heated with phenylhydrazine alone; but when heated with phenylhydrazine in benzene solution, a phenylhydrazine salt is formed with each carboxyl group. A few acids, including crotonic, salicylic, and halogen substituted benzoic acids, fail to react, while many halogen substituted aliphatic acids, such as α-bromopropionic, α-bromo-*n*-caproic, β-bromopropionic, bromoacetic, and β-bromoisobutyric acids, merely split off hydrogen halide to yield a precipitate of the corresponding phenylhydrazine hydrohalide.

In Table I are listed the melting points and elementary analyses of the derivatives with phenylhydrazine not previously reported. The melting points which we have found for the derivatives which have been previously reported, together with the melting points as given in Beilstein[3] (these enclosed in parentheses) are as follows: formic, 143° (145°); acetic 129° (129°); propionic 157° (157°); isobutyric 140° (140°); *n*-butyric 102° (103°); *n*-caproic 98° (96.5°); isocaproic 144° (144°); heptoic 103° (103°); *n*-caprylic 106° (104°); lactic 115° (114.5°); adipic 209° (207°); succinic 210° (209°); benzoic 168° (168°).

TABLE I

MELTING POINTS OF DERIVATIVES OF ACIDS FORMED WITH PHENYLHYDRAZINE

	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Valeric	109	68.72	68.75	8.38	8.39
Capric	105	73.24	73.03	9.99	9.99
Undecanoic	110	73.90	73.54	10.21	9.93
Diethylacetic	145	69.91	69.83	8.80	8.79
Undecylenic	97	74.44	74.60	9.55	9.43
Chloroacetic	111[b]	[a]			
α-Chloropropionic	95[b]	49.89	49.75	6.05	6.07
Trichloroacetic	123[b]	35.36	35.79	3.31	3.53
Sebacic	194	69.12	68.63	7.91	7.89
Malonic	194	63.42	63.67	5.67	5.71
Benzene sulfonic	179[b]	50.69	50.70	5.67	5.74
p-Toluene sulfonic	188[b]	55.71	55.38	5.71	5.71

[a] Molecular weight found by titration with standard base: calcd. 202.6; found 204.7. [b] This indicates that the derivative obtained was a salt.

Experimental

Two general procedures were used in preparing derivatives of the acids examined, the choice depending upon the kind of acid.

Procedure 1.—One gram of the acid was dissolved in 2 cc. of phenylhydrazine, and the solution boiled gently for thirty minutes. The crystalline product which separated when the solution cooled was filtered off with suction and washed with small quantities of benzene or ether until the crystals were completely white. When a large excess of phenylhydrazine was used, it was sometimes necessary to dilute the mixture with benzene in order to bring about precipitation of the product. It was found that the derivatives of the lower monobasic acids were best recrystallized from hot benzene, while those of the higher acids and dibasic acids were best recrystallized from alcohol or alcohol-water mixtures. The derivatives obtained from dibasic acids by this method proved to be bis-β-phenylhydrazides.

Procedure 2.—One gram of the acid was mixed with 2 cc. of phenylhydrazine dissolved in 5 cc. of benzene. In some cases a white solid precipitated immediately and was recrystallized from alcohol. If no solid separated, the mixture was refluxed for thirty minutes, and the product which precipitated upon cooling was filtered, washed with ether, and recrystallized from benzene or alcohol. Sulfonic acids, halogen substituted aliphatic acids, and aliphatic dibasic acids yielded salts by this procedure.

Phenylhydrazides were obtained from the aliphatic monobasic acids, formed in the saponification of esters, in the following manner.

The ester was saponified in the usual way. The solution of the salt of the acid was evaporated nearly to dryness, acidified with a slight excess of dilute phosphoric acid, and extracted with ether. A large excess of phosphoric acid must be avoided to prevent the precipitation of the phosphoric acid salt of phenylhydrazine. The acid obtained after the evaporation of the ether was treated with phenylhydrazine in the same manner as indicated in Procedure 1 to obtain the derivative.

The authors are indebted to Mr. George T. Williamson, who ran many of the analyses which appear in the table.

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PITTSBURGH, PA. RECEIVED OCTOBER 22, 1941

(3) Beilstein, "Handbuch der organischen Chemie," Vol. XV.

Steryl Sulfates. III. Preparation of 3,5,6-Cholestantriol-I

BY ALBERT E. SOBEL,[1] IRVING ALLAN KAYE AND PAUL E. SPOERRI

The unusual stability of the ester linkage of steryl sulfates in alkaline media makes this derivative valuable for the study of the reactions of sterols in basic solutions while protecting the hydroxyl group. This is especially so because such derivatives are water soluble and form in quantitative yields.[2] The present paper deals with the result of such studies in which a new method for the preparation of 3,5,6-cholestantriol I was found by treating pyridonium dibromocholesteryl sulfate with aqueous potassium carbonate at room temperature as indicated below.

(1) Partially from the dissertation submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940. Previous paper, THIS JOURNAL, **64**, 361 (1942).

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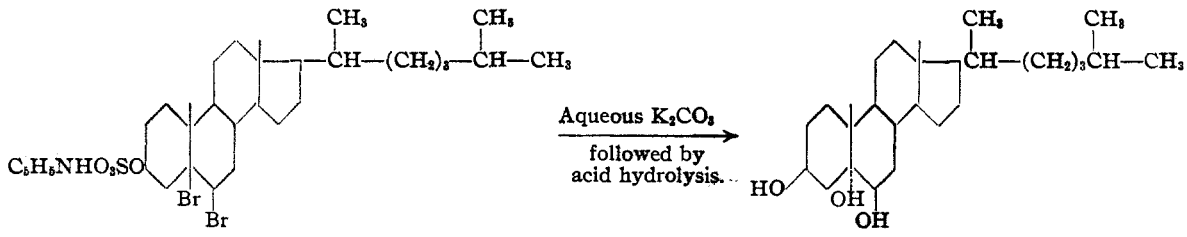

Pyridonium dibromocholesteryl sulfate

3,5,6-Cholestantriol I

This reaction is especially interesting because the treatment of cholesterol dibromide with bases or water results in the formation of cholestenediols, one of which recently has been shown to be Δ^4-cholestenediol-3,6.[3] Thus the presence of the sulfate ester in the 3 position tends to increase substitution in the 5 position instead of loss of hydrogen bromide on treatment with aqueous alkali.

3,5,6-Cholestantriol-I hitherto was obtained either directly from cholesterol by treating it with hydrogen peroxide or by the hydrolysis of α-cholesterol oxide.[4] Its constitution was established by Ellis and Petrow.[5] It has been recently isolated from the ox liver by Haslewood[6] and thus its formation in aqueous medium at room temperature is of some interest in speculating the possible mechanisms of its formation in the animal body from the relatively abundant cholesterol.

Experimental

Preparation of 3,5,6-Cholestantriol I.—Ten grams of pyridonium dibromocholesteryl sulfate[2] was dissolved in 450 ml. of 0.5 molar potassium carbonate. This was placed in a shaking machine for twenty-four hours and three 250-ml. portions of 0.5 molar potassium carbonate added at six-hour intervals during the shaking. The reaction mixture was treated with sulfur dioxide and a precipitate formed which was separated by centrifuging. The precipitate was then transferred with five 40-ml. portions of the hydrolyzing mixture (375 ml. 95% alcohol, 75 ml. water and 50 ml. concentrated sulfuric acid) to a liter Erlenmeyer flask and refluxed for one hour. The reaction mixture was poured into 1500 g. of water and ice and then extracted with two 300-cc. portions of ether. The ether extracts were washed once with dilute potassium carbonate and once more with water and then dried over anhydrous sodium sulfate. The dried ether extract was evaporated to dryness and the dry residue extracted in 50 ml. of hot ethylene dichloride. On cooling, white crystals appeared (m. p. 214) which were recrystallized once more; yield 1.0 g., m. p. 234. Calcd. for $C_{27}H_{48}O_3$: C, 77.09, H, 11.52. Found: C, 76.06; H, 11.39.

3,6-Diacetate of Cholestanetriol-3,5,6.—In a 50-cc. glass-stoppered Erlenmeyer flask 100 mg. of the above cholestanetriol was treated with 5 cc. of acetyl chloride reagent (2.36 cc. of acetyl chloride in 100 cc. of toluene) and 0.5 cc. of pyridine at 60° for one hour, cooled and the excess acetyl chloride neutralized by titrating it with 0.1 N sodium hydroxide in the presence of phenolphthalein indicator. The neutralized reaction mixture was extracted with ether. The ether extracts were washed with a little dilute hydrochloric acid and dried over anhydrous sodium sulfate. The dried extracts were filtered, the ether evaporated on a steam-bath and the toluene slowly evaporated in a vacuum desiccator, attached to a water pump. The residue melted at 158–159°; recrystallized twice from alcohol–water, m. p. 166°. Calcd. for $C_{31}H_{52}O_5$: C, 73.78; H, 10.38. Found: C, 73.57; H, 10.33.

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Distribution of Benzoic Acid between Water and Benzene

BY FREDERICK T. WALL

It is well known that the distribution of benzoic acid between water and benzene can be expressed approximately by the equation

$$C_W/\sqrt{C_B} = K_1 \qquad (1)$$

where C_W and C_B are the concentrations of the acid in water and in benzene and K_1 is a constant. Equation (1) can be derived on the assumption that the acid exists as a dimer when dissolved in benzene and as a monomer when dissolved in water. Equation (1) is not exact, however, because some ionization takes place in the aqueous solution and because the association is not quite complete in the benzene. If α equals the degree of ionization in the aqueous solution and β the degree of dissociation of the dimer in the benzene solution, then eqn. (1) should be replaced by the following more exact expression:

$$C_W(1 - \alpha)/\sqrt{C_B(1 - \beta)} = K_2 \qquad (2)$$