[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

2,3,4,5-Dibenzylidene-D-mannitol and Some of its Derivatives

BY W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

The readily available dibenzoyl-D-mannitol of Einhorn and Hollandt[1] has been shown conclusively to be the 1,6-dibenzoyl derivative by Brigl and Grüner.[2a] Ohle and co-workers[2b] had condensed this dibenzoate, which they thought to be 4,5-dibenzoyl-D-mannitol, with benzaldehyde by heating the mixture with anhydrous sodium sulfate at 130°, obtaining in 26% yield a crystalline substance (m. p. 117°, $[\alpha]^{20}D$ + 28.04° in chloroform) which Brigl and Grüner[2a] showed later to be 1,6-dibenzoyl-3,4-benzylidene-D-mannitol. In an attempt to improve the yield of this last derivative, we condensed 1,6-dibenzoyl-D-mannitol with benzaldehyde at 25°, using fused zinc chloride as catalyst; the dibenzoate, which is insoluble in benzaldehyde, dissolved within fifteen minutes after the addition of the zinc chloride, and after a few hours crystalline material separated. It proved to be a new condensation product, a dibenzoyl-dibenzylidene-D-mannitol (m. p. 169–170° (cor.), $[\alpha]^{20}D$ +45.2° in chloroform). In this experiment it was the main product of the reaction (yield 59%); the mother liquor yielded 24% of the known 1,6-dibenzoyl-3,4-benzylidene-D-mannitol showing the m. p. 119–120° (cor.) and $[\alpha]^{20}D$ +31.8° in chloroform. The proportions of the two products of the condensation (the mono- and the di-benzylidene derivatives) were found to vary irregularly according to the experimental conditions, as is described later. The co-existence of the two acetals would suggest that the mono-derivative is the precursor of the other and that the end-product has the structure 1,6-dibenzoyl–2,5:3,4-dibenzylidene-D-mannitol. Although we have been able to convert the mono- into the di-derivative in a yield of 64% by further treatment with benzaldehyde and zinc chloride, we do not consider that an acetal rearrangement under these conditions is excluded and therefore for the present we prefer to designate the new substance merely as 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol. The debenzoylation of it yields the new 2,3,4,5-dibenzylidene-D-mannitol (m. p. 203–205° (cor.), $[\alpha]^{20}D$ +76.7° in chloroform), which on tosylation is converted to 1,6-ditosyl-2,3,4,5-dibenzylidene-D-mannitol (m. p. 185–186° (cor.), $[\alpha]^{20}D$ +87.5° in chloroform). The tosyl groups in this substance were readily replaceable by iodine, yielding 1,6-diiodo-2,3,4,5-dibenzylidene-D-mannitol (m. p. 184–185° (cor.), $[\alpha]^{20}D$ +58.0° in chloroform), which in turn was reduced by hydrogen and Raney nickel to 1,6-didesoxy-2,3,-4,5-dibenzylidene-D-mannitol (m. p. 159–160° (cor.), $[\alpha]^{20}D$ +49.5° in chloroform). The acid hydrolysis of this last substance yielded the known 1,6-didesoxy-D-mannitol.[3]

We express our appreciation to Dr. A. T. Ness for performing the microchemical analyses.

Experimental

1,6-Dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol and 1,6-Dibenzoyl-3,4-benzylidene-D-mannitol from 1,6-Dibenzoyl-D-mannitol, Benzaldehyde and Fused Zinc Chloride.—The 1,6-dibenzoyl-D-mannitol was readily prepared according to the directions of Brigl and Grüner.[2a] A suspension of 5.0 g. of this dibenzoate, 5.0 g. of powdered fused zinc chloride (fused stick, reagent grade, from General Chemical Co.) and 10 cc. of benzaldehyde was shaken until solution of the dibenzoate was complete (15 min.); after three days the thick mass of crystals was thinned with 10 cc. of alcohol and filtered (yield 4.3 g., 59%). The crystals were insoluble in water, nearly insoluble in cold alcohol or ether but readily soluble in cold pyridine or warm dioxane. They were recrystallized from a mixture of 10 parts of alcohol and 4 parts of dioxane and formed prisms which showed $[\alpha]^{20}D$ +45.2° (*c*, 0.8) in chloroform. Analysis showed the substance to be 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol.

Anal. Calcd. for $C_{34}H_{30}O_8$: C, 72.07; H, 5.34; C_6H_5-CO, 37.1. Found: C, 72.01; H, 5.34; C_6H_5CO, 37.2.

The melting phenomena of the substance are unusual and very characteristic; when it is heated in a capillary tube it melts at 169–170° (cor.), then soon resolidifies and melts again at 179–180° (cor.). It was kept somewhat above 180° for some time and then allowed to cool slowly and crystallize; these crystals showed the same characteristic double melting point. The substance is apparently dimorphic, but we have not studied the phenomenon further and can make no statement concerning a transition temperature.

The mother liquor from which the 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol had been separated was saturated with petroleum ether and upon allowing the solution to stand in the refrigerator for twenty-four hours a crop of

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[1] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898).

[2] (a) Brigl and Grüner, *Ber.*, **65**, 641 (1932); *ibid.*, **66**, 931 (1933); (b) *cf.* Ohle, Erlbach, Hepp and Toussaint, *Ber.*, **62**, 2982 (1929); Müller, *Ber.*, **65**, 1055 (1932).

[3] Micheel, *Ann.*, **496**, 93 (1932); Haskins, Hann and Hudson, THIS JOURNAL, **65**, 67 (1943).

fine needles was deposited. The yield was 1.5 g. (24%). The material, after recrystallization by solution in 5 parts of chloroform and the addition of 15 parts of petroleum ether, melted at 119–120° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +31.8° in chloroform (*c*, 0.9). Ohle, Erlbach, Hepp and Toussaint[2b] reported a melting point of 117° and a specific rotation $[\alpha]^{20}\mathrm{D}$ of +28.04° in chloroform for this compound, which Brigl and Grüner[2a] have shown to be 1,6-dibenzoyl-3,4-benzylidene-D-mannitol. The analysis of the material in our hands agrees with this composition and confirms the analysis which Ohle and collaborators have published.

In other experiments, as reported in Table I, the quantities of 1,6-dibenzoyl-D-mannitol, benzaldehyde and zinc chloride were varied; considerable variation in the yields of the two crystalline reaction products was noted, and the amounts of mono and diacetal dibenzoate that were obtained under the same reaction conditions were not always consistent in different runs. Different lots of zinc chloride did not give like results. We have reported similar anomalies in the condensation of 1,6-dibenzoyl-dulcitol with benzaldehyde when zinc chloride is used as catalyst.[4]

Table I

Condensation of 1,6-Dibenzoyl-D-Mannitol with Benzaldehyde, Using Zinc Chloride as Catalyst

1,6-Dibenzoyl-D-mannitol, g.	Benzaldehyde, cc.	Fused zinc chloride, g.	Diacetal dibenzoate g.	Diacetal dibenzoate %	Mono-acetal dibenzoate g.	Mono-acetal dibenzoate %
5	10	5[a]	4.3	59	1.5	24
5	10	5[a]	4.0	55	1.2	20
7.5	10	5[a]	2.7	25	4.7	51
5	20	5[a]	1.8	25	3.4	56
5	10	5[b]	3.8	52	1.5	24
10	20	10[b]	4.3	30	4.3	35
20	40	20[b]	7.0	24	11.7	48

[a] General Chemical Company, fused stick, reagent grade, Code 2439. [b] J. T. Baker, c. p. analyzed, fused stick, Lot number 2740.

1,6-Dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol from 1,6-Dibenzoyl-3,4-benzylidene-D-mannitol.—A solution of 2.0 g. of 1,6-dibenzoyl-3,4-benzylidene-D-mannitol in a mixture of 2.0 g. of fused zinc chloride and 4 cc. of benzaldehyde was allowed to stand at 25° for two weeks, during which time a magma of crystals was formed. The reaction mixture was thinned by the addition of 5 cc. of alcohol and the crystalline product (1.5 g.; m. p. 164–167°) was separated by filtration and recrystallized from a mixture of dioxane and alcohol. The recrystallized substance (1.4 g., 58%) rotated $[\alpha]^{20}\mathrm{D}$ +45.1° in chloroform (*c*, 0.8) and showed the characteristic double melting point behavior of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol, melting at 169–170° (cor.) then resolidifying and remelting at 178–180° (cor.); a mixed melting point determination with an authentic sample of the latter substance showed no change in the melting points.

3,4-Benzylidene-D-mannitol.—To an ice-cold solution of 4.0 g. of 1,6-dibenzoyl-3,4-benzylidene-D-mannitol in 50 cc. of chloroform, 10 cc. of 0.1 *N* sodium methylate solution was added and the reaction mixture was allowed to stand at 5° for eighteen hours; the alcohol and methyl benzoate were removed by concentrating the solution to dryness *in vacuo* and the crystalline residue was extracted with 20 cc. of warm ethyl acetate. The 3,4-benzylidene-D-mannitol which deposited from the cooled solution (1.5 g., 68%) was recrystallized from 14 parts of ethyl acetate; it consisted of fine needles which melted at 136–137° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +29.0° in water (*c*, 0.8). Ohle, Erlbach, Hepp and Toussaint[2b] reported a melting point of 136° and a specific rotation $[\alpha]^{20}\mathrm{D}$ of +28.83° in water for this acetal.

1,2,5,6-Tetrabenzoyl-3,4-benzylidene-D-mannitol.—To an ice-cold solution of 2.0 g. of 1,6-dibenzoyl-3,4-benzylidene-D-mannitol in 10 cc. of pyridine, 1.5 cc. of benzoyl chloride was added dropwise and the reaction mixture was allowed to stand for eighteen hours at 25°; crushed ice was then added and the heavy sirup which precipitated gradually crystallized. The yield was 2.9 g. (quantitative). The tetrabenzoate was recrystallized by solution in 13 parts of absolute alcohol and formed clusters of needles; it melted at 126–127° (cor.) and showed a rotation $[\alpha]^{20}\mathrm{D}$ of −27.9° in chloroform (*c*, 0.8) in agreement with the recorded values of Brigl and Grüner,[2a] who prepared the substance by the further benzoylation of 1,2,6-tribenzoyl-3,4-benzylidene-D-mannitol.

1,6-Dibenzoyl-2,3,4,5-tetraacetyl-D-mannitol.—A solution of 2.0 g. of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol in an acid acetylating solution, prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid, was allowed to stand for nineteen hours at 25° and then poured upon 200 g. of crushed ice. The precipitate (2.0 g., quantitative) was separated by filtration and upon recrystallization from 4 parts of alcohol it formed six-sided prisms, which melted at 126–127° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +38.9° in chloroform (*c*, 0.8). The same compound was obtained by the acetylation of 1,6-dibenzoyl-D-mannitol in pyridine solution with acetic anhydride. Ohle, Erlbach, Hepp and Toussaint report a melting point of 126° and a specific rotation $[\alpha]^{20}\mathrm{D}$ of +41.35° in chloroform (*c*, 4.644) for the substance.

Anal. Calcd. for $C_{28}H_{30}O_{12}$: C, 60.20; H, 5.41. Found: C, 60.21; H, 5.53.

2,3,4,5-Dibenzylidene-D-mannitol.—A solution of 4.0 g. of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol in 50 cc. of chloroform was cooled to 0° and 10 cc. of 0.1 *N* sodium methylate was added; after standing at 5° for eighteen hours the reaction mixture was concentrated *in vacuo* to remove the chloroform and methyl benzoate and the crystalline residue (2.3 g., 92%) was washed with water and recrystallized from 20 parts of absolute alcohol. The diacetal formed quadrilateral plates which decomposed at 203–205° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +76.7° in pyridine (*c*, 0.8). It is soluble in dioxane and in hot alcohol and insoluble in chloroform and in water.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02: H, 6.19. Found: C, 66.96: H, 6.14.

1,6-Diacetyl-2,3,4,5-dibenzylidene-D-mannitol.—A solution of 1.0 g. of 2,3,4,5-dibenzylidene-D-mannitol in a mixture of 5 cc. of pyridine and 5 cc. of acetic anhydride was allowed to stand at room temperature for twenty hours and then poured upon crushed ice. The precipitated di-

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(4) Haskins, Hann and Hudson, This Journal, **64**, 136 (1942).

acetate was separated by filtration and recrystallized from a mixture of 25 parts of absolute alcohol and 3 parts of dioxane; it formed quadrilateral plates, which melted at 185–186° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +100.0° in chloroform (*c*, 0.8). It was readily soluble in chloroform, dioxane, pyridine and acetone, slightly soluble in ether and hot alcohol and insoluble in cold alcohol, petroleum ether and water. The yield was 1.2 g. (quantitative).

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92; CH_3CO, 19.4. Found: C, 65.27; H, 5.92; CH_3CO, 19.6.

1,6-Ditosyl-2,3,4,5-dibenzylidene-D-mannitol.—A solution of 3.5 g. of 2,3,4,5-dibenzylidene-D-mannitol and 5.0 g. of *p*-toluenesulfonyl chloride in 25 cc. of pyridine was allowed to stand at room temperature for twenty-four hours and the reaction mixture was then poured upon crushed ice. The 1,6-ditosyl-2,3,4,5-dibenzylidene-D-mannitol which precipitated (6.5 g., quantitative) was separated by filtration and upon recrystallization from 20 parts of chloroform it formed fine needles, melting at 185–186° (cor.) and rotating $[\alpha]^{20}\mathrm{D}$ +87.5° in chloroform (*c*, 0.8); it was soluble in warm chloroform and dioxane, moderately soluble in pyridine and chloroform at 25°, and insoluble in alcohol, acetone and water.

Anal. Calcd. for $C_{34}H_{34}O_{10}S_2$: C, 61.24; H, 5.14. Found: C, 61.50; H, 5.21.

1,6-Ditosyl-2,3,4,5-tetraacetyl-D-mannitol.—This compound was obtained from 1,6-ditosyl-2,3,4,5-dibenzylidene-D-mannitol by treatment with an acid acetylating mixture as described for the preparation of 1,6-dibenzoyl-2,3,4,5-tetraacetyl-D-mannitol. The yield from 2.0 g. of the ditosyl-diacetal was 1.7 g. (85%). The compound deposited from its solution in 7 parts of alcohol as small quadrilateral plates melting at 119–120° (cor.) and rotating $[\alpha]^{20}\mathrm{D}$ +22.9° in chloroform (*c*, 0.8).

Anal. Calcd. for $C_{28}H_{34}O_{14}S_2$: C, 51.05; H, 5.20. Found: C, 50.83; H, 5.21.

1,6-Di-iodo-2,3,4,5-dibenzylidene-D-mannitol.—A suspension of 1.0 g, of 1,6-ditosyl-2,3,4,5-dibenzylidene-D-mannitol and 1.5 g. of sodium iodide in 50 cc. of acetone was heated for two hours at 100° in a pressure flask. The sodium *p*-toluene sulfonate which had formed (0.60 g.; theory for two molecular equivalents, 0.58 g.) was separated by filtration and the acetone mother liquor was concentrated *in vacuo* to dryness; the residual solid was washed with water to remove the excess sodium iodide and the insoluble 1,6-di-iodo-2,3,4,5-dibenzylidene-D-mannitol was recrystallized by solution in 10 parts of chloroform and the addition of 20 parts of ether. The yield was 0.85 g. (98%). The substance, which melted at 184–185° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ +58.0° in chloroform (*c*, 0.8), formed glistening elongated prisms; it was insoluble in methyl alcohol, water and ether, soluble in acetone, warm chloroform, ethyl acetate and dioxane and moderately soluble in chloroform at 25°.

Anal. Calcd. for $C_{20}H_{20}O_4I_2$: C, 41.54; H, 3.49. Found: C, 41.53; H, 3.60.

1,6-Didesoxy-2,3,4,5-dibenzylidene-D-mannitol.—A suspension of 3.5 g. of 1,6-di-iodo-2,3,4,5-dibenzylidene-D-mannitol and 1.0 g. of Raney nickel in a mixture of 350 cc. of methyl alcohol and 25 cc. of 0.795 *N* barium methylate solution was agitated vigorously at 25° while hydrogen under a slight positive pressure was introduced.[5] In twenty minutes 315 cc. (calcd., 297 cc.) of hydrogen was taken up and the di-iodo diacetal, which is insoluble in methyl alcohol, had been reduced as evidenced by its complete solution. The catalyst was removed by filtration and the filtrate, upon concentration *in vacuo*, deposited a crystalline precipitate which was extracted with water to remove soluble barium salts and then recrystallized from 40 parts of methyl alcohol. The yield of 1,6-didesoxy-2,3,4,5-dibenzylidene-D-mannitol was 1.9 g. or 96%. The substance is soluble in chloroform and hot methyl and ethyl alcohols and practically insoluble in water and cold methyl and ethyl alcohols. It crystallizes in the form of elongated prisms which melt at 159–160° (cor.) and rotate $[\alpha]^{20}\mathrm{D}$ +49.5° in chloroform (*c*, 0.8).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.49; H, 6.87.

1,6-Didesoxy-D-mannitol.—A solution of 1.0 g. of 1,6-didesoxy-2,3,4,5-dibenzylidene-D-mannitol in 25 cc. of 80% acetic acid was refluxed for one hour; the reaction mixture was concentrated *in vacuo* to dryness and the dry residue was extracted with ether to remove any remaining benzaldehyde and then recrystallized by solution in a small amount of alcohol and the addition of ether. The yield was 0.3 g. (65%). The compound, after one further recrystallization by solution in 16 parts of alcohol and the addition of 50 parts of ether, melted at 147–148° (cor.) and rotated $[\alpha]^{20}\mathrm{D}$ −21.4° in aqueous solution (*c*, 0.8). This rotation is slightly lower than that previously recorded,[3] namely, −22.5°; the latter value was determined on a very small amount of material and we regard the specific rotation −21.4° as the more accurate value. A mixed melting point with 1,6-didesoxy-D-mannitol prepared from 1,6-didesoxy-2,3,4,5-dimethylene-D-mannitol showed no depression. Micheel[3] recorded a melting point of 148° and a specific rotation $[\alpha]^{18}\mathrm{D}$ of −17.6° in chloroform for 1,6-didesoxy-D-mannitol.

Summary

The condensation of the known 1,6-dibenzoyl-D-mannitol and benzaldehyde by fused zinc chloride at 25° formed a mixture of the known 1,6-dibenzoyl-3,4-benzylidene-D-mannitol and a new substance, which is 1,6-dibenzoyl-dibenzylidene-D-mannitol. The latter compound was also obtained by condensing 1,6-dibenzoyl-3,4-benzylidene-D-mannitol with benzaldehyde by fused zinc chloride at 25°, but because of the recognized possibility of acetal rearrangement when zinc chloride is used as an adjunct in acetal formation the diacetal is designated merely as 1,6-dibenzoyl-2,3,4,5-dibenzylidene-D-mannitol. Upon debenzoylation it yielded 2,3,4,5-dibenzylidene-D-mannitol, which was successively converted by customary reactions to 1,6-ditosyl-2,3,4,5-dibenzylidene-D-mannitol, 1,6-di-iodo-2,3,4,5-di-

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[5] Attention is called to this use of barium methylate in the reduction; use of the customary methyl alcoholic potassium hydroxide proved unsuccessful for obtaining a crystalline reduction product.

benzylidene-D-mannitol, 1,6-didesoxy-2,3,4,5-dibenzylidene-D-mannitol and the known 1,6-didesoxy-D-mannitol of Micheel.

BETHESDA, MARYLAND RECEIVED APRIL 30, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Tertiary Alkyl Primary Amines, $RR'R''CNH_2$. III[1]

BY HENRY R. HENZE AND THOMAS R. THOMPSON[2]

It has been demonstrated that carbinamines result from interaction of allylmagnesium bromide and α-alkoxyalkyl cyanides,[3,4] alkyl cyanides,[4] an aralkyl cyanide,[4] alkenyl cyanides,[4] and keto nitriles.[5] Because of the more satisfactory yields of amines obtained in use of α-alkoxyalkyl cyanides, we have continued our utilization of alkoxyacetonitriles and have extended the investigation to include both α- and β-substituted ethoxypropionitriles.

It is of interest to note that β-ethoxypropionitrile reacts, essentially as do α-ethoxypropionitrile and α-alkoxyacetonitriles, with two equivalents of allylmagnesium bromide to form the diallyl-2-ethoxyethylcarbinamine. However, in contrast to the behavior of the α-alkoxynitriles, β-ethoxypropionitrile does not react with propylmagnesium bromide to form an adduct capable of further interaction with allylmagnesium bromide. Nor does this β-alkoxynitrile react smoothly with propylmagnesium bromide to yield the anticipated ketone.

Ability of an adduct, formed initially by interaction of an α-alkoxynitrile with an alkylmagnesium bromide, to react further with the allyl Grignard reagent has been again demonstrated utilizing the adducts produced from *n*-propoxyacetonitrile and isoamoxyacetonitrile, respectively, with methylmagnesium bromide.

All of the allylcarbinamines prepared in this study were reduced catalytically to the corresponding *n*-propyl analogs. Both types of amines are but sparingly soluble in water but readily form picrates and other salts. Unsaturation in the allylcarbinamines can be tested for satisfactorily by mixing acetone solutions of the amine and potassium permanganate. However, chloroform solutions of bromine are decolorized with virtually the same rapidity by both the allyl and propyl amines.

Through the courtesy of Eli Lilly and Company, four of these carbinamines have been tested for possible effect upon blood pressure. The methylisoamoxymethyl-allyl and *n*-propyl carbinamines and the methyl-*n*-propoxymethyl-allyl and *n*-propyl carbinamines were tested by injection into the vein of a pitted cat. Their action seems to be comparable to that of less complex aliphatic amines in lowering blood pressure instead of raising it.

Experimental

α-Ethoxypropionitrile.—α-Chloroethyl ethyl ether[6] (140 g.) was added to 112 g. of dry cuprous cyanide suspended in 200 cc. of anhydrous benzene and the mixture was stirred for two hours before being warmed on the steam-bath for four hours. Distillation and refractionation of the product produced 65 g. (51% yield) of α-ethoxypropionitrile[7]; b. p. 129–130° (751 mm.); d^{20}_{4} 0.8743; n^{22}_{D} 1.3890.

β-Ethoxypropionitrile.—Ethylene cyanohydrin was prepared from ethylene chlorohydrin and sodium cyanide[8] and was converted into β-chloropropionitrile[9] by reaction with thionyl chloride in chloroform solution. The chloronitrile was obtained in 60% yield, b. p. 175° (747 mm.)[10]; d^{20}_{4}1. 1573; n^{20}_{D} 1.4360; *MR* calcd. 20.67; *MR* found 20.22.

Twenty-three grams of freshly cut sodium was added in portions to 350 cc. of ethanol and gently warmed until solution was complete. With cooling in an ice-bath and vigorous stirring, 73.5 g. of β-chloropropionitrile was added slowly. After the initial reaction had subsided, the mixture was warmed for two hours on the steam-bath. Excess sodium ethylate was decomposed by addition of 5 cc. of water and saturation with carbon dioxide. Inorganic material was removed by centrifugation. The alcohol was distilled and the residue upon fractionation yielded 46.6 g.

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[1] From the Ph.D. dissertation of T. R. Thompson, June, 1942. Presented before the Division of Organic Chemistry at the 105th meeting of the American Chemical Society at Detroit, Michigan, April 12–16, 1943.

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[3] Allen and Henze, THIS JOURNAL, **61**, 1790 (1939).

[4] Henze, Allen and Leslie, *ibid.*, **65**, 87 (1943).

[5] Rehberg with Henze, *ibid.*, **63**, 2785 (1941).

[6] Henze and Murchison, *ibid.*, **53**, 4077 (1931).

[7] Gauthier [*Ann. chim. phys.*, (8) **16**, 313 (1909)] reported b. p. 129–130° (730 mm.); d^{16}_{4} 0.878; n^{16} 1.390.

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 57. Our material b. p. 220–221° (746 mm.); d^{20}_{4} 1.0554; n^{20}_{D} 1.4247; γ^{20} 49.42 dynes/sq. cm.; *MR* calcd. 17.34; *MR* found 17.19; *P* calcd. 179.0; *P* found 178.4.

[9] Chapman and Stephen, *J. Chem. Soc.*, **127**, 888 (1925).

[10] Henry [*Chem. Zentr.*, **69**, II, 22 (1898)] reported b. p. 174–176°; $d^{18.5}$ 1.1443.