benzoyl)-3-nitrobenzoic acid were prepared and attempts made to resolve them into optical components without success. A discussion of the relation of the compounds to optically active diphenyl compounds is included.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

ADDITION REACTIONS OF UNSATURATED ALPHA-KETONIC ACIDS. II

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It has been previously shown[1] that the action of sunlight on the methyl ester of benzalpyruvic acid brings about addition of two molecules at the ethylenic linkage, cyclobutane derivatives being formed. The fact that *p*-methoxybenzalpyruvic acid and its methyl ester did not form such addition products, being entirely unaffected by sunlight, led to a comparative study of the addition reactions of the two ketonic acids and their esters with bromine[2] in which it was found that the ease with which both compounds combined with bromine was the same.

This study of unsaturated α-ketonic acids has now been continued with benzalpyruvic acid in which a substituting methoxyl group is in the *ortho* instead of the *para* position to the side chain. It has been found that the *o*-methoxybenzalpyruvic acid and its methyl ester also combine readily with bromine but that in almost all other respects the properties of the compound have been changed to a marked degree by this shift in the position of the methoxyl group. The color is deepened, that of *o*-methoxybenzalpyruvic acid being a brilliant orange, that of the *p*-methoxy acid a bright yellow.[3] The solubilities of the *o*-methoxy acid, its sodium salt and its methyl ester in the appropriate solvents are greater than those of the corresponding *p*-methoxy compounds; the acid and its esters do not combine with solvent of crystallization, a conspicuous characteristic of benzalpyruvic acid and its *p*-methoxy derivatives; the dibromo addition products are less stable than those of the other unsaturated α-ketonic acids studied, hydrogen bromide being lost with great ease. The most striking difference between the two methoxy derivatives is that *o*-methoxybenzalpyruvic acid and its methyl ester are sensitive to light; the aqueous solution of the acid is hydrolyzed rapidly in the sunlight; the acid, exposed in the dry condition, slowly loses its brilliant color; the methyl ester exposed to bright sunlight liquefies within a few minutes due to admixture with a light product.

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

[2] Reimer, *ibid.*, **48**, 2454 (1926).

[3] Hodgson and Handley, *J. Chem. Soc.*, **1928**, p. 162.

Benzalpyruvic acid and its *p*- and *o*-methoxy derivatives react with concentrated sulfuric acid to give brilliantly colored solutions as is ordinarily the case with α,β-unsaturated ketones. That the ketone group in these ketonic acids is essential for this color reaction is proved by the fact that loss of this group by oxidation with hydrogen peroxide to give derivatives of cinnamic acid is accompanied by loss in the ability to form these brilliantly colored compounds. Most striking is the unexpected effect of the bromine atom in the methoxy compounds, the *ortho* and *para* compounds in this case giving similar results. If bromine is in the side chain, a distinct series of color changes, yellow to red-violet, takes place on addition of concentrated sulfuric acid; if there is also bromine in the ring another quite different series of color changes to blue or green ensues. The difference is so marked that it is possible by this reaction to determine, with very small quantities of material, whether bromine is present in the side chain, also in the ring or absent, as well as to detect the presence of the ketone group. This behavior is described more fully in the experimental part.

Experimental Part

Preparation of *o*-Methoxybenzalpyruvic Acid

Seventeen and six-tenths grams (0.2 mole) of pyruvic acid was added to 160 cc. of 10% sodium hydroxide solution (0.4 mole), the solution cooled to 0°, 27.2 g. (0.2 mole) of *o*-methoxybenzaldehyde added and the mixture shaken vigorously. At the end of an hour the emulsion which was at first formed had entirely disappeared and the brownish colored solution was clear. There was no separation of a sodium salt as in the preparation of benzal- and *p*-methoxybenzalpyruvic acids. When this reaction mixture was allowed to stand overnight, a procedure necessary with *p*-methoxybenzalpyruvic acid to insure good yields, the *o*-methoxy compound was found to have been almost completely hydrolyzed to *o*-methoxybenzaldehyde and pyruvic acid. Addition of chilled concentrated hydrochloric acid to the cooled, strongly alkaline solution immediately after one hour of shaking precipitated the bright yellow sodium salt of *o*-methoxybenzalpyruvic acid in about 80% yield. The hydrochloric acid was added with vigorous stirring until the first traces of an orange-colored substance appeared. The yellow, granular sodium salt was filtered, freed from mother liquor by suction, dissolved in cold water and the solution acidified. The *o*-methoxybenzalpyruvic acid precipitated as a granular solid of a brilliant orange color. A less pure product was obtained in small quantity from the mother liquor.

The acid separates from boiling water in long, fine needles; from benzene in compact needles of a brilliant red-orange. As boiling with water or exposure of the aqueous solution to the light brings about hydrolysis of the acid, crystallization from benzene is to be recommended. The acid is readily soluble in the usual organic solvents. It melts at 131°.

Anal. Subs., 0.2035: CO_2, 0.4804; H_2O, 0.0904. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.85. Found: C, 64.37; H, 4.97.

On exposure of the dry, finely powdered acid to bright sunlight, the brilliant color soon fades noticeably. The colorless, light product protects most of the acid from the light so that this reaction proceeds with extreme slowness.

The Methyl Ester of the acid was obtained in pure condition with great difficulty owing to its extreme solubility in almost all solvents and to its unusual ease of hydrolysis. The ester was repeatedly prepared by the reaction of methyl alcohol and hydrogen chloride, by the use of dimethyl sulfate and of diazomethane from carefully purified acid. In all cases it separated as a heavy oil from which, after long standing, a few crystals separated. The oily product, very soluble in the usual solvents, was purified by dissolving it in a large volume of ligroin, cooling the solution slowly, finally in a freezing mixture. The ester separated in long, bright yellow needles melting at 48°.

Anal. Subs., 0.1167: CO_2, 0.2782; H_2O, 0.0581. Calcd. for $C_{12}H_{12}O_4$: C, 65.43; H, 5.57. Found: C, 65.01; H, 5.49.

After standing for several weeks in the dark, but exposed to the moisture of the air, a sample was found to have been largely hydrolyzed to the bright, orange-colored acid. When the ester was exposed to the bright sunlight it liquefied within a few minutes due to admixture with light products. There was no hydrolysis. The two crystalline products of this light reaction will be reported on in a later paper.

The Ethyl Ester prepared by the action of ethyl alcohol saturated with hydrogen chloride is a bright yellow oil boiling at 223° (15 mm.).

Anal. Subs., 0.1630: CO_2, 0.3971; H_2O, 0.0926. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.44; H, 6.35.

Reactions with Bromine

***o*-Methoxybenzalpyruvic Acid Dibromide,** *o*-$CH_3OC_6H_4CHBrCHBrCOCOOH$.—The addition of bromine to the acid was carried out in the usual way in cooled chloroform solution. The bromine was decolorized rapidly. When the product was poured out and the chloroform evaporated in a current of moist air, there was a copious evolution of hydrogen bromide; in a current of dry air there was no evidence of loss of hydrogen bromide. The oily residue gradually solidified. After washing the product with cold ligroin, a straw-colored solid remained, which melted with vigorous decomposition at about 90°. As analyses of the product, crystallized from chloroform or benzene, gave results much too high in carbon and hydrogen for the dibromide, the crude product, washed rapidly with cold ligroin, was analyzed.

Anal. Subs., 0.1589: CO_2, 0.2147; H_2O, 0.0530. Calcd. for $C_{11}H_{10}O_4Br_2$: C, 36.06; H, 2.73. Found: C, 36.84; H, 3.70.

The substance is evidently the impure dibromide. Repeated analyses of different products gave no better results. It would seem to be impossible to prepare the dibromide without loss of some hydrogen bromide.

***β*-Bromo-*o*-methoxybenzalpyruvic Acid,** *o*-$CH_3OC_6H_4CH{=}CBrCOCOOH$ (173°).—This acid is readily obtained by warming the dibromide just described in benzene solution, boiling it with water, or heating it on a water-bath until there is no further evolution of hydrogen bromide. It crystallizes from chloroform, chloroform mixed with ligroin, or methyl alcohol in stiff, colorless needles melting at 173°.

Anal. Subs., 0.1859: CO_2, 0.3153; H_2O, 0.0581. Calcd. for $C_{11}H_9O_4Br$: C, 46.31; H, 3.15. Found: C, 46.27; H, 3.51.

By oxidation of this acid in alkaline solution with hydrogen peroxide, bromomethoxycinnamic acid (171°) was obtained in quantitative yield. Since the bromine atom lost from the dibromide is undoubtedly the one in the position *beta* to the ketonic group and *gamma* to the carboxyl, the oxidation product of the compound thus formed must have the bromine atom in the *alpha* position to the carboxyl group.

$$CH_3OC_6H_4CHBrCHBrCOCOOH \longrightarrow CH_3OC_6H_4CH{=}CBrCOCOOH \longrightarrow CH_3OC_6H_4CH{=}CBrCOOH$$

The acid (171°) is therefore α-bromo-*o*-methoxycinnamic acid.[4] It is described in the latest edition of Beilstein[5] as "α or β bromo" *o*-methoxycinnamic acid.

The Methyl Ester of β-bromo-*o*-methoxybenzalpyruvic acid can be prepared in quantitative yield by the reaction of an ethereal solution of diazomethane on the purified acid. It separates from methyl alcohol in firm clumps of colorless needles melting at 88–89°.

Anal. Subs., 0.1540: CO_2, 0.2708; H_2O, 0.0542. Calcd. for $C_{12}H_{11}O_4Br$: C, 48.16; H, 3.69. Found: C, 47.95; H, 4.00.

When the acid was treated with methyl alcohol saturated with hydrogen chloride, almost the entire amount was recovered unchanged, a behavior like that of other unsaturated α-ketonic acids. Only a minute quantity of a substance crystallizing in fine, yellow needles, melting at 86°, possibly an isomeric ester, was isolated.

By the action of bromine on the methyl ester of *o*-methoxybenzalpyruvic acid, neither the methyl ester of the dibromide nor of the unsaturated bromo acid was obtained. The product, crystallized from diluted methyl alcohol, was a mixture of the unsaturated bromo acid (173°) and of an unsaturated bromo acid (210°) with bromine in the ring, to be described later. The reaction had evidently consisted in addition of bromine, loss of hydrogen bromide, bromination in the ring and hydrolysis of the ester.

Reaction with Excess of Bromine

5-Bromo-*o*-methoxybenzalpyruvic Acid Dibromide, (2)-CH_3O-(5)-BrC_6H_3CHBr-CHBrCOCOOH.—*o*-Methoxybenzalpyruvic acid was dissolved in chilled chloroform, one gram molecular proportion of bromine added slowly, then a second gram molecular proportion of bromine added and the mixture was allowed to stand in the ice chest from three to four days. The product, after evaporation of the chloroform in a current of dry air, was a straw-colored solid melting with vigorous decomposition at 95–100°. It is soluble in the usual organic solvents except ligroin. That the substance contained bromine in the ring was proved by its oxidation with a hot solution of potassium permanganate to 5-bromo-2-methoxybenzoic acid. Analyses of the substance washed with cold ligroin gave results consistently high in carbon and hydrogen and low in bromine for a tribromo compound, showing loss of hydrogen bromide during the manipulation. When the crude product of bromination was stirred for a few minutes with cold methyl alcohol it was changed to a colorless solid which proved to be the methyl ester of the tribromo acid. The substance separates from hot methyl alcohol in clear, firm crystals melting at 103–106°. Analyses of the substance as in the case of the acid gave results about 1% high in carbon and hydrogen for a tribromo ester, showing loss of hydrogen bromide. The same product was obtained in no purer form by the action of diazomethane on the tribromo acid.

β-Bromo-5-bromo-2-methoxybenzalpyruvic Acid, (2)-CH_3O-(5)-$BrC_6H_3CH{=}CBr$-COCOOH, (colorless, 210°).—This acid was prepared in practically quantitative yield by boiling the tribromo acid just described in 40% acetic acid, from which it separated in fine, colorless needles melting with vigorous decomposition at 210°.

Anal. Subs., 5.928 mg.; CO_2, 7.97 mg.; H_2O, 1.31 mg. Calcd. for $C_{11}H_8O_4Br_2$: C, 36.26; H, 2.19. Found: C, 36.67; H, 2.47.

On oxidation with cold potassium permanganate 5-bromo-2-methoxybenzoic acid was obtained. Treatment with hydrogen peroxide in alkaline solution gave α-bromo-2-methoxycinnamic acid (221°).[4]

The Methyl Ester prepared by the action of diazomethane on an ethereal solution

[4] Reimer and Howard, THIS JOURNAL, **50**, 196 (1928).

[5] Vol. X, p. 293.

of the acid is a colorless solid separating from a small volume of boiling ether in firm clumps melting at 131°.

Anal. Subs., 4.431 mg.; CO_2, 6.23 mg.; H_2O, 1.05 mg. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.65. Found: C, 38.35; H, 2.65.

When the methyl ester of 5-bromo-2-methoxybenzalpyruvic acid dibromide (103–106°) was hydrolyzed an acid, isomeric with that just described, and its ester were obtained.

β-Bromo-5-bromo-2-methoxybenzalpyruvic Acid (Yellow, 210°).—The methyl ester of the tribromo acid was covered with a 2% solution of potassium in methyl alcohol and the mixture stirred. The liquid became bright lemon yellow and, as the original colorless ester went into solution, a yellow solid separated. After five minutes the mixture was filtered. A considerable portion of the yellow solid formed was soluble in water. From this solution and from the filtrates hydrochloric acid precipitated an acid which crystallized from benzene in fine needles of a deep yellow color.

Anal. Subs., 6.28 mg.; CO_2, 8.25 mg.; H_2O, 1.45 mg. Calcd. for $C_{11}H_8O_4Br_2$: C, 36.26; H, 2.19. Found: C, 35.78; H, 2.58.

On heating in a melting point tube, the yellow color fades out completely between 145 and 150° and the colorless product melts at 210°. A mixture of the yellow acid and the colorless (210°) acid melted at 210°. The yellow acid is evidently the geometrical isomer of the colorless (210°) acid with a transition temperature of about 150°. On repeated crystallization from benzene and on exposure to the light the same transformation takes place.

The yellow solid formed by the action of potassium methylate on the methyl ester of the tribromo acid (103–106°) which was not soluble in water was crystallized from methyl alcohol. It separates in fine, pale yellow needles melting at 143°.

Anal. Subs., 0.1238; CO_2, 0.1729; H_2O, 0.0327. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.65. Found: C, 38.08; H, 2.91.

The analysis and the fact that the compound gives the yellow acid just described on hydrolysis with alcoholic potassium hydroxide prove it to be the methyl ester of this acid. It can be prepared in quantity by shaking the methyl ester of the tribromo acid (103–106°) with methyl alcohol and a slight excess of potassium acetate in the cold for a few minutes.

Reaction with Bromine in Methyl Alcoholic Solution

This reaction was carried out as previously described.[2] There was no addition of methyl hypobromite under varying conditions of concentration, temperature and speed of addition of bromine. When bromine vapor was passed through the diluted alcoholic solution of the acid as fast as it was decolorized, the product was an oil which gradually solidified. It was proved to be a mixture of the dibromide of *o*-methoxybenzalpyruvic acid and the unsaturated bromo acid (173°) formed from it by loss of hydrogen bromide. By careful manipulation of the mixture a quantitative yield of the unsaturated bromo acid was obtained.

Reaction of Benzalpyruvic Acid and its Methoxy Derivatives with Concentrated Sulfuric Acid

Two to three drops of pure, concentrated sulfuric acid were placed on a glazed porcelain plate, approximately one milligram of the substance to

be tested was added and stirred into the acid. Under this treatment, cinnamic acid, its *p*- and *o*-methoxy derivatives and their bromine substitution products gave no color or a pale to bright yellow, fading out to colorless in a short time. The colors with the ketonic acids are shown in the following table.

TABLE I

COLORS WITH KETONIC ACIDS

Substance	Color	Color with concentrated sulfuric acid
$C_6H_5CH{=}CHCOCOOH$	Pale yellow	Deep yellow ⟶ brown
$C_6H_5CHBrCHBrCOCOOH$	Colorless	Yellow ⟶ red-brown ⟶ dark brown
$C_6H_5CH{=}CBrCOCOOH$	Colorless	Yellow ⟶ red-brown ⟶ dark brown
$C_6H_5CH{=}CBrCOCOOCH_3$	Colorless	Yellow ⟶ red-brown ⟶ dark brown
p-$CH_3OC_6H_4CH{=}CHCOCOOH$	Deep yellow	Orange
p-$CH_3OC_6H_4CHBrCHBrCOCOOH$	Cream color	Orange ⟶ brown ⟶ red-violet
p-$CH_3OC_6H_4CHBrCHBrCOCOOCH_3$	Colorless	Orange ⟶ brown ⟶ red-violet
p-$CH_3OC_6H_4CH{=}CBrCOCOOH$	Colorless	Orange ⟶ brown ⟶ red-violet
p-$CH_3OC_6H_4CH{=}CBrCOCOOCH_3$	Colorless	Orange ⟶ brown ⟶ red-violet
p-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Pale yellow	Orange ⟶ brilliant green ⟶ blue
p-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Pale yellow	Orange ⟶ brilliant green ⟶ blue
o-$CH_3OC_6H_4CH{=}CHCOCOOH$	Orange	Deep cherry-red
o-$CH_3OC_6H_4CHBrCHBrCOCOOH$	Straw color	Yellow ⟶ red-violet
o-$CH_3OC_6H_4CH{=}CBrCOCOOH$	Colorless	Red-brown ⟶ red-violet
o-$CH_3OC_6H_4CH{=}CBrCOCOOCH_3$	Colorless	Red-brown ⟶ red-violet
o-$CH_3OBrC_6H_3CHBrCHBrCOCOOH$	Colorless	Green ⟶ deep blue
o-$CH_3OBrC_6H_3CHBrCHBrCOCOOCH_3$	Colorless	Green ⟶ deep blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Colorless	Green ⟶ greenish-blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Colorless	Green ⟶ greenish-blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Deep yellow	Brown ⟶ olive-green
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Yellow	Olive-green

These color changes are rapid and sharp. The last color given in the table for each substance persists for an hour or more, then gradually changes to brown. If bromine is in the side chain, this brown color persists for several days; if in the ring, all color fades out in two to three hours.

It is noteworthy that these changes of color with sulfuric acid: yellow in the case of benzalpyruvic acid, orange and red with *p*- and *o*-methoxybenzalpyruvic acids, respectively, reddish-violet with a methoxyl group

together with bromine in the side chain, and blue and green with bromine also in the ring are the same and in the same order as the color changes brought about by increased numbers of systems of conjugated double linkages in unsaturated hydrocarbons when treated with concentrated sulfuric acid.[6] The accumulation of substituting groups in our compounds has, in the reaction with sulfuric acid, the same effect as an increase in the condition of unsaturation and of conjugation in these hydrocarbons.

After these experiments had been completed, a paper by Pfeiffer and Wizinger[7] appeared in which the color reactions of sulfuric acid with α, α-dianisylethylenes are described. It is striking that these substances give violet colors with sulfuric acid only when there is halogen in the side chain, as is the case with our compounds.

Summary

For the purpose of comparison with other unsaturated α-ketonic acids, *o*-methoxybenzalpyruvic acid and its reactions with bromine have been studied.

The color reactions of sulfuric acid with benzalpyruvic acid, *p*-methoxybenzalpyruvic acid and *o*-methoxybenzalpyruvic acid are described.

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THE ACTION OF SODIUM BENZYL CYANIDE WITH CINNAMIC ESTER. II[1]

BY S. AVERY

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Introduction

In 1897, Walther and Schickler[2] brought together equal moles of sodium ethylate, benzyl cyanide and cinnamic ester in the presence of ether. From the products of the reaction they isolated a substance melting at 162–163°. This they believed to be cinnamylbenzyl cyanide, but as the analysis indicated the presence of one molecule more of water than this compound would call for, they regarded it as a hydrated derivative.

Three years later Erlenmeyer[3] isolated as a product resulting from the reaction of dry sodium ethylate, cinnamic ethyl ester and benzyl cyanide

[6] Kuhn and Winterstein, *Helv. Chim. Acta*, 11, 151 (1928).

[7] Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

[1] Read at the meeting of the Division of Organic Chemistry, American Chemical Society, St. Louis, April 18, 1928.

[2] Walther and Schickler, *J. prakt. Chem.*, [2] **55**, 347 (1897).

[3] E. Erlenmeyer, Jr., *Ber.*, **33**, 2006 (1900).