dark red to bright fluorescent yellow. The hot solution was then filtered, 50 cc. of acetic acid was added, and the mixture was heated to boiling. Hot water was added until crystals began to form. Boiling was continued for several minutes, and then the solution was cooled. The product was 1,3-di-*p*-chlorophenyl-5,6-dimethylisobenzofuran.

By the same method the 1,3-di-*p*-tolyl-5,6-dimethyl-, 1,3-di-*p*-tolyl-, and 1,3-di-*p*-chlorophenyl-substituted isobenzofurans were prepared. The change of color at the end of the reduction did not always take place, so the length of time for reduction, which apparently varied with the activity of the zinc, had to be estimated in each case.

**Addition of Maleic Anhydride to Isobenzofurans (VII).**—To a solution of 6 g. (1 mol) of 1,3-di-*p*-chlorophenyl-5,6-dimethylisobenzofuran in 200 cc. of benzene was added 1.8 g. (1.1 mols) of maleic anhydride. The reaction was complete in about five minutes in cold solution, as indicated by the sudden disappearance of fluorescence. The solvent was evaporated at room temperature under reduced pressure, and crystals of 1,4-di-*p*-chlorophenyl-1,4-oxido - 6,7 - dimethyl - 1,2,3,4 - tetrahydronaphthalene-2,3-dicarboxylic anhydride separated.

When this compound was crystallized from hot benzene solution, a lower melting isomer was obtained. This isomer was also obtained when the original addition was carried out in hot solution.

By this method the maleic anhydride adducts of 1,3-di-*p*-tolyl-5,6-dimethyl-, 1,3-di-*p*-chlorophenyl-, and 1,3-di-*p*-tolyl-substituted isobenzofurans were also prepared. These products were crystallized from hot solutions and no attempt was made to isolate the higher melting isomers except in the case of 1,3-di-*p*-tolyl-5,6-dimethylisobenzofuran (see Table IV).

**Dehydration of Oxido Tetrahydro Naphthalic Anhydrides (VII) to Form the Corresponding Naphthalic Anhydrides (VIII).**—A suspension of 2 g. of 1,4-di-*p*-chlorophenyl - 1,4 - oxido - 6,7 - dimethyl - 1,2,3,4 - tetrahydronaphthalene-2,3-dicarboxylic anhydride in 200 cc. of absolute methanol was saturated with dry hydrogen chloride gas. The gas was bubbled through the solution slowly to keep it saturated while it was refluxed for two hours. The mixture was then evaporated to dryness. After addition of 50 cc. of 30% aqueous potassium hydroxide and 200 cc. of ethanol, the mixture was refluxed for six hours. The solution was then cooled and acidified. The precipitate was filtered off and purified by dissolving in potassium hydroxide, followed by reprecipitation by acid. The crude 1,4-di-*p*-chlorophenyl-6,7-dimethyl-2,3-naphthalic anhydride was crystallized from hot acetic acid.

By the same method the 1,4-di-*p*-tolyl-6,7-dimethyl-, 1,4-di-*p*-chlorophenyl-, and 1,4-di-*p*-tolyl-substituted 2,3-naphthalic anhydrides were also prepared (see Table IV). Benzene was a more suitable solvent for crystallization of the last two compounds.

## Summary

The new methods reported in a previous paper[2] for the preparation of dihydroisobenzofurans, isobenzofurans, *o*-dibenzoyl benzenes, and aryl- and alkyl-substituted naphthalenes from the butadiene and dimethylbutadiene adducts of dibenzoylethylene were shown to work equally well for the di-*p*-chlorobenzoyl and di-*p*-toluyl ethylenes.

Cyclopentadiene added in good yield to di-*p*-chlorobenzoyl, di-*p*-toluyl, and dimesitoyl ethylenes.

Dimesitoylethylene formed an adduct with butadiene, but did not react with 2,3-dimethylbutadiene.

The dimesitoylethylene adduct to butadiene and all of the adducts from cyclopentadiene could not be converted to furans by the usual procedures.

URBANA, ILLINOIS RECEIVED MARCH 11, 1940

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON AND LEE UNIVERSITY AND HYNSON, WESTCOTT AND DUNNING, INC.]

# The Halogenation of Salicylic Acid

BY LARKIN HUNDLEY FARINHOLT, A. P. STUART* AND DANIEL TWISS

The preparation of polyhalogenated salicylic acids was attempted for several reasons. In the first place, the compounds might have valuable physiological properties and, in the second place, the order in which the halogen atoms enter the available positions is interesting from a theoretical point of view.

The mono- and disubstituted halogen derivatives of salicylic acid have been prepared by previous investigators by the addition of the free halogens to a solution of salicylic acid in a suitable medium. Nothing is known, however, concerning the tri- and tetrahalogenated salicylic acids which form the subject of this investigation.

Starting with 3,5-diiodosalicylic acid prepared according to Woollett and Johnson,[1] numerous methods were applied with the object of obtaining higher iodinated derivatives, but with negative results in each case. The following methods were attempted: (I) refluxing diiodosalicylic acid

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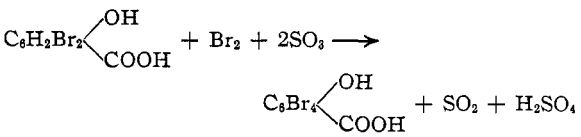
(1) "Organic Syntheses," Vol. XIV, 1934, p. 52.

with iodine in ethyl alcohol, as well as in other solvents, according to Lautemann[2]; (II) using iodine chloride, based on the method of Cofman[3]; (III) following the method of Weselsky,[4] who iodinated in the presence of mercuric oxide; (IV) by the effective method of Likhosherstov and Tzimbalist[5] using dichlorourea and potassium iodide. These methods also were tested on the acetyl derivative of 3,5-diiodosalicylic acid but with equally negative results.

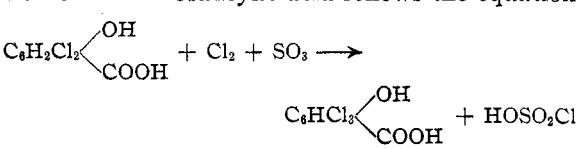
3,5-Dichloro- and 3,5-dibromosalicylic acids were prepared by the method of Earle and Jackson.[6] Attempts to substitute in these compounds more chlorine and bromine, respectively, resulted either in a replacement of the carboxyl group by halogen or no reaction at all.

Juvalta,[7] Rupp[8] and Pratt and Shupp[9] prepared polyhalogenated phthalic anhydrides by halogenating phthalic anhydride in solution in fuming sulfuric acid and Twiss and Farinholt[10] showed that *o*-sulfobenzoic anhydride may be halogenated in the same manner. The present investigation is concerned with the application of this method to salicylic acid and dihalogenosalicylic acids. The experiments with salicylic acid were not successful. The reaction yielded a water-soluble product, indicating substitution of sulfonic acid groups which, apparently, were too firmly bound to the nucleus to be replaced by halogen atoms under the conditions of the reaction. It was found necessary first to prepare the dihalogenosalicylic acids by known methods and use them as the starting materials for further halogenations. No iodine derivatives could be prepared by this method since both diiodosalicylic acid and its acetyl derivative decomposed on contact with fuming sulfuric acid, even in the cold, with liberation of iodine.

Good results were obtained with dibromo- and dichlorosalicylic acids. No attempt was made to interpret the mechanism of the process but it seems likely that the dihalogenosalicylic acids form some sort of unstable addition complex with sulfur trioxide or sulfuric acid which facilitates the substitution of the halogen atoms. According to the amount of bromine, one or two bromine atoms may be introduced into dibromosalicylic acid. The hydrogen bromide evolved in the reaction is oxidized by the sulfur trioxide and the resulting bromine made available again for further substitution. The net result of the formation of tetrabromosalicylic acid may be represented by the equation

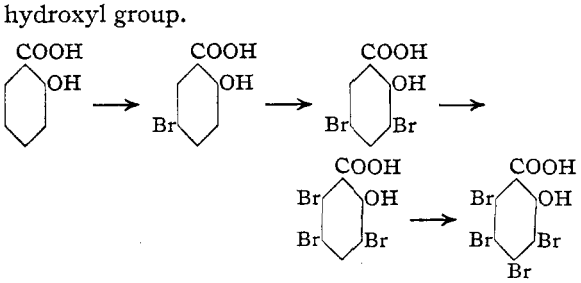


In the chlorination, the hydrogen chloride is not oxidized but combines with sulfur trioxide to form chlorosulfonic acid. It is worthy of note that the trichlorosalicylic acid cannot be chlorinated further but that a bromine atom may be substituted in the remaining free position. The formation of trichlorosalicylic acid follows the equation



The position of the third halogen in trichloro- and tribromosalicylic acids was determined by heating the acid thus formed with soda lime and identifying the resulting trihalogenophenol. It was shown that the substitution takes place in position 6, adjacent to the carboxyl group, presumably under the influence of the two halogen atoms already present. No evidence was found of the formation of isomers. The introduction of a fourth bromine atom in tribromosalicylic acid and of a bromine atom in trichlorosalicylic acid occurs without difficulty.

The order in which bromine atoms, for example, substitute in salicylic acid is represented by the scheme below. The first atom enters mainly in the position meta to the carboxyl and para to the hydroxyl group.



The replacement of the carboxyl group by a halogen atom served as a further check on the

(2) Lautemann, *Ann.*, **120**, 301 (1861).
(3) Cofman, *Gazz. chim. ital.*, **50**, II, 297 (1920).
(4) Weselsky, *Ann.*, **174**, 103 (1874).
(5) Likhosherstov and Tzimbalist, *J. Gen. Chem.* [*U. S. S. R.*], **3**, 177–182 (1933).
(6) Earle and Jackson, THIS JOURNAL, **28**, 109, 111 (1906).
(7) German Patent 50,177 (1889), *Frdl.*, **2**, 93 (1889).
(8) Rupp, *Ber.*, **29**, 1625–1634 (1896).
(9) Pratt and Shupp, THIS JOURNAL, **40**, 203, 254 (1918).
(10) Twiss and Farinholt, *ibid.*, **58**, 1561–1565 (1936).

configurations of the halogenated salicylic acids. The combined action of bromine and water on all these acids produced halogenated phenols of known constitution. In this way tetrabromosalicylic acid gave pentabromophenol, 3,5,6-tribromosalicylic acid yielded 2,3,4,6-tetrabromophenol, while 3,5,6-trichlorosalicylic acid gave 2-bromo-3,4,6-trichlorophenol and 4-bromo-3,5,6-trichlorosalicylic acid formed 2,5-dibromo-3,4,6-trichlorophenol. Similarly, 3,5,6-trichlorosalicylic acid was converted into 2,3,4,6-tetrachlorophenol by the action of chlorine in the presence of water. For complete identification, acetyl and benzoyl derivatives were prepared and the melting points compared with those given in the literature.

## Experimental

### Halogenation of Salicylic Acid

The preparation of the following polyhalogenated salicylic acids was carried out in a three-necked Pyrex flask, fitted with a reflux condenser and a monel metal stirrer. The flask was heated by means of an oil- or water-bath; the temperatures given refer to the bath.

**3,4,5,6-Tetrabromosalicylic Acid.**—In 275 ml. of 60% fuming sulfuric acid, 50 g. of 3,5-dibromosalicylic acid[11] was dissolved and 28 g. (9 ml.) of bromine slowly added through a dropping funnel under the surface of the liquid while stirring vigorously. The addition took place over a period of four hours and during this time the flask was kept in a water-bath at about 30°. Toward the latter part of the reaction a crystalline solid separated. After stirring for two more hours and standing overnight, the tetrabromosalicylic acid was filtered off on a sintered glass funnel. The filtrate gave more tetrabromosalicylic acid by pouring on ice. The yield of the crude product was nearly quantitative.

3,4,5,6-Tetrabromosalicylic acid was purified by crystallization from dilute alcohol, forming clusters of white crystals which gradually decomposed at about 235–240°.

*Anal.* Calcd. for $C_7H_2O_3Br_4$: Br, 70.46. Found: Br, 70.33.

**Acetyl 3,4,5,6-Tetrabromosalicylic Acid.**—In order to furnish a check on the results above and to prepare a suitable derivative for identification, 3,4,5,6-tetrabromosalicylic acid was acetylated by heating a small amount with acetic anhydride and several drops of concentrated sulfuric acid. The solution was then carefully diluted with water, the solid filtered off and allowed to dry spontaneously on a porous plate. The acetyl derivative of 3,4,5,6-tetrabromosalicylic acid crystallizes in needles from ligroin containing a little toluene, m. p. 162.5°.

*Anal.* Calcd. for $C_9H_4O_4Br_4$: Br, 64.49. Found: Br, 64.34.

**3,5,6-Tribromosalicylic Acid.**—After dissolving 30 g. of 3,5-dibromosalicylic acid in 200 ml. of 60% fuming sulfuric acid, 8.1 g. (2.7 ml.) of bromine was added, while stirring, over a period of one and one-half hours. After the addition of the bromine, stirring was continued for another hour. The temperature was kept at about 30° throughout the reaction. Some tribromosalicylic acid precipitated from the oleum solution and was filtered off. The filtrate was diluted by pouring on ice and more of the acid thus obtained. The yield of the crude product was nearly quantitative. 3,5,6-Tribromosalicylic acid crystallizes from toluene in rectangular plates, m. p. 210.5°.

*Anal.* Calcd. for $C_7H_3O_3Br_3$: Br, 63.98. Found: Br, 63.70.

**Acetyl 3,5,6-Tribromosalicylic Acid.**—The compound was prepared following the same procedure as for the tetrabromosalicylic acid. On dilution of the acetic anhydride solution, the acetyl derivative of 3,5,6-tribromosalicylic acid separated as an oil which, after scratching and shaking, was converted into a solid. The product crystallized from ligroin in needles, m. p. 145°.

*Anal.* Calcd. for $C_9H_5O_4Br_3$: Br, 57.52. Found: Br, 57.73.

**3,5,6-Trichlorosalicylic Acid.**—3,5-Dichlorosalicylic acid was first prepared by the method of Earle and Jackson.[6] A solution of 83 g. of this material in 200 ml. of 60% fuming sulfuric acid was heated in an oil-bath to 80–90°. While stirring vigorously, a slow stream of chlorine was passed through the solution for about fifteen hours. On cooling, crystals of trichlorosalicylic acid separated and were filtered off on a sintered glass funnel. A second crop was obtained by pouring the filtrate on ice. Based on the crude product, the yield was about 70%. 3,5,6-Trichlorosalicylic acid may be crystallized from benzene, toluene, dilute acetic acid or dilute ethyl alcohol. It forms white plates, m. p. 207°.

*Anal.* Calcd. for $C_7H_3O_3Cl_3$: Cl, 44.08. Found: Cl, 44.06.

**Acetyl 3,5,6-Trichlorosalicylic Acid.**—Prepared by the procedure described above, this compound crystallizes from ligroin in needles, m. p. 129.5°.

*Anal.* Calcd. for $C_9H_5O_4Cl_3$: Cl, 37.53. Found: Cl, 37.77.

**Attempted Preparation of Tetrachlorosalicylic Acid.**—A solution of 60 g. of 3,5-dichlorosalicylic acid in 250 ml. of 60% fuming sulfuric acid was chlorinated for six hours at 40–45°, then for six hours at 65–75° and finally for seventeen hours at 100°. The resulting compound was not the anticipated tetrachloro derivative but was 3,5,6-trichlorosalicylic acid. The addition of iodine as a catalyst did not produce different results, while an attempt to chlorinate trichlorosalicylic acid with dichlorourea, according to Likhosherstov,[5] left the starting material unaltered.

**4-Bromo-3,5,6-trichlorosalicylic Acid.**—To a solution of 25 g. of recrystallized 3,5,6-trichlorosalicylic acid in 175 ml. of 60% fuming sulfuric acid was added 8.1 g. [2.7 ml.] of bromine through a dropping funnel over a period of about two hours while stirring. The temperature was kept at about 30°. After the addition, the solution was stirred for another hour and then diluted by pouring over ice. The white solid which separated was obtained in nearly a quantitative yield. 4-Bromo-3,5,6-trichlorosalicylic acid crystallizes from dilute alcohol in clusters of white crystals, m. p. 213°.

(11) This compound was prepared by the method of Earle and Jackson.[6] A pure product was obtained in an 87% yield.

*Anal.* Calcd. amount of silver to precipitate all halogen in a 0.3181 g. sample of $C_7H_2O_3BrCl_3$: 3.971 milliequivalents. Found: 3.962.

**Acetyl 4-Bromo-3,5,6-trichlorosalicylic Acid.**—The acetyl derivative of 4-bromo-3,5,6-trichlorosalicylic acid was prepared in the usual manner. It separates from ligroin in white crystals, m. p. 144°.

*Anal.* Calcd. amount of silver to precipitate all halogen in a 0.3236 g. sample of $C_9H_4O_4BrCl_3$: 3.572 milliequivalents. Found: 3.579.

**Attempted Preparation of 3,5-Dichloro-4,6-diiodosalicylic Acid.**—As the instability of 3,5-diiodosalicylic acid in fuming sulfuric acid may be due to the fact that the iodine atoms are in the activated positions, ortho and para to the phenolic hydroxyl, an attempt was made to iodinate 3,5-dichlorosalicylic acid in the less reactive positions 4 and 6.

To a solution of 60 g. of 3,5-dichlorosalicylic acid in 200 ml. of 60% fuming sulfuric acid, 74.5 g. of iodine was added gradually over a period of sixteen hours. The temperature was kept at 50–60° and the mixture was stirred continuously. The procedure was marked by foaming which ceased at the end of this time. Heating was then continued at 100° with 100 ml. additional fuming sulfuric acid until the foaming subsided and the cooled reaction mixture poured on ice. A dark colored solid separated and this was shown to be free iodine. No other solid precipitated and no dichlorosalicylic acid could be recovered.

### Establishment of the Positions of the Halogen Atoms by Decarboxylation

The determination of the positions of the halogen atoms in the halogenosalicylic acids was accomplished by two methods. The first consisted in decarboxylating the acid, to form the corresponding phenol, by heating in a retort with an excess of dry soda lime. The desired phenol sublimed into the neck of the retort and was removed by dissolving in alkali, then reprecipitated with acid and recrystallized from a suitable solvent. As an additional check, a functional derivative was prepared and, if already known, its melting point compared with that recorded in the literature.

**2,3,4,5-Tetrabromophenol** was formed by heating 2,3,4,5-tetrabromosalicylic acid with powdered soda lime in a retort at 195°. It crystallizes in white needles from dilute alcohol, m. p. 123°, and has not been reported previously in the literature.

*Anal.* Calcd. for $C_6H_2OBr_4$: Br, 78.03. Found: Br, 78.08.

**2,3,4,5-Tetrabromophenyl acetate** was prepared in the usual manner with acetic anhydride and a drop of concentrated sulfuric acid. It crystallizes from dilute acetic acid in white needles, m. p. 110.5°.

*Anal.* Calcd. for $C_8H_4O_2Br_4$: Br, 70.78. Found: Br, 70.93.

**2,3,4,5-Tetrabromophenyl benzoate** was prepared by the Schotten–Baumann reaction. It crystallizes from ethyl alcohol in clusters of white needles, m. p. 133°.

*Anal.* Calcd. for $C_{13}H_6O_2Br_4$: Br, 62.24. Found: Br, 62.23.

**2,4,5-Tribromophenol**[12] (m. p. 80°) was obtained by decarboxylating 3,5,6-tribromosalicylic acid with soda lime at 200°; benzoate, m. p. 97–98°.

**2,4,5-Trichlorophenol**[13] (m. p. 67.5°) was obtained by decarboxylating 3,5,6-trichlorosalicylic acid with soda lime at 185°; benzoate, m. p. 89–90°.

**3-Bromo-2,4,5-trichlorophenol** was obtained by heating 4-bromo-3,5,6-trichlorosalicylic acid with soda lime in a retort at 185°. This compound, which has not been prepared previously, crystallizes from ligroin in clusters of white needles, m. p. 126°.

*Anal.* Calcd. amount of silver to precipitate all halogen in a 0.3055 g. sample of $C_6H_2OBrCl_3$: 4.421 milliequivalents. Found: 4.399.

**3-Bromo-2,4,5-trichlorophenyl benzoate** was prepared by the usual method. It crystallizes from dilute alcohol in clusters of needles, m. p. 125°.

*Anal.* Calcd. amount of silver to precipitate all halogen in a 0.1313 g. sample of $C_{13}H_6O_2BrCl_3$: 1.381 milliequivalents. Found: 1.372.

### Action of Bromine and Chlorine Water on the Halogenated Salicylic Acids

Another aid in determining the position of the halogen atoms in the halogenated salicylic acids was the replacement of the carboxyl group by bromine or chlorine, thus obtaining known halogenated phenols. For complete identification, the acetyl or benzoyl derivatives were prepared and compared with the literature.

**2,3,4,5,6-Pentabromophenol.**—A solution of bromine in acetic acid was added to a suspension of 2,3,4,5-tetrabromosalicylic acid in 30% acetic acid. Carbon dioxide was evolved slowly. Excess bromine solution was added, the mixture was warmed to about 60° and stirred at that temperature until no more carbon dioxide was liberated. More water was added, the mixture shaken and the solid filtered off and washed thoroughly. The yield of the phenol was nearly quantitative. 2,3,4,5,6-Pentabromophenol[14] crystallizes from dilute acetic acid in white needles, m. p. 229–230°. The acetyl derivative crystallizes from acetic acid in prisms, m. p. 198–199°.

**2,3,4,6-Tetrabromophenol.**—Following the same procedure as in the preparation of pentabromophenol, 3,5,6-tribromosalicylic acid in dilute acetic acid was treated with bromine to give a nearly quantitative yield of 2,3,4,6-tetrabromophenol.[15] It crystallizes from dilute alcohol in clusters of needles, m. p. 112–113°. Its acetyl derivative separates from dilute acetic acid in flat plates, m. p. 105°.

**2-Bromo-3,4,6-trichlorophenol.**—In the same manner as above, 3,5,6-trichlorosalicylic acid was treated with bromine water. The crude phenol thus obtained was dissolved in 5% sodium hydroxide solution, filtered from a small amount of insoluble material of unknown composition, and precipitated with hydrochloric acid. 2-Bromo-

(12) *Cf.* Kohn and Pfeifer, *Monatsh.*, **48**, 211–229 (1927).

(13) *Cf.* (a) Holleman, *Rec. trav. chim.*, **39**, 736–750 (1920); (b) Kohn and Fink, *Monatsh.*, **58**, 73–91 (1931).

(14) *Cf.* Zincke and Birschel, *Ann.*, **362**, 227 (1908); Lucas and Kemp, THIS JOURNAL, **43**, 1660 (1921).

(15) *Cf.* Hodgson, Walker and Nixon, *J. Chem. Soc.*, 1054 (1933); Zincke, *Ann.*, **363**, 262–263 (1908).

3,4,6-trichlorophenol crystallizes from dilute acetic acid in white needles, m. p. 83–84°. The melting point is several degrees higher than that given by previous investigators[13b,16] but there seems to be little doubt concerning its constitution since the benzoyl derivative is identical with that prepared by Kohn and Fink. This compound crystallizes from acetic acid in prisms, m. p. 116–117°.

**2,5-Dibromo-3,4,6-trichlorophenol.**—Following the same procedure, 4-bromo-3,5,6-trichlorosalicylic acid was treated with bromine water. The resulting 2,5-dibromo-3,4,6-trichlorophenol[13b] crystallizes from dilute alcohol in clusters of needles, m. p. 195°. The benzoyl derivative separates from glacial acetic acid in prisms, m. p. 177–178°.

**2,3,4,6-Tetrachlorophenol.**—Chlorine was passed through a suspension of 3,5,6-trichlorosalicylic acid in 30% acetic acid for several hours. A heavy oil precipitated. It was washed with water several times and treated with 5% sodium hydroxide solution, in which most of the material dissolved. The alkaline solution was filtered and then acidified with hydrochloric acid. The oil which separated soon solidified. On recrystallizing several times from ligroin, the resulting needles melted at 68–69°, the melting point of 2,3,4,6-tetrachlorophenol.[17] Its acetyl derivative[18] crystallizes from dilute alcohol, and melts at 66°.

(16) *Cf.* Fox and Turner, *J. Chem. Soc.*, 1863 (1930).

**Acknowledgment.**—We are indebted to David Norvell Walker for his aid in carrying out part of this investigation.

## Summary

1. Tri- and tetrahalogeno substituted products of salicylic acid were prepared by halogenation in fuming sulfuric acid.

2. The positions of the halogen atoms were determined (a) by decarboxylation and identification of the resulting halogenated phenols and (b) by substitution of the carboxyl groups by bromine or chlorine and subsequent identification of the halogenated phenols.

(17) *Cf.* Tiessens, *Rec. trav. chim.*, **50**, 116 (1931); Lock and Nottes, *Monatsh.*, **67**, 320 (1936).

(18) *Cf.* Blitz and Giese, *Ber.*, **37**, 4014 (1904).

LEXINGTON, VIRGINIA
BALTIMORE, MARYLAND RECEIVED FEBRUARY 23, 1940

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY COLLEGE, CORK]

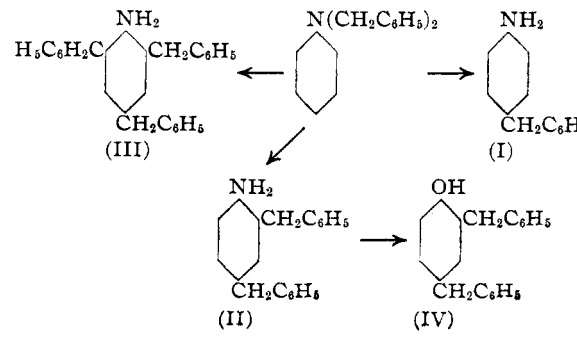
# The Molecular Rearrangement of Tertiary Aryl Alkyl Anilines

BY PETER J. DRUMM, W. F. O'CONNOR AND J. REILLY

The well-known Hofmann–Martius reaction involving the rearrangement of N-substitution products of the arylamines to C-substitution compounds has, in recent years, received considerable attention. Three theories which have been put forward are that the rearrangement, which is admittedly intermolecular, consists in the migration of the alkyl group, (1) as alkyl halide, (2) as a free radical and (3) as an olefin.

It seems to the present authors, in certain cases at any rate, that another possibility may be envisaged, *viz.*, a combination of the free radical and olefin mechanisms, in which the free radical is first produced and then dissociates to give an olefin. In support of this view F. O. Rice[1] from his work on propyl radicals has concluded that all radicals higher than ethyl dissociate to give olefins. It would seem possible, therefore, in certain cases, such as in the rearrangement of isoamylaniline, where trimethylethylene has been obtained,[2] that the first step is the splitting off of the free radical isoamyl which then loses a hydrogen atom to yield the olefin trimethylethylene.

To obtain further evidence, if possible, of the mechanism involved, the authors studied the rearrangement of dibenzylaniline hydrochloride. The products isolated were *p*-aminodiphenylmethane (I), 1-amino-2,4-dibenzylbenzene (II) and an aminotribenzylbenzene which is probably 1-amino-2,4,6-tribenzylbenzene (III). The orientation of the benzyl groups in (II) was determined by its conversion into 2,4-dibenzylphenol (IV).




(1) Rice, "Annual Reports on the Progress of Chemistry," The Chemical Society, London, 1937, p. 268.

(2) Hickinbottom, *J. Chem. Soc.*, 2396 (1932).