tion of potassium (3 g., 72 mmoles) in *t*-butyl alcohol (100 ml.) and 2-bromopyridine (4 g., 25 mmoles) gave an oily residue after the usual work up. This residue was crystallized from acetone to give 1 g., m.p. 218–231° (10%). Recrystallization from acetone raised the m.p. to 251.5–252.5°; $[\alpha]_D$ −28° (chloroform). The infrared spectrum was identical to that of an authentic sample.[9]

Anal. Calcd. for $C_{25}H_{36}O_6$ (432.54): C, 69.42; H, 8.39. Found: C, 69.26; H, 8.45.

Treatment of the above product (VII) with 1% methanolic sulfuric acid (1 hr. reflux) gave a 77% yield (m.p. 204–205°) of 13α,21-epoxy-11β-hydroxy-17β-methyl-18-nor-17α-Δ^4-pregnene-3,20-dione. Recrystallization from acetone–petroleum ether raised the m.p. to 206–208°; $[\alpha]_D^{25}$ +52° (chloroform); λ_{max} 242 mμ (ε 16,900). The infrared spectrum was identical to that of an authentic sample.[9,14]

11β-Hydroxy-17α,21-methylenedioxy-5-pregnene 3,20-bisethylene ketal (VIII). To a solution of potassium (1.7 g.) in *t*-butyl alcohol (100 ml.) under nitrogen was added a slurry of 11β,17α,21-trihydroxy-5-pregnene 3,20-bisethylene ketal (I, 6.0 g.) in *t*-butyl alcohol (100 ml.) followed by the addition of methylene bromide (5.0 ml.). The mixture was stirred and refluxed for 3 hr. After cooling, chloroform (800 ml.) was added and the mixture washed to neutrality with water. The extract was dried and evaporated to give a solid residue which was crystallized from acetone–petroleum ether; yield 3.85 g., m.p. 220–240°. Several recrystallizations from the same solvent pair raised the melting point to 252–255°; $[\alpha]_D^{25}$ −42° (chloroform); ν_{max} 3448, 1092, 1052, and 956 cm.$^{-1}$

Anal. Calcd. for $C_{26}H_{38}O_7$ (462.56): C, 67.51; H, 8.28. Found: C, 67.56, 67.09, 67.42; H, 8.52, 8.59, 8.36.

11β-Hydroxy-17α,21-methylenedioxy-4-pregnene-3-one 20-ethylene ketal (IX). A solution of 11β-hydroxy-17α,21-methylenedioxy-5-pregnene 3,20-bisethylene ketal (VIII) (250 mg.) in methanol (50 ml.) containing sulfuric acid (8%, 5 ml.) was refluxed for 1 hr. It was poured into water and the mixture neutralized with solid sodium bicarbonate. The resulting crystalline product was collected by filtration. This gave 200 mg., m.p. 195–197° (88%). Recrystallization from acetone–petroleum ether raised the melting point to 235–237°; $[\alpha]_D^{25}$ +97° (chloroform); $\lambda_{max}^{CH_3OH}$ 241 mμ (ε 16,900); ν_{max} 3436, 1664, 1612, 1046, and 956 cm.$^{-1}$

Anal. Calcd. for $C_{24}H_{34}O_6$ (418.51): C, 68.87; H, 8.19. Found: C, 68.35; H, 8.20.

11β-Hydroxy-17α,21-methylenedioxy-4-pregnene-3,20-dione (X). *A. Hydrolysis with 1% sulfuric acid.* A solution of 11β-hydroxy-17α,21-methylenedioxy-4-pregnene-3-one 20-ethylene ketal (IX, 207 mg.) in methanol (50 ml.) containing sulfuric acid (8% v/v) (10 ml.) was refluxed for 24 hr. Water was added and the methanol evaporated to give a crystalline product which was collected by filtration; yield 139 mg. (75%), m.p. 180–185°. Recrystallization from acetone–petroleum ether raised the m.p. to 211–213°; $[\alpha]_D^{25}$ +185° (chloroform); λ_{max} 241 mμ (ε 16,500); ν_{max} 3460, 1714, 1667, 1618, 1118, and 1047 cm.$^{-1}$

Anal. Calcd. for $C_{22}H_{30}O_5$ (374.46): C, 70.56; H, 8.08. Found: C, 70.25; H, 8.15.

B. Hydrolysis with formic acid. A solution of IX in 60% formic acid was heated on a steam bath for 1 hr., and after the usual work-up and crystallization from acetone–petroleum ether, a 72% yield of 11β-hydroxy-17α,21-methylenedioxy-4-pregnene-3,20-dione (X) was obtained.

Acknowledgment. We wish to thank Messrs. A. Pellicano and J. Poletto for excellent technical assistance and Dr. H. G. Arlt, Jr. for his kind cooperation during this investigation. Thanks are also due to E. Heyder, A. Monteforte, S. Mauer, and I. Ringler of the Experimental Therapeutics Research Section for the biological assays, to Mr. L. Brancone and staff for microanalyses and to Mr. W. Fulmor and staff for the spectral and polarimetric determinations.

ORGANIC CHEMICAL RESEARCH SECTION
LEDERLE LABORATORIES DIVISION
AMERICAN CYANAMID CO.
PEARL RIVER, N. Y.

---

[14] R. Hirschmann, G. A. Bailey, G. I. Poos, R. Walker, and J. M. Chemerda, *J. Am. Chem. Soc.*, **78**, 4814 (1956); J. E. Herz, J. Fried, P. Grabowich and E. F. Sabo, *J. Am. Chem. Soc.*, **78**, 4812 (1956).

4-Dibutylamino-2-methylpyrimidine-5-carboxaldehyde Semicarbazone

THEODORE D. PERRINE

Received March 9, 1961

The recent note by Wiley and Yamamoto[1] listing the various methods by which pyrimidine carboxaldehydes have been prepared prompts us to report on a further method with which we have had success, namely the reaction of hexamethylenetetramine on a 5-chloromethylpyrimidine.

EXPERIMENTAL

4-Dibutylamino-5-ethoxymethyl-2-methylpyrimidine. 4-Chloro-5-ethoxymethyl-2-methylpyrimidine[2] (110 g.) and 228 g. of dibutylamine were heated on the steam bath. An exothermic reaction ensued, the temperature of the reaction mixture rising to 145–150°. After 1 hr. the dibutylamine hydrochloride was removed by filtration, the filter cake was washed with ether, the combined filtrate and wash were concentrated, and the residue was distilled *in vacuo*. The product had b.p. 130° (0.23 mm.) and n_D^{24} 1.5022.

Anal. Calcd. for $C_{16}H_{29}N_3O$ (mol. wt. 279.41): C, 68.77; H, 10.46. Found: C, 68.32; H, 10.50.

The *picrate* had a m.p. of 87–88.5°, and is soluble in ether. The *chloroplatinate* crystallized with great difficulty.

5-Chloromethyl-4-dibutylamino-2-methylpyrimidine hydrochloride. A solution of 10 g. of the above dibutylaminopyrimidine in 50 ml. of glacial acetic acid was saturated with hydrogen chloride at 0°, and the solution heated in a sealed glass tube at 150–160° for 5 hr. The product,[3] a white waxy solid, was obtained by concentrating the solution. Yield, 13.8 g.

4-Dibutylamino-2-methyl-pyrimidin-5-carboxaldehyde semicarbazone. A 13.8-g. portion of the above material, which was soluble in water and alcohol, was recrystallized from glacial acetic acid, precipitated from ice cold aqueous solution with sodium bicarbonate, and the free base immediately extracted with ether. After drying the extract, the ether was removed and the residue dissolved in 140 ml. of 2-propanol. Water (3 ml.) and 4.8 g. of hexamethylenetetramine were added and the solution refluxed for 6 hr. After removal of the 2-propanol, the resultant product was ex-

---

[1] R. M. Wiley and Y. Yamamoto, *J. Org. Chem.*, **25**, 1906 (1960).

[2] A generous sample of this material was supplied by Merck and Co.

[3] This was reconverted to 4-dibutylamino-5-ethoxymethyl-2-methylpyrimidine with sodium ethoxide. The product had n_D^{24} 1.5032. The picrate had a m.p. of 87–89.5°, showing no depression on admixture with authentic material.

tracted with ether. No attempt was made to isolate the free aldehyde but it was at once converted to the *semicarbazone*, white crystals from ether; m.p. 155–156°. The yield was poor.

Anal. Calcd. for $C_{15}H_{26}N_6O$ (mol. wt. 306.41); C, 58.79; H, 8.55. Found: C, 58.98; H, 8.32.

NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MD.

A Convenient Method for the Preparation of Di-*n*-butylfluoroborane

E. J. DE WITT

Received March 10, 1961

Hennion, McCusker, and Rutkowski[1] have recently reported the preparation of diisobutylfluoroborane by treatment of the corresponding chloroborane with antimony trifluoride. Antimony trifluoride is known to replace the other halides for fluoride, but it is unusual for this reagent to replace an alkyl group for fluoride. Such a reaction was used to prepare di-*n*-butylfluoroborane in a very convenient one step process. Tri-*n*-butylborane was heated with antimony trifluoride. At about 135°, the di-*n*-butylfluoride began to distill, and an antimony mirror formed on the flask walls. The reaction was completed by heating to 180°. The lower boiling butyldifluoroborane might be expected to form, but none was detected.

Buls, Davis, and Thomas[2] have reported the di-*n*-butylfluoroborane to boil at −5°/100 mm. The material reported here had a much higher boiling point, 48°/20 mm. (d_4^{24} 0.783). Hennion *et al.* reported their isobutyl isomer to boil at 49°/52 mm. (d_4^{25} 0.7662). The higher boiling point (48°/20 mm.) would be expected since it lies between the monoalkyldifluoroborane (36.3°/742 mm.)[3] and the tri-*n*-butylborane (90°/9 mm.).[3]

EXPERIMENTAL

Di-n-butylfluoroborane. The reaction system consisted of all glass connections, and all operations were carried out under nitrogen. A flask was charged with 32 g. of antimony trifluoride and 50 g. of tri-*n*-butylborane. On heating to 135°, a volatile material began to distill and was collected in a cooled receiver. The temperature was gradually increased to 180°, and when distillation ceased, the heat was removed. The water-white product weighed 41.3 g. This material was distilled twice through a 1-ft. × $^1/_4$-in spiral wire packed column. The water-white mobile liquid weighed 25 g. and was flammable in air. The product distilled at 47°/20 mm. (d_4^{24} 0.783).

Anal. Calcd. for $C_8H_{18}BF$: F, 13.18. Found: F, 12.91, 13.09.

---

(1) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, 80, 617 (1958).

(2) V. W. Buls, O. L. Davis, and R. L. Thomas, *J. Am. Chem. Soc.*, 79, 337 (1957).

(3) M. F. Lappert, *Chem. Rev.*, 56, 1053, 1028 (1956).

Acknowledgment. The author wishes to thank Dr. L. Kreider for obtaining some of the physical data on this reaction; and the Goodrich analytical staff for the fluorine analysis.

THE B. F. GOODRICH RESEARCH CENTER
THE B. F. GOODRICH CO.
BRECKSVILLE, OHIO

Synthesis of Cyanotriphenylmethane from Hexaphenylethane

C. W. SCHIMELPFENIG

Received March 1, 1961

The postulation of the involvement of the cyanyl radical in the reaction of mercuric cyanide with disilicon hexachloride[1] has prompted a search for further examples in which a carbon-nitrogen pair might react as an uncharged unit. By the reaction of hexaphenylethane and mercuric cyanide, cyanotriphenylmethane has been formed in 15% yield.

Whether this reaction has involved the cyanyl radical or the cyanide ion is not certain. It is of interest to note earlier reactions between organic radical precursors and mercury salts other than mercuric cyanide[2] and to note reactions between hexaphenylethane and several inorganic salts.[3]

EXPERIMENTAL

A solution of 0.09 mole of hexaphenylethane in 250 ml. of benzene was prepared.[4] Silver chloride and excess silver were removed by filtration under nitrogen. A suspension composed of the benzene solution and 0.1 mole of mercuric cyanide was stirred magnetically for 10 days at room temperature beneath an atmosphere of nitrogen. The suspension was filtered. The filtrate was extracted with water. The washed benzene filtrate containing the crude product was evaporated to dryness. This residue was extracted with boiling ethanol. From the ethanol-soluble portion was isolated by fractional sublimation and fractional crystallization (ethanol solvent) 7.55 g. (0.028 mole) of cyanotriphenyl methane. This product was shown to be identical with an authentic sample prepared by the method of Fischer[5] by the identity of their infrared spectra and on the basis of a mixture melting point.

---

(1) A. Kaczmarczyk and G. Urry, *J. Am. Chem. Soc.*, 81, 4112 (1959).

(2) A. D. Ainley, L. A. Elson, and W. A. Sexton, *J. Chem. Soc.*, 776 (1946); Z. M. Manulkin, *Zhur. Obshcheĭ Khim.*, 16, 235 (1946); G. A. Razuvaev, Yu. A. Ol'dekop, and N. A. Maĭer, *Zhur. Obshcheĭ Khim.*, 25, 697 (1955); G. A. Razuvaev Yu. A. Ol'dekop, and N. A. Maĭer, *Doklady Akad. Nauk, S.S.S.R.*, 98, 613 (1954); Yu. A. Ol'dekop and N. A. Maĭer, *Doklady Akad. Nauk, S.S.S.R.*, 131, 1096 (1960); B. S. Wildi and J. S. Dunn, U. S. Patent 2,957,935 (Oct. 25, 1960).

(3) M. Gomberg and H. R. Gamrath, *Trans. Faraday Soc.*, 30, 24 (1934); H. D. Hetzner, Dissertation, University of Michigan, 1939.

(4) M. Gomberg, *J. Am. Chem. Soc.*, 22, 757 (1900).

(5) E. Fischer and O. Fischer, *Ann.*, 194, 242 (1878).