centrated at reduced pressure and washed with aqueous sodium bicarbonate and with water, and dried over anhydrous magnesium sulfate. The residue (4.4 g., 82% yield) left by complete removal of solvent was relatively pure ester, m. p. 40–45°. Three recrystallizations from ether–petroleum ether gave 3.0 g. of pure material of constant melting point (41–43°).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.51, 64.18; H, 7.32, 7.17.

A trial distillation at 2 mm. of a small sample of the pure hydroxy ester resulted in elimination of methanol, identified in the Dry Ice trap, and partial conversion to lactone.

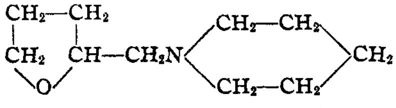
CHEMICAL LABORATORY
SMITH COLLEGE
NORTHAMPTON, MASSACHUSETTS

RECEIVED FEBRUARY 6, 1945

Pyridine from Furfural

BY CHRISTOPHER L. WILSON

The following observations with furfurylamine confirm and extend the recent findings of Kline and Turkevich.[1] Passage over typical dehydrating catalysts at elevated temperatures failed to give pyridine[2] but catalytic reduction in the liquid phase led first to tetrahydrofurfurylamine and then, under more drastic conditions, to piperidine (9%) and N-tetrahydrofurfurylpiperidine (formula inset, 43%). These experiments could be the basis of a satisfactory synthetic method for pyridine.



Hydrogenation of Furfurylamine.—Furfurylamine (193 g.), Raney nickel catalyst (30 g.) and hydrogen (137 atm. (20°)) were introduced into a 2-l. rotating autoclave. Two moles of hydrogen were rapidly absorbed at 140° and a third slowly at 200–215°. The product on fractionation consisted of (a) b. p. below 110°, which after drying over potassium carbonate gave piperidine (15 g.) identified as picrate, and (b) N-tetrahydrofurfurylpiperidine (new, 73 g.), b. p. 102–104° (11 mm.).

Anal. Calcd. for $C_{10}H_{19}ON$: C, 71.0; H, 11.35; N, 8.3; mol. wt., 169. Found: C, 70.7; H, 10.9; N, 8.9; equiv. by titr., 171.

The **picrate** had m. p. 140–141°.

Anal. Calcd. for $C_{16}H_{22}O_8H_4$: N, 14.1. Found: N, 13.8.

An authentic specimen was prepared by heating tetrahydrofurfuryl bromide and excess piperidine together at 100° for one hour.

---

(1) Kline and Turkevich, THIS JOURNAL, **66**, 1710 (1944).

(2) Such a reaction was first envisaged by Ciamician and Dennstedt, *Ber.*, **14**, 1059, 1475 (1881).

UNIVERSITY COLLEGE, LONDON

RECEIVED JANUARY 29, 1945

NEW COMPOUNDS

Propylene Glycol *p*-Nitrobenzoate

Propylene glycol was converted to the *p*-nitrobenzoate by treatment with *p*-nitrobenzoyl chloride in pyridine according to the general procedure outlined by Shriner and Fuson.[1] After three recrystallizations from alcohol the product melted at 126–127°.

Anal: Calcd. for $C_{17}H_{14}N_2O_8$: C, 54.55; H, 3.77; N, 7.48. Found: C, 54.75; H, 3.99; N, 7.60.

---

(1) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, p. 137.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
HENNING EKLUND
CHARLES C. PRICE

RECEIVED FEBRUARY 5, 1945

Di-(*p*,*p*′-dichlorobenzohydryl) Ether

Three grams (12 millimoles) of *p*,*p*′-dichlorobenzohydrol (prepared by the reduction of *p*,*p*′-dichlorobenzophenone with zinc and sodium hydroxide[1]) was dissolved in 15 cc. of dry chloroform and 5 cc. of concentrated sulfuric acid was added slowly dropwise with vigorous stirring. After standing at room temperature for ten minutes the brown mixture was poured onto 50–60 g. of ice. The chloroform layer was separated, washed with 5% sodium carbonate solution and water until neutral, and then dried over anhydrous potassium carbonate. After filtering and removal of the chloroform on the steam-bath with reduced pressure, a viscous oil remained which was dissolved in 5 cc. of petroleum ether (60–70°) and the solution cooled in an ice-bath until crystals formed. These were collected by suction filtration and then crystallized twice from absolute ethanol, using a small amount of Norit each time. The yield of colorless crystals was 1.5 g., 51% of the theoretical, melting 126–127°.

Anal. Calcd. for $C_{26}H_{18}Cl_4O$: Cl, 29.1; mol. wt., 488. Found: Cl, 28.8; mol. wt., 490.

The ether was further characterized by cleavage with 3,5-dinitrobenzoyl chloride to form *p*,*p*′-dichlorobenzohydryl 3,5-dinitrobenzoate: 1.0 g. of the ether, 0.5 g. of 3,5-dinitrobenzoyl chloride and 0.15 g. of anhydrous zinc chloride were heated on the steam-bath for one hour and in an oil-bath at 150° for one-half hour. The oily product was poured into 50 cc. of ice water with stirring and the mixture allowed to stand forty-eight hours. The crude product slowly solidified and after washing with warm 2% sodium carbonate solution and crystallization from 2:1 benzene–alcohol there was obtained 0.2 g. of *p*,*p*′-dichlorobenzohydryl 3,5-dinitrobenzoate, m. p. 174–176°. A mixed melting point with the authentic ester[2] gave 174–176°. Attempts to cleave the ether with acetic acid–sulfuric acid, as Nef had done on benzohydryl ether,[3] gave only the unreacted ether. The ether was not appreciably hydrolyzed by heating with 5% sulfuric acid in a sealed tube at 150° for two hours.

---

(1) Montagne, *Rec. trav. chim.*, **24**, 115 (1905).

(2) Grummitt, Buck and Joseph, THIS JOURNAL, **67**, 693 (1945).

(3) Nef, *Ann.*, **298**, 234 (1897).

SHERWIN-WILLIAMS LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
OLIVER GRUMMITT
ALLEN BUCK

RECEIVED JANUARY 20, 1945

p,*p*′-Dichlorobenzohydryl 3,5-Dinitrobenzoate

A mixture of 2.0 g. (8 millimoles) of *p*,*p*′-dichlorobenzohydrol (prepared by the reduction of *p*,*p*′-dichlorobenzophenone with zinc and sodium hydroxide[1]), 1.5 g. (6 millimoles) of 3,5-dinitrobenzoyl chloride and 5–6 cc. of dry pyridine was heated on the steam-bath for one hour. It was then poured with stirring into 100 cc. of cold water and allowed to stand until the oil layer solidified. The water was decanted, the solid was pulverized and then thoroughly washed with several portions of warm 2% sodium carbonate solution. The solid was collected by

---

(1) Montagne, *Rec. trav. chim.*, **24**, 115 (1905).