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SCHIFF BASES DERIVED FROM 5-CHLOROVANILLIN

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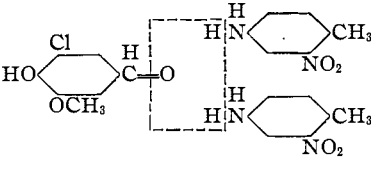
The intermolecular condensation of aldehydes and amines with subsequent loss of water leads to the formation of the well-known Schiff's bases. Compounds of this class containing the vanillin nucleus as an integral part of their structure have been investigated by a number of workers. Senier and Forster,[1] in carrying out a series of studies upon the thermotropic properties and the effect of actinic light upon Schiff's bases, prepared a series of vanillin amines. Hann[2] studied the effect of the introduction of iodine into the vanillin residue upon the thermotropic properties of the resulting bases when the iodinated aldehyde was condensed with various amines. Hann and Spencer[3] isolated chlorovanillalaniline and chlorovanillal-α-naphthylamine. 2-Bromovanillin and 6-bromovanillin have been condensed with benzidine by Raiford and Stoesser,[4] and a number of bases from 5-bromovanillin and 5,6-dibromovanillin have been prepared by Raiford and Hilman.[5]

In the present paper is described a further series of compounds of 5-chlorovanillin with aromatic amines. In a majority of cases the reaction products were obtained quite readily in crystalline condition upon cooling an organic solvent containing molecular proportions of the necessary components.

In one instance, that of *m*-toluidine, no crystalline product could be isolated although the marked deepening of the color as the reaction mixture was heated indicated a progressive formation of the chromophore C=N—. That this conclusion was warranted was proved by separation of the picrate of 5-chlorovanillal-*m*-toluidine upon addition of alcoholic picric acid. Hantzsch and Schwab[6] reported derivatives of a type in which one molecule of aldehyde condensed with two molecules of an amine, and in this study such a reaction product was encountered with nitro-*p*-toluidine. The reaction in this case may be considered to proceed in the following manner



[1] Senier and Forster, *J. Chem. Soc.*, **107**, 452 (1915).

[2] Hann, *J. Wash. Acad. Sciences*, **14**, 79 (1924).

[3] Hann and Spencer, THIS JOURNAL, **49**, 535 (1927).

[4] Raiford and Stoesser, *ibid.*, **49**, 1077 (1927).

[5] Raiford and Hilman, *ibid.*, **49**, 1571 (1927).

[6] Hantzsch and Schwab, *Ber.*, **34**, 834 (1901).

Unsuccessful attempts were made to prepare derivatives of chlorovanillin with *o*- and *p*-nitro-anilines, 2,4-dichloro-aniline and trinitroaniline.

Experimental

The general procedure adapted was to weigh out 3 g. of chlorovanillin and an equimolecular proportion of the desired amine, add 25 cc. of 95% alcohol (or more if necessary for complete solution), heat to boiling and allow to digest at boiling temperature for two to two and one-half hours. Upon cooling, the reaction product usually separated in crystalline condition, or if an oil it could be induced to crystallize by scratching with a glass rod. The crude reaction product was recrystallized from alcohol to constant melting point, dried and analyzed. All melting points were taken with Anschütz thermometers and stems totally immersed in the heating bath. Table I gives a summary of the results.

TABLE I

SCHIFF'S BASES DERIVED FROM 5-CHLOROVANILLIN

Name	Formula	Appearance	M. p., (corr.), °C.	Analysis (Kjeldahl–Gunning–Arnold Method) 0.1 *N* HCl consumed, Wt., g.	cc.	Nitrogen, % Found	Calcd.
5-Chlorovanillal *o*-toluidine	$C_{15}H_{14}O_2NCl$	Almost colorless cryst. powder	115	0.1022	3.5	4.80	5.10
5-Chlorovanillal *p*-toluidine	$C_{15}H_{14}O_2NCl$	Canary-yellow glistening leaflets	142	.1125	4.0	4.98	5.10
5-Chlorovanillal *m*-nitro-aniline	$C_{14}H_{11}O_4N_2Cl$	Light yellow powder	160	.1141	7.4	9.08	9.14
5-Chlorovanillal *p*-chloro-aniline	$C_{14}H_{11}O_2NCl_2$	Orange-yellow cryst. powder; light yellow with gentle heat	128	.1548	4.8	4.34	4.73
5-Chlorovanillal cymidine	$C_{18}H_{20}O_2NCl$	Sl. yellow glistening truncated prisms	146–147	.1068	3.4	4.46	4.41
5-Chlorovanillal *p*-anisidine	$C_{15}H_{14}O_3NCl$	Brilliant straw-colored needle-like crystals	131	.2352	7.9	4.70	4.80
5-Chlorovanillal benzidine	$C_{28}H_{22}O_4N_2Cl_2$	Yellow powder	251–252	.1041	4.1	5.52	5.38
5-Chlorovanillal *m*-aminobenzoic acid	$C_{15}H_{12}O_4NCl$	Yellow hard cryst. crust	207	.1541	5.2	4.73	4.58
5-Chlorovanillal *p*-aminophenol	$C_{14}H_{12}O_3NCl$	Iridescent brick-red granules	150	.1229	4.3	4.90	5.05
5-Chlorovanillal *o*-dianisidine	$C_{22}H_{21}O_4N_2Cl$	Orange powder	188	.1226	5.8	6.63	6.79

The picrates of the Schiff's bases crystallize readily from alcoholic solutions and it is sometimes possible to obtain the picric acid addition product when the base itself cannot be isolated. In the present study the picrates were obtained by dissolving one gram of the pure base in 10 cc. of 10% alcoholic picric acid, heating to boiling and then allowing to cool, when the picrate separated. It was usually pure, but was recrystallized once from 95% alcohol before analysis. The results are given in Table II.

TABLE II

PICRATES OF SCHIFF'S BASES DERIVED FROM 5-CHLOROVANILLIN

Picrate of	Formula	Appearance	M. p. (corr.), °C.	Analysis Salicyl sulfonic acid method 0.1 *N* HCl Wt., g.	consumed, cc.	Nitrogen, % Found	Calcd.
5-Chlorovanillal *m*-toluidine	$C_{21}H_{17}O_9N_4Cl$	Soft granular yellow micro-crystals	224	0.1237	9.8	11.10	11.10
5-Chlorovanillal *p*-toluidine	$C_{21}H_{17}O_9N_4Cl$	Soft brilliant golden yellow needles	230	.1206	9.3	10.80	11.10
5-Chlorovanillal *m*-nitro-aniline	$C_{20}H_{14}O_{11}N_5Cl$	Orange iridescent cryst. crusts	190	.1062	9.6	12.66	13.08
5-Chlorovanillal *p*-chloro-aniline	$C_{20}H_{14}O_9N_4Cl$	Orange-yellow granules	215	.1298	10.0	10.79	10.67
5-Chlorovanillal *p*-anisidine	$C_{21}H_{17}O_{10}N_4Cl$	Bright orange needles	229–230	.1188	9.1	10.73	10.76
5-Chlorovanillal benzidine	$C_{40}H_{28}O_{18}N_8Cl_2$	Micro-cryst. fine orange powder	250–260 (dec.)	.1660	13.3	11.22	11.44
5-Chlorovanillal[a] *m*-aminobenzoic acid alcoholate	$C_{21}H_{15}O_{11}N_4Cl \cdot C_2H_5OH$	Orange-red hard granules	241	.1079 .2036 g. lost	7.4 .0170 g. at 120°	9.61 8.35	9.65 7.93
5-Chlorovanillal *p*-aminophenol	$C_{20}H_{13}O_{10}N_4Cl$	Orange needles	224–225 (dec.)	.1712	13.2	10.80	11.06
o-Dianisidine	$C_{26}H_{22}O_{16}N_8$	Soft golden yellow needles	Darkens, dec. 225°	.1018	11.4	15.69	15.96
5-Chlorovanillal *m*-aminobenzoic acid	$C_{21}H_{15}O_{11}N_4Cl$	Orange-yellow powder	236	.1144	8.5	10.41	10.48

[a] Dried at 120° for five hours.

5-Chlorovanillal-*bis*-nitro-*p*-toluidine.—Five g. of nitrotoluidine (1-CH_3-2-NO_2-4-NH_2) and 6.1 g. of pure chlorovanillin were dissolved in 25 cc. of absolute alcohol and the solution was refluxed for two and one-half hours. Upon standing overnight in the ice box, the reaction mixture solidified to a mass of orange-yellow crystals. These were recrystallized twice from 95% alcohol, from which the compound separated in hard yellow flower-like crystalline rosets which melted at 125° (corr.) to a clear yellow oil. Although the experiment was repeated three times no compound formed by a condensation of a single amine molecule could be isolated.

The picrate of the *bis*-compound separated in bright yellow micro-crystals when one gram of base was treated with 10 cc. of 10% alcoholic picric acid. It melted, although not sharply, at 148° to a clear red oil.

Anal. Base, subs., 0.1697: 0.1 *N* HCl, 14.1 cc. Calcd. for $C_{22}H_{21}O_6N_4Cl$, 11.85. Found: 11.64. Picrate, subs., 0.2019: 0.1 *N* HCl, 20.1 cc. Calcd. for $C_{28}H_{24}O_{13}N_7Cl$: N, 13.97. Found: N, 13.94.

Summary

Chlorovanillin has been condensed with *o*-, *m*- and *p* toluidines, *m*-nitro-aniline, *p*-chloro-aniline, cymidine, *p*-anisidine, nitro-*p*-toluidine, benzidine, *m*-aminobenzoic acid, *p*-aminophenol and dianisidine, and the condensation products have been characterized by the preparation of their addition products with picric acid.

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