(XII) in 50 cc. of ether was cooled in an ice-bath and a solution of 5.0 g. of sodium azide, in 20 cc. of water, was added slowly with vigorous stirring. The stirring was continued for an additional two hours, and the ether layer was separated and washed with ice cold 10% sodium bicarbonate and was dried over sodium sulfate. Evaporation of the ether *in vacuo* gave the oily azide (XIII) which was dissolved in 50 cc. of absolute alcohol and decomposed as described for the preparation of (IV). The alcohol was then removed *in vacuo*, the resulting oil was dissolved in a small amount of ether, and the ether solution placed in a refrigerator, where crystallization occurred. The crystals were washed with ether and recrystallized from a small volume of ethyl acetate; 2.6 g. (46% of the theoretical yield) of prismatic crystals was obtained, which melted at 89–91°.

Anal. Calcd. for $C_{20}H_{31}O_6N_3$: C, 58.68; H, 7.63; N, 10.25. Found: C, 58.40; H, 7.49; N, 10.33.

3,4-Diaminocarbobenzyloxy-2-furanvaleric Acid Piperidide (XV).—Nineteen grams of the acid chloride (XII) was transformed into the azide (XIII) and the azide was dissolved in a mixture of 100 cc. of benzene and 13.2 cc. of benzyl alcohol, and was decomposed under nitrogen as described above. The solvents were removed *in vacuo*, and the resulting oil was placed in the refrigerator where crystallization soon occurred. The crude material was washed with ether and was purified by recrystallization from methanol; 13.5 g. (48% of the theoretical yield) of needles was obtained, which melted at 129–131°.

Anal. Calcd. for $C_{28}H_{35}O_6N_3$: C, 67.52; H, 6.61; N, 7.87. Found: C, 67.58; H, 6.67; N, 7.86.

Acknowledgment.—The authors wish to express their appreciation to Mrs. Florence Baker and to Miss Lola Ward for their valuable assistance in certain phases of this work.

Summary

A method for the preparation of 3,4-diaminofuran derivatives has been described, and a number of these compounds have been prepared.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF GEORGE A. BREON & COMPANY]

Preparation of Phenyl Ketones from Bile Acids[1]

BY WILLARD M. HOEHN AND ROBERT BRUCE MOFFETT

The use of diphenylcadmium for the preparation of phenyl ketones from acid chlorides[2] has had no known application with the steroid acids.[3,4] The preparation of acid chlorides of bile acids has been described by Cortese and Bauman[5] in which the formates of hydroxylated bile acids were treated with thionyl chloride. In the present work it was found that formates of the bile acids studied could be crystallized directly from the formic acid reaction mixture in pure form. In most instances no further crystallization of formates was necessary.

These compounds together with their physical constants and analyses are given in Table I.

Several of the acid chlorides crystallized on removal of the thionyl chloride and in such cases they were recrystallized from dry ether (Table II).

The acid chlorides were dissolved in dry benzene and treated with a solution of diphenylcadmium prepared by adding cadmium chloride to phenylmagnesium bromide. The best results were obtained when a large excess of diphenylcadmium solution was added dropwise to the acid chloride solution with vigorous stirring at reflux temperature. A solid complex separated at once and could be filtered off, but usually the entire reaction mixture was decomposed by adding dilute hydrochloric acid.

The product was extracted with ether, which was removed by steam distillation. This steam distillation also served to remove biphenyl which was always a by-product of the preparation of the diphenylcadmium. The formate groups[6] were removed by hydrolysis and the phenyl ketone crystallized generally from methanol.

To further characterize these products the acetates were prepared from the hydroxyl-containing phenyl ketone. The formates of four of them were made. To establish the presence of the ketone group the oximes were prepared from four of the phenyl ketones. On mild oxidation the phenyl ketones from desoxycholic acid and from 3-hydroxy-12-ketocholanic acid gave the same triketone.

A Wolff–Kishner reduction on the phenyl ketone from desoxycholic acid gave 3,12-dihydroxy-24-phenylcholane, which failed to crystallize, but could be oxidized to the crystalline 3,12-diketo-24-phenylcholane.

Additional evidence of the structure of the phenyl ketones was obtained by the oxidation of their acetates to the next lower homolog of the bile acid from which they were prepared; thus on chromic acid oxidation followed by hydrolysis 3,12-diacetoxy-*nor*-cholanyl phenyl ketone gave *nor*-desoxycholic acid and 3-acetoxy-12-keto-*nor*-cholanyl phenyl ketone gave 3-hydroxy-12-keto-*nor*-cholanic acid.

(1) Reported in part at the April, 1944, meeting of the American Chemical Society at Cleveland, Ohio, and at the meeting of the Missouri Academy of Science, St. Louis, Missouri.

(2) Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

(3) Riegel and Kaye, THIS JOURNAL, **66**, 723 (1944), prepared isopropyl ketones from steroid acids by this method but no phenyl ketones were reported.

(4) Since the report of this paper at the A. C. S. meeting,[1] Jacobsen has published a communication to the Editor of THIS JOURNAL, **66**, 662 (1944), in which the phenyl ketone from cholic acid was prepared by this method.

(5) (a) Cortese and Bauman, THIS JOURNAL, **57**, 1393 (1935); (b) *J. Biol. Chem.*, **113**, 779 (1936).

(6) In one case (the phenyl ketone from 3-hydroxy-12-ketocholanic acid) the intermediate formate was isolated in pure form, showing that the diphenylcadmium does not react with these formic ester groups.

TABLE I

FORMATES OF BILE ACIDS

Formate of acid	M. p., °C.	$[\alpha]^{25}D$ (10 mg./cc. dioxane)[a]	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Formyl analyses, %[a] Calcd.	Formyl analyses, %[a] Found	Saponification equivalent[a] Calcd.	Saponification equivalent[a] Found
Desoxycholic (5b)	195–196	+105.0°	$C_{26}H_{40}O_6$					12.96	12.3	149.5	147
nor-Desoxycholic	165–166	+102.5°	$C_{25}H_{38}O_6$	69.10	8.81	68.84	9.20[c]	13.42	13.58	144.8	144
bis-nor-Desoxycholic	214–216	+ 90°	$C_{24}H_{36}O_6$	68.54	8.63	68.73	8.76[b]	13.8	13.4	140.3	139
3-Hydroxy-12-ketocholanic	207–208	+117.5°	$C_{25}H_{38}O_5$	71.74	9.15	71.57	9.27[b]	6.95	7.0	204.3	207.5
Lithocholic	139–141	+ 50°	$C_{25}H_{40}O_4$	74.21	9.96	73.96	9.98[b]	7.19	7.38	202.3	203
nor-Lithocholic	189–191	+ 63°	$C_{24}H_{38}O_4$	73.82	9.81	74.18	9.72[b]	7.45	7.42	195.3	195.5
bis-nor-Lithocholic	179–181	+ 35°	$C_{23}H_{36}O_4$	73.36	9.64	73.74	9.65[b]	7.72	7.72	188.3	189
Cholic (5a)	205–209	+ 90°	$C_{27}H_{40}O_8$					17.63	18.1	123.2	123.2
3(β)-Hydroxy-Δ^5-cholenic	172–176	− 45°	$C_{25}H_{38}O_4$	74.58	9.52	74.35	9.48[b]	7.23	7.1	201.3	199.5
3,12-Dihydroxy-7-keto-cholanic	204–208	+ 65°	$C_{26}H_{38}O_7$	67.51	8.28	67.14	8.18[c]	12.55	12.5	154.2	157

[a] Rotations, formyl analyses and saponification equivalents by J. Stickley. [b] C–H Analyses by J. Delucia, New York, N. Y. [c] C, H and N Analyses by Arlington Laboratories.

TABLE II

ACID CHLORIDES

Chloride	M. p., °C.	$[\alpha]^{25}D$ (10 mg./cc. dioxane)[a]	Empirical formula	Chlorine analyses, % Calcd.	Chlorine analyses, % Found	Formyl analyses,[a] Calcd.	Formyl analyses,[a] Found	Saponification equivalent[a] Calcd.	Saponification equivalent[a] Found
3-Formoxy-12-ketocholanyl	164–168	+100°	$C_{25}H_{37}O_4Cl$	8.11	8.11	6.65	6.66	145.7	151
3-Formoxycholanyl	132–135	+ 55°	$C_{25}H_{39}O_3Cl$	8.38	8.24	6.87	6.66	141.0	141
3-Formoxy-*nor*-cholanyl	169–175	+ 50°	$C_{24}H_{37}O_3Cl$	8.67	8.23	7.12	7.27	136.3	136
3(β)-Formoxy-Δ^5-cholenyl	137–140	− 48.5°	$C_{25}H_{37}O_3Cl$	8.42	8.31	6.87	6.56	140.3	142
Cholanyl[b]	108.5–111	+ 30°	$C_{24}H_{39}OCl$	9.36	9.08	..	..	189.5	190
3,12-Diformoxy-*bis-nor*-cholanyl	116–119	+ 78.6°	$C_{24}H_{35}O_6Cl$	8.08	8.09			109.7	110.5

[a] See Table I. [b] Borsche, *Ber.*, **52**, 1365 (1919).

All the phenyl ketones and their derivatives are listed in Table III.

The phenyl ketone from *bis-nor*-desoxycholic acid was only obtained in amorphous form, but its acetate and formate were crystalline. These compounds as well as the phenyl ketone from *bis-nor*-lithocholic acid and its acetate showed broad melting points and fractional crystallization gave fractions with different melting points. It is possible that under the condition of preparation some racemization may have taken place at one or more of the asymmetric carbon atoms, possibly the C_{20} atom since this position is alpha to a ketone.

Experimental

Formates of Bile Acids.—The formates prepared are listed with their properties and analyses in Table I. The following is the general method by which they were prepared.

A solution (or suspension) of the bile acid in formic acid (sp. gr. 1.20) (2 cc. per gram) was heated in a water-bath at 70–80° for five hours. In most cases the bile acid dissolved completely and on cooling in the refrigerator the formate crystallized. The product was collected, washed with formic acid and dried. The product could be recrystallized from formic acid, but if pure bile acids were used this was not necessary. An additional amount could be obtained by concentrating the formic acid filtrate and cooling. The yields were generally 90–95% of pure material. In a few cases the formate separated before all the bile acids had dissolved and consequently there was little change in appearance during the reaction, but even in these cases the formate was obtained pure in good yield.

Acid Chlorides.—Those which crystallized easily and were isolated are listed in Table II. A mixture of 0.02 mole of the bile acid formate and 15 ml. of thionyl chloride (redistilled from cottonseed oil) was allowed to stand at room temperature with occasional shaking for one hour. The bile acid soon dissolved with evolution of hydrogen chloride and sulfur dioxide. In some cases the solution darkened somewhat. An equal volume of a mixture of dry ether and benzene was then added and the solvent was removed *in vacuo*. More ether and benzene were added and again removed *in vacuo*. The residue was used for the preparation of the phenyl ketones without further purification. In cases where the residue crystallized, a sample was recrystallized from a mixture of dry ether and benzene, and collected and dried with as little contact as possible with moist air. The acid chlorides appeared stable for short periods if kept dry, but on standing several months even in tightly stoppered bottles, they smelled strongly of hydrogen chloride.

Phenyl Ketones.—Table III gives the properties of the phenyl ketones and their derivatives. The preparation of 3-12-dihydroxy-*nor*-cholanyl phenyl ketone from desoxycholic acid is described below in detail and will serve as an example.

Diphenylcadmium was prepared by carefully adding with cooling 8.8 g. of anhydrous cadmium chloride to a solution of phenylmagnesium bromide prepared from 1.95 g. (0.08 g. atom) of magnesium, 8.85 ml. (0.084 mole) of bromobenzene, and 50 ml. of dry ether. After standing for about one-half hour at room temperature with occasional shaking, a Michler ketone test was negative.

The crude (non-crystalline) acid chloride (prepared as described above) was dissolved in 100 ml. of dry benzene in a 500-ml. flask fitted with a stirrer, reflux condenser (protected by a calcium chloride tube) and a dropping funnel. The solution was heated to boiling and the diphenylcadmium solution was added dropwise during one-

TABLE III

PHENYL KETONES OF BILE ACIDS

-*nor*-cholanyl phenyl ketone	M. p., °C.	$[\alpha]^{25}D$ (10 mg./cc. dioxane)[a]	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Saponification equivalent[a] Calcd.	Found
3,12-Dihydroxy-	203–205	+ 47.5°	$C_{30}H_{44}O_3$	79.61	9.80	79.49	9.75[b]	...	...
3,12-Diacetoxy-[c]	136–137	+ 92.5°	$C_{34}H_{48}O_5$					268.4	270
3,12-Diformoxy-[c]	122–125	+ 87.5°	$C_{32}H_{44}O_5$					254.3	255
Oxime of 3,12-dihydroxy-	194.5–198	+ 30°	$C_{30}H_{45}O_3N$	N, 3.00		3.03; 2.92		...	...
3,12-Diketo-	170–171.5	+ 87.5°	$C_{30}H_{40}O_3$	80.32	8.99	79.90	9.90[b]	...	...
3,12-Dihydroxy-*bis*-	105–115	+ 59.0°	$C_{29}H_{42}O_3 \cdot 1/2CH_3OH$	77.94	9.76	78.06	9.57[b]	...	...
3,12-Diacetoxy-*bis*-	141–142	+ 90°	$C_{33}H_{46}O_5$					261.7	262.5
Oxime of 3,12-dihydroxy-*bis*-	280–285, dec.		$C_{29}H_{43}O_3N$	76.79	9.56	77.17	9.64	...	...
				N, 3.09		2.95[d]			
3,12-Diacetoxy-*ter*-	193–195.5	+122.5°	$C_{32}H_{44}O_5$	75.55	8.72	75.83	8.74[d]	254.3	250
3,12-Diformoxy-*ter*-	242–245	+125°	$C_{30}H_{40}O_5$					240.3	246
3-Hydroxy-12-keto-	176–178	+ 77.5°	$C_{30}H_{42}O_3$	79.96	9.40	79.66	9.38[b]	...	...
3-Acetoxy-12-keto-	196.5–197.5	+ 85°	$C_{32}H_{44}O_4$					492.7	490
3-Formoxy-12-keto-[e]	183–184	+102.5°	$C_{31}H_{42}O_4$					478.6	475
Dioxime of 3-hydroxy-12-keto-	186–189	+125°	$C_{30}H_{44}O_3N_2$	N, 5.83		5.63; 6.12		...	...
3-Hydroxy-	146–147	+ 40°	$C_{30}H_{44}O_3$	82.52	10.16	82.23	10.11[b]	...	...
3-Acetoxy-	171–172	+ 60°	$C_{32}H_{46}O_4$					478.7	480
3-Hydroxy-*bis*-	121.5–123	+ 27.5°	$C_{29}H_{42}O_3$	82.42	10.02	81.88	10.13[d]	...	...
3-Acetoxy-*bis*-	95–99	+ 45°	$C_{31}H_{44}O_4$	80.12	9.54	80.20	9.69[d]		
3-Hydroxy-*ter*-	150–155	+ 52.5	$C_{28}H_{40}O_3 \cdot 1/2CH_3OH$	80.62	9.97	81.15	10.20[d]	...	...
3-Acetoxy-*ter*-	174.5–180	+ 57.5°	$C_{30}H_{42}O_5$					450.6	455
3,7,12-Trihydroxy-[f]	175–177	+ 39°	$C_{30}H_{44}O_4 \cdot 1/2CH_3OH$	75.57	9.57	75.36	9.50[b]	...	...
3,7,12-Triacetoxy-[f]	122–123	+ 78.5	$C_{36}H_{50}O_7$					198.2	197
3,12-Dihydroxy-7-keto	180–181.5	0°	$C_{30}H_{42}O_4$	77.22	9.07	77.07	9.26[d]	...	...
3,12-Diacetoxy-7-keto-	164–166	+ 75°	$C_{34}H_{46}O_6$					175.4	175
3(β)-Hydroxy-Δ^5	129–134	− 30°	$C_{30}H_{42}O_3$	82.90	9.74	82.76	10.06[d]	...	...
3(β)-Acetoxy-Δ^5	157–158	− 30°	$C_{32}H_{46}O_4$					478.7	485
3(β)-Formoxy-Δ^5	150–153	− 32.5°	$C_{31}H_{42}O_4$					462.6	472
Phenyl ketone									
nor-Cholanyl	137.5–138.5	+ 27.5°	$C_{30}H_{44}O$	85.66	10.54	85.73	10.68[d]	...	...
Oxime of *nor*-cholanyl	133.5–135	+ 15°	$C_{30}H_{45}ON$	N, 3.22		3.25		...	...
3,12-Diketo-24-phenyl-cholane	117–119	+ 90°	$C_{30}H_{42}O_2 \cdot CH_3OH$	79.77	9.94	79.92	10.24	...	...

[a] See Table I. [b] See Table I. [c] Formyl analysis: Calcd.: 11.4. Found: 11.9. [d] See[a] Table I. [e] Formyl analysis: Calcd.: 6.05. Found: 6.05.

half hour with vigorous stirring and refluxing. A solid complex separated immediately. After refluxing for ten minutes more the mixture was cooled and decomposed by adding dilute hydrochloric acid. The layers were separated and the aqueous layer was extracted with ether. The combined ether-benzene solution was washed with dilute hydrochloric acid and then with water. The solvent was removed by steam distillation which was continued for about one hour or until little more biphenyl came over. The residue was hydrolyzed by refluxing for one hour with 70 ml. of 5% methanolic sodium hydroxide solution. The mixture was diluted to about 500 ml. by adding water a little at a time with shaking to induce crystallization. The crude product was collected and after drying weighed 8.6 g. It was mixed with 50 ml. of ether, heated to boiling, cooled, and filtered. Considerable colored material was removed by this procedure and 7.4 g. (81% of a nearly white product melting at 202–204°) was obtained. This was dissolved in about 200 ml. of methanol, filtered, concentrated to about 25 ml. and cooled. A nicely crystalline product melting at 203–205° was obtained which weighed 5.83 g. (63.8%).

The other phenyl ketones were prepared by essentially the same procedure except that the treatment of the crude product with ether was usually omitted. All were crystallized from methanol except the following: 3-hydroxy-*nor*-cholanyl phenyl ketone was crystallized from a mixture of ether and petroleum ether; 3,12-dihydroxy-7-keto-*nor*-cholanyl phenyl ketone was crystallized first from moist isopropyl alcohol and then from benzene; 3(β)-hydroxy-Δ^5-*nor*-cholenyl phenyl ketone was crystallized first from methanol and then from ethanol; and *nor*-cholanyl phenyl ketone was crystallized from isopropyl ether. 3,12-Dihydroxy-*ter*-*nor*-cholanyl phenyl ketone failed to crystallize and the crude product was used to prepare the acetate and formate.

Acetates of the Phenyl Ketones.—All of the hydroxyl containing phenyl ketones were converted to their acetates (Table III) by refluxing them in a solution of acetic acid and acetic anhydride (2:3 by volume). In several cases the acetates separated from the reaction mixture on cooling and needed no further purification. This was the case with 3-acetoxy-12-keto-*nor*-cholanyl phenyl ketone, 3-acetoxy-*nor*-cholanyl phenyl ketone, 3-acetoxy-*ter*-*nor*-cholanyl phenyl ketone, and 3(β)-acetoxy-Δ^5-*nor*-cholenyl phenyl ketone. When the reaction mixture did not crystallize the solvent was removed *in vacuo* and the residue was crystallized. 3,12-Diacetoxy-*ter*-*nor*-cholanyl phenyl ketone, 3-acetoxy-*bis*-*nor*-cholanyl phenyl ketone, 3,7,12-triacetoxy-*nor*-cholanyl phenyl ketone, and 3,12-diacetoxy-7-keto-*nor*-cholanyl phenyl ketone all crystallized from methanol. 3,12-Diacetoxy-*nor*-cholanyl phenyl ke-

tone crystallized from acetone and 3,12-diacetoxy-*bis-nor*-cholanyl phenyl ketone crystallized from ethanol.

Formates of the Phenyl Ketones.—Four of the hydroxyl containing phenyl ketones were converted to their formates (Table III) by a process similar to that used for the preparation of the formates of bile acids. 3-Formoxy-12-keto-*nor*-cholanyl phenyl ketone, 3,12-diformoxy-*ter-nor*-cholanyl phenyl ketone, and 3(β)-formoxy-Δ^5-*nor*-cholenyl phenyl ketone crystallized from the formic acid reaction mixture and could be recrystallized from formic acid if necessary. 3,12-Diformoxy-*nor*-cholanyl phenyl ketone was obtained by removing the formic acid *in vacuo* and crystallizing the residue from methanol.

3-Formoxy-12-keto-*nor*-cholanyl phenyl ketone was also obtained from the crude reaction product of 3-formoxy-12-ketocholanyl chloride with diphenylcadmium.[6] A sample of the residue left from the steam distillation was extracted with methanol and recrystallized from acetone giving a product with a melting point and mixed melting point identical with that obtained as above.

Oximes of the Phenyl Ketones.—A solution of 0.7 g. of the phenyl ketone, 0.7 g. of hydroxylammonium chloride, and 1 g. of sodium acetate (trihydrate) in 7 ml. of ethanol and 2 ml. of water was refluxed for one hour. In the case of *nor*-cholanyl phenyl ketone a mixture of dioxane, methanol and water was used as the solvent. The oximes of 3,12-dihydroxy-*bis-nor*-cholanyl phenyl ketone and of 3-hydroxy-12-keto-*nor*-cholanyl phenyl ketone separated from the reaction mixture and needed no further purification. The oximes of 3,12-dihydroxy-*nor*-cholanyl phenyl ketone were obtained by adding water to the reaction mixture, extracting with ether, removing the ether and crystallizing the residue, the former from benzene and the latter first from methanol and then from ethanol. Most of these oximes (Table III) proved to be moderately soluble in organic solvents, but 3,12-dihydroxy-*bis-nor*-cholanyl phenyl ketone oxime proved to be exceedingly insoluble in all organic solvents tried.

3,12-Diketo-*nor*-cholanyl Phenyl Ketone.—To a cooled solution of 0.906 g. (0.002 mole) of 3,12-dihydroxy-*nor*-cholanyl phenyl ketone in 20 ml. of acetic acid was slowly added 2.4 ml. (40% excess) of 4.66 normal chromic acid solution (in acetic acid and water). After standing one hour below room temperature the solution was poured into water giving a precipitate which was collected and dried giving a quantitative yield of material melting at 165–170°. After recrystallization from isopropyl alcohol it melted at 168–169°.

In a similar way a sample of 3-hydroxy-12-keto-*nor*-cholanyl phenyl ketone was oxidized to the same triketone, m. p. 170–171.5°. A mixed melting point gave no depression (see Table III for rotation and analysis).

3,12-Diketo-24-phenylcholane.—A mixture of 5.0 g. of 3,12-dihydroxy-*nor*-cholanyl phenyl ketone, 6 ml. of 85% hydrazene hydrate and 100 ml. of 6% methanolic sodium methoxide was heated in a bomb at 180–190° for three hours. After pouring into water the mixture was extracted with ether and the ether solution was evaporated *in vacuo* leaving a colorless amorphous residue.[7] Repeated attempts failed to yield a crystalline product.

(7) This work was done by Jacob Linsk in this Laboratory.

A sample of 1 g. of this amorphous 3,12-dihydroxy-24-phenylcholane was dissolved in 10 ml. of acetic acid and 4 ml. of 4.74 normal chromic acid solution (in acetic acid and water) was added. After standing at room temperature for three hours the solution was poured into water and extracted with ether which was washed with dilute hydrochloric acid and water, and dried over anhydrous sodium sulfate. The ether was removed *in vacuo* and the amorphous residue was recrystallized from methanol giving 0.8 g. of crystals melting at 113–115°. After a second crystallization from methanol it melted at 117–119° (see Table III for rotation and analysis).

Oxidation of Acetates of Phenyl Ketones.—A solution of 0.537 g. (0.001 mole) of 3,12-diacetoxy-*nor*-cholanyl phenyl ketone in 10 ml. of acetic acid was heated with 1.3 ml. of a 4.8 normal chromic acid solution in acetic acid and water, and 3 drops of sulfuric acid were added. After heating at 50° for one hour the solution was allowed to stand at room temperature overnight. The solution was poured into water, extracted with ether, and the ether solution was extracted with 40 ml. of dilute sodium hydroxide solution. After adding 1.2 g. of solid sodium hydroxide, the basic solution was refluxed for one hour, diluted, filtered, and acidified. A small yield of *nor*-desoxycholic acid was obtained which melted at 209–210° after crystallization from acetone. A mixed melting point with an authentic sample gave no depression.

In a similar way 3-acetoxy-12-keto-*nor*-cholanyl phenyl ketone gave a small yield of 3-hydroxy-12-keto-*nor*-cholanic acid which melted at 245–248° after one crystallization from ethanol. A mixed melting point with a known sample[8] gave no depression.

Summary

Phenyl ketones have been prepared from certain bile acids by treating the acid chlorides of their formates with diphenylcadmium followed by saponification. The intermediate formates of most of these acids were prepared, and several crystalline acid chlorides were isolated. The phenyl ketones were characterized either by their acetate, formate or oxime.

The phenyl ketones from desoxycholic acid and from 3-hydroxy-12-ketocholanic acid were oxidized to the same triketone. A Wolff–Kishner reduction followed by mild oxidation converted the phenyl ketone from desoxycholic acid to 3,12-diketo-24-phenylcholane. The acetates of two of the phenyl ketones were converted to the next lower homolog of the acid from which they were prepared by chromic acid oxidation followed by saponification.

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(8) Schwenk, Riegel, Moffett and Stahl, THIS JOURNAL, 65, 549 (1943).