[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE ISOMERIC ESTERS OF PARA-PHENOXY-BENZOYLACRYLIC ACID

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In a continuation[1] of the investigation of unsaturated ketonic acids it seemed of interest to study substances with a phenoxyl group in the molecule; for this purpose *p*-phenoxy-benzoylacrylic acid and its methyl and ethyl esters have been prepared.

The stable yellow esters are transformed into their corresponding colorless, lower-melting, unstable isomers when their benzene or ether solutions are exposed to the sunlight. The transformation of the colorless to the yellow isomers takes place very rapidly in a benzene solution containing iodine and also in contact with concd. hydrochloric acid. The behavior of the yellow methyl and ethyl esters when exposed to the sunlight as solids, however, is different; the ethyl ester, like all the ethyl esters of this series studied, melts in the sunlight and turns slowly to the colorless isomer but the methyl ester shows a remarkably rapid change of color from yellow to white with the formation of a polymeric substance which behaves like the polymer of yellow methyl *p*-methoxy-benzoylacrylate formed under the same conditions but much more slowly. A further study of the polymer of the phenoxy ester can be included conveniently in a later study of the polymeric acids and esters obtained from the *p*-methoxy substituted substances.

Though *p*-methoxy-benzoylacrylic acid shows the greatest ease of polymerization, the *p*-phenoxy acid does not polymerize in the sunlight; this was contrary to expectation after it was found that the methyl ester of the *p*-phenoxy acid shows a more rapid polymerization than the methyl ester of the *p*-methoxy acid. Of the four unsaturated ketonic acids studied, that with a *p*-methoxy group, then, is the only one which forms a polymer. In spite of the fact that it has not been possible to isolate the unstable form of benzoylacrylic acid or of its methoxy and ethoxy substitution products, it was hoped that it might be possible to isolate unstable *p*-phenoxy-benzoylacrylic acid, but attempts to prepare it have been unsuccessful.

The unstable ethyl ester of the *p*-phenoxy acid, like the unstable ethyl ester of the *p*-ethoxy acid, is a liquid. In order to prove the isomerism it has been shown that the two isomers give different products on treatment with semicarbazide. The colorless ethyl ester, like the colorless methyl ester, gives an α-semicarbazido addition product, whereas both yellow esters give, along with the addition products, isomeric semicarbazones.

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[1] Rice, THIS JOURNAL, **45**, 222 (1923); **46**, 214, 2319 (1924).

The semicarbazones of the α-semicarbazido compounds are not formed in any of the reactions with the esters of *p*-phenoxy-benzoylacrylic acid and semicarbazide; otherwise the respective products correspond to those obtained with the esters of both the methoxy and ethoxy acids.

Experimental Part

***p*-Phenoxy-benzoylpropionic Acid** was prepared from diphenyl ether and succinic anhydride by the Friedel and Crafts reaction.[2] A mixture of finely powdered anhydrous aluminum chloride, 114 g., and succinic anhydride, 76 g., was added gradually to a carbon disulfide solution of diphenyl ether, 132 g.; after the violence of the reaction had subsided the product was warmed for three hours with hot water, the carbon disulfide removed and the red addition product decomposed with ice water. The colorless solid was filtered off by suction, washed thoroughly with water and allowed to dry. After one recrystallization from toluene, 119.2 g. of chalk-white acid melting at 118–119° was separated; yield, 58%.

Methyl *p*-Phenoxy-benzoylpropionate, $C_6H_5OC_6H_4COCH_2CH_2CO_2CH_3$.—The methyl ester was obtained as a liquid by heating its methyl alcoholic solution containing concd. sulfuric acid; on standing for several weeks the product, which distilled at 252° (16 mm.), turned to a solid; m. p., 59°. This solid separated when a methyl alcoholic solution of the acid was saturated with dry hydrogen chloride; yield, 91%.

Anal. Subs., 0.1868: CO_2, 0.4940; H_2O, 0.0970. Calcd. for $C_{17}H_{16}O_4$: C, 71.83; H, 5.63. Found: C, 72.12; H, 5.76.

Ethyl *p*-Phenoxy-benzoylpropionate, $C_6H_5OC_6H_4COCH_2CH_2CO_2C_2H_5$.—The ethyl ester obtained by both methods of preparation was a colorless liquid boiling at 255° (15 mm.).

Anal. Subs., 0.1619: CO_2, 0.4297; H_2O, 0.0887. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.38; H, 6.08.

The yellow methyl and ethyl esters of *p*-phenoxy-benzoylacrylic acid were prepared by bromination of the corresponding saturated esters and elimination of hydrogen bromide from these bromo esters.[1]

Methyl *p*-Phenoxy-benzoylacrylate, $C_6H_5OC_6H_4COCH:CHCO_2CH_3$.—The ester crystallized as its methyl alcohol solution cooled; it was washed free of potassium bromide with ice water and purified by two recrystallizations from methyl alcohol; yield, 84.5%. The firm, yellow needles melt at 93° and are soluble in ether, carbon disulfide, benzene, chloroform and boiling methyl alcohol.

Anal. Subs., 0.1623: CO_2, 0.4316; H_2O, 0.0741. Calcd. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96. Found: C, 72.52; H, 5.07.

Ethyl *p*-Phenoxy-benzoylacrylate, $C_6H_5OC_6H_4COCH:CHCO_2C_2H_5$.—The crude solid was washed with ice water, dried and recrystallized from alcohol; yield, 74%. The yellow needles melting at 46° are readily soluble in benzene, ether and hot alcohol, less so in petroleum ether from which they separate in large, well-formed crystals.

Anal. Subs., 0.1556: CO_2, 0.4167; H_2O, 0.0777. Calcd. for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 73.03; H, 5.54.

Methyl *p*-phenoxy-benzoylacrylate does not give a solid dibromo addition product but the ethyl ester reacts with bromine with the formation of a solid melting at 78° with evolution of gas.

Anal. Subs., 0.1577: CO_2, 0.2757; H_2O, 0.0513. Calcd. for $C_{18}H_{16}O_4Br_2$: C, 47.37; H, 3.51. Found: C, 47.68; H, 3.61.

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[2] Kipper, *Ber.*, **38**, 2491 (1905).

***p*-Phenoxy-benzoylacrylic Acid**, $C_6H_5OC_6H_4COCH:CHCO_2H$.—The acid was prepared by the Friedel and Crafts reaction from maleic anhydride[3] and diphenyl ether. After the rapid evolution of hydrogen chloride had ceased, the product was heated for two hours, the red solid decomposed with ice water and the mixture freed from carbon disulfide and diphenyl ether by distillation with steam. The yellow unsaturated acid was purified by recrystallization from benzene from which it separated in fine, powdery needles melting at 121°. It is readily soluble in ether, alcohol, chloroform and glacial acetic acid, sparingly soluble in boiling water; yield, 25.5%.

Anal. Subs., 0.2231: CO_2, 0.5834; H_2O, 0.0913. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.47. Found: C, 71.31; H, 4.54.

The unsaturated acid was also prepared by bromination of the saturated acid in glacial acetic acid solution and elimination of hydrogen bromide from the bromo acid; yield of pure acid 76%.

p-Phenoxy-benzoylacrylic acid, like *p*-methoxy-benzoylacrylic acid, gives different stereoisomeric dibromo addition products depending upon the solvent used. A glacial acetic acid solution of the unsaturated acid, cooled in ice, was treated with bromine; the solid left on evaporation of the solvent, after washing with 50% acetic acid, melted at 156° with decomposition. It is very readily soluble in the usual organic solvents; as recrystallization lowers its melting point, the crude solid was used for analysis.

Anal. Subs., 0.1546: CO_2, 0.2516; H_2O, 0.0409. Calcd. for $C_{16}H_{12}O_4Br_2$: C, 44.86; H, 2.80. Found: C, 44.38; H, 2.93.

When the unsaturated acid was brominated in chloroform solution, a solid was obtained which melted at 116–119° with decomposition after the crude product had been washed with 50% acetic acid; a mixture of the two isomers melted at 125–140°.

Anal. Subs., 0.1715: CO_2, 0.2807; H_2O, 0.0468. Calcd. for $C_{16}H_{12}O_4Br_2$: C, 44.86; H, 2.80. Found: C, 44.63; H, 3.03.

Colorless **Methyl *p*-Phenoxy-benzoylacrylate**, $C_6H_5OC_6H_4COCH:CHCO_2CH_3$.—A saturated benzene solution of 3.5 g. of yellow methyl *p*-phenoxy-benzoylacrylate was exposed for three weeks to intermittent winter sunlight until the yellow color had disappeared; on spontaneous evaporation of the solvent, a colorless solid was left which melted at 83° after several recrystallizations from methyl alcohol; yield, 96%. It separates from petroleum ether in large, transparent needles and is very readily soluble in the common organic solvents.

Anal. Subs., 0.1602: CO_2, 0.4240; H_2O, 0.0723. Calcd. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96. Found: C, 72.18; H, 5.01.

The change from the yellow to the colorless isomer takes place to a limited extent only, when a dilute benzene solution (1 g. in 100 cc. of benzene) is exposed to the sunlight. The colorless ester is transformed completely into the yellow isomer in benzene solution holding a trace of iodine and, like the yellow ester, it does not form a solid dibromo addition product.

When the powdered yellow ester (15 g.) is exposed to the sunlight in a thin layer an astonishingly rapid change of color takes place with the formation of a polymeric substance. After 18 hours of exposure to the sunlight the solid was removed from the tray, washed with methyl alcohol and recrystallized from a mixture of chloroform and methyl alcohol; fine, colorless needles melting at 167° separated; yield, 88%.

Anal. Subs., 0.1526: CO_2, 0.4042; H_2O, 0.0707. Subs., 0.3593, 0.6445: $CHCl_3$, 65.6, 65.6; ΔTB, 0.035°, 0.062°. Calcd. for $C_{34}H_{28}O_8$: C, 72.34; H, 4.96; mol. wt., 564. Found: C, 72.23; H, 5.14; mol. wt., 561, 568.

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[3] Terry and Eichelberger, THIS JOURNAL, **47**, 1076 (1925).

Colorless Ethyl *p*-Phenoxy-benzoylacrylate, $C_6H_5OC_6H_4COCH{:}CHCO_2C_2H_5$.—The yellow ethyl ester isomerizes when exposed to the sunlight in benzene and absolute ether solution; the isomer is a liquid which could not be induced to crystallize. After exposure of the ether solution until it was colorless, the ether was removed with dry air and the liquid analyzed.

Anal. Subs., 0.1563: CO_2, 0.4173; H_2O, 0.0780. Calcd. for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 72.81; H, 5.54.

The isomer is also formed when the powdered yellow ester is exposed to the sunlight. That the liquid separated in both these reactions is an isomer was indicated by its behavior with semicarbazide[4] and by the fact that it is changed rapidly and completely into the yellow ester melting at 46° when its benzene solution is allowed to stand with a crystal of iodine.

p-Phenoxy-benzoylacrylic acid in benzene solution was exposed to the sunlight for four weeks but no change in color of the solution took place nor could any substance be separated except the unchanged unsaturated acid. When the powdered yellow acid was exposed for three weeks during the cold weather, there was no evidence of change but decomposition, with the appearance of a carrot-colored layer on the surface of the acid, resulted when the solid was left in the sunlight in hot weather.

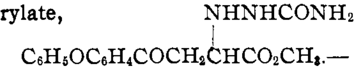
In marked contrast to the behavior of the other esters of the series, the esters of *p*-phenoxy-benzoylacrylic acid are not hydrolyzed by 10% sodium carbonate solution with the formation of the yellow unsaturated acid.

With concd. hydrochloric acid the colorless methyl ester, like the colorless methyl ester of *p*-ethoxy-benzoylacrylic acid, is changed into its isomer but the reaction is a much more rapid one; on contact with the acid the color of the ester begins to change at once and at the end of three hours the transformation is complete resulting in a quantitative separation of yellow isomeric ester.

Acid hydrolysis of the yellow phenoxy esters results in the formation of products analogous to those obtained with the other esters studied but the reactions are much slower and much less complete. After the mixture had boiled for three hours with dil. hydrochloric acid (1:4) 90% of ester was recovered and only traces of *p*-phenoxy-benzoylacrylic acid and a saturated acid were obtained; a very small quantity of this saturated acid, together with unsaturated acid, was formed on boiling the yellow ester for three hours with concd. hydrochloric acid but in this reaction, too, hydrolysis was not complete. Since the properties of the second acid indicated that it was probably α-hydroxy-*p*-phenoxy-benzoylpropionic acid, an attempt was made to prepare it by the method used for the preparation of the hydroxy acids of benzoyl and substituted benzoylpropionic acids; but after boiling 4 g. of *p*-phenoxy-benzoylacrylic acid for 30 hours with dil. hydrochloric acid (1:4) only 0.2 g. of the impure saturated acid could be separated and the unsaturated acid turned black and could not be recovered pure. Change of concentration of the hydrochloric acid gave no better results. Analysis indicates that the substance is an hydroxy acid and since benzoylacrylic acid and its methoxy derivative give α-hydroxy acids when boiled with dil. hydrochloric acid, this substance is probably α-hydroxy-*p*-phenoxy-benzoylpropionic acid. It is readily soluble in alcohol, ether, chloroform and warm water and was purified by recrystallization from a mixture of chloroform and petroleum ether; m. p. of colorless needles, 120°.

Anal. Subs., 0.1502: CO_2, 0.3660; H_2O, 0.0670. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 66.45; H, 4.95.

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



$C_6H_5OC_6H_4COCH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCO_2CH_3$.—

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[4] See p. 274 of this article.

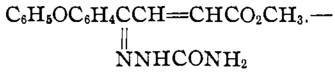
Colorless methyl *p*-phenoxy-benzoylacrylate, dissolved in methyl alcohol, was treated with two molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate. After the reaction had proceeded for several hours, the solid which began to form almost at once was filtered by suction, washed and dried. It can be recrystallized by long boiling in methyl alcohol but it is only slightly soluble and recrystallization is not necessary if the dry solid is washed thoroughly with warm methyl alcohol; it is left as a white crystalline powder melting at 184° and is insoluble in the usual organic solvents.

Anal. Subs., 0.1576: CO_2, 0.3499; H_2O, 0.0755. Calcd. for $C_{18}H_{19}O_5N_3$: C, 60.50; H, 5.32. Found: C, 60.55; H, 5.32.

No solid product could be separated when the filtrate, left after removal of this substance, was poured into water. The reaction was repeated using one molecular equivalent of reagent and though it is not as clean a reaction as when two molecular equivalents of reagent are used, the only product isolated was the substance just described.

α-Semicarbazido-methyl-*p*-phenoxy-benzoylacrylate was also obtained in 87% yield when yellow methyl *p*-phenoxy-benzoylacrylate was treated with two molecular equivalents of semicarbazide; in this reaction, too, it was the sole product isolated.

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



$C_6H_5OC_6H_4\underset{\overset{\|}{NNHCONH_2}}{C}CH{=}CHCO_2CH_3$.—

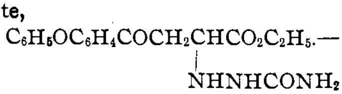
Isomeric semicarbazones are formed as the chief products of the reaction when the yellow methyl ester is treated with one molecular equivalent of semicarbazide. Along with these a quantity of the substance melting at 184° is formed but it can be kept small by increasing the volume of methyl alcohol used as a solvent for the ester, and this small amount can be readily isolated by taking advantage of its insolubility in methyl alcohol and ether. The separation of the semicarbazones was made difficult by the presence of some unused ester which invariably crystallized with them. The crude product of the reaction was treated with cold methyl alcohol which left most of the α-semicarbazido product as a solid; the first crop of crystals to separate from the solution was chiefly one of the isomeric semicarbazones which was purified by recrystallization from methyl alcohol. It separated with methyl alcohol of crystallization in the form of faintly yellow crystals softening at 75° and melting at 141°. On boiling the crystals with ether, they change to an almost colorless powder which melts sharply at 141°.

Anal. Subs., 0.1548: CO_2, 0.3597; H_2O, 0.0706. Calcd. for $C_{18}H_{17}O_4N_3$: C, 63.71; H, 5.01. Found: C, 63.37; H, 5.06.

The second crop of crystals which separated from the methyl alcoholic solution was chiefly a mixture of unused ester and a trace of α-semicarbazido compound; the residue contained the second semicarbazone which was deposited as a solid when the residue was dissolved in ether. On recrystallization from methyl alcohol heavy, transparent crystals softening at 75° and melting at 150° were formed; they turned to a colorless powder, melting at 150° when they were boiled with ether, and the same transparent crystals separated again when the powder was dissolved in methyl alcohol.

Anal. Subs., 0.0834: CO_2, 0.1940; H_2O, 0.0394. Calcd. for $C_{18}H_{17}O_4N_3$: C, 63.71; H, 5.01. Found: C, 63.44; H, 5.24.

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

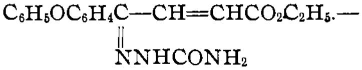


$C_6H_5OC_6H_4COCH_2\underset{\overset{|}{NHNHCONH_2}}{C}HCO_2C_2H_5$.—

The reaction between colorless ethyl *p*-phenoxy-benzoylacrylate and semicarbazide was carried out in the way described in the case of the colorless methyl ester, using a portion of the product made by exposing the absolute ether solution of the yellow ethyl ester. The sole product was a fine, white crystalline powder melting at 178° and insoluble in the common organic solvents. The reaction was repeated with a specimen of colorless ester made by exposure of the solid yellow ester and in this case also the substance melting at 178° was the only product isolated. Again, it was the sole product in the reaction with the yellow ethyl ester and two molecular equivalents of semicarbazide.

Anal. Subs., 0.1606: CO_2, 0.3625; H_2O, 0.0852. Calcd. for $C_{19}H_{21}O_5N_3$: C, 61.45; H, 5.66. Found: C, 61.55; H, 5.89.

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



$C_6H_5OC_6H_4\underset{\substack{\| \\ NNHCONH_2}}{C}—CH{=}CHCO_2C_2H_5$.—

When the yellow ethyl ester was treated with one molecular equivalent of semicarbazide, isomeric semicarbazones were formed together with the α-semicarbazido compound; they were separated by laborious fractional crystallization using alcohol and ether as solvents. One isomer forms in fine colorless needles melting at 156°; the other in clumps of heavy, faintly-yellow needles melting at 85.

Anal. Subs. (156°), 0.1510: CO_2, 0.3578; H_2O, 0.0746. Calcd. for $C_{19}H_{19}O_4N_3$: C, 64.58; H, 5.38. Found: C, 64.62; H, 5.48.

Anal. Subs. (85°), 0.1649: CO_2, 0.3902; H_2O, 0.0825. Calcd. for $C_{19}H_{19}O_4N_3$: C, 64.58; H, 5.38. Found: C, 64.53; H, 5.55.

Summary

The stable yellow methyl and ethyl esters of *p*-phenoxy-benzoylacrylic acid are transformed on exposure to the sunlight in benzene and ether solution into the corresponding labile isomers. The reverse transformation takes place rapidly when the colorless isomers are dissolved in benzene containing iodine or in the presence of concd. hydrochloric acid.

The yellow methyl ester forms a polymer when exposed to the sunlight as a powdered solid; under the same conditions the yellow ethyl ester gradually turns to a liquid and isomerizes. *p*-Phenoxy-benzoylacrylic acid forms neither a polymer nor an isomer.

Hydrolysis of the esters and their reactions with semicarbazide have been studied.

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