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

THE ACTION OF ACETIC ANHYDRIDE OF SOME BENZYLIDENE ANTHRANILIC ACIDS.

[SECOND PAPER.]

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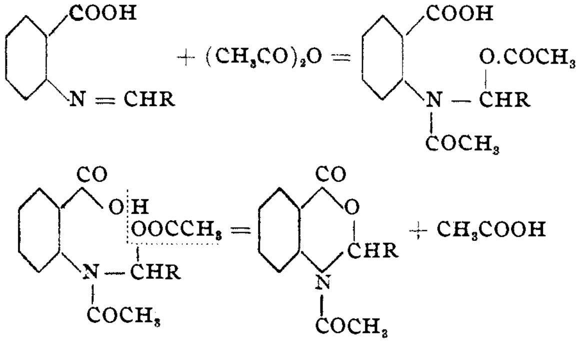
A number of acet-keto-dihydro-benzmetoxazines have been obtained by Ekeley and Dean[1] by the action of acetic anhydride on benzylidene anthranilic acids, according to the following reactions:



The reaction seems to be a general one, and this paper will describe the benzylidene anthranilic acids obtained from protocatechuyl aldehyde, bromosalicyl aldehyde, *o*-nitrobenzaldehyde, *o*-methoxysalicyl aldehyde, resorcyl aldehyde and *p*-dimethylamino benzaldehyde, and the benzmetoxazines obtained from them by means of acetic anhydride.

Protocatechuylidene Anthranilic Acid.—Molecular proportions of anthranilic acid and protocatechuyl aldehyde were allowed to react in concentrated alcoholic solution in a beaker packed in ice and salt. After a few moments an orange-red, crystallin powder separated out. This was pressed out upon a porous plate and recrystallized from alcohol. Orange-red crystals. M. p. 204°.

Calculated for $C_{14}H_{11}NO_4$: N, 5.44; found: N, 5.54.

3,4 - Dihydroxyphenylacetketodihydrobenzmetoxazine. — Protocatechuylidene anthranilic acid was heated with an excess of acetic anhydride on the water-bath for three hours. By means of a bent, glass tube the vapors of acetic anhydride were drawn off from the solution while still on the water-bath until it was sufficiently concentrated for the oxazine to crystallize out. The product, pressed out on a porous plate and recrystallized from methyl alcohol, yielded colorless needles. Soluble in the ordinary organic solvents. M. p. 121°.

Calculated for $C_{16}H_{13}NO_5$: N, 4.63; found: N, 4.34.

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[1] THIS JOURNAL, **34**, 161.

Bromosalicylidene Anthranilic Acid.—Molecular proportions of bromosalicylaldehyde and anthranilic acid react under cooling in alcohol solution. The bromosalicylidene anthranilic acid soon separates out. Recrystallized from alcohol, it yields yellow needles. Soluble in the ordinary organic solvents. M. p. 198°.

Calculated for $C_{14}H_{10}NO_3Br$: N, 4.30; found: N, 4.25.

2,4-Hydroxybromophenylacetketodihydrobenzmetoxazine.—Heated on the water-bath for several hours with an excess of acetic anhydride and the reaction product separated out as before, the oxazine was obtained in the form of colorless hexagonal pyramids, when recrystallized from methyl alcohol. Soluble in the ordinary organic solvents. M. p. 170°.

Calculated for $C_{16}H_{12}NO_4Br$: N, 4.09; found: N, 4.29.

o-Nitrobenzylidene Anthranilic Acid.—*o*-Nitrobenzaldehyde was heated with an equivalent amount of anthranilic acid in benzene solution for two days under reflux upon the water-bath. The solution was placed in a refrigerator for several days, after which the *o*-nitrobenzylidene anthranilic acid separated out in the form of straw-colored needles. These change to a brown on exposure to the light, the change taking place rather quickly. Recrystallized from alcohol. M. p. 67°.

Calculated for $C_{14}H_{10}N_2O_4$: N, 10.37; found: N, 9.98.

o - Nitrophenylacetketodihydrobenzmetoxazine. — *o*-Nitrobenzylidene anthranilic acid, heated with an excess of acetic anhydride and treated as in the previous cases, yields an oxazine. Recrystallized from methyl alcohol, very light yellow needles. M. p. 167.5°.

Calculated for $C_{16}H_{12}N_2O_5$: N, 61.39; found: N, 61.49.

o-Methoxybenzylidene Anthranilic Acid.—Molecular proportions of the methyl ether of salicylaldehyde and anthranilic acid were allowed to react in alcohol solution at the temperature of a mixture of ice and salt. Yellow crystals of *o*-methoxybenzylidene anthranilic acid separated out, which were recrystallized from alcohol. M. p. 122°.

Calculated for $C_{15}H_{13}NO_3$: N, 5.49; found: N, 5.54.

o-Methoxyphenylacetketodihydrobenzmetoxazine.—When *o*-methoxy benzylidene anthranilic acid is heated with an excess of acetic anhydride on the water-bath, the excess of anhydride removed as in the previous cases, and the crude product recrystallized from methyl alcohol, very light yellow prisms of *o*-methoxyphenylacetketodihydrobenzmetoxazine are obtained. M. p. 165°.

Calculated for $C_{17}H_{15}NO_4$: N, 4.70; found: N, 4.39.

Resorcylidene Anthranilic Acid.—As in the previous cases, molecular proportions of the aldehyde and the acid react in alcohol solution with the formation of the benzylidene anthranilic acid. Recrystallized from alcohol, resorcylidene anthranilic acid appears as yellow needles. No definit melting point was obtained; begins to change color at about 150° with decomposition.

Calculated for $C_{14}H_{11}NO_4$: N, 5.44; found: N, 5.11.

1,3 - Dihydroxyphenylacetketodihydrobenzmetoxazine. — Treated on the water-bath as above described, resorcylidene anthranilic acid with acetic anhydride yields the oxazine. 1,3-Dihydroxyphenylacetketodihydrobenzmetoxazine crystallized from methyl alcohol in colorless crystals. M. p. 192°.

Calculated for $C_{16}H_{13}NO_4$: N, 4.68; found: N, 4.63.

p-Dimethylaminobenzylidene Anthranilic Acid.—In a cooled alcohol solution, molecular amounts of dimethylaminobenzaldehyde and anthranilic acid react with the formation of *p*-dimethylaminobenzylidene anthranilic acid. Bright red needles from alcohol. M. p. 176°.

Calculated for $C_{16}H_{16}N_2O_2$: N, 10.44; found: N, 10.34.

p-Dimethylaminophenylacetketodihydrobenzmetoxazine.—With excess of acetic anhydride, *p*-dimethylaminobenzylidene yields the corresponding oxazine when heated on the water-bath. Dark yellow crystals from xylol. M. p. 162°.

Calculated for $C_{18}H_{18}N_2O_3$: N, 9.03; found: N, 9.08.

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THE DIRECT DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS.

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Oxygen is one of the most frequently occurring constituents of organic compounds, and yet there is no direct method known for its quantitative determination. In the analysis of a compound the universal custom has been to determin the percentage of all the elements present with the exception of oxygen, subtract the sum of these from one hundred, and call the remainder the percentage of oxygen. Although this has presented no serious impediment to the development of organic chemistry, yet many instances have occurred in which a method for the quantitative estimation of oxygen would have been a great convenience. No doubt most organic chemists have in the course of their synthetic investigation work met with reactions involving considerable alteration in the oxygen content of a compound without changing to any appreciable extent the percentages of carbon and hydrogen present as, for instance, in the replacement of the amino group by hydroxyl. Moreover, a direct method for oxygen is also needed for its determination in commercial products as asphalt, rubber, etc., and for following the course of reactions involving the fixation of atmospheric oxygen in compounds. Several indirect