

chloride at 80° for several hours yielded the corresponding hydroxy compound, m. p. 141.5–142.5°.

*Anal.* Calcd. for  $C_{19}H_{28}O_2$ : C, 79.2; H, 9.68. Found: C, 79.7; H, 9.89.

This hydroxy ketone was further characterized by the orange colored 2,4-dinitrophenylhydrazone, m. p. 230–232°, which it formed.

*Anal.* Calcd. for  $C_{26}H_{32}N_4O_5$ : C, 64.0; H, 6.89. Found: C, 63.2; H, 6.99.

**Androstenedione.**—To a solution of 2.5 g. of  $\Delta^{4,6}$ -androsthenol-17 in 200 cc. of acetic acid was added at 35–45° and with stirring a solution of 3 g. of chromic acid in 50 cc. of 90% acetic acid. The addition required one-half hour and the solution was then kept at 45° for one-half hour. The solution was poured into water and the product was extracted with ether. The ether solution was

washed well with sodium carbonate solution and water and concentrated to a small volume. On cooling this solution for some time crystals formed and were filtered. They were recrystallized from ether to yield androstenedione, m. p. 168–170°, identical with the known product.

### Summary

Cholestene dibromide was oxidized to  $\Delta^{5,6}$ -androsthenone-17 which was converted to desoxotestosterone acetate and  $\Delta^{4,5}$ -androsthenone-17. These new compounds on oxidation were converted to testosterone acetate and androstenedione. An isomeric 7-keto- $\Delta^{5,6}$ -androsthenol-17 was also obtained.

STATE COLLEGE, PENNA.  
DETROIT, MICH.

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## NOTES

### An Attempted Synthesis of Morphenol

BY ALFRED BURGER AND S. AVAKIAN

A recent announcement by Gilman and Cheney<sup>1</sup> that these authors are studying the closure of a six-membered ring between positions 1 and 9 in dibenzofuran types prompts us to report unsuccessful attempts to synthesize methylmorphenol through 6-methoxy-9-hydroxy-phenanthrylene oxide and subsequent selective reduction of the 9-hydroxy group. 4-Methoxy-dibenzofuran-1-acetic acid was treated with (a) concentrated sulfuric acid, (b) 85% sulfuric acid, (c) anhydrous hydrogen fluoride at room temperature,<sup>2</sup> and (d) stannic chloride in the cold, and at the boiling point of the condensing agent. The acid chloride was treated with aluminum chloride in ice-cold benzene (e), and the acid bromide with aluminum chloride in nitrobenzene solution at room temperature (f), and with boiling stannic chloride (g), but none of these reactions yielded phenanthrene derivatives. It is possible that Gilman and his co-workers will achieve ring closure by using compounds containing strongly *para*-orienting groups in position 6 of the dibenzofuran system.<sup>1</sup>

Since the distance between sulfur and carbon atoms is greater than that between oxygen and carbon atoms, the positions 1 and 9 in dibenzothio-

phene should be closer to each other than in dibenzofuran, and ring closure should be easier in the dibenzothiophene series. In investigating the effect of substituting sulfur atoms for —CH=CH— groups in polycyclic aromatic systems we are now studying the intramolecular dehydration and decarboxylation of 1-carboxy-dibenzothiophene-9-acetic acid, which should lead to derivatives of 4,5-phenanthrylene sulfide, a possible isomer of pyrene.

### Experimental

4-Methoxydibenzofuran-1-carboxylic acid<sup>3</sup> was converted into the chloride by the action of thionyl chloride. The acid chloride crystallized from benzene-ligroin as colorless needles, m. p. 162.5–163.5°. The yield was 93%.

*Anal.* Calcd. for  $C_{14}H_9ClO_3$ : C, 64.48; H, 3.48. Found: C, 64.22; H, 3.62.

The acid chloride was stirred with an ethereal solution of diazomethane for sixteen hours. The diazo ketone crystallized out. Recrystallization from benzene-petroleum ether rendered yellow crystals, m. p. 150–151° (dec.). The yield was 86%.

*Anal.* Calcd. for  $C_{16}H_{11}N_2O_3$ : C, 67.39; H, 4.15. Found: C, 67.50; H, 4.00.

The diazo ketone was treated with ammonium hydroxide in dioxane solution according to Arndt and Eistert.<sup>3,4</sup> 4-Methoxydibenzofuran-1-acetamide crystallized from ethanol as colorless needles, m. p. 203°. The yield was 75%.

*Anal.* Calcd. for  $C_{15}H_{13}NO_3$ : C, 70.56; H, 5.14. Found: C, 70.93; H, 5.34.

(1) Gilman and Cheney, *THIS JOURNAL*, **61**, 3149 (1939).

(2) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939).

(3) Gilman, Parker, Baillie and Brown, *ibid.*, **61**, 2836 (1939).

(4) Arndt and Eistert, *Ber.*, **68**, 200 (1935).

The acid amide was boiled under reflux with thirty parts of a 20% alcoholic solution of potassium hydroxide for three hours. The alcohol was replaced by water and evaporated, and the 4-methoxydibenzofuran-1-acetic acid was precipitated from the filtered solution. It was recrystallized from ethanol and appeared as colorless needles, m. p. 223–224°. The yield was 90%.

*Anal.* Calcd. for  $C_{15}H_{12}O_4$ : C, 70.28; H, 4.73. Found: C, 70.31; H, 4.43.

UNIVERSITY, VIRGINIA RECEIVED NOVEMBER 21, 1939

### The Preparation of Acetyl Bromide\*

BY THEODORE M. BURTON WITH ED. F. DEGERING

Acetyl bromide was prepared as early as 1863 by distilling it as formed from a mixture of glacial acetic acid, bromine and phosphorus.<sup>1</sup>

Investigations have shown, however, that acetyl bromide undergoes substitution with bromine to form bromo-acetyl bromides with decrease in the yield of acetyl bromide. Further improvements designed to increase the yield of acetyl bromide have also resulted in increased bromination in the nucleus.<sup>2</sup>

By the elimination of free bromine it was thought possible to increase the yield of acetyl bromide according to the reaction



Phosphorus tribromide (b. p. 169–170° at 740 mm.) can be prepared readily in 99.5% yield by slowly adding dried bromine from a dropping funnel into a slight excess of freshly washed and dried red phosphorus placed in a round-bottomed flask equipped with a mechanical stirrer and a reflux condenser.

The acetyl bromide was prepared by adding slowly through the dropping funnel, with stirring, a slight excess of 99.5% glacial acetic acid (3.075 moles of  $CH_3COOH$  per mole of phosphorus tribromide) to the cold phosphorus tribromide. The mixture separated into two layers which were distilled separately into a common receiver packed in ice. The crude acetyl bromide was rectified in a modified Podbielniak column to produce a water-white fraction boiling from 73–76° at 740 mm. The yield varied from 71.4 to 73.4% of the theoretical.

\*Presented before the Indiana Academy of Science at Terre Haute, Indiana, November, 1939.

(1) H. Gal, *Ann.*, **129**, 53 (1863); M. Hanriot, *Ann. chim. phys.*, [5] **17**, 83 (1879).

(2) H. Gal, *Compt. rend.*, **56**, 1258 (1863); F. Urech, *Ber.*, **13**, 1687 (1880); J. Volhard, *Ann.*, **242**, 144 (1887); C. Hell, *Ber.*, **21**, 1726 (1888); C. F. Ward, *J. Chem. Soc.*, **123**, 2207–2213 (1923); H. B. Watson, *ibid.*, **127**, 2067–2082 (1925); Bernard Gwynn and Ed. F. Degering, *Proc. Indiana Acad. Sci.*, **87** (1939).

In other experiments the phosphorus tribromide was purified before use, but yields were increased only by a slight amount to 74.9% of the theoretical. In an effort to test the effect of temperature, the acetyl bromide was distilled from the reaction mixture at room temperature under reduced pressure. The product was collected in a gas bottle immersed in a bath cooled with solid carbon dioxide. No change, however, was observed in the yield. In all cases large amounts of hydrogen bromide were liberated so that the reaction probably does not proceed as indicated in the above equation.

It was found possible to prepare acetyl bromide without the formation of hydrogen bromide by adding phosphorus tribromide slowly, with stirring, to an excess of boiling acetic anhydride. The boiling point dropped as acetyl bromide was formed and when the addition of phosphorus tribromide was completed, the acetyl bromide was distilled from the mixture and rectified as before. The yield was 81.7% of the theoretical.

By using the readily prepared phosphorus tribromide, instead of free bromine with glacial acetic acid, substitution reactions are avoided and the yield of acetyl bromide can be increased to about 80% of the theoretical.

CHEMICAL LABORATORY  
PURDUE UNIVERSITY

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### Hydrogen Bonds Involving the C–H Link. IX.<sup>1</sup> Nitriles and Dinitriles as Solvents for Hydrogen Containing Halogenated Methanes

BY M. J. COPLEY, G. F. ZELHOFER AND C. S. MARVEL

Nitriles should be capable of bonding with hydrogen in halogenated methanes of the  $CH_2X_2$  and  $CHX_3$  types and hence should be good solvents for these products. Work reported earlier<sup>1</sup> shows that valeronitrile and benzonitrile do dissolve methylene chloride and monochlorodifluoromethane in excess of the amount calculated from Raoult's law. It is interesting to find that the aliphatic dinitriles, succinonitrile and glutaronitrile, dissolve less than the calculated amounts of these two halogenated methanes. Adiponitrile dissolves almost the exact calculated amount and sebaconitrile takes up more than the calculated amount. These results are interesting when considered with the boiling points of the dinitriles.

(1) For the eighth communication in this series see THIS JOURNAL, **61**, 3550 (1939).