

finally showing signs of crystallization. The oil was left under water for some days to allow its crystallization to become complete. The substance was obtained in colorless crystals having a melting point of 145–146°. It was analyzed and was found to be 3,5-dichloro-2,4,6-triketoheptane.

0.1852 g. gave 0.2708 g. CO<sub>2</sub> and 0.0551 g. H<sub>2</sub>O, C = 39.58; H = 3.40. 0.2331 g. gave 0.3157 AgCl, Cl = 33.50. Calc. for C<sub>7</sub>H<sub>3</sub>Cl<sub>2</sub>, C = 39.81; H = 3.79; Cl = 33.65.

Further investigations on similar lines are being continued.

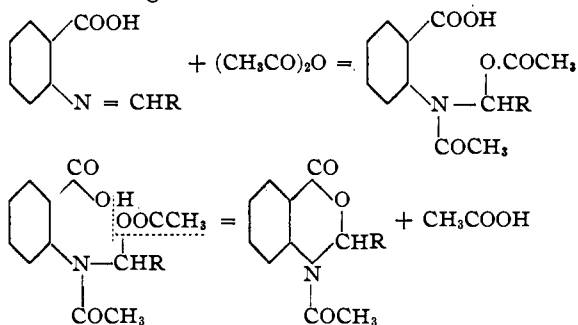
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]  
**THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS. IV.**

By JOHN B. EKELEY AND CHARLES F. POE.

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Eighteen members of a series of acetketodihydrobenzmetoxazines have been described in previous papers.<sup>1</sup> These were obtained by the action of acetic anhydride upon the corresponding benzylidene anthranilic acids, according to the following reactions:



The previous members of this series, as described, were made by heating the benzylidene anthranilic acid with excess of acetic anhydride on the water bath for several hours, then evaporating off the excess of anhydride, and allowing the benzmetoxazine to crystallize out of the cooled concentrated solution. This method failed with certain benzylidene anthranilic acids, notably those derived from anisaldehyde and from piperonal, acetanthranilic acid being obtained instead of the expected benzmetoxazine. By a variation of the method, these benzmetoxazines have also been prepared. The benzylidene anthranilic acid was heated with molecular proportions of acetic anhydride in xylol solution for several hours, the excess of xylol was then distilled off, and the solution cooled in ice water. The benzmetoxazine derivative then crystallized out in a very

<sup>1</sup> THIS JOURNAL, 34, 161; 35, 282; 36, 604.

pure condition. The yield was much greater than had been obtained by the previous method of heating the two substances together without a solvent. Thus from 66 g. of benzylidene anthranilic acid 70 g. of phenylacetketodihydrobenzmetoxazine were obtained, whereas theory required 78 g. It was found, however, that in some cases the first method gives better results; for instance, in the case of salicylidene anthranilic acid, the latter method gives a syrupy mass from which it is difficult to obtain the benzmetoxazine, while by heating the benzylidene anthranilic acid directly with an excess of anhydride the benzmetoxazine is obtained easily and with a very satisfactory yield.

This paper will describe the benzylidene anthranilic acids obtained from *o*-toluylaldehyde, dibromosalicylaldehyde, 1,4- $\alpha$ -naphtholaldehyde, anisaldehyde, piperonal, methylvanillin, and *m*-methoxysalicylaldehyde, and the benzmetoxazine derivatives obtained from them.

In the condensation products from dibromosalicylaldehyde and from 1,4- $\alpha$ -naphtholaldehyde, it was found that the hydrogen of the hydroxyl group had been replaced by acetyl.

#### Experimental Part.

***o*-Toluylideneanthranilic Acid.**—Molecular amounts of *o*-toluylaldehyde and anthranilic acid in concentrated alcohol solution give a white, crystalline mass on standing, which may be recrystallized from a small amount of alcohol. Difficultly soluble in the ordinary organic solvents except methyl and ethyl alcohols, in which it is very soluble, and xylol. M. p. 143°.

Calc. for  $C_{15}H_{13}O_2N$ : N, 5.57; found: N, 5.6.

***o*-Methylphenylacetketodihydrobenzmetoxazine.** — *o*-Toluylideneanthranilic acid was heated with acetic anhydride in excess on the water bath for three hours. The excess acetic anhydride was then evaporated off, a stream of air being drawn over the liquid as it was being heated on the water bath. On cooling, the benzmetoxazine crystallized out. Recrystallized from alcohol it gave colorless prisms. Soluble in the ordinary organic solvents except ether. M. p. 166°.

Calc. for  $C_{17}H_{15}O_3N$ : N, 4.98; found: N, 4.9.

**Dibromosalicylideneanthranilic Acid.**—Dibromosalicylideneanthranilic acid separates out as a red crystalline mass when molecular amounts of dibromosalicylaldehyde and anthranilic acid are mixed in a cold alcohol solution. Recrystallized from alcohol, it yields scarlet needles, soluble in the ordinary organic solvents. M. p. 176°.

Calc. for  $C_{14}H_9NBr_2$ : N, 3.51; found: N, 3.22.

**Acetyldibromophenylacetketodihydrobenzmetoxazine.**—After heating dibromosalicylideneanthranilic acid with an excess of acetic anhydride and evaporating off the excess of anhydride as before, the benzmetoxazine

was obtained, mixed with a small amount of an intensely yellow crystalline substance, which probably is the unacetylated metoxazine. Colorless prisms, soluble in the ordinary organic solvents, except ether. M. p. 153°.

Calc. for  $C_{18}H_{13}O_5NBr_2$ : N, 2.89; found, N, 2.87.

**Dibromophenylacetketodihydrobenzmetoxazine.**—The yellow crystals remaining behind after heating the compound just described with alcohol were recrystallized from boiling xylol, giving yellow needles, insoluble in most organic solvents. M. p. 274°.

Calc. for  $C_{16}H_{11}O_4NBr_2$ : N, 3.22; found: N, 3.17.

**1,4- $\alpha$ -Naphtholideneanthranilic Acid.**—Molecular amounts of  $\alpha$ -1,4-naphthaldehyde and anthranilic acid mixed in cold alcohol solution gave in a short time a maroon-colored mass. This was recrystallized from *warm* nitrobenzol, giving maroon-colored microscopic needles. Insoluble in the ordinary organic media, except acetone, methyl and ethyl alcohols. When boiled with nitrobenzol it decomposes partially. M. p. 195°.

Calc. for  $C_{18}H_{13}O_3N$ : N, 4.81; found: N, 5.04.

**Acetyl- $\alpha$ -hydroxy-1,4-naphthoacetketodihydrobenzmetoxazine.** — Heated on the water bath with excess acetic anhydride, 1,4- $\alpha$ -naphtholideneanthranilic acid yields the corresponding benzmetoxazine, the hydroxyl group being at the same time acetylated. Soluble in the ordinary organic solvents, difficultly in alcohol, from which it was recrystallized. Colorless microscopic needles. M. p. 238°.

Calc. for  $C_{22}H_{17}O_5N$ : N, 3.72; found, N, 3.57.

**Anisylideneanthranilic Acid.**—This was obtained as before by mixing a cold concentrated solution of anthranilic acid with anisaldehyde. The yellow crystals thus obtained were recrystallized from alcohol. Soluble in the ordinary organic solvents, except ether. M. p. 146°.

Calc. for  $C_{15}H_{13}O_3N$ : N, 5.49; found: N, 5.39.

***p*-Methoxyphenylacetketodihydrobenzmetoxazine.** — Molecular amounts of anisylideneanthranilic acid and acetic anhydride were heated for two and one half hours in xylol solution under reflux. The greater portion of the xylol was then distilled off and the remaining solution cooled in ice water. Sandy, colorless crystals separated out. These were filtered under suction, and, when washed with ether on the filter, were found to be snow-white in appearance. Soluble in the ordinary organic solvents except ether. M. p. 118°.

Calc. for  $C_{17}H_{15}O_4N$ : N, 4.70; found: N, 4.55.

**Piperonalideneanthranilic Acid.**—When molecular amounts of piperonal and anthranilic acid were brought together in cold alcohol solution, piperonalideneanthranilic acid separated out in a crystalline mass. Recrystallized from chloroform, it gave yellow crystals, soluble in the ordinary organic solvents except ether. M. p. 196°.

Calc. for  $C_{18}H_{11}O_4N$ : N, 5.20; found, N, 5.15.

**3,4 - Methylene-dihydroxyphenylacetketodihydrobenzmetoxazine.** — Molecular amounts of piperonalideneanthranilic acid and acetic anhydride were heated together in xylol solution under reflux for two hours. The greater portion of the xylol was then distilled off and the remaining solution cooled in ice water. The solution separated into two layers, the lower one thick and syrupy. After standing several hours, this solidified into a mass of crystals. These were filtered under suction and washed with ether on the filter, yielding sandy, white crystals of the expected benzmetoxazine. Soluble in the ordinary organic solvents except ether. M. p.  $126^{\circ}$ .

Calc. for  $C_{17}H_{18}O_6N$ : N, 4.50; found: N, 4.31.

**Methylvanillylideneanthranilic Acid.**—Molecular amounts of methyl vanillin and anthranilic acid were brought into concentrated cold alcoholic solution. After standing over night, the methylvanillylidene anthranilic acid appeared as bright yellow needles. These, recrystallized from xylol, were soluble in the ordinary organic solvents except ether. M. p.  $163^{\circ}$ .

Calc. for  $C_{16}H_{16}O_4N$ : N, 4.91; found: N, 4.76.

**3,4-Dimethoxyphenylacetketodihydrobenzmetoxazine.**—As in the two preceding cases, the benzmetoxazine was obtained by heating molecular amounts of the acid and acetic anhydride in xylol solution under reflux, distilling off most of the xylol, and cooling the remaining solution in ice water. The oil which separated out in this case would not crystallize until a small amount of alcohol had been added, whereupon the expected benzmetoxazine separated out as white sandy crystals. These were filtered off under suction, and washed with ether on the filter. Soluble in the ordinary organic solvents, except ether. M. p.  $106^{\circ}$ .

Calc. for  $C_{18}H_{17}O_6N$ : N, 4.28; found: N, 3.99.

***m*-Methoxysalicylideneanthranilic Acid.**—This acid is formed when molecular quantities of *m*-methoxysalicylaldehyde and anthranilic acid are heated in xylol solution for several hours under reflux. On standing the solution deposits red needles. These were recrystallized from chloroform. Soluble in the ordinary organic solvents. M. p.  $113^{\circ}$ .

Calc. for  $C_{18}H_{18}O_8N$ : N, 5.16; found: N, 4.80.

**Acetyl-2-hydroxy-4-methoxyphenylacetketodihydrobenzmetoxazine.**—Molecular proportions of *m*-methoxysalicylideneanthranilic acid and acetic anhydride heated in xylol solution as in previous cases yield colorless crystals of the acetylated oxazine after the concentrated solution has stood in the cold for several days. These were recrystallized from xylol. M. p.  $187^{\circ}$ .

Calc. for  $C_{19}H_{17}O_8N$ : N, 3.97; found: N, 3.76.

**3-Methoxy-4-acetoxyphenylacetketodihydrobenzmetoxazine.** — The preparation of the benzmetoxazine derived from vanillylideneanthranilic

acid and acetic anhydride by the method of heating the two substances in xylol under reflux gave a product which differed in its properties from that described in a previous paper<sup>1</sup> as made by the method of heating the acid and the acetic anhydride in excess. It is evident that the product previously described was not pure. To prepare the pure compound, it is necessary to heat the vanillylideneanthranilic acid with two molecular proportions of acetic anhydride in xylol solution under reflux for one hour. After distilling off the greater portion of the xylol, the acetylated metoxazine separates out on cooling in colorless sandy crystals. Recrystallized from xylol. Soluble in the ordinary organic solvents, except ether. M. p. 141°.

Calc. for C<sub>19</sub>H<sub>17</sub>O<sub>6</sub>N: N, 3.97; found: N, 3.61.

BOULDER, COLORADO.

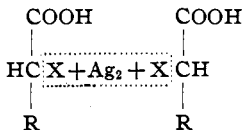
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

## THE ACTION OF FINELY DIVIDED SILVER ON $\alpha$ -BROMO- AND $\alpha$ -IODOPALMITIC ACIDS: SYNTHESIS OF TWO ISOMERIC DITETRADECYLSUCCINIC ACIDS.

By D. BREESE JONES.

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As is well known, the reaction between finely divided silver, so called "molecular silver", and monohalogen substitution products of the fatty acids is by no means a simple one. Besides the removal of halogen from two molecules of the substituted fatty acid and union taking place through the released affinities of the carbon atoms with formation of dibasic acids,



there are always formed several other products of the reaction. Hell and his co-workers have studied the action of silver on several halogen substituted fatty acids. From ethyl  $\alpha$ -bromoisobutyrate and silver<sup>2</sup> were obtained two isomeric tetramethylsuccinic acids, carbon dioxide, ethyl bromide, isobutyric acid and methylacrylic acid, while ethyl  $\alpha$ -bromobutyrate<sup>3</sup> yielded ethyl bromide, ethyl alcohol, ethyl butyrate, two diethylsuccinic acids, and a sirup whose composition agrees with that of hydroxysuberic acid. Ethyl  $\alpha$ -bromoisovalerianate with silver<sup>4</sup> yielded two isomeric sebacic acids, ethyl bromide, ethyl isovalerianate, and

<sup>1</sup> THIS JOURNAL, 35, 164 (1913).

<sup>2</sup> Hell, *Ber.*, 10, 2229 (1877).

<sup>3</sup> Hell and Mühlhäuser, *Ibid.*, 13, 473-9 (1880).

<sup>4</sup> Hell and Mayer, *Ibid.*, 22, 48 (1888).