1. The methods of preparing the orcinolphthaleins and of separating the isomers have been improved. The effect of conditions of preparation on the amounts of the isomers formed has also been studied.

2. The action of ammonia on γ-orcinolphthalein, on tetrabromo-β-orcinolphthalein, and on tetrabromo-γ-orcinolphthalein has been investigated.

3. The *colorless* and *colored* potassium salts of α-orcinolphthalein have been again prepared and analyzed and an explanation of the color changes of α-orcinolphthalein with alkalies more in accord with the facts than that proposed by Baeyer, has been suggested.

4. α-Orcinolphthalein exists only in the colorless form, while both colored and colorless forms of the isomeric β-compound have been prepared. The γ-phthalein is only known in the colored form. The tetrabromoorcinolphthaleins and the orcinoltetrachlorophthaleins exist only in the colorless forms.

5. The colored compounds of the orcinolphthaleins with hydrochloric acid have been isolated and analyzed.

6. Colorless hydrates, acetyl and benzoyl derivatives, and colorless compounds of the orcinolphthaleins with solvents have also been prepared.

7. The three tetrabromoorcinolphthaleins and the three orcinoltetrachlorophthaleins and their diacetates have been made and studied.

8. The absorption spectra of the orcinolphthaleins, of the tetrabromoorcinolphthaleins, of the orcinoltetrachlorophthaleins and of the tetrabromo-γ-orcinoltetrachlorophthaleins have been investigated and the transmission curves plotted.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

o- AND *p*-CHLOROBENZOYLACETIC ESTERS AND SOME OF THEIR DERIVATIVES.

BY LAMBERT THORP AND E. R. BRUNSKILL.

Received March 16, 1915.

The work presented in this article is a continuation of that begun by one of us upon the halogenated benzoylacetic esters,[1] and had for its object a study of the effect of negative substituents in the aromatic nucleus upon the ease of alkylation and upon the course of the saponification of the substituted benzoylacetic esters. In regard to ease of alkylation the chlorobenzoylacetic esters stand between benzoylacetic ester and its nitro derivatives, a condition of affairs which might be expected *a priori* from other well-known instances of the effect of a substitution of a nitro group for a chlorine atom, such as the relative instability of chloroacetic and nitroacetic acids with respect to the loss of carbon dioxide, the difference

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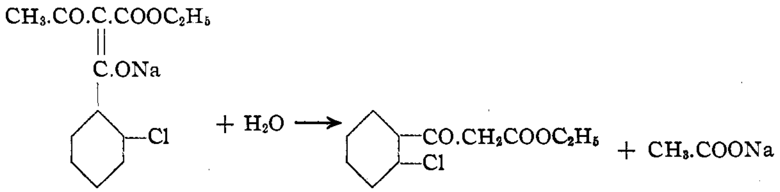
[1] THIS JOURNAL, **35**, 270 (1913).

in the orientating influence of the halogen atom and the nitro group upon the entrance of a second substituent into the benzene ring, the more pronounced effect of the nitro group upon the reactivity of a halogen atom in the aromatic nucleus, etc.

The ketonic decomposition of *o*-chlorobenzoylacetic ester, by means of dilute sulfuric acid, is effected with the same degree of smoothness as obtains in the case of benzoylacetic ester itself, although with even dilute alkali the acid decomposition appears to predominate in the case of certain derivatives of *p*-chlorobenzoylacetic ester.

Experimental.

***o*-Chlorobenzoylacetic Ethyl Ester.**—To one-half (160 cc.) of a solution of sodium ethylate, prepared by dissolving 20.7 g. of sodium (2 equiv. wts.) in 320 cc. of absolute alcohol, 58.5 g. (1 mol) of acetoacetic ester were added. The solution of sodium acetoacetic ester, so obtained, was cooled to 5°, and then 28.25 cc. (0.5 mol) of *o*-chlorobenzoyl chloride were gradually admitted from a buret, the temperature of the reaction mixture being maintained under 12°. It is important that the solution be constantly stirred during this addition. After the lapse of half an hour 80 cc. of the sodium ethylate solution were added and, when the temperature of the mixture had become sufficiently low, 14.12 cc. of the acid chloride were dropped in as before. In this way, always employing one-half of the remaining sodium ethylate and *o*-chlorobenzoyl chloride, the operation was completed after five successive additions. In order that the separation of the sodium salt might be complete, the reaction mixture was allowed to remain in a cold place for 24 hrs. The salt was filtered with the aid of suction, and washed several times with dry ether. Yield, 123 g. Whereas the sodium salts of other tautomeric esters of this series are distinctly yellow in color, the sodium salt of *o*-chlorobenzoylacetoacetic ester is pure white. When warmed with dilute ammonia solution it is decomposed in accordance with the scheme:



One hundred and twenty grams of the sodium salt of *o*-chlorobenzoylacetoacetic ester were dissolved in 600 cc. of water, 54 g. of ammonium chloride and 60 cc. of concentrated aqueous ammonia were added, and the solution maintained at a temperature of 40–50° for 2–3 hrs., with frequent shaking. The product, which had separated as a heavy, yellow oil, was extracted with ether. The ethereal solution was dried over calcium chloride, the ether removed, and the residue placed over sulfuric acid *in vacuo*. The yield of ester amounted to 70 g.

o-Chlorobenzoylacetic ester is a pale yellow, viscous liquid, heavier than water, and possessing a faint, though pleasant, aromatic odor. It is only very slightly soluble in water, but miscible with the common organic solvents. It cannot be distilled under 30 mm. pressure without suffering decomposition.

0.4364 g. subs. required 20.4 cc. 0.1 *N* $AgNO_3$. Calc. for $C_{11}H_{11}O_3Cl$: Cl, 15.6; found: 15.1.

Ketonic Decomposition of *o*-Chlorobenzoylacetic Ester. *o*-Chloroacetophenone.—In a flask, provided with a reflux condenser, a mixture of 54 g. of the ester, 240 cc. of water and 60 cc. of concentrated sulfuric acid was boiled until the evolution of carbon dioxide had apparently ceased, a condition which seemed to have been realized after 10–12 hrs. The mixture was cooled, and the ketone, which floated as an oily layer on the surface of the acid, was taken up with ether. In order to remove any unchanged ester the ethereal solution was shaken with 10% potassium hydroxide solution; it was then washed with water, separated and dried over calcium chloride. After the ether had been removed the residual ketone distilled entirely between 223 and 230°. After further fractionation, a pure product, boiling at 227–228° under 738 mm., was obtained in a yield of 80% of the theoretical.

o-Chloroacetophenone is a colorless liquid, very slightly soluble in water, and with a very agreeable, aromatic odor. The index of refraction was determined by means of an Abbé refractometer.

$N_{D25°} = 1.685$. Specific gravity: $d_{25}^{25} = 1.1884$.

0.2000 g. subs. required 12.92 cc. 0.1 *N* $AgNO_3$. Calc. for C_8H_7OCl: Cl, 22.94; found: 22.88.

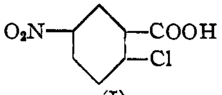
***o*-Chloroacetophenone Oxime.**—To a solution of 3 g. of hydroxylamine hydrochloride and 2 g. of sodium hydroxide in 10 cc. of water, 5 g. of the ketone were added, and then sufficient alcohol, 20 cc., to make the mixture homogeneous. The oxime began to crystallize from the solution after the latter had remained at room temperature for 3 hrs., and after 24 hrs. the separation appeared to be complete. The product was filtered, and hot water added to the filtrate, whereupon a further quantity of oxime was obtained. Recrystallization from 50% alcohol furnished a pure product in a yield of 90% of the theoretical.

o-Chloroacetophenone oxime crystallizes in the form of beautiful, silky needles which melt at 103°. The substance is very slightly soluble in cold water, more readily in hot water; slightly soluble in ligroin; easily soluble in alcohol or benzene; very easily soluble in ether or chloroform.

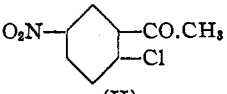
0.2448 g. subs. gave 19.0 cc. N_2 (24°, 743 mm., over KOH). Calc. for C_8H_8ONCl: N, 8.27; found: 8.56.

Nitration of *o*-Chloroacetophenone.—One hundred grams of nitric acid (sp. gr. 1.52) were cooled to 0°, and then 10 g. of *o*-chloroacetophenone were added gradually by means of a dropping funnel, the mixture being constantly stirred and the temperature maintained below 5°. After the solution had been allowed to remain in the freezing mixture for 3 hrs. it was poured into 500 g. of ice water, whereupon the nitro compound separated as a white, flocculent precipitate. The product was filtered, washed thoroughly with water and then recrystallized from alcohol. Yield, 85% of the theoretical.

The orientation of the nitro group in the nitrochloroacetophenone was effected by oxidation with a 2% potassium permanganate solution. The nitrochlorobenzoic acid obtained by this oxidation process showed a melting point of 164.7°. To the acid whose structure is represented by Formula I the literature assigns a melting point of 165°; consequently the ketone must have the nuclear substituents in the positions as represented by Formula II:



(I).



(II).

2-Chloro-5-nitroacetophenone crystallizes from alcohol in the form of small, colorless prisms, and has a melting point of 62°. It is insoluble in water, very slightly soluble in ligroin, slightly soluble in cold alcohol or ether, readily soluble in benzene, chloroform or hot alcohol.

0.2423 g. subs. gave 0.1752 g. AgCl. Calc. for $C_8H_6O_3NCl$: Cl, 17.77; found: 17.88.

***p*-Chlorobenzoylacetic Ester.**—This ester was obtained in a manner analogous to that for the preparation of the corresponding ortho compound, as outlined above. It was found advantageous, however, to employ the *p*-chlorobenzoyl chloride in ether solution since, under these circumstances, the separation of the sodium salt of *p*-chlorobenzoylacetoacetic ester is much facilitated. The quantities of the various substances used were as follows: acetoacetic ester, 37 g.; *p*-chlorobenzoyl chloride, 50 g. in 90 cc. of anhydrous ether; sodium, 13.12 g.; absolute alcohol, 200 cc. The yield of sodium salt was 90 g. This substance is of a yellow color, and much less soluble in water than the corresponding ortho compound.

One hundred and twenty grams of the sodium salt of *p*-chlorobenzoylacetoacetic ester were suspended in 600 cc. of water, 30 g. of ammonium chloride and 60 cc. of concentrated aqueous ammonia were added, and the mixture maintained at a temperature of 40–45° for 3 hrs., with continual shaking. The product was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled. In this way the ester was obtained as a yellow, viscous oil, which, upon being cooled in a freezing mixture, solidified to a mass of crystals. The crystals were freed from traces of adhering mother liquor by means of a porous plate, and then recrystallized from dilute alcohol.

p-Chlorobenzoylacetic ester crystallizes in the form of colorless, flat prisms, and has a melting point of 38°. It is insoluble in water, readily soluble in alcohol, ether, benzene or ligroin.

0.4387 g. subs. gave 0.2880 g. AgCl. Calc. for $C_{11}H_{11}O_3Cl$: Cl, 15.67; found: 15.79.

Potassium Salt of *p*-Chlorobenzoylacetic Ester.—Five grams of *p*-chlorobenzoylacetic ester were treated with two equivalent weights of potassium hydroxide in 10% solution at the ordinary temperature. Upon stirring the mixture the potassium salt separated out as a white, voluminous mass, which was filtered off and recrystallized from absolute alcohol. The salt is slightly soluble in water, easily soluble in alcohol. It melts with decomposition at 265°.

0.2132 g. subs. gave 0.0682 g. K_2SO_4. Calc. for $C_{11}H_{10}O_3ClK$: K, 14.37; found: 14.78.

***p*-Chlorobenzoylacetic Acid.**—Three and one-half grams of *p*-chlorobenzoylacetic ester were allowed to react with 2.4 g. (3 mols) of potassium hydroxide in 50 cc. of water at the ordinary temperature for a period of 3 days. At the end of this time the solution was filtered, and then extracted with ether in order to remove traces of unchanged ester and *p*-chloroacetophenone. From the cold solution the *p*-chlorobenzoylacetic acid was precipitated by means of dilute sulfuric acid. The substance was recrystallized from a mixture of ether and ligroin.

p-Chlorobenzoylacetic acid is very slightly soluble in water; slightly soluble in benzene or ligroin; readily soluble in alcohol or ether.

When heated gradually the substance decomposes into *p*-chloroacetophenone; but when quickly brought to a temperature in the vicinity of its melting point it melts at 232°.

0.0784 g. subs. gave 0.0568 g. AgCl. Calc. for $C_9H_7O_3Cl$: Cl, 17.88; found: 17.89.

Alkylation of *p*-Chlorobenzoylacetic Ester.

Phenacyl *p*-Chlorobenzoylacetic Ethyl Ester, $ClC_6H_4.CO.CH(CH_2.CO.C_6H_5).COOC_2H_5$.—To a solution of sodium ethylate, prepared from 2.05 g. of sodium and 35 cc. of absolute alcohol, 20 g. of *p*-chlorobenzoylacetic ester were added. The solution of the sodium salt of *p*-chlorobenzoylacetic ester was cooled, and then treated gradually with one equivalent weight (17.6 g.) of phenacyl bromide. The mixture became warm, and sodium bromide separated. The reaction was driven to completion by warming the contents of the flask on the water bath for fifteen minutes. Water was added to dissolve the sodium bromide, and the reddish oil which separated was taken up with ether. The ethereal solution was dried over calcium chloride, filtered, and the ether removed. The residual oil, after being allowed to remain in a cold place for several days, was transformed into a crystalline mass. The crystals were pressed out on a porous plate, and then recrystallized from dilute alcohol. The yield was 50% of the theoretical.

Phenacyl *p*-chlorobenzoylacetic ethyl ester crystallizes in the form of colorless prisms, and has a melting point of 63°. It is insoluble in water, slightly soluble in ligroin, fairly soluble in alcohol, readily soluble in ether, benzene or chloroform.

0.2238 g. subs. gave 0.1342 g. AgCl. Calc. for $C_{19}H_{17}O_4Cl$: Cl, 10.33; found: 10.36.

4-Chlorodiphenacyl, $C_6H_5.CO.CH_2.CH_2.CO.C_6H_4Cl$.—The ketonic decomposition of phenacyl *p*-chlorobenzoylacetic ester, by means of dilute alkali, is not effected with the same smoothness as obtains in the case of the correspondingly substituted, nonhalogenated benzoylacetic esters, the yield of ketone being diminished by the greater tendency of the former ester to undergo the acid decomposition.

Thirty-five grams of phenacyl *p*-chlorobenzoylacetic ester were added to a solution of 13.6 g. of potassium hydroxide (2 mols) in a mixture of 300 cc. of water and 100 cc. of alcohol, and the solution boiled under a reflux condenser. After 2 hrs. boiling the contents of the flask were cooled, and the product filtered off. Several recrystallizations from alcohol, with the aid of bone black, gave a pure product, melting at 114.5°. The yield was poor.

4-Chlorodiphenacyl crystallizes in the form of colorless leaflets of pearly luster. It is insoluble in water, slightly soluble in ligroin, fairly soluble in alcohol or ether, readily soluble in benzene or chloroform.

0.3378 g. subs. gave 0.1814 g. AgCl. Calc. for $C_{16}H_{13}O_2Cl$: Cl, 13.02; found: 13.28.

***p*-Chlorophenacyl Benzoylacetic Ester,** $C_6H_5.CO.CH(CH_2.CO.C_6H_4Cl).COOC_2H_5$.—This ester was prepared in order to determine the relative yields of 1,4-diketone produced in the saponification of this and of the isomeric ester described above.

Thirty-eight grams of *p*-chlorophenacyl bromide were added gradually to a solution of the sodium salt of benzoylacetic ester, prepared from 3.65 g. of sodium, 80 cc. of absolute alcohol and 30 g. of benzoylacetic ester. The reaction was completed by warming on the water bath for half an hour. The alcohol was distilled, and then water added to dissolve the sodium bromide. The oil which separated was extracted with ether, the ethereal solution dried over calcium chloride, and the greater part of the ether removed on the steam bath. In order to eliminate the last traces of ether the ester was placed *in vacuo* over sulfuric acid, a procedure which caused the transformation of the substance into a crystalline mass. The product was pressed out on a porous plate, and then recrystallized from alcohol. The yield was 75% of the theoretical.

p-Chlorophenacyl benzoylacetic ester crystallizes in the form of colorless needles which have a melting point of 92°. It is insoluble in water, fairly soluble in alcohol, ether or ligroin, readily soluble in benzene or chloroform.

0.2084 g. subs. gave 0.0892 g. AgCl. Calc. for $C_{19}H_{17}O_4Cl$: Cl, 10.33; found: 10.58.

Saponification of 9 g. of the ester by means of a solution of 3.2 g. of potassium hydroxide in a mixture of 75 cc. of water and 25 cc. of alcohol yielded 50% of the theoretical amount of a substance, identical in melting point, and undistinguishable in other physical properties from the 4-chlorodiphenacyl, described above.

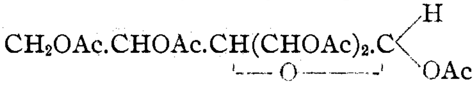
URBANA, ILL.

A COMPARISON OF THE OPTICAL ROTATORY POWERS OF THE ALPHA AND BETA FORMS OF CERTAIN ACETYLATED DERIVATIVES OF GLUCOSE.

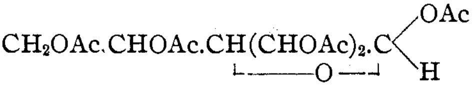
BY C. S. HUDSON AND J. K. DALE.[1]

Received March 5, 1915.

If the alpha and beta forms of glucose pentacetate have the isomeric structures, as generally accepted,

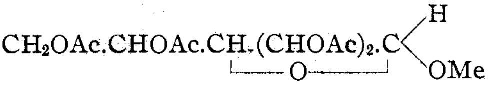


$\mathrm{CH_2OAc.CHOAc.\underbrace{CH(CHOAc)_2.C}_{O}}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OAc}\end{smallmatrix}$ and

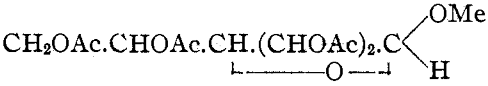


$\mathrm{CH_2OAc.CHOAc.\underbrace{CH(CHOAc)_2.C}_{O}}\begin{smallmatrix}\mathrm{OAc}\\ \mathrm{H}\end{smallmatrix}$

the molecular rotations of the substances may be regarded as having the values (A + B) for one form, and (—A + B) for the other, according to the considerations which have been presented by one of us in a previous article.[2] The quantity A represents the rotation which is due to the end asymmetric carbon atom, and B denotes the rotation of the remainder of the structure. In similar manner, the rotations of the alpha and beta forms of tetracetyl methylglucoside,



$\mathrm{CH_2OAc.CHOAc.\underbrace{CH.(CHOAc)_2.C}_{O}}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OMe}\end{smallmatrix}$ and



$\mathrm{CH_2OAc.CHOAc.\underbrace{CH.(CHOAc)_2.C}_{O}}\begin{smallmatrix}\mathrm{OMe}\\ \mathrm{H}\end{smallmatrix}$

may be written (A′ + B) and (—A′ + B), where A′ is of different value from A, on account of the replacement of the acetyl by the methyl radical, but B remains of constant value. The deduction may be drawn that the

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[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture, and the Laboratory of Physical Chemistry, Princeton University.

[2] THIS JOURNAL, 31, 66 (1909).