br, 49.89. Found: Br, 49.78.

Dibenzoate, $C_{10}H_3(OCOC_6H_5)_2Br_3$(N).—Compound K was treated in pyridine solution with benzoyl chloride. The yellow crystals which formed were changed to an oil with water. The ether solution of the oil was decolorized with charcoal. On mixing the filtered solution with petroleum ether, colorless microscopic plates slowly formed. The substance liquefies with turbidity at 185° but becomes transparent at 189°. It is soluble in ether and in chloroform. insoluble in acetic acid, acetone and carbon tetrachloride.

Anal. Calcd. for $C_{24}H_{13}O_4Br_3$: Br, 39.67. Found: Br, 39.47.

Dimethyl Ether, $C_{10}H_3(OCH_3)_2Br_3$(P).—The crude product was a reddish-purple solid but in alcoholic solution charcoal removed the color; colorless needles, m. p. 149°; easily soluble in benzene and in ether. insoluble in petroleum ether.

Anal. Calcd. for $C_{12}H_9O_2Br_3$: Br, 56.47. Found: Br, 56.26.

Diethyl Ether, $C_{10}H_3(OC_2H_5)_2Br_3$(O).—The crude product crystallized from hot alcohol in colorless needles, m. p. 125°; solubilities as above.

Anal. Calcd. for $C_{14}H_{13}O_2Br_3$: Br, 52.98. Found: Br, 52.68.

2,6,8-Tribromo-5-hydroxy-1,4-naphthoquinone, $C_{10}H_3O_2OHBr_3$(L).—To a suspension of compound K dissolved in 250 cc. of glacial acetic acid was added 20 g. of chromic acid dissolved in very little water. The temperature rose to 55°. It was heated to 80° for about fifteen minutes while vigorous effervescence occurred. It was then heated for ten minutes longer. The solution was filtered and poured into much cold water. The orange-colored precipitate was filtered and washed with water. It was dried and extracted with boiling petroleum ether. The solvent was distilled off and the residue recrystallized from hot glacial acetic acid; rich red needles; m. p. 196°; yield, small. The quinone is very soluble in chloroform and in benzene; slightly soluble in alcohol and in ether.

Anal. Calcd. for $C_{10}H_4O_3Br_3$: Br, 58.49. Found: Br, 58.60.

Monoacetate, $C_{10}H_2O_2OCOCH_3Br_3$(M).—The quinone on boiling for seven hours with acetic anhydride gave an acetate consisting of golden-brown scales, m. p. 234°, when recrystallized from acetic acid; soluble in chloroform, insoluble in alcohol and in petroleum ether.

Anal. Calcd. for $C_{12}H_5O_4Br_3$: Br, 52.98. Found: Br, 52.84.

Tetrabromodihydroxynaphthalene

2,4,6,8-Tetrabromo-1,5-dihydroxynaphthalene, $C_{10}H_2(OH)_2Br_4$(S).—To 10 g. of diacetoxynaphthalene dissolved in 200 cc. of chloroform containing a few crystals of iodine was added 14 cc. of bromine. The solution was well shaken and allowed to stand. Much hydrogen bromide was evolved. After ten minutes the product began to crystallize out; most of the product had formed in ten hours. This was filtered off and a second crop was obtained at the end of two days; total yield, 19.5 g.; colorless glistening feathery needles which did not melt below 300°. It can be recrystallized from hot benzene, 90 cc. of which dissolves 0.5 g. only. The product decomposes if solvents of higher boiling point are used. It is insoluble in most of the organic solvents. Crystals exposed to direct sunlight turn rose-pink in color within two hours.

Anal. Calcd. for $C_{10}H_4O_2Br_4$: Br, 67.23. Found: Br, 67.45.

Dimethyl Ether, $C_{10}H_2(OCH_3)_2Br_4$(T).—The methyl ether was prepared in the usual way and the crude product boiled in benzene with charcoal. It was then filtered and the solvent evaporated off. The residue was dissolved in the least amount of hot benzene, cooled and an equal amount of alcohol added, giving colorless microscopic needles, m. p. 226°; soluble in benzene and in acetic acid, insoluble in ether and in petroleum ether.

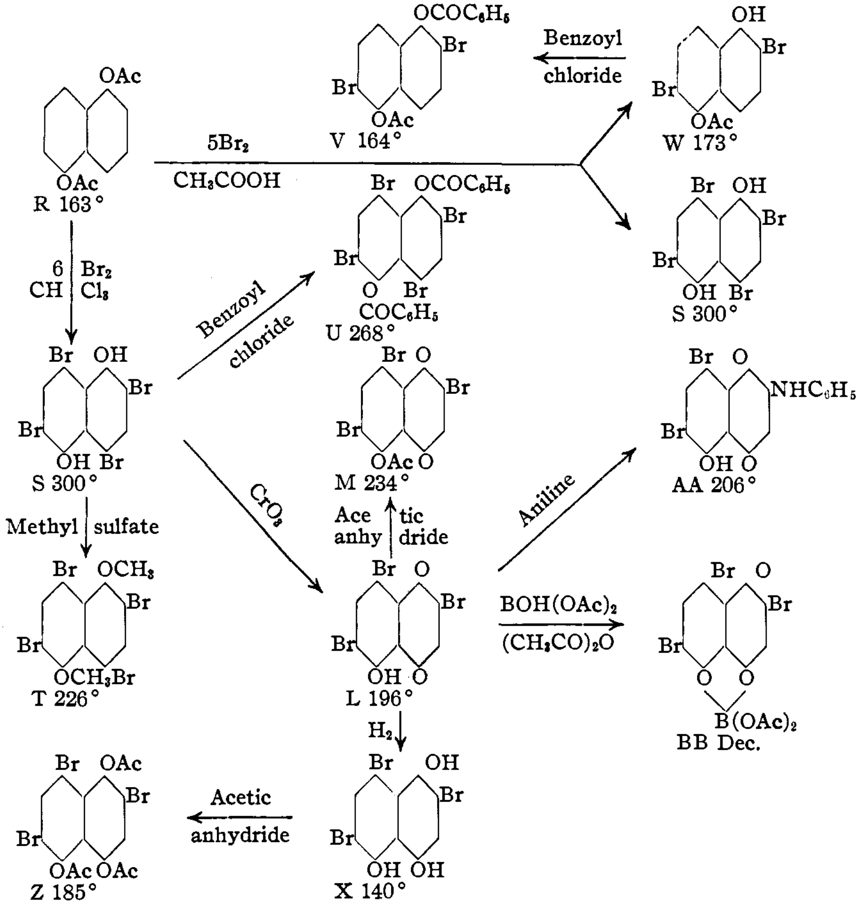
Anal. Calcd. for $C_{12}H_8O_2Br_4$: Br, 63.41. Found: Br, 63.21.

Dibenzoate, $C_{10}H_2(OCOC_6H_5)_2Br_4$(U).—Compound S was benzoylated by the Schotten–Baumann method. The product was purified as was the dimethyl ether, and gave irregularly shaped plates, m. p. 268°; soluble in benzene; insoluble in alcohol and in ether.

Anal. Calcd. for $C_{24}H_{12}O_4Br_4$: Br, 46.92. Found: Br, 46.85.

Further Notes on the Tetrabromonaphthalene.—Compound S was oxidized with chromic acid in acetic acid solution. One atom of bromine was eliminated and a quinone identical with L was obtained, as was shown by its melting point, 196°, by the identity of the acetyl derivatives and by the following analysis.

Anal. Calcd. for $C_{10}H_3O_3Br_3$: Br, 58.39. Found: Br, 58.41.



Compound S gave a product with concd. nitric acid in acetic acid: chrome-yellow needles, m. p. 232° with decomposition. It contains nitrogen but no bromine. It dissolves in dilute sodium hydroxide, the solution coloring the skin red.

Certain dibromo and tribromo derivatives follow since a part of the bromine is eliminated in some reactions.

6,8-Dibromo-2-anilino-5-hydroxy-1,4-naphthoquinone, $C_{10}H_2O_2OHNHC_6H_4Br_2$ (AA).—Two cc. of aniline in 5 cc. of glacial acetic acid was added to a hot solution of 1 g. of L in 40 cc. of acetic acid, giving an abundant yield of dark red glistening needles of hair-like structure, showing a green fluorescence when recrystallized from acetic acid. It melts at 206° is soluble in chloroform and slightly soluble in alcohol and in ether.

Anal. Calcd. for $C_{16}H_9O_3NBr_2$: Br, 37.82. Found: Br, 37.66.

2,6,8-Tribromo-1,4,5-trihydroxynaphthalene, $C_{10}H_2(OH)_3Br_3$(X).—A suspension of 1 g. of the naphthoquinone L in 50 cc. of ether was underlaid with 50 cc. of dilute sulfuric acid. This was shaken with additions of zinc dust until reduction was complete. The ether layer was separated and mixed with an equal volume of petroleum ether. The crystalline precipitate was purified from a like mixture of solvents as long silky flesh-colored needles which decompose at about 140°, soluble in alcohol and in acetic acid;

difficultly soluble in chloroform and in benzene; soluble in dilute sodium hydroxide with a purple color which changes to a reddish-brown. Ferric chloride oxidizes the naphthol back to the quinone.

Anal. Calcd. for $C_{10}H_5O_3Br_3$: Br, 58.11. Found: Br, 57.75.

Triacetate, $C_{10}H_2(OCOCH_3)_3Br_3$(Z).—Compound X was boiled with acetic anhydride for seven hours: white fluffy needles from alcohol, m. p. 185°; soluble in benzene, less soluble in ether.

Anal. Calcd. for $C_{16}H_{11}O_6Br_3$: Br, 44.53. Found: Br, 44.31.

Pyroboro-acetate Ester of Tribromohydroxy-naphthoquinone (BB).—To 1 g. of compound L dissolved in 50 cc. of warm acetic anhydride was added 0.5 g. of pyroboro-acetate dissolved in the smallest amount of acetic anhydride. The flask was stoppered and shaken. A reddish-purple color developed and a fluorescent solid crystallized on cooling. The product was filtered, washed with absolute ether and dried to constant weight over phosphorus pentoxide; weight, 1.2 g.; hexagonal plates, possessing a green metallic luster but red by transmitted light. The ester was easily and completely decomposed to the original quinone by water. It was affected by even a very short exposure to the atmosphere. When heated a red vapor was evolved at 200° but no melting occurred below 300°.

Anal. Calcd. for $C_{14}H_8O_7Br_3$: Br, 44. 54. Found: Br, 44.47.

Determinations were also made for boric acid, acetic acid and for the quinone residue, using the method proposed by Dimroth.[7]

Anal. Calcd. for the quinone residue: 0.4592. Found: 0.4576. Calcd. for acetic acid: 14.9 cc. of 0.1457 N $Ba(OH)_2$. Found: 14.8 cc. Calcd. for boric acid: 7.4 cc. of 0.1457 N $Ba(OH)_2$. Found: 7.4 cc.

Bromination of Diacetoxynaphthalene in Acetic Acid.—When diacetoxynaphthalene is dissolved in glacial acetic acid, treated with 5 moles of bromine and allowed to stand at room temperature, a mixture of products S and W is obtained. The first crop, obtained after a few hours, was found to consist of the naphthol W. The second crop, after twelve hours' standing, was a mixture of W and the tetrabromo compound S. The naphthol was dissolved out from the mixture with acetone. After a week a final crop consisting of S only was recovered. Ten grams of the acetate gave 5 g. of W and 13 g. of S.

2,6-Dibromo-5-acetoxy-1-naphthol, $C_{10}H_4OCOCH_3OHBr_2$(W).—Colorless needles, m. p. 173°, from acetic acid solution.

Anal. Calcd. for $C_{12}H_8O_3Br_2$: Br, 44.44. Found: Br, 44.14.

The fact that one acetyl group was hydrolyzed was shown by the preparation of a monobenzoate in pyridine solution.

2,6-Dibromo-5-acetoxy-1-benzoxynaphthalene, $C_{10}H_3(OCOCH_3)(OCOC_6H_5)Br_2$ (V).—This product, made in the usual way, was recrystallized from a mixture of equal parts of alcohol and petroleum ether as transparent colorless rectangular plates, m. p. 164°; soluble in alcohol, slightly soluble in cold acetic acid and in petroleum ether.

Anal. Calcd. for $C_{19}H_{11}O_4Br_2$: Br, 35.57. Found: Br, 35.48.

Summary

1. 1,5-Dihydroxynaphthalene in acetic acid yields with bromine in the presence of iodine a dibromo and a tribromo substitution product.

2. The diacetate in chloroform solution similarly treated gives a tetrabromo derivative.

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[7] Dimroth, *Ann.*, **446**, 108 (1926).

3. The diacetate in acetic acid solution at room temperature gives a mixture of the tetrabromo derivative and a dibromo-acetoxynaphthol.
4. The dibromo compound is oxidized by chromic acid to a naphthoquinone; so also is the tribromo derivative, but the tetrabromo compound oxidizes with the loss of one bromine atom to the same quinone.
5. The naphthoquinones are easily reduced to dihydric and trihydric naphthols.
6. The hydroxynaphthoquinones have the 1,4-quinoid structure, as proved by the pyroboro-acetate reagent.
7. A variety of derivatives is described.
8. The naphthoquinones are isomeric with certain halogenated juglones but are not identical with any.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

LEVULINIC ACID AND ITS ESTERS

BY PETER P. T. SAH AND SHAO-YUAN MA

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While levulinic acid[1] is formed quite easily from glucose and other carbohydrates by the action of boiling dilute mineral acids, the mechanism of the reaction is still obscure and there is practically no good convenient method for the preparation of a large amount of the acid in the laboratory. The common procedure described by Rischbieth[2] offers experimental difficulties and gives only low yields due to incomplete disintegration of the carbohydrate (starch). McKenzie[3] has recently described a procedure in which cane sugar is hydrolyzed with dilute hydrochloric acid, the solution is evaporated to dryness and the residue extracted with ether. We have not found that the new method has any advantage over those previously described.

By repeated trials we have found commercial glucose to be a better starting material than sucrose. The yields were higher and the amount of humus substance precipitated was comparatively less. Another experimental observation we have made is that the action proceeds rapidly if the temperature of the solution is raised to 110°. At temperatures below this,

[1] (a) Nöldecke, *Ann.*, **149**, 224 (1869); (b) v. Grote and Tollens, *ibid.*, **175**, 181 (1875); (c) v. Grote, Kehrer and Tollens, *ibid.*, **206**, 207, 226, 233, 257 (1881); (d) Tollens, *Ber.*, **14**, 1950 (1881); (e) Kent and Tollens, *Ann.*, **227**, 227 (1884); (f) Block, Kreckeler and Tollens, *ibid.*, **238**, 287 (1887); (g) Wehmer and Tollens, *ibid.*, **243**, 314 (1888); (h) Schuette and Sah, THIS JOURNAL, **48**, 3164 (1926).

[2] Rischbieth, *Ber.*, **20**, 1773 (1887).

[3] McKenzie, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1929, Vol. IX, p. 50.