70.9; H, 5.4; N, 15.0; amino-N, 0.083. Found: C, 69.6; H, 5.5; N, 15.3; amino-N, 0.083.[3]

Poly-L-tryptophan differs in its solubility from the DL-polymer. It is soluble in dimethylformamide and pyridine, but insoluble in dioxane, acetone, butylamine, hot glacial acetic acid, methanol, ethanol and ethyl acetate.

An aqueous suspension of polytryptophan turns deep violet when treated with Hopkins–Cole reagent; it gives a positive ninhydrin reaction and a negative picric acid test.[11]

Hydrolysis of Polytryptophan.—Poly-DL-tryptophan (22.3 mg.) was dissolved in a mixture of dioxane (1 ml.), 4 *N* methanolic sodium methoxide (2 ml.) and water (0.2 ml.). Oxygen was removed by a stream of nitrogen and the hydrolysis carried out by heating in a sealed tube at 110–120° for 72 hours.

The amount of tryptophan in the hydrolysate was determined by its ultraviolet absorption[8] and colorimetrically.[12]

Anal. Calcd. for a hydrolysate of 100 mg. of poly-DL-tryptophan (*n* average 80): tryptophan, 109 mg. Found: tryptophan 105 mg. (ultraviolet absorption[8]); 107 mg. (colorimetric ninhydrin determination[12]).

Poly-L-tryptophan was hydrolyzed analogously to the DL-polymer; as it is insoluble in dioxane, pyridine was used instead. A quantitative yield of tryptophan was obtained also in this case.

A chromatographic analysis of the neutralized hydrolysate of poly-DL- and poly-L-tryptophan carried out as above yielded one spot with R_f 0.46 identical with that of authentic samples of DL- and L-tryptophan.

Acknowledgment.—This investigation was supported by a research grant (PHS G-3677) from the National Institutes of Health, Public Health Service.

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Nicotinyl and Isonicotinyl Hydrazones of Pyridoxal

BY PETER P. T. SAH

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Nicotinyl and isonicotinyl hydrazones of pyridoxal, two new compounds that show interesting biological properties,[1] may be prepared easily by the following procedure.

Pyridoxal hydrochloride (product of Nutritional Biochemicals Corporation, 2 g.) in water (20 ml.) was treated with isonicotinic acid hydrazide[2] or nicotinic acid hydrazide[3] (1.4 g.) in 50% ethanol (20 ml.). Sodium acetate (1 g.) in water (10 ml.) was then added and the reactants were heated on the steam-bath for 10 minutes and allowed to stand for 24 hours at room temperature. The crude crystalline product was recrystallized from a mixture of methanol and benzene (1:2). The yield of the purified product was between 2.4 and 2.6 g.

Equally satisfactory results were obtained by using an alternate procedure which consisted of heating equivalent amounts of the reactants in pyridine and removing the solvent by steam distillation with the addition of sodium acetate.

Pyridoxal isonicotinyl hydrazone forms pale-yellow, small prisms either from dilute ethanol or from a mixture of methanol and benzene, m.p. 261–262° dec. (cor.).

Anal. Calcd. for $C_{14}H_{14}O_3N_4$: C, 58.72; H, 4.94; N, 19.57. Found: C, 58.55; H, 5.03; N, 19.77.

Pyridoxal nicotinyl hydrazone forms practically colorless, fine needles from dilute ethanol or thick platelets from a mixture of methanol and benzene, m.p. 235–236° dec. (cor.).

Anal. Calcd. for $C_{14}H_{14}O_3N_4$: C, 58.72; H, 4.94; N, 19.57. Found: C, 58.68; H, 4.87; N, 19.63.

These two compounds are very slightly soluble in cold water, slightly soluble in cold methanol or ethanol but soluble in hot; soluble in cold 10% sodium hydroxide; very soluble in dilute mineral acids; but insoluble in benzene or petroleum ether. A mixture of methanol and petroleum ether may also be used for recrystallization. Quantitatively, pyridoxal nicotinyl hydrazone is considerably more soluble than pyridoxal isonicotinyl hydrazone in most of the solvents tested.

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(1) Pyridoxal isonicotinyl hydrazone was found by W. B. Sutton of the Lilly Research Laboratories, Indianapolis, Indiana, to possess significant antitubercular activity *in vitro* as well as *in vivo*; its isomer, pyridoxal nicotinyl hydrazone, however, is much less active *in vitro* and inactive *in vivo*. Following this observation, both derivatives were found by Dr. Louis Greenberg of the University of California School of Medicine to be equal to pyridoxine in their vitamin B_6 activity. Recently, both were found by Dr. B. Freedlander of Mount Zion Hospital, San Francisco and Dr. A. Furst of Stanford University School of Medicine to show distinct activity against mammary cancer in mice and certain leukemia in mice. The details of these biological results will be reported by these investigators elsewhere.

(2) H. Meyer and J. Mally, *Monatsh.*, **33**, 393 (1912).

(3) Prepared by Dr. C. T. Peng of University of California College of Pharmacy according to the method described in the literature; "Beilsteins Handbuch der organischen Chemie," Bd. XXII, 41 (1935); Th. Curtius and E. Mohr, *Ber.*, **31**, 2493 (1898). It formed white, stout needles or rods from a mixture of benzene and dioxane, m.p. 163–164° (cor.).

A New Synthesis of Perfluoroaldehydes

BY OGDEN R. PIERCE AND THOMAS G. KANE

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The preparation of perfluoroaldehydes has been described by reduction of the corresponding acid[1] or nitrile[2] with lithium aluminum hydride, by oxidative nitration of 1,1,1-trifluoropropane,[3] and by the Rosemund reduction of the corresponding acid chloride.[4] In this Laboratory it has been found that perfluoroaldehydes can be prepared by reduction of the corresponding perfluoroacid esters with lithium aluminum hydride at −70° in good yield (70–80%). The method employs a reverse addition technique and only small amounts of the by-product fluorine-containing alcohol are formed.

An explanation of the ready formation of aldehydes, in contrast to the usual alcohol formation from esters,[5] is not apparent at this time and is under investigation. Supporting work in this Laboratory has indicated that esters containing halogen atoms in the α- and β-positions will yield aldehydes on similar reductions. This would indicate that a strong inductive effect is a determining factor in the reaction mechanism.

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(2) A. L. Henne, R. L. Pelley and R. M. Alm, *ibid.*, **72**, 3370 (1950).

(3) H. Shechter and F. Conrad, *ibid.*, **72**, 3371 (1950).

(4) Central Research Department, Minnesota Mining and Manufacturing Co., private communication.

(5) W. G. Brown, "Reductions by Lithium Aluminum Hydride," in Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 469–509.