Summary

1. A number of derivatives of *p*-benzyloxy- and *p*-methoxy-triphenyl carbinol have been synthesized.
2. The 2 free radicals, *p*-benzyloxy- and *p*-methoxy-triphenylmethyl, have been prepared. A study has been made of the important reactions of these 2 radicals toward oxygen, iodine, hydrogen chloride and light, and of their capacity to form additive compounds.
3. The degree of dissociation of the 2 hexa-arylethanes into the corresponding triarylmethyls has been determined in 6 solvents over a range of temperature from —17° to +53°, and in concentrations from 1 to 6%. The degree of dissociation was found to be influenced by concentration of the free radical, temperature, and the nature of the solvent. The benzyloxy compound dissociates to the extent of from 26 to 56%, the methoxy, to the extent of from 22 to 42%.

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ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE ISOMERIC ESTERS OF BENZOYLACRYLIC ACID

BY GRACE POTTER RICE

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Up to the time of this investigation the only ester of benzoylacrylic acid known was the yellow methyl ester described by Kozniewski and Marklewski[1] in their paper on this acid and its homologs.

In view of the many examples[2] of the transformation of unsaturated organic compounds into their geometrical isomers on exposure to light, it seemed of interest to study the action of light on this ester. Of the substances investigated, that which bears the closest resemblance to the esters of benzoylacrylic acid is dibenzoylethylene, C_6H_5-$COCH:CHCOC_6H_5$; $C_6H_5COCH:CHCOOR$. Paal and Schulze[3] showed that the yellow *trans* form of this substance is changed completely in the light into the colorless *cis* form.

In the present investigation it has been found that the yellow methyl and ethyl esters of benzoylacrylic acid are transformed on exposure to sunlight into the corresponding stereo-isomeric colorless esters, which have higher melting points than the corresponding yellow substances. The reverse transformation of the colorless into the

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[1] Kozniewski and Marklewski, *Bull. Acad. Sci. Cracow*, **81** (1906).

[2] (a) Stoermer and Simon, *Ann.*, **342**, 1 (1905). (b) Stoermer and Friderici, *Ber.*, **41**, 324 (1908). (c) Stoermer, *ibid.*, **42**, 4865 (1909); **44**, 637 (1911). (d) Stoermer and Stockmann, *ibid.*, **47**, 1786, 1793 (1914). (e) Stoermer and Ladewig, *ibid.*, **47**, 1795 (1914). (f) Stoermer and Prigge, *Ann.*, **409**, 20 (1915). (g) Stoermer and Voht, *ibid.*, **409**, 36 (1915).

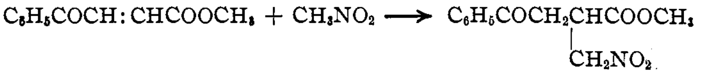
[3] Paal and Schulze, *ibid.*, **35**, 168 (1902).

colored esters is readily brought about by exposing the colorless solids to the sunlight in solutions containing a trace of iodine or bromine.

In view of the work of Stoermer in this field of research there is little doubt but that the yellow esters are the stable forms and the colorless esters the labile forms. Though the stable form usually has the higher melting point there are substances such as α-methylcinnamic acid[2f] and β-methylcinnamic acid, *o*-methoxy-β-methylcinnamic acid and the anilide of β-ethylcinnamic acid[4] whose labile forms have the higher melting points; and though the stable form is usually colorless or less deeply colored than the labile,[5] there are cases known such as dibenzoylethylene[3] and the anilide of 2-nitro-α-phenylcinnamic acid[2f] where the reverse is true.

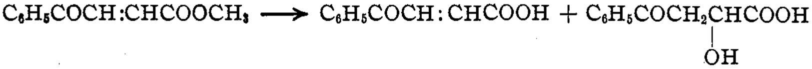
That the colorless methyl ester is the stereo-isomer of the known yellow ester has been established by oxidation and by preparation of its nitromethane addition product which was identified as the same product as was obtained by Kohler and Engelbrecht[6] from the yellow ester and nitromethane. These two reactions may be represented by the following equations.

$$C_6H_5COCH{:}CHCOOCH_3 \xrightarrow{O} C_6H_5COOH + COOH.COOH$$



$$C_6H_5COCH{:}CHCOOCH_3 + CH_3NO_2 \longrightarrow C_6H_5COCH_2\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HCOOCH_3$$

The behavior of the isomeric esters with alkaline reagents is not the same. On boiling the yellow methyl ester with dilute sodium carbonate solution almost complete decomposition takes place, but the colorless methyl ester is saponified by this reagent to give a 60% yield of benzoylacrylic acid. With conc. hydrochloric acid, however, the 2 esters show the same behavior and give the same product of saponification, a mixture of benzoylacrylic acid and α-hydroxybenzoyl-propionic acid.



$$C_6H_5COCH{:}CHCOOCH_3 \longrightarrow C_6H_5COCH{:}CHCOOH + C_6H_5COCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$$

The unsaturated acid has been made in various ways[7] and has been studied extensively by Bougault.[8]

It has now been shown that it corresponds in configuration to the yellow ester and that it is not transformed into its isomer in the sunlight. Moreover, it has not been possible, by any of the usual methods, to prepare an isomeric acid corresponding in configuration to the colorless esters.

In view of the work of Rupe and his co-workers,[9] the behavior of the esters of benzoylacrylic acid when treated with semicarbazide is of interest. The solids obtained with both the yellow and the colorless esters and one molecule of semicarbazide are addition products, which are probably the result of 1,4 addition to the ester and subsequent rearrangement of the substances first formed according to one or the other of the following schemes.

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[4] Stoermer, Grimm and Laage, *Ber.*, **50**, 959 (1917).

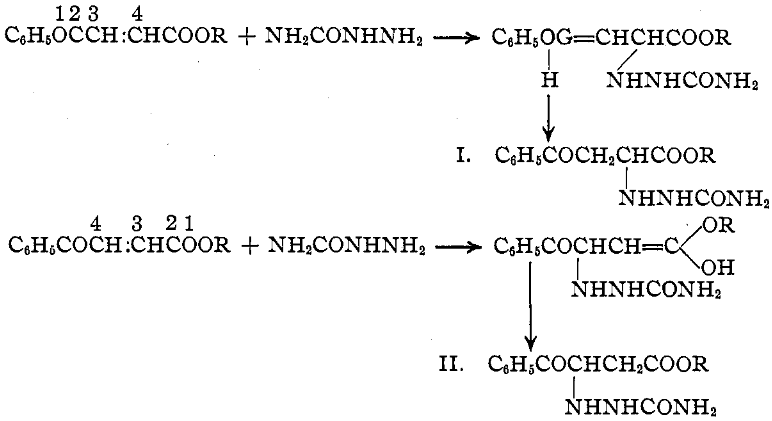
[5] Stoermer and Oehlert, *ibid.*, **55**, 1232 (1922).

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

[7] (a) von Pechmann, *Ber.*, **15**, 885 (1882). (b) Koenigs and Wagstaffe, *ibid.*, **26**, 558 (1893). (c) Gabriel and Colman, *ibid.*, **32**, 397 (1899).

[8] Bougault, (a) *Ann. chim. phys.*, [8] **15**, 491 (1908); *Compt. rend.*, **146**, (b) 140, (c) 936 (1908); **147**, (d) 249, (e) 476 (1908); **148**, (f) 1270 (1909).

[9] (a) Rupe and Schlochoff, *Ber.*, **36**, 4377 (1903). (b) Rupe and Hinterlach, *ibid.*, **40**, 4764 (1907). (c) Rupe and Kessler, *ibid.*, **42**, 4503, 4715 (1909).



$$\overset{1\,2\,3\quad\;4}{\mathrm{C_6H_5OCCH{:}CHCOOR}} + \mathrm{NH_2CONHNH_2} \longrightarrow \mathrm{C_6H_5O\underset{H}{G}{=}CH\underset{NHNHCONH_2}{C}HCOOR}$$

$$\downarrow$$

$$\text{I. }\ \mathrm{C_6H_5COCH_2\underset{NHNHCONH_2}{C}HCOOR}$$

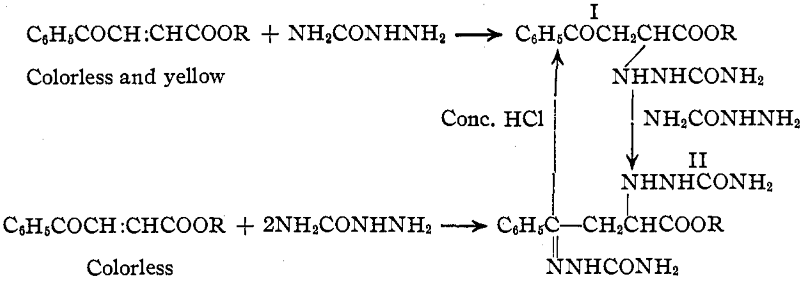
$$\overset{4\quad 3\quad 2\,1}{\mathrm{C_6H_5COCH{:}CHCOOR}} + \mathrm{NH_2CONHNH_2} \longrightarrow \mathrm{C_6H_5CO\underset{NHNHCONH_2}{C}HCH{=}C\begin{smallmatrix}\diagup OR\\ \diagdown OH\end{smallmatrix}}$$

$$\downarrow$$

$$\text{II. }\ \mathrm{C_6H_5CO\underset{NHNHCONH_2}{C}HCH_2COOR}$$

The proof that semicarbazide adds in the manner indicated in the formula instead of $\underset{\mathrm{NHCONHNH_2}}{\text{—CH—}}$ was established by Rupe and Kessler[9c] in their study of the action of semicarbazide on unsaturated aliphatic ketones. Preference is given to Formula I because semicarbazide would be expected to show the same mode of addition with the ester as nitromethane. In this connection it is of interest that Fromm and Siebert[10] have recently explained a product obtained by them in the reaction between phenylhydrazine and a thio-ethylene derivative by 1,4 addition of phenylhydrazine to the unsaturated compound.

The semicarbazide addition product reacts with a second molecule of semicarbazide to give the same derivative as is obtained when the colorless ester is treated with 2 molecules of the reagent; the semicarbazido-semicarbazone thus formed is hydrolyzed by conc. hydrochloric acid with the re-formation of the semicarbazide addition product. The transformations are indicated in the following scheme.

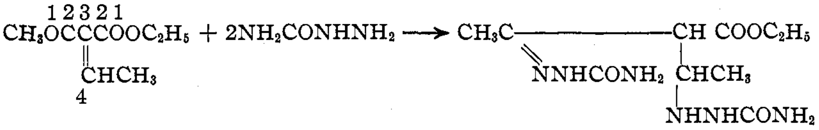


$$\underset{\text{Colorless and yellow}}{\mathrm{C_6H_5COCH{:}CHCOOR}} + \mathrm{NH_2CONHNH_2} \longrightarrow \overset{\text{I}}{\mathrm{C_6H_5COCH_2\underset{NHNHCONH_2}{C}HCOOR}}$$

$$\text{Conc. HCl}\uparrow \qquad \downarrow \mathrm{NH_2CONHNH_2}$$

$$\underset{\text{Colorless}}{\mathrm{C_6H_5COCH{:}CHCOOR}} + \mathrm{2NH_2CONHNH_2} \longrightarrow \overset{\text{II}}{\mathrm{C_6H_5\underset{\underset{NNHCONH_2}{\|}}{C}{-}CH_2\overset{NHNHCONH_2}{C}HCOOR}}$$

The type of substances represented by II was obtained by Rupe and his co-workers[9a,9b] from unsaturated aliphatic ketones and from 1 unsaturated aliphatic ester, ethylideneaceto-acetic ester. The structure of this ester, however, is such that it is not possible to decide which carbonyl group is involved in the addition of the semicarbazide.



$$\overset{1\,2\,3\,2\,1}{\mathrm{CH_3OC\underset{\underset{\underset{4}{CHCH_3}}{\|}}{C}COOC_2H_5}} + \mathrm{2NH_2CONHNH_2} \longrightarrow \mathrm{CH_3\underset{\underset{NNHCONH_2}{\diagdown}}{C}{-\!\!-\!\!-\!\!-}\underset{\underset{NHNHCONH_2}{CHCH_3}}{C}H\ COOC_2H_5}$$

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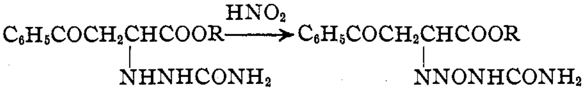
[10] Fromm and Siebert, *Ber.*, **55,** 1020 (1922).

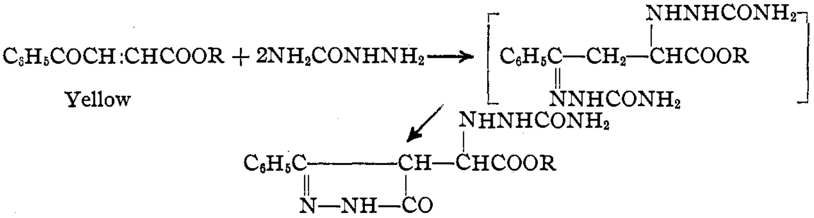
Very recently Auwers[11] has refuted Rupe's statement that aromatic ketones do not give this type of substance by showing that propenylphenyl ketone and substances closely related to it, which have the grouping $C_6H_5COCH:CHR$ in the molecule where R is an aliphatic residue, likewise give semicarbazido-semicarbazones. *Iso*butenyl-*p*-cresyl ketone is the only one of the ketones investigated by Auwers which gives a semicarbazide addition product; Rupe and Kessler,[9c] however, obtained a substance of this type by hydrolysis of the semicarbazido-semicarbazone derived from mesityl oxide and proved its presence without isolating it. They, moreover, prepared from this substance a nitroso derivative[9c] whose structure was established by its behavior on treatment with alkali.

The semicarbazide addition products obtained in this investigation, likewise, give nitroso derivatives whose structure is doubtless analogous to that assigned by Rupe and Kessler to their substance.



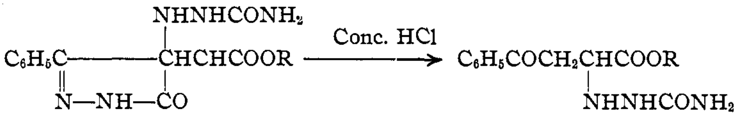
$$\underset{\text{NHNHCONH}_2}{C_6H_5COCH_2CHCOOR} \xrightarrow{HNO_2} \underset{\text{NNONHCONH}_2}{C_6H_5COCH_2CHCOOR}$$

The yellow esters of benzoylacrylic acid give the same products as the corresponding colorless esters when treated with 1 molecule of semicarbazide, but when treated with 2 molecules of reagent the yellow esters give products which are probably pyrazolone derivatives, formed by loss of 1 molecule of ammonia as indicated in the following equation.



$$\underset{\text{Yellow}}{C_6H_5COCH:CHCOOR} + 2NH_2CONHNH_2 \longrightarrow \left[\underset{\text{NNHCONH}_2}{\overset{}{C_6H_5C}}\text{—}CH_2\text{—}\overset{\text{NHNHCONH}_2}{CHCOOR}\right] \longrightarrow \underset{\text{N—NH—CO}}{C_6H_5C\text{———}CH\text{—}\overset{\text{NHNHCONH}_2}{CHCOOR}}$$

Treatment of this substance with conc. hydrochloric acid gives the addition product which was obtained when the ester was treated with 1 molecule of semicarbazide.



$$\underset{\text{N—NH—CO}}{C_6H_5C\text{———}\overset{\text{NHNHCONH}_2}{CHCHCOOR}} \xrightarrow{\text{Conc. HCl}} \underset{\text{NHNHCONH}_2}{C_6H_5COCH_2CHCOOR}$$

This reaction indicates that the group, ($NHNHCONH_2$), which is in the α position to carboxymethyl is not involved in the loss of ammonia. The proof is lacking, however, that ammonia is eliminated in the way shown in the above equation, but it is less likely that ammonia would be eliminated in the only other possible way to form a 6-membered ring nitrogen compound.

Work is in progress in this Laboratory which has for its object the comparison of the esters of *p*-methoxy-benzoylacrylic acid with the esters studied in this paper.

Experimental Part

The yellow methyl ester of benzoylacrylic acid used in this investigation was prepared according to the method of Kohler and Engelbrecht.[6]

[11] Auwers, *Ber.*, **54**, 987 (1921).

The product from vacuum distillation, after solidification, was recrystallized twice from methyl alcohol and was obtained in large lemon-yellow crystals melting at 34°. This solid was exposed to the sunlight both on glass plates and in corked test-tubes. Though the action proceeded more rapidly on the plates, their use was discontinued because of loss of material by evaporation. The yellow crystals melt in the sunlight and re-solidify after the sunlight has left them. In the course of a week of exposure, however, the crystals cease to appear each night and the substance remains a yellow liquid for about 2 weeks. Crystals then begin to separate and continue to increase in quantity until the whole mass is apparently solid. The time of exposure was usually about 6 weeks with test-tubes of 2cm. cross section containing 15 g. of material. When smaller amounts were used the action was complete in a shorter time. The solid was freed from contaminating yellow liquid by filtering with suction; after this was washed with iced methyl alcohol in a funnel surrounded by ice, it was obtained in the form of firm, colorless needles which are pure and melt sharply at 67° after 2 recrystallizations from methyl alcohol. The yield of pure product was 82–90%. The best yields were invariably obtained when not more than 2 g. of material was exposed. There is always a small quantity of the colorless solid held in the yellow liquid which acts as an excellent solvent. This is readily proved by boiling the yellow liquid with water; as the solution cools, colorless crystals separate which melt at 67°. On distillation in a vacuum the residue was shown to contain yellow ester, so part of the yellow liquid at least, is a mixture of the substance melting at 67° and yellow ester.

The colorless solid is very soluble in chloroform, ether, benzene, methyl or ethyl alcohols, and is slightly soluble in boiling water.

Analyses. Subs., 0.1554: CO_2, 0.3964; H_2O, 0.0744. Subs., 0.7420, 0.9493, 1.2130: $(C_2H_5)_2O$, 32.5, 32.5, 32.5; ΔTB, 0.252°, 0.335°, 0.447°. Calc. for $C_{11}H_{10}O_3$: C, 69.47; H, 5.26; mol. wt., 190. Found: C, 69.56; H, 5.31; mol. wt., 195, 188, 180.

Analysis and molecular-weight determinations indicate that the substance is isomeric with the yellow methyl ester of benzoylacrylic acid. That the colorless solid is the stereo-isomeric ester was established by two reactions, first by oxidation and second by addition of nitromethane.

Two g. of the substance was dissolved in acetone and treated gradually at 0° with the calculated quantity of finely powdered potassium permanganate. Instantaneous decolorization took place. The products of oxidation were benzoic acid, obtained in quantitative yield, and oxalic acid.

Addition of nitromethane to the colorless ester would be expected to give the same derivative as was obtained with this reagent and the yellow ester[12] if the two substances are stereo-isomers.

Accordingly, 2.5 cc. of nitromethane was brought into reaction with 0.437 g. of sodium in 12.5 cc. of absolute methyl alcohol, and 3.25 g. of colorless ester, dissolved in 30 cc. of methyl alcohol, was added, drop by drop; after treatment with 2.5 cc. of glacial acetic acid the solution was saturated with hydrogen chloride and poured into iced sodium carbonate. A colorless solid separated, which, on recrystallization from methyl alcohol, melted at 57°: 3 g. of pure product was isolated, a 70% yield.

This is the same substance, methyl α-phenacyl-β-nitropropionate, as was obtained from nitromethane and yellow methyl benzoylacrylate. Their identity was established by comparison of the products from the two reactions.

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[12] Ref. 6, p. 769.

Attempt was made to prove the isomerism of these 2 esters by preparing the same dibromo derivative from them. Both decolorize a chloroform solution of bromine very rapidly in a freezing mixture, but no solid could be separated from the products. Carbon disulfide and carbon tetrachloride were also used as solvents and all 3 solvents were allowed to evaporate very rapidly on extremely cold days out-of-doors in a strong wind. Under these most favorable conditions and with the use of all the ordinary solvents in contact with the products, no solid was obtained though the reaction was carried out several times with each ester. The dibromoderivative of benzoylacrylic acid[13] was then prepared and this crystalline substance esterified in the hope of obtaining seed. No crystals formed. The products are doubtless mixtures due to the presence of 2 unequal asymmetric carbon atoms in the molecule.

The colorless ester is stable in the solid condition in the sunlight; 2 g. was recovered unchanged after exposure in a crystallizing dish for 4 months. It also remained unchanged in chloroform solution in the sunlight.

The yellow ester is stable in the dark; a bottle was filled with the pure product and protected carefully from diffused daylight; at the end of a year and a half it was found that the substance was unchanged.

The change from the colorless to the colored isomer takes place readily in both ether and benzene solutions to which a crystal of iodine has been added. At the end of 12 hours of exposure the product was a mixture of the 2 esters but after 5 winter days, during which the sunlight was very intermittent, the change to the yellow isomer was complete.

In a typical experiment, 2 g. of colorless ester, in a small beaker, was dissolved in benzene containing a crystal of iodine and left in the sunlight until the benzene had evaporated completely. When the beaker was placed in ice, the residue solidified to a yellow crystalline mass; from this 1.9 g. of pure yellow ester was obtained. The change, likewise, takes place in chloroform solution to which 2 drops of bromine have been added.

Saponification of Colorless Methyl Benzoylacrylate

The colorless ester is very sensitive to alkalies, forming a dark red gummy mass with alcoholic potassium hydroxide. This was to be expected from the work of Bougault[8e,8f] on benzoylacrylic acid. Attempt was made to saponify the ester by treating its solution in methyl alcohol, cooled in a freezing mixture, with iced alcoholic potassium hydroxide; the mixture was stirred vigorously for a few minutes and acidified with iced hydrochloric acid as soon as it began to show a yellow color. The ether extract of this solution gives on evaporation a liquid which is completely insoluble in boiling water and, therefore, contains no unchanged ester. The odor of acetophenone is very strong and its presence was proved by preparation of its oxime. No trace of any acid could be found. Acetophenone was the only product identified. Attempt was then made to

[13] Ref. 7a, p. 888.

saponify the ester by boiling with water. Though the solid is soluble in boiling water, it was recovered unchanged after heating the solution for 2 hours. It was finally found possible to saponify the substance with a dilute solution of sodium carbonate. Eight-tenths g. of powdered solid was left overnight floating on a sodium carbonate solution; in the morning the solution was filtered to recover the unchanged ester and acidified with hydrochloric acid. A yellow liquid was precipitated which was purified by extracting its ether solution with sodium carbonate and acidifying the aqueous solution; a colorless solid separated which, after one recrystallization from toluene, formed yellow crystals which melted at 94°; 0.2 g. was obtained and 0.5 g. of ester was recovered.

Saponification is brought about more readily by boiling the ester in a large excess of dil. sodium carbonate solution for 2 or 3 minutes; although there is a slight odor of acetophenone, a 60% yield of acid results when the solution is acidified. This acid is colorless and melts, though not sharply, at 64°; it rapidly turns yellow when left standing on paper in the sunlight and slowly in diffused daylight; in the yellow form it melts at 96–97°.

This answers the description in the literature of benzoylacrylic acid; von Pechmann[7a] gives 64° as the melting point of the colorless hydrated acid, and 96–97° as the melting point of the yellow anhydrous acid. The water of crystallization may be removed by heating the melted acid to 80° for a few minutes; as the liquid cools, the substance solidifies in the yellow form melting at 96–97°.

For purposes of further identification benzoylacrylic acid was prepared by the Friedel and Crafts reaction from maleic anhydride and benzene.[7c] The acid obtained in this way has the same properties as that described above; comparison of the anhydrous acids from the two sources indicated their identity; this was further established by study of their reactions with semicarbazide and hydroxylamine. The 2 specimens of acid give the same derivative with semicarbazide, a colorless solid melting at 198°. This was prepared by Bougault[8a] but described by him as a substance which melts at 190°. The acids from the two sources give the same product on treatment with hydroxylamine, a substance melting at 167.5–168.5° and described by Bougault[8a] as an oxime, though he gives no analysis of the compound or proof of his statement. A second substance, not mentioned by Bougault, is obtained in the reaction with hydroxylamine, a solid melting at 154° with rapid evolution of gas. These substances may be stereo-isomeric oximes, though in view of the work of Posner and his co-workers[14] on the behavior of unsaturated acids and esters with hydroxylamine, it seems possible, at least, that the products are not so simple. Since the reaction was used in this research merely as a step

[14] Posner, *Ber.*, **36**, 4305 (1903); **39**, 3515 (1906). Posner and Oppermann, *ibid.*, **39**, 3705 (1906). Posner, *ibid.*, **40**, 218 (1907). Posner and Rohde, *ibid.*, **42**, 2785 (1909); **43**, 2665 (1910).

in identifying benzoylacrylic acid, the 2 products were not investigated further.

The colorless ester can also be saponified by boiling it with conc. hydrochloric acid or by allowing it to stand in contact with this acid, though it was recovered unchanged after boiling for 2 hours with dil. hydrochloric acid. The product of hydrolysis, however, is not pure benzoylacrylic acid but is a mixture of the unsaturated acid and α-hydroxy-benzoylpropionic acid. The two substances can be separated by extracting the mixture with cold benzene in which the unsaturated acid is very readily soluble. It crystallizes from the benzene solution in a pure state leaving chiefly a small amount of hydroxy acid as a residue. The solid, insoluble in benzene, is slightly impure hydroxy acid which can be purified by recrystallization from chloroform; it melts at 125–126°. That this is the same substance as was obtained by Koenigs and Wagstaffe[15] from chloralacetophenone and was shown by Bougault[8a] to be the α-hydroxy acid, was established by comparison of it with a specimen made from benzoylacrylic acid and hydrochloric acid according to the directions of Bougault. As the hydroxy acid can be prepared in this way from benzoylacrylic acid, it is likely that the first step in the saponification of the ester is the formation of the unsaturated acid, which further reacts in the presence of the hydrochloric acid to form the hydroxy acid.

The yellow benzoylacrylic acid which results from the saponification of the colorless ester undoubtedly corresponds in configuration to the yellow ester. This was indicated by the fact that the yellow ester is formed when the silver salt of the acid is treated with methyl iodide. The possibility that the colorless ester was first formed in this reaction and then isomerized into the colored ester by the trace of iodine present is eliminated by the fact that the reaction took place rapidly and in diffused daylight.

Saponification of Yellow Methyl Benzoylacrylate

The yellow ester is much more sensitive to alkaline reagents than is the colorless ester. On boiling it with sodium carbonate solution under the conditions used with the colorless ester the odor of acetophenone was at once noticed and no acid was precipitated on acidification of the solution. By using a very dilute solution of sodium carbonate and boiling it for a length of time insufficient to saponify all the ester used, it was possible, however, to separate a small quantity of benzoylacrylic acid. Partial decomposition also took place when the yellow ester was boiled in water, but with conc. hydrochloric acid it behaved like the colorless ester and gave a mixture of benzoylacrylic acid and α-hydroxy-benzoylpropionic acid.

Many unsuccessful attempts were made to prepare an isomeric ben-

[15] Ref. 7b, p. 557.

zoylacrylic acid. The yellow acid was exposed for months to the sunlight but was recovered unchanged. In place of hydrochloric acid, weak acids were used in the hope of separating an isomeric acid from the solution of the sodium salt obtained on saponification of the colorless ester. Many variations of procedure were tried but the yellow acid already described was the only product isolated.

A reaction used by Koenigs and Wagstaffe[7b] in the case of the yellow benzoylacrylic acid suggested another method for preparation of an isomeric acid. They treated α-hydroxy-benzoylpropionic acid with conc. sulfuric acid at 0° and obtained the unsaturated acid in very small yield. In the present investigation both acetyl chloride and acetic anhydride were used in place of sulfuric acid in attempts to eliminate a molecule of water. For this purpose it was necessary to prepare the α-hydroxy acid and also the unsaturated acid in quantity. The latter was readily obtained in excellent yield from benzoylpropionic acid by following the directions of Bougault[8a] but in preparing α-hydroxy-benzoylpropionic acid it was found that longer boiling with hydrochloric acid than was recommended by Bougault was necessary in order to keep the quantity of unchanged unsaturated acid a minimum.

Accordingly, benzoylacrylic acid was boiled in 30 times its weight of dil. hydrochloric acid (1:4) for 6 hours. As the solution cooled the unsaturated acid which had failed to react, separated as a solid and was recovered; the filtrate, on evaporation, deposited almost pure α-hydroxy-benzoylpropionic acid. The yield of pure product was 77%.

In an attempt to prepare an isomeric unsaturated acid the α-hydroxy acid was treated in a crystallizing dish with a large excess of acetic anhydride. On spontaneous evaporation of the anhydride a residue was left which solidified completely on contact with water. It was purified both from a mixture of methyl alcohol and water and from benzene; the colorless solid melts at 79° and is soluble in boiling water, methyl alcohol, ether and chloroform, less soluble in benzene. The same solid was obtained, though in poor yield, by boiling the acid with acetic anhydride. It was not possible from the analyses to assign any probable formula to this substance, as it was shown that it was not an acid it was not investigated further.

The α-hydroxy-benzoylpropionic acid was also treated with an excess of acetyl chloride. On complete evaporation of the acetyl chloride, water was added and an orange-colored solid was obtained. This was recrystallized from glacial acetic acid from which it separates as an orange-colored powder which is not an acid. Its color indicates that it is probably a complicated product so it was not analyzed or studied further. It is interesting to note that von Pechmann[16] obtained a red solid by heating the unsaturated acid to 150–160° with acetic anhydride.

β-Hydroxy-benzoylpropionic was used in place of the α-hydroxy acid

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[16] Ref. 7a, p. 886.

in an attempt to prepare an isomeric benzoylacrylic acid; the β acid was first made by Fischer and Stewart[17] though they did not identify their product as the β-hydroxy acid; their method, modified slightly, was used in the preparation of the substance.

Benzoylpropionic acid was brominated in chloroform solution and the purified β-bromo-benzoylpropionic acid was obtained in quantitative yield as a colorless solid melting at 126°; 10 g. of the bromo acid was shaken in a machine for 7 hours with 200 cc. of a 10% solution of sodium carbonate and the product acidified. The solution, which contains β-hydroxy-benzoylpropionic acid and a small amount of colored impurity, probably unsaturated hydrocarbon, was extracted with ether. The colored impurity is so much more soluble in ether than the acid that it can be separated completely from the bulk of the acid by using a small quantity of ether for the first extraction. The acid was obtained as a colorless solid from the subsequent combined ether extracts and was purified by using a mixture of ether and petroleum ether from which it crystallizes in needles melting at 116°. The yield of pure product was 58%.

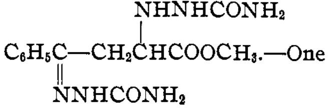
The reaction between β-hydroxy-benzoylpropionic acid and acetic anhydride gave a mixture from which it was possible to separate a small quantity of a solid, found to be very soluble in all the ordinary organic solvents except petroleum ether; it melted at 94°; as neither this solid nor the mixture was acid in character, they were not investigated further.

The hydroxy acid was left overnight in a crystallizing dish with acetyl chloride; in the morning the very small quantity of liquid left was removed and water was added to the remaining crystals. The substance is best purified, though with loss of material, by recrystallization from benzene, from which it separates in needles melting at 144°. From the analyses no formula could be assigned to the compound and as it was not an acid it was not investigated further.

Therefore, neither α-hydroxy nor β-hydroxy-benzoylpropionic acid gives an isomeric benzoylacrylic acid on treatment with either acetic anhydride or acetyl chloride.

Reactions Between Colorless Methyl Benzoylacrylate and Semicarbazide

Semicarbazone of α-Semicarbazido-methyl-benzoylpropionate,



$$C_6H_5\underset{\underset{\textstyle NNHCONH_2}{\|}}{C}—CH_2\overset{\overset{\textstyle NHNHCONH_2}{|}}{C}HCOOCH_3$$

.—One g. of ester, dissolved in methyl alcohol, was treated with a mixture of aqueous solutions of 1.3 g. of semicarbazide hydrochloride and 1.6 g. of sodium acetate, which is in the proportion of 1 molecule of ester to 2 molecules of semicarbazide. A colorless solid begins to separate almost at once; after the mixture has stood overnight the reaction is complete. The solid was filtered by suction, dried and washed with boiling methyl alcohol. After one recrystallization from boiling water it is obtained in quantitative yield as a colorless powder melting at 177–178° with rapid evolution of gas. The reaction takes place readily if the powdered ester is suspended in water and treated with 2 molecules of

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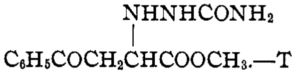
[17] Fischer and Stewart, *Ber.*, **25**, 2560 (1892).

semicarbazide hydrochloride in the presence of sodium acetate, and the same solid melting at 177–178° is the only product. It is soluble in boiling water, less so in ether and chloroform and almost insoluble in methyl alcohol and acetone.

Analyses. Subs., 0.1543: CO_2, 0.2734; H_2O, 0.0769. Subs., 0.1544: 35.2 cc. of N_2(21°, 771.8 mm.). Calc. for $C_{13}H_{18}O_4N_6$: C, 48.44; H, 5.59; N, 26.08. Found: C, 48.32; H, 5.53; N, 26.23.



α-Semicarbazido-methyl-benzoylpropionate, $C_6H_5COCH_2\overset{NHNHCONH_2}{\overset{|}{C}}HCOOCH_3$.—This substance was obtained by the action of 1 molecule of semicarbazide on 1 molecule of ester. A solution of 1 g. of colorless methyl benzoylacrylate, dissolved in methyl alcohol, was treated with a mixture of aqueous solutions of 0.6 g. of semicarbazide hydrochloride and 0.8 g. of sodium acetate. The reaction was allowed to proceed overnight, water was added and the solution filtered. A small quantity of ester was recovered by washing the dried solid with ether and the product was purified by recrystallization from methyl alcohol from which it separates as a colorless powder which melts at 150–150.5°. It is soluble in methyl and ethyl alcohols, chloroform and acetone, and is slightly soluble in benzene and ether. It dissolves in hydrochloric acid and is reprecipitated from the acid solution by sodium carbonate.

Analyses. Subs., 0.1590: CO_2, 0.3162; H_2O, 0.0784. Calc. for $C_{12}H_{15}O_4N_3$: C, 54.34; H, 5.66. Found: C, 54.23; H, 5.47.

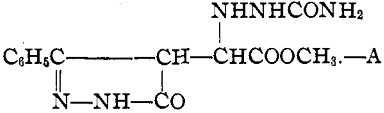
This same substance was also obtained by treating the semicarbazone of α-semicarbazido-methyl-benzoylpropionate with warm, dil. hydrochloric acid and neutralizing the acid solution after a minute with sodium carbonate. The colorless solid which separates in almost pure condition was identified by comparison with a specimen made by treating the colorless ester with 1 molecule of semicarbazide. The α-carbazido-methyl-benzoylpropionate reacts with a molecule of semicarbazide to give the semicarbazido-semicarbazone. The solid melting at 150–150.5° was dissolved in methyl alcohol and treated with 2 molecules of semicarbazide hydrochloride in the presence of sodium acetate. After the mixture had stood overnight, water was added and a solid melting at 177.5° separated. Comparison with a specimen of the product obtained by treating the ester with 2 molecules of semicarbazide proved the identity of the substance. The reaction between α-semicarbazido-methyl-benzoylpropionate and semicarbazide can also be carried out by suspending the powdered solid in a solution of semicarbazide. On evaporation of the water, a quantitative yield of product melting at 177–178° was obtained.

Nitroso-α-semicarbazido-methyl-benzoylpropionate, $C_6H_5COCH_2\overset{NNONHCONH_2}{\overset{|}{C}}HCOOCH_3$.—One g. of solid melting at 150–150.5° was treated with a little more than the calculated quantity of conc. hydrochloric acid. On slightly warming the mixture the solid was dissolved completely; the solution was diluted, cooled with ice water and treated with constant stirring with a dilute, ice-cold solution of sodium nitrite until starch-potassium iodide paper showed a blue color. The colorless solid which separated very rapidly, was filtered by suction, washed repeatedly with cold water and dried. After it was washed once with methyl alcohol it melted sharply with evolution of gas at 125°. It gives Liebermann's nitroso reaction and is soluble in chloroform, acetone and warm methyl alcohol, very slightly soluble in ether and insoluble in cold water.

Analyses. Subs., 0.1520: CO_2, 0.2737; H_2O, 0.0648. Calc. for $C_{12}H_{14}O_5N_4$; C, 48.97; H, 4.76. Found: C, 49.10; H, 4.73.

Reactions Between Yellow Methyl Benzoylacrylate and Semicarbazide

Methyl Ester of Semicarbazido-methylphenyl-pyrazolone-carboxylic Acid,



$$\begin{array}{lll} & & NHNHCONH_2 \\ & & \quad | \\ C_6H_5C & \text{————}CH & \text{—}CHCOOCH_3 \\ \quad \| & \quad | & \\ \quad N\text{—}NH\text{—}CO & & \end{array}$$

.—A solution of 1.3 g. of semicarbazide hydrochloride, mixed with a solution of 1.6 g. of sodium acetate was added to a methyl alcohol solution of 1 g. of the yellow methyl ester, which is in the proportion of 2 molecules of semicarbazide to 1 molecule of ester. After standing overnight the reaction mixture, which had deposited a mass of colorless solid, was poured slowly with stirring into water. The solution was filtered, the solid washed several times with water, dried and then washed with cold methyl alcohol. A yield of 1.1 g. of solid melting at 172° with slow evolution of gas was obtained. The substance is soluble in boiling water and hot methyl alcohol, and slightly soluble in ether, chloroform, benzene and acetone.

Analyses. Subs., 0.1512: CO_2, 0.2814; H_2O, 0.0680. Subs., 0.1537: 31.2 cc. of N_2 (21°, 771.8 mm.). Calc. for $C_{13}H_{15}O_4N_5$: C, 50.75; H, 4.99; N, 23.36. Found: C, 51.14; H, 4.91; N, 22.95.

This substance dissolves in conc. hydrochloric acid. If water is immediately added, a colorless solid separates which dissolves on diluting the solution and is probably a hydrochloric acid addition product, as on addition of sodium carbonate to the solution an insoluble, colorless solid separates which, after recrystallization from methyl alcohol, melts at 150–150.5°. It was identified as α-semicarbazido-methyl-benzoylpropionate, the same substance as was obtained from the semicarbazido-semicarbazone of the colorless ester on treatment with hydrochloric acid. α-Semicarbazido-methyl-benzoylpropionate is obtained as the only product when the yellow methyl-benzoylacrylate is treated with 1 molecule of semicarbazide. The reaction was carried out in the usual way and after the mixture had stood overnight it was poured into water, the solution filtered and the product recrystallized from methyl alcohol. The small quantity of ester which had not reacted was left in the alcohol.

Ethyl Benzoylacrylate, $C_6H_5COCH:CHCOOC_2H_5$.—Ethyl benzoylacrylate was prepared by the same general series of reactions as were used in the case of the methyl ester. Thirty-four g. of benzoylpropionic acid was esterified, giving 35 g. of a colorless liquid boiling at 194° (32 mm.). The saturated ester was brominated and hydrobromic acid eliminated from an absolute ethyl alcohol solution of the bromine compound. The unsaturated ester is a pale yellow, mobile liquid which distilled at 184–185° (25 mm.); yield 26 g. Analyses indicated that the product was not pure, so material was accumulated and the liquid subjected to fractional distillation in a vacuum. Analyses of several fractions gave results which agreed very closely, but carbon was persistently 1% lower than that required for the ester. The liquid does not solidify in a freezing mixture of ice and conc. hydrochloric acid but it readily solidifies in solid carbon dioxide and alcohol. By working very rapidly it was possible to filter the partially melted solid in a double funnel filled with a freezing mixture. The filtrate was the ethyl ester and the product which remained for a few moments on the filter paper as a solid contained most of the impurity.

Analyses. Subs., 0.1695: CO_2, 0.4427; H_2O, 0.0902. Calc. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88. Found: C, 71.23; H, 5.91.

This ester was also prepared directly from benzoylacrylic acid, but the product from this source was very difficult to purify.

Colorless Ethyl Benzoylacrylate, $C_6H_5COCH{=}CHCOOC_2H_5$.—Ten g. of the pure product from vacuum distillation was exposed in a corked test-tube to the sunlight for

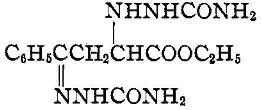
10 weeks. At the end of this time it was possible to make the liquid solidify partially by cooling it in a freezing mixture. The firm, colorless needles were separated from the yellow liquid by filtering in a funnel surrounded by ice, washed quickly with iced alcohol and recrystallized from that solvent; yield, 6.1 g. No more colorless solid could be isolated, though the yellow liquid was again exposed to the sunlight for a month. In a second experiment, 2 g. of yellow ethyl ester was exposed to the sunlight, and at the end of 2 weeks crystals appeared in the liquid. In this case 1.45 g. of colorless solid was isolated. The ester melts at 54° and is very soluble in ether, methyl and ethyl alcohols.

Analyses. Subs., 0.1515: CO_2, 0.3905; H_2O, 0.0815. Calc. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88. Found: C, 70.29; H, 5.97.

In ether solution containing a trace of iodine, the colorless ethyl ester is transformed in the sunlight into the yellow ester. One g. of colorless ester was completely changed in 5 hours of exposure; the product failed to crystallize in a freezing mixture even on contact with a crystal of the colorless ester. That it was the yellow ester was shown by making the semicarbazide derivative; the sole product, a solid melting at 171° with evolution of gas, was identified by comparison with a specimen made from the yellow methyl ester and semicarbazide.

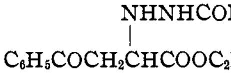
Reactions Between Colorless Ethyl Benzoylacrylate and Semicarbazide

Semicarbazone of α-Semicarbazido Ethyl Benzoylpropionate,



$C_6H_5C(=NNHCONH_2)CH_2CH(NHNHCONH_2)COOC_2H_5$.—One g. of colorless ethyl ester was dissolved in alcohol and treated with an aqueous solution of 2 molecules of semicarbazide hydrochloride in the presence of sodium acetate. After the solution had stood overnight it was poured into water and the solid filtered by suction, washed repeatedly with water and dried. After it had been washed twice with alcohol, it melted sharply at 187° with rapid evolution of gas. A second crop of the same substance separated as the solvent evaporated. The yield of pure product, 1.6 g., was quantitative. It is slightly soluble in ether, benzene, chloroform and acetone, and insoluble in alcohol and cold water.

Analyses. Subs., 0.1552: CO_2, 0.2850; H_2O, 0.0861. Calc. for $C_{14}H_{20}O_4N_6$: C, 50.00; H, 5.95. Found: C, 50.08; H, 6.16.



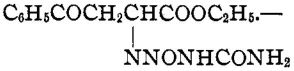
α-Semicarbazido-ethyl-benzoylpropionate, $C_6H_5COCH_2CH(NHNHCONH_2)COOC_2H_5$.—When the reaction with the colorless ethyl ester and 1 molecule of semicarbazide was carried out in exactly the same manner as it was with the colorless methyl ester, a mixture of substances resulted, one of them the same product as was obtained when 2 molecules of semicarbazide were used. If, however, less than 1 molecule of semicarbazide was used and the solution was filtered after 4 hours, the yield of addition product was practically quantitative. The ester which failed to react could be recovered by washing the dry product with ether, and the remaining mixture could be separated by boiling it with methyl alcohol and filtering. The trace of insoluble material melts at 187° with rapid evolution of gas. The methyl alcohol solution deposits a colorless powder melting at 151–152°. It is soluble in methyl and ethyl alcohols, chloroform and acetone, slightly soluble in ether. It dissolves in conc. hydrochloric acid and is reprecipitated from the acid solution by sodium carbonate.

Analyses. Subs., 0.1500: CO_2, 0.3066; H_2O, 0.0830. Calc. for $C_{13}H_{17}O_4N_3$: C, 55.91; H, 6.09. Found: C, 55.74; H, 6.14.

This substance was also obtained by treating the semicarbazone of α-semicarbazido-ethyl-benzoylpropionate with a little more than the calculated amount of conc. hydrochloric acid and neutralizing the solution at once with solid sodium carbonate. The product which separated was recrystallized from methyl alcohol and identified by comparison with a specimen obtained by the reaction between the ester and 1 molecule of semicarbazide.

The semicarbazide addition product reacts with a second molecule of semicarbazide as did the corresponding methyl derivative to give a semicarbazido-semicarbazone.

Nitroso-α-semicarbazido-ethyl-benzoylpropionate,



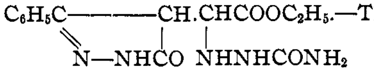
$C_6H_5COCH_2\underset{\substack{|\\ NNONHCONH_2}}{C}HCOOC_2H_5$.—

One g. of α-semicarbazido-ethyl-benzoylpropionate was dissolved in a small excess of conc. hydrochloric acid, 3 cc. of water added, the solution cooled in ice water and treated with constant stirring with ice-cold sodium nitrite solution until starch-potassium iodide paper was colored blue. The solid was collected at once, washed and dried. After being powdered and washed with methyl alcohol, it melted at 127° with rapid evolution of gas; yield 1.1 g. The nitroso derivative is soluble in warm water, and slightly soluble in alcohol, acetone and chloroform; it gives Liebermann's nitroso reaction

Analyses. Subs., 0.1510: CO_2, 0.2776; H_2O, 0.0686. Calc. for $C_{13}H_{16}O_5N_4$: C, 50.64; H, 5.19. Found: C, 50.13; H, 5.04.

Reactions Between Yellow Ethyl Benzoylacrylate and Semicarbazide

Ethyl ester of semicarbazido-methylphenyl-pyrazolone-carboxylic acid,



.—This substance is the product of the reaction between the yellow ethyl ester and 2 molecules of semicarbazide. It separates as a colorless solid when the mixture which has stood overnight is poured into ice water. After washing it with water several times the solid melted sharply at 171° with slow evolution of gas. The yield was quantitative. The substance is sparingly soluble in ether, alcohol, benzene and chloroform.

Analyses. Subs., 0.1613, 0.1503: CO_2, 0.3119, 0.2897; H_2O, 0.0863, 0.0801. Calc. for $C_{14}H_{17}O_4N_5$: C, 52.66; H, 5.32. Found: C, 52.73, 52.56; H, 5.94, 5.92.

On treatment with cold conc. hydrochloric acid, the pyrazolone behaves like the corresponding ring compound derived from the yellow methyl ester. The product was identified as α-semicarbazido-ethyl-benzoylpropionate, the same substance as was obtained from the semicarbazido-semicarbazone of the colorless ethyl ester and hydrochloric acid. With 1 molecule of semicarbazide the yellow ethyl ester gives the same product as the colorless ethyl ester but the yield is small. The reaction was carried out in a variety of ways but more than half of the product was always the same substance as is obtained with the yellow ester and 2 molecules of semicarbazide; the mixture can be separated, however, by taking advantage of the comparative insolubility of the ring compound in methyl alcohol.

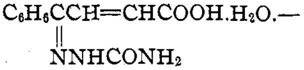
Reaction Between Benzoylacrylic Acid and Semicarbazide

In view of the behavior of the isomeric esters it seemed of interest to investigate the reaction between semicarbazide and benzoylacrylic acid itself, particularly as the melting point of the derivative obtained in this investigation does not agree with the melting point given by Bougault for the substance which he calls a semicarbazone.

The same product was invariably obtained, whether 1 molecule of semicarbazide was used or 2 molecules, whether the reaction was allowed to proceed for half an hour or overnight, and whether the solution was dilute or concentrated. It is not a pure substance, however, as was indicated by comparison of the results of analyses of the product after washing it thoroughly with water, with the results of analyses of the same product after it had been washed with alcohol.

The reaction was best carried out by adding the finely powdered acid to the mixture of solutions of semicarbazide hydrochloride and sodium acetate and stirring rapidly for a half hour; copious precipitation of solid resulted. The reaction mixture was allowed to stand for an hour, the solid was filtered by suction, washed thoroughly with water and allowed to dry. The yield of crude product was quantitative. The mixture can be separated, but with difficulty, by the use of glacial acetic acid. Cold glacial acetic acid effects a partial separation, but on boiling the mixture in this solvent an insoluble colorless solid is left which melts at 225° with rapid evolution of gas. The glacial acetic solution deposits on cooling a solid which melts at 190° with charring. Complications are usually introduced into this method of separation because the high-melting solid is slightly soluble in glacial acetic acid and because the solid which melts at 190° is slowly changed by boiling in glacial acetic acid into a substance which melts at 205°. It is troublesome to separate the mixture of the 3 substances completely, though it is possible to isolate most of the solids melting at 205° and 225° by heating this mixture in boiling ethyl alcohol; the undissolved portion is the solid melting at 225°. As the solvent cools, a mass of the solid melting at 205° separates in almost pure condition and the residue, left on evaporation of the alcohol, is a mixture of the two substances melting at 190° and 205° which is very difficult to separate, when working with a small quantity of material. It was, therefore, easier not to try to separate such a mixture, but to purify it as was the solid melting at 205° by boiling it in glacial acetic acid. When the length of time the crude product is boiled and the quantity of glacial acetic acid used are regulated with extreme care it is possible to bring all of the solid melting at 190° into solution without changing an appreciable quantity of it and to leave all the substance melting at 225° undissolved.

Hydrate of Semicarbazone of Benzoylacrylic Acid,

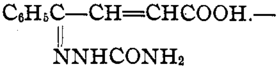


$C_6H_6\underset{\underset{NNHCONH_2}{\|}}{C}CH{=}CHCOOH.H_2O$.—

This solid, melting at 190°, is slightly soluble in cold water, acetone, benzene, ether and chloroform, soluble in boiling glacial acetic acid and in boiling alcohol. It is changed on long boiling in water into the solid melting at 205° but decomposes on heating in the dry state before water is eliminated.

Analyses. Subs., 0.1305, 0.1361: CO_2, 0.2508, 0.2588; H_2O, 0.0590, 0.0600. Calc. for $C_{11}H_{11}O_3N_3{\cdot}H_2O$: C, 52.58; H, 5.17. Found: C, 52.41, 51.86; H, 5.02, 4.89.

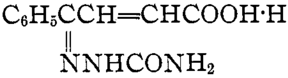
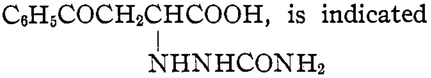
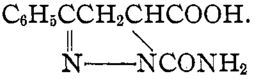
Isomeric Semicarbazones of Benzoylacrylic Acid,



$C_6H_5\underset{\underset{NNHCONH_2}{\|}}{C}{-}CH{=}CHCOOH$.—

The solid (205°) is soluble in methyl and ethyl alcohols and in boiling water; the solid (225°) is insoluble in water and the ordinary organic solvents.

Analyses. Subs. (205°), 0.1507, 0.1463: CO_2, 0.3112, 0.3028; H_2O, 0.0687, 0.0656. Calc. for $C_{11}H_{11}O_3N_3$: C, 56.65; H, 4.72. Found: C, 56.31, 56.44; H, 5.06, 4.98. Subs. (225°), 0.1440: CO_2, 0.2945; H_2O, 0.0613. Calc. for $C_{11}H_{11}O_3N_3$: C, 56.65; H, 4.72. Found: C, 55.77; H, 4.73.

These analyses indicate that substances analogous in structure to those obtained with the esters and semicarbazide are not formed in the reaction with benzoylacrylic acid itself, and that the crude product may be a mixture of stereo-isomeric semicarbazones, one of which holds a molecule of water in combination. That the solid melting at 190° is an unsaturated substance holding a molecule of water,  $C_6H_5\underset{\substack{\| \\ NNHCONH_2}}{C}CH{=}CHCOOH\cdot H_2O$, and not an isomeric addition product of semicarbazide and benzoylacrylic acid,  $C_6H_5COCH_2\underset{\substack{| \\ NHNHCONH_2}}{C}HCOOH$, is indicated by its behavior on treatment with bromine. It reacts with bromine in ice-cold solutions both of chloroform and glacial acetic acid, without eliminating a trace of hydrobromic acid, to give the same bromine compound which is obtained from the solids melting at 205° and 225° on treatment with bromine in glacial acetic acid solution. The latter substances likewise behave toward bromine as if they were unsaturated. In view of the fact that the hydrazone of benzoylacrylic acid described by Gabriel and Colman[18] was later shown by Bougault[8a] to be the isomeric ring compound, it was expected that the reaction with semicarbazide and benzoylacrylic acid might likewise give an analogous ring compound,  $\begin{array}{l} C_6H_5CCH_2CHCOOH \\ \qquad\ \ \| \qquad \diagdown \\ \qquad\ \ N{-\!\!-\!\!-}NCONH_2 \end{array}$. Such a substance should react with bromine with the elimination of hydrobromic acid and the product would have 1 bromine atom in the molecule; but all 3 substances react with bromine in exactly the same way to give the same bromine compound which has 2 bromine atoms in the molecule. This can be explained readily if 2 of the substances are stereo-isomeric semicarbazones and the third a hydrated form of one of them. The reaction with bromine was carried out in the same way with the 3 substances, by suspending the powdered solid in ice-cold glacial acetic acid and adding the calculated quantity of bromine in the same solvent. The reaction proceeds as the solution is stirred and the bromine compound separates as the semicarbazone goes into solution. After the crude product is filtered and washed once with ice-cold glacial acetic acid, it is obtained as a colorless powder which melts sharply at 171° with rapid evolution of gas. The substance is exceedingly sensitive to all solvents, and is decomposed completely into a yellow liquid even on contact with warm solvents, so that the usual methods of purification could not be applied.

Attempt was made to purify it by dissolving in a large volume of cold methyl alcohol but analyses of different fractions of crystals obtained as the solution evaporated indicated that decomposition was taking place and that it was useless to attempt to purify the substance. Since there is a difference of 9 in the percentage of carbon between the ring bromine compound with 1 bromine atom in the molecule and the isomeric unsaturated substance which has added 2 atoms of bromine, it was possible to use the crude product for analyses.

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[18] Ref. 7c, p. 398.

Analyses. Subs., 0.1541: CO_2, 0.1837; H_2O, 0.0390. Subs., 0.1594, 0.1506: 16.2 cc. of N_2 (23°, 749.5 mm.); 14.8 cc. of N_2 (27°, 763 mm.). Calc. for $C_{11}H_{11}O_3N_3Br_2$: C, 33.58; H, 2.79; N, 10.68. Found: C, 32.5; H, 2.8; N, 11.2, 10.8.

Summary

The yellow methyl and ethyl esters of benzoylacrylic acid are transformed in the sunlight into the corresponding stereo-isomeric colorless esters. The reverse transformation of the colorless into the yellow esters takes place if the former are exposed to the sunlight in solutions containing a trace of iodine or bromine.

The hydrolysis of these esters with both alkaline and acid reagents has been studied.

Attempts have been made to prepare an isomeric benzoylacrylic acid corresponding in configuration to the colorless esters.

The colorless esters react with 1 molecule of semicarbazide to form addition products and with 2 molecules of this reagent to form semicarbazones of the addition products. The yellow esters form the same product as the colorless esters with 1 molecule of semicarbazide but with 2 molecules of this reagent they form pyrazolone derivatives.

Benzoylacrylic acid reacts with semicarbazide to form isomeric semicarbazones.

New York, N. Y.

[Contribution from the Chemical Laboratories of Columbia University]

RESEARCHES ON SELENIUM ORGANIC COMPOUNDS. II. SYNTHESIS OF DIARYL THIOPHENES AND DIARYL SELENOPHENES[1]

By Marston Taylor Bogert and Pilar Perez Herrera

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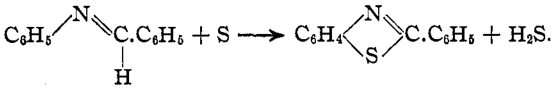
Introductory

In view of the ease with which benzal aniline condenses to the thiazole (I) on fusion with sulfur, it was hoped that a similar fusion of acetophenone anil with sulfur would give the *p*-thiazine (II), or possibly the thionaphthene (III). When the actual experiments were carried out, however, neither thiazine nor thionaphthene was obtained, but a fair yield of 2,4-diphenyl-thiophene (IV).



(I)

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[1] The acetophenone used in these experiments was supplied by Mr. Burton T. Bush, President, Antoine Chiris Co., and the selenium by Mr. E. W. Rouse, of the Baltimore Copper Smelting and Rolling Co., to both of whom we are most grateful.