CCXCVI.—*The Abnormal Reaction of Certain Aromatic Aldehydes with Schiff's Reagent.*

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WIELAND and SCHEUING (*Ber.*, 1921, **54**, 2527) have recently carried out an investigation on the nature of Schiff's reagent and the colour obtained in its reaction with aldehydes, and conclude that the essental constituent of the reagent is an *N*-sulphinic acid of pararosaniline-*C*-leucosulphonic acid,

$$SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NH{\cdot}SO_2H.$$

To the soluble violet dyestuff produced on the admixture of the reagent with acetaldehyde they ascribe the formula

$$NH{:}C_6H_4{:}C[C_6H_4{\cdot}NH{\cdot}SO{\cdot}O{\cdot}CH(OH){\cdot}CH_3]_2.$$

There are several references to abnormalities in the Schiff aldehyde reaction in the literature (compare Lorenz, *Ber.*, 1881, **14**, 789; Schmidt, *ibid.*, p. 1840; Bela von Bitto, *Z. anal. Chem.*, 1897, **36**, 369; Paula and von Buttlar, *Annalen*, 1911, **383**, 230), and one of us has remarked on the behaviour of salicylaldehyde (J., 1923, **123**, 2700) and β-resorcylaldehyde (*ibid.*, p. 2705) in giving yellow colorations and precipitates, in place of the usual soluble dyestuff, under certain conditions.

Investigations have been carried out with a view to discovering (1) the class of aldehyde which gives these abnormal yellow precipitates with Schiff's reagent; (2) the conditions under which these precipitates are formed—because it was afterwards discovered that red colorations and precipitates are produced under other conditions; and (3) the nature of this abnormal reaction and the composition of the precipitates.

Of the large number of aldehydes examined ortho-hydroxy-aromatic aldehydes most readily give yellow precipitates; indole-aldehyde behaves similarly. The reaction product is chiefly dependent on the quantity of sulphur dioxide capable of neutralising iodine (afterwards referred to as "free" sulphur dioxide) present in the reagent, as is seen from the Table, in which Y = yellow, O = orange, R = red, P = purple, B = brown, subscript p = precipitate, subscript c = coloration, and g. = g. of "free" sulphur dioxide per 100 c.c. of reagent.

	g. = 19	10	1·0	0·25	0·1
Aldehyde.			Reaction.		
Salicylaldehyde	P_c	P_p	Y_p	Y_p	Y_p
p-Hydroxybenzaldehyde	P_c	P_c	P_p	Y_p	Y_c
β-Resorcylaldehyde	P_p	Y_p	Y_p	Y_p	Y_p
Dihydroxy*iso*phthalaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2 : 3 : 4-Trihydroxybenzaldehyde	Y_c	Y_c	Y_c	Y_c	Y_c
p-Methoxysalicylaldehyde	R_p	R_c+Y_p	Y_p	Y_p	Y_p
Vanillin	P_p	B_p	Y_p	Y_p	Y_p
Orcylaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
a-Orcindialdehyde	R_p	Y_p	Y_p	Y_p	Y_p
Indole-3-aldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-3-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-4-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-5-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-1-naphthaldehyde	O_p	O_p	O_p	O_p	O_p
1-Hydroxy-2-naphthaldehyde	R_c+O_p	O_p	O_p	O_p	O_p
Cinnamaldehyde	P_p	P_p	P_p	B_p	B_p

The following aldehydes, chosen as representatives of other classes, behave normally, in that red or purple solutions are obtained under all the above conditions: Benzaldehyde, *m*-hydroxy-, and *o*-, *m*-, and *p*-methoxy-benzaldehydes; *o*-, *m*-, and *p*-nitro-, *o*-chloro-, *o*- and *m*-fluoro-, *m*- and *p*-bromo-, *p*-methyl-, 2-nitro-4-methoxy-,* 3-nitro-4-methoxy-benzaldehydes; 3 : 4-methylenedioxybenzaldehyde ($P_p + V_c$); *iso*propyl- and 2-carboxy-3 : 4-methylenedioxybenzaldehydes; α-naphthaldehyde, and its 3-* and 5-methoxy- and 5-bromo-derivatives; 5-bromo-2-naphthaldehyde; acrolein (deep blue), *iso*butyric aldehyde, glycollaldehyde, and glyoxal. It is noteworthy that 2 : 4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde,† and thioacetaldehyde were neutral towards the reagent, and that resacetophenone and 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone gave a violet coloration very slowly—in sharp contrast to β-resorcylaldehyde, which reacts rapidly.

In general, *o*-hydroxy-aromatic aldehydes give the yellow precipitates most readily, but exceptions to the rule are afforded by *p*-hydroxybenzaldehyde, which gives the yellow reaction when only a trace of " free " sulphur dioxide is present, by vanillin, by cinnamaldehyde and indole-aldehyde.

In order to ascertain the composition of the precipitates, that obtained from β-resorcylaldehyde was examined in detail. They cannot be separated as pure compounds owing to their insolubility in organic solvents or water, and to their instability towards acids and alkali. Analytical results were therefore only approximate, but a satisfactory clue to the constitution of the precipitate in each case was obtained from the interaction of the aldehyde with reagents in which the base employed was analogous to pararosaniline.

Neither the yellow nor the red *precipitates* have a constitution approximating to that proposed by Wieland and Scheuing for the dyestuff. The two classes of precipitates have very nearly, but not quite, the same constitution. When they are first formed their behaviour corresponds with that which would be expected of sulphites of hydrated Schiff's bases formed from the aldehyde and pararosaniline-*C*-leucosulphonic acid, $SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_3$—the basic constituent of Schiff's reagent. These sulphites, on drying over calcium chloride or potassium hydroxide, slowly lose sulphur dioxide; and after complete removal of the " sulphite " sulphur dioxide by dilute aqueous sodium bicarbonate, the final dried

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* These aldehydes have not been described in the literature and were prepared in connexion with other investigations, an account of which, it is hoped, will be published shortly.

† This is probably due to steric hindrance, because in another investigation it was found impossible to convert the aldehyde to the alcohol by the well-known methods which readily served in other cases.

substance has properties that would be associated with, and a composition approximating to that of, a hydrated Schiff's base of formula $SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_3(OH)_2]_3$. On careful hydrolysis with 10% aqueous sodium hydroxide, in which the precipitates are soluble, it was possible to recover the aldehyde in a quantity corresponding to that expected from the above formula, but the recovered pararosaniline could not be estimated. Hence we regard the reaction with this type of aldehyde as being $SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_3 + 3R{\cdot}CHO + xH_2SO_3 \longrightarrow SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH)R]_3(H_2SO_3)_x$, the sulphurous acid acting as a catalyst in the formation of the "Schiff's base."

This suggestion is substantiated by the production of the yellow precipitates from pure pararosaniline-*C*-leucosulphonic acid and β-resorcylaldehyde in sulphurous acid solution, and also of precipitates, which are analogous in appearance, constitution, and general properties, from the aldehyde and the following: (*a*) the leucosulphonic acid in hydrochloric acid solution, this acid taking the place of sulphurous acid as a catalyst, and the resulting precipitate being a hydrochloride, and not a sulphite; (*b*) sulphurous acid solutions of *p'p''p'''*-triaminotriphenylmethane; (*c*) *p'p''*-diaminotriphenylcarbinol; (*d*) *p'p''*-diaminotriphenylmethane; or (*e*) *p*-aminotriphenylmethane. It was not possible to obtain the simplest analogue of Schiff's reagent, *i.e.*, a sulphurous acid solution of *p*-aminotriphenylcarbinol.

The reaction of Schiff's reagent in the normal case is considered by Wieland and Scheuing to involve the production of a compound in which carbon and nitrogen are indirectly united through sulphur dioxide, *i.e.*, the formation of an aldehyde-bisulphite type, whilst in the abnormal cases the C–N union is direct, *i.e.*, of the Schiff's base or anil type. The presence of large quantities of sulphur dioxide in the reagent favours the bisulphite reaction and also retards the Schiff's base reaction, and thus in some of the cases examined, *e.g.*, salicylaldehyde, a small quantity of the red dyestuff is produced with Schiff's reagent saturated with sulphur dioxide. The red precipitates are therefore really yellow ones which have adsorbed a little of the red dyestuff, but not sufficient to make the analytical results for the two classes markedly different.

It is not yet understood why the aldehydes given above should behave in this abnormal manner towards Schiff's reagent.

EXPERIMENTAL.

Reaction of β-Resorcylaldehyde towards Schiff's Reagent.

The reagent was prepared by allowing 10 g. of pure pararosaniline (Kahlbaum) to stand at the ordinary temperature in 500 c.c. of saturated aqueous sulphur dioxide; when the solution became colourless 200 c.c. were added to a (saturated) solution of 8 g. of β-resorcylaldehyde in 1000 c.c. of water at 20°. The freshly prepared reagent produced a red coloration followed by a red precipitate; a yellow precipitate then formed slowly under ordinary conditions, but very rapidly if sulphur dioxide was removed from the solution under diminished pressure. From a separate portion of the reagent, the sulphur dioxide was removed, and samples were used at various concentrations of " free " sulphur dioxide (1) to estimate the amount of sulphur dioxide present, by titration with iodine, and (2) to investigate the effect of loss of sulphur dioxide from the reagent on the nature of the reaction. The results are summarised on p. 2222.

The solids were filtered and they then dissolved in aqueous alkali—the yellow with an orange colour, the red with a purple colour—and from these solutions the original solid could be immediately reprecipitated by the addition of acid. If allowed to stand in such a solution, the solids were hydrolysed (very rapidly if the solutions were heated) and a purple solid, pararosaniline, was precipitated along with a little tar. After this was filtered off, acidification of the alkaline solution produced a strong odour of sulphur dioxide, and β-resorcylaldehyde could be extracted from the acid liquid with ether, thus showing the essential constitution of the solids to be: aldehyde, pararosaniline, and sulphur dioxide.

For analysis, the solids were filtered and dried in a desiccator. The red remained unchanged in colour, but the yellow slowly lost sulphur dioxide and water, becoming dark green, and only became yellow again on the addition of *sulphurous acid*, and not on the addition of either water or sulphur dioxide alone. The loss of sulphur dioxide and the concomitant colour change were continuous as shown by sulphur estimations (see below) at intervals. The last trace of sulphur remaining in the solids as sulphite (but not that on the central carbon atoms of the rosaniline) was removed by dilute aqueous sodium bicarbonate, which caused the sample which was originally yellow to become deep green, but did not affect the colour of the red sample.

Sulphur estimations (*Carius*). Yellow solid: 2 days, 7·16; 1 week, 5·6; 2 months, 4·0; after washing with $NaHCO_3$, 2·8%. (Last sample had N, 4·4%.) Red solid: 1 week, 6·0; 2 months, 4·3; after washing with $NaHCO_3$, 3·2%. (Last sample had N, 5·1%.) The last sample from the yellow compound, which had been thoroughly dried over calcium chloride, was further dried over concentrated sulphuric acid in a vacuum. The last treatment caused a loss of 7·2%, which is ascribed to loss of water from any

–NH·CH(OH)– groups present (compare Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 996).

In order to demonstrate the catalytic action of the sulphurous acid, pararosaniline-*C*-leucosulphonic acid (Wieland and Scheuing, *loc. cit.*) was dissolved in (*a*) sulphurous acid and (*b*) dilute hydrochloric acid, and on the addition of an aqueous solution of β-resorcylaldehyde to these solutions, a yellow precipitate {Found : N, 4·4; S, 2·9. $SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_3(OH)_2]_3$ requires N, 5·4; S, 4·1%} was produced in the former case, identical in all respects with that from the aldehyde and Schiff's reagent, and a greenish-yellow precipitate {Found: N, 4·4; Cl, 8·5; S, 2·75. $SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_3(OH)_2,HCl]_3$ requires N, 4·7; Cl, 11·8; S, 3·5%} in the latter case; this differed from the yellow precipitate in containing hydrolysable chlorine, *i.e.*, it was the hydrochloride instead of the sulphite. Since it was impossible to recrystallise either of the solids, the analytical results only approximate to those of pure compounds, and it appears as if some of the nitrogen atoms combined with two aldehyde residues, causing the low results for S, N, and Cl.

The quantity of aldehyde present in the precipitate was determined as follows, the method being trustworthy to within ± 2% : A weighed quantity of the solid was hydrolysed with boiling 8% aqueous sodium hydroxide, the solution cooled, filtered from pararosaniline, almost neutralised with dilute hydrochloric acid, and made up to 50 c.c. Phenolphthalein was added, followed by hydrochloric acid drop by drop until the solution was just colourless; methyl-orange was then added and the solution titrated with standard acid. This was a measure of the aldehyde in the original compound, since β-resorcylaldehyde is acid to phenolphthalein,* but does not affect methyl-orange. An addition of 0·1 c.c. of the acid was required to correct for the change from p_H 7—9 (sensitivity to phenolphthalein) to p_H 3—5 (sensitivity to methyl-orange). The yellow solid contained 56% of aldehyde, and the red 50%; $SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_3(OH)_2]_3$ requires 52%. The aldehyde content should be higher than that given by the titration method but the tar probably contained a little aldehyde which resisted aqueous extraction.

Influence of Sulphurous and Hydrochloric Acids on the Rate of Precipitation of Schiff's Base.—A standard solution of each acid

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* Although *β*-resorcylaldehyde behaves as a monobasic acid towards alkali in presence of phenolphthalein (compare *Annalen*, 1911, **383**, 288), 4 : 6-dihydroxy*iso*phthalaldehyde behaves partly as a mono- and partly as a di-basic acid, and cannot be estimated in the same manner.

was in turn added to a dilute aqueous solution of aniline (3%), which was then immediately added to a 5% solution of β-resorcylaldehyde, the tube shaken, and the time (*t*) noted for the appearance of the precipitate. In each case, increasing concentration of acid first diminished and then increased the time required :

G. of SO_2 per 100 c.c. of solution.	*t* (secs.).	G. of HCl per 100 c.c. of solution.	*t* (secs.).
0·0	115	0·0	110
0·026	75	0·0073	100
0·066	60	0·0803	15
0·092	20	0·3285	15
0·118	20	0·4280	20
0·170	45	0·5840	95
0·298	200	0·8760	>300

Condensation of Resorcylaldehyde with Bases analogous to Triphenylmethane-C-leucosulphonic Acid.

Preparation of Bases.—p'p''p'''-*Triaminotriphenylmethane.* Finely powdered, dried triphenylmethane (10 g.) was slowly added to a constantly stirred mixture of 78 g. of nitric acid (*d* 1·42) and 120 g. of concentrated sulphuric acid at — 5—0°, and after the temperature of the whole had been allowed to rise slowly to about 15° (½ hour), the reaction mixture was poured into much cold water, and the solid trinitrotriphenylmethane was filtered off, boiled with 75% acetic acid, filtered, dried, and recrystallised from chloroform–ether; m. p. 212·5° (yield, 65%).

The trinitro-compound was dissolved in boiling glacial acetic acid, and to the red solution zinc powder was added until the colour had disappeared. The whole was diluted with water, excess of zinc filtered off, ammonia added to the solution, and the base filtered, dried, dissolved in dilute hydrochloric acid, the hydrochloride precipitated by the addition of concentrated hydrochloric acid, and finally dissolved in water, from which the free base was precipitated with ammonia, filtered, dried, and recrystallised from absolute alcohol. It had m. p. 201°.

pp'-*Diaminotriphenylmethane.* This was prepared by a slight modification of Baeyer and Villiger's method (*Ber.*, 1904, **37**, 2860); part of it was acetylated, and the diacetyl derivative (m. p. 233—234°) was oxidised to the carbinol, which was purified by conversion to the hydrochloride (Doebner's violet) and reprecipitation with ammonia. It had m. p. 173°.

p-*Aminotriphenylmethane.* A mixture of benzhydrol (5 g.) (from benzophenone), aniline hydrochloride (3·5 g.), and powdered anhydrous zinc chloride (4 g.) was immersed for 20 hours in the vapour of a mixture of toluene and xylene at 140°—this temperature is of extreme importance. The whole was cooled, the tube broken, washed with water, shaken with a mixture of ether and sulphuric acid, and the curdy, insoluble amine sulphate filtered off, recrystallised from water, dried, extracted with ether (Soxhlet) until no brown coloration of the ether was observed, and finally dissolved in much boiling water; the base was then precipitated by sodium hydroxide and crystallised from light petroleum (aggregates of colourless plates, m. p. 84·5°). The acetyl derivative had m. p. 167° (compare Baeyer and Villiger, *loc. cit.*).

p-*Aminotriphenylcarbinol.* The methane was oxidised as in the case of the diamino-compound (compare Baeyer and Lohr, *Ber.*, 1890, **23**, 1623). *p*-Acetamidotriphenylcarbinol crystallises in fine, lustrous needles, m. p. 175·5°. To obtain the free amine, the pure acetyl derivative (4·5 g.) was mixed with 250 c.c. of dilute sulphuric acid (1 in 5) and 30 c.c. of alcohol, and the whole was boiled until clear (3 hours). The solution was filtered and caustic soda added to the hot filtrate (not sufficient to neutralise it) until a few drops gave a crystalline deposit on cooling. The bulk of the solution was then allowed to cool, and the aminotriphenylcarbinol sulphate crystallised in orange plates, which were dried and extracted in a Soxhlet, as in the case of the diamino-compound. The pure sulphate was then dissolved in hot water and the base precipitated with ammonia. It had m. p. 115°, but could not be obtained in a crystalline condition from any solvent (compare Baeyer and Lohr, *loc. cit.*).

Unlike the di- and tri-amino-derivatives, the mono-amino-carbinol is not readily soluble in sulphurous acid, and in an attempt to prepare the *C*-leucosulphonic acid by dissolving the carbinol in hot sulphurous acid solution, a crystalline solid was obtained of m. p. 125—128° (decomp.) (Found: N, 3·72; S, 5·6). The compound most nearly corresponding to this is the sulphite

$$[(C_6H_5)_2C(OH)\cdot C_6H_4\cdot NH_2]_2,H_2SO_3,$$

which requires N, 4·4; S, 5·1%. When heated on the water-bath, the crystals became deep orange in colour, in agreement with the fact that feebly coloured salts of the carbinol become deeply coloured when heated. Hence the *C*-leucosulphonic acid could not be obtained because of the insoluble nature of the sulphite first formed on the addition of sulphurous acid to the carbinol.

Aqueous solutions of the aldehyde were mixed with sulphurous acid solutions of the above bases in order to trace the regularity in sulphur and nitrogen content of the precipitates. The estimations were carried out after the solids had been washed with aqueous sodium bicarbonate and dried, and the results are summarised as follows.

			Calc. for 1 aldehyde to each NH_2-group	
Amine.	N%.	S%.	N%.	S%.
$CH(C_6H_4{\cdot}NH_2)_3$	5·3	trace	5·97	0·0
$CHPh(C_6H_4{\cdot}NH_2)_2$	4·6	,,	5·06	0·0
$CPh(OH)(C_6H_4{\cdot}NH_2)_2$	4·1	3·4	4·43	5·1
$CHPh_2{\cdot}C_6H_4{\cdot}NH_2$	3·5	0·0	3·5	0·0

It is thus seen that only in the cases of the carbinols where *C*-leucosulphonic acids are formed is any appreciable quantity of sulphur left in the solids, and the proportion of nitrogen falls quite regularly with number of amino-groups present. It is also noteworthy that all the precipitates contained sulphur until washed with dilute bicarbonate, and that the colour change was not so marked in the case of the methanes as the carbinols.

Condensations of Other Aldehydes with Schiff's Reagent.—The aldehydes used here were prepared by the methods given in the literature.* The majority of these were almost insoluble in water and hence were first dissolved in alcohol, which had to be freed from traces of aldehyde. For this purpose it was boiled with solid caustic soda and distilled, the middle fraction being mixed with about 2 c.c. of Schiff's reagent and again fractionated; the first portion was rejected, but about 1 l. of alcohol, which gave a very faint pink colour with Schiff's reagent only after the lapse of ½ hour, was thus obtained. The aldehyde to be tested (0·25 g. approx.) was then dissolved in 5 c.c. of the alcohol, 5 c.c. of the reagent (made up as before) were added, and the mixture was very gently shaken to avoid atmospheric oxidation of the alcohol. The results are given on p. 2222.

Note on the Stability of Schiff's Reagent.—As is well known, Schiff's reagent when heated develops a red colour similar to that obtained in normal aldehyde reactions. It has been found that this colour disappears when the solution is cooled if it has not been either boiled or heated for a considerable time, for the appearance and disappearance of the colour depend on the amount of sulphur dioxide present in this solution. Damianovich (*Chem. Abs.*, 1910, 4, 1681) heated Schiff's reagent in a sealed tube, and therefore noted the same phenomenon. *pp'*-Diaminotriphenylcarbinol behaves in exactly the same way, the development of a deep violet colour in the heat and its disappearance in the cold being very striking. Absorption spectra were photographed and the bands were almost identical in the first case with those observed in pararosaniline hydrochloride, and in the second case with those in Doebner's violet. A colour change was also noted in the case of

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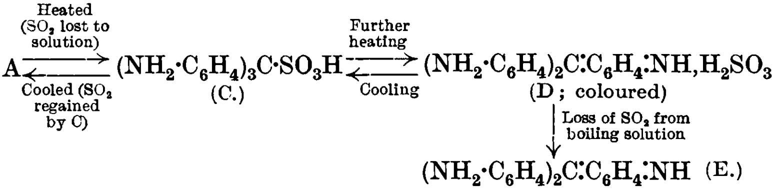
* Neither orcinol nor indole condenses with diphenylformamidine to give an aldehyde-anil (compare Shoesmith and Haldane, J., 1923, **123**, 2705).

the mono-amino-compound and here the hot solution was yellow and the cold colourless, but for reasons given this was not so satisfactory as the others. Wieland and Scheuing (*loc. cit.*) have proved that when Schiff's reagent is boiled until a precipitate appears the following reaction takes place :

$$\underset{\text{(A.)}}{2C(NH_2{\cdot}C_6H_4)_2(SO_3H){\cdot}C_6H_4{\cdot}NH{\cdot}SO_2H} \longrightarrow \underset{\text{(B.)}}{C(NH_2{\cdot}C_6H_4)_3{\cdot}SO_3{\cdot}NH_2{:}C_6H_4{:}C(C_6H_4{\cdot}NH_2)_2}.$$

The formation of the colour suggests that an intermediate stage has been observed and that the full cycle of changes is as follows :



$$\begin{tikzcd}[column sep=large]
A \arrow[r, shift left, "\text{Heated (SO}_2\text{ lost to solution)}"] & \underset{\text{(C.)}}{(NH_2{\cdot}C_6H_4)_3C{\cdot}SO_3H} \arrow[l, shift left, "\text{Cooled (SO}_2\text{ regained by C)}"] \arrow[r, shift left, "\text{Further heating}"] & \underset{\text{(D ; coloured)}}{(NH_2{\cdot}C_6H_4)_2C{:}C_6H_4{:}NH,H_2SO_3} \arrow[l, shift left, "\text{Cooling}"] \arrow[d, "\text{Loss of SO}_2\text{ from boiling solution}"] \\
 & & (NH_2{\cdot}C_6H_4)_2C{:}C_6H_4{:}NH \text{ (E.)}
\end{tikzcd}$$

Unchanged C combines with E to form B by salt formation.

In order to avoid this disadvantage of Schiff's reagent, a " modified reagent " has been suggested independently by Prudhomme (*Bull. Soc. Ind. Mulhouse*, 1904, **74**, 169) and by Wertheim (*J. Amer. Chem. Soc.*, 1922, **44**, 1834), which is prepared from pararosaniline and sodium hyposulphite. Towards such a reagent the *o*-hydroxybenzaldehydes behave as towards a Schiff's reagent containing about 1 g. of " free " sulphur dioxide per 100 c.c.

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