p-Acetophenone-azo-β-naphthol, $CH_3COC_6H_4N:NC_{10}H_6OH$.—Two grams of *p*-aminoacetophenone, dissolved in 12 cc. 5 *N* hydrochloric acid, diazotized and added to 2.5 grams *β*-naphthol dissolved in 12 cc. 5 *N* sodium hydroxide, gave a bright red precipitate, insoluble in both acid and alkalies. It can be purified by crystallization from glacial acetic acid or acetone, the former being preferable. M. p., 181°–3°.

Calculated for $CH_3COC_6H_4N_2C_{10}H_7O$: N, 9.69. Found, 9.32.

Properties.—This compound crystallizes in small red prisms with a yellowish green reflex. It is soluble in alcohol, chloroform, toluene, carbon disulphide, and in hot glacial acetic acid, acetone, ligroin and ethyl acetate. Like benzeneazo-*β*-naphthol it is *insoluble* in aqueous alkalies. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid with a deep purple color and somewhat less readily in concentrated hydrochloric acid with a crimson color. It dissolves in alcoholic potash. It gives an *oxime* when heated with hydroxylamine hydrochloride and sodium acetate in alcohol for several hours.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

VANILLIDENE- AND PIPERONYLENEBENZIDINES.

BY HENRY A. TORREY AND E. D. CLARKE.

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The observation that benzidine gives with vanillin a very abundant precipitate of vanillidene benzidine led us to study this reaction more closely in the hope that possibly it might be used in a quantitative determination of vanillin. The fact, however, that both a mono- and a divanillidene derivative can be obtained according to the amount of benzidine added and certain other disadvantages led us to abandon this idea in our work and to turn our attention to the study of other similar derivatives. The other benzidine derivatives described by us are all condensation products in which two molecules of the aldehyde have condensed with one molecule of benzidine. Unfortunately the work had to be discontinued before definite information regarding the existence of the corresponding mono-aldehyde derivatives had been obtained.

Action of Benzidine on Vanillin, 3-Methoxy-4-hydroxybenzalbenzidine, $C_6H_3(OH)(OCH_3)CH:NC_6H_4.C_6H_4NH_2$ and *Bis-3-methoxy-4-hydroxybenzalbenzidine*, $C_6H_3(OH)(OCH_3)CH:NC_6H_4.C_6H_4N:HCC_6H_3.(OH).(OCH_3)$.—When two grams of vanillin, dissolved in a hot mixture of 25 cc. alcohol and 50 cc. water, were mixed with one molecule of benzidine dissolved in hot 58 per cent. alcohol, a bright yellow precipitate came down immediately, but the mixture was allowed to stand some time in order that the precipitation might become quite complete, after which the substance was washed, dried and purified by crystallization from hot benzene. The melting point finally obtained was 181°, although the body began to draw together at about 170°, and did not finally become clear below 184°–5°. The lack of sharpness in the melting point may be attributed to the formation of liquid crystals, a phenomenon often observed in this class of compounds. The analyses show this to be the mono-vanillidene derivative of benzidine, and different in properties from the di-vanillidene derivative obtained by Wolfson,[1] who gives the melting point of his product as 204°. The yield of the mono-vanillidene derivative is almost quantitative, 3.95 g. being obtained instead of the calculated 4.18 g. With glacial acetic acid, a red solution was formed, which on cooling deposited a mass of fine moss-like crimson crystals. When these were washed with a mixture of water and alcohol (4–1), the substance acquired its original yellow color.

Calculated for $C_6H_3(OH).(OCH_3)CH{:}\,NC_6H_4.C_6H_4NH_2$: C, 75.47; H, 5.66; N, 8.81. Found: C, 75.23, 75.04; H, 5.85, 5.82; N, 8.44, 8.67.

When *two* molecules of vanillin were used for each molecule of benzidine, the proportions employed by Wolfson, the *bis*-3-methoxy-4-hydroxybenzalbenzidine described by him was obtained. Crystallization from benzene finally gave a product of a yellow color that melted fairly sharply at 220°–221.5° (Wolfson 204°), although some drawing together was noticed below this point. The analysis shows that it is a divanillidene derivative.

Calculated for $(C_6H_3(OH)(OCH_3)CH{:}\,)_2C_{12}H_8N_2$: N, 6.19. Found: N, 5.80.

The vanillin residue is replaced by the hydroxybenzal group when it is treated in hot alcoholic solution with salicylaldehyde.

Bis-monobromvanillidenebenzidine $(CH_3OC_6H_2Br(OH)CH{:}\,)_2C_{12}H_8N_2$.—The monobromvanillin used in this preparation was made by treating 5 grams of vanillin dissolved in glacial acetic acid with a little iodine and then with 3.2 grams bromine. The reaction product was poured into water and crystallized from alcohol. The yield of the crude product was 4.5 grams. Its purity was established by its melting point, 160°–1° and by analysis. Bromine calculated for $(CH_3O)C_6H_2Br(OH)CHO$, 34.42; found, 34.40. This bromvanillin is identical with that described by Tiemann and Haarmann,[2] but our method of preparation proved to yield more satisfactory results than that given by them.

On mixing 1.5 grams benzidine dissolved in 30 cc. hot alcohol with 4 grams (2 mols.) of bromvanillin dissolved in 40 cc. hot alcohol, the divanillidene derivative was obtained as a yellow body, which separated out on cooling. It was allowed to stand four hours, filtered, washed, dried and crystallized from benzene. It decomposes to a black liquid

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[1] Inaugural dissertation, Albert-Ludwigs Univ., 1905, F. Wolfson.

[2] *Ber.*, 7, 615.

rather slowly at 232°. It gives a bright red color with acids and is soluble with a yellow color in aqueous sodium hydroxide.

Calculated for $((CH_3O)C_6H_2Br(OH)CH:)_2C_{12}H_8N_2$: Br, 26.23. Found, 25.91, 26.10.

Bis-nitropiperonylenebenzidine, $(CH_2O_2C_6H_2NO_2CH:)_2C_{12}H_8N_2$.—This derivative was made by mixing hot alcoholic solutions of 6-nitropiperonal[1] (m. p. 97°) and benzidine, made up as follows: 5 grams nitropiperonal in 100 cc. alcohol and 2.4 grams benzidine in 50 cc. alcohol. The reddish yellow precipitate that appeared in a few minutes was allowed to stand some time before filtering and then crystallized from xylene. It decomposes when heated to 273° and when pure is of a dark yellow color, which changes rather rapidly to dark brown on exposure to sunlight.

Calculated for $(CH_2O_2C_6H_2NO_2CH:)_2C_{12}H_8N_2$: N, 10.41. Found, 10.10, 10.25.

Bis-mono-brompiperonylenebenzidine, $(CH_2O_2C_6H_2BrCH:)_2C_{12}H_8N_2$.—When two molecules of brompiperonal[2] (m. p. 129°) were dissolved in hot alcohol and mixed with a hot alcoholic solution of one molecule of benzidine, a yellow substance precipitated almost immediately. The mixture was allowed to stand overnight, and after washing and drying, the compound was crystallized from benzene. M. p. 257° with decomposition. Analysis shows that both amino groups have reacted with the brompiperonal.

Calculated for $(CH_2O_2C_6H_2BrCH:)_2C_{12}H_8N_2$: Br, 26.40. Found, 26.84, 26.44, 26.18.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

DI-ISOBUTYL OR 2,5-DIMETHYL-HEXANE.

BY LATHAM CLARKE.

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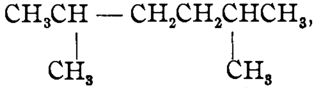
Although di-isobutyl or 2-5 dimethylhexane,  $CH_3\underset{\substack{|\\ CH_3}}{C}H - CH_2CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3$, has been known for many years, a new synthesis of it has been considered necessary in the research on the octanes now in progress in this laboratory. The value of this research depends to a great extent on the accuracy of the physical constants, and the data in regard to di-isobutyl vary considerably according to the observations of different investigators, so that they do not appear to have the desired accuracy.

Di-isobutyl was first made by Kolbe[3] in 1849, by the electrolysis of potassium isovalerianate. Kolbe published the boiling point 108°, and the specific gravity, 0.694 at 18°. According to Kopp,[4] to whom

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[1] Fittig, Remsen, *Ann.*, **159**, 134. F. Haber, *Ber.*, **24**, 624.

[2] Oelker, *Ber.*, **24**, 2593.

[3] *Ann.*, **69**, 261.

[4] *Ibid.*, **95**, 335.