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°.

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.

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

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

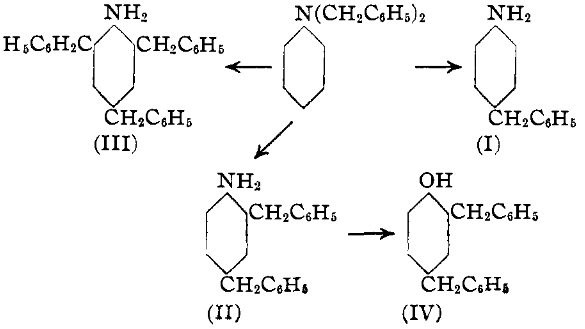
The Molecular Rearrangement of Tertiary Aryl Alkyl Anilines

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).



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

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

The authors were unable to obtain evidence of the formation of dibenzyl which might be expected to occur on the basis of the "free radical" theory. An olefin mechanism is also excluded for obvious reasons. It would appear, therefore, that under the conditions employed the theory of primary dissociation into aniline and benzyl halide may be an intermediate step in the rearrangement and in support of this view it was found that on heating dibenzylaniline hydrobromide in a current of nitrogen and so removing volatile products from the sphere of reaction benzyl bromide was obtained and identified as the benzyl ester of *p*-nitrobenzoic acid. It was found that dibenzylaniline undergoes rearrangement at temperatures below 200° which is considerably lower than that necessary in the case of the alkylanilines. A similar facility of migration has been observed by Hickinbottom[3] in the case of alkylanilines with heavy groups such as the cetyl and octyl groups. A further point of interest in connection with this work is the formation of aminotribenzylbenzene. This is the first instance so far as the authors are aware where more than two groups have been introduced into the aniline ring during the molecular rearrangement of either secondary or tertiary aniline bases.

Experimental

Seventy-eight grams of dry dibenzylaniline hydrochloride was heated in a sealed tube for seven hours at 200–220°. The viscous amber-colored product was treated with dilute sodium carbonate solution, and the liberated bases extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, the ether distilled off and the residual oil fractionated. The following fractions were collected: I, 15.6 g., b. p. 180–220° at 20 mm.; II, 24.2 g., b. p. 250–285° at 20 mm.; III, 15.0 g., b. p. 290–300° at 20 mm.

_p_-Aminodiphenylmethane.—Fraction I was redistilled and yielded 14.1 g. of an oil boiling at 185–190° at 14 mm. This oil readily dissolved, on heating, in dilute hydrochloric acid. On cooling the hydrochloride was deposited as colorless plates melting at 219°.

Anal. Calcd. for $C_{13}H_{14}NCl$: Cl, 16.17. Found: Cl, 16.26.

On conversion of this hydrochloride into the base, the latter was obtained as a solid which separated from ligroin in the form of colorless plates which melted at 36° alone or when mixed with a specimen of pure *p*-aminodiphenylmethane.[4] Benzoyl-*p*-aminodiphenylmethane crystallizes from alcohol in long, thin, prismatic needles, m. p. 165°.

Anal. Calcd. for $C_{20}H_{17}ON$: N, 4.88. Found: N, 4.82.

Diphenylmethane - 4 - azo - β - naphthol forms scarlet needles from alcohol, m. p. 141°.

Anal. Calcd. for $C_{23}H_{18}ON_2$: N, 8.28. Found: N, 8.34.

Fraction II.—This fraction on redistillation gave 22.8 g. of a light-yellow colored viscous oil, b. p. 250–260° at 11 mm. On dissolving in hot aqueous alcoholic hydrochloric acid and allowing the solution to cool slowly the hydrochloride separated and was subsequently crystallized from a mixture of chloroform and light petroleum (b. p. 60–80°) from which it separated in the form of needles melting at 171°.

Anal. Calcd. for $C_{20}H_{20}NCl$: Cl, 11.47. Found: Cl, 11.69.

The free base crystallizes from light petroleum (b. p. 40–60°) in colorless needles melting at 50°.[3]

Anal. Calcd. for $C_{20}H_{19}N$: C, 87.91; H, 6.96; N, 5.12. Found: C, 87.83; H, 7.08; N, 5.13.

Identification of above Base as 1-Amino-2,4-dibenzylbenzene.—Twenty-two grams of the above base was dissolved in dilute sulfuric acid. The solution was cooled to 5° and diazotized by the addition of an aqueous solution of 5.6 g. of sodium nitrite. The whole was then heated slowly to 60° and maintained at this temperature until evolution of nitrogen was complete. The product was extracted with ether and the residue after evaporation of the latter was distilled under reduced pressure giving a pale-yellow oil, b. p. 250–255° at 10 mm. This oil which was phenolic in character was still contaminated with traces of unchanged amine which interfered with its subsequent characterization. To remove the last traces of amine the oil was boiled with tin and hydrochloric acid and the cold acid solution extracted with ether. On removal of the latter the phenol was obtained as a colorless oil, b. p. 252–254° at 10 mm. It was converted into its α-naphthyl urethan derivative by heating with α-naphthyl carbimide almost to the boiling point for a few minutes. The oily product was extracted repeatedly with hot ligroin and filtered from the di-α-naphthyl carbamide. From the filtrate the α-naphthyl urethan separated in light yellow crystals m. p. 143–144°. A mixture of this substance with the α-naphthyl urethan of 2,4-dibenzylphenol[5] melted at 143–144°, with which substance it was identical. The base melting at 50°, obtained from fraction II above, is therefore 1-amino-2,4-dibenzylbenzene.

1-Benzoylamino-2,4-dibenzylbenzene separates as long, colorless needles from alcohol, m. p. 158°.

Anal. Calcd. for $C_{27}H_{23}ON$: N, 3.71. Found: N, 3.66.

2,4-Dibenzylbenzene-1-azo-β-naphthol.—It was found advantageous to carry out the diazotization of the amine in glacial acetic acid solution. The azo-β-naphthol was obtained from alcohol–chloroform in long red needles melting at 154°.

Anal. Calcd. for $C_{30}H_{24}ON_2$: N, 6.54. Found: N, 6.73.

Fraction III.—This oil, b. p. 290–300° at 20 mm., was dissolved in warm glacial acetic acid and concentrated hydrochloric acid added. The precipitated hydrochloride

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(3) Hickinbottom, *J. Chem. Soc.*, 1119 (1937).

(4) Basler, *Ber.*, 16, 2718 (1883).

(5) Short and Stewart, *J. Chem. Soc.*, 553 (1929).

was collected and recrystallized several times from ethyl acetate from which solvent it was obtained in clusters of needles melting at 186°.

Anal. Calcd. for $C_{27}H_{26}ClN$: Cl, 8.89. Found: Cl, 8.94.

The free base from the above hydrochloride crystallizes from ligroin in colorless, prismatic plates, m. p. 61–62°.

Anal. Calcd. for $C_{27}H_{25}N$: N, 3.86. Found: N, 3.78.

This substance is a primary amine and the results of analysis of itself and its derivatives agree with its formulation as an aminotribenzylbenzene. Hofmann, in his study of the molecular rearrangement of phenyltrimethylammonium iodide, obtained mesidine.[6] By analogy it is probable that the above aminotribenzylbenzene is 1-amino-2,4,6-tribenzylbenzene.

Benzoylaminotribenzylbenzene.—This compound crystallizes from alcohol in needles, m. p. 149°. *Anal.* Calcd. for $C_{34}H_{29}ON$: N, 3.00. Found: N, 3.01.

Tribenzylbenzene-azo-β-naphthol.—Crystallizes from alcohol in scarlet prisms with copper glance, m. p. 146°. *Anal.* Calcd. for $C_{37}H_{30}ON_2$: N, 5.41. Found: N, 5.61.

Summary

The molecular rearrangement of dibenzylaniline hydrochloride has been studied. The rearrangement proceeded at a comparatively low temperature with formation of *p*-aminodiphenylmethane, 1-amino-2,4-dibenzylbenzene and a third amine which is probably 1-amino-2,4,6-tribenzylbenzene. This would appear to be the first instance where three migrating groups have been introduced into the aniline ring during the rearrangement of a secondary or tertiary aniline base.

CORK, IRELAND RECEIVED NOVEMBER 29, 1939

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[6] Hofmann, *Ber.*, **5**, 715 (1872).

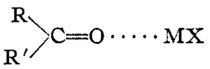
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Coördinate Compounds in the Color Test for Organometallic Compounds[1]

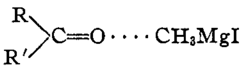
BY HENRY GILMAN AND R. G. JONES

The color test[2] is probably the most useful laboratory tool in studies on organometallic compounds. However, because Michler ketone, the essential compound in the color test, can form coördinate compounds with Grignard reagents, it is necessary to examine the possible interference effects of coördinate compounds.

The formal relationship of organometallic compounds to salts, made it a relatively short step from Werner's[3] coördination structures of the carbonyl type with salts [A], to the suggestion, which probably first was proposed by Straus,[4] for coördination compounds of ketones with the Grignard reagent [B]. Later, v. Braun[5] and then, particularly, Meisenheimer and co-workers[6] and Hess and Rheinboldt[7] used the coördination structures as a basis for interpreting some reactions of carbonyl compounds with the Grignard reagent.[8]



[A]



[B]

There is no doubt that coördination complexes of some sort are formed with many ketones and Grignard reagents. Not only have some of the complexes been isolated and analyzed, but they have been hydrolyzed to the original ketones.[9] The most interesting and suggestive recent study is by Pfeiffer and Blank.[10] They examined the molecular compounds derived by interaction of some Grignard reagents with benzophenone, *p*-aminobenzophenone, *p*-dimethylaminobenzophenone, and, of especial interest at this time, *p,p'*-tetramethyldiaminobenzophenone or Michler ketone. In each case, the complex formed by a 1:1 ratio of ketone and Grignard reagent regenerated the ketone on hydrolysis. With benzo-

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[1] This is Paper XXX in the series of "Relative reactivities of organometallic compounds; the preceding paper is: THIS JOURNAL, **62**, 980 (1940).

[2] (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925); (b) *Bull. soc. chim.*, **41**, 1479 (1927); (c) Gilman and Heck, *Rec. trav. chim.*, **48**, 193 (1929); (d) *ibid.*, **49**, 218 (1930); (e) *Ber.*, **62**, 1379 (1929); (f) Gilman, Sweeney and Heck, THIS JOURNAL, **52**, 1604 (1930); (g) Gilman and Heck, *ibid.*, **52**, 4949 (1930).

[3] Werner, *Ann.*, **322**, 296 (1902).

[4] Straus, *ibid.*, **393**, 241 (1912).

[5] Von Braun and Kirschbaum, *Ber.*, **52**, 1725 (1919).

[6] Meisenheimer and Casper, *ibid.*, **54**, 1655 (1921); Meisenheimer, *ibid.*, **61**, 708 (1928); *Ann.*, **442**, 180 (1925); **446**, 76 (1925).

[7] Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921). See, also, Hess and Wustrow, *Ann.*, **437**, 256 (1924).

[8] Earlier adaptations of coördinate structures were proposed for the structures of Grignard reagents. Some selected references are: Baeyer and Villiger, *Ber.*, **35**, 1202 (1902); Grignard, *Compt. rend.*, **136**, 1262 (1903); Chelinzeff, *Ber.*, **38**, 3665 (1905). Modern electronic concepts of valence are discussed by Johnson in Chap. 19 of Gilman, "Organic Chemistry," John Wiley and Sons, New York, 1938. See, particularly, p. 1673, for the preliminary coördination and subsequent migrations in the reaction of ketones with Grignard reagents.

[9] Leroide, *Compt. rend.*, **148**, 1611 (1909). Fischer and Hess, *Ber.*, **45**, 912 (1912).

[10] Pfeiffer and Blank, *J. prakt. Chem.*, **153**, 242 (1939).