complexes of the amides with boron trifluoride. This is in agreement with the work of Bowlus and Nieuwland on acetamide.[3]

No method was devised for the purification of the complexes. The reaction products were very hygroscopic and were immediately decomposed by water. Tetrahydrofuran and ethanol reacted rapidly with the complexes, yielding precipitates of ammonium fluoborate.

The compounds did not possess sufficient thermal stability to allow high vacuum distillation or sublimation. The complex with formamide decomposed on warming in vacuum, with evolution of carbon monoxide and hydrogen cyanide, which gases were identified by their infrared spectra. Ammonium fluoborate was one of the solid reaction products, but since the solid reaction product was very soluble in water no boron nitride was considered to be formed.

Anal. Calcd. for NH_4BF_4: HBF_4, 83.44. Found: HBF_4, 83.89.

The complex of acetamide with boron trifluoride began to decompose in vacuum at about 90°, with liberation of a small amount of acetic acid. At 130–140° and 0.1 mm. a yellow viscous oil distilled over. Efforts to purify and characterize this oil were not successful. The boron present in the oil was in the form of a fluoborate salt.

(3) H. Bowlus and J. A. Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

DEPARTMENT OF CHEMISTRY
MALLINCKRODT LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

Some Amides of Piperazines

BY C. B. POLLARD AND BETTY SUE GRAY

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Since 1,4-bis-(benzenesulfonyl)-piperazine[1] exhibited marked activity in inhibiting growth of tubercle bacillus in serum, twelve new amides of piperazines were synthesized for testing against this organism. These compounds were prepared by modifications of the method of Pollard and Adelson.[2] Anhydrous piperazines were used; anhydrous sodium carbonate was added; and propanol-2 or benzene was employed as a reaction solvent instead of ether. Data concerning these compounds are given in Table I.

TABLE I

DATA CONCERNING SOME AMIDES OF PIPERAZINES

Compound, piperazine	Crystallized from	Yield, % purified product	M.p., °C. (cor.)	Nitrogen, % Calcd.	Found
1-(*p*-Chlorobenzoyl)-4-phenyl	Methanol	29.2	119–121	9.32	9.24
1-(*o*-Chlorobenzoyl)-4-phenyl	Methanol	22.5	109–111	9.32	9.17
1-(*m*-Nitrobenzenesulfonyl)-4-phenyl	Formamide	43.2	153–154	12.10	12.29
1-(*p*-Bromobenzenesulfonyl)-4-phenyl	Methanol	38.6	180–182	7.35	7.35
1,4-Bis-(*p*-chlorobenzoyl)	Propanol-2	36.0	238.8–239.8	7.71	7.75
1,4-Bis-(*p*-toluenesulfonyl)	Boiling dioxane	42.0	295.3–296.3	7.11	7.09
1,4-Bis-(*o*-chlorobenzoyl)	Methanol	22.9	214–215.5	7.71	7.71
1,4-Bis-(*m*-nitrobenzenesulfonyl)	Formamide	34.4	262–264	12.28	12.14
1,4-Bis-(*p*-chlorobenzoyl)-2,5-dimethyl	Chlorobenzene	38.2	288–289	7.16	6.93
1,4-Bis-(*o*-chlorobenzoyl)-2,5-dimethyl	Formamide	48.2	296–298	7.16	7.15
1,4-Bis-(*m*-nitrobenzenesulfonyl)-2,5-dimethyl	Formamide	48.5	249–250	11.57	11.25
1,4-Bis-(*p*-bromobenzenesulfonyl)-2,5-dimethyl	Formamide	51.5	262–263	5.07	5.21

These new amides were ineffective against tubercle bacillus.

The authors express their sincere appreciation for the *in vitro* tuberculostatic testing of these compounds. The tests were performed in the laboratory of Dr. Guy P. Youmans, Department of Bacteriology, Northwestern University Medical School, and made available by arrangement with Parke, Davis and Company.

(1) M. E. Smith and C. B. Pollard, THIS JOURNAL, **63**, 630 (1941).
(2) C. B. Pollard and D. E. Adelson, *ibid.*, **56**, 150 (1934).

ORGANIC CHEMISTRY LABORATORIES
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

Homologs of Some Steroid Hormones

BY AUGUST I. RYER, WILLIAM H. GEBERT AND NATHANIEL M. MURRILL

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In connection with other work in progress in these laboratories, some homologs of testosterone and one homolog of ethinyltestosterone were prepared. These new steroids in which the hydroxyl is at C_{25} instead of C_{17} possess no androgenic activity. These compounds were synthesized from 25-ketonorcholesteryl acetate (I), a by-product of the oxidation of cholesteryl acetate dibromide.[1]

25-Hydroxy-Δ^4-norcholestene-3-one (IX) was obtained using a procedure similar to that described for the synthesis of testosterone.[2] 25-Ketonorcholesteryl acetate (I) was reduced to the diol monoacetate (II); this was then benzoylated and the resulting 3-acetate-25-benzoate partially hydrolyzed to give 25-benzoxynorcholesterol (V). Oxidation by a modification of the method of Oppenauer[3] followed by hydrolysis produced the ketone (IX).

25-Ethinyl-Δ^4-norcholestene-25-ol-3-one (X) was prepared by the ethynation of I with potassium acetylide to give the 25-ethinyl derivative (VI) followed by Oppenauer oxidation. The reaction of ethylmagnesium iodide with I yielded 26-methyl-25-hydroxycholesterol (VII). Both VII and 25-hydroxycholesterol[4] were oxidized to XI and XII, respectively. A derivative of IX, 25-chloro-Δ^4-norcholestene-3-one (XV), was also prepared in which the hydroxyl at C_{25} was replaced with chlorine.

(1) L. Ruzicka and W. H. Fischer, *Helv. Chim. Acta*, **20**, 1291 (1937).
(2) L. Ruzicka, A. Wettstein and H. Kägi, *ibid.*, **18**, 1478 (1935).
(3) R. V. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).
(4) A. I. Ryer, W. H. Gebert and N. M. Murrill, THIS JOURNAL, **72**, 4247 (1950).