

such that the styrene should have polymerized thermally. These peroxides thus actually acted as effective inhibitors of the polymerization. That this effect is due to the nitro group was established by addition of as little as 1-2% of nitrobenzene to reaction mixtures which would normally have yielded thermally- or benzoyl peroxide-catalyzed polystyrene. No polymer was obtained in either instance.¹⁴

Summary

The polymerization of styrene and of methyl

(14) Foord [*J. Chem. Soc.*, 48 (1940)] has reported that nitro groups retard the thermal polymerization of styrene.

methacrylate in the presence of such catalysts as *p*-bromobenzoyl peroxide, anisoyl peroxide and chloroacetyl peroxide has yielded polymers with an average of from one-half to two and one-half fragments from the peroxide per polymer molecule. These observations are in complete accord with the suggestion that peroxides serve as catalysts for addition polymerization by decomposition to generate free radicals.

URBANA, ILLINOIS

RECEIVED JUNE 11, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY, AND THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

Branched-Chain Fatty Acids. I. Synthesis of 17-Methyloctadecanoic Acid

BY JAMES CASON

Although branched-chain fatty acids rarely occur in nature, there seems to be a special significance attached to those which do occur, such as the bile acids and the series of fatty acids isolated by Anderson and co-workers¹ from acid-fast bacteria. The acids isolated by Anderson are of both chemical and physiological interest, especially phthioic acid which induces in animals the development of typical tubercular lesions; yet very little is known concerning their structures except that tuberculostearic acid is probably 10-methyloctadecanoic acid.² Some evidence concerning the structure of phthioic acid has been published.³ Determination of structure in this series is rendered rather difficult by lack of knowledge of the properties of pure synthetic branched-chain fatty acids. Fordyce and Johnson⁴ have synthesized isostearic, isopalmitic and isomyristic acids, Spielman⁵ has synthesized 10-methyloctadecanoic acid and Schneider and Spielman⁶ have synthesized several 10-methyl and 2-methyl acids; however, in no case have several physical properties of an entire series of branched-chain acids been investigated. Since knowledge of this kind should be of help in deducing the structures of the naturally-occurring acids, the task of synthesizing the series of methyl-

stearic acids has been inaugurated by the synthesis of 17-methyloctadecanoic acid.

Of the various methods which have been applied to building long aliphatic chains the reaction of an organometallic compound with the acid chloride of a half ester has proved especially satisfactory and in the present communication dialkyl cadmium compounds are shown to be quite useful for this purpose. Isononyl bromide, required for synthesis of 17-methyloctadecanoic acid, was conveniently prepared from isoamyl bromide by either of two methods. By use of the conventional reaction between a Grignard reagent and ethylene oxide isoamyl bromide may be converted to isoheptyl alcohol, and this in turn converted to its bromide and isononyl alcohol (IV). A more novel procedure begins with the reaction of di-isoamyl cadmium and β -carboxymethoxypropionyl chloride (I) according to the method of Gilman and Nelson.⁶ Such a reaction has previously been mentioned by Carter.⁷ De Benneville⁸ has reported a 30% yield of keto acid in the reaction between diphenyl cadmium and succinic anhydride; however, this yield is based on the anhydride and the yield calculated on the basis of the bromide used is only 12%. In the reaction between di-isoamyl cadmium and succinic anhydride the yield of 4-keto-7-methyloctoic acid was only 5-10% and the zinc compound gave no better results, so the use of the acid chloride (I) seems a definite advantage. When an effort

(1) For references consult Anderson, *Physiol. Rev.*, **12**, 166 (1932); Anderson, *Chem. Reviews*, **29**, 225 (1941).

(2) Spielman, *J. Biol. Chem.*, **106**, 87 (1934).

(3) Spielman and Anderson, *ibid.*, **112**, 759 (1936); Wagner-Jauregg, *Z. physiol. Chem.*, **247**, 135 (1937); Robinson, *J. Chem. Soc.*, 505 (1940); Stenhagen and Ställberg, *J. Biol. Chem.*, **139**, 345 (1941).

(4) Fordyce and Johnson, *THIS JOURNAL*, **55**, 3368 (1933).

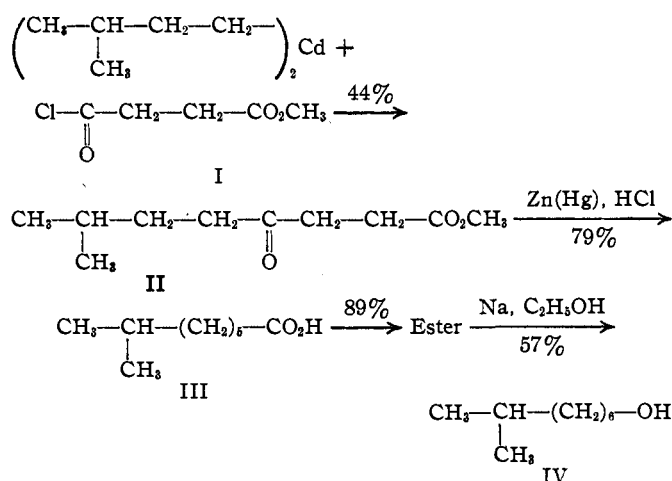
(5) Schneider and Spielman, *J. Biol. Chem.*, **142**, 345 (1942).

(6) Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

(7) Carter, *Iowa State Coll. J. Sci.*, **15**, 63 (1940).

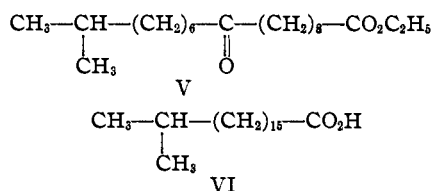
(8) De Benneville, *J. Org. Chem.*, **6**, 462 (1941).

was made to obtain 4-keto-7-methyloctioic acid from the reaction of isoamylmagnesium bromide with succinic anhydride, only higher-boiling products were obtained, in agreement with the observations of several workers⁹ for aliphatic Grignard reagents. A by-product obtained in the preparation of methyl 4-keto-7-methyloctoate was identified as methyl ethyl succinate. This di-ester doubtless arises from reaction of the acid chloride (I) with the diethyl ether used as solvent, a type of reaction which has previously been reported by Whitmore and co-workers.¹⁰ The di-ester could not arise from equilibrium of the ester acid chloride with the corresponding di-ester and di-acid chloride, for such a disproportionation would lead to dimethyl succinate. Methyl 4-keto-7-methyloctoate (II) was reduced in good yield by the Clemmensen method to 7-methyloctioic acid (III), and the ester of this acid was reduced with sodium and alcohol to the desired isononyl alcohol (IV). This alcohol has previously been prepared from isoamyl bromide by Levene and Allen¹¹ by use of the more laborious malonic ester synthesis.



Ethyl 10-keto-17-methyloctadecanoate (V) was readily prepared by the reaction of di-isononyl cadmium with ω -carbomethoxypropionyl chloride. Fordyce and Johnson⁴ prepared ketones of this type by use of the Grignard reagent, while Spielman^{2,5} employed the corresponding zinc derivatives to advantage. The use of cadmium gives about the same yields as does that of zinc but offers the

advantage that anhydrous cadmium chloride is more easily handled than is anhydrous zinc chloride. Reduction of the keto ester (V) by the Clemmensen method to 17-methyloctadecanoic acid (VI) proceeded rather slowly but the yield was satisfactory.



In view of the purpose of this investigation several physical constants of 17-methyloctadecanoic acid were determined.

Experimental Part¹²

β -Carbomethoxypropionyl Chloride (I).—Methyl hydrogen succinate was prepared by heating a mixture of 200 g. of succinic anhydride and 128 g. of absolute methyl alcohol under reflux for two hours, according to Bone, Sudborough and Sprankling¹³; however, instead of isolating the product by crystallization, the reaction mixture was distilled *in vacuo* through an 18-inch packed column. After removal of excess alcohol and a small fore-run of dimethyl succinate, the half ester was collected at 110–111° (2 mm.). The white crystalline product melted at 53–57° and weighed 219 g. (83%, average of three runs).

Two hundred and five grams of half ester was treated with 330 g. of phosphorus pentachloride during about twenty minutes, then the mixture was heated on the steam-bath for one and one-half hours. Distillation of the mixture through a packed column gave 216.5 g. (92.5%) of the acid chloride (I); b. p. 85–87° (15 mm.).

Methyl 4-Keto-7-methyloctoate (II).—The Grignard solution prepared from 60.3 g. of isoamyl bromide and 9.7 g. of magnesium in 250 cc. of ether was cooled in ice and 44 g. of dried cadmium chloride was added in one portion. After stirring for ten minutes, the ice-bath was removed and stirring continued an additional one and one-half hours. To the brown solution of the organo-cadmium compound there was added, in about five minutes, a solution of 39 g. of β -carbomethoxypropionyl chloride in 50 cc. of ether. The resulting grayish-brown solution was stirred for forty-five minutes at room temperature and an additional hour with refluxing (during this period the solution becomes very viscous). After decomposition with ice and sulfuric acid, the ether layer was washed twice with 5% sodium carbonate solution and twice with water, then dried and distilled. The residue remaining after removal of ether was distilled through an 18-inch Podbielniak column at 13 mm. pressure, and after 8.3 g. of fore-run, b. p. 93–122°, had distilled the keto ester was

(9) For references see Runge, "Organometallverbindungen," Wissenschaftliche Verlagsgesellschaft m. b. H., Stuttgart, 1932, p. 168.

(10) Whitmore, Whitaker, Mattil and Popkin, *THIS JOURNAL*, **60**, 2790 (1938); Whitmore and Wheeler, *ibid.*, **60**, 2899 (1938).

(11) Levene and Allen, *J. Biol. Chem.*, **27**, 433 (1916).

(12) All melting points corrected.

(13) Bone, Sudborough and Sprankling, *J. Chem. Soc.*, **85**, 539 (1904).

collected at 122–125°; yield, 21.3 g. (44% based on acid chloride). Use of a larger ratio of acid chloride did not increase the quantity of keto ester obtained.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.50; H, 9.75. Found: C, 63.99; H, 9.53.

The fore-runs from several preparations of this keto ester were combined and redistilled, yielding a chief fraction boiling at 204–205° (756 mm.) and consisting of methyl ethyl succinate. Saponification of this ester gave pure succinic acid, m. p. 182–184°; and its non-identity with dimethyl succinate was established by a direct comparison with pure dimethyl succinate

	B. p. (756 mm.), °C.	F. p., °C.	d_{20}^4
Methyl ethyl succinate	204–205	< –20	1.076
Dimethyl succinate	195.0–195.2	18.5	1.121

Weger¹⁴ has reported for methyl ethyl succinate: b. p. 208.2°; f. p. < –20°; d^0 –1.0925.

In one run the Grignard reagent from 43.4 g. of isoamyl bromide in 150 cc. of ether was added during one hour to 37.6 g. of the acid chloride in 50 cc. of ether, while cooling in ice and salt. After stirring had been continued for fifteen minutes with cooling, the mixture was allowed to stand overnight, then worked up as above. The keto ester fraction weighed only 4.9 g. (10.5%) and there was a large amount of higher-boiling material.

The semicarbazone, which was obtained crystalline with much difficulty, crystallized very slowly from aqueous alcohol as heavy colorless prisms; m. p. 78–84° (sinters at 70°).

Anal. Calcd. for $C_{11}H_{21}O_3N_3$: C, 54.29; H, 8.71. Found: C, 54.34; H, 8.66.

4-Keto-7-methyloctioic Acid.—Six and one-half grams of the keto ester (II) was saponified by heating at 60 ± 5° for two hours with 75 cc. of 1 *N* sodium hydroxide. After acidification, the product was taken up in ether and distilled through an 18-inch Podbielniak column. After a small fore-run the 4-keto-7-methyloctioic acid distilled at 134° (2 mm.); m. p. 47–49°; yield, 5.6 g. (94%). After two crystallizations from petroleum ether (30–60°), this acid was obtained as slender blades with mother-of-pearl luster; m. p. 48–50°.

Anal. Calcd. for $C_8H_{16}O_3$: C, 62.78; H, 9.35. Found: C, 63.08; H, 9.43.

The semicarbazone, prepared from a sample of distilled acid, crystallized from 50% aqueous alcohol as fluffy white needles; m. p. 138–140° (gas evolution) varying somewhat with the rate of heating.

Anal. Calcd. for $C_{10}H_{19}O_3N_3$: C, 52.40; H, 8.36. Found: C, 52.42; H, 8.30.

In one run in which di-isoamyl cadmium was allowed to react with 0.5 equivalent of succinic anhydride in refluxing ether solution for twenty-four hours, an 11% yield (on basis of bromide used) of ether-soluble acidic material was obtained, which gave the semicarbazone of 4-keto-7-methyloctioic acid. In another run in which the reaction was continued for forty-eight hours, only 5% yield of pure keto acid was obtained. The zinc compound (prepared from isoamylmagnesium bromide and anhydrous zinc chlo-

ride) gave about the same yield in the reaction with succinic anhydride.

7-Methyloctioic Acid (III).—Forty and one-half grams of the keto ester (II) was reduced by the Clemmensen procedure with 100 g. of amalgamated zinc, 75 cc. of water, and 175 cc. of concentrated hydrochloric acid. Vigorous refluxing was continued for forty-six hours, during which time were added 325 cc. of concentrated hydrochloric acid and a 50-g. charge of amalgamated zinc. The colorless product was extracted with three portions of hexane, and after the extract had been washed and dried and the solvent distilled, the acid was distilled through a Podbielniak column at 2 mm. pressure. The methyloctioic acid distilled at 103–105°, after which the temperature rose rapidly, and there was obtained 1.1 g. of keto acid; b. p. 132–134°. The yield of 7-methyloctioic acid¹¹ was 26.4 g. (79%, based on keto acid consumed). When the reduction was continued for only twenty-eight hours, 16% of keto acid was recovered.

For preparation of the amide, 1 g. of acid and 1.3 g. of phosphorus pentachloride were warmed on the steam-bath for thirty minutes, the phosphorus oxychloride was removed *in vacuo*, and, after cooling, 10 cc. of cold concentrated ammonium hydroxide was added in one portion. A white crystalline solid separated immediately, and after warming for fifteen minutes at 60–70° it was collected. The crude amide, which melted at 99–103°, weighed 0.8 g., and after one crystallization from ligroin (75–90°) gave the constant m. p. of 104–105° (Levene and Allen,¹¹ 106.5°).

Isononyl Alcohol (IV).—(A) Ethyl 7-methyloctioate¹¹ was prepared by refluxing for two hours a mixture of 32.8 g. of acid (III), 115 cc. of absolute alcohol, and 5 cc. of concentrated sulfuric acid; yield, 34.5 g. (89.5%); b. p. 102° (12 mm.). This ester (30 g.) was reduced with sodium and alcohol as described by Ford and Marvel,¹⁵ the reduction being completed in about four minutes. The reaction mixture was diluted with about 1 liter of water and extracted with four 100-cc. portions of hexane. After the extract had been washed with 5% sodium carbonate solution, water and saturated sodium chloride solution, and the solvent had been distilled, the alcohol was distilled from a Claisen flask; b. p. 100° (13 mm.); yield, 13.2 g. (57%). The phenyl urethan, after one crystallization from petroleum ether (30–60°), melted at 64–65° and gave no depression with the sample prepared as described under (B). Levene and Allen¹¹ have reported this m. p. as 66.4°.

(B) The reaction between a Grignard solution prepared from 90.5 g. of isoamyl bromide and 14.7 g. of magnesium in 225 cc. of ether, and a solution of 40 g. of ethylene oxide in 75 cc. of ether was carried out essentially as described by Dreger.¹⁶ After the reaction mixture had been decomposed with ice and acid the organic layer was washed with 20% sodium hydroxide and water, dried, and then fractionated through a packed column. After 5.5 g. of fore-run, b. p. 73–98° (45 mm.), isoheptyl alcohol distilled at 98–101° (45 mm.); yield, 36.5 g. (52.5%). The phenyl urethan, crystallizing from aqueous alcohol as white needles, melted at 80.0–81.5°; literature,¹¹ 82.5°

(15) Ford and Marvel, "Organic Syntheses, Vol. X, p. 62 (1930)

(16) Dreger, *ibid.*, Coll. Vol. I, p. 229 (1932).

(14) Weger, *Ann.*, **221**, 38 (1883).

Isoheptyl bromide, prepared with hydrobromic and sulfuric acids in 89% yield, boiled at 83° (45 mm.).

Anal. Calcd. for $C_7H_{15}Br$: C, 46.96; H, 8.43. Found: C, 47.37; H, 8.59.

The Grignard solution from 93.5 g. of isoheptyl bromide and 12.9 g. of magnesium in 200 cc. of ether was treated with a solution of 34.5 g. of ethylene oxide in 75 cc. of ether, as described above; however, in this case, the second stage of the ethylene oxide reaction occurred during refluxing of the ether solution. The reaction mixture was worked up as before and the product fractionated through a packed column. After a small fore-run there was obtained 4.0 g. of isononyl alcohol, b. p. 110–115° (25 mm.), and 33.0 g., b. p. 115–120° (25 mm.) (90% at 118°); total yield, 49%. The phenyl urethan, prepared from the low-boiling fraction, formed white needles from aqueous alcohol or hexane, and after two crystallizations melted at 64.4–65.4°.

Isononyl bromide, prepared in 91% yield by refluxing a mixture of 44 g. of isononyl alcohol, 102 cc. of 48% hydrobromic acid, and 12.3 cc. of concentrated sulfuric acid for six hours, boiled at 92–93° (13 mm.).

Anal. Calcd. for $C_9H_{19}Br$: C, 52.19; H, 9.24. Found: C, 52.87; H, 9.38

ω -Carbathoxynonyl Chloride.—Ethyl hydrogen sebacate was prepared according to Swann, Oehler and Buswell,¹⁷ except that the reaction mixture was distilled through an 18-inch heated Vigreux column. In this way a yield of 67–71% was obtained, b. p. 173–176° (2 mm.), after a single distillation. The acid chloride was prepared with phosphorus pentachloride, as described for β -carbomethoxypropionyl chloride. The product was distilled rapidly (in 50–60-g. lots) from a Claisen flask, b. p. 171–172° (12 mm.); yield, 81%.

Ethyl 10-Keto-17-methyloctadecanoate (V).—Di-isononylcadmium was prepared from 22 g. of isononyl bromide in 100 cc. of ether, as described for di-isoamylcadmium, and to this was added in about two minutes a solution of 26.4 g. of ω -carbathoxynonyl chloride in 40 cc. of ether. The mixture was stirred one hour at room temperature and three hours under reflux, then worked up as described before. The keto ester was distilled from a Claisen flask at 1–2 mm. pressure; b. p. 190–200°; yield, 16.7 g. (46%). There was also obtained about 5 g. of low-boiling material. The product was sufficiently pure for the next step, but for analysis a sample was redistilled and a center cut taken; b. p. 197° (1–2 mm.).

Anal. Calcd. for $C_{21}H_{40}O_2$: C, 74.07; H, 11.84. Found: C, 74.34; H, 12.11.

One run was made in which the Grignard reagent from 8 g. of isononyl bromide in 50 cc. of ether was added dropwise to a stirred solution of 9.6 g. of ω -carbathoxynonyl chloride in 25 cc. of ether, during forty-five minutes while cooling in ice. After stirring the resulting mixture for one hour at room temperature and an additional half hour under reflux the reaction was worked up as above, yielding 2.6 g. (20%) of keto ester. It was found relatively unsatisfactory to saponify the crude product and isolate the keto acid by crystallization,⁴ due to the interference of sebacic acid.

10-Keto-17-methyloctadecanoic Acid.—A solution of 4.1 g. of keto ester (V) in 40 cc. of 1 *N* alcoholic potassium hydroxide was warmed for two hours at 60 \pm 5°. A small precipitate was removed from the warm solution by suction filtration and then dissolved in a few cc. of water. The precipitate obtained on acidification (90 mg.) melted at 112–122°, and after recrystallization from water the m. p. was 131.5–132.2°; no depression with sebacic acid. This acid probably arises from diethyl sebacate not completely separated by distillation from a Claisen flask, and arising from interaction of the acid chloride with ether.¹⁰ It does not arise from ethyl hydrogen sebacate, for exhaustive extraction of the keto ester with sodium carbonate solution failed to remove the source of the sebacic acid. The alcoholic filtrate obtained above was diluted with water and acidified, and the keto acid was collected. The white product weighed 3.5 g. (95%) and melted at 70.0–73.5°. After three crystallizations from hexane the analytical sample formed large irregular blades; m. p. 73.5–74.5°.

Anal. Calcd. for $C_{17}H_{34}O_2$: C, 73.03; H, 11.62. Found: C, 72.91; H, 11.30.

The **semicarbazone**, prepared in 50% aqueous alcohol, crystallized from acetone as fine white needles; m. p. 97.5–97.7°.

Anal. Calcd. for $C_{20}H_{38}O_2N_2$: C, 65.01; H, 10.64. Found: C, 64.96; H, 10.55.

17-Methyloctadecanoic Acid (VI).—Ten grams of the keto ester (V) was reduced by the Clemmensen procedure, the reduction being continued for sixty-five hours and three 25-g. portions of zinc amalgam being used. The reaction mixture was cooled and the white crystalline acid collected together with the zinc. The acid was dissolved in 50 cc. of absolute methyl alcohol, the zinc was removed by filtration, and after addition of 2.5 cc. of concentrated sulfuric acid the mixture was refluxed for two hours. After dilution with water the product was collected in hexane and the extract was washed with 5% sodium carbonate and water, then dried and distilled. The residue was fractionated through a Podbielniak column. After a very small fore-run, methyl 17-methyloctadecanoate distilled at 171–172° (1–2 mm.); yield, 7.7 g. The colorless distillate crystallized on cooling to about 22° and melted at 25–27.5°. A center cut, m. p. 26–28°, was used for analysis.

Anal. Calcd. for $C_{20}H_{40}O_2$: C, 76.86; H, 12.90. Found: C, 77.25; H, 12.85.

The ester (6.6 g.) was saponified by refluxing for one hour with 25 cc. of 10% alcoholic potassium hydroxide. The 17-methyloctadecanoic acid obtained after dilution with water and acidification weighed 6.0 g. (77% from keto ester) and melted at 61–65.5°. After two crystallizations from acetone there was obtained 4.7 g. of acid melting at 67.0–67.6°. After additional crystallizations from acetone and hexane, the analytical sample formed feathery, irregular blades melting at 67.3–67.8°; n_D^{20} 1.4336; d_4^{20} 0.8420.

Anal. Calcd. for $C_{19}H_{38}O_2$: C, 76.45; H, 12.83; mol. wt., 298.5. Found: C, 76.69; H, 12.78; mol. wt., 297.0, 297.2.

In one run in which the acid was crystallized directly from acetone, omitting purification by distillation of the ester, acid of the same melting point was readily obtained

(17) Swann, Oehler and Buswell, "Org. Syn.," **19**, 45 (1939).

but in considerably lower yield. The **amide**, prepared in 60% yield as described for 7-methyloctioic acid, after crystallization from ligroin (75–90°), methyl alcohol and acetone, separated in rosetts of small white blades; m. p. 100.2–101.3°.

Anal. Calcd. for $C_{19}H_{39}ON$: C, 76.71; H, 13.21. Found: C, 77.01; H, 13.39.

The **tribromoanilide** was prepared in 74% yield (m. p. 111.5–112.5°) by heating the acid chloride from 0.50 g. of acid with 0.58 g. of tribromoaniline for one and one-half hours on the steam-bath. After two crystallizations from ethyl alcohol, slender white needles were obtained; m. p. 112.0–112.5°.

Anal. Calcd. for $C_{25}H_{40}ONBr_3$: C, 49.21; H, 6.60. Found: C, 49.13; H, 6.62.

The **lead salt** was prepared by pouring an alcoholic solution of the sodium salt into aqueous lead acetate.

Anal. Calcd. for $C_{38}H_{74}O_4Pb$: Pb, 25.81. Found: Pb, 25.65.

This salt was very sparingly soluble in ether (15–20 mg. per 100 cc.).

Summary

Ethyl 10-keto-17-methyloctadecanoate has been synthesized by the reaction of di-isononyl cadmium with ω -carbethoxynonyl chloride. This keto ester has been converted to 17-methyloctadecanoic acid by Clemmensen reduction. 4-Keto-7-methyloctioic acid was prepared as an intermediate in this synthesis.

NASHVILLE, TENN.

RECEIVED FEBRUARY 4, 1942

[COMMUNICATION NO. 844 FROM THE KODAK RESEARCH LABORATORIES]

The Synthesis of Some New Glucose and Gentiobiose Derivatives

BY DELBERT D. REYNOLDS AND WILLIAM O. KENYON

Many esters of glucose derived from monobasic organic acids are known, and intramolecular or cyclic carbonic acid esters of glucose have been synthesized.¹ However, as far as the authors are aware, the intermolecular esters containing two glucose units and one dibasic acid, or a derivative of such interesters, are not known. Recently, the authors had occasion to prepare di-(1,2,3,4-tetraacetyl- β -*D*-glucosyl) carbonate, and it was obtained in good yields. This paper describes the method of preparing this compound and some of its derivatives.

As substantiation for the structures assigned, the di-(1,2,3,4-tetraacetyl- β -*D*-glucosyl) carbonate was converted to di-(1,2,3,4,2',3',4'-heptaacetyl- β -gentiobiosyl) carbonate as illustrated in Fig. 1. The latter compound was hydrolyzed to gentiobiose which was converted to β -gentiobiose octaacetate and compared with a specimen of pure octaacetate synthesized by another method.²

The unusual stability of the di-(1-bromo-2,3,4-triacetyl- β -*D*-glucosyl) carbonate is worthy of note. A sample of the pure compound was exposed to laboratory conditions for several months without any noticeable decomposition or change of melting point.

A similar series of compounds has been pre-

pared from other sugars and other dibasic acids. We hope to report these in subsequent papers.

The plan of the experimental work and the structures of the compounds produced are shown in Fig. 1.

Experimental

Di-(1,2,3,4-tetraacetyl- β -*D*-glucosyl) Carbonate (II).—Twenty grams of β -*D*-glucose 1,2,3,4-tetraacetate (I), prepared as described by Reynolds and Evans,² and 5 g. of Drierite were added to 50 cc. of dry pyridine. This mixture was cooled in an ice-water-bath and a solution of 2.8 g. of phosgene in 10 cc. of dry toluene was added slowly. The mixture soon formed a firm gel. Fifty cc. of pyridine was added, the mixture shaken at room temperature for fifteen hours, and then warmed on the steam-bath for two hours. The resulting solution was poured into ice water containing acetic acid in excess of the pyridine used. The precipitate was dried and recrystallized by dissolving in chloroform and adding ether until crystallization began; average yield 17 g. (82% of theory); m. p. 195–196°; twice recrystallized by the above method, the m. p. was 198–199°; $[\alpha]_{D}^{20.5} + 12.15^{\circ}$ (*c*, 4.026; *l*, 2; $CHCl_3$). *Anal.* Calcd. for $C_{28}H_{48}O_{21}$: C, 48.17; H, 5.30. Found: C, 48.06; H, 5.23.

Di-(1-bromo-2,3,4-triacetyl- β -*D*-glucosyl) Carbonate (III).—Twenty grams of II dissolved in 200 cc. of a 32% solution of hydrogen bromide in glacial acetic acid was allowed to stand two hours at room temperature and then 200 cc. of chloroform was added. The solution was poured into 1 liter of ice water. The resulting chloroform layer containing III was separated, washed well with ice

(1) W. N. Haworth and C. R. Porter, *J. Chem. Soc.*, 151 (1930).

(2) D. D. Reynolds and W. L. Evans, *THIS JOURNAL*, **60**, 2559 (1938).

(3) We wish to thank Mr. T. F. Murray, Jr., of these Laboratories, for the optical rotation measurements.