4. Application of the data to the preparation of pure and commercial calcium arsenates has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

The Action of Light on Beta-Bromobenzalpyruvic Acid

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The action of sunlight on the methyl ester of benzalpyruvic acid results in polymerization of the ester to cyclobutane derivatives[1] as is the case with the cinnamic acids and many other ethylenic compounds. In a study of other unsaturated α-ketonic acids, in this Laboratory, it has been found[2] that benzalpyruvic acids in which methoxyl groups are substituted in the nucleus are less affected by light than the unsubstituted ester. The most active substance encountered is β-bromobenzalpyruvic acid which is extraordinarily sensitive to light. The present paper describes results so far obtained in the study of this light reaction.

When a colorless solution of β-bromobenzalpyruvic acid in benzene is allowed to stand in the diffused light of the laboratory it takes on a yellow color and, after two to three days, has become a brilliant lemon yellow. This color change does not take place in the dark.

On exposure of this yellow solution in thin layers to the direct sunlight the color fades quickly and the solution remains colorless for hours if kept in the direct rays of the sun. As soon as it is removed from the sunlight the yellow color reappears. The change from a yellow to a colorless solution in direct sunlight and from colorless to yellow in diffused light is rapid and can be repeated many times. The solution is so sensitive to the difference in intensity of the light that moving it a few cm. out of the direct rays is sufficient to bring back the yellow color and even the passing of a cloud over the sun has the same effect. After several hours of exposure a white crystalline substance begins to separate on the walls of the containing vessel. This is a dimeric form of β-bromobenzalpyruvic acid. The filtered solution, colorless after a day of exposure to the sunlight, becomes brilliantly yellow overnight. This yellow intermediate compound is, in all probability, a geometrical isomer of the original acid which forms an equilibrium mixture with that acid in diffused light. The effect of light on β-bromobenzalpyruvic acid is then, in part, as follows

$$\overbrace{\underbrace{\underset{\text{(colorless)}}{C_6H_5CH{=}CBrCOCOOH} \rightleftarrows \underset{\text{(yellow)}}{\text{intermediate compound}} \rightleftarrows \underset{\text{(colorless)}}{\text{polymer}}}_{\text{In bright light}}}^{\text{In diffused light}}$$

The cause of the rapid change in color of the solution as it is moved into and out of the direct rays of the sun is evidently the difference in rate of polymerization in bright and in diffused light, the speed of polymerization outstripping that of isomerization in bright light but falling far behind it in diffused light, a sensitivity to difference of light intensity recalling that of lactoflavine, recently described.[3]

If the tubes used for exposure are tightly stoppered another effect of light becomes apparent in the formation of a volatile substance which, as soon as it has saturated the benzene solution, changes the course of the reaction. This substance was found to be hydrogen bromide formed evidently by photodecomposition of some of the bromine compounds present. In its presence there is no appearance of the yellow compound, the polymer is formed in but small quantity, much of the original acid being recovered unchanged. The solution slowly takes on a brown color due to formation of decomposition products. When the tubes are left open to the air, so that the hydrogen bromide escapes, there is no evidence of such products until the solution has been exposed for several weeks. The containers used were at first loosely stoppered to allow the escape of this gas but, as it was found that the solutions were sensitive to the oxygen of the air, later experiments were conducted in an atmosphere of nitrogen. The best yields of polymer were obtained in this way.

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

(2) Reimer and Kamerling, *ibid.*, **55**, 4643 (1933); Reimer, Tobin and Schaffner, *ibid.*, **57**, 211 (1935).

(3) Karrer, Köbner, Salomon and Zehender, *Helv. Chim. Acta*, **18**, 270 (1935).

The yellow solutions, saturated with nitrogen and exposed to bright sunlight with a stream of nitrogen running through, rapidly lost their yellow color. The polymeric compound was deposited in yields of 75 to 80%. The characteristics of this compound are like those of the substance formed from the unsubstituted benzalpyruvic ester in the sunlight[1] which has been proved to be a cyclobutane derivative. If these two reactions are, indeed, analogous, exposure to the light of the unsaturated bromo acid without a solvent would be expected to give directly a polymeric product, without the intermediate formation of an isomer, which should then be different from the polymer obtained from benzene solution. This has been found to be the case. On exposure of bromobenzalpyruvic acid to the sunlight without solvent, there is no change in color. The crystalline acid slowly crumbles to a fine powder from which there can be separated, in small quantity, a crystalline dimeric compound isomeric with the one obtained in benzene solution. The space relation of these isomeric polymers is still under investigation.

When freshly prepared, colorless solutions of β-bromobenzalpyruvic acid were exposed to bright sunlight with a stream of dry oxygen running through the solution, they took on a brownish-yellow color almost at once, a color which did not fade at all in the light, and a pale brownish solid was deposited slowly. This is a mixture, the chief components of which are the dimer, obtained previously from benzene solution, melting at 201°, and a bromo acid melting at 109°. This acid has the formula $C_{10}H_8O_4Br_2$, differing from the original unsaturated bromo acid, $C_{10}H_7O_3Br$, by the elements of hypobromous acid. It is evidently formed in the oxidizing mixture by the addition of hypobromous acid to the unsaturated acid as it can be readily obtained by suspending β-bromobenzalpyruvic acid in water and drawing bromine vapor through the liquid. It is the presence of this bromo acid (109°) that gives the brownish-yellow color to the solution.

The most interesting product of the action of light on β-bromobenzalpyruvic acid appeared after the experiments had been in progress for some time when the solvent was benzene from another source than that previously used. The yellow solutions, in tubes open to the air, began to deposit colorless crystals with a brilliant pearly luster almost immediately on exposure to the sunlight. After several hours the solution became slightly cloudy and the polymeric compound (201°) was slowly deposited. In many repetitions of this experiment the separation of the shining solid began within a few seconds of exposure to the sunlight and stopped abruptly after several hours. The fact that this compound had not been obtained when benzene from another source was used as a solvent and that its formation stopped completely after a limited time suggested that it was a product of reaction of the unsaturated acid with some foreign substance in the benzene. On investigation the benzene was found to contain moisture; after its removal the reaction proceeded as previously described. The new compound is, therefore, a hydrolytic product. It is a saturated acid free from bromine, fairly soluble in cold water, melting with vigorous decomposition at 134°. It has the formula $C_{10}H_{10}O_6$. Oxidation of a dilute solution of the sodium salt of the acid with hydrogen peroxide gave two soluble products which were proved to be mandelic and oxalic acids. The properties of the substance and these two products of oxidation suggest that the compound $C_{10}H_{10}O_6$ is an hydroxy acid, $C_6H_5CHOHCOCOCOOH{\cdot}H_2O$. The acid, however, is colorless and it does not lose water on standing for many weeks over sulfuric acid. Because of these facts and because the ketone groups in such a compound would be highly activated, more probable structures would be $C_6H_5CHOHCOC(OH)_2COOH$ or $C_6H_5CHOHC(OH)_2COCOOH$. That there are two hydroxyl groups attached to neighboring carbon atoms and the second of these formulas therefore correct is shown by the behavior of the acid toward the Criegee[4] reagent; when treated with lead tetraacetate, benzaldehyde is formed immediately.

It is to be expected that an acid of this constitution could be obtained from β-bromobenzalpyruvic acid by oxidation and hydrolysis at the double linkage and subsequent hydrolysis of the bromine atom and it has, in fact, been found possible to reproduce the light reaction by use of potassium permanganate under carefully controlled conditions. The products of this reaction were the bromo acid (109°), mandelic and oxalic acids and a 35 to 40% yield of the hydroxy acid. The possibility of preparing from this acid compounds with several highly activated groups makes it of more than usual interest. These experiments are now in progress.

[4] Criegee, *Ber.*, **64**, 260 (1931).

It is evident, from the foregoing account, that the products formed by action of light on β-bromobenzalpyruvic acid are determined by the conditions of the reaction. The acid, exposed to light in the solid condition, is very slowly polymerized to a dimeric form. In benzene solution it changes fairly rapidly to a yellow compound, probably a geometrical isomer, which in bright sunlight is transformed into a colorless, isomeric diamer. In the presence of oxygen the chief products obtained from the benzene solution are this same diamer and a bromo acid formed by addition of hypobromous acid to the original unsaturated acid. If moisture as well as oxygen is present, an hydroxy acid, $C_6H_5CHOHC(OH)_2COCOOH$, separates rapidly from the benzene solution on exposure to the light. Such a light reaction, resulting in the addition of two hydroxyl groups to an ethylenic linkage, was postulated by Ciamician[5] to account for the final products obtained by him from the mixture of substances formed by action of light on methylheptenone but the compound was not isolated. A parallel behavior, "hydroxylation" at the double linkage, has recently been suggested[6] to account for the formation of azafrin in the escobedia plant and mentioned as a possible first step in the change of β-carotene to vitamin A. Certainly the compound here described is the result of photochemical "hydroxylation" in the presence of moisture and oxygen of the air.

Experimental Part

Beta-bromobenzalpyruvic acid was obtained as previously described[1] from benzalpyruvic acid prepared by a later method.[7] The pure bromo acid in saturated benzene solution was exposed to bright sunlight in quartz test-tubes or flasks fitted with grooved stoppers so that the hydrogen bromide, that had been found to block the reaction, could escape. The intermediate yellow compound, under these conditions, changed to the polymer as fast as it was formed. On moving the solution out of the direct rays of the sun, the yellow color became apparent. After several hours of exposure, fine crystals of the polymeric compound began to separate. These were filtered out at frequent intervals. After about two weeks of exposure there was no further separation of this compound. The benzene filtrates, now of a pale brownish color, contain a complex mixture of material from which benzoic and oxalic acids, an unidentified bromo acid and a tarry residue have been obtained. When dry nitrogen was passed through the solutions during exposure the yield of polymeric compound was increased from about 50 to nearly 80%.

The solid polymer, washed with benzene, separates slowly from methyl alcohol in large, brilliant, clear, rhombic crystals which rapidly become opaque on exposure to the air. The pure substance melts with vigorous decomposition at 201°. It is readily soluble in acetone, fairly soluble in ether and in boiling methyl alcohol, insoluble in benzene, chloroform and ligroin.

Anal. Clear crystals: Calcd. for $C_{20}H_{14}O_6Br_2 \cdot 2CH_3OH$: C, 45.99; H, 3.83. Found: C, 45.51; H, 3.66. Opaque crystals: Calcd. for $C_{20}H_{14}O_6Br_2$: C, 47.06; H, 2.74. Found: C, 47.03; H, 2.56.

The compound decomposes to give yellow solutions on long heating in organic solvents and, in the dry condition in the light, it takes on also a yellow color.

All attempts to replace the bromine atoms with hydrogen or to eliminate the bromine atoms so that the compound could then be reduced in the hope of obtaining one of the unsubstituted cyclobutane acids formerly prepared[1] have been unsuccessful. The acid is either not attacked at all by the reagents used or suffers deep-seated decomposition. It is interesting to find that Stoermer in his latest work on cyclobutane acids[8] has met with the same difficulty in the case of a brominated γ-truxillic acid.

The **methyl ester** of the acid could not be prepared by the action of methyl alcohol, saturated with hydrogen chloride, but was readily formed by action of diazomethane. The ester is very slightly soluble in ether and alcohols, more readily in acetone and benzene. It separates from boiling methyl alcohol in colorless prisms melting at 212° with slow decomposition above the melting point.

Anal. Calcd. for $C_{22}H_{18}O_6Br_2$: C, 49.07; H, 3.34; mol. wt., 538. Found: C, 49.08; H, 3.29; mol. wt. (Rast), 526.

The ester does not decompose on long boiling with methyl alcohol nor in the light but solutions in benzene turn yellow slowly on heating. It is extremely resistant to saponification. This same ester can be prepared by exposing methyl β-bromobenzalpyruvate to sunlight in benzene solution.[9]

When finely ground crystals of β-bromobenzalpyruvic acid were exposed to the sunlight without solvent they crumbled slowly to a fine powder, strongly triboelectric. After two to three months' exposure, the mass was extracted repeatedly with small quantities of boiling benzene from which the original unsaturated acid crystallized on cooling. The small amount of residue, not soluble in benzene, was a colorless acid which separated from boiling methyl alcohol in stocky needles melting with decomposition at 285°. The acid does not crystallize with methyl alcohol. It is readily soluble in boiling benzene and in ether.

Anal. Calcd. for $C_{20}H_{14}O_6Br_2$: C, 47.06; H, 2.74; mol. wt., 510. Found: C, 47.47; H, 3.17; mol. wt. (Rast), 468.

The *methyl ester* was prepared with diazomethane in the

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(5) Ciamician and Silber, *Ber.*, **46**, 3077 (1913).

(6) Kuhn and Brockmann, *Ann.*, **516**, 111 (1935).

(7) Reimer, THIS JOURNAL, **53**, 3147 (1931).

(8) Stoermer and Stroh, *Ber.*, **68**, 2102 (1935).

(9) The methyl ester of bromobenzalpyruvic acid previously prepared[10] was described as an oil. The oil is evidently a mixture of isomers as the ester obtained by action of diazomethane on the monobromo acid crystallizes from diluted methyl alcohol in shining plates melting at 62°. *Anal.* Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 49.05; H, 3.19.

(10) Reimer, THIS JOURNAL, **48**, 2454 (1926).

usual manner. It crystallizes from methyl alcohol in fine, shining colorless needles melting at 233–234°.

Anal. Calcd. for $C_{22}H_{18}O_6Br_2$: C, 49.06; H, 3.34. Found: C, 48.95; H, 3.60.

α-Keto-β,β,γ-trihydroxy-γ-phenylbutyric Acid, $C_6H_5CHOHC(OH)_2COCOOH$.—This acid, obtained when benzene containing a trace of moisture was used as solvent in the light reactions, separated from solution in small plate-like crystals which are conspicuous because of their brilliant pearly luster. It was purified by repeated extraction with boiling benzene, the residue then dissolved in the smallest possible quantity of dioxane, in which it is readily soluble, and double the volume of benzene added. The acid separates in fine needles melting with vigorous decomposition at 134°. It is readily soluble in alcohols and acetone, fairly soluble in water.

Anal. Calcd. for $C_{10}H_{10}O_6$: C, 53.09; H, 4.42; mol. wt., 226. Found: C, 53.26; 53.38; H, 4.47; 4.42; mol. wt., 232.

Proof of Structure.—To one-half gram of the acid in the calculated quantity of dilute sodium carbonate solution, 10 cc. of hydrogen peroxide (13 vol.) was added. After twenty-four hours the solution was acidified, extracted with ether, the ether evaporated and the residue crystallized repeatedly from boiling benzene. Clear needles separated which rapidly became opaque in the air and then melted at 118°. These properties indicated mandelic acid and this was confirmed by a mixed melting point with an authentic sample. The crystals left from evaporation of the residual aqueous solution were identified as oxalic acid.

These two products proved that the groups C_6H_5CHOHC— and —COCOOH were present in the molecule. The proof that there are two hydroxyl groups attached to neighboring carbon atoms and that the formula of the acid is, therefore, $C_6H_5CHOHC(OH)_2COCOOH$, was obtained by oxidation with lead tetraacetate prepared according to the directions of Dimroth.[11] After half an hour, steam was passed through the reaction mixture which smelled strongly of benzaldehyde. *p*-Nitrophenylhydrazine added to the distillate gave a brick red solid which, after crystallization from glacial acetic acid, melted at 192–194° alone and when mixed with a sample of the *p*-nitrophenylhydrazone prepared from pure benzaldehyde.

As the yields of the hydroxy acid were small, rarely more than 5%, attempts were made to obtain it in larger quantity. The obvious procedure of adding more water to the benzene before exposure was not satisfactory; if but a small excess of water was added, the hydrate of bromobenzalpyruvic acid crystallized out and the reaction stopped. By passing moist oxygen through the benzene solution, however, the yields of hydroxy acid were increased to 10 to 12%. After this acid had crystallized out, a mixture of solids slowly formed from which have been separated the dimeric compound (201°), unchanged β-bromobenzalpyruvic acid, mandelic acid and the bromo acid (109°).

Synthesis.—Four grams of β-bromobenzalpyruvic acid was dissolved in a mixture of 130 cc. of acetone and 30 cc. of water and a few drops of sulfuric acid. A solution of 1 g. of potassium permanganate in 200 cc. of acetone was added slowly, the mixture mechanically stirred, and kept at a temperature of 0 to −3°. Small amounts of dilute sulfuric acid were added as needed to keep the solution faintly acid. The oxidation required two and one-half hours. After spontaneous evaporation of the acetone there remained about 12 cc. of water and a mixture of crystalline solids, which were washed with a very little cold water and dried over sulfuric acid for forty-eight hours. The mixture, 3.5 g., was then repeatedly extracted with 5-cc. portions of hot benzene. The shining residue, not soluble in benzene, was the pure hydroxy acid (134°). A further small amount was deposited from the benzene extracts as they cooled. The yield in all was 1.3 g. (36%). On standing the yellow benzene solutions deposited slowly clear shining crystals of the bromo acid, melting at 109°, described below. From the aqueous filtrate 0.34 g. of mandelic acid and 0.2 g. of oxalic acid were obtained, showing that about one-half of the unsaturated acid was oxidized and hydrolyzed to the hydroxy acid and that about one-fourth of this product was oxidized further to mandelic and oxalic acids.

The hydrogen bromide formed by the hydrolysis was evidently oxidized in the permanganate solution to hypobromous acid which formed an addition product with part of the unsaturated acid.

Hydrated Dibromohydroxybenzylpyruvic Acid, $C_6H_5CHBrCBrOHCOCOOH \cdot H_2O$ or $C_6H_5CHOHCBr_2COCOOH \cdot H_2O$.—This acid was synthesized in quantitative yield as follows: 5 g. of β-bromobenzalpyruvic acid was suspended in 400 cc. of water, the mixture cooled with ice and 3 g. of bromine vapor drawn through slowly with a current of air. The bromine was at first rapidly decolorized, then more slowly, and a pure white granular solid separated. The compound can also be prepared by dropping bromine into a cooled, aqueous suspension of the unsaturated acid. The substance crystallizes from benzene in clear fine needles melting to an opaque liquid at about 107°, to a clear liquid at 109°. It is readily dehydrated over sulfuric acid.

Anal. Calcd. for $C_{10}H_8O_4Br_2 \cdot H_2O$: C, 32.43; H, 2.70. Found: C, 32.58, 32.73; H, 2.78, 2.63. Calcd. for $C_{10}H_8O_4Br_2$: C, 34.09; H, 2.27. Found: C, 34.18; H, 2.61.

When benzene solutions of the acid are heated or left standing in the air they take on the deep brownish-yellow color characteristic of benzene solutions of β-bromobenzalpyruvic acid exposed to light in the presence of oxygen.

Summary

The action of light on β-bromobenzalpyruvic acid results in products differing according to the conditions of the reaction. Two isomeric diamers, a hydrated bromo acid and a trihydroxy ketonic acid are here described.

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[11] Dimroth, Friedemann and Kämmerer, *Ber.*, **53**, 485 (1920).