[Contribution from the Chemical Laboratory of Barnard College]

THE ISOMERIC ESTERS OF PARA-ETHOXY-BENZOYLACRYLIC ACID

By Grace Potter Rice

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In view of the fact that the behavior of *p*-methoxy-benzoylacrylic acid and its methyl and ethyl esters,[1] in certain reactions carried out in this Laboratory, was found to be very different from that of benzoylacrylic acid and the corresponding esters,[2] it seemed of interest to investigate another group of substances closely related to those already studied. For this purpose *p*-ethoxy-benzoylacrylic acid and its esters have been chosen. It has been found, contrary to expectation, that the acid, like benzoylacrylic acid, does not form a polymer when exposed to the sunlight or to the light from a mercury-vapor lamp; this seems remarkable when comparison is made with the ease with which *p*-methoxy-benzoylacrylic acid polymerizes under a variety of conditions.

The stable, yellow esters of *p*-ethoxy-benzoylacrylic acid, like those of the methoxy acid, are isomerized on exposure to the sunlight in benzene solution, but the yellow methyl ester of *p*-ethoxy-benzoylacrylic acid when exposed as a solid to the sunlight is changed into its isomer, in marked contrast to the behavior of the corresponding ester of the methoxy acid which, under the same conditions, is polymerized without the formation of a trace of isomer. It is worthy of notice that the methoxy-methyl ester (72°), with a melting point 10° lower than that of the ethoxy-methyl ester (81.5°), undergoes polymerization in the sunlight without the slightest evidence of melting; the ethoxy ester under identical conditions of exposure softens but does not liquefy during the formation of its isomer. This is of interest because it has been thought that the difference in behavior of the methyl and ethyl esters of the methoxy acid might be due to the fact that the methyl ester (72°) remained solid while the ethyl ester (43°) melted in the sunlight. Apparently polymerization and isomerization are not determined, with these esters at least, solely by the physical state of the substance during exposure.

The yellow esters of *p*-ethoxy-benzoylacrylic acid are the stable forms and have the higher melting points; in benzene solutions containing a crystal of iodine, the colorless isomers are transformed quantitatively, both in the dark and in the sunlight, into their yellow isomers.

The yellow and colorless esters are partially saponified by dil. sodium carbonate solution to give *p*-ethoxy-benzoylacrylic acid, which is also their only product of hydrolysis with cold concd. hydrochloric acid; on boiling with dil. hydrochloric acid a second product, α-hydroxy-*p*-ethoxy-benzoyl-

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[1] Rice, This Journal, 46, 214 (1924).

[2] *Ibid.*, 45, 222 (1923).

propionic acid, was obtained. In both hydrolysis reactions with hydrochloric acid the colorless esters are transformed into the yellow isomers, which is of interest in view of the fact that in the case of the esters of the other unsaturated ketonic esters investigated it has not been possible to prove this isomerization. It is, therefore, probable that with all the esters studied the products of hydrolysis are those obtained from the respective yellow isomers: $\underset{\text{colorless}}{C_2H_5OC_6H_4COCH{=}CHCOOCH_3} \longrightarrow$

$\underset{\text{yellow}}{C_2H_5OC_6H_4COCH{=}CHCOOCH_3} \longrightarrow C_2H_5OC_6H_4COCH{=}CHCOOH +$

$C_2H_5OC_6H_4COCH_2CHOHCOOH$.

The unstable ethyl ester of *p*-ethoxy-benzoylacrylic acid has not been obtained as a solid; that it is isomeric with the yellow stable ester was proved by the reaction with semicarbazide. Two substances were formed, an addition product and its semicarbazone, which correspond to the two substances obtained with the colorless methyl ester and the reagent. The yellow esters give in addition to these two products, isomeric semicarbazones not a trace of which could be found in the reaction with the liquid ethyl ester, in spite of the fact that the reaction was carried out several times under a variety of conditions.

The respective products obtained on treatment of *p*-ethoxy-benzoylacrylic acid and the isomeric esters with semicarbazide correspond to those obtained with the methoxy acid and esters. Benzoylacrylic acid and its esters show a different behavior with semicarbazide.

Experimental Part

p-Ethoxy-benzoylpropionic acid was prepared by the Friedel and Crafts reaction from succinic anhydride and phenetole.[3] On decomposition of the bright red addition product with ice and concd. hydrochloric acid, the colorless acid separated as a solid. It was filtered, washed and dried and used in the crude state for the preparation of its methyl and ethyl esters; yield, 59%.

The methyl ester begins to crystallize as soon as the methyl alcohol solution of the acid is saturated with dry hydrogen chloride. The fine, colorless needles, which melt at 53° after several recrystallizations from methyl alcohol, are very soluble in the usual organic solvents.

Anal. Subs., 1502: CO_2, 0.3650; H_2O, 0.0912. Calc. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 66.27; H, 6.74.

The ethyl ester separates in long, silky crystals which melt at 51°.

Anal. Subs., 0.1514: CO_2, 0.3722; H_2O, 0.0966. Calc. for $C_{14}H_{18}O_4$: C, 67.20; H, 7.20. Found: C, 67.04; H, 7.09.

The yellow methyl and ethyl esters of *p*-ethoxy-benzoylacrylic acid were prepared

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[3] Gabriel and Colman, *Ber.*, 32, 404 (1899).

by elimination of hydrobromic acid from the corresponding bromo esters of *p*-ethoxybenzoylpropionic acid.[4]

Both unsaturated esters crystallized when their alcoholic solutions were cooled, and were filtered off and washed free from potassium bromide with ice water.

Methyl *p*-Ethoxy-benzoylacrylate, $C_2H_5OC_6H_4COCH:CHCOOCH_3$.—The methyl ester was purified by recrystallization from methyl alcohol from which it separates in fine, yellow needles which melt at 81.5°; yield of pure product, 91%.

Anal. Subs., 0.1511: CO_2, 0.3696; H_2O, 0.0789. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.71; H, 5.80.

Ethyl *p*-Ethoxy-benzoylacrylate, $C_2H_5OC_6H_4COCH:CHCOOC_2H_5$.—The ethyl ester crystallized from alcohol in long, yellow, silky needles which melt at 54°; yield, 87%.

Anal. Subs., 0.1576: CO_2, 0.3915; H_2O, 0.0881. Calc. for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45. Found: C, 67.74; H, 6.21.

Both esters are readily soluble in methyl and ethyl alcohols, ether, chloroform, benzene and acetone.

***p*-Ethoxy-benzoylacrylic Acid,** $C_2H_5OC_6H_4COCH:CHCOOH$.—The acid was prepared by the Friedel and Crafts reaction from maleic anhydride and phenetole with carbon disulfide as a solvent, using an efficient electric stirrer until the hardening of the addition product made stirring impossible. On decomposition of the solid red cake with ice and concd. hydrochloric acid, the unsaturated acid separated as a solid and was filtered off with suction; yield, 62%. It was purified by recrystallization from benzene from which it separates in yellow needles melting at 141–142°. It is soluble in methyl and ethyl alcohols and ether, in boiling benzene and toluene and also in boiling water.

Anal. Subs., 0.1524: CO_2, 0.3671; H_2O, 0.0757. Calc. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.69; H, 5.51.

The unsaturated esters can be prepared directly from the unsaturated acid. A methyl alcoholic solution of the acid was saturated with dry hydrogen chloride and the solution allowed to stand overnight. No crystals formed even on seeding, so the liquid was poured onto ice and solid sodium carbonate, the neutral solution was extracted with ether, the ether extract dried and the ether allowed to evaporate. Since the residue failed to crystallize, it was dissolved in methyl alcohol and warmed with potassium acetate. On pouring the mixture onto ice the unsaturated ester separated as a solid; 7 g. of ester was obtained from 12 g. of acid. The residue is a yellow liquid which could not be induced to crystallize.

Methyl and ethyl *p*-ethoxy-benzoylacrylates react with bromine in chloroform solution to give quantitative yields of solid dibromo addition products. The residue left from the reaction with the methyl ester, after rapid evaporation of the solvent, was purified by washing it with warm methyl alcohol. The colorless crystals, which melt at 92°, are readily soluble in ether, benzene, chloroform and hot methyl alcohol.

Anal. Subs., 0.1533: CO_2, 0.2234; H_2O, 0.0497. Calc. for $C_{13}H_{14}O_4Br_2$: C, 39.59; H, 3.55. Found: C, 39.74; H, 3.60.

The viscous residue from the reaction with the ethyl ester solidified in contact with benzene and glacial acetic acid; the solid was perfectly colorless and melted sharply at 81° after washing with ice-cold methyl alcohol.

Anal. Subs., 0.1600: CO_2, 0.2392; H_2O, 0.0540. Calc. for $C_{14}H_{16}O_4Br_2$: C, 41.17; H, 3.92. Found: C, 40.77; H, 3.75.

α,β-Dibromo-*p*-ethoxy-benzoylpropionic Acid, $C_2H_5OC_6H_4COCHBrCHBrCOOH$.—

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[4] Kohler and Engelbrecht, THIS JOURNAL, **41**, 764 (1919). Ref. 1.

p-Ethoxy-benzoylacrylic acid was treated with bromine in glacial acetic acid solution. The solid residue obtained after rapid evaporation of the solvent was recrystallized from 50% acetic acid; the substance separated as a fine, white powder which melted with decomposition at 151°; yield, quantitative.

Anal. Subs., 0.1515: CO_2, 0.2106; H_2O, 0.0429. Calc. for $C_{12}H_{12}O_4Br_2$: C, 37.89; H, 3.15. Found: C, 37.91; H, 3.14.

Action of Sunlight on the Stable, Yellow Esters

Colorless Methyl *p*-Ethoxy-benzoylacrylate, $C_2H_5OC_6H_4COCH{:}CHCOOCH_3$.—A benzene solution of yellow methyl *p*-ethoxy-benzoylacrylate was exposed in a quartz test-tube to the sunlight until the color of the solution had disappeared. On spontaneous evaporation of the solvent, a liquid was left which crystallized readily when stirred. After four recrystallizations from methyl alcohol the ester formed large, colorless, transparent needles which melted at 53° and were extremely soluble in organic solvents except ligroin.

Anal. Subs., 0.1543: CO_2, 0.3771; H_2O, 0.0840. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.65; H, 6.04.

This isomeric, colorless ester was also obtained in a yield of 92.4% when 8.8 g. of powdered, yellow ester was exposed to the sunlight for 24 hours on a porcelain tray. A smaller yield of isomeric ester was obtained when the tray was allowed to become very warm. In this reaction 0.4 g. of a mixture of two high-melting, colorless solids was obtained from 19.5 g. of yellow ester. It is probable that these substances are polymers, although a quantity of them sufficient for analysis was not obtained.

The colorless ester is extremely stable in the solid state. It was not changed on long exposure to the sunlight and to the light from a mercury-vapor lamp. It is partially transformed into the yellow isomer on distillation in a vacuum.

It is transformed quantitatively in benzene solution containing a crystal of iodine in the dark as well as in the sunlight into the yellow isomer.

The colorless ester forms the same solid dibromo addition product that was obtained with the yellow ester.

Colorless Ethyl *p*-Ethoxy-benzoylacrylate, $C_2H_5OC_6H_4COCH{:}CHCOOC_2H_5$.—Yellow ethyl *p*-ethoxy-benzoylacrylate isomerizes when exposed to the sunlight in benzene solution. On removing the benzene from the colorless solution by drawing dry air through it, a straw-colored liquid was left which could not be made to crystallize even when frozen in a mixture of solid carbon dioxide and alcohol. The crystalline yellow ester was also exposed to the sunlight in quartz test-tubes; after a few hours of exposure, out-of-doors in cold winter weather, the solid liquefied and remained a liquid during the two months over which the test-tubes were exposed. No solid formed in the viscous mass obtained when the liquid was frozen with solid carbon dioxide, even on seeding it with crystals of yellow ester. It was not possible to purify the product by distillation in a vacuum because, like the colorless methyl ester, it isomerizes when heated under diminished pressure. Analysis indicates that the substance may be slightly impure ethyl *p*-ethoxy-benzoylacrylate.

Anal. Subs., 0.1608: CO_2, 0.3956; H_2O, 0.0937. Calc. for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45. Found: C, 67.10; H, 6.47.

An open beaker containing 0.8 g. of the straw-colored liquid in benzene solution, to which had been added a crystal of iodine, was exposed on the roof in the sunlight for four hours. At the end of this time the solvent and iodine had evaporated completely, leaving 0.8 g. of yellow crystals melting at 54°. The liquid ester is also transformed quantitatively into the yellow solid when its benzene solution containing a crystal of iodine is left for several days protected from all light. Warming such a solution for six hours on a water-bath brings about the transformation, but the reaction is not as clean as the other isomerization reactions described.

The proof that the liquid is isomeric with the yellow ester rests on its behavior with semicarbazide (see p. 2324). It gave with this reagent substances which correspond to those obtained with the colorless methyl ester and not a trace of isomeric semicarbazones which were invariably obtained with both the methyl and ethyl yellow esters.

p-Ethoxy-benzoylacrylic acid was dissolved in benzene in a flask and the solid allowed to crystallize in a thin layer on the surface of the glass. After three months of exposure, 65% of the unsaturated acid used was recovered unchanged; no solid could be separated from the residue which was a dark red oil. Duplication of this procedure gave exactly the same results. The solid unsaturated acid was exposed to the light from a mercury-vapor lamp for 40 hours; no change in color took place nor was there evidence of decomposition. The behavior of this substance in the light was unexpected in view of the ease of polymerization of *p*-methoxy-benzoylacrylic acid.

Saponification of the Esters of Para-ethoxy-benzoylacrylic Acid

The yellow and colorless methyl esters of the unsaturated acid were boiled for three minutes with an excess of a 10% solution of sodium carbonate. In each reaction 80% of the ester was recovered and a small quantity of *p*-ethoxy-benzoylacrylic acid was separated on acidifying the carbonate solutions. Longer boiling and also warming the esters with sodium carbonate solution for several hours on a water-bath resulted in their decomposition without the formation of a larger quantity of unsaturated acid.

The yellow methyl ester was suspended in dil. hydrochloric acid (1:4) and the mixture boiled for three hours; 30% of the ester used was left as an oil floating on the surface of the liquid and could be removed by filtering the hot solution. The yellow unsaturated acid formed by hydrolysis separated as the filtrate cooled and was removed. On complete evaporation of the filtrate a colorless acid was left which was purified by recrystallization from chloroform. It melts at 132° and is soluble in alcohol, hot chloroform and warm water and slightly soluble in ether. It can be recrystallized from water.

Anal. Subs., 0.1530: CO_2, 0.3413; H_2O, 0.0822. Calc. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.88. Found: C, 60.83; H, 5.96.

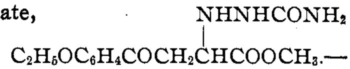
This analysis indicates that the substance is an hydroxy acid, and since the esters of both benzoylacrylic acid and *p*-methoxy-benzoylacrylic give α-hydroxy acids on hydrolysis it is probable that this acid also has the hydroxyl group in the alpha position.

Hydrolysis of the yellow methyl ester with concd. hydrochloric acid is a very slow reaction; 60% of the quantity used was recovered after standing in contact with the acid for 24 days, but in twice that length of time the hydrolysis was complete. The only product isolated was the unsaturated acid. The colorless methyl ester was changed to its yellow isomer both on boiling it with dil. hydrochloric acid (1:4) and on leaving it covered with concd. hydrochloric acid for several weeks; the unsaturated acid was the only product of hydrolysis with concd. acid, but with boiling dil. acid the α-hydroxy acid was also formed.

The unsaturated acid can be changed into the α-hydroxy acid by boiling with dil. hydrochloric acid but the reaction is not complete even after the boiling has been continued for ten hours.

Reaction between the Colorless Esters and Semicarbazide

α-Semicarbazido-methyl-*p*-ethoxy-benzoylacrylate,

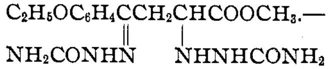


$$C_2H_5OC_6H_4COCH_2\overset{\overset{\displaystyle NHNHCONH_2}{|}}{C}HCOOCH_3$$

—One g. of colorless methyl ester was dissolved in 75 cc. of methyl alcohol and the solution treated with two molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate. After the reaction had proceeded for 15 hours the solid was removed and the filtrate allowed to evaporate to dryness. The solid (1.1 g.) was recrystallized from methyl alcohol, in which it is sparingly soluble; it separates as a colorless powder melting at 169°. It can also be recrystallized from acetone and from a mixture of glacial acetic acid and water.

Anal. Subs., 0.1500: CO_2, 0.2998; H_2O, 0.0840. Calc. for $C_{14}H_{19}O_5N_3$: C, 54.36; H, 6.14. Found: C, 54.50; H, 6.22.

Semicarbazone of α-Semicarbazido-methyl-*p*-ethoxy-benzoylacrylate,



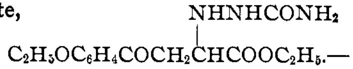
$C_2H_5OC_6H_4\underset{\underset{NH_2CONHN}{\|}}{C}CH_2\underset{\underset{NHNHCONH_2}{|}}{C}HCOOCH_3$.—

The residue left on evaporation of the filtrate was extracted with water to remove inorganic material and the sticky, semi-solid treated with methyl alcohol which precipitated a white solid. This was purified by recrystallization from acetone from which it separates as a chalk-white powder melting at 176° with evolution of gas; 0.2 g. was separated.

Anal. Subs., 0.1362: CO_2, 0.2464; H_2O, 0.0725. Calc. for $C_{15}H_{22}O_5N_6$: C, 49.18; H, 6.01. Found: C, 49.33; H, 5.91.

When the reaction was carried out with one molecular equivalent of semicarbazide the sole product was α-semicarbazido-methyl-*p*-ethoxy-benzoylacrylate. The semicarbazone of the addition product (176°) can also be obtained by treating the addition product (169°) directly with semicarbazide, and it can be hydrolyzed with concd. hydrochloric acid to give the addition product (169°).

α-Semicarbazido-ethyl-*p*-ethoxy-benzoylacrylate,

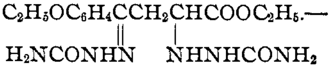


$C_2H_5OC_6H_4COCH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCOOC_2H_5$.—

One g. of liquid ethyl ester was dissolved in alcohol and treated with semicarbazide; the mixture was left overnight and the solid removed and purified by recrystallization from alcohol; it is a crystalline powder melting at 154°; yield, 0.65 g.

Anal. Subs., 0.1477: CO_2, 0.3027; H_2O, 0.0861. Calc. for $C_{15}H_{21}O_5N_3$: C, 55.72; H, 6.50. Found: C, 55.89; H, 6.47.

Semicarbazone of α-Semicarbazido-ethyl-*p*-ethoxy-benzoylacrylate,



$C_2H_5OC_6H_4\underset{\underset{H_2NCONHN}{\|}}{C}CH_2\underset{\underset{NHNHCONH_2}{|}}{C}HCOOC_2H_5$.—

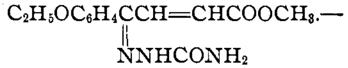
The filtrate left after removal of the solid (154°)was allowed to evaporate to dryness; the residue was treated with water, the solid was filtered off, washed and dried and then washed with alcohol, which removed a small quantity of the solid (154°) and left behind the second product of the reaction which was freed from impurity by warming in acetone in which it is only very slightly soluble and then recrystallizing it from alcohol; it separates as a fine, white powder melting at 183° with evolution of gas.

Anal. Subs., 0.1496: CO_2, 0.2805; H_2O, 0.0875. Calc. for $C_{16}H_{24}O_5N_6$: C, 50.52; H, 6.31. Found: C, 51.13; H, 6.49.

This substance is also obtained on treatment of the semicarbazido addition product with semicarbazide; it is hydrolyzed by hydrochloric acid with the formation of the addition product (154°).

Reaction between the Yellow Esters and Semicarbazide

Isomeric Semicarbazones of Methyl *p*-Ethoxy-benzoylacrylate,



$C_2H_5OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH{=}CHCOOCH_3$.—

The reaction between semicarbazide and the yellow methyl ester was carried out in the way described in the case of the colorless methyl ester. The colorless solid, which began to separate almost as soon as the solutions were mixed, was filtered off after the reaction had been allowed to proceed for 20 hours. A mixed melting point showed that it was the addition product (169°) obtained from the colorless ester. When water was added to the filtrate a solid separated with approximately the same melting point as this substance but the mixture of the two melted at 155–160°. After several recrystallizations from methyl alcohol the second product, fine, very pale yellow needles, melted at 173°. It is the semicarbazone of the unsaturated ester.

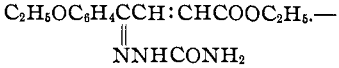
Anal. Subs., 0.1393: CO_2, 0.2937; H_2O, 0.0723. Calc. for $C_{14}H_{17}O_4N_3$: C, 57.73; H, 5.84. Found: C, 57.50; H, 5.76.

On complete evaporation of the aqueous filtrate and extraction of the residue with water a small quantity of solid, melting at 120–125° with evolution of gas, was isolated and finally identified as the semicarbazone of the addition product (176°) obtained in the reaction with the colorless ester. The substance on recrystallization from methyl alcohol melts at 120–125° with evolution of gas, and on boiling this solid with acetone the substance (176° with evolution of gas) is obtained. It is possible that the lower-melting solid holds methyl alcohol.

The reaction with the yellow methyl ester and semicarbazide was carried out several times using various quantities of reagent and of solvent. The mixtures obtained when the volume of methyl alcohol was sufficient to keep the addition product (169°) in solution were separated only after laborious fractional crystallization. A fourth product, the isomeric semicarbazone of the ester, melting at 149°, was invariably obtained when the volume of methyl alcohol was large and the yield of the addition product small. This substance can be separated from the mixture by extracting it with cold methyl alcohol; the residue from the evaporation of methyl alcohol, on dissolving in hot glacial acetic acid with the addition of water, deposits firm, colorless crystals that are pure after one recrystallization from methyl alcohol.

Anal. Subs., 0.1485: CO_2, 0.3146; H_2O, 0.0792. Calc. for $C_{14}H_{17}O_4N_3$: C, 57.73; H, 5.84. Found: C, 57.77; H, 5.92.

Isomeric Semicarbazones of Ethyl *p*-Ethoxy-benzoylacrylate,



$$C_2H_5OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH{:}CHCOOC_2H_5.—$$

When the reaction between the yellow ethyl ester and semicarbazide was carried out in the usual way with sufficient alcohol to keep the ester in solution the mixture of the four substances formed was separated only after repeated recrystallizations with the use of various solvents. Three of these products can be isolated with comparative ease if the quantity of solvent is small and the ester, precipitated from its alcohol solution when the aqueous solution is added, dissolves gradually as the reaction proceeds. The first substance to separate is the addition product (154°) which was filtered off and identified as the product obtained in the reaction with the isomeric ethyl ester. When the yellow oil which was precipitated on addition of water to the filtrate was dissolved in hot glacial acetic acid with addition of water, the solution deposited firm, shining plates which were pure and melted at 155° after one recrystallization from acetone.

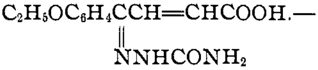
Anal. Subs., 0.1495: CO_2, 0.3227; H_2O, 0.0857. Calc. for $C_{15}H_{19}O_4N_3$: C, 59.01; H, 6.22. Found: C, 58.86; H. 6.36.

The isomeric semicarbazone was isolated from the residue, from the complete evaporation of the aqueous filtrate, by taking advantage of the fact that it is more soluble in alcohol than the addition product which is mixed with it. It crystallizes from alcohol in fine, pale yellow needles melting at 140°.

Anal. Subs., 0.1390: CO_2, 0.3022; H_2O, 0.0781. Calc. for $C_{15}H_{19}O_4N_3$: C, 59.01; H, 6.22. Found: C, 59.29; H, 6.24.

The fourth product, the semicarbazone of α-semicarbazido-ethyl-*p*-ethoxy-benzoylacrylate, was always obtained in the reaction with the yellow ethyl ester when the solid (154°) remained in solution in the quantity of alcohol used and could be separated by taking advantage of the fact that it is not soluble in acetone.

Semicarbazone of *p*-Ethoxy-benzoylacrylic Acid,



$C_2H_5OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH{=}CHCOOH$.—The semicarbazone of the unsaturated acid was prepared by treating a methyl alcohol solution of the acid with semicarbazide. After the mixture had stood for two hours, the product was filtered off, washed with water and methyl alcohol and dried. It melted at 212° with decomposition.

Anal. Subs., 0.1503: CO_2, 0.3107; H_2O, 0.0751. Calc. for $C_{13}H_{15}O_4N_3$: C, 56.31; H, 5.41. Found: C, 56.37; H, 5.55.

Summary

The yellow methyl and ethyl esters of *p*-ethoxy-benzoylacrylic acid isomerize when exposed to the sunlight both as solids and in benzene solution. The unstable, colorless esters thus formed are transformed quantitatively, both in the dark and in the sunlight when in benzene solutions containing a crystal of iodine, into the stable yellow isomers. Hydrochloric acid brings about the same change.

Hydrolysis of the esters has been studied. With semicarbazide the colorless isomers form addition products and semicarbazones of these addition products. The yellow isomers give in addition to these, two substances, namely, the isomeric semicarbazones; *p*-ethoxy-benzoylacrylic acid forms a semicarbazone. The behavior of the ethoxy compounds is like that of the corresponding methoxy compounds and different from that of benzoylacrylic acid and its esters.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME REDUCTION PRODUCTS OF 1-NITRO- AND 3-NITROCARBAZOLE

BY T. C. WHITNER, JR.

RECEIVED JUNE 6, 1924 PUBLISHED OCTOBER 4, 1924

It has been shown[1] that when carbazole is nitrated, using acetic acid as the solvent and keeping the temperature of the mixture at 80°, two mononitro compounds are formed; both are easily reduced to the corresponding amino compounds. Also the two nitro compounds can be easily separated due to their different solubilities in acetic acid, the 3-nitrocarbazole being relatively insoluble, while the 1-nitrocarbazole is much more soluble in this solvent. While this is the first mention of the 1-amino compound, the 3-amino derivative had previously been made from

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[1] Ziersch, *Ber.*, **42**, 3797 (1909).