tion of sodium carbonate. The yellow, alkaline solutions, on treatment with hydrogen peroxide, rapidly lost their color and on acidification of the clear, colorless solutions deposited a colorless acid, which, after two crystallizations from benzene, separated in opaque rods melting at 180–181°.

Anal. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.71; H, 4.06. Found: C, 48.60; H, 4.10.

The methyl ester (XV) of this acid was prepared by the diazomethane reaction and by methanol saturated with hydrogen chloride. It separates from methanol in rosets of soft fibrous needles, melting at 51–52°.

Anal. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.53; H, 4.56. Found: C, 50.64; H, 4.74.

Reactions with Sulfuric Acid.—Approximately 1 mg. of substance was stirred into two to three drops of pure concentrated sulfuric acid on a porcelain plate. *p*-Ethoxycinnamic acid and its derivatives gave a pale yellow color, which faded rapidly. The ketonic acids and their esters dissolved with brilliant red color followed rapidly by a series of changes to a final solution the color of which persisted for hours. With *p*-ethoxybenzalpyruvic acid, its esters and its dibromo addition product the colors were red ⟶ red orange ⟶ reddish yellow. In the case of the isomeric bromo acids the color differences are striking: with the colorless, apparently chelated acid VI, cherry-red ⟶ deep red ⟶ violet ⟶ deep brown and its esters the same. With the yellow, isomeric acid XI and its esters, brilliant red ⟶ purple ⟶ purple-blue ⟶ green.

Summary

The influence of the *p*-ethoxyl group on the behavior of the side chain of benzalpyruvic acid has been shown to be similar to that of the *p*-methoxyl group. Isomeric β-bromo-*p*-ethoxybenzalpyruvic acids have been prepared, the differences in physical and chemical properties of these isomers indicating a chelated form for the colorless acid, an open chain form for the yellow isomer.

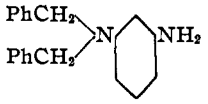
NEW YORK, N. Y. RECEIVED OCTOBER 21, 1940

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

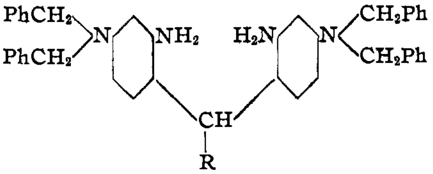
Reactions of Aldehydes with Amines. II. A New Aldehyde Reagent[1]

BY F. G. SINGLETON[2] AND C. B. POLLARD

Preliminary attempts to condense N,N-dibenzyl-*m*-phenylenediamine (I) with aromatic aldehydes to form substituted tetraminotriphenylmethanes (II) were unsuccessful. However, it was noticed that the addition of an aldehyde to an alcoholic solution of (I) containing a small amount of mineral acid caused the immediate formation of a red color which was followed by a strong green fluorescence. This paper deals with the color and fluorescence and describes a new test for aldehydes based upon these properties.

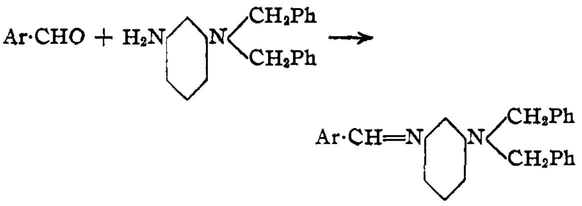


(I)



(II)

The Color.—When (I) was heated with aromatic aldehydes in neutral alcohol solution, yellow oils separated which were shown to be Schiff bases



Purification gave yellow, amorphous solids which could not be crystallized. Treatment with dry hydrogen chloride in anhydrous ether gave blood-red, resinous monohydrochlorides. Further treatment gave almost colorless dihydrochlorides which lost hydrogen chloride slowly in air, forming the red mono- salts. The di- salts were hydrolyzed by water in the cold to (I) and the original aldehydes. The six derivatives prepared are described in Table I. All of these compounds softened gradually on heating and became liquids below 100°.

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(1) This paper is abstracted from a portion of a dissertation submitted by F. G. Singleton to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1940.

(2) Present address: Kansas State College, Manhattan, Kansas. Part of this work was done in the laboratory of Mme. Ramart-Lucas, Professor at the Sorbonne while Mr. Singleton was Research Fellow (1938–39) of the Société des Amis de l'Université de Paris.

Table I

Schiff Bases from N,N-Dibenzyl-*m*-phenylenediamine

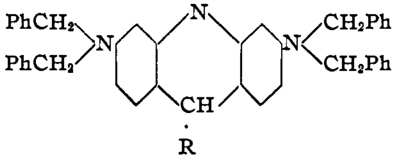
Aldehyde	Color	Yield, %	Formula	Analyses, % N Calcd.	Found
Benzaldehyde	Pale yellow	76	$C_{27}H_{24}N_2$	7.48	7.44
Salicylaldehyde	Yellow	82	$C_{27}H_{24}N_2O$	7.15	7.17
Cinnamaldehyde	Yellow	62	$C_{29}H_{26}N_2$	6.77	6.97
p-Chlorobenzaldehyde	Pale yellow	87	$C_{27}H_{23}N_2Cl$	6.62	6.83
Anisaldehyde	Pale yellow	52	$C_{28}H_{26}N_2O$	6.77	6.90
o-Methoxybenzaldehyde	Pale yellow	60	$C_{28}H_{26}N_2O$	6.82	6.90

Moore and Gale[3] found that Schiff bases from N,N-dimethyl-*p*-phenylenediamine showed similar color reactions, but were crystalline solids. They suggested that the color of the mono- salt was caused by the addition of hydrogen chloride to form a para-quinonoid structure, and that the addition of a second molecule restored the benzenoid form. The diethyl homologs showed the same properties.

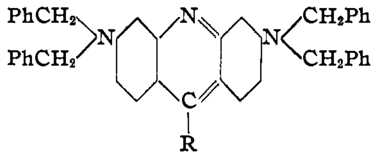
In a later paper Moore[4] found support for this theory in the observation that Schiff bases from dimethyl- and diethyl-*m*-phenylenediamines, which are incapable of forming quinonoid structures, did not give the color changes shown by their para isomers. This evidence was weakened by the fact that the compounds were not crystalline.

Since it seemed strange that the *m*-dialkylamino bases should differ radically from the *m*-dibenzylamino compounds in the color of their salts, the work of Moore was repeated. The *m*-dimethylamino derivatives gave intensely colored monohydrochlorides and almost colorless dihydrochlorides just as did their para isomers. Therefore, the color cannot be accounted for on a basis of quinonoid structure.

The Fluorescence.—Since the Schiff bases are not fluorescent, a secondary reaction must occur. Although repeated efforts to isolate another pure compound have failed, the fluorescence is probably caused by the formation of acridine derivatives by the condensation of (I) with aldehydes to form the series (II) and the subsequent loss of ammonia to form dihydroacridines (III) which oxidize in the air to the acridines (IV).



(III)



(IV)

Acridine Yellow and other acridines are prepared by similar series of reactions. Several acridines have been prepared in this Laboratory by similar reactions starting from the acetyl derivative of (I), and these compounds show fluorescence similar to that in the test.

The Test.—The stock solution consists of a 1% solution of (I) in 95% ethanol and the reagent solution is prepared by adding 1 ml. of concentrated hydrochloric acid to 100 ml. of this solution. In this form the reagent oxidizes rapidly and should not be used after forty-eight hours.

The test is carried out by placing 2 drops of the substance in a test-tube and adding 5 ml. of the reagent solution. The test differentiates between three classes of aldehydes.

(1) **Saturated aliphatic aldehydes** give a light red initial color which is followed within ten minutes by a bright green fluorescence which becomes stronger on standing and completely masks the color. The strength of the fluorescence increases with the length of the chain to a maximum at butyraldehyde and then decreases. Mixed aldehydes such as phenylacetaldehyde and hydrocinnamaldehyde fall in this class. Exception: formaldehyde gives a yellow initial color and no fluorescence.

(2) **Unsaturated aliphatic aldehydes** give a darker red initial color than the saturated compounds. A dull brownish-green fluorescence appears within ten minutes. Exceptions: hexadiene-2,4-al and cinnamaldehyde show unusually dark red initial colors but no fluorescence. This is probably because of the absorption of certain wave lengths of the incident light by the conjugated systems of double bonds.

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[3] Moore and Gale, This Journal, 30, 394 (1908).

[4] Moore, *ibid.*, 32, 382 (1910).

(3) **Aromatic aldehydes** give initial colors which vary from bright yellow to dark red. The chlorine atom and the nitro group decrease the color while the hydroxy, methoxy and dimethylamino groups increase the color. A bright green fluorescence similar to that of the saturated aliphatics appears only after two or more hours. Exceptions: nitro-aldehydes do not give fluorescence.

Furfuraldehyde is unique in that the original red color changes slowly to dark green on standing, and furfuraldehyde can be detected even in the presence of other aldehydes.

The presence of aldehydes as impurities in solvents may be detected by adding 5 ml. of the reagent to 10 ml. of the solvent. At concentrations of 1% and 0.1% the color appears immediately. At 0.01% it is necessary to wait several hours or preferably overnight before comparing with a blank. The limit of sensitivity of the test is about 0.002%.

The aldehydes tested were: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, hexaldehyde, heptaldehyde, octaldehyde, 2-ethylhexaldehyde, phenylacetaldehyde, hydrocinnamaldehyde, glyoxal, α-(*n*-amyl)-cinnamaldehyde, acrolein, crotonaldehyde, 2-vinyl-crotonaldehyde, hexene-2-al, hexadiene-2,4-al, citronellal, citral, cinnamaldehyde, dibutyraldehyde, dicrotonaldehyde, furfuraldehyde, chloral, benzaldehyde, *m*- and *p*-tolualdehydes, *o*-, *m*- and *p*-nitrobenzaldehydes, *o*- and *p*-chlorobenzaldehydes, *o*- and *p*-bromobenzaldehydes, 2-chloro-5-nitro-benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, *o*- and *p*-methoxybenzaldehydes, vanillin, piperonal, veratric aldehyde, *p*-aminobenzaldehyde, *p*-dimethylaminobenzaldehyde. Of these only chloral failed to give a positive test.

Experimental Part

N,N-Dibenzyl-*m*-nitraniline was prepared by a modification of the method of Desai.[5]

In a 1-liter flask were placed 138 g. (1 mole) of *m*-nitraniline, 253 g. (2 moles) of benzyl chloride and 164 g. (2 moles) of powdered anhydrous sodium acetate. One and five-tenths grams of iodine was added as a catalyst and the mixture was heated at 125–130° for seven hours in an oil-bath with constant mechanical stirring. The black oil was poured with stirring into water while hot to remove acetic acid and excess sodium acetate. The oil solidified during the stirring and was washed several times with water and then treated overnight with 500 cc. of alcohol. Filtration gave bright yellow crystals which were washed with alcohol and then recrystallized from alcohol. If the product melts at 71° or above, a second recrystallization is unnecessary. The melting point of the highly purified substance was 72° (Desai 73–74°). It sometimes shows dimorphic properties in which case it melts at 72°, resolidifies, and melts again at 78°. A second batch was recovered from the mother liquor and recrystallized. The yield was 200 g. or 65%.

N,N-Dibenzyl-*m*-phenylenediamine (I) was prepared by Desai[6] who described it as a black oil which oxidized rapidly in the air. It has been obtained in pure crystalline form in this Laboratory by the following method. One hundred grams of dibenzyl-*m*-nitraniline was dissolved in a mixture of 200 cc. of alcohol and 500 cc. of concentrated hydrochloric acid. Sufficient mossy zinc (200–250 g.) to complete the reduction was then slowly added. As long as any of the nitro compound remains, a few drops of the reaction mixture, when poured into water, will give the yellow color of the free base (the hydrochloride is colorless). The solution was filtered and allowed to remain in the icebox overnight. The white crystals of the hydrochloride of (I) were filtered off and stirred thoroughly with 1500 cc. of water to free the amine. This process was repeated and the product was filtered, washed with water, and suspended in 1 liter of 5% sodium hydroxide solution and allowed to remain overnight in the refrigerator. Filtration followed by thorough washing with water and drying gave 72 g. (90%). Recrystallization from 500 cc. of alcohol gave 63 g. of white crystals which melted sharply at 101°.

Anal. Calcd. for $C_{20}H_{20}N_2$: N, 9.73. Found: N, 9.71.

Summary

1. A new test for aldehydes has been described.
2. Six new Schiff bases from N,N-dibenzyl-*m*-phenylenediamine have been prepared and described.

GAINESVILLE, FLORIDA RECEIVED OCTOBER 24, 1940

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(5) Desai, *J. Indian Chem. Soc.*, **5**, 425 (1928).