did not depress the m.p. of authentic 2-butanone *p*-nitrophenylhydrazone. *p*-Nitrophenylhydrazones were not obtained from fractions B or C. Semicarbazones were not obtained from any of the fractions.

Acknowledgment.—The authors wish to express their appreciation to the American Gilsonite Co., Salt Lake City, Utah, for a research grant that made this investigation possible.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH

17β-Methyl-Δ⁵-androstene-3β-ol

BY RICHARD T. RAPALA AND EUGENE FARKAS

RECEIVED AUGUST 31, 1955

A report by Ghosh[1] on the isolation of a $C_{20}H_{32}O$ compound, called serposterol from a Rauwolfia serpentina plant, suggested the tentative structure as methylandrostenol. We have prepared the postulated compound, 17β-methyl-Δ⁵-androstene-3β-ol, previously unknown, and found that it is not identical with the natural material.[2]

The mixture of 17-methylene-3β-acetoxy-$\Delta^{5,6;17,20}$-androstadiene and 17-methyl-3β-acetoxy-$\Delta^{5,6;16,17}$-androstadiene, resulting from dehydration of 3β-acetoxy-17α-methyl-$\Delta^{5,6}$-androstene-17β-ol, was selectively reduced with palladium-on-charcoal catalyst to give a single compound. Hydrolysis gave the compound proposed as serposterol. Comparison of the X-ray pattern and a mixed melting point determination showed that the two compounds were different. Comparison of the infrared spectra however showed great similarities but the curves were not superimposable.

That the hydrogenation gave the 17β-methyl compound was shown by the work of Heusser[3] in the hydrogenation of the same 17-methylene-3β-acetoxy-$\Delta^{5,6;17,20}$-androstadiene with platinum catalyst to give, after mild hydrolysis, the known 17β-methylandrostane-3-ol. Furthermore, Hershberg[4] obtained a 17β-ethyl compound by the reduction of $\Delta^{5,16}$-pregnadien-20-yne-3β-ol with palladium-on-charcoal as in the present series.

Experimental

3β-Acetoxy-17α-methyl-Δ⁵-androstene-17β-ol.—The acetate was prepared from 2.0 g. of 17α-methyl-Δ⁵-androstene-3β-17β-diol in 12 cc. of anhydrous pyridine and 6 cc. of acetic anhydride. After 6 hours the mixture was poured into ice, and the product filtered. Recrystallization from ethyl acetate yielded 1.15 g. of colorless needles, m.p. 164–165° (first crop), and 0.750 g., m.p. 162–164° (second crop); lit.[5] reports m.p. 160–161°.

A Mixture of 3β-Acetoxy-17-methyl-$\Delta^{5,6;16,17}$-androstadiene and 3β-Acetoxy-17-methylene-$\Delta^{5,6;17,20}$-androstadiene.—The acetate was dehydrated by the procedure of Julia and Heusser[3] using phosphorus oxychloride–pyridine. From 1.9 g. of acetate there was obtained 0.8 g. of product, m.p. 116–118°. This was found to be a mixture of dienes which could be used directly in the hydrogenation without separation.

3β-Acetoxy-17β-methyl-Δ⁵-androstene.—The reduction of the mixture of dienes (800 mg.) in absolute ethanol was carried out using 400 mg. of prereduced 5% palladium-on-charcoal catalyst in an atmosphere of hydrogen. One mole of hydrogen was absorbed in 20 minutes. Recrystallization of the product from methanol, after removal of catalyst and solvent, gave 250 mg. of fine needles, m.p. 129–131°, $[\alpha]^{26}D$ −64°.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.71; H, 10.21.

17β-Methyl-Δ⁵-androstene-3β-ol.—To a solution of 500 mg. of potassium carbonate in 10 cc. of water, 10 cc. of dioxane and 100 cc. of methanol was added 250 mg. of the acetoxyandrostene. The solution was refluxed for one hour, then evaporated to dryness and water added. The solid was collected and recrystallized from methanol to give 0.190 g. of colorless rods, m.p. 163–165°. The analytical sample was recrystallized two additional times from methanol, m.p. 164–165°, $[\alpha]^{26}D$ −65.7°; $\lambda_{max}^{CHCl_3}$ 2.84, 3.40, 6.85, 7.27, 9.56.

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.09; H, 11.30.

Upon admixture with authentic serposterol (m.p. 151–153°) there was a depression in melting point to 124–131°. In addition, X-ray pattern and infrared spectra were not identical.

LILLY RESEARCH LABORATORIES
ELI LILLY AND COMPANY
INDIANAPOLIS, INDIANA

(1) G. B. Ghosh and R. K. Basu, *Naturwiss.*, **42**, 130 (1955).
(2) We are indebted to Dr. B. P. Ghosh for an authentic sample of serposterol.
(3) S. A. Julia and H. Heusser, *Helv. Chim. Acta*, **35**, 2080 (1952).
(4) E. B. Hershberg, E. P. Oliveto, C. Gerold and L. Johnson, THIS JOURNAL, **73**, 5073 (1951).
(5) K. Miescher and W. Klarer, *Helv. Chim. Acta*, **22**, 962 (1939).

Derivatives of Piperazine. XXVIII. Synthesis of 1-Aryl-4-thioaryloylpiperazines and 1-Aryl-4-thioalkanoylpiperazines by the Kindler Modification of the Willgerodt Reaction

BY C. B. POLLARD AND JOHN C. BRAUN

RECEIVED AUGUST 8, 1955

The Kindler modification of the Willgerodt reaction has been found to be applicable to both ketones[1,2] and aldehydes of the aromatic series[3,4] and the aliphatic series.[5,6]

Heterocyclic amines such as morpholine[7] and piperazine[8] were found to be especially suitable, since their use permitted reactions to be run in vessels which were open to the atmosphere.

The authors have found that N-phenylpiperazine and N-phenylpiperazines which have substituents on the benzene ring also undergo the reaction when refluxed with an aldehyde or ketone and sulfur in pyridine solution.

Purification of the products was rather difficult, and considerable differences in procedure were required, depending on whether the aldehyde or ketone was aliphatic or aromatic. Thioamides derived from the latter are moderately to slightly soluble in ethanol, while those derived from the former are generally very soluble.

Experimental

The N-phenylpiperazines were prepared by the methods of Pollard and Wicker[9] and Pollard and MacDowell.[10] The

(1) K. Kindler, *Arch. Pharm.*, **265**, 389 (1927).
(2) K. Kindler and T. Li, *Ber.*, **74**, 321 (1941).
(3) K. Kindler, German Patent 385,376 (Nov. 23, 1923).
(4) K. Kindler, *Ann. Chem., Justus Liebigs*, **431**, 193, 222 (1923).
(5) L. Cavalieri, D. B. Pattison and M. Carmack, THIS JOURNAL, **67**, 1783 (1945).
(6) E. Cerwonka, R. C. Anderson and E. V. Brown, *ibid.*, **75**, 28 (1953).
(7) E. Schwenk and E. Bloch, *ibid.*, **64**, 3051 (1942).
(8) P. Chabrier and S. T. Renard, *Compt. rend.*, **228**, 850 (1949).
(9) C. B. Pollard and T. H. Wicker, Jr., THIS JOURNAL, **76**, 1853 (1954).
(10) C. B. Pollard and L. G. MacDowell, *ibid.*, **57**, 2363 (1935).