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RESEARCHES ON UNSATURATED KETONIC ACIDS. II. SOME EXPERIMENTS WITH BETA-BENZOYLACRYLIC ACID AND RELATED COMPOUNDS

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Introductory

In spite of repeated efforts on the part of various investigators to obtain the geometrical isomer of the ordinary β-benzoylacrylic acid, it has eluded capture so far, although Mrs. Rice has succeeded in preparing stereoisomeric esters of the acid[2] and of its *p*-methoxy[3] and *p*-ethoxy[4] derivatives.

Since we began our experiments in this field four years ago, the papers by Rice, by Conant and Lutz[5] and by Oddy[6] have appeared and others have been announced, which in part duplicated results that we had obtained already and in part anticipated lines of attack well under way.

Our interest in the preparation of the geometrical isomer of β-benzoylacrylic acid orginally arose from the belief that, assuming the ordinary form to be *trans*, if the *cis* isomer could be obtained it might be condensed to α-naphthaquinone, a reaction which the known form does not undergo. As we have pointed out in a recent paper,[7] however, the failure of the naphthaquinone condensation is not due to the stereoconfiguration of the benzoylacrylic acid, but to the preference of the latter for lactone formation; just as β-benzoylpropionic acid when dehydrated gives phenylcrotolactone and not dihydronaphthaquinone $\rightleftharpoons$ 1,4-dihydroxynaphthalene. Many of the data recorded in this communication had been accumulated before this fact was established.

The use of actinic light for the transformation of the stable into the labile isomer[4,5,8] proved unsuccessful in the case of benzoylacrylic acid, although

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[1] Grateful acknowledgment is made to the Barrett Company, to whose courtesy we are indebted for the maleic acid used in the prosecution of this investigation.—M. T. B. and J. J. R.

[2] Rice, THIS JOURNAL, **45**, 222 (1923).

[3] Rice, *ibid.*, **46**, 214 (1924).

[4] Rice, *ibid.*, **46**, 2319 (1924).

[5] Conant and Lutz, *ibid.*, **45**, 1303 (1923).

[6] Oddy, *ibid.*, **45**, 2156 (1923).

[7] Bogert and Ritter, *Proc. Nat. Acad. Sci.*, **10**, 363 (1924); THIS JOURNAL, **46**, 2871 (1924).

[8] (a) Perkin, *J. Chem. Soc.*, **39**, 409 (1881). (b) Thiele, *Ber.*, **27**, 445 (1894). (c) Paal and Schulze, *Ber.*, **35**, 168 (1902). (d) Ciamician and Silber, *Ber.*, **36**, 4266 (1903). (e) Stoermer and Simon, *Ann.*, **342**, 1 (1905). (f) Stoermer and Friderici, *Ber.*, **41**, 324 (1908). (g) Stoermer, *Ber.*, **42**, 4865 (1909). (h) Smedley, *J. Chem. Soc.*, **95**, 219 (1909). (i) Stoermer, *Ber.*, **44**, 637 (1911). (j) Stoermer and Stockmann,

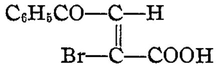
solutions of the acid in various solvents were exposed to sunlight and to ultraviolet light for long periods, alone and also in the presence of traces of iodine. This agrees with the experience of Mrs. Rice with the free acid, although she succeeded in accomplishing such transmutations with its esters[2] and with the esters of its *p*-alkyloxy derivatives.[3,4]

Because of the non-identity of the two groups, (C_6H_5CO and COOH), in union with the —CH:CH— complex, addition of bromine to benzoylacrylic acid can give only racemic mixtures and no internally compensated (*meso*) form. The configuration of the components of these racemic mixtures will differ according as the initial benzoylacrylic acid reacts in *cis* or *trans* position and as the addition follows the behavior of fumaric or maleic acid with permanganate or with bromine.

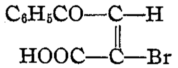
The dibromides so obtained present the same possibilities of stereoisomerism as the tetroses and in addition introduce some interesting complications resulting from keto-enolic tautomerism.

If we disregard these keto-enolic complications and for convenience designate as "normal" the type of addition which changes fumaric to racemic, and maleic to *meso*-tartaric acid, and as "abnormal" the opposite type by which fumaric yields a *meso*-dibromide and maleic a racemic one, the elimination of one molecule of hydrogen bromide from the dibromides gives rise to the following possibilities: (*a*) if the benzoylacrylic acid is actually of *trans* configuration and adds bromine "normally," or if it reacts in the *cis* form and adds bromine "abnormally," a racemic mixture should result, both of whose components (I and II) should yield one and the same α-bromobenzoylacrylic acid (III) when the β-bromine is the one removed, or one and the same β-bromo acid when the α-bromine is the one eliminated as hydrogen bromide. Similarly, "normal" addition to *cis*-benzoylacrylic acid, or "abnormal" addition to its *trans* isomer, also should give a racemic mixture, whose components (V and VI) are different from I and II. Both of these should yield one and the same α-bromo-benzoylacrylic acid (VII), which is not identical with III; and one and the same β-bromo acid (VIII), which is different from IV. The difference between III and VII, for example, is evident from their configurations.

(VII)



$$\begin{array}{r@{}c@{}l} C_6H_5CO— & C & —H \\ & \| & \\ Br— & C & —COOH \end{array}$$



$$\begin{array}{r@{}c@{}l} C_6H_5CO— & C & —H \\ & \| & \\ HOOC— & C & —Br \end{array}$$

(III)

The dibromide of benzoylacrylic acid already known melts at 147.5° (corr.) and is easily prepared by the direct addition of bromine to the acid in chloroform or glacial acetic acid solution.[9] Our search for the

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Ber., **47**, 1786, 1793 (1914). (k) Stoermer and Ladewig, *Ber.*, **47**, 1795 (1914). (l) Stoermer and Prigge, *Ann.*, **409**, 20 (1915). (m) Stoermer and Voht, *Ann.*, **409**, 36 (1915).

[9] (a) Von Pechmann, *Ber.*, **15**, 883 (1882). (b) Bougault, *Ann. chim. phys.*, [8] **15**, 491 (1908).

other stereo-isomer was in vain. Mrs. Rice, however, was more fortunate in her investigation of *p*-methoxy-benzoylacrylic acid[3] for, although only one dibromide was formed in glacial acetic acid solution, she isolated two when the bromination was conducted in chloroform as solvent. On the other hand, she found that both stereo-isomeric methyl *p*-ethoxy-benzoylacrylates,[4] in chloroform solution, gave the same dibromide.

Assuming that benzoylacrylic acid is of fumaroid type and that the addition of bromine follows the same ("abnormal") course that it does with fumaric acid itself,[10] its dibromide should be a racemic mixture of V and VI, as noted above.

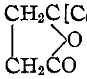
Removal of hydrogen bromide from the dibromide prepared by us yielded a monobromo-benzoylacrylic acid, m. p., 109.4°, which probably carried its bromine on the alpha carbon; whereas the removal of a molecule of bromine regenerated the initial benzoylacrylic acid (m. p., 97°).

McKenzie[10a] has shown also that the addition of bromine to maleic acid follows the "abnormal" course. The *iso*-dibromide of benzoylacrylic acid was prepared, therefore, from *iso*-dibromosuccinic anhydride, benzene and aluminum chloride. It melted at 142° (corr.) and apparently was not identical with the dibromide melting at 147.5° (corr.) yet it gave the same monobromo-benzoylacrylic acid (m. p., 109.4°) as the latter on elimination of hydrogen bromide (by the action of fused sodium acetate), and the ordinary benzoylacrylic acid (m. p., 97°) by removal of a molecule of bromine, instead of the stereo-isomers expected.

As the addition of hydrogen or halogens to an acetylene linkage leads generally to *cis*-ethylene types, attempts were made to prepare benzoylpropiolic acid by the removal of 2HBr from the dibromo-benzoylpropionic acids, but these efforts were futile.

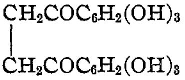
Dodge[11] has described the mutual interconversion of coumaric and coumarinic acids through the addition and splitting off of the elements of sulfurous acid. From benzoylacrylic acid we prepared a crystalline addition product with sulfurous acid, but attempts to eliminate this again, in the hope of getting the *cis*-benzoylacrylic acid, proved fruitless, hydrolysis or decomposition of the benzoylacrylic acid occurring instead.

Georgievics[12] condensed pyrogallol with succinic anhydride in the presence of fused zinc chloride and obtained both a succinein (IX) and a digallacyl (X), the latter dyeing yellow shades on an alum mordant.



$$\begin{array}{l} CH_2C[C_6H_2(OH)_3]_2 \\ | \quad \rangle O \\ CH_2CO \end{array}$$

(IX)



$$\begin{array}{l} CH_2COC_6H_2(OH)_3 \\ | \\ CH_2COC_6H_2(OH)_3 \end{array}$$

(X)

Experiments were undertaken, therefore, with maleic anhydride, in the

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[10] (a) McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912). (b) Lossen and Riebensahm, *Ann.*, **292**, 295 (1896).

[11] Dodge, This Journal, **38**, 446, 457 (1916).

[12] Georgievics, *Monatsh.*, **20**, 450 (1899).

belief that the analogous maleic derivatives would possess greater tinctorial power because of the presence therein of the double bond. No malein was isolated, but the maleic derivative corresponding to X was secured in 15% yield, and proved disappointing in that its dyeings were weak and poor.

Similar condensations attempted with maleic anhydride and phenol, or catechol, in the presence of fused zinc chloride, were unsuccessful, tarry products resulting. When benzene was used as solvent, however, and aluminum chloride as condensing agent, the maleic anhydride united with the phenol, and not with the benzene, giving hydroxy-benzoylacrylic acid.

Von Pechmann[9a] reported that when he condensed citraconic anhydride with benzene, in the presence of aluminum chloride, the product was the β-methyl-β-benzoylacrylic acid, m. p. 113°. The product separated by us, on the other hand, proved to be the isomeric α-methyl-β-benzoylacrylic acid, m. p. 153° (corr.), which gave no Pechmann dye when boiled with an excess of acetic anhydride.

We had prepared the naphthoylacrylic acids before the appearance of Oddy's article.[6] According to our observations, when naphthalene was condensed with maleic anhydride in benzene solution, in the presence of aluminum chloride, the product consisted of approximately 40% of the β(α-naphthoyl)acrylic acid and 60% of the β(β-naphthoyl) isomer. Oddy isolated and identified only the latter.

Experimental Part

Maleic Anhydride, prepared from the acid and phosphorus pentoxide, formed large, colorless, glassy prisms (from ether), m. p. 53°, in agreement with the value reported by Anschütz;[13] yield, 90%.

β-Benzoylacrylic Acid was synthesized from this maleic anhydride and benzene, with aluminum chloride as catalyst, following the method of von Pechmann,[9a,14,2] modified in accordance with the observations of Haller and Guyot,[15] of McMullen,[16] and of others, in the analogous benzoylbenzoic acid reaction. It crystallized from toluene in pale yellow, glistening prisms, m. p. 97° (corr.), which is in harmony with the melting point recorded by Bougault.[17]

Decomposition of the aluminum salt by boiling it with sodium carbonate solution, as practised in the preparation of benzoylbenzoic acid, proved unsatisfactory because it caused hydrolysis of some of the benzoylacrylic acid to acetophenone which latter prevented the solidification of the acid and was removed, but with great difficulty by distillation with steam. Further, some of the acetophenone was apt to unite with the benzoyl-acrylic acid to form diphenacylacetic acid, $(C_6H_5COCH_2)_2CHCOOH$, as pointed out by Bougault.[18]

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[13] Anschütz, *Ber.*, **12,** 2281 (1881).

[14] Koenigs and Wagstaffe, *Ber.*, **26,** 558 (1893). Gabriel and Colman, *Ber.*, **32,** 397 (1899).

[15] Haller and Guyot, *Compt. rend.*, **119,** 139 (1894).

[16] McMullen, This Journal, **44,** 2055 (1922).

[17] Bougault, *Compt. rend.*, **146,** 140 (1908).

[18] Bougault, *ibid.*, **147,** 476 (1908).

The presence of an excess of benzene did not result in the formation of any dibenzoylethylene, $C_6H_5COCH:CHCOC_6H_5$, nor could it be obtained from benzoylacrylic acid, benzene and aluminum chloride. Similarly, an excess of maleic anhydride did not lead to the production of any detectable quantity of acids of the types, $C_6H_4(COCH:CHCOOH)_2$, $C_6H_3(COCH:CHCOOH)_3$, etc., nor could such products be obtained by the action of maleic anhydride on benzoylacrylic acid either in carbon disulfide or benzene solution, with aluminum chloride as catalyst. This is in harmony with the observation of Friedel and Crafts[19] that only one mole of phthalic anhydride reacts with one of benzene, even when the former is used in large excess.

β-Benzoylacrylic Acid Dibromide was prepared by interaction of equimolar amounts of the acid and bromine in glacial acetic acid solution. The nearly colorless solution was poured into water. The dibromide separated as an oil which soon solidified. It crystallized from benzene in minute, colorless needles; m. p., 147.5° (corr.) (von Pechmann[9a] gave the melting point as 135°, Bougault[9b] as 148°); yield, approximately that calculated.

Anal. Calcd. for $C_{10}H_8Br_2O_3$: Br, 47.60. Found: 47.50.

This method proved more convenient than that used by von Pechmann and others wherein chloroform was the solvent. The product lost hydrogen bromide very gradually when heated, the rate of evolution being so low that it did not affect the sharpness of the melting-point.

***iso*-Dibromosuccinic Anhydride** was obtained conveniently by adding bromine (1 mole) to molten maleic anhydride (1 mole) at 95–98°. No evolution of hydrogen bromide occurred and the weight of the product equalled that calculated. This method is simpler than that of Pictet[20] which involves the use of sealed tubes.

Since our product exhibited the properties noted by Pictet, being an oily substance which reacted vigorously with water and solidified in a freezing mixture, no effort was made to purify it to the point of checking the melting point (32°) that he found.

***iso*-β-Benzoylacrylic Acid Dibromide** was obtained from the *iso*-dibromosuccinic anhydride, benzene and aluminum chloride, by the method used for the production of benzoylacrylic acid itself. After removal of the excess of benzene, the crude dibromide remained as an oil which soon solidified to a brownish, crystalline mass. This was dried and washed repeatedly with small amounts of benzene, which freed it from tarry impurities. Recrystallized from benzene, it formed colorless, glassy crystals; m. p., 142° (corr.); yield, 80–85%. A mixture of this product with the isomeric dibromide (m. p., 147.5°) melted at about 125°.

Anal. Calcd. for $C_{10}H_8Br_2O_3$: Br, 47.60. Found: 47.41.

The compound dissolved readily in alcohol or glacial acetic acid, was slightly soluble in benzene and practically insoluble in ligroin or in water.

Monobromo-benzoylacrylic Acid.—When a glacial acetic acid solution (25 cc.) of either of the two stereo-isomeric benzoylacrylic acid dibromides (10 g.) was heated for a few minutes at 70–80° with fused sodium acetate (3 g.),[21] sodium bromide precipitated. The mixture was poured into water, the precipitated oil collected with ether and the ether removed. The sirupy residue gradually solidified in large, prismatic crystals. Recrystallized from benzene, it was obtained in short, thick, colorless, transparent prisms of vitreous luster, m. p. 109.4°, soluble in alcohol, ether, carbon disulfide or glacial acetic acid, less readily in benzene and practically insoluble in water or ligroin. By slow evaporation of its solution in carbon disulfide, it crystallized in large prisms.

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[19] Friedel and Crafts, *Bull. soc. chim.*, [2] **35**, 503 (1881).

[20] Pictet, *Ber.*, **13**, 1670 (1880).

[21] Zincke and Schmidt, *Ber.*, **27**, 2758 (1894).

Anal. Calcd. for $C_{10}H_7O_3Br$: Br, 31.34. Found: 31.68.

Cold concd. hydrochloric acid attacked the acid with the formation of tarry decomposition products. When it was boiled with acetic anhydride, a red solution resulted.

Both stereo-isomeric benzoylacrylic acid dibromides yielded the same monobromobenzoylacrylic acid by this treatment.

Inasmuch as the mutual interconversion of geometrical isomers in some instances has been accredited to the addition and splitting off of acetic acid, alcoholic potassium hydroxide solution was used upon the benzoylacrylic acid dibromides in place of sodium acetate and acetic acid. Potassium bromide was precipitated immediately in the calculated amount (1 mole). From the reaction product, about half of the original dibromide was recovered unaltered, but no benzoylpropiolic acid or other alteration product was isolated in sufficient purity to be identified.

The products obtained by the action of aqueous sodium hydroxide solution varied with the amount and concentration of the alkali, the temperature and duration of the action and other factors. With 2 *M* alkali, acetophenone and oxalic acid were obtained in small quantities. If this reaction proceeded through the intermediate formation of a monobromo-benzoylacrylic acid, the formation of acetophenone would indicate that this intermediate monobromo acid carried its bromine in the alpha position.

When 2 moles of 3 *M* sodium hydroxide solution per mole of acid were used and the solution was subsequently distilled with steam, a colorless, waxy solid was collected in the distillate, which melted at about 50°, absorbed bromine rapidly, decolorized potassium permanganate solution, and was halogen-free (Beilstein test). The yield was low, due to the formation of much tar. It may have been the benzoylacetylene, C_6H_5-COC⋮CH, resulting from a reaction analogous to that by which cinnamic acid dibromide yields phenylacetylene, but the quantity of material available was insufficient for its identification.

When more than 3 moles of 3*M* sodium hydroxide solution were employed per mole of acid, there resulted a yield of benzoic acid practically equal to that calculated, but the other products were not isolated or identified.

Elimination of Bromine from the Stereo-isomeric Benzoylacrylic Acid Dibromides.—The following experiments were conducted with the two stereo-isomers, using either the free acids or their methyl esters, according to the needs of the case.

Either zinc dust and glacial acetic acid,[8b] or zinc dust and methyl alcohol,[22] reduced the dibromides to benzoylpropionic acid. Zinc dust in the presence of water[23] was apparently without action. The use of sodium shot with an ether or benzene solution of the ester gave no reaction at the boiling point of these solvents; at higher temperatures, in toluene or xylene solution, dark colored decomposition products were formed; nor could the desired reaction be effected by the use of a 1% sodium amalgam with the ester.

A smooth dehalogenation was accomplished, however, by the action of potassium iodide in alcoholic solution.[24] When a solution of 20 g. of the dibromide in 200 cc. of saturated alcoholic potassium iodide solution was refluxed for 30 minutes on a steam-bath, it soon turned dark from separated iodine and potassium bromide precipitated. A 30% conversion was thus effected, and was carried to completion by the gradual addition of finely ground hydrated sodium thiosulfate in an amount equivalent to the iodide used; or a saturated aqueous solution of the thiosulfate was found to give equally good results. It was necessary also to add a little water, when alcoholic solutions were used, in order to hold the inorganic salts in solution. The pale yellow solution obtained by

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[22] Röhm, *Ber.*, **34,** 573 (1901).

[23] Biilmann, *J. prakt. Chem.*, [2] **61,** 220, 491 (1900).

[24] Zotta, *Ann.*, **192,** 102 (1878).

this dehalogenation was diluted with water until all benzoylacrylic acid was precipitated. This oil was collected with ether and purified as described already. Only the ordinary form of the acid was obtained from either dibromide.

Sulfo-β-benzoylpropionic Acid.—Benzoylacrylic acid (1 mole) was added to a solution of sodium sulfite (2 moles) in a small volume of hot water. The solution was boiled for 5 minutes and allowed to cool. The crystals of disodium salt which separated were recrystallized from water and then formed colorless, flattened, lustrous needles which darkened slightly at 260°, but did not melt; yield, 85–90%.

Anal. Calcd. for $C_{10}H_8O_6SNa_2$: S, 10.60. Found: 10.65.

The product dissolved freely in water, less readily in alcohol or acetic acid and was practically insoluble in benzene. Long boiling of the substance with acetic anhydride gave a red solution, probably from regeneration of some benzoylacrylic acid and the formation of Pechmann dye from the latter. Hot aqueous 3 *M* sodiumh ydroxide solution hydrolyzed the acid, with formation of acetophenone. Concd. sulfuric acid was without action when cold, but decomposed it when warm.

Since the addition of hydrogen bromide to β-acetylacrylic acid gives the α-bromo derivative,[25] it seems likely that sulfurous acid adds in a similar manner and that the acid is therefore the α-sulfo-β-benzoylpropionic. The production of acetophenone from it by the action of alkali is a further argument in favor of this assumption.

β-(*m*-Nitro)benzoylacrylic Acid, $O_2NC_6H_4COCH{:}CHCOOH$.—Finely ground benzoylacrylic acid (1 part) was added gradually to fuming nitric acid (5 parts) at 0°, during constant stirring. The solution was filtered rapidly through glass wool, to remove undissolved benzoylacrylic acid, and the filtrate allowed to run into ice-water. The precipitated nitro derivative crystallized from alcohol in odorless, yellow, microscopic needles; m. p., 188° (corr.); yield, 90%.

Anal. Calcd. for $C_{10}H_7O_5N$: C, 54.30; H, 3.17. Found: C, 53.93; H, 3.20.

When this compound was oxidized with potassium permanganate, *m*-nitrobenzoic acid (m. p., 140°, uncorr.) was formed.

β-(Hydroxybenzoyl)acrylic Acid, $HOC_6H_4COCH{:}CHCOOH$.—To a solution of 15 g. of phenol and a like amount of maleic anhydride in 15 cc. of dry benzene was added 27 g. of anhydrous aluminum chloride in small portions at laboratory temperature. The mixture was then refluxed on a steam-bath until evolution of hydrogen chloride ceased, after which it was acidified with 10% hydrochloric acid, the benzene layer separated and extracted with 5% sodium carbonate solution. The filtered alkaline solution was acidified with 10% hydrochloric acid, the precipitate collected, dried and crystallized from benzene. Long colorless needles resulted; m. p., 134.5° (corr.); yield, 25%.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.17. Found: C, 61.34, 61.56; H, 4.35, 4.25.

The compound dissolved readily in glacial acetic acid or in alcohol, but was less soluble in benzene or water. The hydroxyl group is probably in the *para* position with reference to the maleic acid attachment.

The action of zinc chloride upon a molten mixture of maleic anhydride and phenol gave only tarry products.

***sym*-Di(trihydroxybenzoyl)ethylene,** $[(HO)_3C_6H_2COCH{:}]_2$.—A mixture of 2 parts of maleic anhydride, 4 parts of pyrogallol and 1.6 parts of coarsely ground zinc chloride was constantly stirred and heated at a temperature not above 120°, for higher temperatures gave dark products difficult to purify. The reaction was exothermic and the temperature rose rapidly unless controlled carefully.

The cooled melt was dissolved in an equal volume of water containing a few cubic

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[25] Wolff, *Ann.*, **264**, 234 (1891).

centimeters of concd. hydrochloric acid and the solution was allowed to stand for 24 hours. The crude diketone separated in grayish crystals that were collected and recrystallized from 20% alcohol. These crystals were dissolved in the minimum quantity of hot 95% alcohol, benzene was added to faint turbidity, the solution filtered hot and allowed to cool slowly. Clusters of pale yellow, silky needles were thus secured; yield, about 15%. Heated to 180°, these crystals darkened and at 195° decomposed with evolution of a dark red vapor. In a sealed tube, they softened at about 225° and melted at 231° (corr.), congealing again to a dark mass when cooled.

Anal. Calcd. for $C_{16}H_{12}O_8$: C, 57.81; H, 3.64. Found: C, 56.80, 57.12; H, 3.94, 4.33.

The compound dissolved freely in alcohol, rather less readily in glacial acetic acid, still more difficultly in water, ether or aniline, and was practically insoluble in ligroin, benzene or ethyl acetate. In aqueous potassium hydroxide solution, it dissolved to form a deep reddish-brown solution, acidification of which with mineral acid discharged the color and re-precipitated the original substance. Attempts to nitrate this compound, under various conditions,[26] were uniformly unsuccessful, the products being mainly tars.

In the absence of zinc chloride, heat alone did not effect the condensation, although in its presence pyrogallol reacted far more violently with maleic than it did with succinic anhydride.

The other product expected in this reaction, namely the malein, probably was represented by a deep red substance, soluble in water, alcohol or ether, which remained in the mother liquors from the purification of the diketone. Extracted from the aqueous solution by ether, it was left as a dark red, gummy mass when the ether was removed.

DYEING EXPERIMENTS WITH THE DIKETONE were carried out using an amount of dye equal to 2% of the weight of the fabric. The dyeings were uniformly weak and poor. The colors were as follows: (a) on silk, direct, a pink; with acetic acid, a purple; with alum and sodium thiosulfate, a lilac; with chromium oxychloride and sodium thiosulfate, a yellow; (b) on cotton, with potassium carbonate, a yellow; with alum and potassium acid tartrate, a lilac; with sodium dichromate, a blue-black; with sodium dichromate and potassium acid tartrate, a purple; after-chromed, a green-brown.

α-Methyl-β-benzoylacrylic Acid was prepared from citraconic anhydride, benzene and aluminum chloride, following the method employed for the synthesis of benzoylacrylic acid itself. The crude product formed a pale yellow oil, nearly equal in weight to that calculated. Prolonged treatment of the crude product with steam removed small amounts of an oily substance, and the residue then partially solidified. By filtration, this solid was separated from contaminating oil. Crystallized from water, it appeared in colorless, long needles of silky luster; m. p., 153° (corr.); yield, 20%.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.47; H, 5.26. Found: C, 69.34; H, 5.33.

The product was readily soluble in alcohol or glacial acetic acid, but dissolved with more difficulty in water. Boiling barium hydroxide solution hydrolyzed it with the formation of acetophenone, and no Pechmann dye was observed when it was boiled with excess of acetic anhydride.[7]

Von Pechmann[9a] carried out this same reaction with citraconic anhydride and separated, instead of our product, the isomeric β-methyl derivative, m. p. 113°, hydrolysis of which yielded propiophenone and oxalic acid.

β-(α-Naphthoyl)acrylic Acid, $C_{10}H_7COCH:CHCOOH$.—Maleic anhydride (1 mole) and naphthalene (1.5 moles) were dissolved in dry benzene (4 moles), and finely ground anhydrous aluminum chloride (2 moles) was added in small portions, while the solution

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[26] Barth, *Monatsh.*, **1,** 882 (1880). Benedikt, *Ber.*, **13,** 362 (1880). Benedikt and Weselsky, *Monatsh.*, **3,** 386 (1882).

was stirred vigorously and the temperature kept below 20°. When all the aluminum chloride had been added, the temperature was raised and the liquid refluxed on a steam-bath until the evolution of hydrogen chloride ceased. The deep red solution was poured into water containing slightly more than 1 mole of hydrogen chloride. The upper layer was separated, extracted with 5% sodium carbonate solution and the alkaline extract acidified. The resultant yellow, viscous mass was extracted with ether and the ether evaporated, leaving the mixed crude acids as a light yellow, crystalline solid; yield, 70–80%. Of this crude product, approximately 40% proved to be α-naphthoyl and 60% β-naphthoyl derivative. The two were separated by fractional crystallization from toluene, in which the alpha is less soluble than the beta acid.

This method is an adaptation of that of Heller and Schülke[27] for the synthesis of naphthoyl- and anthroyl-benzoic acids.

The crude α-naphthoyl derivative was further purified by repeated crystallization from benzene, and then appeared in pale yellow, glassy scales or plates, m. p. 150.2° (corr.), freely soluble in alcohol or acetic acid, much less soluble in benzene or toluene, and practically insoluble in water.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.43. Found: C, 73.96; H, 4.63.

Oxidized by potassium permanganate, in the presence of magnesium sulfate, the compound yielded α-naphthoic acid, m. p. 160° (uncorr.), from which naphthalene was obtained by distillation with calcium oxide. In concd. sulfuric acid the substance dissolved to form a deep red solution which when warmed changed in color to a pale yellow with an intense green fluorescence. When this solution was poured into water, a colorless crystalline solid separated.

β-(β-Naphthoyl)acrylic Acid retained very tenaciously traces of an ocher-colored impurity; these were finally removed by boiling an alcohol solution of the acid with animal charcoal. Recrystallized from benzene, it formed clusters of pale yellow needles, m. p. 188° (corr.), whose solubilities were in the main similar to those of the alpha isomer. Oddy[6] gave the melting point as 189–190°.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.43. Found: C, 73.85; H, 4.71.

The product gave β-naphthoic acid, m. p. 181–182° (uncorr.), when oxidized by potassium permanganate in the presence of magnesium sulfate. In concd. sulfuric acid, it dissolved to give a deep red solution; but when this solution was warmed, tarry substances were formed, and on pouring the solution into water, only decomposition products separated.

Summary

1. The stereo-isomer of β-benzoylacrylic acid is not obtained by the physical or chemical methods employed.
2. Elimination of hydrogen bromide from the two stereo-isomeric benzoylacrylic acid dibromides yields one and the same monobromo-benzoylacrylic acid, and removal of a molecule of bromine gives only the well-known form of benzoylacrylic acid.
3. Benzoylacrylic acid adds the elements of sulfurous acid with the formation of the sulfo-benzoylpropionic acid but, under the conditions recorded, the *cis* form of benzoylacrylic acid is not obtainable from this addition product.
4. Nitration of benzoylacrylic acid gives the *m*-nitro derivative in good yield.

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[27] Heller and Schülke, *Ber.*, **41**, 3633 (1908).

5. Hydroxy-benzoylacrylic acid can be prepared from maleic anhydride, phenol and aluminum chloride, in benzene solution.

6. Pyrogallol condenses with maleic anhydride, in the presence of fused zinc chloride, to the *sym*-di(trihydroxybenzoyl ethylene), which is a poor and weak dye.

7. α-Methyl-β-benzoylacrylic acid can be prepared from citraconic anhydride, benzene and aluminum chloride.

8. Naphthalene, maleic anhydride and aluminum chloride yield a mixture of naphthoylacrylic acids consisting of approximately 40% β-(α-naphthoyl) and 60% of β-(β-naphthoyl) derivative.

9. The following new compounds have been synthesized and studied: *iso*-benzoylacrylic acid dibromide, monobromo-β-benzoylacrylic acid, monosulfo-β-benzoylpropionic acid, β-(*m*-nitrobenzoyl)acrylic acid, β-(hydroxybenzoyl)acrylic acid, α-methyl-β-benzoylacrylic acid and β-(α-naphthoyl)acrylic acid.

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ESTERS OF FURFURYL ALCOHOL

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The esters of furfuryl alcohol have been little investigated. Wissell and Tollens[1] obtained the acetate and benzoate, but so far no others have been prepared. As remarked by these authors, the ordinary methods of esterification cannot be employed with furfuryl alcohol, as mineral acids quickly decompose it. Resort must be had to the action of acid anhydrides or to reactions like the Schotten-Baumann.

The first of these methods was employed in this work. To one mole of furfuryl alcohol, a little over one mole of anhydride was added and the the mixture heated in an oil-bath to 130–150° for two hours. After cooling, the reaction mixture was neutralized with sodium carbonate solution, washed with cold water to remove as much as possible of the unconverted alcohol, dried with calcium chloride and fractionated. It was found that when the fractionation was conducted under reduced pressure, the esters, although boiling constantly, quickly became colored on standing. This, it is thought, was due to traces of furfuryl alcohol which could not readily be removed by fractionation under reduced pressure, owing to the fact that the boiling points of the alcohol and the esters were too close together under reduced pressure. When, however, the separation was conducted at ordinary atmospheric pressure, the boiling points of the two were far enough apart to insure a satisfactory separation. Some decomposition always

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[1] Wissell and Tollens, *Ann.*, **272**, 303 (1893).