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.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

RECEIVED MAY 10, 1951

---

[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.

---

[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]

DEPARTMENT OF CHEMISTRY
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA

RECEIVED JUNE 20, 1951

Preparation of Some Heterocyclic Biurets[1,2]

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

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

---

[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).

successfully employed in the preparation of two heterocyclic biurets. Reduced to its simplest terms, this reaction may be represented by the equation

$$RNH_2 + H_2NCONHCONHNO_2 \longrightarrow RNHCONHCONH_2 + N_2O + H_2O$$

In this way we have prepared 1-(2-pyridyl)- and 1-(2-thiazolyl)-biuret in yields of 34 and 13%, respectively.

Experimental[4]

1-(2-Pyridyl)-biuret.—2-Aminopyridine (47 g., 0.5 mole) and nitrobiuret[5] (74.1 g., 0.5 mole) were dissolved in 830 ml. of water which had been heated to 70°. The temperature of the stirred solution was raised from 65 to 75° over a period of 2.75 hours; during this time gaseous evolution and precipitation occurred. The temperature of the reaction mixture was then raised to 90° over a period of 1 hour. The colorless granular crystals were filtered from the cooled solution and dried under vacuum over phosphorus pentoxide, yield 30.5 g. (33.8%), m.p. 194–195.5° with gaseous decomposition. Recrystallization from 95% ethanol gave an 87% recovery of colorless platelets, m.p. 197–198° with slight gaseous decomposition. Recrystallization of these crystals from water gave fine crystals, m.p. 196.2–197.2°. *Anal.* Calcd. for $C_7H_8N_4O_2$: C, 46.66; H, 4.48; N, 31.10. Found: C, 46.46; H, 4.50; N, 31.56, 30.76.

1-(2-Thiazolyl)-biuret was prepared in an analogous manner, yield 12.5%, m.p. 205–214° with gaseous decomposition and resolidification. The melting point may be raised to 217–218° by recrystallization from 95% ethanol. *Anal.* Calcd. for $C_5H_6N_4O_2S$: C, 32.25; H, 3.25; N, 30.09; S, 17.22. Found: C, 32.37; H, 3.43; N, 29.74; S, 17.05.

Biuret Tests.—Phenylbiuret and 1-(2-pyridyl)-biuret gave a blue-violet color when treated with dilute copper sulfate and sodium hydroxide. 1-(2-Thiazolyl)-biuret gave an emerald green color.

---

[4] All melting points have been corrected for thermometer stem-emergence.

[5] J. Thiele and E. Uhlfelder, *Ann.*, **303**, 93 (1893).

DEPARTMENT OF CHEMISTRY
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA

RECEIVED JUNE 20, 1951

The Exchange of Deuterium for Hydrogen in *n*-Heptane[1]

BY JOSEPH A. DIXON[2] AND ROBERT W. SCHIESSLER

The simultaneously-occurring hydrogenation and hydrogen exchange reactions of an olefin and deuterium over nickel or platinum have been the subject of numerous investigations,[3] and the exchange of deuterium for hydrogen between a saturated hydrocarbon and deuterium has been well demonstrated.[4] The hydrogen atoms of benzene and ethylene have been shown to participate in an exchange with deuterium atoms of heavy water.[5] Horrex, Greenhalgh and Polanyi published the only report of exchange between heavy water and a saturated hydrocarbon[6] over metal catalysts. They obtained exchange between both cyclohexane and isopentane and a water containing 14% D_2 at 100° and one-half atmosphere over a platinum catalyst. The product cyclohexane was reported to contain 0.67% deuterium.

Ingold, Raisin and Wilson examined hydrogen exchange between sulfuric acid and aliphatic hydrocarbons.[7] Little exchange was obtained with *n*-hexane or *n*-heptane.

While examining various routes for the preparation of a perdeuterated normal paraffin we have studied the liquid and vapor phase reactions of a saturated straight-chain hydrocarbon with heavy water.

In Table I are shown the results of experiments with deuterium oxide or hydrogen oxide and *n*-heptane. The *K* of the last column of the Table is a measure of the extent of exchange and is defined by

$$(C–H) + (O–D) \leftrightarrows (C–D) + (O–H)$$

$$K = \frac{(C–D)\,(O–H)}{(C–H)\,(O–D)}$$

where (C–D) and (C–H) refer to the number of carbon–deuterium and carbon–hydrogen bonds, respectively, in the hydrocarbon and the (O–D) and (O–H) represent the oxygen–deuterium and oxygen–hydrogen linkages in the water. The density is a linear function of the ratio of hydrogen to deuterium in hydrocarbons and heavy water. The number of C–D, C–H, O–D and O–H bonds is obtained from the densities of the product water and product hydrocarbon by simple calculations.

The experiments indicate: (1) Nickel and platinum catalysts are ineffective for the catalysis of hydrogen exchange between water and a straight-chain paraffin in the liquid phase. (2) Vapor phase interchange of the hydrogen isotopes between heavy water and a normal paraffin takes place readily over a kieselguhr-supported nickel catalyst. Exchange proceeded at 135° in the vapor and did not take place at 150° in the liquid.

Undoubtedly the inability of the hydrocarbon to compete with the water for catalyst surface is the dominant factor in the failure of the present liquid phase experiments.[8]

The exchange is accompanied by scission of carbon–carbon bonds. This is very unfortunate if the goal is a completely deuterium-substituted straight-chain hydrocarbon. Experiments 11 to 13 were performed with ordinary water. The change in density is excellent evidence that the hydrocarbon skeleton is being altered. Infrared spectra[9] of the hydrocarbon product from Experi-

---

[1] American Petroleum Institute Project 42. Advisory Committee: H. Sutherland (Chairman), E. M. Barber. J. R. Bates, L. C. Beard, G. H. Denison, L. M. Henderson, R. G. Larsen, R. F. Marschner, L. A. Mikeska and J. H. Ramser.

[2] California Research Corp., Richmond, California.

[3] V. H. Dibeler and T. I. Taylor, *J. Chem. Phys.*, **16**, 1008 (1948); K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1795 (1936); K. Morikawa, N. R. Trenner and H. S. Taylor, *ibid.*, **59**, 1103 (1937); G. H. Twigg and E. K. Rideal, *Proc. Roy. Soc.*, (*London*). **A171**, 55 (1939); J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[4] K. Morikawa, W. S. Benedict and H. S. Taylor, ref. 3; K. Morikawa, N. R. Trenner and H. S. Taylor, ref. 3; A. Farkas, *Nature*, **143**, 244 (1939); *Trans. Faraday Soc.*, **35**, 917 (1939): *ibid.*, **36**, 522 (1940); R. K. Greenhalgh and M. Polanyl, *ibid.*, **35**, 520 (1938).

[5] J. Horiuti and M. Polanyi, *Nature*, **134**, 377 (1934); G. Joris, H. S. Taylor and J. C. Jungers, THIS JOURNAL, **60**, 1982 (1938); P. I. Bowman, W. S. Benedict and H. S. Taylor, *ibid.*, **57**, 960 (1935).

[6] C. Horrex and M. Polanyi, *Mem. Proc. Manchester Lit. and Phil. Soc.*, **80**, 33 (1935–1936); *C. A.*, **31**, 2503 (1937); C. Horrex, R. K. Greenhalgh and M. Polanyi, *Trans. Faraday Soc.*, **35**, 511 (1937).

[7] C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936).

[8] The serious retardation of nickel-catalyzed hydrogenations by small amounts of water has been observed frequently in this and other laboratories.

[9] These spectra were determined by The Petroleum Refining Laboratory of The Pennsylvania State College. The infrared spectrometer was a Perkin and Elmer Model 12-A.