methanol. On standing overnight in the ice-box, there was obtained 54.5 g. of crystalline material. The mother liquors gave an additional 1.5 g. on dilution with methanol. Recrystallization from benzene–methanol gave 35 g. (30%) of long needles, m.p. 140–155°. An analytical sample had m.p. 155° (bubbly melt) with sintering at 150°, $[\alpha]_D$ +92° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{30}H_{46}O_5S_3$: C, 61.82; H, 7.96. Found: C, 61.64; H, 7.95.

Methyl Dehydrocholate Trihemithioethylene Ketal (III).—The above acid (33.5 g.) in 400 ml. of ether was treated with an excess of ethereal diazomethane. The crude product after drying and distillation of the ether weighed 34 g. (99%), m.p. 173–178°. Crystallization from methanol gave small feathery needles, m.p. 183° with sintering at 177°, $[\alpha]_D$ +90° (dioxane). The analytical sample was dried under vacuum at 100° for one hour.

Anal. Calcd. for $C_{31}H_{48}O_5S_3$: C, 62.38; H, 8.11. Found: C, 62.30; H, 7.86.

24-Hydroxycholane-3,7,12-trione Trihemithioethylene Ketal (IV).—The above ester (31 g.) in one liter of dry ether was added dropwise with stirring to a suspension of 3.8 g. of lithium aluminum hydride in 400 ml. of dry ether. The mixture was heated at the reflux temperature for two hours and allowed to stand overnight. The reaction mixture was worked up with dilute sulfuric acid in the usual manner. The crude product (29 g., 98%) had m.p. 222–228° and two recrystallizations from benzene–methanol gave needles with m.p. 233–235°, $[\alpha]_D$ +95° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{30}H_{48}O_4S_3$: C, 63.34; H, 8.51. Found: C, 62.95; H, 8.57.

Hydrolysis of 24-Hydroxycholane-3,7,12-trione Trihemithioethylene Ketal. A.—The above alcohol (2.0 g.) was dissolved in 150 ml. of dry methanol containing 3 ml. of acetyl chloride and the solution heated under reflux for five hours. The methanol was distilled, the residue taken up in ether, washed with sodium bicarbonate, the ether distilled and the residue chromatographed on silica. Elution with 15% ethyl acetate–benzene gave 0.74 g. (41%) of 24-hydroxycholane-3,7,12-trione 7,12-dihemithioethylene ketal (V). The product, thick needles after two crystallizations from benzene–cyclohexane, had m.p. 212.6–214.2°, $[\alpha]_D$ +43° (dioxane). The analytical sample was dried under vacuum at 118° for 5 hours.

Anal. Calcd. for $C_{28}H_{44}O_4S_2$: C, 66.10; H, 8.72. Found: C, 66.15; H, 8.77.

B.—Compound IV (7.0 g.) was dissolved in 315 ml. of dioxane containing 35 ml. of water and 8 ml. of concentrated sulfuric acid. The solution was heated under reflux for 22 hours, neutralized with solid sodium bicarbonate, and filtered. The filtrate was concentrated under reduced pressure and the residue taken up in methanol. On standing, 0.5 g. of material crystallized, m.p. 192–206°. The mother liquor was distilled to dryness, taken up in 15 ml. of benzene and diluted with 75 ml. of ether to give 1.7 g., m.p. 202–207°. The mother liquor was diluted with ether and gave 0.4 g., m.p. *ca.* 178° with previous sintering. Evaporation of the mother liquor to dryness and trituration with ether gave 1.5 g., m.p. *ca.* 170°.

Crops 3 and 4 (1.9 g.) were combined and crystallized twice from methanol, yielding 0.55 g. of 24-hydroxycholane-3,7,12-trione 12-hemithioethylene ketal (VI), m.p. 182–183°, $[\alpha]_D$ +57.5° (dioxane).

Anal. Calcd. for $C_{26}H_{40}O_4S$: C, 69.31; H, 8.99; S, 7.15. Found: C, 69.33; H, 8.93; S, 7.13.

Crops 1 and 2 (2.2 g.) were crystallized from methanol and gave 1.3 g. of 24-hydroxycholane-3,7,12-trione (VII), m.p. 212–213°, $[\alpha]_D$ +28° (dioxane).

Anal. Calcd. for $C_{24}H_{36}O_4 \cdot {}^1/_2CH_3OH$: C, 72.74; H, 9.47. Found: C, 72.47; H, 9.12; S, 0.0.

The triketone alcohol (0.5 g.) was acetylated with pyridine and acetic anhydride. The product was recrystallized from benzene–petroleum ether (b.p. 60–70°) and gave 24-acetoxycholane-3,7,12-trione (VIII), m.p. 203–204°, $[\alpha]_D$ +26° (dioxane). The analytical sample was dried under vacuum at 56°.

Anal. Calcd. for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90. Found: C, 72.37; H, 8.95.

C.—Trihemithioethylene ketal alcohol (2.0 g.) was dissolved in 50 ml. of glacial acetic acid. One ml. of concentrated hydrochloric acid was added and the solution heated under reflux for 22 hours. The acid was distilled under reduced pressure and the residue triturated with ether which gave 0.9 g. (59%) of 24-acetoxycholane-3,7,12-trione, m.p. 191–200°. Crystallization from benzene–petroleum ether (b.p. 60–70°) yielded 0.7 g. of needles, m.p. 202°, which did not depress the melting point of authentic cholanetrione acetate (m.p. 202–203°).

The acetate (0.207 g.) was dissolved in 8 ml. of 4% potassium hydroxide in methanol, the solution concentrated to 5 ml. and allowed to stand, giving in two crops 0.139 g. (74%) of long colorless needles. The analytical sample was crystallized from 80% methanol, had m.p. 212.2–212.8°, and was dried under vacuum at 118° for 5 hours. The infrared spectrum was identical with that of the triketone alcohol (m.p. 212–213°) obtained previously.

DIVISION OF CHEMICAL RESEARCH
G. D. SEARLE AND CO.
CHICAGO 80, ILLINOIS

Heterocyclic Derivatives of Arsenic: Some Corrected Statements

BY F. G. MANN

RECEIVED NOVEMBER 28, 1955

It has been stated by Weston[1] that Chatt and Mann[2] have resolved 5,10-di-*p*-tolyl-5,10-dihydroarsanthrene into optically active forms. A statement to the same effect is made by Costain and Sutherland.[3] Actually Chatt and Mann separated this compound into two geometric isomers. Each isomer possesses a plane of symmetry and therefore no question of optical resolution arises.

Garascia and Mattei[4] have stated that Cookson and Mann[5] have "prepared several 9-substituted arsafluorenes." Our compounds were, however, 10-substituted 9,10-dihydroarsanthridines, the central ring system being six-membered and not five-membered. Garascia and Mattei's further statement that we record 9-arsafluorinic acid, m.p. 299°, is therefore also incorrect, for no arsafluorene compounds are described in our paper.

---

[1] R. E. Weston, THIS JOURNAL, **76**, 2645 (1954).

[2] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1184 (1940).

[3] C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

[4] R. J. Garascia and I. V. Mattei, THIS JOURNAL, **75**, 4589 (1953).

[5] G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2888 (1949).

UNIVERSITY CHEMICAL LABORATORY
CAMBRIDGE, ENGLAND

Condensation of Chloral Hydrate with 8-Quinolinol

BY KONOMU MATSUMURA AND MOTOKO ITO

RECEIVED JULY 26 1955

Chloral hydrate reacts with 8-quinolinol to form predominantly 5-(α-hydroxy-β-trichloroethyl)-8-quinolinol (I). On alkaline hydrolysis with methanolic potassium hydroxide I yielded 5-carboxy- and 5-formyl-8-quinolinol (IV) and a compound which is soluble in sodium bisulfite. Hydrolysis with sodium methoxide in methanol gave IV and a compound V which is insoluble in sodium bisulfite and which gives some indication of possessing the carboxy and methoxy groups. Thus, I on alkaline hydrolysis appears to undergo only partial hydrolysis to V; the remainder of V undergoes