Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.32; H, 5.12. Found: C, 81.11; H, 5.15.

The **p-nitrobenzoate** separates from alcohol as rosets of colorless needles which melt at 109.5–109.8°.

Anal. Calcd. for $C_{24}H_{17}O_5N$: N, 3.51. Found: N, 3.49.

Conversion to 2-Phenylfuran.—The oxime of 2-phenyl-4-benzoylfuran was prepared in absolute alcohol solution in the presence of pyridine. It is readily soluble in the common organic solvents and separates from dilute alcohol as colorless needles which melt at 149.0–149.4°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.70; H, 5.13; N, 5.46, 5.40.

The Beckmann rearrangement was carried out by adding phosphorus pentachloride to a solution of the oxime in absolute ether. After crystallization from alcohol with the aid of Norite the **anilide** of 2-phenyl-4-furoic acid was obtained as colorless plates which melted at 192.0–193.0°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: N, 5.32. Found: N, 5.44.

The anilide was hydrolyzed with alcoholic potassium hydroxide; it was necessary to heat the solution under reflux for twenty-four hours to cause complete reaction. The aniline was separated by steam distillation and identified as 1-phenylazo-2-naphthol, m. p. 128–129°. The residue was treated with Norite and acidified. Crystallization from alcohol produced colorless needles of **2-phenyl-4-furoic acid** which melted at 208.0–209.0°.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.25; H, 4.25; neut. equiv., 188. Found: C, 70.20; H, 4.49; neut. equiv., 191, 190.

The acid is readily soluble in acetone, moderately soluble in alcohol, sparingly soluble in benzene, xylene, ether and chloroform. It forms a yellow solution in concentrated sulfuric acid.

The acid was not converted to the corresponding pyrrole when treated with ammonium hydroxide in a bomb at 180°. Decarboxylation did not occur when it was subjected to the following treatments:

1. A mixture of the acid and copper bronze was heated to 250°.
2. A mixture of the acid and copper bronze in quinoline was heated at 225° in a stream of nitrogen.
3. A mixture of the acid and copper bronze in benzylmethylaniline was heated at 280° for one hour.
4. A mixture of the sodium salt of the acid and soda-lime was heated for two hours at 375° under a pressure of 10 mm.

The reaction was finally carried out by heating the acid overnight at 275° in a high-pressure bomb. The **2-phenylfuran** obtained in this way had the following properties: b. p. 107–108° (18 mm.); $n^{20}{}_D$ 1.5968; $d^{20}{}_4$ 1.083. These data are in agreement with those found for a sample prepared by the method described by Kondo and Suzuki.[6]

Summary

1,2-Dibenzoyl-1-propene is transformed into 2-phenyl-4-benzoylfuran by treatment with selenium dioxide. The furan is readily hydrolyzed by aqueous alkalies to give 1,2-dibenzoylethane and formic acid. Ammonia and aniline react to give the corresponding pyrroles. By a series of reactions the benzoylfuran was degraded to the known 2-phenylfuran.

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[6] Kondo and Suzuki, *J. Pharm. Soc. Japan*, No. **544**, 501 (1927); *C. A.*, **21**, 3362 (1927).

URBANA, ILLINOIS RECEIVED MAY 31, 1938

NOTES

The Structure of Cholesteryl Chloride

BY ERNST BERGMANN

In work with cholesteryl chloride, as carried out in various laboratories and also in this Institute, certain conflicting evidence has accumulated with regard to its usual formula (I). The main point is the following one: while the two epimeric cholestyl chlorides react with sodium acetate under Walden inversion,[1] cholesteryl chloride has been found in our laboratory to give the same cholesteryl acetate which is obtained by direct acetylation of cholesterol.[2] Recently, Marker and co-workers[3] have reported that 7-oxocholesteryl chloride, the constitution of which follows from the characteristic absorption band at 270 mμ of α,β-unsaturated ketones[4] behaves "normally" toward sodium acetate, giving an acetate under configurational inversion. Besides that, Marker and his co-workers have pointed out that cholesteryl chloride reacts under much less drastic conditions than the other chlorides mentioned.[5]

Reactions of halogenides with acetate ions are

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[1] Marker and co-workers, THIS JOURNAL, **57**, 1755, 2358 (1935).

[2] That cholesterol and cholesteryl chloride have identical configuration, has been discussed in *Helv. Chim. Acta*, **20**, 590 (1937).

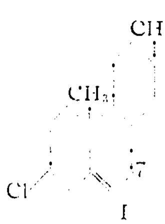
[3] Marker and co-workers, THIS JOURNAL, **59**, 619 (1937).

[4] Unpublished results from our laboratory (Miss F. Goldschmidt); compare for 7-oxocholesteryl acetate, Eckhardt, *Ber.*, **71**, 461 (1938).

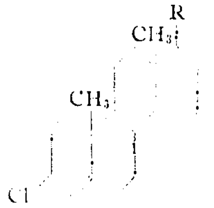
[5] Compare Mauthner, *Chem. Central.*, **80**, II, 1537 (1909).

now generally accepted to occur with Walden inversion,[2-6] with one exception, if the halogenide belongs to the allyl derivatives. In this case the possibility of allylic rearrangement prevents any prediction of the steric course taken by a substitution reaction. Therefore, the above difficulty would be overcome if cholesteryl chloride were able to react in the form (II),[7] deriving from *allo*-cholesterol.[8] The reaction of form (II) with sodium acetate would be accompanied by a shift of the double bond.[9] In the case of 7-oxocholesteryl chloride the conjugation with the carbonyl group would stabilize the $C{=}C$ double bond in the "classical" 5,6-position.

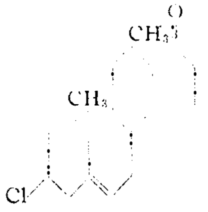
It is interesting to note that similar conditions have been observed by Linstead and Rydon[10] in the case of buten-(1)-ol-(4), which is converted by a mixture of sulfuric and hydrobromic acids partly into 4-bromobutene-(1), and partly into 4-bromobutene-(2). On the basis of Juvala's[11] results, the high substitution velocity, too, of cholesteryl chloride would be understood more easily.



I



II



III

Analogous considerations apply to the case of chloroandrostenone (III), which in contrast with the corresponding saturated chloroandrosterone is able to react with sodium benzoate without configurational inversion. This behavior may again be due to the possibility of III reacting in an allylic form.

Finally, it may be mentioned that this possibility is not necessarily limited to (I) and (III), but may apply to corresponding derivatives of other strong acids as, *e. g.*, toluenesulfonic acid.[12]

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(6) *Cf.* also Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937). Fieser, in "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, 1937, p. 392, has not yet taken these facts into account.

(7) The allylic nature of certain reactions of cholesteryl chloride has been discussed by Wagner-Jauregg and Werner [*Z. physiol. Chem.*, **213**, 119 (1932)] on the basis of the old allylic formula for cholesterol.

(8) The preparation of the chloride corresponding with *allo*-cholesterol is prevented by the easy dehydration of this substance: Schoenheimer and Evans, THIS JOURNAL, **58**, 182 (1936); *J. Biol. Chem.*, **114**, 567 (1936).

(9) The ability of cholesteryl chloride to react as (I) will account for the hydrogenative formation of a cholestane and not a coprostane derivative.

(10) Linstead and Rydon, *J. Chem. Soc.*, 1995 (1934).

(11) Juvala, *Ber.*, **63**, 1989 (1930).

(12) Compare Stoll, *Z. physiol. Chem.*, **246**, 6 (1937).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
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Racemization During Esterification by Diazomethane

BY ERNST BERGMANN AND YAÏR SPRINZAK

In the course of experiments on Walden inversion, we had to prepare optically active methyl bromosuccinate. While esterification with methyl alcohol in the presence of concentrated sulfuric acid[1] gave satisfactory results, a series of experiments carried out with diazomethane gave invariably a racemic ester.

(−)-Bromosuccinic acid (1.5 g., rotation in acetone: c 3.000; l 9.9 cm.; α_D −2.18°, hence $[\alpha]_D$ −72.7°), finely pulverized, was added at zero temperature to a solution of diazomethane, prepared from ethyl nitrosomethylcarbamate (5 g.) and 25% methyl-alcoholic potash solution (7 cc.) in ether (30 cc.). The acid disappeared quickly; after thirty minutes of standing, the yellow solution was evaporated and the remaining racemic methyl bromosuccinate distilled *in vacuo;* b. p. 87° (2.5 mm.); yield 1.4 g. (Calcd. for $C_6H_9O_4Br$: Br, 35.5. Found: Br, 35.4).

As check experiments, a sample of the same (−)-bromosuccinic acid was kept for thirty minutes with a mixture of ether and methyl alcohol (6:1) and the optically active methyl ester in contact with diazomethane solution, prepared as above, for two hours. In both cases, no changes in optical rotation were observed.

Therefore we are inclined to assume that the racemization is connected in some way with the esterification mechanism. An analogous observation has been made incidentally by Stoermer and Starck[2] in the case of the optically active acid

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(1) Holmberg, *Ber.*, **59**, 125 (1926).

(2) Stoermer and Starck, *ibid.*, **70**, 479 (1937).