Aqueous solutions, both of the acid and of its salts, were rapidly decomposed by the emanation, the concentrated more rapidly than the dilute, but the increased velocity was not proportional to the concentration and is clearly influenced by secondary reactions.

In conclusion, allusion should be made to three new attempts to prepare periodic tables which shall prove more satisfactory than that of Mendeléeff, or others now in use. These are respectively by Schmidt (*Z. physik. Chem.*, **75**, 651), Emerson (*Am. Chem. J.*, **45**, 160) who proposes a "Helix chemica," and Van den Broek (*Physik. Ztschr.*, **12**, 490), in whose table each group has three series instead of two, and which is based on "ideal" atomic weights, which often differ to the extent of several units from those which have been experimentally determined.

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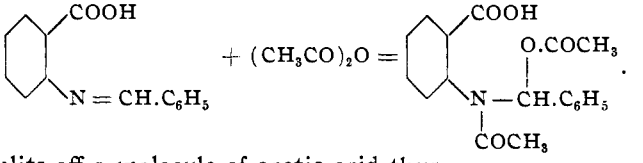
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]

THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS.

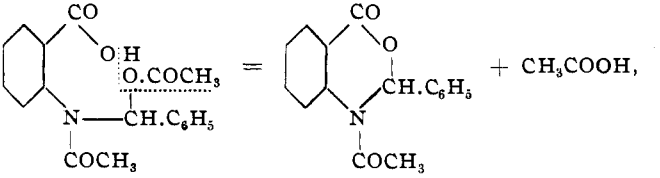
BY JOHN B. EKELEY AND PAUL M. DEAN.

Received November 21, 1911.

Anthranilic acid reacts with aromatic aldehydes with the formation of benzylidene derivatives. These derivatives react with acetic anhydride, giving a series of oxazines. The reaction probably passes through an intermediate stage in which a molecule of the benzylidene derivative adds a molecule of acetic anhydride thus:



Heating splits off a molecule of acetic acid thus,



giving an acetketodihydrobenzmetoxazine.[1]

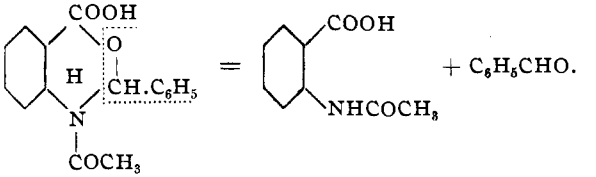
The reaction seems to be general, since in the cases thus far studied with aromatic aldehydes, the condensation takes place with ease. This paper will deal with the oxazines obtained from benzylidene, metanitrobenzylidene, paranitrobenzylidene, paraoxybenzylidene, salicylidene, and vanillylidene anthranilic acids. These oxazines are colorless,

[1] The Badische Anilin und Soda Fabrik has patented a process for making a series of compounds containing the metoxazine ring, abstracts of which are given in the *Chem. Zentralblatt*, 1910, I, 308, 309, 1564; 1911, I, 853.

crystallin solids, with the exception of the one from vanillin, which is straw colored, and are very stable, requiring boiling with acids or alkalis to affect decomposition. The compounds obtained from meta- and paranitrobenzylidene anthranilic acid may be boiled with concentrated sodium hydroxide with only slight decomposition.

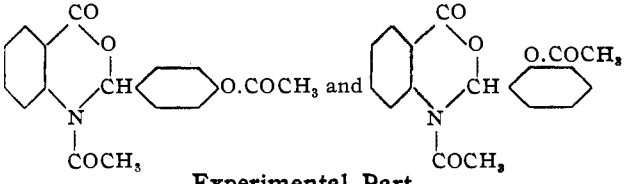
Just as this paper was being finished, we noted an abstract of a paper by Wolf,[1] in which he describes the benzylidene derivatives (except that from vanillin) from which we have made our condensation products. Since the methods of preparation are different, we are also including them in this paper.

The constitution of the condensation product from benzylidene anthranilic acid and acetic anhydride was proved from the decomposition products obtained when it was heated with strong hydrochloric acid. Benzaldehyde was given off and a crystallin substance separated out, which proved to be acetanthranilic acid, melting at 185°. The decomposition evidently takes place as follows:



The compound therefore is phenylacetketodihydrobenzmetoxazine.

In the condensation products from *p*-hydroxybenzylidene and salicylidene anthranilic acids, it was found that the hydrogen of the hydroxyl group had been replaced by acetyl, thus:



Experimental Part.

Benzylidene Anthranilic Acid.—One gram-molecule of anthranilic acid in benzene solution was heated with 1 gram-molecule of benzaldehyde under reflux on the water bath. A little animal charcoal was added, and the solution filtered. Light straw-colored needles separated out on cooling. These were contaminated with a small amount of anthranilic acid, so that several recrystallizations from benzene were necessary to obtain the substance pure. Melting point, 126°.

Calculated for $C_{14}H_{11}NO_2$: N, 6.22. Found, 6.52.

Phenylacetketodihydrobenzmetoxazine.—Benzylidene anthranilic acid was heated in an Erlenmeyer flask with an excess of acetic anhydride for 4

[1] *Monatsheft*, 31, 903–16.

hours on the water bath. By means of a bent glass tube connected with a suction pump, the vapors of acetic anhydride were drawn off from the solution, while still on the water bath, until it was sufficiently concentrated to allow the oxazine to crystallize out. On cooling the flask, the contents solidified. The crystals were filtered off, pressed out on a porous plate, and recrystallized from methyl alcohol. Colorless prisms, soluble in the ordinary organic solvents. Melting point 108°.

Calculated for $C_{16}H_{13}NO_3$: N, 5.24; C, 71.91; H, 4.87.
Found: N, 5.50; C, 71.80; H, 4.78.

m-Nitrobenzylidene Anthranilic Acid.—One gram-molecule of anthranilic acid was dissolved in just enough alcohol to hold it in solution when placed in a freezing mixture of ice and salt. One gram-molecule of pulverized *m*-nitrobenzaldehyde was then added with constant stirring of the solution. In a short time, the *m*-nitrobenzylidene anthranilic acid separated out, so that the contents of the beaker became solid. The crystals were filtered off by suction, pressed out on a porous plate, and recrystallized from alcohol. Light straw-colored needles, soluble in the usual organic solvents. Melting point, 202°.

Calculated for $C_{14}H_{10}N_2O_4$: N, 10.37. Found, 10.76.

m-Nitrophenylacetketodihydrobenzmetoxazine. — One gram-molecule of metanitrobenzylidene anthranilic acid was heated with an excess of acetic anhydride on the water bath, until, in a short time, the oxazine crystallized out. The crystals were filtered off by suction, and washed with alcohol and then ether to remove the excess acetic anhydride. The substance was recrystallized from boiling xylene. Thick, colorless crystals, insoluble in the ordinary organic solvents, soluble in hot xylene. Melting point, 192°.

Calculated for $C_{16}H_{12}N_2O_5$: N, 8.98; C, 61.51; H, 3.80.
Found: N, 9.05; C, 61.30; H, 3.98.

p-Nitrobenzylidene Anthranilic Acid.—*p*-Nitrobenzylidene anthranilic acid was prepared in the same manner as the corresponding *meta* product. Straw-colored needles, soluble in the ordinary organic solvents. Melting point, 164°.

Calculated for $C_{14}H_{10}N_2O_4$: N, 10.37. Found, 10.68.

p-Nitrophenylacetketodihydrobenzmetoxazine.—This oxazine was prepared in exactly the same manner as that from metabenzylidene anthranilic acid. The oxazine crystallized out from the acetic anhydride solution in silky white needles, which were filtered off by suction, washed with alcohol and then with ether, after which treatment they were found to be pure. Insoluble in the ordinary organic solvents. Soluble in hot xylol. Melting point, 199°.

Calculated for $C_{16}H_{12}N_2O_5$: N, 8.98; C, 61.51; H, 3.80.
Found: N, 9.19; C, 61.46; H, 4.10.

p-Oxybenzylidene Anthranilic Acid.—*p*-Oxybenzylidene anthranilic acid was made in alcoholic solution in the same way as the *p-nitro* compound. This substance crystallized out in the form of lemon-yellow needles. Soluble in the ordinary organic solvents. Melting point, 207°.

Calculated for $C_{14}H_{11}NO_3$: N, 5.80. Found, 5.98.

Acetyl-p-oxyphenylacetketodihydrobenzmetoxazine.—This compound was made in exactly the same way as the preceding oxazines. In this case the hydrogen of the hydroxyl group is replaced by acetyl. Recrystallized from methyl alcohol, it yields colorless prisms. Melting point, 148°.

Calculated for $C_{18}H_{15}NO_5$: N, 4.31; C, 66.46; H, 4.61.
Found: N, 4.68; C, 66.11; H, 4.94.

Salicylidene Anthranilic Acid.—Salicylidene anthranilic acid was prepared in a manner analogous to that of the other benzylidene products. Orange-red crystals from alcohol. Soluble in ordinary organic solvents. Melting point, 195°.

Calculated for $C_{14}H_{11}NO_3$: N, 5.81. Found, 6.03.

Acetyl-o-oxyphenylacetketodihydrobenzmetoxazine.—This compound was prepared from salicylidene anthranilic acid in the same way as the preceding oxazines. Colorless crystals from methyl alcohol. Melting point, 162°.

Calculated for $C_{18}H_{15}NO_5$: N, 4.31; C, 66.46; H, 4.61.
Found: N, 4.64; C, 65.85; H, 4.75.

Vanillylidene Anthranilic Acid.—Equimolecular solutions of anthranilic acid and vanillin in benzene were mixed. On standing, lemon-yellow needles crystallized out. Recrystallization from boiling benzene yielded a product melting at 170°.

Calculated for $C_{15}H_{13}NO_4$: N, 5.16. Found, 5.01.

3-Methoxy-4-oxyphenylacetketodihydrobenzmetoxazine.—This compound was prepared from vanillylidene anthranilic acid and acetic anhydride in the same manner as the preceding oxazines. Light straw-colored crystals, melting at 184°.

Calculated for $C_{19}H_{17}NO_5$: N, 3.94; C, 64.22; H, 4.78.
Found: N, 4.19; C, 63.94; H, 5.02.

Condensation products from other benzylidene anthranilic acids are being prepared and will be described in a succeeding paper.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

THE ACTION OF ALCOHOLATES AND AMINES ON BENZOYLISOCYANCHLORIDE.

BY TREAT B. JOHNSON AND LEWIS H. CHERNOFF.

Received December 1, 1911.

Of the three classes of acylimidocarbonates, I, II and III, only the