to give β-bromo-ethyl-bromomalonic ester. It is suggested that substitution, followed by splitting of the ring with addition of hydrobromic acid, may be the normal mechanism of the breaking of the cyclopropane ring by bromine.

3. A number of cyclopropane derivatives showed no reaction with HOCl, HOBr or ICl.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE ADDITION OF ETHYL AND TERTIARY BUTYL HYPOCHLORITES TO CINNAMIC ACID

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The addition of methyl hypochlorite to cinnamic acid and other ethylene derivatives, by the reaction of chlorine with the unsaturated compounds in methyl alcohol solution, was reported in a previous paper.[1] The question of the applicability of this reaction to other alcohols led to the investigation of ethyl and *tert.*-butyl alcohols, the results of which are given in this paper.

Chattaway and Backeberg[2] have recently shown that in the chlorination of ethyl alcohol, ethyl hypochlorite and hydrogen chloride are the primary products and that in the presence of unchanged alcohol the ethyl hypochlorite quickly eliminates hydrogen chloride from its molecule with the formation of acetaldehyde, the chlorination of which follows. One would expect, therefore, the addition of ethyl hypochlorite to cinnamic acid, by the reaction of chlorine with the unsaturated compound in ethyl alcohol solution, to be complicated by a number of side reactions. The principal reactions follow.

$$CH_3CH_2OH + Cl_2 \longrightarrow CH_3CH_2OCl + HCl \qquad (1)$$

$$C_6H_5CH{=}CHCOOH + CH_3CH_2OCl \longrightarrow C_6H_5CH(OC_2H_5)CHClCOOH \qquad (2)$$

$$CH_3CH_2OCl \longrightarrow CH_3CHO + HCl \qquad (3)$$

$$3CH_3CHO \xrightarrow{HCl} (CH_3CHO)_3 \xrightarrow{Cl_2} (CH_2ClCHO)_3 \longrightarrow \text{, etc.} \qquad (4)$$

$$C_6H_5CH{=}CHCOOH + Cl_2 \longrightarrow C_6H_5CHClCHClCOOH \qquad (5)$$

By introducing a slow stream of dry chlorine into an efficiently stirred solution of cinnamic acid in absolute ethyl alcohol, we were able to add ethyl hypochlorite to the double linkage of the unsaturated compound. The chlorine concentration was kept as low as practicable and the temperature was either that of the Laboratory, or 0–10°, the results being about the same in both cases. Most of the chlorine went into the side

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[1] Jackson, THIS JOURNAL, **48,** 2166 (1926).

[2] Chattaway and Backeberg, *J. Chem. Soc.*, **125,** 1097 (1924).

reactions, about three times the calculated amount being required to complete the reaction and large quantities of aldehyde being evident in the chlorinated mixture. The products, which were isolated by saponification of the esters resulting from the chlorination, were α-chloro-β-ethoxyphenylpropionic acid, α-chlorocinnamic acid, and α-chloro-β-hydroxyphenylpropionic acid, while the presence of allocinnamic acid was strongly indicated. The yield of the chloro-ethoxy acid was low (about 6%). The α-chloro-β-hydroxyphenylpropionic acid was formed by the addition of hypochlorous acid to cinnamic acid, while α-chlorocinnamic acid was doubtless produced by the action of sodium hydroxide with ethyl α-β-dichloro-β-phenylpropionate during the saponification reaction.[3] The reaction of chlorine with an alcoholic solution of ethyl cinnamate was found to give a somewhat higher yield (10%) of the chloro-ethoxy acid.

A number of experiments with alcoholic solutions of cinnamic acid were tried with a view to improving the yield of the chloro-ethoxy acid by eliminating the hydrochloric acid formed in the reaction. Oxidation of the hydrochloric acid by means of potassium chlorate gave a 9% yield of the chloro-ethoxy acid, while 22% of the cinnamic acid was converted into α-chloro-β-hydroxyphenylpropionic acid. Although the yield of the chloro-ethoxy acid was not materially improved by this method, the amount of chlorine required was only one-third that necessary in the absence of potassium chlorate. When calcium carbonate was suspended in the reaction solution, we could isolate only α-chloro-β-hydroxyphenylpropionic acid. With the use of pyridine and the calculated amount of chlorine, 80% of the cinnamic acid was recovered unchanged. On the basis of the equation $C_2H_5ONa + Cl_2 \longrightarrow C_2H_5OCl + NaCl$, we tried without success the reaction of the calculated amount of chlorine with a suspension of sodium cinnamate in an absolute alcohol solution of sodium ethylate.

Inasmuch as Goldschmidt[4] has shown that the addition of ethyl hypochlorite to 1,4-dihydronaphthalene may be accomplished in carbon tetrachloride solution, we hoped to utilize this method for the addition of ethyl hypochlorite to cinnamic acid. It was found, however, that cinnamic acid failed to react with ethyl hypochlorite in carbon tetrachloride, a pure, dry solution of which was prepared by the procedure of Taylor, MacMullin and Gammal,[5] although tests showed the presence of ethyl hypochlorite in the solution during three days.

The stability of *tert.*-butyl hypochlorite[5,6] led to the hope that chlorina-

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[3] Sudborough and James, *J. Chem. Soc*, **89**, 105 (1906).

[4] Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).

[5] Taylor, MacMullin and Gammal, THIS JOURNAL, **47**, 395 (1925).

[6] Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

tion of a solution of cinnamic acid in *tert.*-butyl alcohol would result in a more satisfactory addition of the hypochlorite than was obtained in the case of ethyl hypochlorite, where the rate of decomposition apparently exceeds the rate of the addition reaction. We found, in fact, that *tert.*-butyl hypochlorite may be readily added to cinnamic acid in this manner, although only a 14% yield of pure α-chloro-β-*tert.*-butyloxy-phenylpropionic acid results. It was necessary to use almost three times the calculated amount of chlorine, because of side reactions between chlorine and *tert.*-butyl alcohol.

(The principal reaction between *tert.*-butyl alcohol and chlorine seems to be substitution of the hydrogen in the methyl groups.[7] On the basis of the facts at present available, it is not possible to state whether the *tert.*-butyl hypochlorite formed in our reaction is a result of the direct action of chlorine with the alcohol, or is formed by the action of the alcohol with hypochlorous acid, which might result from the reaction of chlorine with small amounts of water present in the alcohol.)

Although the addition of *tert.*-butyl hypochlorite to benzalacetophenone, by its reaction with chlorine and *tert.*-butyl alcohol, could not be established, we were able to isolate a stereo-isomer of α,β-dichloro-β-phenylpropiophenone, which has hitherto not been reported. The new isomer melts at 82–83° and is more soluble in alcohol than the high-melting isomer (113°). That the substance is a stereo-isomer of benzalacetophenone dichloride, and not a structural isomer, was established by its reaction with hydroxylamine to give diphenylisoxazole, which Goldschmidt[8] has shown to be the product of this reaction with the high-melting dichloride.

The Mode of Addition

In the addition of methyl hypochlorite to cinnamic acid, the chlorine atom has been shown[1] to go exclusively to the carbon atom in the alpha position to the carboxyl group, while the methoxyl radical combines with the carbon in the beta position. This result is analogous to the well-known mode of addition of hypochlorous acid, the methoxyl and hydroxyl groups assuming the same position in the addition product. We found, likewise, that in the addition of ethyl and *tert.*-butyl hypochlorites to cinnamic acid, the chlorine combines with the alpha carbon while the alkoxyl group attaches itself to the beta carbon. Our evidence for the structure of the ethyl and *tert.*-butyl hypochlorite addition products is based upon the preparation of acetophenone by their reaction with alcoholic potassium hydroxide, followed by hydrolysis of the resulting oils with dil. sulfuric acid solution. In the case of the *tert.*-butyl hypochlorite addition product, both acetophenone and α-chloro-β-hydroxyphenyl-

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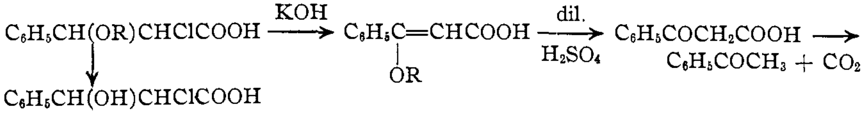
[7] Davis and Murray, *Ind. Eng. Chem.*, **18**, 845 (1926).

[8] Goldschmidt, *Ber.*, **28**, 2540 (1895).

propionic acid were obtained by this treatment. The formation of acetophenone and α-chloro-β-hydroxyphenylpropionic acid from the α-chloro-β-alkoxy acid (I) is readily explained as shown by the equations below, while the β-chloro acids (II) would not be expected to yield these products.

$$\underset{\text{I}}{C_6H_5CH(OR)CHClCOOH} \qquad \underset{\text{II}}{C_6H_5CHClCH(OR)COOH}$$

$$(R = C_2H_5 \text{ or } (CH_3)_3C)$$



$$\begin{array}{l} C_6H_5CH(OR)CHClCOOH \xrightarrow{KOH} C_6H_5\underset{\displaystyle OR}{\underset{|}{C}}{=}CHCOOH \xrightarrow[H_2SO_4]{dil.} C_6H_5COCH_2COOH \longrightarrow C_6H_5COCH_3 + CO_2 \\ \qquad\downarrow \\ C_6H_5CH(OH)CHClCOOH \end{array}$$

Although the unsaturated alkoxyl acids resulting from the reaction with alcoholic potassium hydroxide were not isolated, the oils thus obtained were shown to decolorize bromine in carbon tetrachloride solution and to reduce potassium permanganate rapidly in sodium carbonate solution. Perkin[9] has shown that benzoylacetic acid, on heating with dil. sulfuric acid solution, is quantitatively decomposed into acetophenone and carbon dioxide. One would expect, therefore, our treatment of the product, resulting from the reaction with alcoholic potassium hydroxide, with dil. sulfuric acid solution and steam to yield acetophenone. The formation of α-chloro-β-hydroxyphenylpropionic acid in the reactions with the *tert.*-butyl hypochlorite addition product was doubtless due to hydrolysis of some of the chloro-*tert.*-butyloxy acid.

Experimental Part

Addition of Ethyl Hypochlorite

The ethyl alcohol used in this work was refluxed over quicklime and distilled through a fractionating column. With the exception indicated, the temperature of the experiments was that of the Laboratory.

Reaction of Cinnamic Acid with Chlorine and Absolute Ethyl Alcohol.—Twenty g. of cinnamic acid was dissolved in 100 cc. of absolute ethyl alcohol. A slow stream of chlorine, dried by bubbling through concd. sulfuric acid, was introduced into the vigorously stirred solution. The concentration of chlorine was kept as low as possible, so that several hours were required to complete the reaction. A number of experiments showed that approximately 9 liters of chlorine (about thrice the calculated amount) gave the best results with 20 g. of cinnamic acid. Upon completion of the chlorination the solvent, which had a strong aldehyde odor, was distilled under diminished pressure. The residue was an oil, nearly all of which (20.5 g.) boiled at 122–124° (5 mm.). This material, a mixture of acid esters, was boiled with a small excess of 0.5 *N* sodium hydroxide solution until saponification was complete. The chlorostyrene, formed by the reaction of sodium hydroxide with the dichloride of cinnamic acid, was extracted with ether. Acidification of the alkaline solution precipitated an oil which slowly crystallized. The crystals were filtered off and dried. Recrystallization from benzene gave 2 g. of substance melting at 134–138° and an oil. On further recrystallization of the

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[9] Perkin, *J. Chem. Soc.*, **45**, 178 (1884).

substance melting at 134–138° long, transparent needles melting at 137–138° were obtained. The oil crystallized only after long standing. Suction filtration of the sirupy material thus obtained yielded 2 g. of colorless crystals melting at 69–78°, which after several recrystallizations from benzene melted at 78–79°. The oily filtrate from the substance melting at 69–78° was suspended in dil. aqueous sodium hydroxide and boiled until solution was complete and the odor of chlorostyrene was no longer perceptible. Acidification of this solution precipitated an oil, which crystallized on standing; m. p., 57–61°. The substance in dil. sodium carbonate solution rapidly decolorizes aqueous potassium permanganate at room temperature, producing the odor of benzaldehyde. It probably consists chiefly of allocinnamic and isocinnamic acids. In one experiment, by oxidation of this material with potassium permanganate solution and acidification of the resulting solution, there was obtained a small amount of α-chloro-β-hydroxyphenylpropionic acid; m. p., 79–81°. A mixture with the known acid melted at the same temperature.

The crystals melting at 137–138° were shown to be α-chlorocinnamic acid, which was doubtless formed by the reaction of aqueous sodium hydroxide with ethyl α,β-dichloro-β-phenylpropionate during the saponification described above.

Anal. Calcd. for $C_9H_7O_2Cl$: Cl, 19.42. Found: 19.35.

No depression of the melting point was produced on mixing with known α-chlorocinnamic acid; m. p., 137–138°. Also, the melting point of the acid amide, 120–121°, prepared by the procedure of Stoermer,[10] corresponds with that of the acid amide of α-chlorocinnamic acid.

The substance melting at 78–79°, obtained as described above, is α-chloro-β-ethoxyphenylpropionic acid containing one molecule of crystal water. The water of crystallization was determined by heating to constant weight at 115°; the ethoxyl analysis was made by the Zeisel method.

Anal. Calcd. for $C_{11}H_{13}O_3Cl.H_2O$: H_2O, 7.31; OC_2H_5, 18.26; Cl, 14.37. Found: H_2O, 7.50; OC_2H_5, 18.26; Cl, 14.21.

By chlorinating a solution of 10 g. of cinnamic acid in 50 cc. of absolute ethyl alcohol cooled in ice water, the yield of the chloro-ethoxy acid was 1 g. (6%).

Structure of the Chloro-ethoxy Acid.—The sample used in the following experiment was shown by an ethoxyl determination to contain 87% of the chloro-ethoxy acid. One and one-half g. of this substance, melting at 77–79°, was added to a solution of 2.4 g. of potassium hydroxide in 13 cc. of absolute alcohol. After boiling under a reflux condenser for six hours, the alcohol was distilled, the residue dissolved in water and acidified, the oil thus precipitated being extracted with ether. To the oil obtained by distillation of the ether there was added 100 cc. of 10% aqueous sulfuric acid; this mixture was then steam distilled until oily material ceased to pass over. From the distillate there was obtained by extraction with ether 0.6 g. of oil which resembled acetophenone in appearance and odor. In order to identify the substance, the semicarbazone was prepared by the reaction of the oil with semicarbazide hydrochloride and sodium acetate according to the usual procedure; m. p., 195–196°; yield, 0.6 g., which corresponds to an amount of acetophenone equal to 65% of the calculated amount, on the basis of a quantitative conversion of the chloro-ethoxy acid into acetophenone. The melting point of the substance showed no depression when mixed with known acetophenone semicarbazone; m. p., 195–196°. From the aqueous solution left in the distilling flask in the steam distillation described above, there was obtained by extraction with ether about 0.1 g. of an oil which was not investigated. Since the formation of acetophenone by these reactions is most logically explained on the assumption that the ethoxyl group is in the

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[10] Stoermer, *Ber.*, **44**, 647 (1911).

beta position to the carboxyl group, it is concluded that the substance is α-chloro-β-ethoxyphenylpropionic acid.

Reaction with Ethyl Cinnamate.—A solution of 29 g. of ethyl cinnamate in 100 cc. of absolute ethyl alcohol was treated with 10 l. of chlorine in the manner described above. At the end of the reaction the product was heated with dil. sodium hydroxide solution until saponification of the esters was complete. After extracting the chlorostyrene thus formed, the solution was acidified and an oil precipitated. This on standing partially crystallized. By means of a fractional crystallization from benzene, there were obtained 4 g. of α-chlorocinnamic acid melting at 135–138°, 3 g. of substance melting at 50–105° and 8 g. of oil containing some crystals. By allowing the 8 g. of sirupy material to stand for about three weeks, there were separated with the aid of benzene 4 g. of α-chloro-β-ethoxyphenylpropionic acid melting at 78–80° (10% yield). An ethoxyl determination showed the substance to contain 89% of the chloro-ethoxy acid.

Reaction of Cinnamic Acid with Chlorine and Ethyl Alcohol in the Presence of Calcium Carbonate.—Into a thoroughly stirred suspension of 10 g. of cinnamic acid and 20 g. of finely powdered calcium carbonate in 55 cc. of absolute ethyl alcohol, there was introduced about 4.5 liters of chlorine at such a rate as to maintain only a slight excess. The reaction mixture was then diluted with water and acidified, an oil being precipitated. The oil crystallized on standing; m. p., 60–75°; wt., 7 g. By recrystallization from benzene this material was separated into hydrated α-chloro-β-hydroxyphenylpropionic acid melting at 79–81° (4.5 g.) and 1.5 g. of substance melting at 50–70°, which probably consists chiefly of the low-melting isomers of cinnamic acid. The substance melting at 79–81° is easily soluble in hot water, from which it crystallizes in long needles. A qualitative test by the Zeisel method showed that it contained no ethoxyl group.

Anal. Calcd. for $C_9H_9O_3Cl.H_2O$: Cl, 16.22. Found: 15.61.

Its identity was confirmed by converting it into α-chlorocinnamic acid by reaction with acetic anhydride and sodium acetate,[11] and by the preparation of α,β-dichloro-β-phenylpropionic acid by heating it in a sealed tube with fuming hydrochloric acid.

Reaction in the Presence of Potassium Chlorate.—A vigorously stirred suspension of 20 g. of cinnamic acid and 2.6 g. of potassium chlorate in 100 cc. of absolute ethyl alcohol was treated with 3 liters of chlorine (one molecular equivalent) at the rate of about one bubble per second, seven hours being required to complete the reaction. Qualitative tests showed that the solid, suspended in the solution at the end of the reaction, was a mixture of potassium chloride and potassium chlorate. After the chlorination had been completed, the solution was poured into about 1000 cc. of water. The oil, thus precipitated, partially crystallized on standing for about 24 hours. The oily material was separated from the solid by suction filtration. The solid thus obtained weighed 9 g. and melted at 60–77°. By recrystallization from benzene 6.5 g. of hydrated α-chloro-β-hydroxyphenylpropionic acid was obtained; m. p., 79–81°. No depression of the melting point was produced on mixing with the known acid. The oil obtained in the above described-filtration was heated with 0.5 *N* sodium hydroxide solution for an hour. After extracting the insoluble material with ether, the solution was acidified, an oil being precipitated. This crystallized on standing for several hours; wt., 6 g.; m. p., 55–63°. This material contains α-chloro-β-ethoxyphenylpropionic acid mixed with the low-melting isomers of cinnamic acid. For purification it was dissolved in dil. sodium carbonate solution and treated with potassium permanganate solution in slight excess. After filtering off the manganese dioxide, extracting the benzaldehyde with ether and acidifying, an oil was precipitated which immediately crystallized. This was filtered off and air dried; wt., 1.8 g.; m. p., 68–75°. A Zeisel test showed the substance

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[11] Forrer, *Ber.*, **16**, 854 (1883).

to be an ethoxyl compound. Recrystallization from benzene gave pure α-chloro-β-ethoxyphenylpropionic acid; m. p., 78–79°. A mixture with the known acid melted at the same temperature. By extracting the filtrate from the substance melting at 68–75° with ether and distillation of the solvent, after drying over sodium sulfate, there was obtained an oil which soon crystallized. From this 1.2 g. of α-chloro-β-ethoxyphenylpropionic acid melting at 65–75° was obtained. One recrystallization from benzene gave the pure chloro-ethoxy acid; m. p., 78–79°.

Addition of Tertiary Butyl Hypochlorite

The *tert.*-butyl alcohol used was the "anhydrous" grade manufactured by the Petroleum Chemical Corporation. The commercial product was found to give about the same results as *tert.*-butanol boiling at 81–82°.

Reaction of Cinnamic Acid with Chlorine and *tert.*-Butyl Alcohol.—A vigorously stirred solution of 25 g. of cinnamic acid in 350 cc. of *tert.*-butyl alcohol was treated with a stream of dry chlorine until approximately 10.5 liters (about 2.8 times the calculated amount) had reacted. The use of less chlorine gave an incomplete reaction of the cinnamic acid because of side reactions between chlorine and *tert.*-butyl alcohol. The temperature was that of the Laboratory, and the rate of introduction of chlorine was such as to maintain only a small excess, about 15 hours being required to complete the reaction. At the end of the reaction the *tert.*-butyl alcohol was distilled under diminished pressure, the bath temperature being 60–70°. The residue was an oil, which was dissolved in ether and thoroughly extracted with saturated aqueous sodium carbonate. The small amount of insoluble material remaining in the ether was not investigated. The sodium carbonate solution was heated at the boiling point for about three minutes. This treatment decomposes cinnamic acid dichloride to give chlorostyrene, which is removed by means of ether. On acidifying the sodium carbonate solution, there precipitated an oil, which was extracted with ether. After drying and distilling the solvent, an oil was obtained. The oil showed slight tendency to crystallize upon standing and with the use of the common solvents, except benzene. It was dissolved in benzene and allowed to evaporate almost to dryness at room temperature. The crystalline mass thus obtained was separated from the oily material by means of suction filtration; m. p., 60–70°. This is principally α-chloro-β-*tert.*-butyloxyphenylpropionic acid contaminated with the low-melting isomers of cinnamic acid. The substance may be obtained completely pure by further recrystallization from benzene; however, the purification may be facilitated by oxidation of the unsaturated compounds with dil. potassium permanganate solution, which was shown to be without action on the chloro-*tert.*-butyloxy acid under the conditions employed. The substance melting at 60–70° was dissolved in dil. aqueous sodium carbonate and to this solution there was added potassium permanganate solution until its color persisted for a few minutes, a large excess being avoided. After filtering off the manganese dioxide thus precipitated, the filtrate was immediately extracted with ether to remove benzaldehyde. Acidification of the sodium carbonate solution gave an oil which readily crystallized. Another crystallization from benzene gave pure α-chloro-β-*tert.*-butyloxyphenylpropionic acid; yield, 6 g., or 14%. The remainder of the material was an oil containing some crystals. The colorless crystals of the chloro-*tert.*-butyloxy acid retain benzene and, on standing, the melting point (83–85°) slowly rises because of the loss of benzene. Before analysis the finely powdered substance was allowed to stand in a vacuum desiccator over phosphorus pentoxide for about a week, when its melting point became constant at 94–94.5°. The benzene may also be removed by crystallization from chloroform.

Anal. Calcd. for $C_{13}H_{17}O_3Cl$: C, 60.80; H, 6.67; Cl, 13.81. Found: C, 60.81; H, 6.68; Cl, 14.15.

Structure of the Chloro-*tert.*-Butyloxy Acid.—To a solution of 5.4 g. of potassium hydroxide in 28 cc. of absolute ethyl alcohol there was added 3.8 g. of the chloro-*tert.*-butyloxy acid melting at 92–94°. After boiling under a reflux condenser for five hours, the alcohol was distilled, the residue dissolved in water and acidified. The oil thus precipitated was extracted with ether; after drying the ether solution and distilling the solvent, 3 g. of red, mobile oil was obtained. Efforts to separate a pure compound from the oil were without success. That it contained an unsaturated compound was indicated by the fact that it decolorized a solution of bromine in carbon tetrachloride, and its sodium carbonate solution rapidly reduced potassium permanganate. The oil was mixed with 100 cc. of 10% sulfuric acid solution and steam distilled until oil ceased to pass over. Extraction of the distillate with ether and distillation of the solvent, after drying, gave 0.9 g. of oil resembling acetophenone in appearance and odor. By treating it with semicarbazide hydrochloride and sodium acetate, acetophenone semicarbazone was obtained; m. p., 195–196°. A mixture of this substance with known acetophenone semicarbazone melted at the same temperature. The identity of the oil was further established by its reaction with hydroxylamine hydrochloride to give acetophenone oxime; m. p., 58–59°.

The aqueous solution remaining in the distilling flask after the steam distillation described above was extracted with ether. From this there was obtained 1.5 g. of reddish oil, which partially crystallized on adding a small amount of water and cooling in ice; wt., 0.3 g.; m. p., 82–84°. After this had been recrystallized from benzene several times and allowed to stand in a vacuum desiccator over phosphorus pentoxide, it melted at 104–105°, which corresponds with the melting point of anhydrous α-chloro-β-hydroxyphenylpropionic acid given by Glaser.[12]

Anal. Calcd. for $C_9H_9O_3Cl$: C, 53.86; H, 4.52; Cl, 17.67. Found: C, 53.89; H, 4.70; Cl, 17.31.

The formation of acetophenone and α-chloro-β-hydroxyphenylpropionic acid by these reactions shows that the alkoxyl group is in the beta position to the carboxyl group, and the substance is α-chloro-β-*tert.*-butyloxyphenylpropionic acid.

Reaction of Benzalacetophenone with Chlorine and *tert.*-Butyl Alcohol.—A solution of 15 g. of benzalacetophenone in 150 cc. of *tert.*-butyl alcohol was treated with 4.5 l. of chlorine in the manner described for cinnamic acid. Distillation of the *tert.*-butyl alcohol gave a colorless oil, which partially crystallized upon standing for several days. After filtering and allowing the filtrate to stand for about four weeks, another crop of crystals was obtained. From the first fraction there was obtained by recrystallization from alcohol 3.5 g. of α,β-dichloro-β-phenylpropiophenone melting at 113–114°. A mixture with the known dichloride of benzalacetophenone melted at the same temperature. The second fraction of crytsals obtained as described above weighed 2 g. and melted at 80–90°. A fractional crystallization from alcohol yielded colorless crystals melting at 82–83°. This was found to be a stereo-isomer of α,β-dichloro-β-phenylpropiophenone, which has not hitherto been described.

Anal. Calcd. for $C_{15}H_{12}OCl_2$: C, 64.52; H, 4.33; Cl, 25.41. Found: C, 64.26; H, 3.99; Cl, 25.32.

That the substance is a stereo-isomer of benzalacetophenone dichloride, and not a structural isomer, was shown by its reaction with hydroxylamine to give diphenylisoxazole, which Goldschmidt[8] showed to be the product of the same reaction with α,β-dichloro-β-phenylpropiophenone melting at 113°. To a solution of 0.35 g. of the low-melting dichloride (82–83°) in 13 cc. of 80% aqueous ethyl alcohol, there was added 0.18 g. of hydroxylamine hydrochloride. After bringing into solution by warming, dil. sodium hydroxide solution was added until tests with litmus showed an excess.

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[12] Glaser, *Ann.*, **147**, 82 (1868).

Crystals of diphenylisoxazole soon began to separate. After standing for 30 minutes, the solution was filtered and the filtrate was immediately poured into water, which precipitated the diphenylisoxazole; yield, 0.2 g. By recrystallization from alcohol, colorless flakes of the pure substance were obtained; m. p., 140.5–141°. No depression of the melting point was produced on mixing with known diphenylisoxazole (m. p. 140.5–141°), which was prepared by the reaction of hydroxylamine with the dichloride of benzalacetophenone melting at 113–114°.

The principal portion of the material resulting from the reaction of benzalacetophenone with chlorine and *tert.*-butyl alcohol was an oil which did not crystallize after standing for several months and which could not be obtained in the solid state by the use of solvents. In the hope of isolating the *tert.*-butyl hypochlorite addition product, the oil was subjected to a distillation at 5 mm. pressure. This, however, produced deep-seated decomposition, large quantities of gas being evolved. From the fraction boiling at 125–150° ω-chloro-acetophenone was separated; the other products were not identified, although the presence of benzoyl chloride was evident. The ω-chloro-acetophenone, after recrystallization from alcohol, melted at 55–55.5° and possessed the lachrymatory properties characteristic of this substance. Inasmuch as the melting point given in the literature is 58–59°, the crystals melting at 55–55.5° were further identified.

Anal. Calcd. for C_8H_7OCl: C, 62.12; H, 4.57; Cl, 22.93. Found: C, 61.68; H, 4.60; Cl, 23.24.

When treated with hydroxylamine hydrochloride according to the procedure of Korten and Scholl,[13] it gave synphenylchloromethylketoxime (m. p., 88–89°), a reaction characteristic of ω-chloro-acetophenone.

Summary

1. The reaction of chlorine with a solution of cinnamic acid in absolute ethyl alcohol results in a low yield of α-chloro-β-ethoxyphenylpropionic acid. Oxidation of the hydrochloric acid formed in the reaction by means of potassium chlorate was shown to reduce greatly the amount of chlorine required, although the yield of the chloro-ethoxy acid was not materially improved. A solution of ethyl hypochlorite in carbon tetrachloride was found to be without action on cinnamic acid.

2. The reaction of chlorine with a solution of cinnamic acid in *tert.*-butyl alcohol results in the formation of α-chloro-β-*tert.*-butyloxy-phenylpropionic acid.

3. The addition of *tert.*-butyl hypochlorite to benzalacetophenone, by its reaction with chlorine and *tert.*-butyl alcohol, could not be established. However, a new stereo-isomer of α,β-dichloro-β-phenylpropiophenone was isolated.

CLEVELAND, OHIO

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[13] Korten and Scholl, *Ber.*, **34**, 1901 (1901).