

bromoaniline demanded by theory have been synthesized and their structures determined.

5. Further work is in progress in this Laboratory.

IOWA CITY, IOWA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

## BENZALPYRUVIC ACID DIBROMIDE

BY MARIE REIMER

RECEIVED JUNE 6, 1931

PUBLISHED AUGUST 5, 1931

The action of sunlight on  $\beta$ -bromobenzalpyruvic acid has been the subject of study in this Laboratory for several years.<sup>1</sup> The fact that large quantities of this unsaturated bromo compound have been required has led to improved methods of preparation of benzalpyruvic acid and of its dibromide from which the unsaturated bromo compound is prepared and to the observation that a marked characteristic of the dibromide is the ease with which it forms addition compounds with various solvents. In view of a recent paper by Musajo<sup>2</sup> in this same field it seems advisable to publish results already obtained.

The melting points of different samples of benzalpyruvic acid dibromide prepared in the early work varied from 125 to 142° and this variation was ascribed to contamination of the substance with the unsaturated bromo compound formed from it by loss of hydrogen bromide. It has now been found that the dibromide readily forms a hydrate in the presence of even traces of moisture and that the purest sample of the dibromide described previously contained enough of this hydrate to lower the melting point although not enough to affect the analytical results. In the present work, in which benzalpyruvic acid and the reagents used in the bromination reaction were thoroughly dried, the crude dibromide, obtained in 92 to 97% yield, has been found to melt at 148–150°; recrystallized from dried benzene, at 150–151°. The compound described by Musajo as melting at 147–150° is probably this substance and is certainly not a racemic isomer of the acid melting at 142° as he suggests. Under the conditions used in this Laboratory for the bromination no isomer is formed.

### Experimental Part

**Preparation of Benzalpyruvic Acid.**—For the preparation of pure samples of the acid its methyl ester, obtained readily from crude acid and easily purified, was hydrolyzed in methyl alcoholic solution with potassium hydroxide. The marked insolubility of the potassium salt of the acid in methyl alcohol suggested the following procedure for the condensation reaction which is found to give better yields of pure product and in a much shorter time than the former method adapted from that of Erlenmeyer.

<sup>1</sup> Reimer, *THIS JOURNAL*, **48**, 2454 (1926).

<sup>2</sup> Musajo, *Gazz. chim. ital.*, **60**, 669 (1930).

Seventeen and six-tenths grams (0.2 mole) of pyruvic acid was mixed with 21.2 g. (0.2 mole) of benzaldehyde, the mixture cooled and 55 cc. of a 25% solution of potassium hydroxide (0.24 mole) in methyl alcohol added slowly with constant shaking and cooling. The solution became dark reddish yellow but there was no evidence of condensation as long as the mixture was kept at or below 10°. As the temperature rose, crystals of the potassium salt of benzalpyruvic acid slowly separated and the solution became warm. After twelve hours at room temperature there was an almost solid mass of crystalline potassium salt. This was filtered, washed with a few cubic centimeters of methyl alcohol and with ether and air dried. From 70 to 80% yields of analytically pure salt were obtained.

*Anal.* Calcd. for  $C_{10}H_7O_3K$ : K, 18.22. Found: K, 18.42.

From the alcoholic filtrates, after spontaneous evaporation of the alcohol and acidification of the aqueous solution of the residue, a dark reddish-yellow oil was obtained. This is evidently a mixture containing the oily acid described by Claisen and Claperède.<sup>3</sup>

From cooled, concentrated solution of the potassium salt iced hydrochloric acid precipitated benzalpyruvic acid in more than 90% yield. To prevent the separation of the acid as an oil which subsequently solidifies in impure condition, it was found advisable to seed the potassium salt solution with crystals of the acid before acidification. The product was dried over sulfuric acid and recrystallized from benzene; melting point, 61–62°.

**Reaction with Bromine.**—The bromination was carried out in carefully dried chloroform with bromine freshly distilled from phosphorus pentoxide. To 10 g. of the dried acid in 60 cc. of chloroform, cooled with ice, 3.03 cc. of bromine was added slowly. The solid that separated toward the end of the reaction was filtered and washed with cooled chloroform. From the filtrate the chloroform was evaporated almost completely in a current of dry air. The yield of dibromide from both sources was 92 to 97%. When the bromination was carried out with air-dried acid, a considerable portion of the substance in the chloroform filtrates was found to be the unsaturated acid,  $\beta$ -bromobenzalpyruvic acid. The crude dibromide is faintly yellow. It softens in the melting point tube at 147° and melts with vigorous decomposition at 149–150°. It crystallizes slowly from dried benzene in fine, stiff, almost colorless needles melting at 150–151° with effervescence.

*Anal.* Calcd. for  $C_{10}H_8O_3Br_2$ : C, 35.71; H, 2.38. Found: C, 35.92; H, 2.47.

The hydrate was formed by dissolving 1 g. of the dibromide in 15 cc. of warm benzene to which 0.3 cc. of water had been added. From the moist benzene solution, very fine shining soft white needles separated almost immediately. The crystals soften markedly at about 90°. If the heating is rapid, the substance melts, with vigorous decomposition, at about 140°. If heated slowly, the decomposition may take place at as low a temperature as 120°.

*Anal.* Calcd. for  $C_{10}H_8O_3Br_2 \cdot H_2O$ : C, 33.89; H, 2.82. Found: C, 33.78; H, 2.99.

A sample of this substance sealed in a specimen bottle was unchanged after many months. On exposure to the air, even after four months, the substance softened at 90° and melted at 142–143°.

With methyl alcohol the dibromide also forms a solid addition product which separates from solution when almost all the solvent alcohol has evaporated. The solid softens between 70 and 80° to an opaque mass which melts at about 125° with slow evolution of gas above this temperature. This behavior is unchanged after many weeks.

*Anal.* Calcd. for  $C_{10}H_8O_3Br_2 \cdot CH_3OH$ : C, 35.86; H, 3.26. Found: C, 36.18; H, 3.15.

<sup>3</sup> Claisen and Claperède, *Ber.*, **14**, 2472 (1881).

The stability of this product suggests that it is a hemi-acetal and is in marked contrast with that of the methyl alcoholic addition product of  $\beta$ -bromobenzalpyruvic acid. This addition compound separates from methyl alcohol solution in large transparent prisms which almost immediately become opaque through loss of methyl alcohol.

*Anal.* Calcd. for  $C_{10}H_7O_3Br \cdot CH_3OH$ : C, 45.99; H, 3.83. Found: C, 46.10; H, 4.10.

When benzalpyruvic acid dibromide is boiled with methyl alcohol for five or ten minutes, the methyl ester previously described, melting at  $117^\circ$ , is formed in good yield. There is no loss of hydrogen bromide as is the case when the dibromide is boiled with water<sup>1</sup> nor is there replacement of bromine with methoxyl as with the dibromide of 2,4-dimethoxy-5-bromocinnamic acid.<sup>4</sup>

In ethyl alcohol the dibromide is readily soluble in the cold and does not separate from the solution on spontaneous evaporation of the solvent. The yellow oil remaining gave analytical results indicating it to be a mixture. After standing for several days, the oil deposited a few crystals which melted at  $61-62^\circ$  and were proved to be the ethyl ester of benzalpyruvic acid dibromide by a mixed melting point determination with that substance. The ester was readily obtained in quantity by bromination of ethyl benzalpyruvate.<sup>5</sup> The product crystallizes from ether in very pale yellow stocky needles melting at  $61-62^\circ$ .

*Anal.* Calcd. for  $C_{12}H_{12}O_3Br_2$ : C, 39.56; H, 3.29. Found: C, 39.22; H, 3.39.

The ester crystallized from ethyl alcohol in less pure condition, and, after standing in contact with alcohol for several days, the product was a yellow oil which analyses showed to be a mixture of the ester with that substance in combination with alcohol.

The ease of esterification of benzalpyruvic acid dibromide is interesting when contrasted with the behavior of the unsaturated  $\beta$ -bromobenzalpyruvic acid. The unsaturated acid cannot be esterified directly, crystallizing unchanged after standing for many hours in solution in alcohol saturated with hydrogen chloride.

### Summary

Improved methods of preparation of benzalpyruvic acid and of benzalpyruvic acid dibromide have been described as well as addition compounds of the dibromo compound with various solvents.

NEW YORK, N. Y.

<sup>4</sup> Reimer and Tobin, *THIS JOURNAL*, **52**, 341 (1930).

<sup>5</sup> Reimer, *ibid.*, **46**, 783 (1924).