advantage over chemical methods of applicability in the direct determination of the dyes in the presence of many other dyes.

The spectroscopy of the sodium salts of the indigotin sulfonic acids is unquestionably closely analogous to that of the potassium salts. In the spectrophotometric evaluation of technical indigotin various anomalies are encountered which may be attributed in part to the presence of varying quantities of monosulfonate. Comprehensive data on the absorption of the pure dye throughout the visible spectrum, obtained with particular consideration to the practical requirements of the analysis of mixtures of food dyes, are in course of preparation by H. Wales of the Color Laboratory.

Summary

The absorption of the pure potassium salts of the sulfonated indigotins in the visible spectrum has been measured under a variety of conditions.

Data are supplied for their spectrophotometric identification and evaluation.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE ISOMERIC ESTERS OF PARA-METHOXY-BENZOYLACRYLIC ACID

BY GRACE POTTER RICE

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In a recent communication[1] the transformation in the sunlight of the yellow methyl and ethyl esters of benzoylacrylic acid into the corresponding colorless isomers and the reactions of these esters were described; in a continuation of the investigation of unsaturated ketonic esters the isomeric methyl and ethyl esters of the *p*-methoxy derivative of benzoylacrylic acid have now been prepared and studied. It has been found that the stable yellow esters when exposed to the sunlight in benzene solution are changed into colorless isomers and that the reverse transformation of the colorless into the yellow esters is brought about by exposing solutions of the colorless solids containing a crystal of iodine to the sunlight. The yellow esters of *p*-methoxy-benzoylacrylic acid, like those of the unsubstituted acid, are doubtless the stable forms; as is usually the case with stereo-isomers of this type, the stable methyl *p*-methoxy-benzoylacrylate has the higher melting point, but the reverse is true with ethyl *p*-methoxy-benzoylacrylate whose labile form melts 4° higher than its isomer. The behavior of the two yellow esters when exposed to the sunlight in the solid state is very different; the ethyl ester, like the two esters of benzoylacrylic acid, liquefies in the sunlight and is transformed into its colorless isomer. The methyl ester, with its melting point of 72°, does not liquefy when

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[1] THIS JOURNAL, 45, 222 (1923).

exposed to the sunlight, but the powdered crystalline solid shows a very rapid change to a colorless product which is a polymeric ester and probably a cyclobutane derivative.[2]

p-Methoxy-benzoylacrylic acid also is transformed in the sunlight into a polymeric acid. In this investigation a number of polymeric esters and acids have been isolated and the study of these isomeric substances is being continued in the hope of throwing some light on their configurations. In view of the recent publications of Stobbe,[3] Stoermer[4] and de Jong[5] on the truxinic and truxillic acids, these substances with the possibility for isomerism the same as in the truxinic and truxillic acid series, are of particular interest.

The yellow unsaturated esters are much more readily saponified by sodium carbonate than their colorless isomers; all give the same product, *p*-methoxy-benzoylacrylic acid. With cold concd. hydrochloric acid and with boiling dil. acid the yellow and the colorless esters give a mixture of unsaturated acid and α-hydroxy-*p*-methoxy-benzoylpropionic acid: $CH_3OC_6H_4COCH:CHCOOR \longrightarrow CH_3OC_6H_4COCH:CHCOOH + CH_3OC_6H_4COCH_2C(OH)HCOOH$. In all these saponification reactions there was a separation of a small quantity of the same polymeric acid as that obtained by the action of sunlight on *p*-methoxy-benzoylacrylic acid; apparently polymerization of the unsaturated acid takes place very easily.

The esters of *p*-methoxy-benzoylacrylic acid do not behave in the same way as the esters of the unsubstituted acid on treatment with semicarbazide.[6]

In the reaction between the yellow esters of *p*-methoxy-benzoylacrylic acid and one molecular equivalent of reagent, mixtures of isomeric semicarbazones were formed together with the semicarbazide addition products, and in the reaction with two molecular equivalents of semicarbazide these same substances were formed and also the semicarbazones of the addition products; the semicarbazido-semicarbazones are hydrolyzed by concd. hydrochloric acid to give the semicarbazide addition products which, in turn, react with a molecule of semicarbazide to give the semicarbazido-

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[2] Riiber, *Ber.*, **35**, 2411, 2908 (1902). Ruhemann, *J. Chem. Soc.*, **85**, 1453 (1904). Macleod, *Am. Chem. J.*, **44**, 331 (1910). Reimer, *ibid.*, **45**, 417 (1911). Stobbe and Rücker, *Ber.*, **44**, 869 (1911). Stobbe, *Ber.*, **45**, 3396 (1912). Riiber, *Ber.*, **46**, 335 (1913).

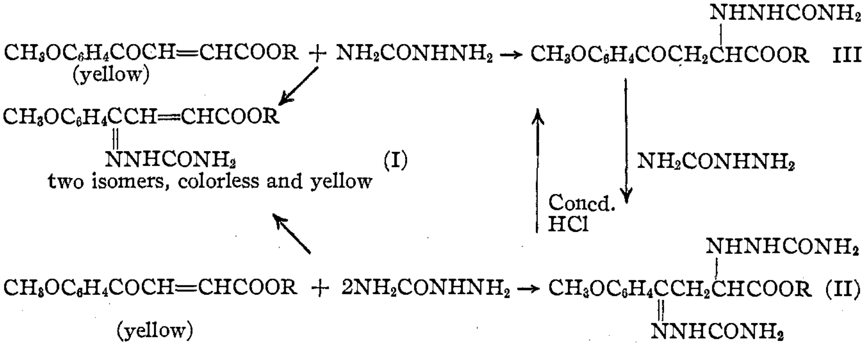
[3] Stobbe, *Ber.*, **52**, 666, 1021 (1919). Stobbe and Steinberger, *Ber.*, **55**, 2225 (1922). Stobbe and Zschoch, *Ber.*, **56**, 676 (1923).

[4] Stoermer and Foerster, *Ber.*, **52**, 1255 (1919). Stoermer and Emmel, *Ber.*, **53**, 497 (1920). Stoermer and Laage, *Ber.*, **54**, 77, 97 (1921). Stoermer and Scholtz, *Ber.*, **54**, 85 (1921). Stoermer and Bachér, *Ber.*, **55**, 1860 (1922). Stoermer, *Ber.*, **56**, 1683 (1923).

[5] de Jong, *Ber.*, **55**, 463 (1922); **56**, 818 (1923).

[6] Ref. 1, p. 223.

semicarbazones. The transformations are indicated in the following scheme.



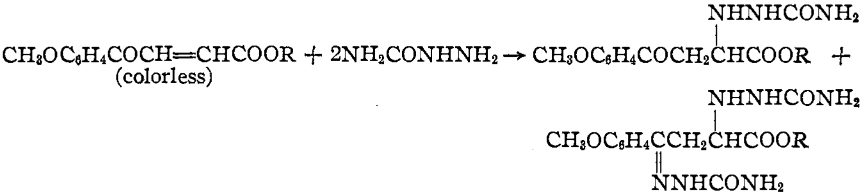
$$\underset{\text{(yellow)}}{CH_3OC_6H_4COCH{=}CHCOOR} + NH_2CONHNH_2 \rightarrow CH_3OC_6H_4COCH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCOOR \quad III$$

$$CH_3OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH{=}CHCOOR \quad (I)$$

$$\text{two isomers, colorless and yellow}$$

$$\underset{\text{(yellow)}}{CH_3OC_6H_4COCH{=}CHCOOR} + 2NH_2CONHNH_2 \rightarrow CH_3OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCOOR \quad (II)$$

The reaction between the colorless esters and one molecular equivalent of semicarbazide was not a clean one and the only substances isolated were the semicarbazide addition products; with two molecular equivalents of reagent a mixture of addition products and their semicarbazones was formed. No trace of isomeric semicarbazones was isolated in the reactions with the colorless esters.



$$\underset{\text{(colorless)}}{CH_3OC_6H_4COCH{=}CHCOOR} + 2NH_2CONHNH_2 \rightarrow CH_3OC_6H_4COCH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCOOR + CH_3OC_6H_4\underset{\underset{NNHCONH_2}{\|}}{C}CH_2\overset{\overset{NHNHCONH_2}{|}}{C}HCOOR$$

Experimental Part

The yellow methyl and ethyl esters of *p*-methoxy-benzoylacrylic acid were prepared from the corresponding esters of *p*-methoxy-benzoylpropionic acid[7] by the same transformations which were used in the preparation of the esters of benzoylacrylic acid.[8] Calculated from the succinic anhydride used, a 50% yield of pure unsaturated esters was obtained; this low figure is explained by the separation of only a 65% yield of crude *p*-methoxy-benzoylpropionic acid in the Friedel and Crafts reaction.

Methyl *p*-Methoxy-benzoylacrylate, $CH_3OC_6H_4COCH{=}CHCOOCH_3$.—The ester separated as a yellow solid when its methyl alcohol solution, obtained on elimination of hydrobromic acid from the saturated bromo ester, was poured onto ice. After four recrystallizations from methyl alcohol it melted at 71–72°. It separates in yellow needles which are soluble in ether, benzene, methyl and ethyl alcohols.

Analyses. Subs., 0.1525: CO_2, 0.3654; H_2O, 0.0715. Calc. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.34; H, 5.20.

Ethyl *p*-Methoxy-benzoylacrylate, $CH_3OC_6H_4COCH{=}CHCOOC_2H_5$.—This ester

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[7] Hahn, THIS JOURNAL, 38, 1533 (1916).

[8] Kohler and Engelbrecht, *ibid.*, 41, 764 (1919). Ref. 1, p. 233.

was purified by distillation under diminished pressure; the yellow liquid boiling at 210–215° (11 mm.) solidified as it cooled and formed large yellow crystals which melted at 42–43° after four recrystallizations from ethyl alcohol. It is very soluble in methyl and ethyl alcohols, ether, benzene, chloroform or acetone, very slightly soluble in ligroin.

Analyses. Subs., 0.1591: CO_2, 0.3868; H_2O, 0.0806. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.30; H, 5.63.

The two esters react in chloroform solution with bromine with the formation of solid dibromo addition products. In each case the residues, after evaporation of the solvent, solidified in contact with methyl alcohol; in the reaction with the methyl ester one substance was separated but in the reaction with the ethyl ester two stereo-isomers were isolated. The yields were quantitative. The three bromine compounds were recrystallized from warm methyl alcohol; the solid from the methyl ester melted at 115° and the isomeric bromo addition products of the ethyl ester at 51° and 66°, respectively.

Analyses. Subs. (115°), 0.1547: CO_2, 0.2159; H_2O, 0.0443. Calc. for $C_{12}H_{12}O_4Br_2$: C, 37.89; H, 3.15. Found: C, 38.06; H, 3.18.

Subs. (51°), 0.1512: CO_2, 0.2218; H_2O, 0.0479. Calc. for $C_{13}H_{14}O_4Br_2$: C, 39.59; H, 3.55. Found: C, 40.00; H, 3.52.

Subs. (66°), 0.1532: CO_2, 0.2212; H_2O, 0.0503. Calc. for $C_{13}H_{14}O_4Br_2$: C, 39.59; H, 3.55. Found: C, 39.37; H, 3.64.

Colorless Methyl *p*-Methoxy-benzoylacrylate, $CH_3OC_6H_4COCH=CHCOOCH_3$.—Two g. of yellow methyl *p*-methoxy-benzoylacrylate in benzene solution was exposed in a quartz test-tube to the sunlight for a week. The yellow color disappeared gradually and on evaporation of the benzene solution, firm, colorless crystals separated, which after two recrystallizations from methyl alcohol melted at 62°. The substance is very soluble in the usual organic solvents except ligroin; yield, 1.8 g. of pure product.

Analyses. Subs., 0.1533: CO_2, 0.3659; H_2O, 0.0708. Calc. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.10; H, 5.13.

When the colorless solid in solution in benzene or ether, in the presence of a crystal of iodine, is exposed for a day to sunlight it is changed completely into the yellow isomer. The rapid transformation of this colorless product into the yellow ester indicates that the two substances are stereo-isomers. In the dry state the colorless ester is stable in the sunlight; its melting point was not changed after four months of exposure. Both esters, when suspended in water, decolorize an aqueous solution of potassium permanganate very rapidly.

Colorless Ethyl *p*-Methoxy-benzoylacrylate, $CH_3OC_6H_4COCH=CHCOOC_2H_5$.—Two g. of yellow ethyl *p*-methoxy-benzoylacrylate in benzene solution was exposed in a quartz test-tube to the sunlight for eight days; 1.8 g. of pure, colorless product, melting at 46–47°, was separated. The substance is exceedingly soluble in all the common organic solvents; it can be purified most readily by dissolving it in a minimum quantity of ethyl alcohol and cooling the solution in ice, when the compound separates in small, shining plates.

Analyses. Subs., 0.1530: CO_2, 0.3733; H_2O, 0.0785. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.54; H, 5.70.

This ester is changed completely into the corresponding yellow ester when its benzene or ether solution, containing a crystal of iodine, is exposed to the sunlight for six hours, but, like the colorless methyl ester, it is stable to the light in the dry state.

Both the colorless esters in chloroform solution add bromine very readily but no solid bromine addition product could be separated in spite of the fact that the reaction was carried out several times under various conditions with each ester. In one reaction 30% of the colorless ester used was transformed into the corresponding yellow ester.

Saponification of the Esters of Para-Methoxy-Benzoylacrylic Acid

The yellow methyl ester was saponified by boiling for five minutes with dil. sodium carbonate solution, but more than half of the ester used was recovered unchanged; longer boiling brings about partial decomposition of the ester. On acidification of the alkaline solution a yellow acid separated which melted at 130–132° and, after purification, was identified as *p*-methoxy-benzoylacrylic acid, by comparison with specimens of this acid made from maleic anhydride and anisole by the Friedel and Crafts reaction and from *p*-methoxy-benzoylpropionic acid.[9]

α,β-Dibromo-*p*-methoxy-benzoylpropionic Acid, $CH_3OC_6H_4COCHBrCHBrCOOH$.—The reaction between the unsaturated acid and bromine was carried out in the usual way in chloroform as a solvent. The solid left after evaporation of the solvent was extracted with cold methyl alcohol, which deposited colorless crystals melting at 140°; the portion which failed to dissolve in methyl alcohol melted at 164° with evolution of gas and charring; the two substances are isomers. When the acid was brominated in glacial acetic acid the lower-melting isomer was the only substance formed; the crude solid was powdered and washed several times with dil. acetic acid (1:3); a quantitative yield of pure product was isolated. The solid (140°) is very soluble in glacial acetic acid, chloroform or methyl alcohol; the solid (164°) is soluble in warm methyl alcohol or glacial acetic acid or in boiling chloroform.

Analyses. Subs. (140°), 0.1496: CO_2, 0.1985; H_2O, 0.0386. Calc. for $C_{11}H_{10}O_4Br_2$: C, 36.06; H, 2.73. Found: C, 36.18; H, 2.86.

Subs. (164°), 0.1489: CO_2, 0.1976; H_2O, 0.0401. Calc. for $C_{11}H_{10}O_4Br_2$: C, 36.06; H, 2.73. Found: C, 36.19; H, 2.99.

Yellow methyl *p*-methoxy-benzoylacrylate is also saponified by boiling for ten hours with dil. hydrochloric acid (1:4), but a mixture of products results.

The first substance to separate from the solution is yellow *p*-methoxy-benzoylacrylic acid and the filtrate on standing deposits either fine, colorless needles which melt at 180°, or a mixture of these needles and the yellow unsaturated acid. The mixture was separated by fractional crystallization from water or by washing it with ether in which the acid (180°) is only slightly soluble.

Analyses. Subs. (180°), 0.1113: CO_2, 0.2609; H_2O, 0.0514. Subs., 0.2166, 0.3761: $(CH_3)_2CO$, 26.8, 26.8; ΔTB, 0.033°, 0.058°. Calc. for $C_{22}H_{20}O_8$: C, 64.07; H, 4.85; mol. wt., 412. Found: C, 63.93; H, 5.13; mol. wt., 418, 413.

A mixed melting point proved that this acid is the same substance that is obtained by the action of sunlight on *p*-methoxy-benzoylacrylic acid.

On complete evaporation of the filtrate from saponification a solid was left which was purified by recrystallization from chloroform. It melts at 122° and is very soluble in methyl and ethyl alcohols, in boiling water and hot chloroform.

Analyses. Subs., 0.1476: CO_2, 0.3184; H_2O, 0.0699. Calc. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.35. Found: C, 58.83; H, 5.26.

Analysis indicates that this substance is an hydroxy acid and since the esters of benzoylacrylic acid on treatment with concd. hydrochloric acid give α-hydroxy-benzoylpropionic acid[10] it is probable that the acid melting at 122° is α-hydroxy-*p*-methoxy-benzoylpropionic acid, $CH_3OC_6H_4COCH_2C(OH)HCOOH$. For purposes of comparison β-hydroxy-*p*-methoxy-benzoylpropionic acid, $CH_3OC_6H_4COC(OH)H{-}CH_2COOH$ was prepared in a way analogous to that used in the preparation of β-hydroxy-benzoyl-

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[9] Bougault, *Compt. rend.*, **146**, (a) 140, (b) 411 (1908); (c) *Ann. chim. phys.*, [8] **15**, 491 (1908).

[10] Ref. 1, p. 229.

propionic acid;[11] *p*-methoxy-benzoylpropionic acid was brominated in chloroform in the usual way and the purified bromo acid[12] melting at 114° was shaken in a machine for 5 hours with a 10% sodium carbonate solution and the product cooled in ice and acidified. On the addition of ether to this solution in a separatory funnel crystals appeared which dissolved only after many extractions with ether. The acid can be purified readily by recrystallization from chloroform or water and separates in colorless needles which melt at 120–121°; yield, 50%. It is very soluble in methyl alcohol, water, boiling ether or chloroform. A mixture of this acid and the acid obtained on hydrolysis of the ester melts at 100–110°.

Analyses. Subs., 0.1528: CO_2, 0.3294; H_2O, 0.0716. Calc. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.35. Found: C, 58.79; H, 5.20.

The yellow methyl ester is saponified on standing in contact with concd. hydrochloric acid to give the same acids which are obtained when it is boiled with dil. acid, namely, the yellow unsaturated acid, the α-hydroxy acid and the acid melting at 180°.

The colorless ethyl ester is saponified by boiling with dil. sodium carbonate solution much more slowly than the yellow ester. Even after boiling for one hour, more than half the ester was recovered unchanged and on acidification of the carbonate solution a mixture of the acid melting at 180° and yellow *p*-methoxy-benzoylacrylic acid separated.

The colorless ester both on standing with cold concd. hydrochloric acid and when boiled with dil. hydrochloric acid behaved in the same way as the yellow ester and gave a mixture of unsaturated acid, α-hydroxy acid and the acid melting at 180°.

p-Methoxy-benzoylacrylic acid, in contact with concd. hydrochloric acid, is changed slowly into the acid melting at 180°, leaving only a trace of α-hydroxy acid, but when the unsaturated acid is boiled with dil. hydrochloric acid a 50% yield of α-hydroxy acid is obtained. The ease with which polymerization of the unsaturated acid takes place is remarkable.

Reaction between Yellow and Colorless Methyl Para-Methoxy-Benzoylacrylate and Semicarbazide

Isomeric Semicarbazones of Methyl *p*-Methoxy-benzoylacrylate, I.—Two g. of yellow ester, dissolved in methyl alcohol, was treated with a mixture of aqueous solutions of 1 g. of semicarbazide hydrochloride and 1 g. of sodium acetate, which is in the proportion of one molecule of ester to one of semicarbazide. After standing overnight the solution was poured onto a watch glass and left in a strong current of air until the methyl alcohol was partly evaporated. Water was added and the precipitated solid was filtered, washed, dried and dissolved in warm methyl alcohol; the first substance to separate, crystallized in fine yellow needles which were pure and melted at 165° after one recrystallization from methyl alcohol; the second substance to separate crystallized in colorless glistening plates melting at 178°. The filtrate contained a mixture of the two substances. After removal of the methyl alcohol the residue was dissolved in hot glacial acetic acid and warm water was added to the solution; pure solid (178°) crystallized, but by this treatment the yellow solid in the mixture was lost. The yield of crude product was quantitative.

Analyses. Subs. (165°), 0.1427: CO_2, 0.2954; H_2O, 0.0663. Calc. for $C_{13}H_{15}O_4N_3$: C, 56.31; H, 5.41. Found: C, 56.45; H, 5.16.

Subs. (178°), 0.1639, 0.1564: CO_2, 0.3357, 0.3208; H_2O, 0.0799, 0.0735. Calc. for $C_{13}H_{15}O_4N_3$: C, 56.31; H, 5.41. Found: C, 55.86, 55.94; H, 5.41, 5.22.

Neither of these substances reacts with semicarbazide.

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[11] (a) Fischer and Stewart, *Ber.*, **25**, 2560 (1892). (b) Ref. 1, p. 231.

[12] Ref. 9c.

After removal of the isomeric semicarbazones from the water-methyl alcohol solution, the latter was left to evaporate; 0.1 g. of a colorless solid melting at 161° was isolated and identified by a mixed melting point as the same substance which was formed when the ester was treated with excess of semicarbazide.

Semicarbazone of α-Semicarbazido-methyl-*p*-methoxy-benzoylpropionate, II.—Four g. of yellow methyl ester was dissolved in methyl alcohol and the solution treated with an aqueous solution of 2 molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate. After standing overnight the solution was poured into water and the solid was filtered, washed with water and dried; yield, 5.5 g. The crude product was boiled with methyl alcohol; a comparatively insoluble residue was recovered which was identical with the first substance to crystallize from the methyl alcohol solution; in all, 1.25 g. of this colorless powder melting at 178° with rapid evolution of gas, was obtained. It is not very soluble in organic solvents but can be recrystallized from methyl alcohol.

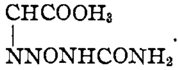
Analyses. Subs., 0.1466, 0.1520: CO_2, 0.2582, 0.2676; H_2O, 0.0738, 0.0791. Calc. for $C_{14}H_{20}O_5N_6$: C, 47.72; H, 5.68. Found: C, 48.03, 48.01; H, 5.59, 5.78.

α-Semicarbazido-methyl-*p*-methoxy-benzoylpropionate, III.—The methyl alcohol solution left after all the solid (m. p. 178° with evolution of gas) had been removed contained a mixture of colorless semicarbazone (178°) and the addition product of the ester and semicarbazide, which could not be separated with methyl alcohol as a solvent. Therefore, this was removed by evaporation and the solid was dissolved in boiling glacial acetic acid with addition of a little hot water; 1.4 g. of semicarbazone (178°) crystallized at once, and later a second crop of crystals formed which melted at 148–154°. By dissolving this mixture in methyl alcohol 0.8 g. of colorless solid melting at 161° was isolated.

Analyses. Subs., 0.1476: CO_2, 0.2861; H_2O, 0.0749. Calc. for $C_{13}H_{17}O_5N_3$: C, 52.88; H, 5.76. Found: C, 52.86, H, 5.63.

This substance was also obtained by treating the semicarbazone of α-semicarbazido-methyl-*p*-methoxy-benzoylpropionate with concd. hydrochloric acid. When the acid solution was diluted and neutralized with sodium carbonate a solid was precipitated which, after recrystallization from methyl alcohol, melted at 161–162°. It was identified by a mixed melting point as the same substance that was formed in the reaction with the ester and semicarbazide. The α-semicarbazido-methyl-*p*-methoxy-benzoylpropionate reacts with semicarbazide to give the semicarbazido-semicarbazone, melting at 178° with evolution of gas. The reaction was carried out in the usual way and the product was identified by comparison with a specimen obtained when the ester was treated with semicarbazide.

Nitroso-α-semicarbazido-methyl-*p*-methoxy-benzoylpropionate, $CH_3OC_6H_4COCH_2$-



$$\begin{array}{l}CHCOOH_3\\ |\\ NNONHCONH_2\end{array}$$

.—Five-tenths g. of solid melting at 161° was dissolved in concd. hydrochloric acid, the solution cooled in ice and treated with cold sodium nitrite solution until starch-potassium iodide paper showed a blue color. The solid was filtered, washed with water and dried; after extraction with methyl alcohol it melted sharply at 132° with evolution of gas.

Analyses. Subs., 0.1510: CO_2, 0.2677; H_2O, 0.0683. Calc. for $C_{13}H_{16}O_6N_4$: C, 48.15; H, 4.93. Found: C, 48.35; H, 5.02.

The reaction between the yellow methyl ester and two molecules of semicarbazide was carried out a second time under conditions as nearly as possible like those used the first time. Only a trace of the colorless semicarbazone was formed, but in its place a quantity of yellow semicarbazone, which was partially separated from the other substances by taking advantage of the fact that it is precipitated more quickly than they when the product of the reaction is poured into water. In two further experiments both semicarbazones were formed in varying quantities, but the conditions which favored the formation of one over the other could not be determined.

The reaction between the colorless methyl ester and two molecules of semicarbazide was carried out in the usual way. From 1 g. of ester 1 g. of crude product melting at 155–160° with evolution of gas was obtained. By fractional crystallization from methyl alcohol this mixture was finally separated into two substances, α-semicarbazido-methyl-*p*-methoxy-benzoylpropionate and the semicarbazido-semicarbazone. No trace of the isomeric semicarbazones was found.

Reaction between Yellow and Colorless Ethyl Para-Methoxy-Benzoylacrylate and Semicarbazide

Isomeric Semicarbazones of Ethyl *p*-Methoxy-benzoylacrylate, I.—Five g. of yellow ester was dissolved in alcohol and the solution treated with a mixture of aqueous solutions of 2.35 g. of semicarbazide hydrochloride and 2.5 g. of sodium acetate, which is in the proportion of one molecule of ester to one molecule of semicarbazide. The mixture was left overnight and then poured into water; the precipitated solid was filtered off, washed and dried. Its melting point indicated that it was not a pure substance. After laborious fractional crystallization, first with ethyl alcohol and then with a mixture of glacial acetic acid and water as solvents, 3 g. of pure product was isolated; of this 2.25 g. was colorless semicarbazone melting at 165°, and 0.25 g., its yellow isomer, melting at 124°. The higher-melting solid was much more readily purified than the lower-melting yellow isomer. By using glacial acetic acid and water the colorless isomer was separated in a pure state, but the yellow isomer was lost and in the other solvents and mixtures of solvents tried the two isomers crystallized together; 0.55 g. of this mixture was not separated.

Analyses. Subs. (124°), 0.1512: CO_2, 0.3194; H_2O, 0.0798. Calc. for $C_{14}H_{17}O_4N_3$: C, 57.73; H, 5.84. Found: C, 57.61; H, 5.86.

Subs. (165°), 0.1500: CO_2, 0.3182; H_2O, 0.0810. Calc. for $C_{14}H_{17}O_4N_3$: C, 57.73; H, 5.84. Found: C, 57.85; H, 6.00.

The third substance (0.5 g.) formed in this reaction melted at 173° and was identified as the same substance that was obtained in the reaction with the yellow ethyl ester and two molecules of semicarbazide.

Semicarbazone of α-Semicarbazido-ethyl-*p*-methoxy-benzoylpropionate, II.—Two g. of yellow ethyl ester, in alcohol solution, was treated with two molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate; 2.7 g. of crude material was precipitated by pouring the mixture into water. This was boiled with alcohol, which left an undissolved portion melting sharply at 182° with rapid evolution of gas; the alcohol solution deposited a further quantity of the same substance; 0.7 g. in all was obtained.

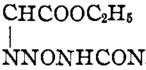
Analyses. Subs., 0.1495: CO_2, 0.2702; H_2O, 0.0814. Calc. for $C_{15}H_{22}O_5N_6$: C, 49.18; H, 6.01. Found: C, 49.29; H, 6.04.

α-Semicarbazido-ethyl-*p*-methoxy-benzoylpropionate, III.—The solid left after removal of the semicarbazido-semicarbazone is a mixture consisting of a small quantity of yellow semicarbazone melting at 124° but chiefly the colorless semicarbazone and the 1,4 addition product of the ester and semicarbazide. The substances were separated by use of ethyl alcohol and the addition product was finally obtained as a colorless, crystalline solid melting at 173°.

Analyses. Subs., 0.1508: CO_2, 0.3001; H_2O, 0.0801. Calc. for $C_{14}H_{19}O_5N_3$: C, 54.36; H, 6.14. Found: C, 54.27; H, 5.90.

It was also obtained by treating the semicarbazido-semicarbazone with concd. hydrochloric acid. On neutralizing the acid solution with sodium carbonate, a solid was precipitated which was identified by comparison with the substance obtained in the reaction with the ester and semicarbazide. This semicarbazide addition product, like the corresponding derivative of the methyl ester, reacts with semicarbazide to give the semicarbazido-semicarbazone.

Nitroso-α-semicarbazido-ethyl-*p*-methoxy-benzoylpropionate, $CH_3OC_6H_4COCH_2\text{-}$



$\underset{NNONHCONH_2}{\underset{|}{CHCOOC_2H_5}}$

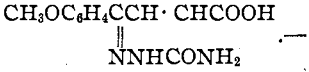
.—α-Semicarbazido-ethyl-*p*-methoxy-benzoylpropionate (0.55 g.) was dissolved in concd. hydrochloric acid and the ice-cold solution treated with cold sodium nitrite solution until starch-potassium iodide paper was colored blue. The solid was filtered off at once and washed thoroughly with water; after washing it with alcohol, 0.5 g. of colorless powder was left which melted at 124–125° with evolution of gas.

Analyses. Subs., 0.1567: CO_2, 0.2878; H_2O, 0.0741. Calc. for $C_{14}H_{18}O_6N_4$: C, 49.70; H, 5.32. Found: C, 50.08; H, 5.25.

Colorless ethyl-*p*-methoxy-benzoylacrylate (0.8 g.) was dissolved in alcohol and treated with 2 molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate. The crude product obtained was separated by the use of alcohol into two substances, the semicarbazido-semicarbazone melting at 182° with evolution of gas and the semicarbazide addition product melting at 173°. The isomeric semicarbazones were not formed. The reaction was also carried out between the colorless ester and one molecule of semicarbazide, and the only substance isolated was the semicarbazide addition product.

Reaction between Para-Methoxy-Benzoylacrylic Acid and Semicarbazide

Semicarbazone of *p*-Methoxy-benzoylacrylic Acid,



$CH_3OC_6H_4\underset{NNHCONH_2}{\underset{\|}{C}}CH\cdot CHCOOH$

.—The acid (0.7 g.) was dissolved in methyl alcohol and the solution treated with two molecular equivalents of semicarbazide hydrochloride in the presence of sodium acetate. Solid began to separate at once and after a half hour the solution was filtered and the solid product washed with water and methyl alcohol; 0.33 g. of slightly yellow solid was obtained, melting at 216° (by the dip method) with evolution of gas and charring. The filtrate was left overnight and poured into water; 0.3 g. of less pure product was precipitated. It is soluble in boiling water, methyl and ethyl alcohols.

Analyses. Subs., 0.1211: CO_2, 0.2423; H_2O, 0.0552. Calc. for $C_{12}H_{13}O_4N_3$: C, 54.75; H, 4.94. Found: C, 54.56; H, 5.06.

Summary

The yellow methyl and ethyl esters of *p*-methoxy-benzoylacrylic acid on exposure to the sunlight in benzene solution are transformed into the corresponding colorless isomeric esters. The reverse transformation of the colorless into the yellow esters results when solutions of the colorless solids containing a crystal of iodine are exposed to the sunlight. Hydrolysis of these esters with alkaline and acid reagents has been studied.

The colorless esters react with semicarbazide with the formation of semicarbazide addition products and semicarbazones of these addition products; the yellow esters give these same substances and also isomeric

semicarbazones. *p*-Methoxy-benzoylacrylic acid reacts with semicarbazide to form a semicarbazone.

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THE INFLUENCE OF HYDROGEN CONCENTRATION ON THE AUTO-OXIDATION OF HYDROQUINONE. A NOTE ON THE STABILITY OF THE QUINHYDRONE ELECTRODE

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It is well known from the work of Manchot,[1] and of Euler and Bolin[2] that the addition of alkali to a solution of hydroquinone causes the latter to act as an auto-oxidizable substance according to the equation: $C_6H_4(OH)_2 + O_2 \longrightarrow C_6H_4O_2 + H_2O_2$. This property of absorbing oxygen in alkaline solution is not confined to hydroquinone alone but is shared in common by a number of substances, particularly those containing phenolic groups. It has been the subject of considerable biological interest as a possible mechanism for respiration in plants.

When the solution is acid, molecular oxygen is unable to effect any detectable oxidizing action upon hydroquinone, although the latter is rapidly oxidized by certain inorganic agents possessing less powerful oxidizing potentials than oxygen, such as ferric ions. This stability of hydroquinone to molecular oxygen in acid solution affords a very simple and accurate means of determining hydrogen-ion concentration in the presence of oxygen, which is impossible with the hydrogen electrode. The method consists simply in dissolving a few crystals of quinhydrone in the liquid and measuring the resulting oxidation potential with an inert electrode of gold or platinum. Under these conditions the following equilibrium[3,4] is set up: $C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2\oplus$, to which the following equation applies: $\pi = \pi_0 + \frac{0.59}{2} \log \frac{[C_6H_4O_2]}{[C_6H_4(OH)_2]} + 0.059 \log H^+$.

The method depends essentially upon the fact that quinhydrone yields equimolecular proportions of quinone and hydroquinone in solution so that the term involving the concentration ratio vanishes and we obtain: $P_H = -\log H^+ = \pi_0 - \pi$ obs./0.059, an equation which differs from the usual hydrogen electrode formula only in the value of π_0. The values of

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[1] Manchot, "Habilitationschrift," Göttingen, **1899**.

[2] Euler and Bolin, *Z. Physiol. Chem.*, **57**, 81 (1908).

[3] Haber and Russ, *Z. physik. Chem.*, **47**, 294 (1904).

[4] Granger, *Dissertation*, Columbia University, March, **1920**. Granger and Nelson, This Journal, **43**, 1401 (1921).