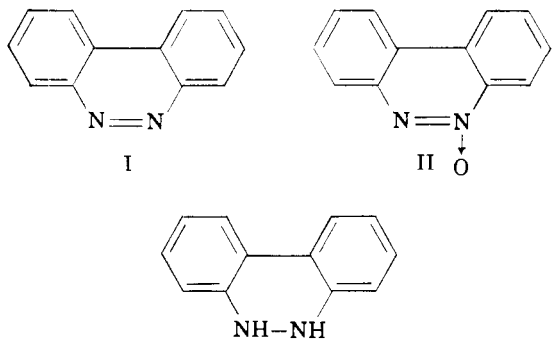
azone, diphenazone, diphenylenazone, 3,4-benzocinnoline, and 5,6-naphthisodiazine has been prepared by the reduction of 2,2′-dinitrobiphenyl: electrochemically,[2] chemically with sodium amalgam and methanol,[3] lithium aluminum hydride,[4] ferrous oxide,[5] or iron[6] and catalytically by hydrogenation with platinum oxide[7] or Raney nickel.[8]

The hydrogenation of either I or benzo[*c*]cinnoline oxide (II) with a platinum oxide catalyst reportedly resulted only in the obtaining of I, although there was evidence[7] that hydrazobiphenyl (III) formed and was readily oxidized to I. The hydrogenation of 2,2′-dinitrobiphenyl at an unspecified but presumably lower temperature and lower pressure in the presence of Raney nickel[8] also gave I. In no case was it reported that the catalytic hydrogenation of I yields 2,2′-diaminobiphenyl.

Upon reduction of 2,2′-dinitrobiphenyl with zinc and alkali a 55% yield of I has now been isolated. When I was catalytically hydrogenated with Raney



nickel, it had been expected that III would be formed. Consequently, the hydrogenation product was recovered under an atmosphere of nitrogen to avoid possible oxidation of III to I which occurs readily in air.[2,7] Contrary to our expectation, only 2,2′-diaminobiphenyl was obtained. Its infrared spectrum was identical with those of authentic samples of 2,2′-diaminobiphenyl obtained both by chemical[9,10] and by catalytic[7,11] reductions of 2,2′-dinitrobiphenyl. Melting points of the mixtures of reduction product and the authentic samples were undepressed.

(2) T. Wohlfahrt, *J. prakt. Chem.*, [2] **65**, 295 (1902).
(3) E. Tauber, *Ber.*, **24**, 3085 (1891).
(4) G. M. Badger, J. H. Seidler, and B. Thompson, *J. Chem. Soc.*, 3207 (1951).
(5) H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).
(6) P. Z. Slack and R. Slack, *Nature*, **160**, 437 (1947).
(7) S. D. Ross, G. J. Kahan, and W. A. Leach, *J. Am. Chem. Soc.*, **74**, 4122 (1952).
(8) J. L. Everett and W. C. J. Ross, *J. Chem. Soc.*, 1972 (1949).
(9) T. F. Macrae and S. H. Tucker, *J. Chem. Soc.*, 1520 (1933).
(10) S. von Niementowski, *Ber.*, **34**, 3325 (1901).
(11) R. B. Carlin and W. O. Forshey, Jr., *J. Am Chem. Soc.*, **72**, 793 (1950).

EXPERIMENTAL[12]

Benzo[c]cinnoline. In a 200-ml. 3-neck r.b. flask fitted with a reflux condenser, stirrer, and thermometer, 10 g. (0.041 mole) of 2,2′-dinitrobiphenyl, 133.4 ml. of absolute ethanol, and 13.4 ml. of an aqueous solution containing 10 g. of sodium hydroxide were heated on a water-bath. When the temperature of the mixture reached 70–80°, 30 g. of granular (30 mesh) zinc was added gradually over a period of 1/2 hour. Heating with stirring at 70–80° was continued for an additional 1/2 hour. The hot mixture was filtered through a Büchner funnel to remove the zinc oxide. The yellow crystalline material which precipitated from the cooled filtrate, was filtered and washed with absolute ethanol. The combined filtrate and wash solution were boiled with the zinc oxide residue and filtered while hot. From the cooled filtrate a second crop of yellow crystals was obtained. The combined yellow crystals of benzo[*c*]cinnoline (I), after recrystallization from absolute ethanol, weighed 4.1 g., yield 55.4%, m.p. 156–158°.

Anal. Calc'd for $C_{12}H_8N_2$: C, 79.98; H, 4.48; N, 15.55. Found: C, 79.87; H, 4.58; N, 15.79.

Reduction of benzo[c]cinnoline to 2,2′-diaminobiphenyl. A teaspoonful of commercial aqueous Raney nickel paste was washed by decanting with three 50-ml. portions of 95% ethanol. Benzo[*c*]cinnoline (0.53 g., 0.0030 mole) dissolved in 10 ml. of absolute ethanol and 10 ml. of an ethanolic suspension of Raney nickel was hydrogenated with shaking at 34–37° in a glass-lined bomb. The vapor-free space was 65 ml. and the pressure dropped from 98 to 70 p.s.i. The ethanolic solution was filtered and concentrated to 8 ml. in an atmosphere of nitrogen. The white colorless crystals of 2,2′-diaminobiphenyl (V) which separated upon cooling weighed 0.35 g., yield 86%, m.p. 77.5–78.5°.

Preparation of 2,2′-diaminobiphenyl from 2,2′-dinitrobiphenyl (IV) *by two different routes:* (*a*). By reduction with tin and hydrochloric acid[10] as described by Macrae and Tucker.[9]

(*b*). By hydrogenation with a platinum oxide catalyst[11] according to the procedure of Ross, Kahan, and Leach.[7]

Anal. Calc'd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: (a) C, 78.24; H, 6.57; N, 15.38. (b) C, 78.25; H, 6.73; N, 15.44.

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(12) The melting points are uncorrected. The analyses were performed by Oakwold Laboratories, Alexandria, Virginia.

The Preparation of Diformylmethylamine

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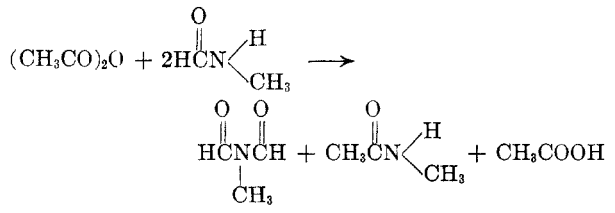
In the course of investigations of the nuclear magnetic resonance spectra of N-substituted amides in this laboratory, diformylmethylamine was synthesized. This compound, which has not been previously reported, was prepared by the reaction of acetic anhydride with N-methylformamide in accordance with the following equation.



EXPERIMENTAL

A solution of 18 ml. of N-methylformamide (0.31 mole) (b.p. 197°) and 25 ml. of acetic anhydride (0.26 mole)was placed in the pot of a 60 plate fractionating column. Acetic acid was distilled off over a period of 15 minutes without prior reflux. The remaining material was separated into two main fractions (b.p. 183 and b.p. 205° respectively).

N-Methylacetamide was identified by its m.p. 28° and its proton nuclear magnetic resonance spectrum which was identical with that of material prepared by the method of Galat and Elion.[1]

The fraction boiling at 183° with m.p. 13.5 to 14.5° was found to be *diformylmethylamine*. Yield 50%.

Anal. Calc'd for $C_3H_5NO_2$: M.W., 87.14; N, 16.09; Moles formate, 2. Found: M.W. (from vapor density at 240°), 86.8; N, 15.85; Moles formate, 1.98.

The diformylmethylamine was further characterized by its proton nuclear magnetic resonance spectrum which consisted of two sharp lines of area ratio 3:2 which is perfectly compatible with the assigned structure.

Use of a higher ratio of acetic anhydride to N-methylformamide resulted in formation of diacetylmethylamine as by-product. Of the several ratios of reactants tried, the one specified above proved to be the optimum. No ratio of reactants employed resulted in formation of any fraction which could be characterized as formylacetylmethylamine.

Diformylmethylamine was also prepared by fractionation of stoichiometric quantities of N-methylformamide and diacetylmethylamine to produce as a by-product, N-methylacetamide. This exchange reaction proved to be very slow.

It is to be noted that the b.p. of N-methylformamide reported by Gautier[2] (180–185°) is not in agreement with that reported in this paper. Gautier's method of preparation of N-methylformamide involved acetic anhydride as a by-product. Thus his products were exactly the starting materials used in the present study. Apparently Gautier's b.p. for N-methylformamide was actually determined on a somewhat impure sample of diformylmethylamine.

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(1) A. Galat and G. Elion, *J. Am. Chem. Soc.*, **65**, 1566 (1943).

(2) A. Gautier, *Ann.*, **151**, 242 (1869).

Kinetin Riboside and Related Nucleosides

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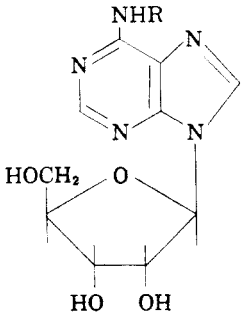
Since Miller and co-workers reported the isolation of kinetin,[1] a cell division factor, from autoclaved DNA samples and its identification as 6-furfurylaminopurine,[2,3] several groups have published on the synthesis of similarly substituted adenine derivatives.[4,5,6] It has been shown[4] that some of these derivatives have kinetin-like activity on plant growth. Because kinetin itself has been isolated from DNA it appeared conceivable that it might actually occur as a riboside or 2-deoxyriboside in nature. In view of our interest in the synthesis of nucleosides and related compounds[7] it seemed pertinent to prepare and test the 9-β-D-ribofuranosyl derivatives (I) of 6-furfurylaminopurine and other substituted adenines.[8] The synthesis of these derivatives, which are listed in Table I, is the subject of this note.



I

A convenient starting material for the preparation of these substituted adenosine derivatives would be a properly blocked 6-chloro-9-β-D-ribofuranosylpurine. The ready replaceability of the 6-chlorine atom in such a nucleoside by ammonia has been demonstrated by Brown and Weliky[9] in their synthesis of adenosine from 6-chloro-9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)purine.[10] However, for our purposes, we have used the corresponding benzoyl blocked 6-chloronucleoside, *i.e.* 6-chloro-9-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)purine (II), because it had been shown previously[11] that the pre-

(1) Miller, Skoog, von Saltza, and Strong, *J. Am. Chem. Soc.*, **77**, 1392 (1955).

(2) Miller, Skoog, Okumura, von Saltza, and Strong, *J. Am. Chem. Soc.*, **77**, 2662 (1955).

(3) Miller, Skoog, Okumura, von Saltza, and Strong, *J. Am. Chem. Soc.*, **78**, 1375 (1956).

(4) Skinner and Shive, *J. Am. Chem. Soc.*, **77**, 6692 (1955).

(5) Daly and Christensen, *J. Org. Chem.*, **21**, 177 (1956).

(6) Bullock, Hand, and Stokstad, *J. Am. Chem. Soc.*, **78**, 3693 (1956).

(7) See for example paper XI of the Puromycin series.[11]

(8) While this work was in progress, R. H. Hall and R. S. de Ropp of these laboratories reported convincing evidence to the effect that kinetin is actually an artifact formed from adenine and 2-deoxy-D-ribose during autoclaving.[15]

(9) Brown and Weliky, *J. Biol. Chem.*, **204**, 1019 (1953).

(10) L. Goldman, J. Marsico, and R. Angier of these laboratories have successfully effected the reaction of 6-chloro-9-(2,5-di-*O*-benzoyl-3-deoxy-3-phthalimido-β-D-ribofuranosyl)purine with aliphatic amines (to be published).

(11) Kissman, Pidacks, and Baker, *J. Am. Chem. Soc.*, **77**, 18 (1955).