when treated with concentrated sulfuric acid, formed a single product which was shown to be 4,4-dimethyl-3-carboxy-1-tetralone (IV)[7] by Clemmensen reduction, anilide formation and exhaustive chlorination to a monochloroanilide.[8]

Thus, both I and II show preference for the formation of six-membered rings to the exclusion of the five-membered alternatives.

Experimental[9]

cis- and *trans*-**4-Methyl-3-carboxy-1-tetralone (III).**—α-Methylbenzylsuccinic anhydride (I) (30.4 g., 0.15 mole) was dissolved in 200 ml. of concentrated sulfuric acid, warmed for two hours on the steam-bath and poured onto ice to give 24.7 g. of crude product. After many recrystallizations from ethanol and water, three fractions were obtained.

Fraction A: high-melting isomer, 6.3 g. (21% of theoretical) m.p. 169.5–171.5° from ethanol; less soluble in ethanol and water than isomer B; crystalline 2,4-dinitrophenylhydrazone, m.p. 286° dec., and semicarbazone, m.p. 255–256° dec.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.93. Found: C, 70.67; H, 6.04.

Fraction B: low-melting isomer, 3.0 g. (10% of theoretical), m.p. 84–86° from water; amorphous 2,4-dinitrophenylhydrazone, m.p. 273° dec., and semicarbazone, m.p. 238–242° dec.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.93. Found: C, 70.60; H, 6.18.

Fraction C: mixed isomers, 7.0 g. (23% of theoretical), m.p. 120–140°; amorphous 2,4-dinitrophenylhydrazone, m.p. 270° dec., and semicarbazone, m.p. 228° dec. From a phase diagram, it was estimated that fraction C contained approximately equal parts of A and B.

cis- and *trans*-**1-Methyl-2-carboxytetralin (V).**—Isomer IIIA (4.33 g.) was reduced by the Clemmensen method to yield 4.16 g. of VA, m.p. 86–88° from petroleum ether.[10]

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.78; H, 7.55.

In a similar manner, 0.88 g. of VB was obtained by the reduction of 1.21 g. of IIIB. The product was recrystallized from petroleum ether, m.p. 64–67°; further purified by sublimation, m.p. 71–73°; mixed melting point with VA, 55–62°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.82; H, 7.56.

1-Methyl-2-carboxynaphthalene (VI).—Isomer VA (1.00 g.) was converted to the methyl ester (0.89 g.) and the latter heated with 0.080 g. of palladium-on-carbon for five hours at 290–310°. Eighty-three per cent. of the theoretical amount of hydrogen was evolved; after saponification, 0.40 g. VIA, m.p. 175–177°[11] when recrystallized from benzene, was obtained. In a similar manner, 0.81 g. of VB yielded 0.46 g. of methyl ester. The ester was heated with 0.021 g. of palladium-on-carbon at 300° for 22 hours at which time 93% of the theoretical amount of hydrogen had been evolved. The product, after saponification, amounted to 0.39 g., m.p. 172–174°[11] after sublimation and recrystallization from benzene, and showed no depression in melting point when mixed with VIA.

4,4-Dimethyl-3-carboxy-1-tetralone (IV).—α,α-Dimethylbenzylsuccinic anhydride (II) (37.2 g.) was treated with concentrated sulfuric acid in the same manner as above to yield 26.5 g. of product, m.p. 157–159° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.53; H, 6.47. Found: C, 71.38; H, 6.67.

1,1-Dimethyl-2-carboxytetralin (VII).—Ten grams of IV was reduced by zinc and hydrochloric acid to yield 10.0 g. of VII, m.p. 145–146° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.45; H, 7.89. Found: C, 76.22; H, 8.11.

1,1-Dimethyl-2-carbanilidotetralin (VIII).—VII (3.6 g.) was converted to the anilide (3.2 g.), m.p. 162–164°, by treatment with thionyl chloride and then with aniline in benzene.

Anal. Calcd. for $C_{19}H_{21}ON$: C, 81.70; H, 7.57; N, 5.01. Found: C, 81.85; H, 7.67; N, 5.08.

1,1-Dimethyl-2-chloro-2-carbanilidotetralin (IX).—After the procedure of von Braun,[8] VIII (0.58 g.) was heated with an excess of phosphorus pentachloride in benzene. The product was recrystallized from ethanol to yield 0.50 g. of IX, m.p. 104–105°.

Anal. Calcd. for $C_{19}H_{20}ONCl$: C, 72.76; H, 6.40; N, 4.44; Cl, 11.30. Calcd. for $C_{19}H_{19}ONCl_2$: C, 65.55; H, 5.50; N, 4.02; Cl, 20.33. Found: C, 73.30; H, 6.47; N, 4.66; Cl, 11.17.

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(7) W. G. Bickford, *et al.*,[4] reported that the structure of II had not been demonstrated with certainty since II could not be oxidized by permanganate, but we found that IV is readily oxidized to α,α-dimethylhomophthalic acid in keeping with the structures proposed for II and IV.

(8) J. von Braun, *et al.*, *Ann.*, **453**, 113 (1927). A five-membered ring would result in a dichloroanilide.

(9) All melting points are uncorrected. Analyses by C. W. Nash, Rohm and Haas Company.

(10) K. V. Auwers and K. Möller, *J. prakt. Chem.*, [2] **109**, 148 (1925), reported the melting point for 1-methyl-2-carboxytetralin to be 83–84°.

(11) Reported[10] melting point for 1-methyl-2-carboxynaphthalene, 177–178°.

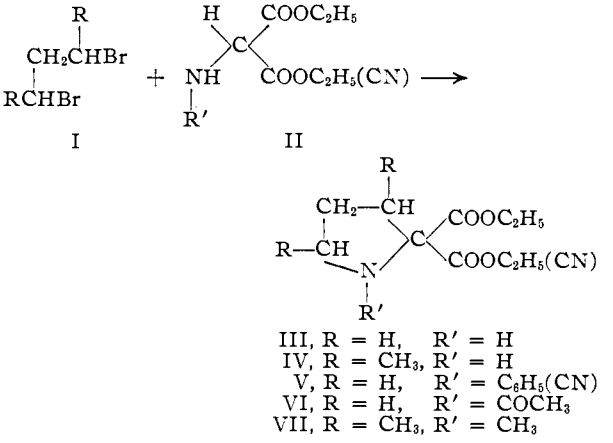
Pyrrolidine Esters

BY EARLE VAN HEYNINGEN

RECEIVED FEBRUARY 6, 1954

In the past the synthesis of 2,2-dicarbethoxypyrrolidines has been accomplished by the use of primary amines and bromoalkylbromomalonates[1] or by the ring closure of an alkyl dibromide with an aminomalonate.[2] The latter method was employed incidentally by Putochin in a synthesis of proline. He did not isolate the diester, however, but saponified it to the dibasic acid which was decarboxylated to give proline.

A brief investigation therefore was made to determine if 2,2-dicarbethoxypyrrolidine could be isolated satisfactorily from this reaction and if the scope of the reaction could be enlarged.



I II

III, R = H, R′ = H
IV, R = CH_3, R′ = H
V, R = H, R′ = $C_6H_5(CN)$
VI, R = H, R′ = $COCH_3$
VII, R = CH_3, R′ = CH_3

In Putochin's procedure, refluxing ethanolic sodium ethoxide effects the ring formation. In the present work I (R = H) and II (R′ = H) under these conditions yielded III in 22% yield. Under like conditions IV was obtained in 35% yield. It was discovered, however, that if the reaction was run in a non-hydroxylic solvent using sodamide to

(1) J. v. Braun and W. Leistner, *Ber.*, **59**, 2329 (1926); R. Willstätter and F. Ettlinger, *Ann.*, **326**, 91 (1903).

(2) N. J. Putochin, *Ber.*, **56**, 2214 (1923).

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).

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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).