form the disodium salt of II (R′ = H), that a much better yield of IV could be obtained (67%). This method was then successfully applied to the preparation of two other pyrrolidines, V and VI, which might be expected to give poor yields by Putochin's original procedure, since the phenyl and acetyl groups greatly decrease or eliminate the basicity of the nitrogen. It was found possible to prepare VII by the methylation of IV.

Experimental[3]

2,2-Dicarbethoxypyrrolidine (III).—The following method is essentially the one Putochin used except the isolation of the diester is described. Sodium (14.1 g., 0.61 atom) was dissolved in 350 ml. of absolute ethanol. Then 107 g. (0.61 mole) of diethyl aminomalonate[4] was added, followed by 246.5 g. (1.22 moles) of trimethylene bromide in large portions. The mixture was refluxed for four hours, and then the alcohol removed in vacuum and the residue dissolved in dilute hydrochloric acid. The acid solution was extracted with ether to remove the excess trimethylene bromide (recovery on distillation, 90 g.), and then basified with dilute sodium hydroxide and extracted with ether. The ether solution was dried and the ether evaporated. The residue was distilled; b.p. 105° (2 mm.), $n^{25}D$ 1.4455; weight 28.8 g. (0.134 mole), 22%.

Anal. Calcd. for $C_{10}H_{17}NO_4$: N, 6.51. Found: N, 6.73.

The crystalline hydrochloride was prepared by bubbling dry hydrogen chloride through an ether solution of the amino ester; white needles from ether–chloroform, m.p. 91–92°.

Anal. Calcd. for $C_{10}H_{18}ClNO_4$: N, 5.57. Found: N, 5.62.

2,2-Dicarbethoxy-3,5-dimethylpyrrolidine (IV). (a).—A solution of 18 g. (0.782 atom) of sodium in 450 ml. of dry ethanol was mixed with 135.5 g. (0.775 mole) of diethyl aminomalonate and then 357 g. (1.55 moles) of 2,4-dibromopentane. It was refluxed 12 hours. A work up in the previously described manner followed by distillations gave 250 g. of recovered dibromide and 66.3 g. (35.6%) of the ester; b.p. 91–94° (1 mm.), $n^{25}D$ 1.4447.

(b).—Sodamide was prepared from 36 g. (1.56 atoms) of sodium in 1 l. of liquid ammonia. The ammonia was evaporated and replaced with 500 ml. of dry benzene which was refluxed to remove traces of ammonia. Then 136.7 g. (0.78 mole) of diethyl aminomalonate was added; dry nitrogen was bubbled through the mixture while it was gently warmed until no more ammonia could be detected. Then with stirring 200 g. (0.87 mole) of 2,4-dibromopentane was added dropwise, and the solution was refluxed for 26 hours. After cooling and addition of water, the product was isolated by benzene extraction, washing, and removal of the benzene. It was distilled; b.p. 89–93° (0.75 mm.), $n^{25}D$ 1.4455; yield 128.2 g. (0.528 mole), 67.7%.

Anal. Calcd. for $C_{12}H_{21}NO_4$: N, 5.76. Found: (a) N, 6.10; (b) N, 5.79.

The hydrochloride was made from anhydrous hydrogen chloride and the amino ester in dry ether. The oil that formed could be crystallized from a chloroform–ether mixture; m.p. 105–107°.

Anal. Calcd. for $C_{12}H_{22}ClNO_4$: N, 5.01. Found: N, 5.14.

2,2-Dicarbethoxy-1,3,5-trimethylpyrrolidine (VII).—2,2-Dicarbethoxy-3,5-dimethylpyrrolidine (66.3 g., 0.273 mole) was added to a suspension of sodamide (made from 6.45 g. of sodium in liquid ammonia) in 200 ml. of toluene. The mixture was refluxed and nitrogen passed through to remove traces of ammonia. Then after cooling slightly 48 g. (0.338 mole) of methyl iodide was dropped in with stirring. After it had been heated for 15 hours, the solution was still basic. It was worked up as usual. Distillation yielded the ester; b.p. 99–105° (0.8–1.1 mm.), $n^{25}D$ 1.4515; yield 29.8 g. (0.116 mole), 42.5%.

Anal. Calcd. for $C_{13}H_{23}NO_4$: N, 5.44. Found: N, 5.33.

1-Phenyl-2,2-dicarbethoxypyrrolidine (V).—Sodamide made from 4.6 g. of sodium was suspended in 200 ml. of toluene. Then 25.3 g. (0.1 mole) of diethyl anilinomalonate[5] was added, ammonia removed, and 20.1 g. (0.1 mole) of trimethylene bromide added and the mixture refluxed. The product, isolated in the usual manner, was purified by distillation; b.p. 145° (0.6 mm.), $n^{25}D$ 1.5132; yield 8.0 g. (0.0275 mole), 27.5%.

Anal. Calcd. for $C_{16}H_{21}NO_4$: C, 65.95; H, 7.27; N, 4.81. Found: C, 65.70; H, 7.20; N, 4.81.

1-Acetyl-2-carbethoxy-2-cyanopyrrolidine (VI).—27.6 g. (1.2 atoms) of sodium was converted to sodamide and suspended in 700 ml. of toluene. Then 100 g. (0.59 mole) of ethyl acetamidocyanoacetate was added, the ammonia removed, and 121.5 g. (0.60 mole) of trimethylene bromide added. After a reflux period of 24 hours, the reaction was worked up in the usual manner except that separation of the bromide was by distillation. The product distilled at 163° (1 mm.), $n^{25}D$ 1.4765, yield 54.0 g. (0.257 mole), 43.5%.

Anal. Calcd. for $C_{10}H_{14}N_2O_3$: N, 13.33. Found: N, 13.54.

A derivative was prepared by refluxing 15 g. of the ester with 9.65 g. of guanidine carbonate in ethanolic sodium ethoxide (2.9 g. of sodium in 75 ml. of ethanol) for eight hours. Simple decantation into water gave the spiro [1-acetylpyrrolidine-2,5′-(2′,4′-di-iminobarbituric acid)]. It could be recrystallized from water; m.p. 311–312°, yield 9 g.

Anal. Calcd. for $C_9H_{13}N_5O_3$: N, 31.38. Found: N, 31.04.

(3) All melting points and boiling points are uncorrected. The microanalyses were performed by W. J. Schenck and H. L. Hunter.

(4) H. R. Snyder and C. W. Smith, THIS JOURNAL, **66**, 350 (1944).

(5) R. Blank, *Ber.*, **31**, 1815 (1898).

THE LILLY RESEARCH LABORATORIES
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Preparation of Crystalline Methyl 4-*O*-Methyl-α-D-glucopyranoside and its Triacetate

BY ROY L. WHISTLER AND STANLEY J. KAZENIAC

RECEIVED FEBRUARY 15, 1954

For investigation of the manner in which starch is oxidized by various oxidants, methyl 4-*O*-methyl-α-D-glucopyranoside is desirable. Here is described an improved method for the preparation of the compound in substantial quantity. The compound is obtained for the first time in crystalline condition as is its triacetate.

Experimental

Methyl 2,3-Di-*O*-acetyl-α-D-glucopyranoside.—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[1] (25 g.) was acetylated with sodium acetate and acetic anhydride at 110° in the usual manner to give methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (26.9 g.), m.p. 109°. This was dissolved in 225 ml. of acetone. Twenty-five ml. of 0.1 *N* hydrochloric acid was added, and the solution was hydrolyzed to constant optical rotation. Methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside was isolated from the solution as a heavy sirup by the method of Levene and Raymond.[2] The yield was 20.1 g., $[\alpha]^{25}D$ +112.4° (*c* 1 in water).

Methyl 2,3-Di-*O*-acetyl-4-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside.—The above sirup was dried by three azeotropic distillations with benzene–absolute alcohol in vacuum and then was converted to crystalline methyl 2,3-di-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside by the method of Bredereck.[3] The yield was 21.9 g., m.p. 162–163°, and $[\alpha]^{25}D$ +79° (*c* 1 in chloroform).

Three methylations by Purdie reagents yielded methyl 2,3-di-*O*-acetyl-4-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside as a sirup (22.0 g.).

Methyl 4-*O*-Methyl-α-D-glucopyranoside.—The trityl group was removed from the above methylated sirup with

(1) K. Freudenberg, H. Toepffer and C. C. Anderson, *Ber.*, **61B**, 1758 (1928).

(2) P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **97**, 763 (1932).

(3) H. Bredereck, *Ber.*, **68B**, 777 (1935).

hydrobromic acid in glacial acetic acid[4] to give methyl 2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranoside (8.8 g.). This was dissolved in 60 ml. of methanol and 3 ml. of 0.5 *N* barium methylate solution was added. After standing overnight at room temperature, the solution was neutralized by treatment with Amberlite resin IRC-50(H). The solution was then evaporated under vacuum to yield a faintly yellow colored sirup (5.8 g. or 31% over-all yield). On standing overnight, this sirup crystallized. Two recrystallizations from isopropyl alcohol gave needles with m.p. 144–145° and $[\alpha]^{25}D$ +154.7° (*c* 1 in water).

Crystals with the same melting point were also obtained by recrystallizations from alcohol–benzene. For best results crude methyl 4-*O*-methyl-α-D-glucopyranoside was dissolved in hot absolute ethanol and benzene added until the solution became turbid. Crystallization occurred on cooling.

Anal. Calcd. for $C_8H_{16}O_6$: C, 46.2; H, 7.7; methoxyl, 29.8. Found: C, 46.2; H, 7.7; methoxyl, 29.6.

Methyl 2,3,6-Tri-*O*-acetyl-4-*O*-methyl-α-D-glucopyranoside.—One-half gram of crystalline methyl 4-*O*-methyl-α-D-glucopyranoside was acetylated with sodium acetate and acetic anhydride at 110° for 30 minutes. After the mixture was poured into ice-water with stirring, the triacetate was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate and was evaporated under vacuum to produce crystals of the triacetate. Two recrystallizations from 95% ethanol gave needles with m.p. 122–123° and $[\alpha]^{25}D$ +150.4° (*c* 1 in chloroform).

Anal. Calcd. for $C_8H_{13}O_6(CH_3CO)_3$: C, 50.3; H, 6.6; acetyl, 38.6. Found: C, 50.3; H, 6.6; acetyl, 38.7.

(4) B. Helferich and W. Klein, *Ann.*, **450**, 219 (1926).

PURDUE AGRICULTURAL EXPERIMENT STATION
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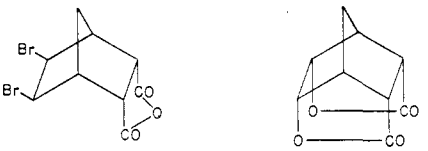
A New Nortricyclene Derivative

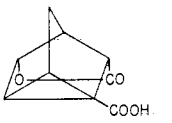
BY ANTHONY WINSTON[1] AND PELHAM WILDER, JR.[2]

RECEIVED DECEMBER 30, 1953

On account of recent investigations of the stereochemistry of bromination of some Diels–Alder adducts,[3,4] it is of interest at this time to report several reactions of *exo-cis*-4,5-dibromo-*endo*-3,6-endomethylenehexahydrophthalic anhydride[5] (I). Upon treatment with boiling aqueous sodium carbonate, the dibromide I yielded a neutral compound, the structure of which was proved to be the dilactone II previously prepared by Alder and Stein.[6] Treatment of this same dibromide with alcoholic potassium hydroxide, on the other hand, resulted in the formation of a monocarboxylic acid which upon analysis was found to be isomeric with the dilactone II above. The absorption at 5.58 μ in the infrared spectrum, Fig. 1, indicated the presence of a γ-lactone structure.[7,8] Several unsuccessful attempts to hydrogenate the acid over platinum oxide made the presence of unsaturation appear unlikely. On the basis of these observations it seems certain that the acid must be the nortricyclenic acid lactone[9] (III)



I II



III

Recently Roberts and his co-workers[10] found that the nortricyclene system was easily prepared by the action of N-bromosuccinimide as well as by the action of bromine in the presence of pyridine upon norbornylene. The infrared absorption at 12.4–12.5 μ exhibited by nortricyclene systems[10,11] is found at 12.40 in the spectrum of the nortricyclenic acid lactone (III).

When dibromide I was treated for fifteen hours at room temperature with sodium methoxide in methanol solution, a small amount of the nortricyclene derivative III was isolated along with a mixture of bromides. When the dibromide was treated briefly with sodium methoxide in methanol solution at the reflux temperature, the only product isolated was a viscous, oily mass from which no single pure substance could be extracted.

NOTE ADDED IN PROOF.—Since this manuscript was submitted for publication, there has appeared a paper by Alder and Brochhagen [*Ber.*, **87**, 167 (1954)] which describes another synthesis of the nortricyclene derivative reported herein. The authors acknowledge the priority of Alder and Brochhagen.

Experimental[12]

Dibromide I.—The dibromide of the cyclopentadiene–maleic anhydride adduct was prepared according to the method of Bartlett and Schneider[13]; micro m.p. 211–212°.

Dilactone II.—Ten grams of the dibromide I, suspended in 100 ml. of 5% sodium carbonate solution was heated under reflux for 3 hours. After acidification with hydrochloric acid the solution was subjected to continuous ether extraction for 24 hours. Upon evaporation of the ether there remained a neutral solid which upon crystallization from water yielded 3.5 g. of colorless crystals, m.p. 274–275° cor, (reported 264–266°[6]). Because of the discrepancy in the melting points, the compound was reanalyzed and the molecular weight was determined by the boiling point elevation of acetic acid.

(1) Du Pont Predoctoral Fellow, 1953–1954.

(2) Author to whom communications should be directed.

(3) H. Kwart and L. A. Kaplan, THIS JOURNAL, **75**, 3356 (1953).

(4) J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953).

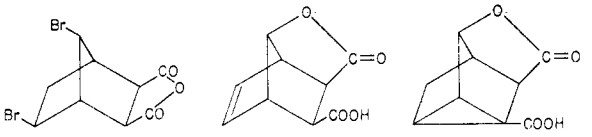
(5) H. Kwart and L. A. Kaplan, reported at the 124th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 6–11, 1953.

(6) K. Alder and G. Stein, *Ann.*, **514**, 1 (1934).

(7) S. Searles, M. Tamres and G. Barrow, THIS JOURNAL, **75**, 71 (1953).

(8) H. Conroy, *ibid.*, **74**, 491 (1952), footnote 26.

(9) As a result of dipole moment studies Kwart and Kaplan (*cf.* reference 3), assigned the structure A to the dibromide I. On the basis of this assignment, the product of alcoholic potassium hydroxide treatment would be acid B or acid C, or possibly both. It is interesting to note that acid C is, indeed, *identical* with acid III; consequently, the isolation of the nortricyclenic acid lactone above, then, may not be considered a proof of the structure of dibromide (I).



A B C

(10) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

(11) E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

(12) Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

(13) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).