as benzoic acid, and that the acidic strength of the second hydrogen of II is about the same as that of the phenol. These results are given in Table II.

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Potential Anticancer Agents.[1] III. 3′-Amino-3′-deoxyadenosine

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The synthesis of 3′-amino-3′-deoxyadenosine from chloromercuri-6-benzamidopurine and 2,5-di-*O*-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride was described by Baker, Schaub, and Kissman in 1955.[2] Since additional amounts of this biologically active nucleoside were required for pharmacological evaluation, its synthesis was repeated; the opportunity was taken to use two later modifications in nucleoside synthesis.

The first modification was the use of pure chloromercuri-6-benzamidopurine, prepared by the Fox method;[3] this procedure has previously led to higher yields of nucleosides.[4] The second modification employed was the deacylation of the blocked nucleoside with *n*-butylamine in boiling methanol.[5] By these two modifications, 3′-amino-3′-deoxyadenosine crystallized from the methanolic butylamine reaction mixture in 66% yield (based on chloro sugar) and was pure as shown by paper chromatography.

The earlier described procedure[2] required ion exchange chromatography for isolation and the over-all yield from the sugar halide was 31%. Thus, the above two new modifications in nucleoside synthesis more than doubled the previous yield.

EXPERIMENTAL[6,7]

3′-Amino-3′-deoxyadenosine. A mixture of 11.8 g. of chloromercuri-6-benzamidopurine[8] and 11.8 g. of Celite[9] suspended in 1180 ml. of xylene was distilled with stirring until no more water was removed (about 360 ml. of distillate). After a warm solution of 10.2 g. of crystalline 2,5-di-*O*-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl chloride[10] in 210 ml. of xylene had been added, the mixture was heated under reflux for 3 hr. The hot solution was filtered and the filter cake was washed with 200 ml. of hot toluene. The combined filtrate and washings were concentrated to dryness *in vacuo*. The filter cake was extracted with five 100-ml. portions of boiling chloroform. The residue from the toluene-xylene concentration was dissolved in the combined chloroform extracts. The chloroform solution was washed with two 200-ml. portions of 30% aqueous potassium iodide solution, then with 200 ml. of water. The chloroform solution was dried over magnesium sulfate, then evaporated to dryness to yield 17.0 g. of cream colored solid; λ_{max}^{KBr} 2.92μ (NH, OH); 5.63μ (imido C=O); 5.81μ (benzoate and imido C=O); 7.90μ (benzoate O=C—O); 8.96μ (C—O—C).

The crude blocked nucleoside (17.0 g.) was dissolved in 210 ml. of methanol containing 30 ml. of *n*-butylamine. This solution was heated under reflux for 6 hr. After 3 hr. heating, the solution began to deposit a white, crystalline solid. The mixture was cooled at 0° overnight, then filtered. The white, crystalline precipitate was washed with methanol, then dried to yield 3.57 g. (66% based on chloro sugar) of 3′-amino-3′-deoxyadenosine, m.p. 265–267° (dec.); λ_{max}^{KBr} 3.00, 3.17μ (OH, NH); 6.00, 6.23, 6.37μ (adenine double bond structure); 9.08, 9.28, 9.64μ (C—O—). The paper chromatogram[7] contained a single spot at R_{Ad} 1.25.

Baker, Schaub, and Kissman[2] reported a m.p. 260–261° (dec.).

The methanol mother liquors contained an additional 2% of 3′-amino-3′-deoxyadenosine along with about 2% of adenine, as shown by paper chromatography.[7]

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(1) This program is under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, and is in collaboration with the Sloan-Kettering Institute for Cancer Research.

(2) B. R. Baker, R. E. Schaub, and H. M. Kissman, *J. Am. Chem. Soc.*, **77**, 5911 (1955).

(3) Footnote 21 of reference (4).

(4) B. R. Baker, K. Hewson, H. J. Thomas, and J. A. Johnson, Jr., *J. Org. Chem.*, **22**, 954 (1957).

(5) L. Goldman, J. W. Marsico, and R. B. Angier, *J. Am. Chem. Soc.*, **78**, 4173 (1956).

(6) The infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer. The melting point was taken on a Fisher-Johns apparatus and is uncorrected.

(7) The paper chromatograms were run with 5% aqueous disodium phosphate by the descending procedure on Whatman No. 1 paper. Adenine was used as a standard and arbitrarily assigned R_{Ad} 1.00. The distance moved by the nucleoside spot was assigned an R_{Ad} value with reference to adenine. The spots were located by visual examination with an ultraviolet lamp.

(8) From 6-benzamidopurine as described for the preparation of chloromercuri-2,6-diacetamidopurine by B. R. Baker and K. Hewson, *J. Org. Chem.*, **22**, 959 (1957).

(9) An analytical grade product of Johns-Manville Corp.

(10) B. R. Baker, J. P. Joseph, and R. E. Schaub, *J. Am. Chem. Soc.*, **77**, 5905 (1955).

Preparation of Acetals and Ketals from Enol Esters

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The reaction of an alcohol and an enol ester to form acetals or ketals is catalyzed by mercuric oxide in combination with boron trifluoride (or mercuric sulfate alone).[1] This catalyst combination was observed to effect a very vigorous reaction, as has been reported. However, we have found that the reaction of ethanol and isopropenyl acetate had an induction period of 5 to 8 minutes when the ester was added to the ethanol containing the mixed catalyst at 30°.

The induction period was eliminated and the yields of ketals were improved by using mercuric

(1) W. J. Croxall, F. J. Glavis, and H. T. Neher, *J. Am. Chem. Soc.*, **70**, 2805 (1948).