The same products were obtained in another experiment in which 0.5 cc. of piperidine was used as a catalyst.

Azobenzene and *p*-Thiocresol.—A solution of 18.2 g. (0.1 mole) of azobenzene and 37.2 g. (0.3 mole) of *p*-thiocresol in 200 cc. of xylene was refluxed for twenty-five hours. As in all other experiments, a trap[2] was used to exclude air. The products obtained were 9.5 g. of aniline, 0.1 g. of benzidine (from a sulfuric acid treatment of the hydrazobenzene present), 5.5 g. of *p*-thiocresol and 90% of the di-*p*-tolyl disulfide which should have formed on the basis of the reduction products isolated.

Miscellaneous.—After heating 0.075 mole of benzophenone-anil with four molecular equivalents of *p*-thiocresylmagnesium iodide in an ether–xylene solution at 103–107° for twelve hours, 96% of the anil was recovered. In addition, 0.3 g. of aniline was isolated. Another experiment under corresponding conditions yielded a 95% recovery of the anil, and traces of aniline and di-*p*-tolyl disulfide.

Subsequent to refluxing three equivalents of *p*-thiocresylmagnesium iodide with benzalaniline in an ether–xylene solution at 114–124° for forty hours, 96% of the *p*-thiocresol was recovered.

The recovery of *p*-thiocresol in an experiment in which four molecular equivalents of it were refluxed with benzophenone in xylene for twenty-six hours was 97.8%. A like recovery of *p*-thiocresol was had in an experiment wherein eight equivalents were heated with nitrobenzene in xylene for twenty-six hours.

Summary

In continuation of studies on the unique 1,4-addition to a conjugated system which is part aliphatic and part aromatic, benzophenone-anil and benzalaniline, respectively, were heated with *p*-thiocresol. No 1,4-addition was observed. Instead the thiocresol acted as a reducing agent, and was converted to di-*p*-tolyl disulfide. It also reduces azobenzene, but not nitrobenzene or benzophenone. *p*-Thiocresylmagnesium iodide did not react with the anils.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE CHLORINE DERIVATIVES OF VANILLIN AND SOME OF THEIR REACTIONS

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In previous work in this Laboratory[1] the bromine substitution products of vanillin were studied for the purpose of completing the list and to obtain derivatives with which to test further the observations of Brady and Dunn,[2] who found that "no evidence of the existence of a second isomeride has been obtained in the cases of any hydroxybenzaldoximes," but that "certain negative substituents in the benzene ring seem to favor the existence of two isomeric oximes." Since stereoisomers were not obtained from

[1] Raiford and Hilman, THIS JOURNAL, **49**, 1077, 1571 (1927); Raiford and Stoesser, **50**, 2556 (1928).

[2] Brady and Dunn, *J. Chem. Soc.*, **105**, 825 (1914); **107**, 1859 (1915).

the bromine derivatives an adequate test of the question required the study of products containing the "more negative" substituent chlorine. The present report covers some of the data collected in that work.

The Action of Chlorine on Vanillin.—Prior to the present work Peratoner[3] chlorinated vanillin and obtained a product that was probably an impure sample of the monochloro derivative, m. p. 165°, more recently isolated by Hann,[4] which was regarded as the 5-chloro compound. Menke and Bentley[5] chlorinated vanillin in a chloroform solution and obtained a product that melted at 166°, and which was reported as a monochloro derivative, but no analytical data were recorded.[6]

To determine the positions of halogen in the three possible isomeric monochloro derivatives of vanillin, the start was made with that amino compound in which the position of the amino radical was fixed[7] as 2 by bringing it into relationship with hemipinic acid. This amino compound was diazotized and the chlorine derivative, m. p., 128°, obtained by Sandmeyer's method must be 2-chlorovanillin.

Direct chlorination of vanillin gave a monohalogenated product, m. p. 163°, in which it has been argued by Hann that chlorine occupies position 5. The third monochloro derivative, m. p. 167–168°,[8] was obtained by chlorination of 3-methoxy-4-acetoxybenzal diacetate.[9] To decide the position of chlorine in this compound, it was converted into a monobromochloro derivative, m. p. 214°, the properties of which were compared with those of an isomeric monobromochloro compound obtained from 2-amino-5-bromovanillin, the structure of which has been established by Raiford and Stoesser.[10] When the amino radical of this substance was replaced by chlorine, a monobromochlorovanillin, m. p. 187°,[11] was obtained which has chlorine in position 2, and the product must be 2-chloro-5-bromovanillin. From this it follows that the substance melting at 214° is the 5-bromo-6-chloro

[3] Peratoner, [*Gazz. chim. ital.*, **28**, 1, 235 (1898)], reported a product that melted at 158–160° and for which he recorded a chlorine content of 20.5% (calcd., 19.0).

[4] Hann, THIS JOURNAL, **47**, 2000 (1925).

[5] Menke and Bentley, *ibid.*, **20**, 316 (1898).

[6] In the present work it was found that although a monochloro compound, m. p. 163°, is the chief product of direct chlorination of vanillin, large excess of chlorine gives also small quantities of the isomeric 2,5- and 5,6-dichloro derivatives. This problem will be studied further to learn whether it is possible to start with pure 5-chlorovanillin and obtain these dichloro compounds in quantity.

[7] Pschorr and Sumuleanu, *Ber.*, **32**, 3408 (1899).

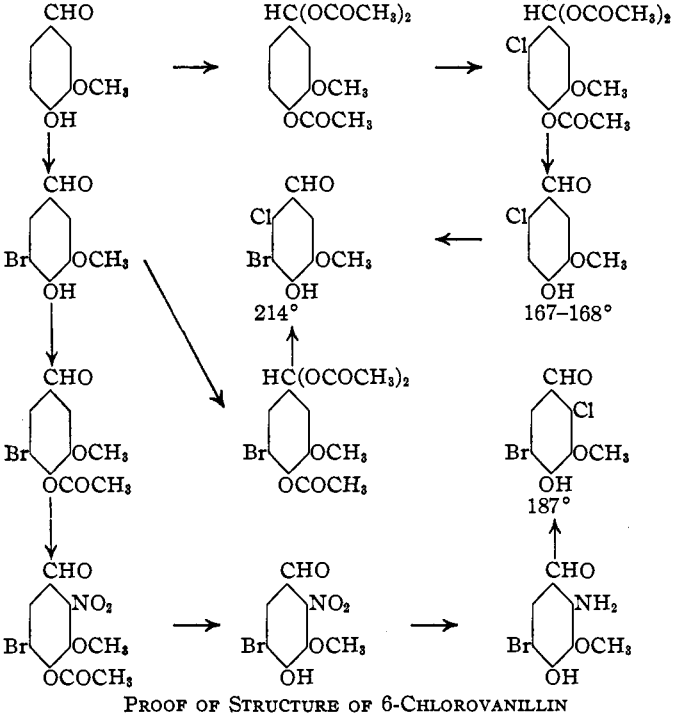
[8] A mixture of this product and that melting at 163° melted between 137 and 146°.

[9] It is of interest here to note that 6-bromovanillin was obtained in high yield [THIS JOURNAL, **49**, 1079 (1927)] by bromination of acetylvanillin in the presence of sodium acetate.

[10] Raiford and Stoesser, *ibid.*, **50**, 2560 (1928).

[11] *Anal.* Subs., 0.2041:AgHal, 0.2544. Calcd. for $C_8H_6O_3ClBr$:Hal., 43.50. Found: Hal., 43.43.

derivative, and that the chlorovanillin, m. p. 167–168°, from which it was prepared must have halogen in position 6. The monochlorovanillin, m. p. 163°, previously recorded must therefore have halogen in position 5. These relations are indicated in the diagrams.



PROOF OF STRUCTURE OF 6-CHLOROVANILLIN

When acetyl-5-chlorovanillin was nitrated it gave a chloronitro derivative, m. p. 137°. Reduction of this product to the corresponding amine and replacement of the amino radical by chlorine gave a dichlorovanillin that melted at 179°. Since this product was also obtained by direct chlorination of 2-chlorovanillin, the positions of the halogen atoms in this dichloro compound are shown to be 2 and 5.

It was shown above that the monochlorovanillin that melts at 167–168° is the 6-derivative. Direct chlorination of this substance gave a dichloro compound, m. p. 192°. Since this product was also obtained by chlorination of 3-methoxy-4-acetoxy-5-chlorobenzal diacetate and subsequent hydrolysis of the acetyl derivative, it follows that the final product must be 5,6-dichlorovanillin.

To obtain the third possible dichloro compound, 3-methoxy-4-acetoxy-6-chlorobenzal diacetate was nitrated, the acetyl groups removed by hydrolysis, the resulting nitro compound reduced and the amino radical replaced by chlorine. This product, melting at 139–140°, is the only remain-

ing dichlorovanillin and must have halogen in positions 2 and 6. Chlorination of this compound gave a low yield[12] of 2,5,6-trichlorovanillin.

Experimental Part

The Three Monochloro Derivatives

2-Chlorovanillin.—A mixture of 14.5 g. of 2-aminovanillin,[13] 20 cc. of hydrochloric acid and 10 cc. of water was cooled below 0° and diazotized by gradually adding 6.5 g. of solid sodium nitrite. After diazotization was complete, a solution of 10 g. of dry cuprous chloride dissolved in 50 cc. of concentrated hydrochloric acid was added. When the copper complex was decomposed, the mixture was heated on a water-bath for a few hours, cooled and filtered. The residue was washed with dilute hydrochloric acid and then with water; yield 88%. Recrystallization from ligroin or chloroform gave pale yellow prisms, m. p. 128–129.

Anal. Subs., 0.4006: 21.65 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_7O_3Cl$; Cl, 19.03. Found: Cl, 19.19.

This chlorovanillin was further characterized by the study of the derivatives indicated in Table I.

TABLE I

DERIVATIVES OF 2-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	85
2	*p*-Bromophenylhydrazone	Dil. alcohol	Brown plates	97
3	Semicarbazone	Alcohol	Colorless plates	86
4	*Bis*-benzidine	Alcohol	Fine orange needles[a]	92

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Found
1	$C_8H_8O_3NCl$	157–158	0.4098	20.37	17.60	17.65
2	$C_{14}H_{12}O_2N_2ClBr$	144–146	.2089	0.1916	32.46	32.54
3	$C_9H_{10}O_3N_3Cl$	220–221[b]	.5510	22.80	14.58	14.69
4	$C_{28}H_{22}O_4N_2Cl_2$	224–226	.2398	0.1280	13.61	13.21

[a] When dried at 120° the color changed to red, but no evidence of solvent of crystallization was obtained.

[b] After removal of alcohol of crystallization. *Anal.* Subs., 0.6346: loss in wt. at 120°, 0.0836. Calcd. for one mole of C_2H_6O: 15.89. Found: 13.17.

5-Chlorovanillin.—This was obtained by a modification of Menke and Bentley's[14] method as indicated below. Excess of chlorine beyond that required for a mono-derivative was bubbled at the rate of about 10 g. of gas in fifteen minutes into a well-stirred solution of 43 g. of vanillin dissolved in 200 cc. of chloroform. Work was begun at room temperature and the temperature of the mixture was not allowed to rise above 60°.

[12] It is of interest to note here that after positions 2 and 6 have been filled by halogen, position 5 is much more readily attacked by bromine than by chlorine. Raiford and Stoesser [THIS JOURNAL, **50**, 2562 (1928)] obtained a 95% yield of tribromovanillin by bromination of the 2,6-derivative. In the present work a yield of only 31% of the trichloro compound was obtained, although twice the theoretical amounts of free chlorine and sulfuryl chloride, respectively, were used in separate experiments. When 2,6-dichlorovanillin was brominated a yield of 96% was obtained.

[13] Pschorr and Sumuleanu, *Ber.*, **32**, 3408 (1899).

[14] Menke and Bentley, THIS JOURNAL, **20**, 316 (1898).

Crystals separated during the experiment and when all the chlorine had been passed in, the mixture was cooled and the solid removed by filtration. Fifty grams of vanillin was placed in the filtrate, enough chloroform added to dissolve all solid, chlorine passed in as before and the product filtered off after cooling. Repetition of the process with a second 50-g. portion of vanillin gave a total yield of 162 g. of chlorinated product or 92%. Recrystallization from acetic acid gave colorless plates; m. p. 163°. Hann found 165°. In a repetition of the experiment, treatment of the first filtrate indicated above with a much larger excess of chlorine gave a small quantity of solid which after repeated crystallizations from alcohol gave colorless needles; m. p. 174–176°. A mixture of this and pure 2,5-dichlorovanillin, m. p. 179° (see below) melted at 175–177°.

Concentration of the filtrate left after removal of the above dichloro product gave a mass of reddish colored crystals. Most of the color was removed by washing with ligroin (70–80°). Repeated crystallization of the residue from alcohol gave pale yellow needles; m. p. 188–191°. A mixture of this and pure 5,6-dichlorovanillin, m. p. 192° (see below), melted at 191–192°.

3-Methoxy-4-hydroxy-5-chlorocinnamic Acid.—A mixture of 48 g. of 5-chlorovanillin, 40 g. of freshly fused sodium acetate and 100 cc. of acetic anhydride was heated under reflux for three hours and then poured into water. The acetyl derivative separated as an oil and later solidified; yield, nearly quantitative. Extraction with boiling alcohol to remove starting material and crystallization from acetic acid gave light yellow granules; m. p. 201°.

Anal. Subs., 0.1715: AgCl, 0.2434. Calcd. for $C_{12}H_{11}O_5Cl$: Cl, 13.12. Found: Cl, 13.23.

Hydrolysis of the above product with a dilute solution of potassium hydroxide gave the free acid, which was crystallized from dilute acetone; m. p. 235–236°, with shrinking a few degrees lower.

Anal. Subs., 0.2171: AgCl, 0.1395. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.53. Found: Cl, 15.89.

5-Chlorovanillin was further characterized by study of the derivatives indicated in Table II.

TABLE II

DERIVATIVES OF 5-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	White needles	92
2	*p*-Bromophenylhydrazone	Dil. alcohol	Yellow plates	Nearly quant.
3	Semicarbazone	Dil. alcohol	Colorless granules	73
4	*Bis*-benzidine	Dil. pyridine	Yellow feathers	90

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Found
1	$C_8H_8O_3NCl$	172	0.2275	11.26	17.60	17.56
2	$C_{14}H_{12}O_2N_2ClBr$	161	.1868	0.1728	32.29	32.06
3	$C_9H_{10}O_3N_3Cl$	201	.1898	.1121	14.57[a]	14.61
4	$C_{28}H_{22}O_4N_2Cl_2$	252–254	.1310	.0725	13.61[b]	13.69

[a] Obtained after drying for eight hours at 125° to remove alcohol of crystallization. *Anal.* Subs., 0.2077: AgCl, 0.1045. Calcd. for $C_9H_{10}O_3N_3Cl \cdot C_2H_6O$: Cl, 12.28. Found: Cl, 12.45. [b] Obtained after drying for two hours at 120°. The volatile product from a second sample was conducted into ice cold water and gave the iodoform test for alcohol. *Anal.* Subs., 0.2460: loss in wt., 0.0387. Calcd. for 2 moles of C_2H_6O: 15.00. Found: 15.37. *Anal.* Subs., 0.2374: AgCl, 0.1079. Calcd. for $C_{28}H_{22}O_4N_2Cl_2 \cdot 2C_2H_6O$: Cl, 11.58. Found: Cl, 11.24.

6-Chlorovanillin.—This was obtained by chlorination of 3-methoxy-4-acetoxybenzal diacetate, which was prepared as follows. To a solution of 10 g. of vanillin dissolved in 25 cc. of acetic anhydride at about 50°, fifteen drops of concentrated sulfuric acid was added, and the red-colored mixture allowed to stand overnight. The solid was filtered off, washed with a little glacial acetic acid and the combined filtrate and washings poured into water; total yield, 97%. Crystallization from alcohol gave colorless plates; m. p. 90–91°.[15] Ten grams of this product was dissolved in 95 cc. of hot glacial acetic acid, 8 g. of finely powdered anhydrous sodium acetate added, the mixture cooled to about 40°, then about twice the calculated amount of chlorine passed in while the whole was stirred. Sodium chloride precipitated as the action proceeded. The mixture was poured into water and allowed to stand; yield, 91%. Repeated crystallization from alcohol gave colorless plates; m. p. 143–144°.

Anal. Subs., 0.2258: AgCl, 0.0989. Calcd. for $C_{14}H_{15}O_7Cl$: Cl, 10.74. Found: Cl, 10.83.

Ten grams of the chlorobenzal diacetate was boiled with a dilute solution of potassium hydroxide until all had dissolved, the mixture was cooled and 6-chlorovanillin precipitated by adding excess of hydrochloric acid; yield, 98%. Crystallization from alcohol gave colorless feathers; m. p. 167–168°.

Anal. Subs., 0.1676: AgCl, 0.1281. Calcd. for $C_8H_7O_3Cl$: Cl, 19.03. Found: Cl, 18.91.

5-Bromo-6-chlorovanillin.—This was obtained in nearly quantitative yield by slowly adding bromine to a warm glacial acetic acid solution of 6-chlorovanillin and anhydrous sodium acetate, with stirring. Crystallization from acetic acid gave colorless needles; m. p. 214°.

Anal. Subs., 0.2590: AgX, 0.3233. Calcd. for $C_8H_6O_3ClBr$: X, 43.50. Found: X, 43.50.

5-Chloro-6-bromovanillin.—Excess of chlorine was bubbled with stirring into a chloroform solution of 6-bromovanillin at about 40°. The product crystallized out during the reaction. By working up the mother liquor an almost quantitative yield was obtained. Recrystallization from alcohol gave nearly colorless needles; m. p. 202°.

Anal. Subs., 0.2202: AgX, 0.2741. Calcd. for $C_8H_6O_3ClBr$: X, 43.50. Found: X, 43.36.

6-Chlorovanillin was further characterized by the study of the derivatives indicated in Table III.

TABLE III

DERIVATIVES OF 6-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	Nearly quant.
2	*p*-Bromophenylhydrazone	Dil. alcohol	Pale brown needles	99
3	Semicarbazone	Alcohol	Colorless needles	98
4	*Bis*-benzidine	Alcohol	Yellow, amorphous powder	92

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Found
1	$C_8H_8O_3NCl$	178	0.2146	0.1534	17.60	17.68
2	$C_{14}H_{12}O_2N_2ClBr$	174	.1779	.1651	32.46	32.34
3	$C_9H_{10}O_3N_3Cl$	241	.1780	.1059	14.57	14.72
4	$C_{28}H_{22}O_4N_2Cl_2$	Dec. at 263	.2403	.1311	13.61	13.50

[15] Tiemann and Nagai, *Ber.*, 8, 1143 (1875), found 88–89° for a product that appears to have the same composition as ours, but they reported no yield.

The Three Dichloro Derivatives

Acetyl-2-nitro-6-chlorovanillin.—Twenty grams of 3-methoxy-4-acetoxy-6-chlorobenzal diacetate was added during a period of three minutes to 50 cc. of fuming nitric acid at 20–30° with shaking, and after standing for fifteen minutes the mixture was poured on cracked ice. The green oil that separated solidified on standing; yield, 61%. Crystallization from alcohol after boiling with norite gave nearly colorless plates that became lemon-yellow on exposure to sunlight; m. p. 81–82°.

Anal. Subs., 0.2083: AgCl, 0.1088. Calcd. for $C_{10}H_8O_6NCl$: Cl, 12.97. Found: Cl, 12.92.

2-Nitro-6-chlorovanillin.—This was obtained by hydrolysis of the acetyl derivative by alkali and by acid. The latter requires a longer time but gives a purer product with less color than was obtained with alkali. Crystallization from water gave colorless needles; m. p. 155–157°.

Anal. Subs., 0.2387: AgCl, 0.1474. Calcd. for $C_8H_6O_5NCl$: Cl, 15.33. Found: Cl, 15.27.

2-Amino-6-chlorovanillin.—Ten grams of the above nitro compound was added in small portions to a boiling mixture made from 100 g. of ferrous sulfate in 350 cc. of water and 110 cc. of concentrated ammonia water. The whole was boiled for fifteen minutes, 200 cc. of boiling water was added and the mixture was filtered while hot. The residue was repeatedly extracted with ammonia water and the collected filtrate was neutralized by dilute sulfuric acid in order to cause the amine to separate; yield, 92%. Crystallization from alcohol gave yellow needles that softened at 190° and melted at 192–193°.

Anal. Subs., 0.2750: AgCl, 0.1958. Calcd. for $C_8H_8O_3NCl$: Cl, 17.61. Found: Cl, 17.61.

2,6-Dichlorovanillin.—The amino group in the above described compound was replaced by chlorine by means of the Sandmeyer reaction; yield, 40%. Crystallization from carbon tetrachloride gave colorless needles; m. p. 139–140°.

Anal. Subs., 0.2246: AgCl, 0.2888. Calcd. for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 31.81.

This compound was further characterized by the study of the derivatives indicated in Table IV.

TABLE IV

DERIVATIVES OF 2,6-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	88
2	*p*-Bromophenylhydrazone	....	....	..
3	Semicarbazone	90% alcohol	Colorless needles	98
4	*Bis*-benzidine	Insoluble	Red, amorphous granules	Nearly quant.

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgCl	Halogen, % Calcd.	Found
1	$C_8H_7O_3NCl_2$	141	0.2391	0.2910	30.08	30.12
3	$C_9H_9O_3N_3Cl_2$	213	.2134	.2199	25.53	25.54
4	$C_{28}H_{20}O_4N_2Cl_4$	232	.1880	.1788	24.06	23.52

Acetyl-5-chlorovanillin.—A mixture of 10 g. of 5-chlorovanillin, 10 cc. of glacial acetic acid and 20 cc. of acetic anhydride was refluxed for an hour and then poured into water. The oil that separated solidified after standing for one day. Many recrystallizations from ligroin gave colorless needles that melted at 67°. When distilled

at 5 mm. it passed over at 167–172°, and solidified to colorless crystals; yield, nearly quantitative.

Anal. Subs., 0.2428: AgCl, 0.1525. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.53. Found: Cl, 15.53.

Acetyl-2-nitro-5-chlorovanillin.—Five grams of the above described product was slowly added to 20 g. of fuming nitric acid with shaking, while the mixture was kept at 20° or below, and then poured on cracked ice; yield, nearly quantitative. Repeated crystallization from alcohol gave colorless needles that contained one molecular proportion of alcohol of crystallization; m. p., 95–96°.

Anal. Subs., 0.2118: AgCl, 0.0957. Calcd. for $C_{10}H_8O_6NCl \cdot C_2H_6O$:[16] Cl, 11.11. Found: Cl, 11.18.

2-Nitro-5-chlorovanillin.—The acetyl derivative was warmed with potassium hydroxide solution until a clear liquid was obtained, and then an excess of dilute sulfuric acid was added. Crystallization of the yellow precipitate from 20% alcohol gave pale yellow needles; m. p. 137°.

Anal. Subs., 0.1950: AgCl, 0.1214. Calcd. for $C_8H_6O_5NCl$: Cl, 15.33. Found: Cl, 15.40.

2-Amino-5-chlorovanillin.—Ten grams of the above nitro compound was reduced by means of ferrous hydroxide as explained above, with the exception that the filtrate was not neutralized by acid. The amine crystallized from the filtrate on cooling, and concentration of the mother liquor gave a second crop; yield, 87%. Recrystallization from water gave light brown needles; m. p. 136–137°.

Anal. Subs., 0.1935: AgCl, 0.1374. Calcd. for $C_8H_8O_3NCl$: Cl, 17.59. Found: Cl, 17.56.

2,5-Dichlorovanillin.—A portion of the amine was dissolved in dilute hydrochloric acid cooled to about 0° and diazotized by slowly adding sodium nitrite. Cuprous chloride dissolved in concentrated hydrochloric acid was now added to the dark red mixture, which was next heated on a water-bath for two hours. The solid was filtered off, washed with dilute acid, dried and extracted with hot acetone. The extract was boiled with norite, filtered and the filtrate mixed with water; yield, 83%. Recrystallization from acetone gave colorless needles; m. p. 179°.

Anal. Subs., 0.2691: AgCl, 0.3494. Calcd. for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 32.12.

When an excess of chlorine was bubbled into 100 cc. of chloroform solution containing 1 g. of 2-chlorovanillin and the solvent distilled off, there was left nearly a quantitative yield of dichloro derivative mixed with some red resinous material. Crystallization from acetone gave colorless needles that melted at 179°, and were found by a mixed melting point to be identical with the 2,5-derivative described above.

This dichlorovanillin was further characterized by a study of the derivatives indicated in Table V.

3-Methoxy-4-acetoxy-5-chlorobenzal Diacetate.—This product was obtained in 97% yield by refluxing for one and one-half hours a solution containing 15 g. of 5-chlorovanillin in 45 cc. of acetic anhydride with one drop of concentrated sulfuric acid and pouring into water. By boiling the alcoholic solution of the deep red solid with norite, filtering and crystallizing, it was obtained in light brown plates; m. p. 115–116°.

[16] A sample dried for six hours under reduced pressure at 80° lost alcohol and left a residue that melted at 112°. *Anal.* Subs., 0.2953: AgCl, 0.1555. Calcd. for $C_{10}H_8O_6NCl$: Cl, 12.98. Found: Cl, 13.03.

TABLE V

DERIVATIVES OF 2,5-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	Nearly quant.
2	*p*-Bromophenylhydrazone	Dil. alcohol	Nearly colorless needles	Nearly quant.
3	Semicarbazone	Dil. pyridine	Colorless needles	89
4	*Bis*-benzidine	Pyridine	Yellow plates	98

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Found
1	$C_8H_7O_2NCl_2$	158	0.2196	0.2671	30.05	30.08
2	$C_{14}H_{11}O_2N_2Cl_2Br$	158	.1745	.2104	38.68	38.33
3	$C_9H_9O_3N_3Cl_2$[a]	228	.1825	.1890	25.51	25.62
4	$C_{28}H_{20}O_4N_2Cl_4$	254–255	.1379	.1325	24.04	23.77

[a] This compound crystallizes with one molecular proportion of water, which was removed by drying to constant weight at 120°. The hydrated form gave the following data. *Anal.* Subs., 0.1565: AgCl, 0.1505. Calcd. for $C_9H_9O_3N_3Cl_2 \cdot H_2O$: Cl, 23.94. Found: Cl, 23.79.

Precipitation from alcoholic solution by addition of water gave a colorless solid of the same melting point.

Anal. Subs., 0.2123: AgCl, 0.0926. Calcd. for $C_{14}H_{15}O_7Cl$: Cl, 10.74. Found: Cl, 10.79.

3-Methoxy-4-acetoxy-5,6-dichlorobenzal Diacetate.—Excess of chlorine was bubbled into a well-stirred solution of 5 g. of the above described diacetate and 4 g. of anhydrous sodium acetate in 75 cc. of glacial acetic acid, the mixture poured into water and allowed to stand for several hours; yield, 85%. Crystallization from alcohol gave colorless needles; m. p. 117–118°. A mixture of this and the starting material melted at 100–105°.

Anal. Subs., 0.1968: AgCl, 0.1544. Calcd. for $C_{14}H_{14}O_7Cl_2$: Cl, 19.44. Found: Cl, 19.41.

TABLE VI

DERIVATIVES OF 5,6-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Alcohol	Colorless plates	99
2	*p*-Bromophenylhydrazone	Acetic acid	Yellow needles	66
3	Semicarbazone[a]	Alcohol	Colorless needles	93
4	*Bis*-benzidine	Alcohol	Fine yellow needles	Nearly quant.

[a] *Anal.* Subs., 0.1789: AgCl, 0.1609. Calcd. for $C_9H_9O_3N_3Cl_2 \cdot C_2H_6O$: Cl, 21.91. Found: Cl, 22.25. *Anal.* Subs., 0.1839: loss in wt., 0.0212. Calcd. for 1 mole of C_2H_6O: 14.19. Found: 11.53.

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Found
1	$C_8H_7O_3NCl_2$	203 with dec.	0.2390	0.2904	30.08	30.06
2	$C_{14}H_{11}O_2N_2Cl_2Br$	163–164[a]	.2307	.2707	37.87	37.30
3	$C_9H_9O_3N_3Cl_2$	237[b]	.1627	.1683	25.53	25.64
4	$C_{28}H_{20}O_4N_2Cl_4$	Dec. at 289°	.2562	.2447	24.04	23.63

[a] On further crystallization the melting point decreased to 147–157°. *Anal.* Subs., 0.2499: AgX, 0.2707. Calcd. for $C_{14}H_{11}O_2N_2Cl_2Br \cdot C_2H_4O_2$: X, 33.55. Found: X, 34.44. [b] Dried to constant weight at 120°.

The compound just described was hydrolyzed by boiling with 10 *N* potassium hydroxide solution into 5,6-dichlorovanillin, which was obtained as the sparingly soluble potassium salt. This was decomposed by dilute sulfuric acid and the product crystallized from alcohol; m. p. 192°.

Anal. Subs., 0.1688: AgCl, 0.2196. Calcd. for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 32.19.

Trichlorovanillin and Derivatives

2,5,6-Trichlorovanillin.—To a saturated chloroform solution of 3 g. of 2,6-dichlorovanillin, 4 cc. of sulfuryl chloride was added, the mixture protected from moisture of the air and allowed to stand for twenty-four hours. The solvent was allowed to evaporate at room temperature and the reddish residue was fractionally crystallized from dilute alcohol. Nearly colorless needles, m. p. 154°, were obtained; yield, 31%.[17]

Anal. Subs., 0.1612: AgCl, 0.2704. Calcd. for $C_8H_5O_3Cl_3$: Cl, 41.68. Found: Cl, 41.49.

2,6-Dichloro-5-bromovanillin.—The required amount of bromine was added to a warm acetic acid solution of 2,6-dichlorovanillin and sodium acetate, the mixture allowed to stand for fifteen minutes and then poured into water; yield, 96%. The product was dissolved in hot acetic acid, hot water was added until precipitation began, the mixture was heated until clear and then allowed to cool. Small colorless needles were formed; m. p. 167°.

Anal. Subs., 0.1715: AgX, 0.2713. Calcd. for $C_8H_5O_3Cl_2Br$: X, 50.33. Found: X, 50.29.

Trichlorovanillin was further characterized by the preparation of the following derivatives. The oxime was obtained in 94% yield by the usual method. Crystallization from alcohol gave colorless needles; m. p. 173°.

Anal. Subs., 0.1665: AgCl, 0.2654. Calcd. for $C_8H_5O_3NCl_3$: Cl, 39.37. Found: Cl, 39.43.

The semicarbazone was obtained in 92% yield. Treatment of its hot alcoholic solution with hot water until precipitation began and allowing to cool gave colorless needles; m. p. 219°.

Anal. Subs., 0.1480: AgCl, 0.2001. Calcd. for $C_9H_8O_3N_3Cl_3$: Cl, 34.07. Found: Cl, 33.45.

Summary and Conclusions

1. The list of possible chlorine substitution products of vanillin has been completed. Each has been characterized by the study of several derivatives.

2. In the reactions which involved the aldehyde radical, the presence of ortho substituents caused no noticeable hindrance.

3. When chlorine is allowed to react on a vanillin derivative it does not always enter the same position as does bromine under the same conditions, which shows that the position taken is, in part, dependent on the character of the entering substituent.

4. In no case was there obtained more than one of the stereoisomeric

[17] Unchanged starting material was recovered from the mother liquors.

oximes demanded by theory. The one obtained, probably the *anti* form, could not be transmuted by hydrogen chloride.

5. Further work is in progress in this Laboratory.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

PYROLYSIS OF ALLYLANILINES

BY F. L. CARNAHAN[1] AND CHARLES D. HURD

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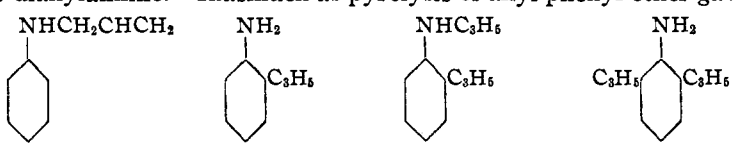
Allylaniline sufficiently resembles ethylamine and allyl phenyl ether in structure so that its pyrolysis may be considered to have points of similarity with theirs, both of which have been previously investigated. Primary effects of dehydrogenation and of deammonation have been shown to be the case[2] with ethylamine

$$CH_3CH_2NH_2 \begin{cases} \nearrow H_2 + CH_3CH{=}NH \\ \searrow NH_3 + CH_2{=}CH_2 \end{cases}$$

Most of the secondary reactions were traceable to the acetaldimide, chief of which was the further dehydrogenation into methyl cyanide or the demethanation into hydrogen cyanide.

For allylaniline to undergo the deammonation reaction the products would be aniline and allene. No allene was found in spite of careful search for it. The dehydrogenation reaction would give rise to acrolein-anil or its products of polymerization: $CH_2{=}CHCH_2NHC_6H_5 \longrightarrow H_2 + CH_2{=}CHCH{=}NC_6H_5$. Diallylaniline, $C_6H_5N(CH_2CH{=}CH_2)_2$, would give rise to acrolein-anil polymers by loss of propylene. Both of these reactions seem to occur. However, the fact that considerable aniline is formed during the pyrolysis of both mono- and di-allylaniline shows that this is not the exclusive feature.

Allyl phenyl ether, on refluxing, has been shown to rearrange[3] into *o*-allylphenol. Similarly, N-allylaniline might be expected to change into *o*-allylaniline, and N,N-diallylaniline into either *o*-allylphenylallylamine or 2,6-diallylaniline. Inasmuch as pyrolysis of allyl phenyl ether gave rise



N-Allylaniline *o*-Allylaniline *o*-Allylphenyl-allylamine 2,6-Diallylaniline

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[1] Du Pont Fellow, 1929–1930.

[2] Hurd and Carnahan, THIS JOURNAL, **52**, 4151 (1930).

[3] For a discussion of this subject, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, 1929, p. 215.