(m. p. 118°, uncor.) is formed and may be precipitated from its alcoholic solution by the addition of water. It is a white, crystalline, almost odorless compound, insoluble in water and soluble in all the usual organic solvents. Hydrolysis cannot be effected by boiling in strong aqueous acid or alkaline solutions.

2,4,6-Trichlorophenyl ethyl carbamate could not be synthesized from the action of ethyl chlorocarbonate on 2,4,6-trichloroaniline.

Preparation of 2,4,6-Trichlorophenyl Methyl Carbamate ($Cl_3C_6H_2NHCOOCH_3$) (mol. wt. 254.5).—When 2,4,6-trichlorophenyl isocyanate is dissolved in an excess of methyl alcohol, 2,4,6-trichlorophenyl methyl carbamate (m. p. 132°, uncor.) is formed and may be precipitated from its alcoholic solution by the addition of water. It is a white, crystalline, almost odorless compound, insoluble in water and soluble in all the usual organic solvents.

Summary

A method of preparation and properties of 2,4,6-trichlorophenyl isocyanate and its corresponding methyl and ethyl alcohol derivatives, namely, 2,4,6-trichlorophenyl methyl carbamate and 2,4,6-trichlorophenyl ethyl carbamate, have been presented.

BALTIMORE, MD. RECEIVED JANUARY 21, 1946

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

The Use of Liquid Phase Oxidation for the Preparation of Nuclearly Substituted Styrenes. I. Methyl *p*-Vinylbenzoate[1]

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS, EARL C. CHAPIN, GRAFTON R. OWENS AND ROBERT W. SHORTRIDGE

The air oxidation of substituted ethylbenzenes to the corresponding acetophenones offers a direct and convenient route to many otherwise difficultly obtainable compounds. While, in the case of ethylbenzene itself, quite a few studies have been made employing oxygen as the oxidizing agent,[2,3,4,5,6] only four examples employing air are mentioned in the literature. As catalysts, copper oxide,[7,8] iron oxide[8,9] and cobalt acetate[10] in acetic acid solution have been used. In the case of cobalt acetate[10] about half as much by-product benzoic acid was obtained as the desired acetophenone.

We have found that in the presence of chromium oxide and calcium carbonate both ethyl *p*-ethylbenzoate and methyl *p*-ethylbenzoate are smoothly oxidized by air to ethyl *p*-acetylbenzoate (41% conversion and 70% yield) and methyl *p*-acetylbenzoate (54% conversion and 66% yield). These ketones were then treated with hydrogen in the presence of copper chromite to give the corresponding carbinols in 63–80% yields.

When ethyl *p*-(α-hydroxyethyl)-benzoate was passed, together with steam, through a column packed with alumina[11] and heated to 300–350°, the product, in two runs, was a low yield of what may be impure ethyl *p*-vinylbenzoate. In a third run there was isolated a small amount of crystalline material having the correct analysis for *p*-vinylbenzoic acid and a larger portion of polymeric material of the same constitution. This latter product swelled to a voluminous gel on long-continued treatment with aqueous alkali, and shrank to its original proportions when again treated with acid.

On the basis of these experiments methyl *p*-(α-hydroxyethyl)-benzoate was heated with potassium bisulfate essentially according to the procedure of Brooks.[12] In this way there was obtained a 49% yield of methyl *p*-vinylbenzoate.

The authors are grateful to Mr. E. L. Ringwald for the preparation of considerable quantities of methyl *p*-ethylbenzoate.

Experimental

Ethyl *p*-Ethylbenzoate.[13]—A solution of 500 g. of HTH (70% $Ca(ClO)_2$ in 2 liters of water and one of 350 g. of potassium carbonate and 100 g. of potassium hydroxide in 1 liter of water were mixed, thoroughly shaken and filtered. The filtrate was placed in a 5-liter, three-necked flask equipped with a stirrer, thermometer, dropping funnel and refluxing condenser, and heated to 65°. While the mixture was stirred and held at 75–80° by the occasional application of a water-bath, 160 g. of *p*-ethylacetophenone was added over a forty-five-minute period. The mixture was stirred thirty minutes more at this temperature and then cooled. A solution of 100 g. of sodium bisulfite in 400 cc. of water was added with continued cooling and the stirring continued for fifteen minutes. This solution was finally acidified with 400 cc. of concentrated hydrochloric acid and the precipitated acid was removed by filtration, washed with water and dried in a 50° oven. This product together with 36 g. from another experiment was refluxed for one and one-half hours with 800 cc. of absolute ethyl alcohol while a vigorous stream of hydrogen chloride was introduced into the boiling mixture. At this

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[1] Since the completion of this work an article has appeared by Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945), which describes the preparation of this compound by an alternate route.

[2] Stephens, THIS JOURNAL, **48**, 2920 (1926).

[3] Stephens, *ibid.*, **50**, 2523 (1928).

[4] King, Swann and Keyes, *Ind. Eng. Chem.*, **21**, 1227 (1929).

[5] Senseman and Stubbs, *ibid.*, **25**, 1286 (1933).

[6] Newitt and Burgoyne, *Proc. Roy. Soc.* (London), **A153**, 448 (1936); *C. A.*, **30**, 2555^9 (1936).

[7] Binapfl and Krey, U. S. Patent 1,813,606; *Chem. Zentr.*, **102**, II, 2058 (1931).

[8] I. G. Farbenindustrie, A.-G., French Patent 646,078; *Chem. Zentr.*, **100**, I, 1507 (1929).

[9] I. G. Farbenindustrie, A. G., U. S. Patent 1,815,985; see French Patent 676,826; *Chem. Zentr.*, **101**, I, 3831 (1930).

[10] Loder, U. S. Patent 2,245,528; *C. A.*, **35**, 5912^8 (1941).

[11] Emerson and Agnew, THIS JOURNAL, **67**, 518 (1945).

[12] Brooks, *ibid.*, **66**, 1295 (1944).

[13] This is an adaptation of the method of Newman and Holmes, "Organic Syntheses," Coll. Vol. II, p. 428.

point 200 cc. more of alcohol was added and the boiling continued for another hour with hydrogen chloride introduction. Upon cooling, 17 g. of inorganic solid was removed by filtration and the filtrate was diluted with water. Distillation of the benzene extract of this material yielded 224 g. (96%) of ethyl *p*-ethylbenzoate, b. p. 122–130° (11 mm.) [129–150° (15 mm.)],[14] n^{25}_{D} 1.5045. An analytical sample boiled at 127.0–127.5° (16 mm.), n^{25}_{D} 1.5065, d^{25}_{25} 1.010.

Anal.[15] Calcd. for $C_{11}H_{14}O_2$: C, 74.2; H, 7.87. Found: C, 74.8; H, 8.13.

Ethyl *p*-Acetylbenzoate.—Air was blown through an alundum disperser for twenty-eight hours into 624 g. of ethyl *p*-ethylbenzoate containing 1% of chromium oxide and 4% of calcium carbonate held at 140–145°. The water produced was collected in a Stark and Dean trap. Upon cooling, the mixture was diluted with a little benzene, filtered free of catalyst and then diluted to 1.5 liter with absolute ethyl alcohol. It was refluxed for two hours, while a vigorous stream of hydrogen chloride was introduced. The introduction of hydrogen chloride was continued for another hour, after which the mixture was diluted with water and the layers separated. Distillation of the benzene fraction yielded 257 g. (41% recovery) of ethyl *p*-ethylbenzoate, b. p. 126–136° (15 mm.), n^{25}_{D} 1.5078; 278 g. (41% conversion, 70% yield) of ethyl *p*-acetylbenzoate, b. p. 154–168° (13 mm.), and 14 g. of higher boiling oil, b. p. 168–196° (13 mm.). There was a large residue from the distillation. A sample of ethyl *p*-acetylbenzoate was crystallized once from alcohol, m. p. 46–49° (57°).[16]

Ethyl *p*-(α-Hydroxyethyl)-benzoate.—Fifty-two grams of ethyl *p*-acetylbenzoate was hydrogenated in standard equipment using 105 cc. of ethanol as solvent and 2.7 g. of copper chromite catalyst. The reaction was run at 140° until there was no further pressure drop. The product, after distillation, boiled at 99–101° (1.3 mm.), n^{25}_{D} 1.5246, 33.2 g., yield 63%. An analytical sample boiled at 112–113° (3 mm.), n^{25}_{D} 1.5240, d^{25}_{25} 1.102.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.22; sapon. equiv., 194. Found: C, 68.5; H, 7.30; sapon. equiv., 194.

A sample of the hydrogenated product was saponified with alcoholic alkali. The acid therefrom, recrystallized from hot water, melted at 137–138° (138–139°[17]). Calcd.: neut. equiv., 162. Found: neut. equiv., 165.

Ethyl *p*-Vinylbenzoate.—Three attempts were made to dehydrate ethyl *p*-(α-hydroxyethyl)-benzoate by passing it through a column packed with alumina, in a steam atmosphere at 300–350° and 50–100 mm. pressure.

In the first run, from 50 g. of starting material there was obtained 2 g. (5% yield) of product, boiling at 135–137° (11 mm.), n^{25}_{D} 1.5450, d^{25}_{25} 1.037.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.84. Found: C, 77.1; H, 7.33.

In the second run, from 51 g. of starting material there was obtained 9.5 g. (21% yield) of material boiling at 140–155° (15 mm.), n^{25}_{D} 1.5444.

In the third run, from 18.6 g. of starting material there was obtained 1.2 g. of crystalline material. After recrystallization from benzene, it melted at 142–143° (143–144°),[1] and gave the correct analysis for *p*-vinylbenzoic acid.

Anal. Calcd. for $C_9H_8O_2$: C, 72.9; H, 5.40. Found: C, 72.6; H, 5.54.

The non-crystalline portion of the reaction product (5 g.) polymerized when distillation was attempted. This product swelled to a voluminous gel on long-continued treatment with aqueous alkali, and shrank to its original proportions when again treated with acid.

Anal. Calcd. for $(C_9H_8O_2)_x$: C, 72.9; H, 5.40. Found: C, 72.4; H, 6.11.

Methyl *p*-Ethylbenzoate.—In a 5-liter, 3-necked flask equipped with a gas inlet tube, stirrer and reflux condenser were placed 860 g. of *p*-ethylbenzoic acid and 3 liters of methanol. These were heated to boiling and dry hydrogen chloride was bubbled in for three hours. After cooling overnight, the lower organic layer was separated, and the upper layer was added to 2 liters of water. The organic layer which separated was combined with the original organic layer, washed with water and dried. On distillation, the product boiled at 127.0–130.5° (24 mm.), n^{25}_{D} 1.5141. It weighed 742 g., a yield of 79%. An analytical sample boiled at 91° (3 mm.), n^{25}_{D} 1.5130, d^{25}_{25} 1.039.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.1; H, 7.31; sapon. equiv., 164. Found: C, 73.1; H, 7.35; sapon. equiv., 164.

Hydrolysis of a small sample of methyl *p*-ethylbenzoate with alkali gave an acid, which, on recrystallization from hexane, melted at 112.2–114.2°. (For *p*-ethylbenzoic acid, a melting-point of 113.5° is recorded[14].)

Methyl *p*-Acetylbenzoate.—This compound was prepared by air oxidation of methyl *p*-ethylbenzoate, using essentially the method already described for ethyl *p*-acetylbenzoate. The air was introduced through a plain glass tube instead of a disperser, dispersion of the gas being obtained by vigorous stirring. At the end of the run the reaction mixture was poured out of the reaction flask while still warm, and diluted with enough benzene to keep the product in solution while it was being filtered from the catalyst. It was deemed unnecessary to re-esterify before distillation. When 500 g. of methyl *p*-ethylbenzoate was oxidized for twenty-four hours at 150°, in the presence of the chromium oxide–calcium carbonate catalyst, 95 g. (19%) was recovered and 290 g. (54% conversion, 66% yield) of methyl *p*-acetylbenzoate was obtained, b. p. 140–145° (4 mm.). An analytical sample, recrystallized from hexane, melted at 95.2–95.4° (94°[18]).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.62; sapon. equiv., 178. Found: C, 67.7; H, 5.86; sapon. equiv., 188.

A sample of the pure ester, saponified with aqueous alkali, gave an acid, which melted at 199–202° (200°[19]) after recrystallization from benzene–hexane–acetone.

Methyl *p*-(α-Hydroxyethyl)-benzoate.—Two hundred twenty-six grams of methyl *p*-acetylbenzoate was hydrogenated in standard equipment, using 400 cc. of methanol as a solvent, and 23 g. of copper chromite catalyst, at 150°, until there was no further pressure drop. The product consisted of 182 g. of material boiling at 145–165° (8 mm.), n^{25}_{D} 1.5334, a yield of 80%. An analytical sample boiled at 134° (4 mm.), n^{25}_{D} 1.5336, d^{25}_{25} 1.144.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.7; H, 6.67; sapon. equiv., 180. Found: C, 66.9; H, 6.72; sapon. equiv., 184.

A small sample of the ester was saponified with aqueous alkali. The acid from the saponification, on recrystallization from benzene, melted at 136.5–138° (138–139).[17] A further recrystallization from benzene gave material of m. p. 136.8–137.5°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.0; H, 6.03; neut. equiv., 166. Found: C, 65.3; H, 6.12; neut. equiv., 166.

Methyl *p*-Vinylbenzoate.—In a Claisen flask carrying a thermometer, and connected to a receiver containing 1 g. of hydroquinone, were placed 75 g. of methyl *p*-(α-hydroxyethyl)-benzoate, 1 g. of potassium bisulfate and 1 g. of hydroquinone. The whole was placed in an oil-bath and evacuated to 20 mm. The bath was rapidly heated to 170°, at which point distillation began. The temperature of the oil-bath was then gradually raised so as to keep the distillation rate at about one drop every two or three seconds, to a maximum of 215–220°, at which time the reaction was complete, leaving a solid polymeric residue in the reaction flask.

A second run was made in exactly the same manner, except that 80 g. of starting material was used, and the oil-

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(14) Kindler, *Ann.*, **452**, 90 (1927).

(15) All of the analyses are microanalyses performed by Arlington Laboratories, Fairfax, Virginia.

(16) Berend and Herms, *J. prakt. Chem.*, [2] **74**, 128 (1906).

(17) Melstrom, *Iowa State Coll. J. Sci.*, **18**, 65 (1943); *C. A.*, **38**, 727 (1944).

(18) Feist, *Ber.*, **67**, 938 (1934).

(19) Ahrens, *ibid.*, **20**, 2952 (1887).

bath was heated to 150° before immersing the reaction flask in it.

The distillates from the two runs were combined, diluted with benzene, most of the water separated, and then the benzene layer was distilled from hydroquinone through a Vigreux column. The product was 69 g. (49% yield) of material boiling at 89–90° (2 mm.), $n^{25}\text{D}$ 1.5568 (supercooled liquid), m. p. 33–34°. An analytical sample melted at 35.0–36.5° (35–36°).[1]

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.0; H, 6.18; sapon. equiv., 162. Found: C, 74.1; H, 6.44; sapon. equiv., 162.

Summary

The liquid phase oxidation of methyl *p*-ethylbenzoate to methyl *p*-acetylbenzoate has been achieved in 54% conversion and 66% yield. This reaction, followed by hydrogenation and dehydration, constitutes a convenient synthesis of methyl *p*-vinylbenzoate.

DAYTON, OHIO RECEIVED JANUARY 31, 1946

[CONTRIBUTION FROM THE PROCTER AND GAMBLE CO.]

The Identity and Polymorphism of Oleyldistearin from Kokum Butter

BY E. S. LUTTON

In 1897 Heise[1] isolated an oleyldistearin from kokum butter and from mkányi fat. Hilditch[2] in 1933 by study of the azelayldistearin from the naturally occurring oleyldistearin indicated the latter glyceride was the symmetrical isomer. The synthesis of pure 2-oleyldistearin and its homologs by Jackson, Daubert, King and Longenecker[3] afforded the opportunity to establish the structure of the natural glyceride with finality. Daubert and Clarke[4] investigated thermally the polymorphism of these compounds. Meara[5] had already found thermal points for the natural oleyldistearin very similar to those reported by Daubert and Clarke for 2-oleyldistearin. He later[6] published additional melting point data on the natural glyceride from several sources including kokum butter, all agreeing quite satisfactorily with the data of Daubert and Clarke.[4]

The weight of evidence is rather convincing, but further confirmation is to be found in X-ray diffraction data. Filer, *et al.*,[7] have very recently reported diffraction patterns for two solvent crystallized forms of (1) synthetic 2-oleyldistearin and (2) a natural oleyldistearin prepared from kokum butter in this laboratory. The corresponding patterns for the two glycerides are practically identical.

By X-ray diffraction and thermal methods an extensive investigation of the polymorphism of the oleyldistearin from kokum butter has been carried out in this laboratory. Through the courtesy of Drs. Longenecker and Daubert it has been possible to make a briefer but similar investigation of their synthetic 2-oleyldistearin. Again the results for the two materials are nearly identical. Deviations from the aforementioned data[7] were observed and will be discussed in a later section.

Materials

1. **Naturally Occurring 2-Oleyldistearin.**—A typical sample of kokum butter was received from the British Food Mission. Analyses of a portion which had been melted and filtered were as follows: iodine value = 36.3, thiocyanogen value = 35.2, acid value = 6.0, saponification value = 189.2, unsaponifiable = 1.36. The filtered portion was then subjected to these steps of fractional crystallization: (a) Three hundred grams was once crystallized from four volumes of acetone at 70°F. (b) The precipitate was crystallized four times from four volumes of acetone at 80°F. (c) The final precipitate of step (b) was crystallized from twenty volumes of petroleum ether at 50°F. The precipitate, Fraction I, was rejected. (d) The filtrate from (c) was crystallized at 32°F. (precipitate = Fraction II, evaporated filtrate = Fraction III). The yield of the main sample, Fraction II, corrected for material removed for analysis was 39%. The stage of purification reached is indicated in some measure by the data of Table I.

TABLE I

FINAL CRYSTALLIZATION FRACTIONS

Fraction	Wt., g.	Iodine value
I	12	28.1
II	75.5	28.3
III	1.3	29.0
Calcd. for 2-oleyldistearin		28.6

2. **Synthetic 2-Oleyldistearin.**—Two solvent crystallized samples in 1-mm. Nylon capillaries were received from Drs. Daubert and Longenecker. The triglyceride had been prepared as described in the literature.[3]

Methods Employed

Samples of the natural glyceride were subjected to examination by m. p., thermal curve and X-ray diffraction as previously described in the case of tristearin and homologs.[8]

The synthetic glyceride was exposed for X-ray diffraction in the Nylon capillaries. For temperature treatment and melting point determination the Nylon capillaries were enclosed in slightly larger thin-walled Pyrex capillaries. Thermal data and X-ray diffraction data appear in Table II.

The various forms were prepared in a variety of ways, but the following are typical. The lowest melting form was obtained by melting the sample and chilling in ice water. The intermediate melting form was obtained by

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(1) Heise, *Tropenflanzer*, **1**, 10 (1897).

(2) Hilditch and Saletore, *J. Soc. Chem. Ind.*, **52**, 101T (1933).

(3) Jackson, Daubert, King and Longenecker, THIS JOURNAL, **66**, 289 (1944).

(4) Daubert and Clarke, *ibid.*, **66**, 690 (1944).

(5) Hilditch, *et al.*, *J. Soc. Chem. Ind.*, **60**, 16–18 (1941).

(6) Meara, *J. Chem. Soc.*, 22 (1945).

(7) Filer, Sidhu, Daubert and Longenecker, THIS JOURNAL, **68**, 167 (1946).

(8) Lutton, *ibid.*, **67**, 524 (1945).