

or methyl alcohol, less easily in absolute alcohol, and is practically insoluble in dry acetone.

Subs., 0.1395; N, 9.4 cc. (21.5°, 770 mm.).

Subs., 0.1817; AgCl, 0.0717.

Calc. for $C_{20}H_{24}O_2N_2.HCl$: N, 7.77; Cl, 9.83. Found: N, 7.91; Cl, 9.76.

NEW YORK, N. Y.

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

THE HALOGENATION OF JUGLONE: A NEW TYPE OF NAPHTHALENE DYES.¹

BY A. S. WHEELER AND J. W. SCOTT.

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Previous to the work of Wheeler and Edwards² the study of the behavior of the hydroxy-naphthoquinones under direct halogenation seems to have been almost overlooked. In the monohydroxy-naphthoquinone series the only halogen derivatives obtained in this way are the 3-bromo-2-hydroxy-naphthoquinone by Diehl and Merz,³ and the analogous iodo compound by Kehrmann and Mascioni.⁴ The 4 known chloro derivatives were obtained by indirect means. In the dihydroxy-naphthoquinone series two chloro derivatives of naphthazarine have been described by Zincke and Schmidt,⁵ the addition compound called the dichloride and the 2-chloro-naphthazarine. This appears to cover the ground up to 1917 when Wheeler and Edwards published their investigation of the bromination of naphthazarine and of 1,4,5,6-tetrahydroxy-naphthalene, in which they showed that the bromination of naphthazarine proceeded analogously to its chlorination and that the bromination of the tetrahydroxy-naphthalene gave isomeric compounds, explained by their earlier discovery that 1,4,5,6-tetrahydroxy-naphthalene is a case of tautomerism,⁶ since it exists in the keto-enol forms. Hence a halogenated quinone would be at least one product of its halogenation.

In this paper we present the initial work upon the chlorination and the bromination of juglone or 5-hydroxy-1,4-naphthoquinone. When juglone in acetic acid solution is treated in the cold with chlorine or bromine, addition products B and G (see chart), are obtained, which lose a mole-

¹ This paper forms part of a thesis submitted by J. W. Scott in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of North Carolina. Mr. Scott succumbed to influenza last October one week after assuming his duties as research chemist with the du Pont Company.

² *THIS JOURNAL*, **39**, 2460 (1917).

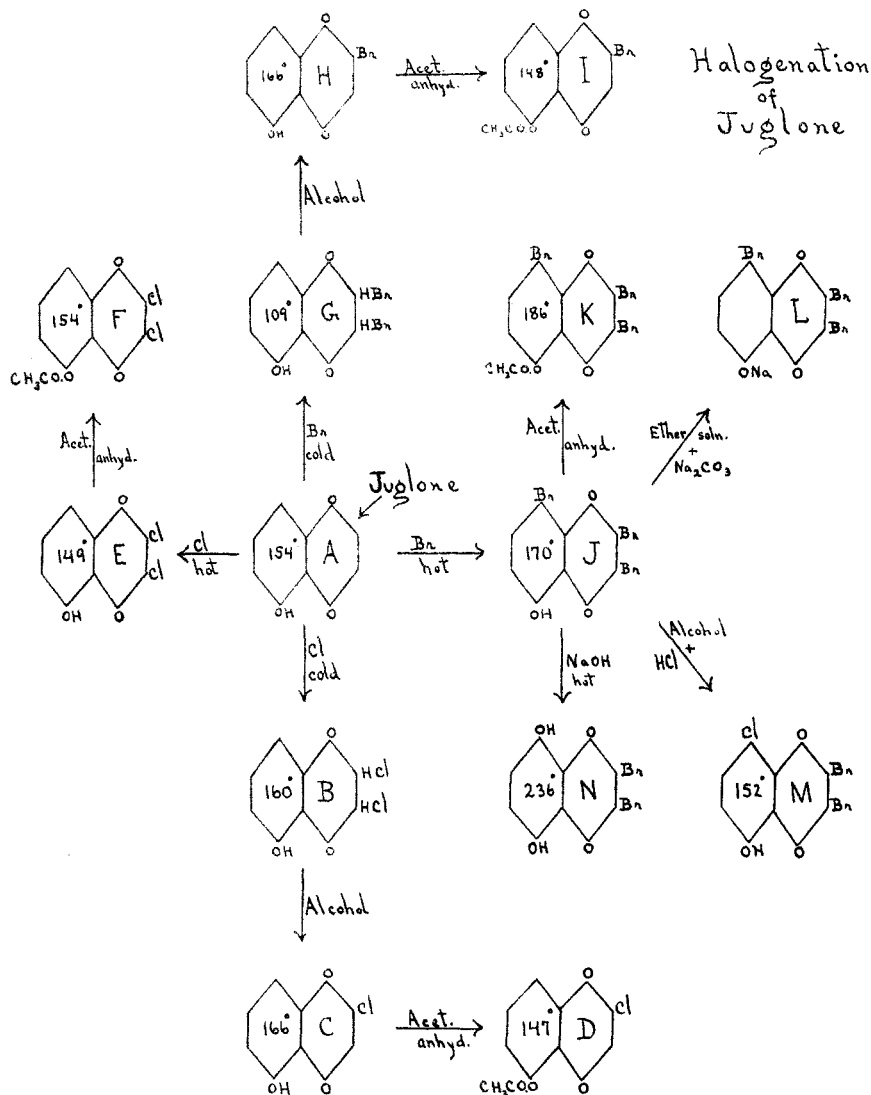
³ *Ber.*, **11**, 1066 (1878).

⁴ *Ibid.*, **28**, 345 (1895).

⁵ *Ann.*, **286**, 41 (1895).

⁶ *THIS JOURNAL*, **38**, 387 (1916).

cule of halogen acid by the action of alcohol, giving the monohalogen substitution products C and H. These still retain the hydroxyl at position 5 as shown by the production of the acetyl derivatives D and I. If juglone in hot acetic acid solution is treated with chlorine, a dihalogen



substitution compound, E, is obtained whereas bromine gives a trihalogen derivative J. This difference in the number of halogen atoms taken up was quite unlooked for. Both compounds yield acetyl derivatives, F and K, with acetic anhydride. The tribromojuglone was also treated

with alcoholic hydrochloric acid, one bromine atom being substituted by a chlorine atom, M. This indicates that one bromine atom is different from the other two and by placing it in Position 8 we have an environment different from that of the other two which are symmetrically placed in the quinone ring. Tribromojuglone also gives up one bromine atom for an hydroxyl group when warmed with alcoholic caustic soda, N.

In tribromojuglone is found a new type of naphthalene dye. This brilliant red compound consists of a quinone ring tied to a phenol ring, so that its character as a dye was to be predicted. Its sodium salt, L, is readily prepared by shaking its ether solution with aqueous sodium carbonate. It is an indigo blue substance which readily dyes silk a beautiful champagne while wool assumes a tan color which may be modified by the use of mordants. Cotton requires a mordant and if tannic acid is used it assumes an ecru color.

Juglone itself should be a dye but it is oxidized when an attempt is made to prepare the sodium salt. And if juglone is halogenated in the cautious way, that is in the cold, it forms an unstable addition product. For these reasons, perhaps, this new group of dyes was not discovered earlier. Five new dyes are described in this paper. To cover this type letters patent have been applied for.

Juglone.

All of the juglone used in this investigation was prepared by the oxidation of 1,5-dihydroxy-naphthalene, obtained before the war from the Badische Anilin u. Soda Fabrik of Ludwigshaven am Rhein who very kindly kept us supplied with this material free of cost. We wish to express here our sincere thanks for this material.

Juglone was first mentioned by Vogel and Reischauer,¹ who obtained it from fresh walnut hulls. It is next referred to by Phipson,² who called it regianin but his product evidently was not pure. Much later Griessmayer³ published Reischauer's notes on juglone (the first appearance of this name), giving an analysis of the compound and its copper salt. The two names given above are derived from the botanical name of the walnut tree, *Juglans regia*. Bernthsen⁴ gave a number of reasons for believing it to be an hydroxy-naphthoquinone. Bernthsen and Semper⁵ extracted 150 kg. of ripe walnut hulls with ether and obtained a yield of 150 g. or 0.10% of pure juglone. By the action of nitric acid they obtained juglonic acid or dinitrohydroxy-phthalic acid, showing that the hydroxyl group in juglone is in the benzene ring. Mylius⁶ fused juglone with pot-

¹ *Buchner Neues Repert. für Pharm.*, 5, 106 (1856); *l'Institut*, 1857, p. 71.

² *Compt. rend.*, 69, 1372 (1869).

³ *Ber.*, 10, 1542 (1877).

⁴ *Ibid.*, 17, 1945 (1884).

⁵ *Ibid.*, 18, 203 (1885).

⁶ *Ibid.*, 18, 463 (1885).

ash and obtained *m*-hydroxybenzoic acid and salicylic acid. Bernthsen and Semper¹ prepared the dioxime, having made the monoxime earlier. These reactions established the constitution of juglone as being 5-hydroxy-1,4-naphthoquinone. Finally Bernthsen and Semper² synthesized juglone by oxidizing 1,5-dihydroxy-naphthalene with chromic acid, obtaining a yield of 30-40%. The acetyl derivative and the monoxime were found to be identical with those obtained from the natural juglone.

Experimental Part.

Juglone Dichloride, (2,3)-C₁₀H₆O₃Cl₂ (B).—One g. of juglone was dissolved in 15 cc. of glacial acetic acid and excess of chlorine was passed into the solution at room temperature. The red solution soon became yellow and after 15 minutes crystals began to separate out. After an hour the product was filtered off. It consisted of yellow crystals, weighing 0.57 g. A second and third crop weighed 0.2 g. each. The crystals of the first crop melted at 156-158° and were recrystallized from 20 cc. of ligroin. The pure product crystallizes in lemon-yellow plates which on heating turn brown at 150° and melt at 159-160°. It is easily soluble in acetone, not readily in ether and is best recrystallized from ligroin or glacial acetic acid.

Subs., 0.1444, 0.1492: AgCl, 0.1687, 0.1752.

Calc. for C₁₀H₆O₃Cl₂: Cl, 28.96. Found: 28.90, 29.05.

Moderately heated with absolute alcohol it is converted into monochloro-juglone by the loss of a molecule of hydrochloric acid.

2-Chlorojuglone (2-Chloro-5-hydroxy-1,4-naphthoquinone), C₁₀H₄O₂·OH.Cl (C).—One g. of juglone dichloride was heated with 70 cc. of absolute alcohol over a water bath at about 60°. The dichloride slowly dissolved forming a yellow solution which gradually changed to a brown. After 2 hours crystals, weighing 0.4 g., were filtered off. These melted at 163-164°. Upon recrystallization from carbon tetrachloride the melting point was raised to 166°, a violet vapor coming off above 130°. The crystals are small, flat, yellowish brown needles. They are not easily soluble in ether or ligroin and are best recrystallized from alcohol or carbon tetrachloride.

Subs., 0.1360, 0.1449: AgCl, 0.0940, 0.1003.

Subs., 0.1497: CO₂, 0.3169; H₂O, 0.0338.

Calc. for C₁₀H₄O₂Cl: Cl, 17.01; C, 57.56; H, 2.40. Found: Cl, 17.10, 17.12; C, 57.73; H, 2.53.

The acetyl derivative is readily obtained with the use of acetic anhydride.

Acetyl-2-chlorojuglone, C₁₀H₄O₂.OCOCH₃Cl (D).—One g of monochloro-juglone was dissolved in 20 cc. of acetic anhydride and the solution

¹ *Ber.*, 19, 164 (1886).

² *Ibid.*, 20, 934 (1887).

was kept near its boiling point for 5 hours. It was then somewhat concentrated, whereupon 0.89 g. of the yellowish brown acetate crystallized out. The crude product melted at 142–144°. It was recrystallized from 10 cc. of alcohol. The pure substance crystallizes in clear, brownish yellow plates which melt at 147°. It is easily soluble in acetic acid and chloroform, less soluble in alcohol and only slightly soluble in ether and ligroin.

Subs., 0.1314, 0.1436: AgCl, 0.0748, 0.0828.

Subs., 0.1495: CO₂, 0.3159; H₂O, 0.0347.

Calc. for C₁₂H₇O₄Cl: Cl, 14.16; C, 57.49; H, 2.79. Found: Cl, 14.08, 14.26; C, 57.62; H, 2.60.

2,3 - Dichlorojuglone (2,3 - Dichloro-5-hydroxy-1,4-naphthoquinone), C₁₀H₃O₂.OH.Cl₂ (E).—An excess of chlorine was passed into a solution of one g. of juglone in 10 cc. of glacial acetic acid. The solution was heated 3 hours on the water bath. The solution was cooled and the product was filtered off. It melted at 144–147° and weighed 0.7 g. The mother liquor gave a further yield of 0.4 g. melting below 125°. The first crop was recrystallized from 40 cc. of alcohol. The pure substance consists of lustrous, golden-brown needles, melting at 149° to a dark red liquid. It is easily soluble in cold acetone, benzene and chloroform. It is best recrystallized from glacial acetic acid or alcohol.

Subs., 0.1456, 0.1432: AgCl, 0.1717, 0.1679.

Subs., 0.1520: CO₂, 0.2764; H₂O, 0.0250.

Calc. for C₁₀H₄O₃Cl₂: Cl, 29.19; C, 49.40; H, 1.65. Found: Cl, 29.17, 29.10; C, 49.61; H, 1.84.

Acetyl Dichlorojuglone, C₁₀H₃O₂.OCOCH₃Cl₂ (F).—One g. of dichlorojuglone was heated with 15 cc. of acetic anhydride for 6 hours. Yield, over one g. Recrystallized from 40 cc. of alcohol it melted at 154° to a dark brown liquid. The pure substance consists of yellow plates, is soluble in chloroform, slightly soluble in ether and best purified by alcohol or carbon tetrachloride.

Subs., 0.1490: AgCl, 0.1508.

Subs., 0.1402: CO₂, 0.2595; H₂O, 0.0298.

Calc. for C₁₂H₄O₄Cl₂: Cl, 24.89; C, 50.54; H, 2.11. Found: Cl, 25.04; C, 50.49; H, 2.38.

Juglone Dibromide, (2,3)-C₁₀H₃O₂.OH.(HBr)₂ (G).—One g. of juglone, suspended in 4 cc. of carbon tetrachloride was treated with 3.8 g. of bromine and shaken 4 hours in a machine. Solution took place in less than an hour and in 4 hours a few yellow crystals had appeared on the walls of the bottle. The liquid was evaporated off *in vacuo*. The residue, weighing 1.83 g., was reddish yellow and melted at 102–104°. On recrystallizing from ligroin yellow prisms with pointed ends, arranged in rosetts and fan-shaped groups, were obtained. These melted at 109° to a deep yellow liquid. They are soluble in acetone and benzene, less soluble in ether, slightly soluble in alcohol and ligroin but easily when hot.

Subs., 0.1461, 0.1515: AgBr, 0.1648, 0.1714.

Subs., 0.1512, 0.1510: CO₂, 0.2002, 0.1992; H₂O, 0.0256, 0.0234.

Calc. for C₁₀H₆O₂Br₂: Br, 47.91; C, 35.93; H, 1.79. Found: Br, 48.00, 48.14; C, 36.12, 35.99; H, 1.89, 1.73.

Juglone dibromide readily loses one molecule of hydrobromic acid with hot alcohol.

2-Bromojuglone (2-Bromo-5-hydroxy-1,4-naphthoquinone), C₁₀H₈O₂·OH.Br (H).—One g. of juglone dibromide was heated with 5 cc. of absolute alcohol on the steam bath. The yellow solution gradually became red, then brown. In an hour crystals began to appear and after two hours the product was filtered off. It weighed 0.54 g. and melted at 165–166°. It was recrystallized from 15 cc. of acetone with only slight loss. The pure crystals are translucent yellowish brown plates which deposit in clusters and melt at 166° to a nearly black liquid. They are easily soluble in chloroform and benzene, much less soluble in cold acetone and acetic acid but readily in the hot, slightly soluble in ether and ligroin.

Subs., 0.1391, 0.1489: AgBr, 0.1041, 0.1105.

Subs., 0.1452: CO₂, 0.2541; H₂O, 0.0258.

Calc. for C₁₀H₆O₂Br: Br, 31.62; C, 47.43; H, 1.98. Found: Br, 31.85, 31.58; C, 47.72; H, 1.99.

An attempt was made to prepare monobromojuglone by warming juglone in glacial acetic acid with one molecule of bromine on the water bath for 3 hours, but only a black decomposition product could be isolated.

Acetyl-2-bromojuglone, C₁₀H₄O₂.OCOCH₃.Br (I).—0.8 g. of monobromojuglone was heated with 10 cc. of acetic anhydride 3.5 hours on the water bath. The liquid was evaporated off and the residue, weighing 0.65 g. and melting at 145–147°, was recrystallized from 25 cc. of alcohol, yielding 0.42 g. of golden brown plates, melting at 148° to a dark yellow liquid. The substance is soluble in cold glacial acetic acid, benzene and chloroform and is best recrystallized from hot alcohol.

Subs., 0.1441, 0.1214: AgBr, 0.0913, 0.0770.

Subs., 0.1502: CO₂, 0.2696; H₂O, 0.0338.

Calc. for C₁₂H₇O₄Br: Br, 27.12; C, 48.81; H, 2.37. Found: Br, 26.96, 26.99; C, 48.97; H, 2.52.

2,3,8-Tribromojuglone (2,3,8-Tribromo-5-hydroxy-1,4-naphthoquinone), C₁₀H₂O₂·OH.Br₃ (J).—This is the most important compound described in this paper. 3.0 g. of juglone was dissolved in 30 cc. of hot glacial acetic acid, 11.0 g. of bromine (4 mols) was added and the solution was heated on a steam bath. Crystals appeared in 2 hours and after 3 hours there was an abundant mass of deep red crystals, which weighed 5.7 g. or 190% of the weight of juglone used. The crude product melted at 167–168°. If 3.0 g. is dissolved in 50 cc. of chloroform and 120 cc. of ligroin added, the first crop of crystals amounts to 2.25 g. The pure substance melts at 170° and consists of brilliant rich red needles, easily ob-

tained 1.5 cm. in length. The powder is light brick red. It is soluble in chloroform and benzene, less soluble in acetone and carbon tetrachloride, difficultly soluble in alcohol and ether.

Subs., 0.1524, 0.1510; AgBr, 0.2085, 0.2070.

Subs., 0.1512, 0.1526; CO₂, 0.1619, 0.1633; H₂O, 0.0088, 0.0138.

Calc. for C₁₀H₈O₃Br₃: Br, 58.39; C, 29.20; H, 0.73. Found: Br, 58.22, 58.33; C, 29.21, 29.18; H, 0.65, 1.01.

Tribromojujgone is insoluble in hot conc. hydrochloric acid, dissolves in strong nitric and in strong sulfuric acid with a red color. It dissolves in hot sodium carbonate solution, forming a purple solution which soon changes to red. It is unaltered by boiling with absolute alcohol 6 hours. The addition of hydrochloric acid to the alcohol causes a substitution of one bromine atom by a chlorine atom. Aqueous or alcoholic caustic soda introduces an hydroxyl group in place of a bromine atom. Tribromojujgone is readily acetylated and forms a sodium salt.

Sodium Salt of Tribromojujgone, C₁₀H₇O₃Br₂Na.—One g. of tribromojujgone is dissolved in 300 cc. of ether and vigorously shaken 15 minutes with a solution of 2.0 g. of sodium carbonate in 20 cc. of water. The ether layer is removed and the purpish deposit in the water layer is filtered off and washed with sodium carbonate solution. The dried powder has an indigo blue color. The yield is quantitative. The salt is easily soluble in water and in alcohol. It reverts to tribromojujgone in acid solutions.

Subs., 0.4997, 0.5004; Na₂SO₄, 0.0861, 0.0836.

Calc. for C₁₀H₇O₃Br₂Na: Na, 5.31. Found: 5.58, 5.41.

It is an active direct dye for silk and wool. If the purple aqueous solution is warmed with silk, it quickly turns yellowish and the silk is dyed a beautiful, rich champagne. The usual mordants have no effect in altering the shade except tin, which imparts an interesting greenish cast. Wool is dyed equally rapidly, taking a tan color. The shade is altered by most mordants especially chrome and copper. The dyeings on both fibers are fast to washing and ironing and fade somewhat only after a long exposure to a southern light, usually sunshine. Cotton is entirely unaffected by the dye but if mordanted with tannic acid it assumes an ecru shade.

Acetyl Tribromojujgone, C₁₂H₉O₄Br₂K.—The action of acetyl chloride is very slow, requiring several days of heating and then giving only a 25% yield. Acetic anhydride is much better. One g. of tribromojujgone is heated with 10 cc. of acetic anhydride 6 hours until the red crystals completely disappear and pure yellow ones form. Yield, 71%. The crystals are silky yellow needles, melting at 186°. The best solvents for purification are alcohol, glacial acetic acid and ligroin.

Subs., 0.1502; AgBr, 0.1864.

Subs., 0.1540; CO₂, 0.1792; H₂O, 0.0163.

Calc. for $C_{12}H_4O_4Br_2$: Br, 52.97; C, 31.79; H, 1.10. Found: Br, 52.80; C, 31.75; H, 1.18.

Attempt to Methylate Tribromojuglone.—One g. of tribromojuglone was heated with 350 cc. of absolute methyl alcohol and 10 cc. of conc. sulfuric acid. Solution took place in an hour and after heating 110 hours the solution was poured into water, boiled up and the red crystals which separated were identified as unchanged tribromojuglone.

Attempts to Oxidize Tribromojuglone.—Tribromojuglone does not dissolve in hot nitric acid of sp. gr. 1.15. It dissolves in hot conc. nitric acid. No organic derivative could be isolated from the solution, however. Tribromojuglone was oxidized in alkaline permanganate solution. The solution was acidified and extracted with ether but no product could be isolated. These reactions will be examined again, however.

8-Chloro-2,3-dibromojuglone (8-Chloro-2,3-dibromo-1,4-naphthoquinone), $C_{10}H_2O_2(OH)_2.Br_2(N)$.—One g. of hydrogen chloride was passed into a solution of one g. of tribromojuglone in 80 cc. of absolute alcohol. Upon heating the solution on the water bath the color changed from red to yellow. When crystals appeared the reaction was complete. The crude product, weighing 0.6 g., melted at 148–150°. It was recrystallized from 40 cc. of alcohol and was obtained in golden-bronze plates, melting at 152° to a dark red liquid. The compound is soluble in cold acetone, benzene and chloroform, difficultly soluble in ether and ligroin.

Subs., 0.1422: AgCl + AgBr, 0.2004. This mixture gave 0.1247 Ag on reduction. Hence; AgCl, 0.0537; AgBr, 0.1467.

Subs., 0.1511: CO_2 , 0.1816; H_2O , 0.0186.

Calc. for $C_{10}H_2O_2ClBr_2$: Cl, 9.68; Br, 43.64; C, 32.76; H, 0.82. Found: Cl, 9.34; Br, 43.89; C, 32.79; H, 1.36.

The reaction may be carried out with a solution of conc. hydrochloric acid in alcohol but the yield is smaller.

8-Hydroxy-2,3-dibromojuglone (1,4-Dihydroxy-2,3-dibromo-1,4-naphthoquinone), $C_{10}H_2O_2(OH)_2.Br_2(N)$.—One g. of tribromojuglone was dissolved in a mixture of 80 cc. of warm alcohol and 40 cc. of 10% sodium hydroxide. The solution, at first violet colored, became blood-red and gave a precipitate. After heating one hour on the water bath the mixture was poured into 100 cc. of cold water and acidified with dil. sulfuric acid. The yellow, flocculent precipitate weighed 0.61 g. and melted at 230–233°. This was warmed in 6 cc. of absolute alcohol, filtered from impurities and cooled. The pure product consists of small golden-brown prismatic needles which on heating begin to give off a vapor about 160° and at 236° melt to a black liquid. It may be recrystallized from alcohol, glacial acetic acid or chloroform.

Subs., 0.1324, 0.1510: AgBr, 0.1436, 0.1624.

Subs., 0.1551: CO_2 , 0.1972; H_2O , 0.0177.

Calc. for $C_{10}H_4O_4Br_2$: Br, 45.93; C, 34.48; H, 1.15. Found: Br, 46.15, 45.77; C, 34.69; H, 1.28.

Work is under way in this laboratory extending this field in a number of directions.

Summary.

1. The chlorination of juglone in cold glacial acetic acid gives a dichloride, an addition product, which loses a molecule of hydrochloric acid with alcohol, giving a monochlorojuglone and this is acetylated with acetic anhydride.

2. The chlorination of juglone in hot glacial acetic acid gives a substitution product, dichlorojuglone, which is a new dye, imparting a rich golden-bronze color to silk. It is acetylated by acetic anhydride.

3. The bromination of juglone in cold glacial acetic acid gives a dibromide which loses one molecule of hydrobromic acid with alcohol, forming a monobromojuglone which is acetylated by acetic anhydride.

4. The bromination of juglone in hot glacial acetic acid gives a substitution product, tribromojuglone, one more halogen atom entering than in the chlorination. Tribromojuglone is acetylated by acetic anhydride. One atom of bromine is replaced (1) by chlorine by the action of alcoholic hydrochloric acid, (2) by hydroxyl by the action of hot caustic alkali.

5. Tribromojuglone is a new type of dye in the naphthalene series. Its sodium salt is soluble and dyes silk a champagne, wool a tan, and cotton, mordanted with tannic acid, is dyed an ecru.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

THE PREPARATION OF β -AMINOPROPIOPHENONE.

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The action of potassium phthalimide upon organic halides to give a potassium halide and a phthalimide derivative of the organic radical, which by hydrolysis was resolved into phthalic acid and an amino derivative of that same radical, was first announced by Gabriel.¹ By this synthesis a large number of amino compounds were made possible of preparation and to Gabriel we owe the advancement made in this direction. It recently became necessary for us, in the course of an investigation soon to be reported, to prepare β -aminopropiophenone and to this purpose we were required to study the possible methods for its preparation. From among the syntheses applicable for amines, only a few can find use where a keto group is present in the radical.

In addition to the Gabriel method we have attempted to prepare this compound by the action of ammonia upon halides of the alkyls contain-

¹ *Ber.*, 20, 2224 (1887).