tor block, it is necessary to employ the utmost care to prevent a re-absorption of water. This difficulty was circumvented by placing enough of the partially dried xylan specimens in a platinum combustion boat to insure a sample of from six to eight milligrams when completely dry. The boat was then quickly transferred to a micro-weighing bottle by holding the mouth of the bottle against the drying tube and tilting the latter to discharge the boat. After weighing the specimen the boat was expeditiously transferred to the combustion tube in the manner described above. Through the use of this technique the absorption of water from the atmosphere was practically nil, as indicated by control weighings made on samples in platinum boats that were transferred back and forth from the combustion tube to the weighing bottle. The carbon and hydrogen values obtained in the highly purified xylan specimens are given below, calculated on the moisture and ash-free basis. Calcd. for $(C_5H_8O_4)_n$: mol. wt., 132.06; C, 45.44; H, 6.11.

In conclusion the writer wishes to express his gratitude to Dr. Arnulf Soltys (Graz) for the generous assistance and helpful suggestions that he contributed to this work.

Summary

The analytical results obtained by subjecting fifteen highly purified xylan specimens from various sources to the ultimate carbon and hydrogen analyses by the Pregl micro-method, indicate that pure xylan has the empirical formula $(C_5H_8O_4)_n$. This is in agreement with the theoretical formula for xylan when formulated as the anhydride corresponding to xylose, $C_5H_{10}O_5$. Judging from the ultimate analyses of xylan preparations reported in the literature, pure xylan has in most cases either not been obtained, or the preparations were analyzed under conditions that did not exclude the absorption or loss of water in the course of the analytical procedure.

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THE STRUCTURAL ISOMERS OF BROMOBENZOYLACRYLIC ACID

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In a recent paper published from this Laboratory[1] two pairs of unsaturated bromo-γ-ketonic esters and the pair of acids corresponding in configuration to them were described and shown to be geometrical isomers, but the position of the bromine atoms in these substances was not determined. In 1925 Bogert and Ritter[2] prepared an unsaturated bromo acid of benzoylacrylic acid and stated that the bromine atom in this substance was probably in the α-position because it gave acetophenone on

[1] Rice, This Journal, 50, 1481 (1928).

[2] Bogert and Ritter, *ibid.*, **47**, 526 (1925).

treatment with sodium hydroxide. This bromobenzoylacrylic acid was prepared by the elimination of hydrogen bromide from the two racemic dibromo acids $C_6H_5COCHBrCHBrCOOH$; the position of the bromine atom in the unsaturated acid is, therefore, determined by the comparative reactivities of the two hydrogen atoms in the dibromo acids. Since the mode of addition to benzoylacrylic ester and its substitution products, which have two conjugated systems of double linkages $\mathrm{C_6H_5\overset{1}{O}\overset{2}{C}\underset{4}{\overset{3}{C}}H{=}\underset{3}{\overset{4}{C}}H\underset{2}{C}\underset{1}{O}OR}$, has been shown to be a result of 1,4-addition according to the scheme $\mathrm{C_6H_5\overset{1}{O}\overset{2}{C}\overset{3}{C}H{=}\overset{4}{C}HCOOR}$,[3,4] it seemed probable that the hydrogen atom α to the C_6H_5CO group would be the reactive one and that the unsaturated acid would, therefore, hold its bromine atom in the β-position to the COOH group. This has been proved to be the case. The proof rests on the synthesis of the structural isomer of the acid of Bogert and Ritter from bromomaleic anhydride by the Friedel and Crafts reaction. This new acid gives phenylglyoxal on ozonization; it is the α-acid, $C_6H_5COCH{=}CBrCOOH$. The acid of Bogert and Ritter must, therefore, be the β-acid $C_6H_5COCBr{=}CHCOOH$.

Since the isomeric unsaturated bromo acids recently described were prepared by elimination of hydrogen bromide from dibromo acids which are substitution products of the dibromobenzoylpropionic acids, they too, undoubtedly, hold their bromine atoms in the β-position. They are, accordingly, $(CH_3O)_2C_6H_2BrCOCBr{=}CHCOOH$ and their esters $(CH_3O)_2C_6H_2BrCOCBr{=}CHCOOR$.

Experimental Part

Before the structure of the bromobenzoylacrylic acids was established, the Friedel and Crafts reaction with bromosuccinic anhydride and benzene was carried out with the idea that if the course of the reaction was such that either α- or β-bromobenzoylpropionic acid was formed exclusively, a clue would be given as to the position of the bromine atom in the bromobenzoylacrylic acid formed in the analogous reaction with bromomaleic anhydride and benzene. The evidence sought was not obtained because not one but two unsaturated bromo acids were isolated from bromomaleic anhydride.

A solution of 14.4 g. of bromosuccinic anhydride in 60 g. of benzene was stirred mechanically and warmed while it was treated gradually with 25 g. of aluminum chloride; the product, which was thrown to the sides of the flask as a solid, was decomposed cautiously with ice and hydrochloric acid and the solution extracted five times with benzene. The benzene deposited 3.7 g. of solid melting at 110–117° which was purified

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[3] Kohler and Engelbrecht, THIS JOURNAL, **41**, 764 (1919).

[4] Rice, *ibid.*, **50**, 233 (1928).

by boiling it with carbon disulfide and crystallizing the residue from benzene; 2.5 g. of α-bromobenzoylpropionic acid, melting at 118° into a red liquid, was obtained.

Anal. Calcd. for $C_{10}H_9O_3Br$: C, 46.69; H, 3.50. Found: C, 47.09; H, 3.93. It is the acid prepared by Bougault[5] by addition of hydrogen bromide to benzoylacrylic acid. Evaporation of the benzene and carbon disulfide filtrates left a red oil from which boiling water extracted 1.6 g. of benzoylacrylic acid. This was formed from the maleic anhydride which separated during the distillation of bromosuccinic anhydride under diminished pressure. Extraction of the original aqueous solution with ether gave 9 g. of bromosuccinic acid; the yield of α-bromobenzoylpropionic acid calculated from the bromosuccinic anhydride which reacted was 30%. No β-bromobenzoylpropionic acid could be found though seed was available for inoculation. The behavior of bromosuccinic anhydride is thus different from that of methylsuccinic anhydride,[6] which gives both α- and β-substituted ketonic acids in the Friedel and Crafts reaction.

α-Bromobenzoylacrylic Acid, $C_6H_5COCH{=}CBrCOOH$.—The bromomaleic anhydride used for the preparation of this acid by the Friedel and Crafts reaction was made from both isodibromosuccinic acid[7] and from dibromosuccinic acid.[8] From dibromosuccinic acid an 81% yield of the unsaturated anhydride was obtained[9] by heating the acid with half its weight of phosphorus pentoxide at 200–210° until hydrogen bromide was no longer eliminated, distilling the product (b. p. 215–216°) and redistilling it under reduced pressure with fresh phosphorus pentoxide—b. p. 110° at 18 mm.

A solution of 24.5 g. of freshly distilled bromomaleic anhydride in 80 g. of benzene was warmed and treated gradually with 38 g. of aluminum chloride with constant stirring. When the vigorous evolution of hydrogen chloride slackened, the product was heated for one hour, the viscous mass treated cautiously with ice and concd. hydrochloric acid and the brownish colored solid filtered off; 18 g. of crude acid melting at 110° into a cherry-red liquid was obtained. The acid was purified by recrystallization from benzene, from which it separates in fine needles; it can also be recrystallized from ether, chloroform, benzene and ligroin, chloroform and ligroin and boiling water. By using water it is possible to get rid of the trace of color which is carried down with other solvents. When impure the acid is extremely sensitive to heat; on evaporation of its solution the residue is a cherry-red oil. From 18 g. of crude product 11.1 g. of pure acid, melting at 129° into a red liquid, was separated.

Anal. Calcd. for $C_{10}H_7O_3Br$: C, 47.05; H, 2.74. Found: C, 47.00; H, 3.01.

The aqueous filtrate, after removal of the crude acid, was extracted four times with benzene; the first crop of crystals from the benzene was 1.5 g. of pure β-bromobenzoylacrylic acid (109°) identified by comparison with a specimen of this acid. The benzene filtrate deposited 2.2 g. of acid, melting at 85–110° into a red oil, from which 1.5 g. of β-bromo acid was separated. This acid gave a colorless melt which solidified on cooling. The residue from benzene as well as the residue left after purifying the α-bromo acid contained a mixture of the α- and β-bromo acids which was contaminated with oily decomposition products. The solid separated from these residues was a mixture of isomeric acids. A trace of the α-bromo acid in the β-bromo acid can invariably be detected because the melt shows the characteristic red color of the α-isomer. The mixture of the α- and β-bromo acids melts at 90–102°. It is an interesting fact that the α-bromo saturated acid and the α-bromo unsaturated acid form red oils on melting, whereas the β-bromo saturated acid and the β-bromo unsaturated acid melt into colorless liquids.

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[5] Bougault, *Ann. chim. phys.*, [8] **15**, 491 (1908).

[6] Mayer and Stamm, *Ber.*, **56**, 1424 (1923).

[7] McKenzie, *J. Chem. Soc.*, **101**, 1200 (1912).

[8] Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

[9] Walden, *Ber.*, **30**, 2886 (1897).

Ozonization of α-Bromobenzoylacrylic Acid.—Ozonized oxygen containing about 5% of ozone was passed for one and one-half hours through a solution of 1 g. of α-bromobenzoylacrylic acid in 25 cc. of glacial acetic acid at ordinary temperature. The ozone was then swept out with a current of nitrogen, the solution diluted with water, neutralized with sodium carbonate and extracted with ether. The ether was pumped off in the presence of water and the resulting water solution treated with a slightly acid solution of phenylhydrazine. This produced a yellow precipitate which was dried and recrystallized from low-boiling petroleum ether. It separated in the characteristic needles of the low-melting phenylhydrazone of phenylglyoxal, with which it was identified by a mixed melting point.

On boiling with water α-bromobenzoylacrylic acid gives acetophenone, which was identified by its semicarbazone. With warm sodium methylate the acid also gives acetophenone. In one case when steam was passed into the crude product from the Friedel and Crafts reaction in order to remove benzene, acetophenone was formed instantly and not a trace of the unsaturated bromo acids was found after steam distillation had been continued for fifteen minutes. The red oil, which separated from the aqueous layer, solidified in contact with ether into a brick red powder which held no bromine and did not melt below 250°. This behavior of α-bromobenzoylacrylic acid suggests the reactions of benzoylacrylic acid by which von Pechmann[10] prepared a red dye.

Before the structure of α-bromobenzoylacrylic acid was established by ozonization, this acid was treated with sodium hydrosulfite in the hope of reducing it to one of the known saturated bromobenzoylpropionic acids, but the reduction product was benzoylpropionic acid. This reaction is similar to that in which chlorodibenzoylethylene is changed into dibenzoylethane.[11]

Methyl α-Chlorobenzoylacrylate, $C_6H_5COCH{=}CClCOOCH_3$.—This unsaturated chloro ester was obtained by saturating a methyl alcohol solution of the α-bromo acid with hydrogen chloride and allowing it to stand. The crude product of reaction was used for analysis.

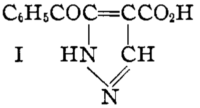
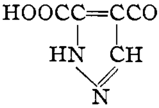
Anal. Calcd. for $C_{11}H_9O_3Cl$: C, 58.79; H, 4.00; Cl, 15.81. Found: C, 58.35; H, 4.17; Cl, 15.76.

The ester remains a yellow liquid after exposure to diffused daylight for a year; it is probably formed by addition of hydrogen chloride followed by elimination of hydrogen bromide.

Methyl α-Bromobenzoylacrylate, $C_6H_5COCH{=}CBrCOOCH_3$.—This ester was prepared by refluxing a methyl alcohol solution of the acid containing a trace of concd. sulfuric acid for three hours. The yellow liquid product is stable in the light but on distillation in a vacuum half of the material was left behind as a red oil; the ester which distilled at 198–200° at 25 mm. was amber colored.

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 49.64, 49.70; H, 3.77, 3.49.

5-Benzoylpyrazole-4-carboxylic Acid or 4-Benzoylpyrazole-5-carboxylic Acid,

I  or  II .—The reaction between α-bromobenzoylacrylic acid and diazomethane was carried out for the purpose of determining whether the yellow liquid ester corresponds in configuration to the acid. An absolute ether

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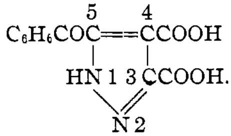
[10] Von Pechmann, *Ber.*, **15**, 885 (1882).

[11] Conant and Lutz, This Journal, **47**, 883 (1925).

solution of diazomethane was added to an absolute ether solution of the acid until evolution of nitrogen ceased; evaporation of the solvent left a yellow oil which gave on analysis a percentage of carbon 3.6% too high for the ester. This yellow oil, after standing for several hours, began to deposit a colorless solid and finally was almost completely changed into this solid. By extracting the mixture with ether the solid was separated from a small quantity of yellow liquid which contained bromine, was insoluble in sodium carbonate solution, was stable in the sunlight, gave acetophenone on warming with water and was probably the ester described above. The solid separated from methyl alcohol in rosets of fine, colorless needles melting at 218° with evolution of gas.

Anal. Calcd. for $C_{11}H_8O_3N_2$: C, 61.11; H, 3.70; N, 12.96. Found: C, 60.76, 61.00; H, 3.71, 4.02; N, 12.86.

The hydrogen bromide is undoubtedly eliminated after formation of the ring nitrogen compound. This reaction is like that of the ester of α-bromocinnamic acid with diazoacetic ester which gives an intermediate product containing bromine.[12] A pyrazole derivative melting at 220° with evolution of gas was made by Wolff,[13] and shown to be  Since the elimination of carbon dioxide from the COOH at 3 is known to take place more readily than from the COOH at 4, it might be possible to determine the structure of the pyrazole formed from the α-bromo acid by obtaining it or its isomer by removal of carbon dioxide[14,15] from the pyrazole of Wolff. The importance of deciding between the two possible structures for the pyrazole, however, did not seem to warrant the laborious synthesis of Wolff's substance. Since it is known that the carbon of the diazomethane molecule adds to the β-carbon atom of an unsaturated substance,[16] it is probable that formula I represents the structure of the pyrazole.

In order to prepare the unsaturated bromo acid[2] now proved to be β-bromobenzoylacrylic acid, for purposes of comparing it with the α-bromo acid, it was necessary to brominate benzoylacrylic acid. Von Pechmann,[10] who recrystallized the dibromo acid prepared in chloroform solution from dilute alcohol, gives a melting point of 135° and Bougault,[5] who recrystallized it from carbon disulfide and benzene, gives 148° as its melting point. Bogert and Ritter[2] report a yield approximately quantitative by bromination of benzoylacrylic acid in glacial acetic acid and give 147.5° as the melting point of the dibromo acid. They state that this is prepared by bromination in chloroform or glacial acetic acid and that search for the second racemic isomer was in vain. In this Laboratory a mixture of racemic isomers was invariably obtained on bromination in both chloroform and glacial acetic acid; this reaction was carried out five times and always a quantitative yield of solid was obtained melting at 110–125°. From this mixture one of the isomers can be separated by boiling the crude solid with benzene and filtering off the less soluble portion, boiling this again with benzene and finally recrystallizing the residue from the same solvent; from 22.6 g. of the mixture 10.1 g. of the dibromo acid which melted at 150° was thus isolated. The rest of the mixture resisted separation though ten different solvents were used. The isomeric dibromo acid can be

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[12] Buchner and Fritsch, *Ber.*, **26**, 256 (1893).

[13] Wolff, *Ann.*, **325**, 187–189 (1902).

[14] Buchner and Dessauer, *Ber.*, **26**, 260 (1893).

[15] Koenigs and Koerner, *ibid.*, **16**, 2153 (1883).

[16] Von Pechmann and Burkard, *ibid.*, **33**, 3590, 3594 (1901).

separated, however, by starting with the product of bromination melting at 110–125° and boiling it in carbon disulfide, filtering off the less soluble portion, boiling the solid which crystallizes from the carbon disulfide again with this solvent, filtering off the less soluble portion and allowing the filtrate to crystallize. The first crop of crystals from this solution melted at 148°; the mixture of this acid and the solid melting at 150° melted at 110–132°.

This lower-melting isomer, described as a solid melting at 142°, has been prepared from isodibromosuccinic anhydride by the Friedel and Crafts reaction.[2] It readily can be obtained by bromination of benzoylacrylic acid in carbon disulfide solution; 2 g. of the acid was suspended in carbon disulfide and the calculated quantity of bromine added with vigorous stirring. Suddenly the bromine color disappeared and the solution at once deposited 2.8 g. of solid melting at 140–145°; including the residue which was a mixture of isomers, the yield was quantitative. The 2.8 g. of solid was recrystallized twice from chloroform, from which it separates in clusters of needles melting at 148°; 50% of the product was separated as this isomer. It crystallizes from benzene in clusters of fine needles while the isomer (150°) separates in long needles from this solvent. There is no depression in the melting point when the isomer (148°) from bromination in carbon disulfide is mixed with the isomer (148°) described above. A mixture of it and the acid (150°) melts at 110–132°. A mixture of the isomers was recrystallized from benzene; the crystals which separated looked like one substance but they melted at 110–143°.

Isomeric Methyl Dibromobenzoylpropionates, $C_6H_5COCHBrCHBrCOOCH_3$.—An absolute ether solution of the isomer (150°) was treated with an absolute ether solution of diazomethane; evaporation of the solvent left a colorless solid in quantitative yield which melted at 58° after one recrystallization from methyl alcohol.

Anal. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.83; H, 3.08.

When the isomer (148°) was likewise treated with diazomethane and the solid recrystallized from methyl alcohol, a quantitative yield of ester melting at 48° was obtained.

Anal. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.80, 37.70; H, 3.08, 3.11.

The mixture of the two esters is a liquid. These esters were prepared in order to confirm a statement made in an earlier paper[17] that bromination of methyl benzoylacrylate gives a product which fails to crystallize because it is a mixture of racemic isomers. The liquid product of bromination of this ester was seeded with the dibromo ester (58°); after standing for several days a crop of crystals which were the ester (58°) separated.

When β-bromobenzoylacrylic acid was prepared from dibromobenzoylpropionic acids,[2] 18% of the dibromo acids was recovered unchanged; it is necessary to heat a glacial acetic acid solution of the dibromo acids in a boiling water-bath for one hour with potassium acetate in order to complete the elimination of hydrogen bromide; the highest yield of unsaturated acid obtained in this work was 55%. β-Bromobenzoylacrylic acid separates from benzene in large, transparent crystals melting at 95–98°; on standing these crystals become opaque and give up their solvent gradually. If the solid (95–98°) is boiled with carbon disulfide, it loses its benzene and shows the melting point reported, 109°.

β-Bromobenzoylacrylic acid does not give a trace of acetophenone on boiling for one hour with water but on heating it for two hours on a boiling water-bath with a 20% sodium carbonate solution, oxalic acid and acetophenone (identified by its semicarba-

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[17] Rice, THIS JOURNAL, **45**, 227 (1923).

zone) were formed. With potassium hydroxide solution (15 g. in 25 cc. of water) the acid gives acetophenone even when the solution is kept cold with ice; after warming this solution for two minutes a 94% yield of benzoic acid was separated. The behavior of the α- and β-bromo acids on hydrolysis shows that treatment with alkaline reagents and even boiling with water can offer no clue as to the position of the bromine atom in the unsaturated bromo acids. That an acetylenic compound was formed[2] from dibromobenzoylpropionic acid in the presence of 3 *M* sodium hydroxide seems improbable in view of the ease of hydrolysis of the unsaturated β-bromo acid which would be the intermediate product formed on treatment with alkali. Further, the tendency which acetylenic compounds of the type $C_6H_5COC{\equiv}CCOC_6H_5$ show to form addition products in the presence of alkaline reagents[1,11] indicates that an acetylenic compound, if formed, would probably not escape reaction. Attempts have been made to prepare benzoylpropiolic acid but it has not yet been obtained in reactions analogous to those used by Lutz[18] for the preparation of dibenzoylacetylene from dibromodibenzoylethane. Further work on this reaction is in progress.

β-Bromobenzoylacrylic acid, like the α-bromo acid, gives benzoylpropionic acid on treatment with sodium hydrosulfite, so that again no conclusion as to structure can be drawn from the reduction reaction.

Methyl β-Bromobenzoylacrylate, $C_6H_5COCBr{=}CHCOOCH_3$.—A liquid mixture of isomers was obtained by bromination of 8.3 g. of methyl benzoylacrylate in carbon disulfide solution; this was dissolved in methyl alcohol, the solution heated for five minutes with 8 g. of potassium acetate and poured onto ice. The yellow liquid, obtained by extraction with ether, gave 10.5 g. of product distilling at 180–185° at 20 mm., a 90% yield. On standing, the yellow liquid deposited a colorless solid which melted at 86° after two recrystallizations from methyl alcohol. In the sunlight the yellow liquid is rapidly and completely transformed into the colorless solid. These esters, therefore, are geometrical isomers.

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: I (86°) C, 49.24; H, 3.54. II (yellow liquid) C, 49.41; H, 3.63.

On treatment of β-bromobenzoylacrylic acid with diazomethane a quantitative yield of the ester (86°) was obtained. This ester, then, corresponds in configuration to the known β-bromo acid (109°). These esters are not reduced even on warming with sodium hydrosulfite.

When the β-bromo esters are boiled with water the vapor at first carries a sharp, tear-producing substance which soon disappears and, after several hours of boiling, acetophenone is formed. On slight warming with potassium hydroxide solution both esters give acetophenone and benzoic acid.

In marked contrast to the behavior of α-bromobenzoylacrylic acid, the β-bromo acid gave a bromo ester when its methyl alcohol solution was saturated with hydrogen chloride. This ester (86°) on standing for two days in methyl alcohol saturated with hydrogen chloride was partially changed into a chloro ester. Micro Pregl determinations gave 20.85, 21.59% of halogen; calcd. for Br, 29.73; for Cl, 15.81.

Summary

α-Bromobenzoylacrylic acid has been prepared and its structure proved. A comparison of its reactions and those of the known bromobenzoylacrylic acid, now shown to be a β-substituted acid, has been made.

NEW YORK CITY

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[18] Lutz, THIS JOURNAL, **48**, 2914 (1926).