which reduction of the copper reagent has taken place. The reducing carbohydrates show up as blue spots against a white background, which gradually becomes somewhat blue.

When examined by this technique, a linear starch degradation product of average size about 3 glucose units, showed clearly resolved spots at least through the octasaccharide, while beyond the octasaccharide partially resolved components through the dodecasaccharide appeared. Beyond this a continuum of components extended to those which failed to move under the chromatographic conditions used. The initial hydrolytic products from α-, β- and γ-dextrins corresponded very exactly in position with the hexasaccharide, heptasaccharide and octasaccharide components of the linear starch hydrolysate. In the 24-hour hydrolysates, it was easily possible to see the spots corresponding to each oligosaccharide from glucose through heptasaccharide (β-dextrin) and from glucose through octasaccharide (γ-dextrin). There was no evidence for components higher than the heptasaccharide or octasaccharide, although as mentioned previously these components were clearly indicated in the linear starch degradation product.

β-Amylase Digestion.—An excess of soybean β-amylase[13] was added to a sample of the 4-hour hydrolysate and the amount of maltose formed determined by alkaline copper reduction[8]: 101, 104, 100%; calcd. for $(C_6H_{10}O_5)_7$-$(C_6H_{12}O_6)$: 104.0. No components other than maltose were detected by paper chromatography of the digest.

Summary

X-Ray crystallographic measurements, acid hydrolysis, paper chromatography and enzyme digestion together with previous periodate oxidation studies indicate that the γ-dextrin is the cyclic octasaccharide of the amylose series, cyclooctaamylose.

(13) Newton and Naylor, *Cereal Chem.*, **16**, 71 (1939).

AMES, IOWA RECEIVED MAY 8, 1950

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

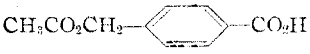
Some Esters Based on *p*-Chloromethylbenzoyl Chloride

BY WILLIAM S. EMERSON AND ROBERT A. HEIMSCH

p-Chloromethylbenzoyl chloride (I), readily preparable in 91–95% yields by the chlorination of *p*-toluyl chloride, constitutes a very versatile intermediate for the preparation of *p*-toluic acid derivatives. In this paper are described certain fundamental reactions of this compound, which involve both the alcohol and acid functions of the molecule.

Treatment of *p*-chloromethylbenzoyl chloride with sodium acetate in acetic acid followed by hydrolysis yielded 72% of *p*-carboxybenzyl acetate (II), which was further hydrolyzed with aqueous alkali to the known *p*-carboxybenzyl alcohol.


I


II


III

p-Chloromethylbenzoyl chloride reacted with cold aqueous alkali to give 98% of *p*-chloromethylbenzoic acid. The *n*-butyl and methyl esters (III) were prepared in 87% and 93% yields, respectively, by using the appropriate alcohol[1] in place of water.

n-Butyl *p*-chloromethylbenzoate did not esterify readily. With sodium butyrate in the presence of triethylamine only 32% of *p*-carbobutoxybenzyl butyrate (IV) was obtained. The adipate was obtained in the same way in 12% yield along with 6% of monocarbobutoxybenzyl adipate.


IV

Methyl *p*-chloromethylbenzoate (III) reacted with alcoholic potassium thiocyanate to give 58% of methyl *p*-isothiocyanomethylbenzoate. The thiocyanate rearranged probably during its isolation. With Raney alloy in boiling water[2] methyl *p*-chloromethylbenzoate yielded principally methyl *p*-toluate (53%) together with 17% of 1,2-bis-(*p*-carbomethoxyphenyl)-ethane (V).


V

Methyl *p*-chloromethylbenzoate reacted with sodium ethyl malonate to give 66% of ethyl *p*-carbomethoxybenzylmalonate.[3] This compound was hydrolyzed, decarboxylated and reesterified to give a 46% over-all yield of methyl β-(*p*-carbomethoxyphenyl)-propionate. The 2-ethylhexyl ester also was prepared.

Experimental

***p*-Chloromethylbenzoyl Chloride.**—*p*-Toluyl chloride was chlorinated at 75–90°. At 42–50% conversions yields ranged from 91% to 95%. A sample, b. p. 140–156° (20 mm.) (150–155° (22 mm.)),[4] solidified on standing. It was crystallized from hexane, m. p. 30–31°,[5] (33–35°).[6]

Anal.[7] Calcd. for $C_8H_6OCl_2$: C, 50.8; H, 3.17. Found: C, 50.7; H, 3.12.

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(1) Blicke and Lilienfeld, THIS JOURNAL, **65**, 2281 (1943), prepared the ethyl ester in 90% yield from the acid chloride and ethanol in the presence of a pyridine catalyst.

(2) Buu-Hoi and Hoán, *J. Org. Chem.*, **14**, 1023 (1949).

(3) Titley, *J. Chem. Soc.*, 2571 (1928), condensed ethyl *p*-bromomethylbenzoate with sodium ethyl chloromalonate, and ethyl *m*-chloromethylbenzoate with sodium ethyl methylmalonate.

(4) Badische Anilin-Soda Fabrik, German Patent 239,311; *Frdl.*, **10**, 118 (1910).

(5) All of the melting points are uncorrected.

(6) P. B. Report No. 82040; Frames 2986–2995.

(7) All of the analyses are microanalyses performed by Mr. P. J. Adams and Mr. Donald Stolz of this laboratory and by the Micro Tech Laboratories, 8000 Lincoln Ave., Skokie, Ill.

***p*-Carboxybenzyl Acetate.**—To a boiling solution of 170 g. of sodium acetate in 500 cc. of glacial acetic acid and 50 cc. of acetic anhydride was added over a ten-minute period, 98 g. of *p*-chloromethylbenzoyl chloride. After the mixture had been boiled under reflux for seven hours, it was cooled, diluted with benzene and filtered. The precipitate was washed with benzene and the combined filtrate and washings were distilled to remove most of the acetic acid, cooled and diluted to 1 l. with benzene. The precipitate was separated by filtration, washed with benzene, slurried with water, again separated by filtration and then dried *in vacuo* over potassium hydroxide. It weighed 92 g. (72%). Further crops from the original solution were gummy. An analytical sample was crystallized twice from benzene–hexane, m. p. 127.5–128.0°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.9; H, 5.15. Found: C, 61.9; H, 5.09.

Hydrolysis with boiling 10% sodium hydroxide yielded *p*-carboxybenzyl alcohol. It was crystallized from aqueous ethanol, m. p. 171–175° (181°).[8]

Anal. Calcd. for $C_8H_8O_3$: C, 63.1; H, 5.26. Found: C, 63.1; H, 5.27.

***p*-Chloromethylbenzoic Acid.**—To 57 g. of *p*-chloromethylbenzoyl chloride held below 40° was added with stirring a solution of 12 g. of sodium hydroxide in 50 cc. of water. After the mixture had been stirred for thirty minutes, it was acidified with concentrated hydrochloric acid. The precipitate was separated by filtration, washed with water and dried *in vacuo* to give 50 g. (98%) of *p*-chloromethylbenzoic acid. A sample was crystallized from benzene, m. p. 199–201° (199°).[9]

***n*-Butyl *p*-Chloromethylbenzoate.**—While 400 cc. of *n*-butanol was stirred below 32°, 433 g. of *p*-chloromethylbenzoyl chloride was added over a thirty-minute period. Then a solution of 88 g. of sodium hydroxide in 600 cc. of *n*-butanol (prepared by boiling the two under a Dean and Stark trap until all the alkali dissolved) was added at such a rate that the temperature was always below 30°. After an hour of stirring, 500 cc. of water was added and the layers were separated. The aqueous portion was extracted twice with benzene. The combined organic layer and extracts were washed with 5% sodium bicarbonate and then with water. Distillation yielded 450 g. (87%) of *n*-butyl *p*-chloromethylbenzoate, b. p. 182–184° (20 mm.), $n^{25}\mathrm{D}$ 1.5188. An analytical sample boiled at 147.5° (0.4 mm.), $n^{25}\mathrm{D}$ 1.5190, d^{25}_{25} 1.109.

Anal. Calcd. for $C_{12}H_{15}O_2Cl$: C, 63.6; H, 6.62. Found: C, 63.4; H, 6.64.

***p*-Carbobutoxybenzyl Butyrate.**—A mixture of 33 g. of sodium butyrate, 57 g. of *n*-butyl *p*-chloromethylbenzoate, 1.0 g. of triethylamine and 100 cc. of toluene was boiled under reflux for ninety minutes.[10] After cooling, the mixture was washed twice with water and distilled to give 18 g. (35%) of what probably was *p*-carbobutoxybenzyl alcohol, b. p. 204–208° (18 mm.), $n^{25}\mathrm{D}$ 1.5070, d^{25}_{25} 1.089 and 22 g. (32%) of *p*-carbobutoxybenzyl butyrate, b. p. 221–222° (18 mm.), $n^{25}\mathrm{D}$ 1.4936, d^{25}_{25} 1.054.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.1; H, 7.91. Found: C, 69.0; H, 7.80.

***p*-Carbobutoxybenzyl Adipate.**—A mixture of 47.5 g. of sodium adipate, 113 g. of *n*-butyl *p*-chloromethylbenzoate, 1.0 g. of triethylamine and 20 cc. of toluene was boiled under reflux for one hour. Upon cooling, the mixture was diluted with 100 cc. of benzene and washed with 100 cc. of 5% sodium bicarbonate and then with 100 cc. of water. Distillation to 200° (4 mm.) yielded 40 g. of *n*-butyl *p*-chloromethylbenzoate. The residue was boiled with 100 cc. of water containing 10 g. of potassium permanganate. After decomposing the permanganate with ethanol, the mixture was filtered, and the layers were separated. The organic layer was washed with 100 cc. of water, heated to 200° (4 mm.), stirred with 10 g. of magnesium carbonate and filtered hot. After the oil had stood in the icebox for several days, crystals appeared. These were separated by filtration and recrystallized from a mixture of benzene and hexane to give 10 g. (6%) of monocarbobutoxybenzyl adipate, m. p. 47–48°.

Anal. Calcd. for $C_{18}H_{24}O_6$: C, 64.3; H, 7.14. Found: C, 64.9; H, 7.13.

The filtrate was washed with 10% sodium bicarbonate and dried. It weighed 32 g. and represented a 12% yield of *p*-carbobutoxybenzyl adipate, $n^{25}\mathrm{D}$ 1.5172, d^{25}_{25} 1.123.

Anal. Calcd. for $C_{30}H_{38}O_8$: C, 68.5; H, 7.23. Found: C, 68.5; H, 7.24.

Methyl *p*-Chloromethylbenzoate.—While 400 cc. of methanol was stirred below 32°, 189 g. of *p*-chloromethylbenzoyl chloride was added over a ten-minute period. A solution of 38 g. of sodium hydroxide in 300 cc. of methanol was added over a twenty-five minute period with the reaction temperature below 15°. While the mixture was stirred for another hour, the temperature rose to 25°. Then 1.5 l. of water was added and the mixture was extracted four times with benzene. The combined benzene extracts were washed once with 5% sodium bicarbonate solution and twice with water. Distillation yielded 172.5 g. (93%) of methyl *p*-chloromethylbenzoate, b. p. 160–165° (30 mm.). An analytical sample was crystallized twice from hexane, m. p. 39–40°.

Anal. Calcd. for $C_9H_9O_2Cl$: C, 58.5; H, 4.88. Found: C, 58.5; H, 5.11.

Methyl *p*-Isothiocyanomethylbenzoate.—To a boiling solution of 32 g. of potassium thiocyanate in 400 cc. of ethanol was added 46 g. of methyl *p*-chloromethylbenzoate. After the solution had boiled for one hour, it was filtered and evaporated to a volume of 60 cc. The slurry was filtered and the precipitate was washed with a little ethanol. Distillation of the combined filtrate and washings yielded 30 g. (58%) of crude methyl *p*-isothiocyanomethylbenzoate, b. p. 138–152° (0.5 mm.). Redistillation yielded 27.5 g. of pure material, b. p. 138–139° (0.3 mm.), $n^{25}\mathrm{D}$ 1.5822, d^{25}_{25} 1.219.

Anal. Calcd. for $C_{10}H_9O_2NS$: C, 58.0; H, 4.35. Found: C, 58.3; H, 4.21.

This compound gave a negative test for the thiocyanate group[11] and a positive test for the isothiocyanate group.[12]

1,2-Bis-(*p*-carbomethoxyphenyl)-ethane.—While a suspension of 12 g. of Raney alloy in 100 cc. of water was stirred at 90–100°, 43 g. of methyl *p*-chloromethylbenzoate was added over a ten-minute period. After two hours of boiling the mixture was cooled and filtered. The precipitate was washed four times with benzene and the filtrate was extracted three times with benzene. After the benzene had been distilled at reduced pressure from the combined extracts and washings, the residue was filtered and the precipitate was washed with hexane. The dried crystals, 6.0 g., m. p. 113–117°, represented a 17% yield of 1,2-bis-(*p*-carbomethoxyphenyl)-ethane. A sample was recrystallized from methanol, m. p. 118.5–119.0° (119°).[13] Distillation of the filtrate yielded 18.5 g. (53%) of methyl *p*-toluate, b. p. 98–104° (13 mm.) (217°, atm. pressure).[14]

Ethyl *p*-Carbomethoxybenzylmalonate.—To a solution of 13.8 g. of sodium in 250 cc. of absolute ethanol which had been cooled to 50° was added 240 g. of ethyl malonate. Then a solution of 111 g. of methyl *p*-chloromethylbenzoate in 50 cc. of ethanol was added over a twenty-minute period. The mixture was boiled for five and one-half hours and then 200 cc. of ethanol was distilled. After cooling, 100 cc. of water, 50 cc. of benzene and 4 cc. of con-

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(8) Löw, *Ann.*, **231**, 361 (1885).

(9) Mellinghoff, *Ber.*, **22**, 3207 (1889).

(10) Method of Tharp, Nottorf, Herr, Hoover, Wagner, Weisgerber, Whitmore and Wilkins, *Ind. Eng. Chem.*, **39**, 1300 (1947).

(11) Wood, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 254.

(12) Mulliken, "Identification of Pure Organic Compounds," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1922, p. 18.

(13) Fischer and Wolfenstein, *Ber.*, **37**, 3215 (1904).

(14) Heilbron, "Dictionary of Organic Compounds," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 777.

centrated hydrochloric acid were added. The layers were separated and the organic layer was washed with 100 cc. of water. Distillation yielded 124.5 g. (52% recovery) of ethyl malonate, b. p. 87–89° (13 mm.), n^{25}D 1.4125; 11.0 g. of intermediate, b. p. 89° (13 mm.)–102° (0.35 mm.), n^{25}D 1.4210; 49 g. (44% recovery) of methyl *p*-chloromethylbenzoate, b. p. 102–118° (0.35–0.60 mm.), n^{25}D 1.5330–1.5298; 6.5 g. of intermediate, b. p. 118–174° (0.60–0.70 mm.); and 68.0 g. (37% conversion and 66% yield based on methyl *p*-chloromethylbenzoate) of ethyl *p*-carbomethoxybenzylmalonate, b. p. 174–184° (0.70–0.80 mm.), n^{25}D 1.4960. There was a 17.0 g. residue.

In another experiment in which the ratio of ethyl malonate to methyl *p*-chloromethylbenzoate was 1.1/1.0 instead of 2.5/1.0 crystals were observed in the distillation residue. They were separated by filtration, washed with hexane and dried. Crystallization from methanol and then from hexane yielded pure ethyl bis-(*p*-carboethoxybenzyl)-malonate, m. p. 82–83°.

Anal. Calcd. for $C_{27}H_{32}O_8$: C, 67.0; H, 6.61. Found: C, 66.9; H, 6.54.

β-(*p*-Carboxyphenyl)-propionic Acid.—A mixture of 31 g. of ethyl *p*-carbomethoxybenzylmalonate, 28 g. of potassium hydroxide and 50 cc. of water was boiled under reflux for three and one-half hours. Upon cooling, the solution was acidified with concentrated hydrochloric acid. The slurry was chilled in an ice-bath, filtered and the precipitate of crude β-(*p*-carboxyphenyl)-propionic acid was washed with water. It was crystallized twice from water. Two crops were obtained: I, 13.5 g., m. p. 270–280°, neut. equiv., 85.2, 85.0 and II, 5.0 g., m. p. 276–286°, neut. equiv., 82.7, 82.6. The neutral equivalent of *p*-carboxybenzylmalonic acid is 79 and that of *p*-carboxyphenylpropionic acid is 87.

A suspension of 43 g. of crude β-(*p*-carboxyphenyl)-propionic acid in 250 cc. of phenyl ether was stirred under reflux for seven hours. After cooling, the mixture was filtered. The precipitate was slurried with hexane, separated by filtration and dried. Recrystallization from glacial acetic acid yielded 29.5 g. of β-(*p*-carboxyphenyl)-propionic acid, m. p. 286–291° (294°).[3]

Methyl β-(*p*-Carbomethoxyphenyl)-propionate.—A mixture of 28 g. of β-(*p*-carboxyphenyl)-propionic acid, 1 l. of methanol and 10 cc. of concentrated sulfuric acid was stirred under reflux for twenty-three hours. After 900 cc. of methanol had been removed by distillation, the mixture was cooled and some product separated by filtration. The filtrate was diluted with 100 cc. of water and extracted four times with a mixture of benzene and hexane. The original precipitate was dissolved in the combined extracts and then the solution was washed once with aqueous sodium bicarbonate and twice with water. After the solution had been dried over calcium chloride, the solvents were distilled and the residue crystallized by chilling in ice. After two recrystallizations from hexane there was obtained 21.5 g. (46% yield based on ethyl *p*-carbomethoxybenzylmalonate) of methyl β-(*p*-carbomethoxyphenyl)-propionate, m. p. 29–31° (33°).[3]

2-Ethylhexyl β-(*p*-Carbo-2-ethylhexoxyphenyl)-propionate.—A solution of 21.5 g. of methyl β-(*p*-carbomethoxyphenyl)-propionate in 65 g. of 2-ethylhexanol containing 1.0 g. of *p*-toluenesulfonic acid was boiled for four hours (until the pot temperature reached 145–150°) under a 24" Vigreux column while the evolved methanol distilled as formed. The residue was diluted with 35 cc. of benzene, washed once with aqueous sodium bicarbonate, twice with water, and then dried over calcium chloride. After the addition of 1 g. of Norit to the solution, the benzene and 2-ethylhexanol were distilled and the residue was heated for one hour at 150° and 0.5 mm. pressure. Filtration through a sintered glass filter removed the Norit and yielded 33.5 g. (80%) of 2-ethylhexyl β-(*p*-carbo-2-ethylhexoxyphenyl)-propionate, n^{25}D 1.4829, d^{55}_{25} 0.983.

Anal. Calcd. for $C_{26}H_{42}O_4$: C, 74.6; H, 10.04. Found: C, 74.1; H, 9.78.

Summary

p-Chloromethylbenzoyl chloride has been found to be a useful intermediate for the preparation of esters involving both the alcohol and acid functions of the molecule.

Methyl *p*-chloromethylbenzoate reacted readily with sodium thiocyanate and with malonic ester and could be coupled to give a diphenylethane derivative.

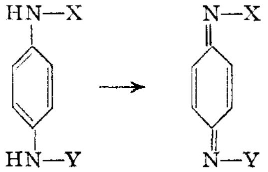
DAYTON 7, OHIO RECEIVED MARCH 29, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. II. *p*-Quinone Diacyl and Diaroylimides

BY ROGER ADAMS AND JOHN L. ANDERSON[1,2]

During the initial investigation of the oxidation of sulfonamides of *p*-phenylenediamine[3] in glacial acetic acid by means of lead tetraacetate, a few experiments to prepare the diimides from the diacetyl and dibenzoyl derivatives of *p*-phenylenediamine were attempted, but no identifiable products were isolated. The present investigation was undertaken in an attempt to find conditions under which these latter compounds could be oxidized to quinone diimides. Studies have shown that temperature and, particularly, solvent and concentration are important factors in the oxidations. By controlling these conditions, the diacyl, diaroyl, and related derivatives of *p*-phenylenediamine can be converted to the *p*-quinone diimides by means of lead tetraacetate in very satisfactory yields. This preliminary paper is confined to a description of the derivatives represented by I and II.



I II

where (a) X = Y = COC_6H_5, (b) X = Y = $COCH_3$, (c) X = Y = $CO_2C_2H_5$, (d) X = Y =

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[1] An abstract of a thesis submitted by John L. Anderson to the Graduate College of the University of Illinois, 1950, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] University of Illinois Fellow, 1948–1949. Allied Chemical and Dye Corporation Fellow, 1949–1950.

[3] Adams and Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).