between these two possibilities have thus far been unsuccessful.

Experimental[5]

N,N-Cleavage of Diphenyltriketone Benzoylphenylhydrazone (IIa), *p*-Nitrophenyl Phenyltriketone (IIIb) and *p*-Nitrophenyl Phenyltriketone *p*-Nitrobenzoylphenylhydrazone (IIIc) on Alumina.—The hydrazone (0.0001–0.0002 mole) was adsorbed on a column of adsorption alumina[6] (10–12 inch long and 0.75–1.25 inch in diameter) from a dry benzene (50–75 cc.) solution. Dry benzene did not effect elution and there was no evidence of reaction until the column was eluted with dry benzene containing from 1 to 10% ethanol. When the mixed solvent was added a warm yellow band which was formed moved down the column. IIa and IIIb each gave benzanilide (59%, m.p. 159–162°, and 75%, m.p. 157–160°, respectively) as shown by m.p. and mixed m.p. with an authentic sample, m.p. 161–162°. Further elution with other solvents gave only a small amount of oily product which could not be induced to crystallize. IIIc gave a 64% yield of *p*-nitrobenzanilide, m.p. 214–215°. The mixed m.p. with an authentic sample, m.p. 216.5–217.5°, was not depressed.

N,N-Cleavage of *p*-Nitrophenyl Phenyltriketone Benzoylphenylhydrazone (IIIb) and Bis-*p*-nitrophenyl Triketone Benzoylphenylhydrazone (IIc) with Dilute Sodium Hydroxide.—A suspension of 0.1 g. of IIIb or IIc in 15 ml. of 0.5% sodium hydroxide and 10 cc. of water was refluxed for 2.5 hours. The anilide was collected by filtration of the cold solution. From IIIb was obtained a 61% yield of benzanilide, m.p. 159–161°. IIc gave a 74% yield of benzanilide, m.p. 156.5–159.5°. Acidification of the filtrate gave, from IIIb, a mixture of *p*-nitrobenzoic acid and benzoic acid in 95 and 65% yields. From the filtrate from IIc was obtained a 70% yield of *p*-nitrobenzoic acid as shown by m.p. and mixed m.p.

Benzophenone *p*-Nitrobenzoylphenylhydrazone (IV).—To a solution of 13 g. (0.048 mole) of benzophenone phenylhydrazone and 30 ml. of dry pyridine cooled in an ice-bath was added 11.2 g. (0.0597 mole) of *p*-nitrobenzoyl chloride in 150 cc. of dry ether over a period of 20 minutes. The mixture was allowed to stand at room temperature for 24 hours and then refluxed for seven hours. Distillation of the filtrate left an oil which crystallized on standing in a refrigerator. The yield of crude benzophenone *p*-nitrobenzoylphenylhydrazone, m.p. 139–146°, was 75%. After repeated recrystallization from ether–ethanol the compound melted at 151.5–152.5°.

Anal. Calcd. for $C_{26}H_{19}N_3O_3$: C, 74.1; H, 4.5; N, 10.0. Found: C, 73.7; H, 4.6; N, 10.0.

An attempt to prepare this compound by adding *p*-nitrobenzoyl chloride (13 g.) to benzophenone phenylhydrazone (15 g.) in 100 cc. of pyridine and allowing the mixture to stand at room temperature overnight gave only 3.5 g. of *p*-nitrobenzoic anhydride and 10 g. of recovered phenylhydrazone.

IV could be hydrolyzed to α-*p*-nitrobenzoylphenylhydrazine, m.p. 191–192° dec., lit.[7] m.p. 195–196°, in 43% yield (57% on the basis of unrecovered starting material) by treatment for 2.5 hours with refluxing 6 *N* hydrochloric acid.

Treatment of 0.10 g. of IV with 5 cc. of refluxing 5% sodium carbonate solution for 12 hours leads only to recovery of 95% of the starting material.

When IV was eluted from an alumina column with benzene a 26% yield (96% based on unrecovered starting material) of benzophenone phenylhydrazone, m.p. 133.5–135.5°, was obtained. A mixed m.p. showed no depression.

Benzil Benzoylphenylhydrazone[8] (V).—V could be recovered unchanged from an alumina column by elution with benzene in 95% yield. When 0.5 g. of V was allowed to stand for nine days, however, in benzene (75 cc.) containing three drops of 95% ethanol in contact with alumina, a 67% yield of benzil phenylhydrazone, m.p. 131–135.5°, was obtained.

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RECEIVED MAY 10, 1951

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(5) All melting points are corrected. Analyses were carried out by Dr. Francine Schwarzkopf, Elmhurst, New York.

(6) Eimer and Amend Adsorption Alumina, 80–200 mesh, activated by heating at 300°.

(7) G. Lockemann, *Ber.*, **43**, 2223 (1910).

(8) K. Auwers and A. Bennecke, *Ann.*, **378**, 243 (1910).

A New Preparation of 2-Amino-4-phenylpyrimidine[1,2]

BY W. K. DETWEILER AND E. D. AMSTUTZ

Several investigators[3-5] have reported the preparation of 2-amino-4-phenylpyrimidine by ring closure methods which involved the use of guanidine salts. We have now found that this compound is also formed by the reaction of phenyllithium with 2-aminopyrimidine in refluxing toluene.

Although it is possible that this substituted pyrimidine was formed by a 1,2-addition of phenyllithium[6] to the nitrogen-to-carbon double bond of the pyrimidine ring, there does not appear to be any evidence to exclude a 1,4-addition to the conjugated system of the iminodihydro form of 2-aminopyrimidine.

Experimental

2-Amino-4-phenylpyrimidine.—2-Aminopyrimidine (9.51 g., 0.1 mole) in 500 ml. of hot dry toluene was added over a half-hour period to phenyllithium[7] (prepared from 31.4 g. of bromobenzene and 2.78 g. of lithium metal) in 140 ml. of anhydrous ether. The ether was allowed to distil from the reaction mixture during this addition; when the bath temperature reached 115°, the condenser was set for reflux and the residual mixture was refluxed with stirring for 7 hours. While cooling the reaction mixture in an ice-bath, a few ml. of water and 300 ml. of a 1:1 mixture of concentrated hydrochloric acid and water were cautiously added with stirring. The acidic extract was separated from the toluene and adjusted to a *p*H 9 by cautiously adding 48% sodium hydroxide to the cooled solution. The precipitated tan solid was filtered, washed with cold water and dried; yield 6.9 g., m.p. 146–157°. Recrystallization from 95% ethanol after treatment with decolorizing charcoal gave 3.4 g. (20%) of cream-colored needles, m.p. 162–164°. Two additional recrystallizations from ethanol gave nearly colorless needles, m.p. 164.4–165.1°. The last trace of color was removed by vacuum sublimation at 9 mm. pressure; the melting point was not significantly altered. *Anal.* Calcd. for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.11; H, 5.37; N, 24.47.

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(1) Abstracted, in part, from a thesis presented by W. K. Detwiler to the Graduate Faculty of Lehigh University of partial fulfillment of the requirements for the Ph.D. degree, June, 1941.

(2) The authors wish to thank the Wm. S. Merrell Company for the financial support of this research.

(3) E. Benary, *Ber.*, **63B**, 2601 (1930).

(4) J. M. Sprague, L. W. Kissinger and R. W. Lincoln, THIS JOURNAL, **63**, 3028 (1941).

(5) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 953 (1946).

(6) For the 1,2-addition of phenyllithium to pyridine see J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 517.

(7) The phenyllithium used in this reaction was prepared according to the instructions given in "Organic Syntheses."[6]

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RECEIVED JUNE 20, 1951

Preparation of Some Heterocyclic Biurets[1,2]

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The Davis–Blanchard[3] method of synthesizing ω-substituted biurets from nitrobiuret has been

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(1) Abstracted, in part, from a thesis presented by W. K. Detweiler to the Graduate Faculty of Lehigh University in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

(2) The authors wish to thank the Wm. S. Merrell Company for the financial support of this research and for helpful discussions in connection with this work.

(3) T. L. Davis and K. C. Blanchard, THIS JOURNAL, **51**, 1803 (1929).