mercury bromide obtained from the addition with mercuric *dl*-mandelate. Thus, no effective synthesis of the optically active bromide was accomplished.

Experimental

Mercuric *dl*-Mandelate.—A solution of 30.4 g. (0.2 mole) of *dl*-mandelic acid in 250 ml. of water was mixed with a solution of 31.9 g. (0.1 mole) of mercuric acetate in 150 ml. of water. The precipitated product was removed by filtration, washed with water, and allowed to stand under 100 ml. of 95% ethanol for 24 hours. A yield of 45.6 g. (91%) of mercuric *dl*-mandelate, m.p. 182–183°, was obtained. The m.p. checks that listed by Hart and Andersen.[2]

Mercuric (+)-Mandelate.—A solution of 6.09 g. (0.04 mole) of (+)-mandelic acid,[3] m.p. 130–131°, $[\alpha]^{25}\text{D}$ 152.5° (2% solution in water), in 100 ml. of water was mixed with a solution of 6.37 g. (0.02 mole) of mercuric acetate in 50 ml. of water. The procedure of product isolation used for the *dl*-salt yielded 9.6 g. (95%) of mercuric (+)-mandelate, m.p. 172–174°, $[\alpha]^{25}\text{D}$ 102.5° (2% solution in 5% aqueous acetic acid).

Anal. Calcd. for $C_{16}H_{14}O_6Hg$: Hg, 39.9. Found: Hg, 39.5.

2-Methoxycyclohexylmercury *dl*-Mandelate.—To a suspension of 10.1 g. (0.020 mole) of mercuric *dl*-mandelate in 50 ml. of methanol was added 2.05 g. (0.025 mole) of cyclohexene. The reaction mixture was allowed to stand for 24 hours. The solid product which precipitated was recrystallized from a hexane fraction (60–70°) to give 3.6 g. (39%) of 2-methoxycyclohexylmercury *dl*-mandelate, m.p. 130–131°.

Anal. Calcd. for $C_{15}H_{20}O_4Hg$: Hg, 43.1. Found: Hg, 42.8.

Treatment of 1.0 g. of the mandelate in methanol with 5% aqueous potassium bromide yielded 0.70 g. (83%) of α-2-methoxycyclohexylmercury bromide, m.p. 112–113°. There was no lowering of the m.p. when this compound was mixed with the bromide prepared from the corresponding acetate.[1]

2-Methoxycyclohexylmercury (+)-Mandelate.—The reaction of 5.0 g. (0.010 mole) of mercuric (+)-mandelate with 1.0 g. (0.012 mole) of cyclohexene in 25 ml. of methanol for 48 hours yielded a clear solution. The solution was neutralized with base and concentrated under reduced pressure. The residue was crystallized from hexane (60–70°) to yield 2.5 g. (54%) of a mixture, m.p. 84–85°.

Anal. Calcd. for $C_{15}H_{20}O_4Hg$: Hg, 43.1. Found: Hg, 42.7.

Fractional crystallization of the mixture from acetone yielded two fractions: m.p.'s 112–115° and 96–99°. Each product when treated with 5% potassium bromide as described for the *dl*-mandelate yielded the α-bromide, m.p. 112–114°, which was optically inactive.

---

[2] M. C. Hart and H. P. Andersen, *ibid.*, **57**, 1059 (1935).

[3] L. Gatterman and H. Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937, p. 228.

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

4-Pyridylacetone

BY ALFRED BURGER, JAMES R. RECTOR AND A. CHANDLER SCHMALZ

RECEIVED OCTOBER 24, 1951

4-Pyridylacetone has been obtained by decarboxylative acylation[1] of 4-pyridylacetic acid with acetic anhydride in analogy to the preparation of the 3-isomer reported by Burger and Walter.[2] 4-Picolylthiomorpholide[3] used as an intermediate in the synthesis of 4-pyridylacetic acid could be desulfurized by the method of Kornfeld[4] to 1-(4-pyridyl)-2-morpholinoethane.

Experimental[5]

4-Pyridylacetone.—A mixture of 40 g. (0.23 mole) of 4-pyridylacetic acid hydrochloride, 31.4 g. (3.8 moles) of anhydrous sodium acetate and 56.4 g. (0.52 mole) of acetic anhydride was refluxed for 18 hours, the dark reaction mixture was hydrolyzed with 100 ml. of water, cleared with Darco, and concentrated under reduced pressure. It was then made carbonate alkaline and extracted exhaustively with ether. The oily pale yellow ketone boiled at 76.5–78° (0.5 mm.) and weighed 15.6 g. (50%).

Anal. Calcd. for C_8H_9NO: C, 71.09; H, 6.71. Found: C, 70.83; H, 6.55.

The **semicarbazone** crystallized from water, m.p. 188–189°.

Anal. Calcd. for $C_9H_{12}N_4O$: N, 29.15. Found; N, 29.20.

Methyl 4-Pyridylacetate.—This ester was prepared from 4-pyridylacetic acid hydrochloride with diazomethane in ether–methanol solution. The colorless oily product boiled at 103–105° (2–3 mm.).

4-Pyridylacetamide.—This amide was obtained in 97% yield from ethyl or methyl pyridylacetate by the procedure described for 3-pyridylacetamide,[2] and recrystallization from dioxane. The colorless crystals melted at 143.5–145°.

Anal. Calcd. for $C_7H_8N_2O$: N, 20.58. Found: N, 20.73.

1-(4-Pyridyl)-2-morpholinoethane.—A solution of 10 g. of 4-picolylthiomorpholide in 200 ml. of absolute ethanol was added to 70 g. of alcohol-moist Raney nickel, and the mixture was refluxed under an atmosphere of nitrogen for three hours. The nickel was filtered, most of the solvent removed under reduced pressure, the residue was treated with alkali and extracted with ether. The amine from the ether extracts boiled at 128–130° (0.7 mm.) and weighed 3.6 g. (41%). The free base was not stable enough to be analyzed.

The dihydrochloride melted at 215.5–217° after recrystallization from methanol–ethyl acetate.

Anal. Calcd. for $C_{11}H_{18}Cl_2N_2O$: N, 10.58. Found: N, 10.82.

The yellow dipicrate crystallized from water, m.p. 190–192°.

Anal. Calcd. for $C_{23}H_{22}N_8O_{15}$: N, 17.23. Found: N, 17.37.

---

[1] J. A. King and F. H. McMillan, THIS JOURNAL, **73**, 4911 (1951).

[2] A. Burger and C. R. Walter, Jr., *ibid.*, **72**, 1988 (1950); H. S. Mosher and J. E. Tessieri [*ibid.*, **73**, 4925 (1951)] working with 3-pyridylacetonitrile have stated that "none of the isomeric pyridylacetonitriles has previously been reported." The 3-isomer had served us as an intermediate in an alternative synthesis of 3-pyridylacetone.

[3] R. L. Malan and P. M. Dean, *ibid.*, **69**, 1797 (1947).

[4] E. C. Kornfeld, *J. Org. Chem.*, **16**, 131 (1951).

[5] All melting points are corrected.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VA.

The Preparation of 1,5-Anhydro-D-mannitol (Styracitol) from D-Mannitol

BY HEWITT G. FLETCHER, JR., AND HARRY W. DIEHL

RECEIVED FEBRUARY 25, 1952

1,5-Anhydro-D-mannitol, originally discovered by Asahina[1] in the husks of the fruit of *Styrax obassia* and named styracitol, was first synthesized by Zervas[2] through the catalytic reduction of tetraacetyl-2-hydroxy-D-glucal. A recent communication[3] from this Laboratory described a more convenient synthesis based on the reduction of tetraacetyl-α-D-mannopyranosyl bromide with lithium

---

[1] Y. Asahina, *Arch. Pharm.*, **245**, 325 (1907); **247**, 157 (1909).

[2] L. Zervas, *Ber.*, **63**, 1689 (1930).

[3] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **72**, 4547 (1950).

aluminum hydride. We wish now to report an even simpler and less expensive method based on the direct dehydration of D-mannitol.

Montgomery and Wiggins[4] investigated the complex mixture which results when D-mannitol is heated with concentrated hydrochloric acid and were able to demonstrate, through the isolation of dibenzylidenestyracitol, that 1,5-anhydro-D-mannitol was present. More recently Foster and Overend[5] have found that when D-mannitol is boiled with concentrated hydrochloric acid for 24 hours the chief product isolated (other than unchanged D-mannitol) is 1,4(=3,6)-anhydro-D-mannitol. We have confirmed Foster and Overend's observation but wish now to add that extension of the reaction time to 48 hours results in the isolation of 1,5- rather than 1,4-anhydro-D-mannitol. While the yield, 10.9%, is low, the starting material is cheap and the styracitol obtained is readily purified. The identity of the styracitol was confirmed through comparison with authentic material and through the preparation of its tetraacetate.

Experimental

In each experiment 50.0 g. of pure D-mannitol was dissolved in 200 ml. of concentrated hydrochloric acid and the solution boiled gently under reflux for the specified time (Table I). The reaction mixture was then concentrated *in vacuo* to a sirup, dissolved in 150 ml. of water, treated with decolorizing carbon and reconcentrated *in vacuo*. After the evaporation (*in vacuo*) of two successive 50-ml. batches of absolute alcohol from the residual sirup it was dissolved in 50 ml. of absolute alcohol. The properties of the various crops of crystalline products obtained thus are listed in Table I.

TABLE I

Run	Hr. reflux	No.	Wt., g.	Fractions M.p.,[a] °C.	Fractions $[\alpha]^{20}D$ (H_2O)[b]
I	24	1	4.4	120–130	−24.8°
		2	2.5	132–137	−35.8
		3	0.9	140–150	−43.6
II	36	1	4.4	146–154	−45.7
		2	0.7	118–122	−31.6
III	48	1	4.9	139–150	−45.6
IV	60	1	4.1	145-152	−46.5
V	72	1	4.2	145–150	−45.6
VI	96	1	3.6	145–151	−45.0

[a] Melting points are corrected. 1,4-Anhydro-D-mannitol melts at 147–148°; 1,5-anhydro-D-mannitol at 156–157°. [b] 1,4-Anhydro-D-mannitol shows $[\alpha]^{20}D$ −23.8° in water; 1,5-anhydro-D-mannitol shows $[\alpha]^{20}D$ −50.9° (H_2O).

A number of crops of crude 1,5-anhydro-D-mannitol (20.4 g., $[\alpha]^{20}D$ *ca.* −45°) were combined and recrystallized from seven parts of ethanol to give 16.3 g. of pure styracitol showing $[\alpha]^{20}D$ −50.3° in water (*c*, 1.06) and melting at 156–157° either alone or in admixture with authentic styracitol.

Three grams of styracitol, made as described above, was acetylated with acetic anhydride in pyridine solution to give 1.5 g. (25%) of its tetraacetate melting at 66–67° and showing in chloroform −42.4° (*c*, 0.826); a mixed melting point with authentic styracitol tetraacetate was undepressed. Fletcher and Hudson[6] reported a value of $[\alpha]^{20}D$ −42.0° for the rotation of 1,5-anhydro-D-mannitol tetraacetate in chloroform.

NATIONAL INSTITUTE OF ARTHRITIS AND
METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE
FEDERAL SECURITY AGENCY, BETHESDA 14, MARYLAND

---

(4) R. Montgomery and L. F. Wiggins, *J. Chem. Soc.*, 2204 (1948).

(5) A. B. Foster and W. G. Overend, *ibid.*, 680 (1951).

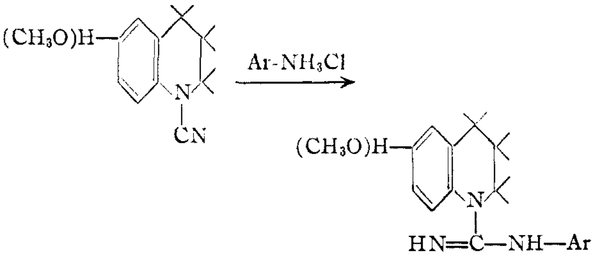
(6) H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **71**, 3682 (1949).

Guanidines Derived from N-Cyanotetrahydroquinolines

BY ROBERT D. GANO WITH R. L. MCKEE AND J. W. AGER, JR.

RECEIVED APRIL 14, 1950

N-Cyano-1,2,3,4-tetrahydroquinoline has been prepared by v. Braun[1] through interaction of 1-alkyltetrahydroquinolines with cyanogen bromide. In the present work, this compound and its 6-methoxy and 6-chloro analogs have been prepared in excellent yield from corresponding 1,2,3,4-tetrahydroquinolines. The cyanamides thus prepared were condensed with aromatic amine hydrochlorides to form guanidines.[1]



Under the conditions employed (prolonged reflux in alcohol or hexanol-1 or heating without solvent to temperatures as high as 250°) methylammonium chloride failed to condense with the cyanamides. Other conditions involving heating 1-cyano-6-chlorotetrahydroquinoline with a mixture of molar quantities of diethylamine and its hydrochloride likewise failed to produce isolable amounts of the alkyl derivatives. A low yield of the desired product was obtained from diethylcyanamide and 6-chlorotetrahydroquinoline hydrochloride.

Experimental

The yields here reported are those obtained in a single experiment and are not considered to be the maximum obtainable.

1-Cyano-6-methoxy-1,2,3,4-tetrahydroquinoline.—To a solution of cyanogen bromide (52 g., 0.49 mole) in 240 cc. of benzene was added dropwise with stirring, a solution of 160 g. (0.98 mole) of thalline in 125 cc. of benzene, the temperature being maintained at 25° by external cooling. After standing overnight, the solution was filtered from the precipitated thalline hydrobromide (110 g., 92%), the benzene distilled at atmospheric pressure, and the product distilled *in vacuo* to yield 82 g. of a pale yellow oil boiling at 160–177° (4.0–4.5 mm.). Redistillation gave 73 g. (79% of the theoretical) of material boiling from 177–182° (4.0–4.5 mm.) which solidified to form white crystals melting at 44–47°. Neither recrystallization of this substance from petroleum ether nor redistillation produced any alteration in melting point.

Anal. Calcd. for $C_{11}H_{12}N_2O$: N, 14.89; CH_3O, 16.49. Found: N, 15.18; CH_3O, 16.73.

1-Cyano-1,2,3,4-tetrahydroquinoline.[1]—Cyanogen bromide (63.1 g., 0.595 mole) and tetrahydroquinoline (159.5 g., 1.19 moles) were allowed to react as above to form a 90% yield of the desired product boiling at 153.5–154.5° (7 mm.) and 169–172° (13 mm.).

1-Cyano-6-chloro-1,2,3,4-tetrahydroquinoline.—6-Chloro-1,2,3,4-tetrahydroquinoline was prepared from tetrahydroquinoline by acetylation, chlorination with sulfuryl chloride in carbon tetrachloride, and acid hydrolysis. It boiled at 125–127° at 3 mm., melted at 41°, and formed a hydrochloride which decomposed at 195° and a picrate melting at 151.5–152.5°.[2] The cyanamide was prepared from 21.2

---

(1) J. v. Braun, *Ber.*, **42**, 2219 (1909).

(2) J. v. Braun, A. Grabowski and M. Rawicz, *ibid.*, **46**, 3169 (1913).