portions. After cooling, filtering, and washing under carbon dioxide with water, ethanol and ether, 2.69 g. of clustered needles was obtained. The product was recrystallized by the addition of 2 ml. of concentrated hydrochloric acid to its solution in a hot mixture of 115 ml. of methanol and 10 ml. of water. It was found to be a hydrochloride with a melting point at about 270°. It is soluble in *N* sodium hydroxide.

Anal. Calcd. for $C_{11}H_{12}ON_4S \cdot HCl$: C, 46.39; H, 4.60; N, 19.68. Found: C, 46.46; H, 4.71; N, 19.51.

1-(4-Acetamidobenzyl)-3-thiosemicarbazide (VI).—To a suspension of 23.6 g. (0.1 mole) of I in 400 ml. of liquid ammonia was added in small pieces 7.3 g. of sodium. A clear solution resulted, after the addition of the first few pieces. By adding 0.6 g. of ammonium chloride, the persistent blue color was discharged. The residue obtained after evaporation was taken up with 200 g. of ice-water and the insoluble material was filtered and washed with water, ethanol and ether; yield 11.18 g. (47%), m.p. 209° (dec.). After recrystallization from 800 ml. of 50% methanol, the product melted at 217–218°. It is insoluble in *N* hydrochloric acid and alkali.

Anal. Calcd. for $C_{10}H_{14}ON_4S$: C, 50.40; H, 5.92; N, 23.51. Found: C, 50.68; H, 5.92; N, 23.24.

RESEARCH LABORATORIES
HOFFMANN-LA ROCHE INC.
NUTLEY 10, N. J.

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Condensation of Nitroparaffins with α,β-Unsaturated Ketones Using Calcium Hydride[1]

BY NORTON FISHMAN[2] AND SAVERIO ZUFFANTI

Introduction.—Kloetzel,[3] in 1947, used diethylamine as a condensing agent for the reaction between nitroparaffins and α,β-unsaturated ketones. At room temperature he obtained yields of 58–97.5% in 6–35 days.

The basic character of calcium hydride[4] led us to investigate its efficacy as a condensing agent in this reaction. 2-Nitropropane, benzalacetophenone and calcium hydride produced no reaction even on prolonged standing over a period of several weeks.

In the presence of methanol, however, an immediate reaction results and within 15 hours a 92% yield of 4-methyl-4-nitro-1,3-diphenyl-1-pentanone is obtained. Nitromethane, 1-nitropropane and 2-nitropropane were condensed with benzalacetone and benzalacetophenone using calcium hydride and methanol. At room temperature the reactions were complete in from 1–21 days and the yields ranged from 65–92%.

Experimental

Purification of Materials.—The methanol and nitroparaffins were purified by allowing them to stand over calcium hydride for several weeks and then filtering and fractionating.

It was noted that although the hydride will not react with the pure alcohol or nitroparaffins individually, an instantaneous evolution of hydrogen is observed if the hydride is added to a mixture of the alcohol and the nitroparaffin. From the reaction mixture can be recovered the entire quantity of alcohol and the calcium salt of the nitroparaffin. The benzalacetone and benzalacetophenone were purified by repeated recrystallizations.

4-Methyl-4-nitro-1,3-diphenyl-1-pentanone.—Into a 250 ml. flask are placed 10 g. (0.048 mole) of benzalacetophenone, 44 g. (0.49 mole) of 2-nitropropane and 40 ml. of dry methanol. These are mixed thoroughly till the ketone is dissolved and 2 g. (0.048 mole) of calcium hydride is added. Thereafter continuous evolution of hydrogen is observed while the reaction progresses.[5] The mixture is allowed to stand stoppered with a calcium chloride tube for 24 hours, and then the solidified contents are extracted with anhydrous chloroform. The extract is concentrated and the crystals are filtered off, washed with alcohol, and dried. The product, 4-methyl-4-nitro-1,3-diphenyl-1-pentanone, melts at 133–135°. Yields of 85–92% are obtained. The purified crystals melt at 146°.

(1) Presented before the Chicago Meeting of the American Chemical Society, September 8, 1950. This note is part of the thesis presented by Norton Fishman to Northeastern University, in partial fulfillment of the requirements of the A.M. degree.

(2) Harvard University, Cambridge, Mass.

(3) M. C. Kloetzel, THIS JOURNAL, **69**, 2271 (1947).

(4) S. Zuffanti and J. Sardella, *ibid.*, **72**, 4322 (1950).

(5) Note the order of addition, for when calcium hydride is added before the ketone, little or no reaction product is obtained.

DEPARTMENT OF CHEMISTRY
NORTHEASTERN UNIVERSITY
BOSTON, MASS.

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5-Methyl-2-nitraminopyridine

BY LUTHER A. R. HALL AND CALVIN A. VANDERWERF

In the course of work aimed toward the synthesis of certain pyridotriazoles, it was of interest to prepare a number of new compounds derived from 2-aminopyridine. All of these except 5-methyl-2-nitraminopyridine have since been reported by Lappin and Slezak.[1]

5-Methyl-2-nitraminopyridine.—The nitration of 5 methyl-2-aminopyridine was carried out by a modification of the general method of Seide.[2] To a cold (0–5°) solution of 15.0 g. (0.139 mole)[3] of 5-methyl-2-aminopyridine[4] in 33 ml. of concentrated sulfuric acid, 9 g. of fuming nitric acid (sp. gr. 1.50) was added carefully with efficient stirring. The nitration mixture was allowed to stand for 2 hours in an ice-bath during which time its color changed from light yellow to dark orange-brown. It was then poured onto about 75 g. of ice. The product, which came down as a yellow precipitate, weighed 14.9 g. (70.0%). After three recrystallizations from water, the pure product melted at 183.0–183.5° (dec.).

Anal. Calcd. for $C_6H_7N_3O_2$: C, 47.1; H, 4.6. Found: C, 47.1; H, 4.6.

(1) G. R. Lappin and F. B. Slezak, THIS JOURNAL, **72**, 2806 (1950).

(2) O. Seide, *Ber.*, **57**, 791 (1924); *ibid.*, **57**, 1802 (1924).

(3) Small scale runs were preferred in order that adequate cooling might be maintained. The reaction is extremely exothermic, with the product decomposing at temperatures above 50°.

(4) Obtained from the Reilly Tar and Chemical Corp.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

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The Preparation of Some Substituted 2-Thiouracils and 2,4-Dimercaptopyrimidines

BY ELVIRA A. FALCO, PETER B. RUSSELL AND GEORGE H. HITCHINGS

The discovery of the chemotherapeutic activity of certain 5-phenoxy-2-thiouracils (I)[1] against vaccinia virus prompted the preparation of a series of 5-phenoxy, and other 2-thiouracils carrying weighty substituents at the 5- or 6-position.

The preparations of these compounds were carried out by conventional methods.[2,3] The compounds are listed in Table I.

(1) R. L. Thompson, S. A. Minton, Jr., E. A. Falco and G. H. Hitchings, *Federation Proc.*, **10**, 421 (1951); *J. Immunol.*, in press (1951).

(2) T. B. Johnson and H. H. Guest, *Am. Chem. J.*, **42**, 271 (1909).

(3) T. B. Johnson and J. C. Ambelang, THIS JOURNAL, **60**, 2941 (1938).