It must be concluded that the oxidation with permanganate of 5-nitrouracil, as well as of uracil itself, under the conditions used does not yield fractions representing specific carbon atoms of the ring system. The conclusions of Lagerkvist,[5] therefore, concerning the role of bicarbonate as a precursor of carbon 6 of uracil must be viewed with considerable doubt.

Experimental

Uracil-4-C^{14}.—The method of Davidson and Baudisch[6] was used for the synthesis of uracil from urea and a sample of malic acid-4-C^{14} prepared in this Laboratory by methods recently described.[7] The identity and purity of the twice-recrystallized uracil-4-C^{14} were established by the determination of the ultraviolet absorption spectrum in 0.01 N hydrochloric acid. Both the ϵ_{max} and the ratio of optical densities at 260 and 280 mμ agreed to within 1% with published data.[8]

5-Nitrouracil-4-C^{14}.—The isotopic nitrouracil was prepared by the method of Johnson and Matsuo[9] from a portion of the uracil-4-C^{14} diluted somewhat with non-radioactive uracil. The increase in weight during this process was 94% of that required by theory. The material was recrystallized once from water.

Oxidation of Uracil-4-C^{14}.—The procedures described by Heinrich and Wilson[1] for the cleavage of the pyrimidine ring, collection of the carbon dioxide, hydrolysis of the oxaluric acid, separation of the calcium oxalate and its subsequent oxidation to carbon dioxide were followed closely, except that the *p*H was maintained between 5 and 7 with the aid of a *p*H meter.

Oxidation of 5-Nitrouracil.—The method of Behrend and Offe[4] was followed for the oxidation step, followed by procedures similar to those mentioned above for uracil.

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A Convenient Preparation of Ethyl 2-Pyridylacetate

BY NEWTON N. GOLDBERG, BRUNO M. PERFETTI AND ROBERT LEVINE

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The following three methods are reported in the literature for the preparation of ethyl 2-pyridylacetate (I): (1) the alcoholysis of 2-pyridylacetanilide, which was prepared by the Beckmann rearrangement of 2-phenacylpyridine oxime,[1,2] (2) in 25% yield by the reaction of the potassium derivative of 2-picoline (prepared from the tar base and potassium amide) with diethyl carbonate[3] and (3) in 35–40% yield by the esterification of the lithium salt of 2-pyridylacetic acid, which was prepared by the carbonation of 2-lithiopyridine, which was in turn prepared from phenyllithium and 2-picoline.[4] These three methods have the common disadvantage that they are lengthy processes.

We have now found that by modifying the method developed in this Laboratory for the acylation of the lithium derivatives of methylated tar bases,[5,6] I may be prepared in 44.5% yield by the addition of a dilute ethereal solution of 2-picolyl lithium to a dilute ethereal solution of diethyl carbonate over a five-hour period. In addition to I, a small amount of di-2-picolyl ketone was isolated as its dipicrate.

Procedure.—2-Picolyllithium (0.4 mole) in 800 ml. of absolute ether was prepared as described previously[5] by the interaction of 0.4 mole of phenyllithium (prepared from 0.8 mole of lithium ribbon[7] and 0.4 mole (62.8 g.) of bromobenzene) and 0.4 mole (37.2 g.) of 2-picoline and was added over a five-hour period to a rapidly stirred cold (ice–salt-bath) solution of diethyl carbonate (0.2 mole, 23.6 g.) in 700 ml. of anhydrous ether. The ether was not allowed to reflux during the addition of the 2-picolyllithium. After the addition of the 2-picolyllithium was complete, the cooling bath was removed. The reaction mixture was heated to reflux, poured onto 200 g. of ice and extracted with several 200-ml. portions of ether. The combined ethereal phases were dried and concentrated and the residue fractionated to give 14.7 g. (44.5%) of ethyl 2-pyridylacetate, b.p. 110–113° (6 mm.); picrate, m.p. 138.8–139.2°.[5] The tarry residue was extracted for 18 hours with petroleum ether, b.p. 60–70°, in a Soxhlet extractor to give a small amount (< 0.1 g.) of a semi-solid material, which contained di-2-picolyl ketone, as indicated by the analysis of its dipicrate, m.p. 190–191° (from 95% ethanol) (undepressed by the dipicrate of the ketone obtained by the carbonation of 2-picolyllithium).

Anal. Calcd. for $C_{25}H_{18}O_{15}N_8$: N, 16.72. Found: N, 16.51.

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Some Brominated Dibenzothiophene Derivatives

BY HENRY GILMAN AND ROBERT K. INGHAM

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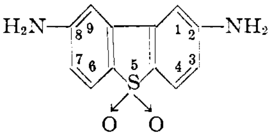
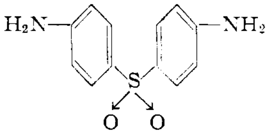
Dibenzothiophene derivatives, especially the substituted 5-dioxides, are closely related to substituted diphenyl sulfones; several compounds possessing high antituberculous activity are diphenyl sulfone derivatives. In view of this relationship and the demonstrated activity of 2-halo-7-aminodibenzofurans[1] the preparation of 2-bromo-



2,8-Diaminodibenzothiophene-5-dioxide



p,*p*′-Diaminodiphenyl sulfone

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