with an equal volume of cold tap water. An extraction with ether was then carried out and the ether extract shaken twice with sodium carbonate and twice with distilled water to remove all traces of acid. The ether extract was then allowed to stand overnight over anhydrous sodium sulfate and finally filtered. The ether is removed by distillation and may be reused.

The chloromethylnaphthalene must be distilled *in vacuo* with great care. Precautions include the use of an oil-bath for even heating, a capillary tube to aid the distillation and the avoidance of too rapid distillation. Care should also be taken to use a flask which has no spots or focal points where decomposition can start. The yield is 238–250 g. (67–70%). There is some naphthalene that distils before the α-chloromethylnaphthalene, which collects in the condenser and must be washed out with benzene.

alpha-Chloromethylnaphthalene distils at 291–292°. Other temperatures are: 134°(3 mm.), 150°(9 mm.), 149.4–150.4°(11 mm.), 150–152°(13 mm.), 158–159°(14 mm.), and 173–174°(35 mm.). A small amount of liquid was distilled over at 170–200°(10–12 mm.), and this liquid crystallized in the receiver.[5] The crystals contain halogen, are insoluble in ether and melt sharply at 125°.[6] alpha-Chloromethylnaphthalene itself polymerizes fairly easily to a chlorine-free polymer,[5] accompanied by changes in physical state and in solubility. The cream-colored polymer melts around 200°.

Preparation of alpha-Naphthaldehyde.—The literature directions[3] for the preparation of this aldehyde are adequate and require no comment. The aldehyde, isolated through the bisulfite compound, is pure enough to employ without a final distillation. It should be stored in the dark and under nitrogen.

Table I

Alpha-Naphthaldehyde Derivatives

Derivatives	M. p., °C.	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
Oxime[b]	98	...	...
4,4-Diphenylsemicarbazide	197	11.50	11.82
p-Nitrophenylhydrazone	237	14.43	14.29
Semicarbazide	219	19.71	19.75
Thio-semicarbazide	217	18.33	18.00
as-Diphenylhydrazone	100.5	8.69	8.48
2,4-Dinitrophenylhydrazone	254	16.66	16.44
β-Naphthylhydrazone	174–175	9.46	9.18
p-Bromophenylhydrazone	136–137	8.72	8.52
Phenylhydrazone	82	11.38	11.30
2,5-Dichlorophenylhydrazone	114	8.88	8.70
Acetone[c]	130	...	...
Anilide	172	6.08	6.24
o-Toluidide	172.5	5.73	5.98

[a] Many of the analyses (micro-Dumas) by Saul Gottlieb, Columbia University. [b] Hinkel, Ayling and Beynon, *J. Chem. Soc.*, 339 (1936). [c] Calcd. for $C_{26}H_{18}O$: C, 89.78; H, 5.43. Found: C, 89.92; H, 5.30.

Summary

An improved method for the preparation of α-chloromethylnaphthalene is described. The properties of α-chloromethylnaphthalene are discussed.

The melting points are given for certain new derivatives of alpha-naphthaldehyde.

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[5] This compound when tested on spayed rats exhibited no oestrogenic properties. The authors are indebted to the Biological Laboratories, E. R. Squibb & Sons, New Brunswick, N. J., for these tests.

[6] All melting points are corrected for stem exposure.

[Contribution from the Chemical Laboratory of The Ohio State University]

The Dimethyl Acetal of *d*-Glucose

By M. L. Wolfrom and S. W. Waisbrot

The dimethyl acetals of the pentamethyl ethers of *d*-glucose and of several other hexoses have been reported by Levene and Meyer.[1] In the unsubstituted sugar structures, acetals of the small carbon atom sugars, glycolaldehyde[2] and glyceraldehyde[3] have long been known. Hudson and co-workers[4] have prepared the dimethyl acetal of *d*-arabinose by a series of reactions discovered by them for the arabinose structure.

In 1895 Emil Fischer[5] concluded that the impure sirup obtained by treating glucose at room temperature with methanol containing 1% of hydrogen chloride, consisted essentially of glucose dimethyl acetal. This conclusion was a reasonable one since he had previously prepared the thioacetal of glucose.[6] A more thorough investigation of this same methanol reaction product made at a later date caused Emil Fischer[7] to characterize the substance as a new methyl glucoside rather than as a dimethyl acetal. By an extension to glucose of the procedure previously reported from

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[1] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **69**, 175 (1926); *ibid.*, **74**, 695 (1927).

[2] A. Pinner, *Ber.*, **5**, 147 (1872); E. Fischer and G. Giebe, *ibid.*, **30**, 3053 (1897).

[3] A. Wohl, *ibid.*, **31**, 1796 (1898); A. Wohl and F. Momber, *ibid.*, **47**, 3346 (1914).

[4] Edna M. Montgomery, R. M. Hann and C. S. Hudson, This Journal, **59**, 1124 (1937).

[5] E. Fischer, *Ber.*, **28**, 1145 (1895).

[6] E. Fischer, *ibid.*, **27**, 673 (1894).

[7] E. Fischer, *ibid.*, **47**, 1980 (1914).

this Laboratory[8] for the synthesis of acetals of galactose, we have obtained the crystalline dimethyl acetal of *d*-glucose. A study of the behavior of this substance under conditions of glucoside formation is in progress and should be of interest since the dimethyl acetal is a probable intermediate in this reaction.

Experimental

***d*-Glucose Dimethyl Acetal Pentaacetate.**—Glucose diethyl mercaptal pentaacetate[9] (20 g.) was dissolved in 200 cc. of absolute methanol and 24 g. of finely powdered cadmium carbonate added. A solution of 65 g. of mercuric chloride in 160 cc. of absolute methanol was then added and the mixture was heated to its boiling point under vigorous mechanical stirring and refluxed for seven hours. At the end of this period the mixture was filtered and the residue was washed with a small amount of methanol. The filtrate was poured into a mixture of chloroform (300 cc.) and water (300 cc.) and the chloroform layer was washed with water (seven times) until free of chlorides. The sirup obtained on solvent removal from the dried chloroform extract was dissolved in ether and brought to crystallization by the addition of heptane to incipient opalescence. Crystallization was completed on standing overnight at ice box temperature; yield 3 g.; m. p. 71–72°; spec. rot. (20°) + 12° (*c*, 2.2; $CHCl_3$).[10] Further recrystallization from a warm mixture of equal parts of ether and heptane did not alter these constants.

Anal. Calcd. for $C_6H_7O_5(OCH_3)_2(CH_3CO)_5$: OCH_3, 14.22; CH_3CO, 11.48 cc. 0.1 *N* NaOH per 100 mg. Found: OCH_3, 14.45; CH_3CO, 11.57 cc.; S, absent.

***d*-Glucose Dimethyl Acetal.**—Glucose dimethyl acetal pentaacetate (8.5 g.) was dissolved in 10 cc. of absolute methanol, 0.5 cc. of 0.4 *N* sodium methylate was added to the cold solution and the mixture kept at ice-box temperature for five hours. At the end of this period ether was added to incipient opalescence and the mixture was maintained at ice-box temperature. At the end of one hour a crystalline product separated that was removed by filtration and recrystallized from a mixture of equal parts of ether and methanol; yield 3.5 g.; m. p. 94–95°; spec. rot. (20°) + 15° (*c*, 3.1; H_2O). Further recrystallization did not alter these constants.

Anal. Calcd. for $C_6H_{12}O_6(OCH_3)_2$: C, 42.47; H, 8.02; OCH_3, 27.44. Found: C, 42.18; H, 7.78; OCH_3, 27.64.

We are indebted to Mr. Howard S. Clark for assistance in the analytical determinations.

Summary

1. The synthesis in crystalline form of *d*-glucose dimethyl acetal and of its pentaacetate is reported.

COLUMBUS, OHIO RECEIVED FEBRUARY 14, 1938

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[8] M. L. Wolfrom, L. J. Tanghe, R. W. George and S. W. Waisbrot, THIS JOURNAL, **60**, 132 (1938). Since the present manuscript was submitted to the Editor, we have noted the publication of H. A. Campbell and K. P. Link [*J. Biol. Chem.*, **122**, 635 (1938)] in which the dimethyl acetal of galactose was synthesized by the same general method.

[9] W. Schneider and J. Sepp, *Ber.*, **51**, 220 (1918); M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[10] All specific rotations are recorded to the D-line of sodium light. *c* is the concentration in grams per 100 cc. of solution.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Substitution of Iodine in Enols by Means of Iodine and Hydrogen Peroxide. The Preparation of Ethyl α-Iodoacetoacetate, *sym*-Iodoacetylacetone and α-Iodotetronic Acid

BY W. D. KUMLER

The use of hydrogen peroxide and iodine to form triiodophenol in practically quantitative yields[1] indicated that hydrogen peroxide might be of use for the synthesis of iodo enols. Iodo enols were prepared readily in good yields in this manner from ethyl acetoacetate, acetylacetone and tetronic acid. The reaction in alcohol with the calculated amounts of iodine and hydrogen peroxide was slow at room temperature but rapid at 70°.

Ethyl α-iodoacetoacetate was prepared by Genvresse[2] and by Schönbrodt[3] and α-iodotetronic acid was made by Wolff and Fertig.[4] Ethyl α-iodoacetoacetate decomposes upon distillation under reduced pressure, so a comparison of the boiling points is not a sure means of identification. α-Iodotetronic acid liberates iodine vapors at a temperature considerably lower than the point at which the compound melts with vigorous decomposition. The temperature of melting (or decomposition) depends upon the rate of heating so the behavior on heating is not a positive means of identification. However, the iodine analysis and equivalent weights of the compounds indicate that they are mono iodo derivatives and their chemical behavior leaves little doubt that the iodine is in the α-position. All of the compounds oxidize iodide quantitatively

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[1] Marsh, *J. Chem. Soc.*, 3164 (1927).

[2] Genvresse, *Ann. chim. phys.*, [6] **24**, 65 (1891).

[3] Schönbrodt, *Ann.*, **253**, 178 (1889).

[4] Wolff and Fertig, *ibid.*, **312**, 164 (1900).