

105° until evolution of hydrogen chloride ceased. The product was then carefully mixed with crushed ice and stirred to decompose excess phosphorus halides. The collected solid was washed acid free with water, dried at 100° and finally extracted with boiling benzene. On concentration of the extract, the chloro compound separated as small rosettes; m. p. 167°.

*Anal.* Calcd. for  $C_8H_9N_2Cl$ : Cl, 21.05. Found: Cl, 20.8.

(e) **Reaction with Aldehydes.** (1) **Formaldehyde.**—A mixture of 3 g. of aminohydroxypyridine in 20 ml. of glacial acetic acid containing 0.11 ml. of concentrated hydrochloric acid and 0.9 g. 37% aqueous formaldehyde was boiled for one hour. Almost immediately a white solid began to separate; on cooling the reaction mixture to 25° and filtering there was obtained 2.7 g. of product; m. p. 360° dec. after drying in a vacuum desiccator. Analyses indicated that this product probably was 3,3'-methylene-bis-(2-hydroxy-4-amino-6,7-dihydroxypyridine) containing one molecule of acetic acid of crystallization.

*Anal.* Calcd. for  $C_{17}H_{20}N_4O_2 \cdot C_2H_4O_2$ : C, 61.3; H, 6.45; N, 15.05. Found: C, 60.91; H, 6.90; N, 15.11.

(2) **Benzaldehyde (XVI).**—A solution of 3 g. of aminohydroxypyridine (II) in 20 ml. of glacial acetic acid containing 0.1 ml. of concentrated hydrochloric acid and 1.06

g. of benzaldehyde was heated for two hours at reflux with stirring. The precipitate which formed almost immediately was collected and washed with acetic acid and dried in a vacuum desiccator; m. p. 360°. The analysis corresponds to the structure of a phenyl dipyridopyridine indicated by the formula XVI on the chart. No attempt was made to identify the product.

*Anal.* Calcd. for  $C_{23}H_{21}N_3O_2$ : N, 11.35. Found: N, 11.49.

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### Summary

Acyl derivatives of iminonitriles (cyanoimines) of the cyclopentane, cyclohexane and benzene series have been found to undergo a ready condensation with sodamide to give 4-amino-2-hydroxypyridine derivatives in excellent yield. Some chemical reactions of these materials, which resemble meta-aminophenol, are described.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

## The Reaction of Aromatic Aldehydes with Aluminum Chloride and Benzene<sup>1</sup>

BY HERBERT E. UNGNADE AND ELBERT W. CRANDALL<sup>2</sup>

Certain aromatic aldehydes lose carbon monoxide when heated with aluminum chloride and benzene.<sup>3,4,5,6,7</sup> The reaction products include the aromatic residue corresponding to the aldehyde, anthracene and triphenylcarbinol.<sup>8</sup> The present investigation is concerned with the conditions of this reaction, the effect of substituents in the aldehyde and the nature of the solvent.

An exhaustive study with *o*-chlorobenzaldehyde indicates that the highest yields of chlorobenzene and triphenylcarbinol are obtained with two to three moles of aluminum chloride per mole of aldehyde and a reaction time of four hours at 60°.

The course of the reaction depends upon the substituents in the aldehyde. Nitrobenzaldehydes fail to lose carbon monoxide and give good yields of nitrotriphenylmethanes. Ortho-para directing groups facilitate the elimination of carbon monoxide and thus the formation of anthracene and triphenylcarbinol. Veratric aldehyde behaves abnormally since it yields only a small amount of guaicol, the main product being vanillin which in turn is recovered when heated with benzene and

aluminum chloride. A similar stability has been observed for 3-phenoxy-4-hydroxybenzaldehyde.<sup>9</sup>

When benzene is replaced by chlorobenzene or nitrobenzene, the aldehyde is recovered unchanged. Even a mixture of equal volumes of benzene and nitrobenzene fails to give a reaction with benzaldehyde. Toluene, however, can be substituted for benzene, giving a mixture of dimethylantracenes but no triarylcarbinol.

### Experimental<sup>9</sup>

**Starting Materials.**—*m*-Methoxybenzaldehyde was prepared by the methylation of *m*-hydroxybenzaldehyde with dimethyl sulfate. *o*-Nitrobenzaldehyde was obtained from *o*-nitrotoluene<sup>10</sup> and *m*-chlorobenzaldehyde from *m*-nitrobenzaldehyde.<sup>11</sup> The remaining aldehydes were commercial products.<sup>12</sup>

**Procedure.**—The reaction of aromatic aldehydes with benzene and aluminum chloride was carried out according to a standardized procedure which is given in detail for *o*-chlorobenzaldehyde.

A solution of *o*-chlorobenzaldehyde (25 g., 0.18 mole) in 150 cc. of thiophene-free benzene was added to 75 g. (0.56 mole) of anhydrous aluminum chloride contained in a three-necked flask equipped with stirrer, condenser and thermometer. The resulting mixture was stirred for six hours at a constant temperature of 60°. During the course of the reaction the mixture turned black. The reaction mixture was poured onto ice and concentrated hydrochloric acid and was steam-distilled. The volatile

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Chicago, April, 1948.

(2) In part from the Master's thesis of E. W. Crandall, 1948.

(3) Hey, *J. Chem. Soc.*, 72 (1935).

(4) Schaarschmidt, Hermann and Szemo, *Ber.*, **58**, 1914 (1925).

(5) Ellison and Hey, *J. Chem. Soc.*, 1847 (1938).

(6) Ungnade and Orwoll, *THIS JOURNAL*, **65**, 1736 (1943).

(7) Dewar and Jones, *J. Chem. Soc.*, **85**, 212 (1904).

(8) Triphenylmethane reported instead by the earlier workers<sup>3,4,5</sup> was undoubtedly a secondary product formed by reduction of the triphenylcarbinol.

(9) All temperatures uncorrected.

(10) "Organic Syntheses," **24**, 75 (1944).

(11) Buck and Ide, *ibid.*, **13**, 28 (1933).

(12) The authors are indebted to the Heyden Chemical Corporation, Garfield, N. J., for generous samples of *o*-chloro-, *p*-chloro-, 2,4-dichloro- and 3,4-dichlorobenzaldehyde.

product was fractionally distilled at atmospheric pressure. The first fraction boiling at 81–83° consisted of benzene. The product boiling at 130–132° (5.62 g.) was shown to be chlorobenzene. The semisolid residue from the steam distillation was extracted with benzene, washed neutral and was dried by distillation with benzene. It weighed 28.07 g. The dry residue was sublimed at 160–200° (2 mm.). The sublimate, dissolved in a minimum amount of Skellysolve C, was adsorbed on aluminum oxide. A blue fluorescent band visible in ultraviolet light was developed and eluted with the same solvent. It yielded 12.70 g. of anthracene, m. p. 212–214°. A brown band, eluted with benzene, contained 7.40 g. of triphenylcarbinol, m. p. 160–162° (from Skellysolve B).

The isomeric methoxy-, chloro- and hydroxybenzaldehydes treated in the same way, yielded phenol and chlorobenzene as volatile products. The non-volatile material consisted of anthracene, triphenylcarbinol and tar. The yields of both volatile and non-volatile substances for aldehydes with equivalent configurations were in the order  $\text{CH}_3\text{O} < \text{Cl} < \text{OH}$ .

**Nitrotriphenylmethanes.**—Each nitrobenzaldehyde (25 g.) was added slowly to a mixture of 50.6 g. of aluminum chloride and 150 cc. of thiophene-free benzene. The mixture was allowed to react as described for *o*-chlorobenzaldehyde, decomposed and steam distilled. The residual material was dissolved in benzene, dried by distillation with benzene and distilled under reduced pressure. The distillates were crystallized from Skellysolve B.

*o*-Nitrotriphenylmethane was obtained in 65.5% yield, b. p. 200–210° (2 mm.), m. p. 88–89°. It depressed the melting point of the *m*- and *p*-isomers. Its melting point is reported as 93–94°. <sup>13</sup>

*m*-Nitrotriphenylmethane boiled at 200–210° (2 mm.)

(13) Kliegl, *Ber.*, **40**, 4941 (1907).

and melted at 91.5–93°, yield 82.4%. The literature melting point is 90°. <sup>14</sup>

The yield of *p*-nitrotriphenylmethane was 67.4%, b. p. 200–210° (2 mm.), m. p. 90–91°. The melting point could be raised to 93–94° by adsorption of the substance on aluminum oxide from Skellysolve C solution. It did not depress the melting point of a sample prepared according to Baeyer and Lohr. <sup>15</sup>

**The Reaction with Disubstituted Benzaldehydes.**—2,4-Dichloro-, 3,4-dichloro-, 2,3-dimethoxy-, 2-hydroxy-3-methoxybenzaldehyde and veratric aldehyde (0.18 mole each) were treated with benzene and aluminum chloride as described before. The volatile products consisted of *o*- and *m*-dichlorobenzene and guaiacol. The non-volatile material from the disubstituted aldehydes with exception of veratric aldehyde contained anthracene and triphenylcarbinol. Veratric aldehyde gave 15.48 g. of pure vanillin, m. p. 79–80°, as the only non-volatile product.

**The Reaction with Toluene.**—Benzaldehyde (0.24 mole) aluminum chloride (67 g.) and toluene (150 cc.) yielded 14.9 g. of chromatographically uniform non-volatile material which melted at 215–217° (from Skellysolve C). The substance is regarded as a mixture of 2,6- and 2,7-dimethylanthracenes. <sup>3</sup>

### Summary

The reaction of aromatic aldehydes with aluminum chloride and aromatic hydrocarbons has been further investigated. The reaction with the nitrobenzaldehydes represents a simple way to prepare nitrotriphenylmethanes.

(14) Tschacher, *ibid.*, **21**, 188 (1888).

(15) Baeyer and Lohr, *ibid.*, **23**, 1621 (1890).

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## A Synthesis of N-(3-Methoxybenzyl)-N-methyl-3-methoxy-4,5-methylenedioxyphenethylamine

By K. E. HAMLIN AND ARTHUR W. WESTON

The synthesis of N-(3-methoxybenzyl)-N-methyl-3-methoxy-4,5-methylenedioxyphenethylamine (I) was undertaken to determine its identity with  $\alpha$ -fagarine, an alkaloid from the plant *Fagara coca*.<sup>1,2</sup> A comparison of physical data has shown I to be different from  $\alpha$ -fagarine, thus confirming the results recently reported by Surrey<sup>3</sup> and by Redemann, Wisegarver and Icke.<sup>4</sup> Inasmuch as our synthesis of 3-methoxy-4,5-methylenedioxyphenethylamine (II) is novel and more direct than those previously reported, we wish to describe it as well as certain other unreported experimental data involved in the synthesis of I. The synthesis of II by the rhodanine method of Gränacher<sup>5,6</sup> has been carried out also. Since it nearly duplicates the work of Redemann and co-workers, only where variations occur in the physical data obtained for the compounds

(1) Stuckert, *C. A.*, **29**, 2298 (1935).

(2) Deulofeu, Labriola and De Langhe, *THIS JOURNAL*, **64**, 2326 (1942).

(3) Surrey, *ibid.*, **70**, 2887 (1948).

(4) Redemann, Wisegarver and Icke, *J. Org. Chem.*, **13**, 886 (1948).

(5) Gränacher, *et al.*, *Helv. Chim. Acta*, **5**, 610 (1922); **6**, 458 (1923).

(6) Julian and Sturgis, *THIS JOURNAL*, **57**, 1126 (1935).

prepared in this synthesis, are such differences indicated in the experimental section.

As shown in the accompanying flow sheet, the starting material used was myristinaldehyde which was obtained in 51% yields by the oxidation of isomyristicin using a modification of the method of Milas.<sup>7</sup> The required isomyristicin was obtained from the isomerization of myristicin by ethanolic potassium hydroxide. A fractionation of heavy oil of nutmeg provided the myristicin.

Myristinaldehyde was converted to the corresponding nitrostyrene by means of nitromethane. Reduction by lithium aluminum hydride<sup>8</sup> provided a ready synthesis of III. The N-(3-methoxybenzyl)-3-methoxy-4,5-methylenedioxyphenethylamine (III) was prepared by catalytic hydrogenation<sup>3,4</sup> of the Schiff base from II and 3-methoxybenzaldehyde. Methylation by the lithium aluminum hydride reduction<sup>8</sup> of the formyl derivative of III resulted in the formation of I in good yield. The isolation and characterization of I and III as free bases, as well as the above mentioned Schiff base, are described.

(7) Milas, *ibid.*, **59**, 2342 (1937).

(8) Nystrom and Brown, *ibid.*, **70**, 3738 (1948).