These hydrolysis runs, with and without the presence of added inhibitor, were carried out in the phosphate buffer (*p*H 7.0) as previously described.[2] All inhibitor dilutions and acetylcholine solutions were freshly prepared before use in the standard sequence of kinetic determinations (at 25.12°) employing a series of inhibitor concentrations varying over the range of 1–10 × 10^{-7} *M*.

The Wilson plot of v/v_I *vs.* concentration for each of the inhibitors III and IV was linear over this concentration range, with least squares fits of about ±6% paralleling the observed magnitudes of precision of the slopes of individual rate plots. The velocity values *v* were obtained as the slopes of these rate plots for the first six to seven minutes of reaction, corresponding to about 10% completion of AC hydrolysis.

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3α-Chloro-B-norcoprostane-6-one

BY MARCEL GUT

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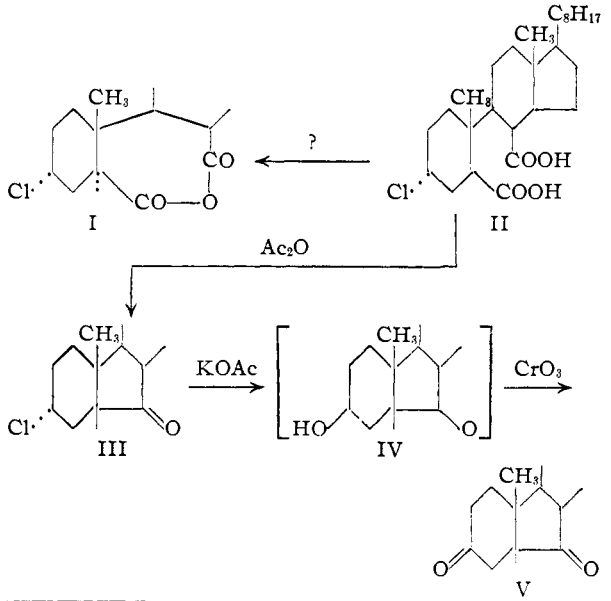
A few years ago we were interested in preparing 3α-chloro-6,7-secocholestane-6,7-dioic acid anhydride (I). Windaus and Stein[1] reported that 3α-chloro-6,7-secocholestane-6,7-dioic acid (II)[2] formed a crystalline anhydride melting at 187°. No further data on this compound were reported. A re-examination of this reaction produced a substance of the indicated melting point, the structure of which was, however, established to be 3α-chloro-B-norcoprostane-6-one (III). Therefore, this ring closure proceeded according to Blanc's rule.[3]

In a recent publication Fieser[4] reinterpreted Butenandt's oxidation and subsequent ring closure of 3,6-diketocholestene yielding B-norcoprostane-3,6-dione (V).[4,5] This prompted us to transform the chloro analog into the known diketone V. The chloro compound III obtained by the ring closure was easily transformed into V and its identity established by comparison with authentic material.[6] 3α-Chloro-B-norcoprostane-6-one (III) was converted under conditions employed by Marker[7] in similar cases to 3-hydroxy-B-norcoprostane-6-one (IV) (mainly the β-epimeride[8]) and the crude mixture was oxidized with chromic anhydride to the known B-norcoprostane-3,6-dione (V).



(1) A. Windaus and G. Stein, *Ber.*, **37**, 3699 (1904).

(2) At that time designated as 3β-chlorocholestane-6,7-dicarboxylic acid.

(3) H. G. Blanc, *Compt. rend.*, **144**, 1356 (1907).

(4) L. F. Fieser, THIS JOURNAL, **75**, 4386 (1953).

(5) A. Butenandt and E. Hausmann, *Ber.*, **70**, 1154 (1937).

Experimental

A solution of 500 mg. of 3α-chloro-6,7-secocholestane-6,7-dioic acid (II) in 15 ml. of acetic anhydride was heated on a steam-bath for 2 hours. Then the mixture was poured into ice, let stand for 2 hours, the solids filtered off, and finally recrystallized from methanol and dried; yield 215 mg., m.p. 180–183°. After sublimation at 140° (0.01 mm.) and recrystallization from acetone the melting point rose to 184–186°, α_D +10.3° Chf (*c* 0.58).

Anal. Calcd. for $C_{26}H_{43}OCl$: C, 76.71; H, 10.65; Cl, 8.71. Found: C, 76.72; H, 10.54; Cl, 8.60.

Treatment of 100 mg. of the above ketone and 450 mg. of potassium acetate in 3 ml. of valeric acid under the same conditions as used by Marker, *et al.*,[7] gave crude 3-hydroxy-B-norcoprostane-6-one (IV), which was oxidized with chromic anhydride in acetic acid. The resulting mixture gave after chromatographing 11 mg. of B-norcoprostane-3,6-dione (V),[4,5] m.p. 114–116°. The diketone could not be isomerized with alkali and the melting point was unchanged after admixture of authentic material.[6] The infrared spectrum shows two carbonyl bands at 5.76 and 5.81 μ.

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(6) Obtained through the courtesy of Dr. L. F. Fieser.

(7) R. E. Marker, F. C. Whitmore and O. Kamm, THIS JOURNAL, **57**, 2358 (1935).

(8) C. W. Shoppee, *J. Chem. Soc.*, 1032 (1948).

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Synthesis of Peptides *via* α-Benzyloximino Acids[1]

BY WALTER H. HARTUNG,[2] DAVID N. KRAMER AND GEORGE P. HAGER

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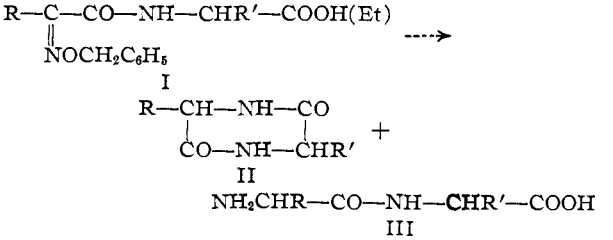
Weaver and Hartung[3] found that catalytic hydrogenation of N-benzyloximinoacylamino acids or their esters, I, in acidic media produced predominantly diketopiperazines, II. Nevertheless, the formation of small amounts of the dipeptide, III, indicated that under other conditions compounds of structure I may prove useful in the synthesis of peptides.



In the earlier conversion of oximes into primary amines acidic media were always employed.[4]

(1) No. 14 in amino acid series; for no. 13 see J. H. R. Beaujon and W. H. Hartung, THIS JOURNAL, **75**, 2499 (1953).

(2) University of North Carolina, Chapel Hill, North Carolina.

(3) W. E. Weaver and W. H. Hartung, *J. Org. Chem.*, **15**, 741 (1950).

(4) W. H. Hartung, THIS JOURNAL, **53**, 2248 (1931).