Calcd. for $C_{19}H_{28}O_3$ (304.4): C, 74.96; H, 9.27. Found: C, 74.69, 74.67; H, 9.69, 9.48. The compound gave a strong depression of the m. p. when mixed with the β-lactone XIVb (see below), and showed a positive color reaction with tetranitromethane. A sample of 11.7 mg. was recovered unchanged after two hours of refluxing with 7 ml. of 1 *N* sulfuric acid and identified by mixed m. p.

A sample of XIIIb (59.5 mg.) was refluxed with aqueous alkali and back-titrated as described above for XIIIa. Calcd. for consumption of one equivalent: 1.95 ml. 0.1 *N* alkali; mol. wt., 304.4. Found: 1.95 ml.; mol. wt., 304.4. Acidification gave a quantitative yield of the unchanged α-lactone XIIIb, identified by mixed m. p.

Sodium Salt of α-Lactone XIIIb (XVd).—A sample of XIIIb (50.5 mg.) was refluxed with 1.7 ml. of 0.1 *N* aqueous sodium hydroxide and 0.9 ml. of water. The clear solution was allowed to stand at −5° for three days, the crystalline sodium salt XVd was separated by centrifuging in the cold, washed with a little ice-water and dried *in vacuo*. *Anal.* Calcd. for $C_{19}H_{29}O_4Na\cdot H_2O$ (362,4): Na, 6.34. Found: Na, 6.12, 6.38.

Acetate of α-Lactone XIIIb (XIIIa).—A sample of the α-lactone XIIIb (150.0 mg.) in 5 ml. of anhydrous pyridine was treated with 3 ml. of acetic anhydride, worked up in the usual way and the α-lactone acetate XIIIa recrystallized three times from aqueous methanol; yield 139 mg., m. p. 176–177°, identified by mixed m. p. and determination of rotation.

β-Lactone XIVb.—The crude β-lactone acetate XIVa (3.53 g., obtained from the mother liquors of the pure XIVa) was refluxed for one hour with 100 ml. of 1 *N* aqueous sodium hydroxide, keeping the sodium salt XVId in solution by addition of 50 ml. of water. Working up as previously described for the hydrolysis of XIIIa there were obtained, after acidification with 50 ml. of 5 *N* sulfuric acid, washing to neutrality, and repeated recrystallization from aqueous methanol, 2.22 g. of β-lactone XIVb; yield 41.3% from XII, m. p. 206–208°, $[\alpha]^{30}D$ −55.5° (in methanol). *Anal.* Calcd. for $C_{19}H_{28}O_3$ (304.4): C, 74.96; H, 9.27. Found: C, 74.82, 75.11; H, 9.02, 9.22. The compound gave a strong depression of the m. p. when mixed with the α-lactone XIIIb, and showed a positive color reaction with tetranitromethane. A sample of 11.1 mg. was recovered unchanged after refluxing for two hours with 10 ml. of 1 *N* sulfuric acid and identified by mixed m. p.

The over-all yield of β-lactone acetate XIVa and β-lactone XIVb obtained from 8.85 g. of thiolbenzyl ester XII was 80.4%.

A sample of XIVb (69.5 mg.) was refluxed with aqueous alkali and back-titrated as described above for XIIIa. Calcd. for consumption of one equivalent: 2.28 ml. of 0.1 *N* alkali; mol. wt., 304.4. Found: 2.30 ml.; mol. wt., 302. Acidification gave a quantitative yield of the unchanged β-lactone XIVb, identified by mixed m. p.

Sodium Salt of β-Lactone XIVb (XVId).—A sample of XIVb (54.5 mg.) was refluxed with 1.79 ml. of 0.1 *N* aqueous sodium hydroxide and 0.7 ml. of water. The clear solution could not be brought to crystallization and was therefore lyophilized. The amorphous sodium salt XVId was washed with a little ice-water and dried *in vacuo*. *Anal.* Calcd. for $C_{19}H_{29}O_4Na\cdot H_2O$ (362.4): Na, 6.34. Found: Na, 6.23, 6.12.

Acetate of β-Lactone XIVb (XIVa).—A sample of XIVb (15.1 mg.) in 1 ml. of dry pyridine was treated with 0.6 ml. of acetic anhydride, worked up in the usual way, the β-lactone acetate XIVa recrystallized from aqueous acetic acid and identified by mixed m. p.

Summary

1. A convenient method for the preparation of the two isomeric monomethyl half-esters of 3(β)-hydroxy-$\Delta^{5,6}$-etiobilienic acid from dehydroisoandrosterone acetate has been described.

2. Conversion of the acetates of the two half-esters to the corresponding half-ester acid chlorides and condensation of the latter with benzyl mercaptan to yield two isomeric methyl-thiolbenzyl esters $C_{29}H_{38}O_5S$, has been carried out, and their constitution established by degradation.

3. Treatment of the latter with Raney nickel at room temperature yielded two isomeric acetoxylactones $C_{21}H_{30}O_4$, which upon alkaline hydrolysis yielded the two isomeric free lactones $C_{19}H_{28}O_3$.

4. One of these, the α-lactone (derived from the α-monomethyl half-ester), was shown to be the lactone of $\Delta^{9,14}$-2,13-dimethyl-2-hydroxymethyl-7(β)-hydroxydodecahydrophenanthryl-1-acetic acid. The isomeric β-lactone (derived from the β-monomethyl half-ester), was shown to possess the structure of the lactone of $\Delta^{9,14}$-2,13-dimethyl-1-hydroxyethyl-7(β)-hydroxydodecahydrophenanthryl-2-carboxylic acid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S. A.]

Steroids. IV.[1a] α-Iodoketones. A Method for the Conversion of *Allo*steroids into Δ^4-3-Ketosteroids[1b]

BY G. ROSENKRANZ, O. MANCERA, J. GATICA AND CARL DJERASSI

Except for 21-iodo-20-ketopregnanes,[2] usually prepared from the corresponding 21-tosylates and not isolated, α-iodoketones of the steroid series appear to be unknown.[2a]

The preparation and reactions, particularly toward dehydrobrominating agents, of brominated derivatives of 3-ketosteroids of both the *allo* (rings A/B *trans*) and *normal* (rings A/B *cis*) series have been studied thoroughly,[3] and it was of interest to extend this work to the corresponding iodo compounds.

The most promising approach appeared to be the well known halogen interchange of bromo compounds by treatment with sodium iodide in acetone solution. When applied to 2-bromo-3-

(1a) Paper III, Rosenkranz, Djerassi, Kaufmann, Pataki and Romo, *Nature*, **165**, 814 (1950).

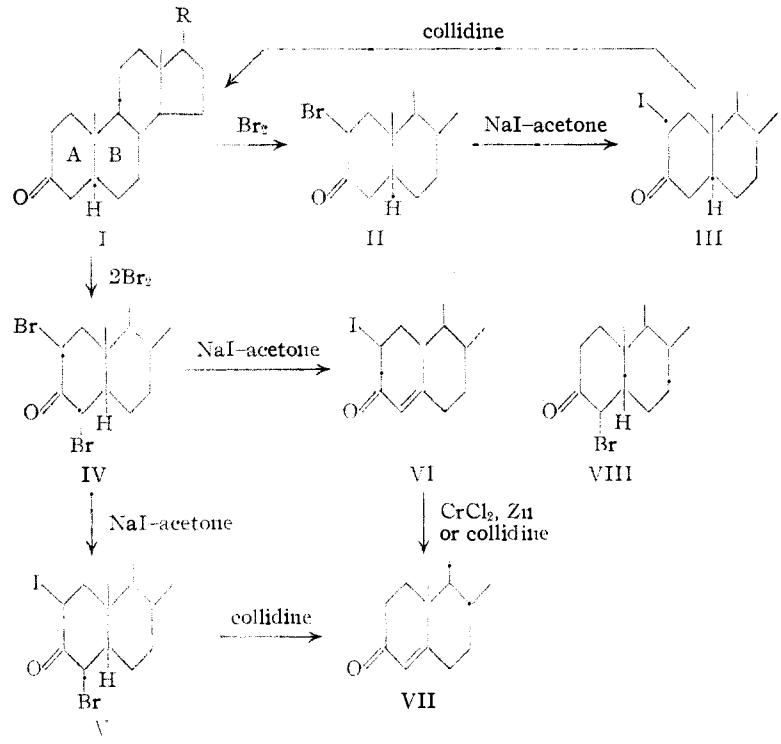
(1b) A part of the experimental portion of this paper is taken from a thesis to be presented by Srta. Josefina Gatica to the Escuela de Ciencias Químicas de la Universidad Nacional Autónoma de México.

(2) Lardon, *Helv. Chim. Acta*, **32**, 1517 (1949), and references cited therein.

(2a) After submission of this manuscript for publication, an article appeared [Julian and Karpel, THIS JOURNAL, **72**, 362 (1950)] in which the preparation and some reactions of a pure 21-iodo-20-ketosteroid were reported.

(3) See Djerassi, *ibid.*, **71**, 1003 (1949), for a brief review and leading references.

keto*allo*steroids (II, R = C_8H_{17}-O, $COOCH_3$), the corresponding α-iodoketones III could be isolated readily in good yield. While the corresponding 2-bromoketones II suffer dehydrobromination[3] on boiling with γ-collidine, the iodo analogs III were deiodinated in up to 70% yield within thirty minutes, regenerating the corresponding saturated ketone I. This unexpected behavior is not generally observed with the analogous bromo ketones, although occasionally small amounts of the corresponding saturated ketone are encountered[4] on long boiling with collidine or dimethylaniline. While collidine obviously acts as an electron source in the reduction of the iodoketones III to I, the exact reaction mechanism[5] is not clear since it was impossible to determine the fate of the collidine portion, which constituted a black semi-solid.



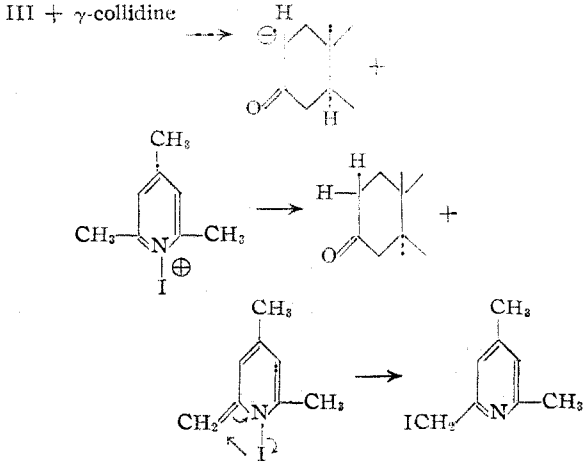
It is of interest to note that all the 2-iodo-3-keto*allo*steroids (III) exhibited remarkably high absorption in the ultraviolet (maxima at 256–258 mμ, log E *ca.* 2.9), while the corresponding bromo ketones (II) show only weak maxima (log E *ca.* 1.6) at 285 mμ in agreement with the extinction observed for certain brominated derivatives of 6- and 7-ketocholestanyl acetate.[6]

When 2,4-dibromo-3-keto*allo*steroids (IV, R = O, $COOCH_3$, $OCOC_6H_{11}$) were subjected to the same reaction conditions (five to twenty hours boiling with sodium iodide in acetone solution), a crystalline monoiodo derivative was isolated with an ultraviolet absorption maximum at 242–244 mμ, characteristic of Δ^4-3-ketones. The structure of the product was shown to be that of a 2-iodo-Δ^4-3-ketosteroid (VI), since the latter was readily deiodinated with collidine, dimethylaniline, chromous chloride[7] or zinc dust to yield the known Δ^4-3-ketosteroids. It should be noted that 2-bromo-Δ^4-3-ketosteroids on boiling with collidine suffer dehydrobromination[3] to give 1,4-dien-3-ones. The conversion of the 2,4-dibromo-*allo* ketone IV to the Δ^4-3-ketone VII can be accomplished in approximately 60% over-all yield without isolation of intermediates, *thus constituting a general synthesis of the important Δ^4-3-ketone moiety (VII) from 3-ketoallosteroids (I).* The mild reaction conditions have proved equally applicable to the sensitive 17-hydroxy-20-ketones of the *allo*pregnane series.[8] In certain instances the isolation of the intermediate 2-iodo-Δ^4-3-ketosteroids (VI) may be of interest in tracer work with isotopic iodine.

Reduction of the reflux time in the reaction of 2,4-dibromoandrostan-17-ol-3-one 17-hexahydrobenzoate (IV, R = $OCOC_6H_{11}$) with sodium iodide to fifty minutes led to a saturated compound, containing iodine and exhibiting a maximum at 258 mμ (typical of III), which gave a correct analysis for a monobromo-monoiodo derivative $C_{26}H_{38}O_3BrI$. Reduction with chromous chloride afforded the saturated ketone I, while short boiling with collidine resulted in the formation of the

(4) Schwenk and Whitman, THIS JOURNAL, **59**, 948 (1937); Jacobsen, *ibid.*, **62**, 1620 (1940); *cf.* however ref. 14.

(5) Dr. Gilbert Stork, Harvard University, in a personal communication, has suggested the following interesting mechanism:



(6) Barr, Heilbron, Jones and Spring, *J. Chem. Soc.*, 334 (1938).

(7) Julian, Cole, Magnani and Meyer, THIS JOURNAL, **67**, 1728 (1945).

(8) Rosenkranz, Kaufmann, Pataki and Djerassi, *ibid.*, **72**, 1046 (1950).

Δ^4-3-ketone VII. Since the C-2 bromine atom is readily replaced by iodine, which in turn is reduced by collidine, while the C-4 bromine atom in 2,4-dibromo-3-keto*allo*steroids (IV) is known to be removed in the form of hydrogen bromide by collidine in a few minutes,[8] it seems most likely that the substance $C_{26}H_{38}O_3BrI$ possesses structure V, *i. e.*, that of a 2-iodo-4-bromo derivative. The isolation of V is of considerable importance in a consideration of the mechanism of the reaction IV→VI. When boiled alone with acetone, V yields a tar exhibiting an ultraviolet absorption maximum at 236 mμ; prior addition of sodium iodide however leads to the expected VI and thence by reduction to the Δ^4-3-ketone VII.

The configuration of the C-4 bromine atom in 2,4-dibromo-3-keto*allo*steroids (IV) is known[3] to be β and is thus favorable to a *trans* elimination of hydrogen bromide. The absolute configuration (with respect to the C-5 hydrogen atom) of the C-2 iodine atom is unknown, but if properly situated the latter could be visualized as acting as an internal base. The above cited experiments render this possibility somewhat unlikely, but a variation of this same mechanism can be postulated since there is a large excess of iodide ion present in the reaction medium, which, acting as an external base, can apparently approach the C-5 hydrogen atom sufficiently closely. An alternate path would be through a 2,4-diiodo derivative, formed from V, but such a substance would of necessity possess the 4α-iodo configuration and thus involve *cis*-elimination, possibly by thermal loss of the elements of hydrogen iodide.

It should be pointed out that 4-bromo-3-ketosteroids of the *normal* series (VIII) were recovered completely unchanged on refluxing with sodium iodide in acetone.[9] While the configuration of the C-4 bromine atom in VIII is not known with certainty, it is probably α and the failure to react with sodium iodide (either with formation of a 4-iodo-3-ketone or a Δ^4-3-ketosteroid) may be due to steric effects only, which do not allow close rearward approach to either the bromine or the hydrogen atom (at C-5).

Experimental[10,11]

2-Iodo-3-keto*allo*steroids (III).—A solution of 4 g. of the 2-bromo-3-keto*allo*steroids (II) in 100 cc. of acetone was refluxed with 4.8 g. of sodium iodide for five and one-half hours, at which time a slight iodine color was noted, which was discharged completely by the addition of sodium thiosulfate solution. The product either crystallized at this point or was precipitated by the addition of water and recrystallized from a mixture of chloroform and ethanol. All of the iodo compounds described in this paper developed a pink color on standing in chloroform solution. Ethyl methyl ketone could be employed instead of acetone, and while refluxing for one hour was insufficient, shaking at room temperature for forty-four hours gave satisfactory results.

2-Bromocholestan-3-one[12] afforded 90% of **2-iodocholestan-3-one** as colorless, long needles, m. p. 125–127° (dec.), 133–136° (Kofler), $[\alpha]^{20}D$ +40°, u. v. maximum at 258 mμ (log E 2.91).

Anal. Calcd. for $C_{27}H_{45}OI$: C, 63.27; H, 8.85; I, 24.76. Found: C, 63.41; H, 8.62; I, 24.87.

2-Iodoandrostane-3,17-dione was obtained in 77% yield as colorless needles from 2-bromoandrostane-3,17-dione[13] and possessed the following constants: m. p. 135–137° (dec.), 140–144° with brown color developing at 112° (Kofler), $[\alpha]^{20}D$ +79°, u. v. maximum at 256 mμ (log E 2.85).

Anal. Calcd. for $C_{19}H_{27}O_2I$: C, 55.08; H, 6.57; I, 30.63. Found: C, 55.33; H, 6.63; I, 30.58.

Methyl 2-iodo-3-ketoetio*allo*cholanate was isolated as long needles (ethanol) in 76% yield from the corresponding 2-bromo derivative[14]; m. p. 136–138° (dec.), $[\alpha]^{20}D$ +82°, u. v. maximum at 256 mμ (log E 2.99).

Anal. Calcd. for $C_{21}H_{31}O_3I$: C, 55.02; H, 6.82; I, 27.69. Found: C, 55.25; H, 6.45; I, 27.87.

Collidine Treatment of 2-Iodocholestan-3-one (III, R = C_8H_{17}).—A solution of 0.8 g. of 2-iodocholestan-3-one was refluxed for thirty minutes with 5 cc. of collidine, during which time a dark sludge separated. After partitioning between ether and dilute acid, and washing of the organic layer with dilute acid, carbonate solution, thiosulfate and water, the nearly colorless ethereal extract was dried, evaporated and the residue was purified by chromatography on alumina. Recrystallization of the hexane–benzene (75/25) eluates from methanol afforded 66–70% of pure cholestan-3-one (I, R = C_8H_{17}), m. p. 127–129°, undepressed on admixture with an authentic specimen, $[\alpha]^{20}D$ +44°. A similar reaction with 2-iodoandrostane-3,17-dione led to androstane-3,17-dione, m. p. 130–132°.

2-Iodo-Δ^4-ketosteroids (VI) from 2,4-Dibromo-3-keto*allo*steroids (IV).—The reaction of 2,4-dibromo-3-keto*allo*steroids with sodium iodide was carried out exactly as described above for the 2-monoiodo derivatives except that it was more advantageous to prolong the reflux period to twenty hours. In these experiments, a very strong iodine color developed, regardless of whether the reaction was carried out in an atmosphere of nitrogen. The 2-iodo-Δ^4-3-ketones were relatively sensitive to various manipulations, *viz.*, the importance of using peroxide-free ether in extractions, and the yields given below refer to *pure crystalline* material only and are not an accurate indication of the total yield. As is indicated in the appropriate experimental sections, it is neither necessary nor desirable to purify the intermediate 2-iodo-Δ^4-3-ketones if the purpose of the experiment is to convert a 3-keto*allo*steroid into the corresponding Δ^4-3-ketone.

2,4-Dibromoandrostane-3,17-dione[15] led in 40% yield to 2-iodo-Δ^4-androstene-3,17-dione; colorless prisms from methanol–chloroform, m. p. 122–128° (dec.) turning brown at 112° (Kofler), $[\alpha]^{20}D$ +139°, u. v. maximum at 242 mμ (log E 4.17).

Anal. Calcd. for $C_{19}H_{25}O_2I$: C, 55.35; H, 6.11; I, 30.78. Found: C, 55.28; H, 6.25; I, 30.97.

Methyl 2-Iodo-Δ^4-3-ketoetiocholenate was obtained in 27% yield from the corresponding 2,4-dibromo derivative[14]

(9) 2-Bromo-Δ^4-androstene-3,17-dione also was found to be resistant toward sodium iodide.

(10) All melting points are uncorrected and determined in capillaries, unless marked Kofler, which were taken on the Kofler block and are corrected. Rotations were determined in chloroform solution and ultraviolet absorption spectra in 95% ethanol. The melting points of all the iodo derivatives described in this paper were very uncharacteristic, since they represented decomposition points, which varied considerably, depending on the rate of heating, the temperature at which the capillary was inserted and whether the determination was carried out in a capillary or in the Kofler block. Rotations and analyses proved to be the only reliable criteria.

(11) We are indebted to the Srtas. Paquita Revaque and Ann Rochman for the rotations and spectra. The C and H analyses were carried out in our Microanalytical Department under the direction of Srta. Amparo Barba, while the iodine analyses are due to Mr. Joseph F. Alicino, Metuchen, New Jersey.

(12) Butenandt and Wolff, *Ber.*, **68**, 2091 (1935).

(13) Butenandt and Dannenberg, *ibid.*, **69**, 1158 (1936).

(14) Djerassi and Scholz, THIS JOURNAL, **69**, 2404 (1947).

(15) Djerassi and Scholz, *J. Org. Chem.*, **13**, 697 (1948).

and crystallized from hexane–acetone; m. p. 128–130° (dec.), $[\alpha]^{20}D$ +164°, u. v. maximum at 244 mμ (log E 4.30).

Anal. Calcd. for $C_{21}H_{29}O_3I$: C, 55.27; H, 6.41; I, 27.81. Found: C, 55.51; H, 6.21; I, 27.54.

2,4-Dibromoandrostan-17-ol-3-one 17-hexahydrobenzoate[16] gave 36% of colorless crystals of **2-iodotestosterone hexahydrobenzoate** from ethanol–chloroform; m. p. 145–147° (dec.), $[\alpha]^{20}D$ +80°, u. v. maximum at 242 mμ (log E 4.24).

Anal. Calcd. for $C_{26}H_{37}O_3I$: C, 59.54; H, 7.11; I, 24.20. Found: C, 60.03; H, 7.07; I, 23.73.

2-Iodo-4-bromoandrostan-17-ol-3-one 17-Hexahydrobenzoate (V, R = $OCOC_6H_{11}$).—A solution of 3 g. of 2,4-dibromoandrostan-17-ol-3-one 17-hexahydrobenzoate and 3.6 g. of sodium iodide in 100 cc. of ethyl methyl ketone was refluxed in a current of nitrogen for fifty minutes and then cooled in ice whereupon crystallization commenced. After addition of thiosulfate and water, the product was filtered (3.02 g., 93%) and recrystallized *quickly* twice from acetone, since prolonged heating caused decomposition. The analytical sample was colorless and possessed m. p. 130–142° (dec.), 146–149° (Kofler), $[\alpha]^{20}D$ +13°, u. v. maximum at 258 mμ (log E 2.96). A strongly positive iodine test was observed after sodium fusion.

Anal. Calcd. for $C_{26}H_{38}O_3BrI$: C, 51.58; H, 6.33. Found: C, 51.71; H, 6.35.

Reactions of 2-Iodo-4-bromoandrostan-17-ol-3-one 17-Hexahydrobenzoate (V, R = $OCOC_6H_{11}$). **A. In Acetone Solution.**—When 0.4 g. of the above iodo-bromo derivative was refluxed with 20 cc. of acetone, the solution assumed a progressively darker and finally black color, which was not discharged by the addition of thiosulfate. After the usual work-up, a black tarry residue was obtained which exhibited a maximum at 236 mμ. Repetition of this reaction in the presence of 0.4 g. of sodium iodide gave a nearly colorless oil (maximum at 242 mμ), which was not crystallized, but was converted directly to testosterone hexahydrobenzoate (m. p. 120–122°) in 60% over-all yield on chromous chloride reduction.

B. **Chromous Chloride Reduction.**—The reduction of the iodo-bromo derivative with chromous chloride was carried out by the procedure given below but entailed considerable losses in view of the notorious difficulty[17] of purifying the product; dihydrotestosterone 17-hexahydrobenzoate,[16,17] m. p. 158–160° was isolated in 33% yield.

C. **Collidine Treatment.**—One-half gram of iodo-bromo compound was refluxed with 5 cc. of collidine and after the usual work-up, including chromatography, afforded 0.15 g. (49%) of testosterone hexahydrobenzoate,[14] m. p. 121–123°, $[\alpha]^{20}D$ 80°, u. v. maximum at 240 mμ (log E 4.21).

Deiodination of 2-Iodo-Δ^4-3-ketosteroids (VI).—The products of the reductions, Δ^4-androstene-3,17-dione with m. p. 169–171°, $[\alpha]^{20}D$ +189°, u. v. maximum at 241 mμ (log E 4.30), and testosterone hexahydrobenzoate m. p. 126–127°, $[\alpha]^{20}D$ +88°, u. v. maximum at 241 mμ (log E 4.31), were identified in each instance by all three physical constants (m. p., rotation, spectrum), but will not be reported below for simplicity's sake.

A. **With Tertiary Amines.**—In each instance, 0.6 to 0.8 g. of 2-iodo-Δ^4-androstene-3,17-dione was refluxed with 5 cc. of amine for thirty minutes, whereupon the solutions turned very dark and then worked up as given above for 2-iodocholestanone. Collidine gave 45% of pure Δ^4-androstene-3,17-dione, dimethylaniline afforded 43% of colored product which required several recrystallizations for complete purification (24%), while pyridine gave a very impure product even after chromatographing.

B. **With Zinc Dust.**—A mixture of 0.5 g. of iodo compound, 7 cc. of dioxane, 30 cc. of ethanol and 5 g. of zinc dust was refluxed for seven hours, filtered, evaporated and crystallized; yield 56% of Δ^4-3-ketosteroid.

C. **With Chromous Chloride.**—Since a detailed method for the preparation of chromous chloride solutions for reduction of brominated steroids[7] is lacking, the following procedure, based on the work of Conant and Cutter,[18] is given in detail: Amalgamated zinc dust (all other types of zinc gave inferior results) was prepared by shaking vigorously 10 g. of zinc dust, 0.8 g. of mercuric chloride, 10 cc. of water and 0.5 cc. of concd. hydrochloric acid for five minutes and decanting the supernatant liquid. After addition of 20 cc. of water and 2 cc. of concd. hydrochloric acid, 5 g. of chromic chloride was added in portions with swirling in a current of carbon dioxide. The dark blue solution was kept under carbon dioxide until ready for use.

One gram of 2-iodo-Δ^4-3-ketosteroid (VI) was dissolved in 50–100 cc. of acetone and treated under carbon dioxide in portions with *ca.* 20 cc. of chromous chloride solution. After ten to thirty minutes, water was added, the product was filtered or extracted with ether and recrystallized. In a number of experiments, the yield of pure Δ^4-3-ketone ranged from 60–63%. For practical purposes in the conversion of 3-keto*allo*steroids to Δ^4-3-ketones, the intermediate 2-iodo-Δ^4-3-ketone need not be isolated, but the crude material (from direct filtration or evaporation of an ether extract) from the sodium iodide reaction is treated immediately with chromous chloride. The over-all yield of Δ^4-3-ketosteroid VII from 2,4-dibromo-3-keto*allo*steroid IV was consistently 50–60%.

Summary

2-Bromo-3-keto*allo*steroids, in contrast to 4-bromo-3-ketosteroids of the *normal* series, react readily with sodium iodide in acetone solution to afford the corresponding 2-iodo ketones. When refluxed with γ-collidine, deiodination occurs and the saturated 3-keto*allo*steroid is regenerated.

Application of these observations to 2,4-dibromo-3-keto*allo*steroids has resulted in a new method for the conversion of 3-keto*allo*steroids to Δ^4-3-ketosteroids. Short treatment of the 2,4-dibromo ketones with sodium iodide yields 2-iodo-4-bromo derivatives, which on boiling with collidine suffer simultaneous deiodination and dehydrobromination, thus leading directly to Δ^4-3-ketosteroids. Longer boiling with sodium iodide affords 2-iodo-Δ^4-3-ketosteroids, which can be deiodinated with collidine, chromous chloride or zinc dust to the desired Δ^4-3-ketosteroids.

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(16) Wilds and Djerassi, THIS JOURNAL, **68**, 2125 (1946).

(17) Ruzicka and Kägi, *Helv. Chim. Acta*, **20**, 1557 (1937).

(18) Conant and Cutter, THIS JOURNAL, **48**, 1016 (1926).