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Anhydrous Acetylbenzilic Acid

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In the course of measurements on the kinetics of saponification of acetylated hydroxy acids, it became necessary to prepare pure acetylbenzilic acid. This compound was first reported by Klinger and Standke[1] (m. p. 98°) and later by Herzig and Schleiffer[2] (m. p. 94–96°) but in neither case was the compound identified quantitatively as acetylbenzilic acid. Using the method of Herzig and Schleiffer, we secured a product of the reported melting point, 94–96°. Recrystallization of this product from benzene, in one case, and from ethyl alcohol–water mixture in another, yielded products melting at 96.5–97.5°, 96.5–96.8°, respectively, with acid equivalent values of 23.19, 23.58 cc. alkali instead of the calculated values of 25.00 cc. for acetylbenzilic acid or 29.60 cc. for benzilic acid. The mixed melting points of these products with benzilic acid were never lowered by more than 4°.

These results showed that the material obtained by Herzig and Schleiffer's method was certainly not pure acetylbenzilic acid. Water, either adsorbed or hydrated, would produce a low acid equivalent and would cause variable melting points by decomposing acetylbenzilic acid to benzilic and acetic acids during melting point determinations. The experimental results reported below demonstrate that the products obtained by previous workers were either a monohydrate or contained water as an impurity.

Preparation of "Hydrated" Acetylbenzilic Acid.

Fifty grams of crude, air-dried benzilic acid[3] and 100 cc. acetic anhydride were heated for fourteen hours on a hot water-bath. The mixture was cooled, and water added in 2–3-cc. portions, with vigorous shaking after each addition so that the solution became clear before adding the next portion. This process was continued until the solution became permanently cloudy (approximately 115 cc. of water required).

The slightly yellow crystals (30–40 g.; a further crop may be obtained by diluting the mother liquor) which separated overnight were filtered and washed with benzene until colorless. The crystals were purified by dissolving in ethyl alcohol, precipitating by careful addition of water, washing with ethanol-water mixture, drying in air, and finally over calcium chloride; yield, 14 g.; m. p. 96° corr., evidently the Herzig and Schleiffer product. However, 0.2004 g. required 23.30 cc. of 0.02968 *M* NaOH for neutralization (calculated for acetylbenzilic acid, 25.00 cc.; calculated for acetylbenzilic acid·H_2O, 23.44 cc.) and required an additional 22.9 cc. for saponification (calculated for acetylbenzilic acid, 25.00 cc.; for acetylbenzilic acid·H_2O, 23.44 cc.). From these figures it can be seen that there is one acetyl group for each free acid group (within 2%), as would be the case for acetylbenzilic acid. Both neutralization and saponification numbers are too low for acetylbenzilic acid, although they are in better agreement with a hydrated acetylbenzilic acid

The presence of water was demonstrated by the following experiments: (1) 0.2004 g. of m. p. 96° was placed in a weighed platinum bucket over concentrated sulfuric acid *in vacuo*. The weight, determined from time to time, decreased and reached a constant value of 0.1886 g. after three weeks. The melting point of this dried product rose to 104.3–105.0° corr.; 0.1866 g. now required 24.67 cc. of 0.02796 *M* NaOH; 24.71 cc. calculated for acetylbenzilic acid.

(2) A 14-g. sample of pure hydrated acetylbenzilic acid was kept *in vacuo* over concentrated sulfuric acid for twenty-five days and occasionally stirred; m. p. 104.5–104.8°; 0.1888 g. required 25.00, 25.02 cc. of 0.02796 *M* NaOH for neutralization; calculated for acetylbenzilic acid: 25.00 cc.; and required an additional 24.9 cc. for saponification; calculated for acetylbenzilic acid: 25.00 cc.

Summary and Conclusions

From these experiments it is evident that approximately one mole of water is present in the compounds described by previous authors, which can be removed by extended drying to yield pure anhydrous acetylbenzilic acid, m. p. 104.5–104.8° corr.

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(1) Klinger and Standke, *Ber.*, **22**, 1212 (1889).

(2) Herzig and Schleiffer, *Ann.*, **422**, 326 (1921).

(3) Gilman, "Organic Syntheses," Collective Vol. I, pp. 82, 88.