Anal. Calcd. for $C_{23}H_{34}O_2$: C, 80.65; H, 10.01. Found: C, 80.82; H, 10.22.

This material gave an acetate which was obtained from acetone–hexane as crystals, m.p. 184–186°; $[\alpha]D -72°$; λ_{max} 232, 239, and 247 mμ (ε 24,800, 27,200, 17,400); λ_{max} 5.75, 5.88, 6.08, 8.10, and 9.91 μ.

6-Chloro-3β-hydroxy-17-ethylpregna-4,6-dien-20-one (VIII) was recrystallized from acetone-hexane to give crystals, m.p. 192–193°; $[\alpha]D -60°$; λ_{max} 237, 244, and 252 mμ (ε 18,600, 21,700, 14,500); λ_{max} 2.89, 5.93, 6.23, and 9.72 μ.

Anal. Calcd. for $C_{23}H_{33}ClO_2$: C, 73.27; H, 8.82; Cl, 9.41. Found: C, 73.09; H, 8.80; Cl, 9.85.

17-Ethylpregna-3,5-dien-20-one (V).—A solution of crude 17-ethyl-3β-hydroxypregn-4-en-20-one (derived from 500 mg. of 17-ethylprogesterone) in 100 ml. of 50% acetic acid was heated at reflux temperature for 45 min. After 10 min. a solid was deposited from the solution. The chilled mixture was filtered to give 360 mg. of white crystals, m.p. 155–158°. This solid was dissolved in benzene and chromatographed on silica gel. The material eluted by benzene was recrystallized from methanol to give 222 mg. (47%) of white needles, m.p. 160–162°; $[\alpha]D -150°$; λ_{max} 228, 234, and 243 mμ (ε 20,200, 21,600, 13,700); λ_{max} 5.91 and 6.05 μ.

Anal. Calcd. for $C_{23}H_{34}O$: C, 84.60; H, 10.50. Found: C, 84.37; H, 10.64.

Acknowledgment.—We thank Mr. W. Fulmor and his associates for the spectral and polarimetric data, Mr. L. Brancone and staff for the microanalyses, Dr. J. L. Fedrick and Mr. R. B. Conrow for a generous supply of 17-ethylprogesterone, and Dr. I. Ringler for assistance in obtaining the biological assays.

New Compounds

Derivatives of 2-Hydroxy-1,3,2-benzodioxastibole[1a]

L. CORTÉS,[1b] J. MANTECÓN,[1b] AND G. CHUCHANI

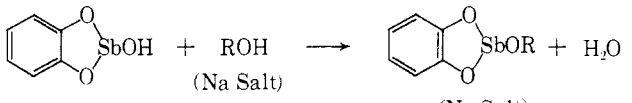
Department of Chemistry, Instituto Venezolano de Investigaciones Científicas (IVIC), Caracas, Venezuela

Received March 2, 1964

A number of derivatives of 2-hydroxy-1,3,2-benzodioxastibole (I) were synthesized as compounds of potential interest in the chemotherapy of several parasitical diseases. Several phenolic compounds containing $-COOH$ and $-SO_3H$ groups were treated with I[2,3] in basic medium to produce the corresponding condensation products. These were isolated as the sodium salts.

TABLE I

1,3,2-BENZODIOXASTIBOLE DERIVATIVES OBTAINED ACCORDING TO THE REACTION



ROH	%	Formula products[a]	% Sb Found	% Sb Calcd.
5-Chlorosalicylic acid	43	$C_{13}H_7ClNaOSb$	28.8	28.8
5-Bromosalicylic acid	39	$C_{13}H_7BrNaO_5Sb$	26.1	26.0
5-Aminosalicylic acid	39	$C_{13}H_9NNaO_5Sb$	30.2	30.1
5-Sulfosalicylic acid	26	$C_{13}H_7Na_2O_8SSb$	25.0	24.8
3-Phenylsalicylic acid	46	$C_{19}H_{12}NaO_5Sb$	26.3	26.2
3-Methylsalicylic acid	37	$C_{14}H_{10}NaO_5Sb$	30.4	30.2
6-Amino-1-naphthol-8-sulfonic acid	40	$C_{16}H_{11}NNaO_6SSb$	24.9	24.8
5-Amino-4-hydroxybenzenesulfonic acid	45	$C_{12}H_9NNaO_6SSb$	27.8	27.7
7-Amino-1-naphthol-3-sulfonic acid	36	$C_{16}H_{11}NNaO_6SSb$	24.9	24.8
8-Amino-1-naphthol-3,6-disulfonic acid	33	$C_{16}H_{10}NNa_2O_9S_2Sb$	20.5	20.6

[a] None of the compounds melts or decomposes below 300°. On acidification with hydrochloric acid, these compounds are rapidly hydrolyzed.

Experimental

2-Hydroxy-1,3,2-benzodioxastibole (I) was prepared as described by Brown and Austin.[3] The derivatives of I were prepared as described,[3] but with the following modification. After the reaction period the solid by-product (hydrated antimony oxide) was filtered and the filtrate neutralized to precipitate the unchanged I. The solution was then concentrated to incipient crystallization and the product washed with small amounts of cold ethanol.

Alternate Method of Condensation.—2-Hydroxy-1,3,2-benzodioxastibole (I) (0.03 mole) in 0.4 *N* sodium hydroxide solution was added to salicylic acid (0.035 mole) in 2 *N* sodium carbonate solution (18 ml.). The mixture was heated for 2 hr. at 70–75° and neutralized after cooling. The precipitated, unchanged I was removed by filtration and the filtrate concentrated until precipitation started. The solid, 2-(*o*-carboxyphenyloxy)-1,3,2-benzodioxastibole, was unchanged at 300°; yield, 70%.

Anal. Calcd. for $C_{13}H_8NaO_5Sb$: Sb, 31.3. Found: Sb, 31.5.

(1) (a) A portion of this paper was presented before the XI Annual Convention of the Venezuelan Association for the Advancement of Science, Caracas, April, 1961. (b) From theses submitted by L. C. and J. M. in partial fulfillment of the requirements for the degree of Licenciado de Química, Universidad Central de Venezuela, June, 1961.

(2) H. Causse, *Bull. soc. chim. France*, 245 (1892).

(3) H. P. Brown and J. Austin, *J. Am. Chem. Soc.*, **63**, 2054 (1941).

Methyl Analogs of Papaverine[1a]

JAMES G. BEASLEY AND ALFRED BURGER

Department of Chemistry, University of Virginia, Charlottesville, Virginia

January 15, 1964

Papaverine and papaveraldine analogs which do not contain ether groups in positions 6 and 7 have not been studied widely. Analogs containing methyl instead of methoxyl groups could contribute to such questions as to the significance of methoxy *vs.* methyl groups,[2] or whether the intramolecular distance between the ether oxygens and the isoquinoline nitrogen[3] has a bearing on the pharmacological activity. Several analogs with methyl groups are described.

(1) Supported by a grant, NB-01445, from the Institute for Neurological Diseases and Blindness, National Institutes of Health, U. S. Public Health Service.

(2) H. L. Friedman, *Symp. Chem.-Biol. Correlation, Natl. Acad. Sci.-Natl. Research Council*, Washington, D. C., 1951, Publ. No. 206, p. 295.

(3) C. C. Pfeiffer, *Science*, **107**, 94 (1948).