

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.<sup>2</sup>

**Mercuric (+)-Mandelate.**—A solution of 6.09 g. (0.04 mole) of (+)-mandelic acid,<sup>3</sup> m.p. 130–131°,  $[\alpha]_D^{25}$  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°,  $[\alpha]_D^{25}$  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  $\alpha$ -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.<sup>1</sup>

**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  $\alpha$ -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.

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### 4-Pyridylacetone

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4-Pyridylacetone has been obtained by decarboxylative acylation<sup>1</sup> of 4-pyridylacetic acid with acetic anhydride in analogy to the preparation of the 3-isomer reported by Burger and Walter.<sup>2</sup>

(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.

4-Picolylthiomorpholide<sup>3</sup> used as an intermediate in the synthesis of 4-pyridylacetic acid could be desulfurized by the method of Kornfeld<sup>4</sup> to 1-(4-pyridyl)-2-morpholinoethane.

#### Experimental<sup>5</sup>

**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,<sup>3</sup> and recrystallization from dioxane. The colorless crystals melted at 143.5–145°.

*Anal.* Calcd. for  $C_7H_9N_2O$ : 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  $C_{11}H_{16}Cl_2N_2O$ : N, 10.58. Found: N, 10.82.

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

*Anal.* Calcd. for  $C_{23}H_{22}N_8O_{16}$ : N, 17.23. Found: N, 17.37.

(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.

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

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1,5-Anhydro-D-mannitol, originally discovered by Asahina<sup>1</sup> in the husks of the fruit of *Styrax obassia* and named styracitol, was first synthesized by Zervas<sup>2</sup> through the catalytic reduction of tetraacetyl-2-hydroxy-D-glucal. A recent communication<sup>3</sup> from this Laboratory described a more convenient synthesis based on the reduction of tetraacetyl- $\alpha$ -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).