the alkaline combustion method are about 2% of the total nitrogen content higher than those obtained by the Kjeldahl method; this cannot be ascribed to sodium hydroxide particles carried off from the combustion tube, since this would make a great difference in the results for the samples of low nitrogen content; we must suppose, therefore, that there are some leakages in our distilling apparatus, or that one hour and a half of distillation is not enough to expel all of the ammonia from the solution.

For the determination of nitrogen in liquids such as milk or beer, we suggest that a measured volume of the liquid be evaporated to dryness in a shallow porcelain dish, lined inside with tin foil free from holes, in order to facilitate the transfer of the residue to the combustion tube.

Summary

A method for the determination of nitrogen by heating with solid sodium hydroxide and sodium acetate is described. The operation takes about thirty minutes.

MEDELLIN, COLOMBIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

ADDITION REACTIONS OF UNSATURATED ALPHA-KETONIC ACIDS

BY MARIE REIMER

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The action of sunlight on methyl benzalpyruvate has recently been described.[1] For further study of the effect of light on unsaturated α-ketonic esters, those of anisalpyruvic acid were chosen since it has been shown in this Laboratory[2] in a comparative study of methyl esters of benzoyl- and of anisoylacrylic acids that, whereas the former isomerizes on exposure to the light, the latter polymerizes with extreme ease. It might be expected, therefore, that the introduction of the *p*-methoxyl group into benzalpyruvic ester would increase the tendency toward polymerization already existing. Experiments have shown, however, that exposure of anisalpyruvic acid and its methyl and ethyl esters to the sunlight leads neither to polymerization nor to isomerization.

Since the polymerization of an ethylenic compound to a cyclobutane derivative is an addition reaction, whatever may be its mechanism, it seemed of interest to study the behavior of benzalpyruvic acid and of anisalpyruvic acid toward various addenda. The blocking effect of the *p*-methoxyl group in light polymerization has recently been reported also in the case of dianisalacetone by Stobbe and Färber[3] who quote, as a parallel

[1] Reimer, THIS JOURNAL, **46**, 783 (1924).

[2] Rice, *ibid.*, **45**, 222 (1923); **46**, 214 (1924).

[3] Stobbe and Färber, *Ber.*, **58**, 1548 (1925).

case, the work of Borsche[4] who did not obtain addition products when he treated dianisalacetone with malonic and aceto-acetic esters. Kohler and his co-workers,[5] investigating these same reactions, have shown, however, that under different conditions, addition does take place although a certain amount of hindrance to the addition was noted in the case of several anisal ketones with malonic ester.

The results of experiments described in this paper are in line with those of Kohler. The reactions of benzalpyruvic and of anisalpyruvic acids with bromine, hydrogen bromide and bromine in methyl alcohol solution were studied. No essential difference in the tendency toward addition of the two ketonic acids was found. As far as one can draw conclusions from these experiments, there would seem to be no connection between ease of addition and tendency toward light polymerization.

In contrast to these results with addition reactions a number of cases have been described in which the course of a reaction has been profoundly influenced by the introduction of methoxyl groups. As examples may be given the influence of the *p*-methoxyl group on the stability of oximes[6] on the reactivity of the carbonyl group in unsaturated ketones,[7] on the ease of dissociation into free radicals[8] and on the migration of the phenyl group.[9] These properties of the *p*-methoxyl group in increasing the activity of certain types of compounds such as those just listed, on the one hand, and in blocking completely the polymerization by sunlight, on the other, are especially interesting in view of the prevalence of this group in naturally occurring compounds such as the alkaloids and the anthocyanins.

Experimental Part

Reactions with Benzalpyruvic Acid

Benzalpyruvic acid was prepared by the method previously described, with the following improvement which saves much time. The crude sodium salt from the condensation reaction should be completely dried and can then be dissolved in boiling water without danger of hydrolysis. The acid precipitated from this solution contains one molecule of water.

An interesting characteristic of the acid is the tenacity with which it holds solvent of crystallization. In one experiment in which the dry acid was crystallized from benzene, long, shining, bright yellow prisms separated; m. p., 70–76°. Analysis showed that these contained benzene. This was lost slowly on exposure to the air, the final melting point being 60–62°.

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[4] Borsche, *Ann.*, **375**, 145 (1910).

[5] Kohler and Helmkamp, THIS JOURNAL, **46**, 1018 (1924). Kohler and Dewey, *ibid.*, **46**, 1267 (1924).

[6] Meisenheimer, Lange and Lamparter, *Ann.*, **444**, 94 (1925).

[7] Straus and Heyn, *Ann.*, **445**, 92 (1925).

[8] Gomberg and Buchler, THIS JOURNAL, **45**, 207 (1923).

[9] McKenzie, Roger and Wills, *J. Chem. Soc.*, **129**, 780 (1926).

From aqueous solution the acid crystallizes with one molecule of water and may subsequently be crystallized several times from benzene without losing all of the crystal water. The first crystals to separate from the benzene solution are transparent, pale yellow plates; later, clumps of opaque, deeper yellow crystals appear. The clear plates melt at 55–57° and are identical with the acid crystallized from water. The opaque crystals melt at 60–62° and contain no water.

Anal. Subs. (55–57°), 0.2013: CO_2, 0.4567; H_2O, 0.0933. Calcd. for $C_{10}H_8O_3.H_2O$: C, 61.85; H, 5.15. Found: C, 61.85; H, 5.18.

Subs. (60–62°), 0.1987; CO_2, 0.4956; H_2O, 0.0897. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.54. Found: C, 68.03; H, 4.55.

Reaction with Bromine

Benzalpyruvic Acid Dibromide, $C_6H_5CHBrCHBrCOCOOH$.—The dibromide of benzalpyruvic acid was prepared by Erlenmeyer[10] who gives a melting point of 138° and by Ciusa,[11] who states that the substance melts at 124°. The several preparations made during this work melted anywhere from 125° to 142°. The differences are due to the ease with which the substance loses hydrogen bromide on heating, especially when moisture is present, to form the unsaturated bromo compound described below. The crude product of bromine addition is a colorless solid; m. p., 135–138°. It is readily soluble in methyl and ethyl alcohols, acetone and hot benzene, fairly soluble in ether and chloroform. From a concentrated solution of chloroform to which an equal volume of ligroin has been added it crystallizes in fine needles; m. p., 142°, with decomposition.

Anal. Subs., 0.1833: CO_2, 0.2396; H_2O, 0.0393. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 35.81; H, 2.41.

β-Bromobenzalpyruvic Acid, $C_6H_5CH{=}CBrCOCOOH$.—Benzalpyruvic acid dibromide was suspended in water and the mixture boiled for about ten minutes. The solid changed to a yellow oil which gradually dissolved. From the cooled solution there separated shining, colorless needles of a brilliant, pearly luster. When heated rapidly the substance melts at about 100°. When heated slowly it resolidifies in the melting-point tube and clears again at about 127°. After repeatedly heating the same sample the melting point is 131–132°. This behavior is due to the fact that the substance crystallizes with one molecule of water which it loses slowly on heating. When the low-melting form is recrystallized from benzene two kinds of crystals separate giving opaque clumps which contain water of crystallization and melt at about 100°, and fine, shining needles, m. p., 131–132°. The acid is best dehydrated by standing in a sulfuric acid desiccator for 48 hours. It is readily soluble in the usual organic solvents.

Anal. Subs. (low melting), 0.1585: CO_2, 0.2538; H_2O, 0.0492. Calcd. for $C_{10}H_7O_3Br.H_2O$: C, 43.95; H, 3.29. Found: C, 43.67; H, 3.44.

Subs. (131–132°), 0.1631: CO_2, 0.2812; H_2O, 0.0400. Calcd. for $C_{10}H_7O_3Br$: C, 47.08; H, 2.74. Found: C, 47.02; H, 2.74.

In benzene solution the acid is extraordinarily light-sensitive. These reactions will be reported in a later paper.

The position of the bromine atom in β-bromobenzalpyruvic acid was proved by identification of the product formed by its oxidation with hydrogen peroxide. The oxidation of several unsaturated α-ketonic acids with

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[10] Erlenmeyer, *Ber.*, **36**, 2527 (1903).

[11] Ciusa, *Gazz. chim. ital.*, [i] **49**, 164 (1919).

hydrogen peroxide has been described.[12] The authors used alcoholic solutions and make the statement that good yields of product were obtained only when no excess of reagent was used, except in one case, that of anisalpyruvic acid, where 1.5 molecular proportions was needed. In the present work aqueous solutions of the sodium salts of the acids were used and a large excess of hydrogen peroxide did not decrease the yield of product which was quantitative in all the reactions. From β-bromobenzalpyruvic acid an acid was obtained which separated from boiling water in long, shining needles; m. p., 130–131°. It was proved to be *trans*-α-bromocinnamic acid by a mixed-melting-point determination with that substance prepared by elimination of hydrogen bromide from cinnamic acid dibromide and subsequent isomerization of the *allo*-α-bromocinnamic acid (m. p., 120°) which was the chief product of this reaction.[13]

Methyl β-Bromobenzalpyruvate, $C_6H_5CH{=}CBrCOCOOCH_3$.—This ester is not formed by treating the acid with methyl alcohol saturated with hydrogen chloride; the acid crystallized from the solution unchanged. The ester was prepared by elimination of hydrogen bromide from the dibromide of methyl benzalpyruvate.

The *methyl ester of benzalpyruvic acid dibromide,* prepared by addition of bromine to methyl benzalpyruvate, is a stable substance that crystallizes from methyl alcohol in pale, straw-colored needles; m. p., 117°.

Anal. Subs., 0.1929: CO_2, 0.2665; H_2O, 0.0503. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.77; H, 2.89.

Four g. of this ester in 75 cc. of methyl alcohol was boiled for one hour with 2.2 g. of potassium acetate. The filtered solution was allowed to evaporate spontaneously. The clear, yellow oil remaining was dissolved in ether, the solution washed, dried and the solvent evaporated. The oil remaining was analyzed.

Anal. Subs., 0.1845: CO_2, 0.3308; H_2O, 0.0635. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 48.89; H, 3.78.

As alkaline solution attacked the double linkage, the ester was hydrolyzed by boiling with concd. hydrochloric acid. β-Bromobenzalpyruvic acid crystallized from the solution.

Experiments with Hydrogen Bromide

No addition product with hydrogen bromide could be isolated. The ease with which the dibromo addition product loses hydrogen bromide readily accounts for this fact.

Reaction with Bromine in Methyl Alcohol Solution

A methyl hypobromite addition product is not formed by the method described by Conant and Jackson.[14] The experiment was carried out at 0°, at room temperature and with ethyl as well as methyl alcohol, with the same results.

Fifteen g. of benzalpyruvic acid was dissolved in 375 cc. of 85% methyl alcohol. A stream of dry air carrying bromine vapor was bubbled through the solution for eight

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[12] Lubryzsiska and Smedley, *Biochem. J.*, **7,** 375 (1913).

[13] Sudburough and Thompson, *J. Chem. Soc.*, **83,** 673 (1903).

[14] Conant and Jackson, THIS JOURNAL, **46,** 1727 (1924).

to ten hours until 5.9 g. of bromine had been decolorized. The alcohol was then distilled and the residue, consisting of oil and a small amount of water, cooled. The aqueous layer was soon filled with white crystals. These were filtered off and the oil remaining was extracted repeatedly with 100cc. portions of ice water which quickly filled with the same white solid. This was proved to be β-bromobenzalpyruvic acid (m. p., about 100°) with water of crystallization previously described. The oily residue from which no more solid could be extracted with water, was dissolved in ether and the solution dried. Evaporation of the solvent left an oil which gradually deposited anhydrous β-bromobenzalpyruvic acid; m. p., 130–131°. The oil remaining gave analytical results agreeing with those for a methyl hypobromite addition product. On exposure in a thin layer to the air, however, it deposited very slowly crystals of β-bromobenzalpyruvic acid (m. p., 130–131°) and evidently was this acid in combination with a molecule of methyl alcohol.

Anal. Subs., 0.1722: CO_2, 0.2923; H, 0.0606. Calcd. for $C_{10}H_7O_3Br.CH_3OH$: C, 45.99; H, 3.83. Found: C, 46.29; H, 3.91.

The only reaction with bromine in methyl alcohol solution was addition of bromine and subsequent loss of hydrogen bromide. A 95% yield of product was obtained.

Reactions with Anisalpyruvic Acid[15]

It is noteworthy that anisalpyruvic acid is much more stable toward alkaline reagents than the corresponding unsubstituted acid, so that the strongly alkaline reaction mixture may stand for many hours without reversal of the reaction. It was prepared by a modification of the method of Ciusa.[11]

Forty g. of pyruvic acid, 68.5 g. of anisic aldehyde and 300 cc. of 10% aqueous sodium hydroxide were brought together at 0° and the mixture was vigorously stirred. After ten minutes a gelatinous paste separated. The yield of product was very small unless this mixture was allowed to stand for at least 12 hours. After this length of time a hard, crystalline mass of sodium anisalpyruvate had formed. This was filtered off, air-dried, dissolved in boiling water and the solution acidified. The bright yellow acid, crystallized from water, melts at 131°. (Ciusa's melting point of 81° is evidently that of the acid with alcohol of crystallization.) The acid is the *trans* form since, on oxidation with hydrogen peroxide, a quantitative yield of *trans-p*-methoxycinnamic acid was obtained, which showed the characteristic behavior of "liquid crystals," melting to an opaque liquid at 170° and to a clear liquid at 185°.[16] It was identified by a mixed-melting-point determination with the acid prepared by Perkin's synthesis.

The *methyl ester* was prepared by dissolving 14 g. of acid in 50 cc. of methyl alcohol saturated with hydrogen chloride. Almost immediately the pale yellow, shining crystals of the methyl ester separated. The ester, crystallized from methyl alcohol, melts at 106°. It is readily soluble in chloroform and acetone, fairly soluble in ether, benzene and alcohol, very slightly soluble in ligroin.

Anal. Subs., 0.1649: CO_2, 0.3964; H_2O, 0.0827. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.55; H, 5.57.

The *ethyl ester* was prepared in the same way. It separated from concentrated alcoholic solution in brilliant, pale yellow plates; m. p., 48°. It is much more soluble in the usual organic solvents than the methyl ester.

Anal. Subs., 0.1633: CO_2, 0.3988; H_2O, 0.0915. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.60; H, 6.22.

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[15] With Alice L. Kreissl.

[16] Rotarski, *Ber.*, **41,** 1994 (1908).

Reactions with Bromine

Anisalpyruvic Acid Dibromide, $4\text{-}CH_3O.C_6H_4CHBrCHBrCOCOOH$.—The dibromo addition compound was prepared in quantitative yield by addition of bromine to the cooled chloroform solution of anisalpyruvic acid. The substance is slightly less stable than benzalpyruvic acid dibromide and could not be purified by recrystallization. The crystals that separated from chloroform and ligroin or from glacial acetic acid were a mixture of the dibromo and the unsaturated monobromo acids. The crude product, m. p. 98–100°, was used for analysis.[17]

Anal. Subs., 0.1779: CO_2, 0.2362; H_2O, 0.0403. Calcd. for $C_{11}H_{10}O_4$: C, 36.06; H, 2.72. Found: C, 36.20; H, 2.52.

The *methyl ester* was prepared by addition of bromine to a cooled chloroform solution of methylanisalpyruvate. The solid melting at 93° was washed with methyl alcohol and analyzed.

Anal. Subs., 0.1757: CO_2, 0.2212; H_2O, 0.0471. Calcd. for $C_{12}H_{12}O_4Br_2$: C, 37.89; H, 3.15. Found: C, 37.76; H, 2.97.

The *ethyl ester* prepared in the same way was left as a colorless oil on evaporation of the chloroform. It solidifies when treated with cold ethyl alcohol but must be handled quickly as it decomposes on exposure to the air. The solid, m. p. 100–108°, washed with alcohol, was used for analysis.

Anal. Subs., 0.1567: CO_2, 0.2290; H_2O, 0.0560. Calcd. for $C_{13}H_{14}O_4Br_2$: C, 39.59; H, 3.52. Found: C, 39.82; H, 3.33.

β-Bromo-anisalpyruvic Acid, $4\text{-}CH_3OC_6H_5CH{=}CBrCOCOOH$.—The substance was prepared by boiling the dibromo acid in water, from which it separates in shining, cream-colored plates. The purest specimen was obtained by dissolving the acid in hot glacial acetic acid and adding an equal volume of hot water. The lustrous crystals that separated contained one molecule of water and melted at 100° to 125°. Different specimens of this acid have various amounts of water so that they may begin to melt as low as 85°. The acid dried over sulfuric acid melted at 136°.

Anal. Subs. (low melting), 0.1402: CO_2, 0.2236; H_2O, 0.0465. Calcd. for $C_{11}H_9O_3Br.H_2O$: C, 43.56; H, 3.63. Found: C, 43.49; H, 3.69.

Subs. (136°), 0.1497: CO_2, 0.2559; H_2O, 0.0466. Calcd. for $C_{11}H_9O_3Br$: C, 46.31; H, 3.15. Found: C, 46.61; H, 3.45.

The substance is readily soluble in the usual organic solvents except ligroin in which it is very slightly soluble.

There is no esterification when this acid is allowed to stand for many hours in methyl alcohol saturated with hydrogen chloride. This behavior is like that of β-bromobenzalpyruvic acid. To prove the structure of this acid it was oxidized with hydrogen peroxide.

α-Bromo-*p*-methoxycinnamic Acid, $4\text{-}CH_3OC_6H_4CH{=}CBrCOOH$.—The product of oxidation of β-bromo-anisalpyruvic acid with hydrogen peroxide crystallized from boiling water in pale, straw-colored needles. A purer product is obtained from methyl alcohol from which it separates in stiff, almost colorless needles; m. p., 188°. The acid is soluble in methyl and ethyl alcohols, ether and acetone, fairly soluble in glacial acetic acid and chloroform.

Anal. Subs., 0.1159: CO_2, 0.1967; H_2O, 0.0374. Calcd. for $C_{10}H_9O_3Br$: C, 46.68; H, 3.50. Found: C, 46.28; H, 3.57.

The position of the bromine atom is indicated by the fact that the acid decolorizes potassium permanganate solution in the cold with the odor of anisic aldehyde.

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[17] Ciusa's melting point of 125° must be that of the unsaturated bromo acid.

The *methyl ester* was prepared in quantitative yield by allowing a saturated solution of hydrogen chloride in methyl alcohol to stand in contact with the acid overnight. It crystallizes from a small volume of methyl alcohol in stiff, colorless needles; m. p., 55°.

Anal. Subs., 0.1722: CO_2, 0.3065; H_2O, 0.0635. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.70; H, 4.05. Found: C, 48.54; H, 4.09.

On hydrolysis a quantitative yield of the acid (188°) was obtained. For identification of this acid, attempts were made to prepare it from *p*-methoxycinnamic acid dibromide. In this reaction an unstable, isomeric acid (155°) was obtained. From the ester of the dibromide, however, the stable acid (188°) was prepared. The treatment of *p*-methoxycinnamic acid dibromide with aqueous potassium hydroxide is described by Eigel,[18] who obtained *p*-methoxyphenyl-bromo-ethylene, $CH_3OC_6H_4CH = CHBr$ (m. p., 55°), as the only product. By using potassium acetate, however, an acid product also is obtained. Five g. of *p*-methoxycinnamic acid dibromide was suspended in 50 cc. of alcohol, 2.7 g. of potassium acetate added and the mixture was boiled for several hours. The alcohol was then evaporated and the aqueous solution of the residue extracted with ether. The ether, after repeated washing with sodium carbonate solution, deposited a quantity of the substituted ethylene melting at 55°. The sodium carbonate washings on acidification gave a small amount of acid melting at about 155° after repeated crystallization from methyl alcohol.

Anal. Subs., 0.1573: CO_2, 0.2678; H_2O, 0.0613. Calcd. for $C_{10}H_9O_3Br$: C, 46.68; H, 3.50. Found: C, 46.43; H, 4.32.

Esterification of this acid gave an oil from which no crystalline compound could be obtained. Hydrolysis of this oil with a strong solution of potassium hydroxide in methyl alcohol gave a crystalline potassium salt which separated almost immediately. This was filtered off, dissolved in water and the solution acidified. The colorless precipitate was pure acid; m. p., 188°. The acid melting at 155° had, therefore, isomerized during some stage of the reaction to the higher-melting acid and is, then, the unstable geometrical isomer of this acid. This high-melting acid (188°) can be obtained in good yield by treating the methyl ester of *p*-methoxycinnamic acid dibromide with 10% alcoholic potassium hydroxide in the cold. The potassium salt, which separated rapidly in 75% yield, deposited pure acid, m. p. 188°, on acidification of its solution. This experiment was carried out by Eigel,[18] who did not investigate the mixture of impure acids that he obtained.

With hydrogen bromide, anisalpyruvic acid does not react.

Reaction with Bromine in Methyl Alcoholic Solution

When anisalpyruvic acid was treated with bromine in aqueous methyl alcoholic solution, different substances were obtained, depending on the speed with which the bromine was carried into the solution. From none of the experiments was any methyl hypobromite addition compound obtained; in all of them there was a considerable quantity of oil that could not be purified, together with various amounts of crystalline product.

The reaction was carried out as previously described in the case of benzalpyruvic acid. The brownish oil left after removal of the alcohol from the reaction product gradually deposited crystals. These were filtered out and further amounts of crystalline compound obtained by treating the remaining oil with benzene. When the bromine vapor was carried through the solution very slowly (10–12 hours), the crystals were found to be hydrated β-bromo-anisalpyruvic acid; m. p., 90–100°. From 15 g. of anisalpyruvic acid, 12 g. of unsaturated bromo acid was obtained.

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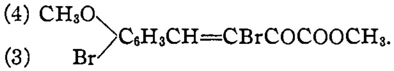
[18] Eigel, *Ber.*, **20**, 2537 (1887).

A more rapid reaction (four to five hours) gave a compound that crystallized from the oily reaction product in stiff, compact needles. Three g. was obtained from 15 g. of the original acid. The only other crystalline product of this reaction was the hydrated β-bromo-anisalpyruvic acid (90–100°). The new crystalline compound was crystallized from a large volume of boiling methyl alcohol from which it separated in fine, pale yellow needles; m. p., 145°.

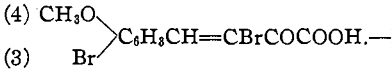
Anal. Subs., 0.1455: CO_2, 0.2047; H_2O, 0.0365. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.64. Found: C, 38.36; H, 2.78.

The compound is an ester and is unsaturated since its acetone solution instantly decolorizes potassium permanganate in the cold. The product of this oxidation, an acid containing bromine, m. p. 212°, was proved to be 3-bromo-anisic acid by a mixed-melting-point determination with that acid prepared by bromination of anisic acid. The ester (145°) is, therefore, methyl β - bromo - 3 - bromo - anisalpyruvate,



$\begin{matrix}(4)\ CH_3O\\(3)\ \ \ Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOCOOCH_3$.

The rapid reaction with bromine and methyl alcohol has caused bromine to enter the ring as well as to add at the double linkage and has brought about esterification of the acid.

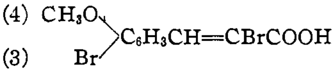


$\begin{matrix}(4)\ CH_3O\\(3)\ \ \ Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOCOOH$

β-Bromo-3-bromo-anisalpyruvic Acid, $\begin{matrix}(4)\ CH_3O\\(3)\ \ \ Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOCOOH$.—Hydrolysis of the ester (m. p., 145°) was carried out by treating it with just enough of a 0.5% solution of potassium in methyl alcohol to bring it into solution. After an hour the potassium salt that had separated was filtered out, dissolved in water and the solution acidified. The yellowish acid that separated holds water of crystallization which accounts for its low, irregular melting point of about 135°. It was crystallized once from boiling water and analyzed.

Anal. Subs., 0.1497: CO_2, 0.1959; H_2O, 0.0330. Calcd. for $C_{11}H_8O_4.{}^1/_2H_2O$: C, 35.38; H, 2.41. Found: C, 35.68; H, 2.44.

From a solution of this acid in methyl alcohol saturated with hydrogen chloride the characteristic pale yellow needles of the ester (m. p., 145°) separated in quantitative yield.



$\begin{matrix}(4)\ CH_3O\\(3)\ \ \ Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOOH$

α-Bromo-3-bromo-4-methoxycinnamic Acid, $\begin{matrix}(4)\ CH_3O\\(3)\ \ \ Br\end{matrix}\!\!>C_6H_3CH{=}CBrCOOH$.—By oxidation of the acid just described with hydrogen peroxide a colorless acid, m. p. 181°, was obtained. It was proved to be α-bromo-3-bromo-4-methoxycinnamic acid by preparing it from 3-bromo-4-methoxycinnamic acid dibromide. This substance, melting at 162°, was studied by Eigel[18] who did not obtain an acid product when he treated it with potassium hydroxide. The acid (m. p., 181°) can be obtained from it, however, by hydrolysis of the ester formed by dissolving 3-bromo-4-methoxycinnamic acid dibromide in methyl alcohol and hydrochloric acid. This mixture was allowed to stand overnight, then poured into dil. sodium carbonate solution and the solution extracted with ether. On evaporation of the ether an ester separated in hard, shining clumps. After crystallization from a small volume of boiling methyl alcohol it melted at 91°.

Anal. Subs., 0.1523: CO_2, 0.2089; H_2O, 0.0496. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Calcd. for $C_{11}H_{11}O_3Br_3$: C, 30.62; H, 2.65. Found: C, 37.40; H, 3.60.

The tribromide has evidently lost hydrogen bromide on esterification. The ester is that of α-bromo-3-bromo-4-methoxycinnamic acid. By hydrolysis with a concentrated alcoholic solution of potassium hydroxide a potassium salt separated which, on acidification of its solution, gave the acid melting at 181°.

In his discussion of bromomethoxycinnamic acid dibromide (m. p., 162°) Eigel states that it is decomposed by water and alcohol but gives no account of the decomposition products. In an attempt to prepare the acid (m. p., 181°) in quantity, this decomposition was investigated. Four g. of the acid (m. p., 162°) was suspended in 120 cc. of cold water and the mixture allowed to stand for 12 hours and frequently shaken. The flocculent, pure white solid which separated was filtered off, washed with water and crystallized from a small volume of methyl alcohol: yield, 80%. The solid has the properties of the substance obtained by Eigel by hydrolysis of the acid (m. p., 162°), described by him and quoted in the new edition of Beilstein as "2- or 3-bromo-4-methoxyphenylacetylene." It crystallizes in leaves, melts at 76°, is volatile with water vapor and gives a greenish precipitate when its alcoholic solution is treated with an aqueous solution of ammoniacal cuprous chloride. The appearance and the odor of the substance are, however, exactly like those of bromo-*p*-methoxyphenylethylene (m. p., 55°) previously described. Analysis proves that it is in reality an ethylenic compound.

Anal. Subs., 0.1570: CO_2, 0.2149; H_2O, 0.0455. Calcd. for $C_9H_8OBr_2$: C, 36.98; H, 2.74. Calcd. for C_9H_7OBr: C, 51.18; H, 3.31. Found: C, 37.33; H, 3.22.

The compound was recovered unchanged from boiling alcoholic and from boiling aqueous potassium hydroxide solutions. The same compound was obtained by boiling bromomethoxycinnamic acid dibromide (m. p., 162°) with 30% aqueous potassium hydroxide for one-half hour. The greenish, crystalline precipitate formed by treatment of its alcoholic solution with aqueous ammoniacal cuprous chloride solution was proved to be the original substance precipitated from alcoholic solution by the addition of water.

Oxidation of the ethylenic compound (m. p., 76°) with a solution of potassium permanganate gave 3-bromo-anisic acid, thus establishing the position of the bromine atom in the ring.

Summary

The reactions of benzalpyruvic acid and of anisalpyruvic acid with bromine, hydrogen bromide and bromine in methyl alcoholic solution have been studied. No essential difference in the tendency toward addition of the two ketonic acids was found. They both gave quantitative yields of dibromo addition products; the bromine atom β to the ketone group was readily eliminated as hydrogen bromide to form β,γ unsaturated β-bromo-α-ketonic acids. As was to be expected from this behavior, no addition product with hydrogen bromide was formed. Addition of bromine in methyl alcoholic solution yielded not a methyl hypobromite addition product, but compounds formed by addition of bromine and subsequent loss of hydrogen bromide.

For identification of the products formed, the oxidation of the products by hydrogen peroxide was studied and a number of substituted cinnamic acids were prepared.

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