pared by the method of Page and Pinder.[4] Its noted[23] instability precluded accurate microanalysis.

**Reduction of 2-Carboethoxy-2-azabicyclo[2.2.2]octan-5-one (XX) to 2-Carboethoxy-2-azabicyclo[2.2.2]octane (X).**—2-Carbethoxy-2-azabicyclo[2.2.2]octan-5-one (500 mg., 2.5 mmoles) was placed in a Parr shaker bottle containing platinic oxide (83.62%) (*ca.* 1 g.), aqueous hydrochloric acid (30 ml., 2 *N*), and ethanol (30 ml.) and was hydrogenated at 26 p.s.i. overnight.

The catalyst was removed by filtration through Celite and the filtrate was evaporated to dryness. The residue was partitioned between ether and water (50 ml. each) and the aqueous phase was washed with a fresh portion (50 ml.) of ether. The combined ether phases were washed with dilute hydrochloric acid (6 *N*), dilute sodium hydroxide (10%), and water. Evaporation yielded 2-carbethoxy-2-azabicyclo[2.2.2]octane (X, 211.4 mg.) identical with that prepared by direct reduction of 2-carboethoxy-2-azabicyclo[2.2.2]oct-5-ene (VII).

Soxhlet extraction of the catalyst with methanol yielded 265.3 mg. of colorless oil, the infrared spectrum of which, in chloroform, closely resembled the mixture of alcohols XVIII and XIX. This material was not further investigated.

(23) I. G. Morris and A. R. Pinder, *J. Chem. Soc.*, 1841 (1963).

**Acknowledgment.**—One of us (D. R. D.) gratefully acknowledges financial support in the form of a Public Health Service Fellowship (7-F2-GM-14,470-01A1) from the National Institutes of General Medical Sciences.

# Steroids. IV. A Synthetic Route to A-Bisnorsteroids[1]

M. P. CAVA AND B. R. VOGT

*Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210*

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A-Bisnorcholestan-1-one (XXIII) and several other 1-substituted cholestanes have been synthesized, starting with cholestan-1-one. The multistep reaction sequence included, as key steps, the photolytic Wolff rearrangement of 2-diazocholestan-1-one and 2-diazo-A-norcholestan-1-one.

A number of modified steroids are known in which one of the four rings is contracted by one carbon atom relative to the normal tetracyclic steroid nucleus.[2] We now wish to report the synthesis of some A-bisnorcholestane derivatives which represent the first examples of steroids containing a four-membered A-ring. The synthetic route employed, starting with the readily available cholest-1-en-3-one (I), represents a sequence of general applicability for the preparation of other 1-substituted A-bisnorsteroids, as well as an improved route to steroidal A-nor-1-ketones.

Cholest-1-en-3-one (I) was converted *via* the corresponding 1$\alpha$,2$\alpha$ epoxide (II)[3] to cholest-2-en-1$\alpha$-ol (III) by use of the general method of Wharton.[4,5] Mild chromic acid oxidation of III using the general method of Brown[6] afforded the corresponding ketone (IV). The over-all yield in the conversion of cholest-1-en-3-one to cholest-2-en-1-one was as high as 50%. Catalytic reduction of IV gave cholestan-1-one (V). Base-catalyzed oximination of cholestan-1-one (V) afforded, in 70% yield, *anti*-2-oximinocholestan-1-one (VI), m.p. 198–201° dec. The *anti* configuration was assigned to oximino ketone VI on the basis of its reaction with divalent copper and cobalt ions,[7] as well as on the basis of the bathochromic shift of its ultraviolet spectrum which was observed in alkaline solution.[8]

Oximino ketone VI was converted to the corresponding $\alpha$-diazo ketone by means of the Forster reaction.[9] Thus, oximino ketone VI reacted with chloramine to give, in 78% yield, 2-diazocholestan-1-one (VII), m.p. 98–100°. Diazo ketone VII underwent a photolytic Wolff rearrangement when irradiated in aqueous tetrahydrofuran containing sodium bicarbonate. The acidic reaction product, m.p. 198–201°, obtained in 63% yield, was assigned the structure 1$\beta$-carboxy-A-norcholestane (VIII). Esterification of VIII with diazomethane afforded 1$\beta$-carbomethoxy-A-norcholestane (IX), isolated as an oil. Treatment of the nor acid (VIII) with lithium aluminum hydride in tetrahydrofuran provided, in 60% yield, 1$\beta$-hydroxymethyl-A-norcholestane (X), m.p. 104–105°.

The carboxyl group of acid VIII was expected to have the $\beta$ configuration on mechanistic grounds, since hydration of the intermediate ketene formed in the photolysis reaction should take place from the less hindered $\alpha$ side of the molecule.[10] Chemical confirmation of the stereochemistry of acid VIII was obtained by converting it into the previously described[11] 1$\beta$-amino-A-norcholestane (XI) *via* a Schmidt reaction, a transformation which is known to proceed with retention of configuration.[12] Amine XI was obtained in this manner in 89% yield as a crystalline solid, m.p. 93–95°, although it had been described previously only as an oil; synthesis of XI by the previously described procedure [lithium aluminum hydride reduction of 1-oximino-A-norcholestane (XII)] afforded, in our hands,

(1) (a) For a preliminary communication of a portion of these results, see M. P. Cava and B. R. Vogt, *Tetrahedron Letters*, **No. 39**, 2813 (1964), which is considered to be part III of this series. (b) Reprints may be obtained from M. P. Cava at the Department of Chemistry, Wayne State University, Detroit, Mich.

(2) For examples involving rings A, B, C, and D, respectively, see (a) H. R. Nace and D. H. Nelander, *J. Org. Chem.*, **29**, 1677 (1964); (b) F. Šorm and H. Dykova, *Collection Czech. Chem. Commun.*, **13**, 407 (1948); (c) N. L. Wendler, R. F. Hirschmann, H. R. Slates, and R. W. Walker, *J. Am. Chem. Soc.*, **77**, 1632 (1955); (d) M. P. Cava and E. Moroz, *ibid.*, **84**, 115 (1962).

(3) P. Streibel and C. Tamm, *Helv. Chim. Acta*, **37**, 1094 (1954).

(4) P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).

(5) The conversion of II to III by Wharton's method was reported independently during the course of our investigation: C. Djerassi, D. H. Williams, and B. Berkoz, *ibid.*, **27**, 2205 (1962). Details of our procedure, however, are reported in the Experimental Section of this paper since they appear to represent both in yield and in work-up an improvement over the previously published procedure.

(6) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(7) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, Oxford, 1937, pp. 195–196.

(8) (a) D. H. R. Barton and J. Beaton, *J. Am. Chem. Soc.*, **83**, 4083 (1961); (b) A. Hassner and I. H. Pomerantz, *J. Org. Chem.*, **27**, 1760 (1962).

(9) For some recent examples of the use of this reaction as well as some earlier references, see M. P. Cava and P. M. Weintraub, *Steroids*, **4**, 41 (1964).

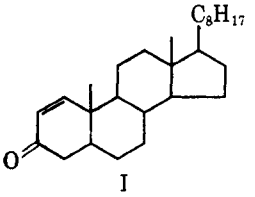
(10) For a more detailed discussion of this point, see J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 5445 (1960).

(11) C. W. Shoppee, S. K. Roy, and B. S. Goodrich, *J. Chem. Soc.*, 1583 (1961).

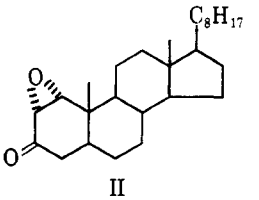
(12) A. Campbell and J. Kenyon, *ibid.*, 26 (1946).

crystalline amine XI, identical with the material obtained from the Schmidt reaction.

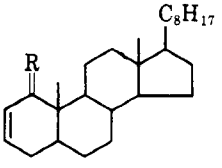
Treatment of noramine XI with 1 equiv. of *t*-butyl hypochlorite in ether, followed by boiling with sodium ethoxide in ethanol, and finally hydrolysis with 10% sulfuric acid, gave, in 73% yield, the known A-norcholestan-1-one (XIII), m.p. 73–74°.[13,14] In view of the present ease of preparation of cholestan-1-one, the reaction sequence described above affords a considerably more convenient route to A-norcholestan-1-one than those previously reported.[11,13,15]



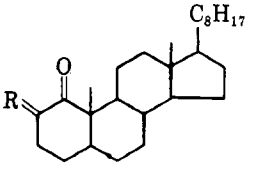
I



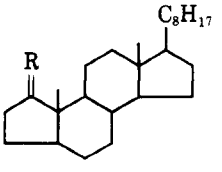
II



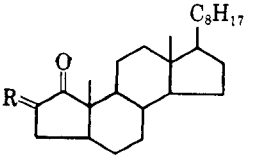
III, R = H, OH
IV, R = O



V, R = H, H
VI, R = NOH
VII, R = $N_2$



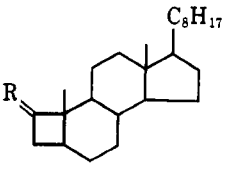
VIII, R = H, $CO_2H$
IX, R = H, $CO_2CH_3$
X, R = H, $CH_2OH$
XI, R = H, $NH_2$
XII, R = NOH
XIII, R = O



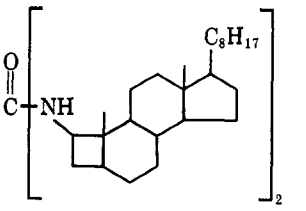
XIV, R = NOH
XV, R = $N_2$

The reaction sequence employed in the conversion of cholestan-1-one to A-norcholestan-1-one was found to be applicable, in somewhat modified form, to the synthesis of A-bisnorcholestan-1-one (XXIII) from its cyclopentanone analog XIII. Treatment of norketone XIII with *n*-butyl nitrite and potassium *t*-butoxide gave *syn*-2-oximino-A-norcholestan-1-one (XIV) as an amorphous solid. The *syn* configuration was assigned to the oximino ketone on the basis of the failure of the oximino ketone to form colored metal complexes[7] and on the basis of the fact that its ultraviolet spectrum failed to shift bathochromically upon addition of alkali.[8]

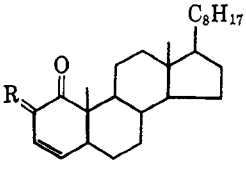
The Forster reaction of the oximino norketone (XIV) with chloramine in aqueous ether proceeded satisfactorily to give, in 63% over-all yield (based on norketone XIII), 2-diazo-A-norcholestan-1-one (XV), m.p. 102–104°. Irradiation of diazo ketone XV in aqueous tetrahydrofuran containing sodium bicarbonate afforded,i n 32% yield, 1β-carboxy-A-bisnorcholestane (XVI), m.p. 165–167°. Acid XVI probably has the β configuration, as would be expected on mechanistic grounds[10]; definite proof of the stereochemistry of the carboxyl group in this molecule must await further investigation. Acid XVI reacted with diazomethane to give the corresponding methyl ester XVII as a low-melting solid, m.p. 34–36°; attempted epimerization of the ester with hot ethanolic sodium ethoxide, followed by alkaline hydrolysis, afforded a slightly impure sample of acid XVI in 56% yield as the only product that could be isolated. Lithium aluminum hydride reduction of XVI in tetrahydrofuran afforded, in 74% yield, 1β-hydroxymethyl-A-bisnorcholestane (XVIII), m.p. 104–105°.



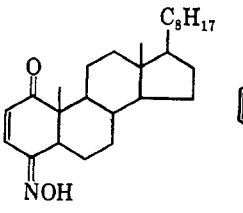
XVI, R = H, $CO_2H$
XVII, R = H, $CO_2CH_3$
XVIII, R = H, $CH_2OH$
XX, R = H, $CON_3$
XXI, R = H, $NHCO_2CH_2C_6H_5$
XXII, R = H, $NH_2$
XXIII, R = O



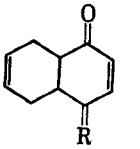
XIX



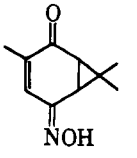
XXIV, R = NOH, *anti*
XXV, R = NOH, *syn*
XXX, R = $N_2$



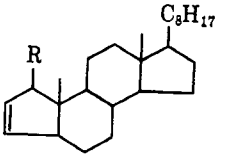
XXVI



XXVII, R = O
XXVIII, R = NOH



XXIX



XXXI, R = H, $CO_2H$
XXXII, R = H, $CH_2OH$

Degradation of the carboxyl to an amino function presented greater difficulties in the A-bisnor series than in the A-nor series. Thus, attempts to degrade acid XVI by way of the Schmidt reaction afforded only an oil from which no crystalline product could be isolated. Conversion of acid XVI into 1β-amino-A-bisnorcholestane (XXII) was then attempted, using the Lindemann modification[16] of the Curtius reaction; the only product isolated from this reaction was a high-melting solid, the infrared spectrum of which was consistent with the urea formulation (XIX) corresponding to the desired amine. Amine XXII was successfully prepared from bisnor acid XVI using the benzylurethan variant of the Curtius procedure. Thus, acid XVI was converted *via* its acid chloride to the corresponding azide XX which was decomposed thermally in the presence of benzyl alcohol. The resulting benzylurethan (XXI), obtained in excellent over-all yield (82%, based on the acid), underwent hydrogenolysis in methanolic hydrogen chloride solution to give amine XXII, characterized as the nicely crystalline hydrochloride.

(13) H. P. Sigg and Ch. Tamm, *Helv. Chim. Acta*, **43**, 1402 (1960).

(14) For earlier examples of the conversion of an amine to the corresponding ketone by this type of chloramine degradation, see W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Am. Chem. Soc.*, **76**, 5554 (1954).

(15) B. Fuchs and H. J. E. Loewenthal, *Tetrahedron*, **11**, 199 (1960).

(16) H. Lindemann, *Helv. Chim. Acta*, **11**, 1027 (1928).

The chloramine degradation of bisnoramine XXII was carried out in a manner similar to that used with noramine XI. Although this degradative method proceeded much less smoothly in the four-membered series, the desired A-bisnorcholestan-1-one (XXIII), m.p. 93–95°, was obtained in moderate yield (22%). The cyclobutanone-type carbonyl in this compound was observed in the infrared at 5.65 $\mu$, a value almost identical with that observed for the similar carbonyl function of D-norandrostane-3,16-dione.[17]

It was of some interest to determine the position of oximination in cholest-2-en-1-one (IV), since introduction of an oximino function could take place at either C-2 or C-4. Base-catalyzed oximination of cholest-2-en-1-one gave an amorphous solid which, after chromatography on silica gel, afforded, in 48% yield, the crystalline *anti*-2-oximinocholest-3-en-1-one (XXIV). The assignment of structure XXIV to this oximino ketone is in accord with the shift of its ultraviolet maximum from 260 to 308 m$\mu$ upon the addition of base. More significantly, compound XXIV afforded colored complexes with both cupric and cobaltous ions; this observation cannot be rationalized with either the isomeric *syn*-2-oximino ketone structure (XXV) or the 4-oximinocholest-2-en-1-one (XXVI) structure. It may be noted that a second oximination product of ketone IV was also obtained, but in very low yield (*ca.* 3%). This compound analyzed fairly well as an isomer of oximino ketone XXIV, although its high melting point (>300°) suggested that it might be dimeric; this material was not investigated further because of the small quantity available.

Although the vinylogous oximino ketone, 4-oximinocholest-2-en-1-one (XXVI), was not encountered in the reaction described above, a spectral model for a compound of this type was prepared. Thus, the readily prepared diketone XXVII[18] was converted into the corresponding crystalline monooxime XXVIII by reaction with 1 equiv. of hydroxylamine hydrochloride in the presence of sodium acetate. This vinylogous oximino ketone shows ultraviolet absorption bands at 220 and 282 m$\mu$, which are shifted in the presence of alkali to 235 and 346 m$\mu$, respectively. The ultraviolet absorption of the known 3-caren-2,5-dione 2-oxime (XXIX)[19] proved to be quite similar to that of compound XXVIII, except for an expected bathochromic shift due to the presence of the C-4 methyl group and the fused cyclopropane ring. Thus, vinylogous oximino ketone XXIX absorbed at 225 and 298 m$\mu$ in the absence of base, and at 244 and 260 m$\mu$ in the presence of base. These spectral characteristics were different from those of the products isolated from the oximination of cholest-2-en-1-one. The reaction of *anti*-2-oximinocholest-3-en-1-one with chloramine furnished the unsaturated diazo ketone, 2-diazocho est-3-en-1-one (XXX), as red-orange crystals of only moderate stability. Irradiation of 2-diazocholest-3-en-1-one (XXX) afforded the crystalline unsaturated acid, 1$\beta$-carboxy-A-norcholest-2-ene (XXXI). The unsaturated nor acid XXXI was not contaminated with any of the isomeric $\alpha,\beta$-unsaturated acid, as was evidenced by its lack of any appreciable ultraviolet absorption at 222 m$\mu$ characteristic of $\alpha,\beta$-unsaturated cyclopentenecarboxylic acids.[20] Acid XXXI was further characterized by lithium aluminum hydride reduction to 1$\beta$-hydroxymethyl-A-norcholest-2-ene (XXXII). The assigned stereochemistry of the unsaturated acid (XXXI) was confirmed by its catalytic reduction to 1$\beta$-carboxy-A-norcholestane (VIII).

(17) J. Meinwald, G. G. Curtis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 116 (1962).

(18) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

(19) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **78**, 174 (1956).

## Experimental Section[21]

**1$\alpha$,2$\alpha$-Oxidocholestan-3-one (II).**—Cholest-1-en-3-one[22] (10.00 g., 0.026 mole) was dissolved in methanol (1080 ml.). The temperature of the stirred solution was brought to 29° and 5 *N* aqueous sodium hydroxide solution (5.5 ml.) was added, followed by 30% hydrogen peroxide (35 ml.). Precipitation of the product commenced approximately 2 min. after addition of the hydrogen peroxide. After 15 min., the reaction vessel was cooled in an ice–salt bath and diluted with 40 ml. of water. The product was separated by filtration and dried *in vacuo* to give 7.80 g. (75%) of white crystals melting at 122–124° (cor.). Recrystallization from ether–absolute ethanol gave white platelets, m.p. 126–127° (cor.) (lit.[3] m.p. 123–124°).

**Cholest-2-en-1$\alpha$-ol (III).**—A mixture of 1$\alpha$,2$\alpha$-oxidocholestan-3-one (10.0 g., 0.025 mole), hydrazine sulfate (20 g., 0.153 mole), and 100% hydrazine hydrate (60 ml., 1.23 mole) was stirred under reflux for 20 min. The reaction mixture was cooled and diluted with water (100 ml.) and the aqueous phase was extracted with three 60-ml. portions of ether. The combined ether extracts were dried over sodium sulfate and evaporated *in vacuo* to an oil which was chromatographed on Woelm neutral alumina (activity III, 100 g.) with benzene. The first fraction (125 ml.) was evaporated to dryness *in vacuo* to give 7.2 g. (74%) of a light yellow solid which was recrystallized from acetone and ether, in that order, to give white needles, m.p. 92–103°, $[\alpha]^{25}D$ +127° (*c* 1.02) [lit.[5] double m.p. 90–92° and 103–104°, $[\alpha]D$ +124° (*c* 1.4)].

**Cholest-2-en-1-one (IV).**—A solution of cholest-2-en-1$\alpha$-ol (6.8 g., 0.017 mole) in ether (50 ml.) was stirred and cooled in an ice bath and treated with 8.8 ml. of a solution containing 5.0 g. of sodium dichromate dihydrate and 3.75 ml. of concentrated sulfuric acid diluted to 25 ml. with water. After 40 min. the cooling bath was removed and the reaction mixture was stirred at room temperature for an additional 1.5 hr. The aqueous phase was separated and extracted with two 15-ml. portions of ether and the combined ether extracts were washed with two 50-ml. portions of saturated sodium bicarbonate solution, dried over magnesium sulfate, treated with charcoal, filtered through Celite, and evaporated to an oil. The oil was crystallized from methanol to give 5.1 g. (75%) of white prisms, m.p. 68–69°, $[\alpha]^{26}D$ +134° (*c* 0.98) (lit.[3] m.p. 69–70°, lit.[5] $[\alpha]D$ +128°).

**Cholestan-1-one (V).**—Cholest-2-en-1-one (15.26 g., 0.039 mole) dissolved in ethyl acetate (100 ml.) was hydrogenated in a Parr apparatus at ambient temperature under 40-p.s.i. hydrogen pressure in the presence of 1.5 g. of 5% palladium on charcoal. At the end of 2 hr. the solution was filtered through Celite and the solvent was removed to give 14.9 g. (98%) of the product, which was not contaminated with starting material as shown by its infrared spectrum and melting point: m.p. 83–85°, $[\alpha]^{27}D$ +110° (*c* 0.91) [lit.[3] m.p. 85–86°, $[\alpha]^{24}D$ +112° (*c* 1.06)].

(20) O. H. Wheeler, *ibid.*, **78**, 3216 (1956).

(21) All melting points were determined on a Fisher-Johns apparatus and are uncorrected unless otherwise indicated. Infrared spectra were recorded on a Perkin-Elmer Model 137 sodium chloride spectrophotometer (potassium bromide pellets). Ultraviolet absorption spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer (95% ethanol solutions unless otherwise indicated); basic solutions were obtained by adding 0.1 *N* aqueous sodium hydroxide to the neutral solution. All optical rotations were taken in chloroform. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Detailed work-up procedures are given only for the first experiment of the following reactions: irradiation, oximination, diazotization, esterification, Schmidt reaction, chloramine degradation, and hydride reduction of acids. In addition, the standard drying agent used was magnesium sulfate (unless otherwise indicated) and solvents were removed on a rotary evaporator. Reactions were run at room temperature or cooled to room temperature unless otherwise indicated.

(22) Cholest-1-en-3-one was obtained from 2$\alpha$-bromocholestan-1-one *via* cholest-1-en-3-one 2,4-dinitrophenylhydrazone according to the method of J. Demaecker and R. H. Martin, *Bull. soc. chim. Belges*, **68**, 365 (1959).

*anti*-2-**Oximinocholestan-1-one** (VI).—A solution of cholestan-1-one (4.0 g., 9.7 mmoles) in dry *t*-butyl alcohol (60 ml.) was added to a stirred base solution prepared from potassium (2.0 g., 0.051 mole) and dry *t*-butyl alcohol (40 ml.). *n*-Butyl nitrite (2.4 ml., 0.022 mole) was added and the solution was stirred for 1 hr. under nitrogen; a second portion of *n*-butyl nitrite (1.0 ml., 0.009 mole) was added and the reaction was continued for an additional 2.5 hr. Water (300 ml.) was then added; the solution was acidified to pH 6 with 6 *N* hydrochloric acid and extracted with three 300-ml. portions of ether. The combined ether extracts were washed with two 45-ml. portions of saturated aqueous sodium bicarbonate solution, 100 ml. of saturated aqueous sodium chloride solution, and 50 ml. of saturated aqueous ammonium chloride solution, in that order, dried over magnesium sulfate, and evaporated to a yellow gel which was dried overnight *in vacuo*. Crystallization of the gel from absolute ethanol gave 2.34 g. of white prisms.

Further work with the mother liquor gave an additional 0.23 g. of the product. Thus, the solvent was removed from the mother liquor on a rotary evaporator and the residual gum was dissolved in chloroform and chromatographed on Davison silica gel (2 × 30 cm. column). The first fraction (chloroform), which was yellow, was rejected. Further development of the column with 1:9 ethyl acetate–chloroform gave a fraction which was evaporated to dryness *in vacuo*. Recrystallization of the residue from absolute ethanol gave an additional 0.23 g. of product (white prisms). The total weight of oximino ketone was 2.77 g. (65%): m.p. 197–200° dec.; $[\alpha]^{31}D$ +90.5° (*c* 1.31); $\nu_{max}$ 3.07, 5.85, 6.18, and 10.50 $\mu$; $\lambda_{max}^{neutral}$ 236 m$\mu$ ($\epsilon$ 6370), $\lambda_{max}^{basic}$ 290 m$\mu$ ($\epsilon$ 12,400).

*Anal.* Calcd. for $C_{27}H_{45}NO_2$: C, 78.02; H, 10.91; N, 3.37. Found: C, 77.92; H, 11.05; N, 3.42.

The metal complexes of the oximino ketone were studied by dissolving *ca.* 1 mg. of oximino ketone in 1–2 ml. of 95% ethanol and adding 1 drop of a 5% aqueous solution of the metal acetate. $Co^{+2}$ formed a yellow complex, while $Cu^{+2}$ formed a green complex

**2-Diazocholestan-1-one** (VII).—To a solution of *anti*-2-oximinocholestan-1-one (2.0 g., 4.82 mmoles) in tetrahydrofuran (6.8 ml.) was added 5 *N* sodium hydroxide (5.2 ml.), ether (100 ml.), and concentrated ammonium hydroxide (8 ml.). The reaction mixture was stirred under nitrogen and treated with 10 ml. of a 5.25% solution of sodium hypochlorite ("Clorox"), injected through a syringe cap. After 1.5 hr., more Clorox (10 ml.) was added and finally, 2.5 hr. after the first addition, a final 10-ml. portion of hypochlorite was injected. After 4.5-hr. total reaction time, the organic layer was separated and diluted with ether (25 ml.). The resulting ether solution was washed with four 25-ml. portions of water, dried over magnesium sulfate, and evaporated to a yellow oil which was dissolved in pentane and chromatographed on a column of Woelm neutral alumina (8 g., activity II). The column was developed with pentane until the eluate no longer appeared yellow. The eluate was evaporated to dryness *in vacuo* and the resulting yellow crystalline material was dried further under high vacuum. The product weighed 1.55 g. (78%). Recrystallization from ether–methanol provided the analytical sample, yellow needles, m.p. 98–100°, $[\alpha]^{31}D$ −0.22° (*c* 0.63), $\nu_{max}$ 4.85 and 6.17 m$\mu$, $\lambda_{max}^{dioxane}$ 276 m$\mu$ ($\epsilon$ 8890).

*Anal.* Calcd. for $C_{27}H_{44}NO_2$: C, 78.58; H, 10.75; N, 6.79. Found: C, 78.59; H, 10.99; N, 6.48.

**1β-Carboxy-A-norcholestane** (VIII).—To a solution of 2-diazocholestan-1-one (1.45 g., 3.2 mmole) in tetrahydrofuran (140 ml.) previously distilled from lithium aluminum hydride was added a solution of sodium bicarbonate (1.3 g.) in distilled water (75 ml.). The resulting mixture was irradiated under nitrogen for 30 min. with a 450-w. Hanovia medium-pressure lamp (quartz probe). The solution was acidified with 6 *N* hydrochloric acid, saturated with sodium chloride, and the resulting two-phase system was extracted with three 100-ml. portions of ether. The combined ether extracts were dried and evaporated to a gummy residue which gave white prisms weighing 0.89 g. (63%), m.p. 198–201°, on crystallization from acetone. Recrystallization from acetone gave the analytical sample, m.p. 202–203°, $[\alpha]^{31}D$ −22.6° (*c* 1.06), $\nu_{max}$ 5.86 and 3.1–4.0 $\mu$.

*Anal.* Calcd. for $C_{27}H_{46}O_2$: C, 80.54; H, 11.52. Found: C, 80.52; H, 11.49.

**1β-Carbomethoxy-A-norcholestane** (IX).—Crystalline 1β-carboxy-A-norcholestane (0.400 g., 0.962 mmole) was added to an ethereal solution of excess diazomethane. The reactants were allowed to stand overnight at room temperature and the solvent was then removed. The residue was chromatographed on Alcoa basic alumina (1 × 20 cm. column, activity II) with Skellysolve F (200 ml.). The norester was obtained as an oil and weighed 0.384 g. (92% yield). The product showed one spot ($R_f$ 0.3) on thin layer chromatography (silica gel, 20:1 cyclohexane–ethyl acetate), $[\alpha]^{27}D$ −23° (*c* 0.85), $\nu_{max}$ 5.77 and 8.67 $\mu$.

*Anal.* Calcd. for $C_{28}H_{48}O_2$: C, 80.71; H, 11.61. Found: C, 80.94; H, 11.36.

**1β-Hydroxymethyl-A-norcholestane** (X).—1β-Carboxy-A-norcholestane (0.253 g., 0.63 mmole) was treated with lithium aluminum hydride (0.700 g., 0.018 moles) in dry tetrahydrofuran (50 ml.) for 16 hr. Excess hydride was decomposed with saturated aqueous sodium sulfate solution. The resulting slurry was acidified with 6 *N* hydrochloric acid, saturated with sodium chloride, and extracted with two 50-ml. portions of ether. The combined ether extracts were washed with saturated aqueous salt solution (50 ml.) and dried. The solvent was removed and the residue was chromatographed on Woelm neutral alumina (15 g., activity II). The first fraction (30 ml. of 1:1 Skellysolve F–benzene) was discarded, but the second fraction (250 ml. of chloroform) was evaporated to yield an oil which was crystallized from acetone after treatment with charcoal. The resulting white needles weighed 0.136 g. (62%), m.p. 103–105°, $[\alpha]^{31}D$ −9.7° (*c* 1.35), $\nu_{max}$ 3.05 $\mu$.

*Anal.* Calcd. for $C_{27}H_{48}O$: C, 83.43; H, 12.45. Found: C, 83.83; H, 12.41.

**1β-Amino-A-norcholestane** (XI).—1β-Carboxy-A-norcholestane (4.5 g., 0.011 mole) was dissolved in chloroform (36 ml.). Concentrated sulfuric acid (18 ml.) was added and the reaction vessel was placed in an oil bath at 52°. Sodium azide (1.47 g., 0.022 mole) was added in small portions during 5–10 min. and the reaction mixture was then stirred under reflux for 2.5 hr. At the end of this time, the vessel was cooled and the contents were poured into a separatory funnel containing ice (*ca.* 100 g.). Chloroform (120 ml.) was added and the two-phased system was made strongly basic with 5 *N* sodium hydroxide. The aqueous layer was separated and washed with additional chloroform (first 200 ml., then 100 ml.). The combined chloroform extracts were washed with 70 ml. of 1:4 5 *N* aqueous sodium hydroxide solution–saturated aqueous sodium chloride solution. The aqueous layer was re-extracted with two 70-ml. portions of chloroform and the combined chloroform extracts were dried first over sodium sulfate and then over solid potassium hydroxide. The solvent was evaporated to give the light yellow product which was recrystallized from absolute ethanol. White prisms were obtained which weighed 3.74 g. (89%), m.p. 93–95°, $[\alpha]^{29}D$ −5.3° (*c*, 2.63) [lit.[11] b.p. 200–220° (0.15 mm.), $[\alpha]D$ −5° (*c* 0.9)], $\nu_{max}$ 2.96 and 6.19 $\mu$.

*Anal.* Calcd. for $C_{26}H_{47}N$: C, 83.57; H, 12.68; N, 3.75. Found: C, 83.57; H, 12.75; N, 3.68.

**A-Norcholestan-1-one** (XII).—1β-Amino-A-norcholestane (0.200 g., 0.536 mmole) was dissolved in anhydrous ether (4 ml.). Sodium bicarbonate (0.044 g.) was added, the flask was placed in an ice bath, and a solution of *t*-butyl hypochlorite (0.066 g., 0.608 mmole) in ether (3 ml.) was pipetted with stirring into the reaction mixture. After 20 min. the ice bath was removed and the reaction mixture was treated with a solution of sodium ethoxide in absolute ethanol (prepared from 0.13 g. of sodium and 7.2 ml. of ethanol). The reaction mixture was boiled on a steam bath until a negative test was obtained with acidified starch–iodide paper, after which enough water was added to dissolve the precipitated salt. The resulting solution was made strongly acid with 10% sulfuric acid and boiled for 30 min. After cooling to room temperature, an equal volume of saturated salt solution was added and the aqueous phase was extracted with two 50-ml. portions of ether. The combined ether extracts were dried and the solvent was removed to give a residue which was chromatographed on a column of Woelm acid alumina (6 g., activity II) with Skellysolve F (50 ml.) followed by a Skellysolve F–benzene mixture (3:2, 100 ml.). The latter eluent provided an oil, weighing 0.146 g. (73%), which was crystallized and recrystallized from methanol to give the crystalline product, white needles, m.p. 72.5–73.5° (cor.), $[\alpha]^{27}D$ +10° (*c* 1.2) [lit.[13] m.p. 74–76°, $[\alpha]^{22}D$ +11° (*c* 0.84)], $\nu_{max}$ 5.76 $\mu$ (cyclopentanone C=O).

**1-Oximino-A-norcholestane** (XII).—A-Norcholestan-1-one (0.200 g., 0.535 mmole) was refluxed with hydroxylamine hydrochloride (0.300 g., 4.32 mmoles) and sodium acetate (0.240 g.) in a mixture of absolute ethanol (8 ml.) and tetrahydrofuran (1 ml.) for 3.5 hr. The solution was cooled, an equal volume of saturated ammonium chloride solution was added, and the

aqueous phase was extracted with two 50-ml. portions of ether. The combined ether extracts were dried and evaporated to dryness. Crystallization from absolute ethanol gave 0.181 g. (87%) of white prisms, m.p. 173–175° (lit.[11] m.p. 170–172°), $\nu_{max}$ 3.02 and 5.96 $\mu$.

**Reduction of 1-Oximino-A-norcholestane (XII).**—Oxime XII (0.148 g., 0.382 mmole) was reduced with lithium aluminum hydride (0.400 g., 10.5 mmoles) in refluxing ether (45 ml.) for 4 hr. Excess hydride was decomposed with saturated aqueous sodium sulfate solution and the reaction mixture was acidified with 6 *N* hydrochloric acid and then made strongly alkaline with 5 *N* sodium hydroxide. The resulting solution was extracted with three 50-ml. portions of ether, and the combined ether extracts were washed with two 50-ml. portions of water and were dried first over sodium sulfate and then over solid potassium hydroxide. The solvent was removed and the residue was chromatographed on Woelm neutral alumina (12 g., activity II). Elution with benzene (40 ml.) followed by chloroform (100 ml.) gave 0.092 g. (62%) of 1$\beta$-amino-A-norcholestane, m.p. 89.5–90.5° (from absolute ethanol), identical with the noramine obtained from 1$\beta$-carboxy-A-norcholestane *via* the Schmidt reaction as shown by a mixture melting point determination (m.m.p. 92–94°) and comparison of the infrared spectra ($\nu_{max}$ 2.97 and 6.18 $\mu$).

**2-Oximino-A-norcholestan-1-one (XIV).**—A-Norcholestan-1-one (1.0 g., 2.68 mmole) was added to a stirred solution of potassium *t*-butoxide in *t*-butyl alcohol [prepared from potassium (0.67 g., 0.017 mole) and dry *t*-butyl alcohol (32 ml.)] under nitrogen. *n*-Butyl nitrite (0.66 ml., 6.45 mmole) was added, followed by an equivalent amount of nitrite 1 hr. later. After a total reaction time of 4 hr., the solution was worked up in the usual way to give 1.046 g. of a light yellow amorphous solid: m.p. 223–224° dec. (darkening at 210°); $\nu_{max}$ 3.12, 5.73, 6.04, and 10.67 $\mu$; $\lambda_{max}^{neutral}$ and $\lambda_{max}^{basic}$ 236 m$\mu$ ($\epsilon$ 7400). Negative tests were obtained with 5% aqueous cobaltous and cupric acetate solutions.

*Anal.* Calcd. for $C_{26}H_{43}NO_2$: C, 77.75; H, 10.79; N, 3.49. Found: C, 78.23; H, 10.73; N, 4.03.

**2-Diazo-A-norcholestan-1-one (XV).**—Crude 2-oximino-A-norcholestan-1-one (3.31 g., 8.23 mmoles) was dissolved in tetrahydrofuran (11.3 ml.) and treated with 5 *N* sodium hydroxide (8 ml.). Ether (150 ml.) was added, followed by concentrated ammonium hydroxide (13.3 ml.) and Clorox (16.5 ml.). The reaction mixture was stirred under nitrogen at *ca.* 20° for 1 hr., a second portion of Clorox (16.5 ml.) was added, and stirring was continued 2 hr. longer. After the usual work-up, the product was isolated as a yellow crystalline solid weighing 2.27 g. (67% over-all yield, based on A-norcholestan-1-one). Recrystallization from ether–methanol gave the analytical sample, m.p. 102–104°, $[\alpha]^{26}D$ +142.5° (*c* 0.88), $\nu_{max}$ 4.82 and 5.97 $\mu$, $\lambda_{max}$ 255 m$\mu$ ($\epsilon$ 16,700) and 300 m$\mu$ ($\epsilon$ 3200).

*Anal.* Calcd. for $C_{26}H_{42}N_2O$: C, 78.34; H, 10.62; N, 7.03. Found: C, 78.33; H, 10.83; N, 7.21.

**1$\beta$-Carboxy-A-bisnorcholestane (XVI).**—2-Diazo-A-norcholestan-1-one (2.273 g., 5.70 mmoles) was photolyzed under the usual reaction conditions and worked up in the usual manner to give a light yellow oil. The oil was dissolved in acetone and the resulting solution was decolorized with charcoal and filtered; the solvent was removed and the residue was redissolved in a minimum volume of acetone. Crystals were obtained by allowing the solution to evaporate slowly. The resulting oil-covered solid was treated with a small volume of acetone and filtered, and the crystals were rinsed with cold acetone. The first three crops, totaling 0.834 g., were recrystallized from acetone to give 0.630 g. of white prisms, m.p. 165–167°. The fourth and fifth crops weighed 0.078 g. combined, giving a total yield of 32%, $[\alpha]^{31}D$ −40.1° (*c* 0.5), $\nu_{max}$ 3.00–4.00 and 5.84 $\mu$.

*Anal.* Calcd. for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found: C, 80.41; H, 11.58.

**1$\beta$-Carbomethoxy-A-bisnorcholestane (XVII).**—1$\beta$-Carboxy-A-bisnorcholestane (0.185 g., 0.476 mmole) was added to excess diazomethane in ether and the resulting solution was allowed to stand overnight at room temperature. The reaction mixture was worked up in the usual way to give 0.170 g. (89%) of an oil which was subjected to low-temperature recrystallization from acetone (−78°). The product was filtered rapidly and dried *in vacuo* to give the solid bisnorester, m.p. 35–36°, $[\alpha]^{28}D$ −51.8° (*c* 1.08), $\nu_{max}$ 5.79 and 8.53 $\mu$.

*Anal.* Calcd. for $C_{27}H_{46}O_2$: C, 80.54; H, 11.52. Found: C, 80.90; H, 11.74.

**Attempted Epimerization of 1$\beta$-Carbomethoxy-A-bisnorcholestane.**—A solution of the bisnorester (0.100 g., 0.249 mmole) and sodium ethoxide [prepared from 0.025 g. (10.7 mg.-atoms) of sodium] in absolute ethanol (15 ml.) was refluxed under nitrogen for 72 hr. At the end of this time 10% sodium hydroxide (*ca.* 0.15 ml.) and absolute ethanol (*ca.* 4 ml.) were added and the reaction mixture was refluxed under nitrogen for an additional 7 hr. A saturated salt solution (15 ml.) and water (5 ml.) were added and the resulting solution was acidified with 6 *N* hydrochloric acid and extracted with three 15-ml. portions of ether. The ether extracts were combined and evaporated *in vacuo*. The last trace of water was removed as an azeotrope with benzene; the residue was dissolved in benzene and chromatographed on Baker silica gel (1 × 8 cm. column) with benzene (225 ml.). The solvent was evaporated, leaving a crystalline product which was recrystallized from acetone to give 0.050 g. (54%) of white prisms, m.p. 156–160°. 1$\beta$-Carboxy-A-bisnorcholestane (XVI) melted at 165–167°. The infrared spectra of the epimerization product and XVI are superimposable.

**1$\beta$-Hydroxymethyl-A-bisnorcholestane (XVIII).**—1$\beta$-Carboxy-A-bisnorcholestane (0.066 g., 0.173 mmole) was stirred with lithium aluminum hydride (0.155 g., 4.08 mmole) in dry tetrahydrofuran (6 ml.) for 18 hr. under nitrogen. The reaction mixture was worked up in the usual manner to give an oil which was chromatographed on Woelm neutral alumina (1 × 11 cm. column, activity III) with a mixture of Skellysolve F–benzene (1:1). The first fraction (40 ml.) was discarded, but the second fraction (45 ml.) yielded 0.047 g. (73%) of crystalline alcohol. Recrystallization from acetone provided the analytical sample, m.p. 104–105°, $[\alpha]^{31}D$ −0.2° (*c* 0.5), $\nu_{max}$ 2.95 $\mu$.

*Anal.* Calcd. for $C_{26}H_{46}O$: C, 83.35; H, 12.38. Found: C, 83.86; H, 12.56.

**Conversion of 1$\beta$-Carboxy-A-bisnorcholestane (XVI) to Benzylurethan XXI.**—The bisnor acid (1.00 g., 3.57 mmoles) was dissolved in dry ether (20 ml.) and treated with thionyl chloride (0.7 ml., 9.65 mmoles) in the presence of pyridine (1 drop). After the mixture was stirred for 1.5 hr., the solvent was evaporated and residual thionyl chloride was removed by distillation on a rotary evaporator with several portions of dry Skellysolve F. The acid chloride was dried *in vacuo* (1.0–0.5 mm.) for 1 hr. and dissolved in dry acetone (30 ml.). The solution was cooled to *ca.* 3° in an ice–water bath and treated with a solution of sodium azide (0.320 g., 4.92 mmoles) in water (2 ml.). The reaction mixture was stirred for 15 min. at 3° and then for 7 min. at ambient temperature (3–7°). Saturated aqueous salt solution (100 ml.) was added and the mixture was extracted with benzene (30 ml.) and ether (25 ml.). The combined organic extracts were dried over molecular sieves, filtered through a sodium sulfate column (2 × 5 cm.), and concentrated to 30 ml. *in vacuo*. The concentrated extract was added dropwise during 3 min. to a refluxing solution of benzyl alcohol (2.7 ml., 0.026 mole) in dry benzene (30 ml.). Some solvent (*ca.* 10 ml.) was distilled off and the reaction mixture was stirred and refluxed for 3 hr. under a drying tube. The solvent was removed and the residue was chromatographed on Woelm neutral alumina (160 g., activity II). The first fraction (250 ml. of 1:1 Skellysolve F–benzene) was discarded and the second fraction (350 ml. of chloroform) was evaporated to give 1.54 g. of a light yellow oil. The oil was dried *in vacuo* overnight and was rechromatographed on Baker silica gel (3 × 24 cm. column). The first and second fractions (250 ml. of 1:1 Skellysolve F–benzene and 175 ml. of benzene) were rejected. The third and fourth fractions (250 ml. of 1:1 benzene–chloroform and 350 ml. of chloroform) provided the desired benzylurethan (XXI) as an oil weighing 1.04 g. (82% over-all yield from the bisnor acid), $[\alpha]^{27}D$ +10.8° (*c* 3.17), $\nu_{max}$ 3.02 and 5.80–5.90 $\mu$.

*Anal.* Calcd. for $C_{33}H_{51}NO_2$: C, 80.27; H, 10.41. Found: C, 80.49; H, 10.64.

**1$\beta$-Amino-A-bisnorcholestane Hydrochloride.**—Benzylurethan XXI (0.50 g., 1.01 mmoles) was dissolved in absolute methanol (200 ml.). Hydrogen chloride gas was bubbled into the solution for 1 min., 5% palladium on charcoal (0.625 g.) was added, and the mixture was hydrogenated on a Parr apparatus for 4.5 hr. under 45-p.s.i. hydrogen pressure. The solution was filtered through a Celite pad and the solvent was removed *in vacuo* leaving a pale yellow crystalline material. Recrystallization from absolute methanol afforded 0.338 g. (85%) of white needles: m.p. 236–242° dec.; $[\alpha]^{26}D$ −30.9° (*c* 0.97); $\nu_{max}$ 3.52, 5.02, 6.22, 6.31, and 6.61 $\mu$.

*Anal.* Calcd. for $C_{25}H_{46}ClN$: C, 75.87; H, 11.62; N, 3.53. Found: C, 75.77; H, 11.74; N, 3.88.

**A-Bisnorcholestan-1-one (XXIII).**—1β-Amino-A-bisnorcholestane (XXII) was obtained by treating a suspension of the hydrochloride salt with strong aqueous base solution, evaporating the ether layer to dryness, and chromatographing the residue on Woelm neutral alumina (activity II) with chloroform.

Bisnoramine XXII (0.282 g., 0.78 mmole) was treated with a solution of *t*-butyl hypochlorite (0.087 g., 0.80 mmole) in ether in the usual manner and the reaction product was boiled with sodium ethoxide and then with 10% sulfuric acid. The reaction mixture was cooled, mixed with saturated aqueous salt solution (40 ml.), and extracted with three 30-ml. portions of ether. The combined ether extracts were filtered to remove an insoluble white precipitate, washed with saturated aqueous salt solution (25 ml.), dried over molecular sieves, and evaporated to dryness *in vacuo*. A small quantity of ether (15 ml.) was added to the residue and the insoluble material was filtered off. The ether was removed and the resulting oil was chromatographed on Alcoa basic alumina (1 × 20 cm. column, activity I) with a mixture of Skellysolve F–benzene (4:1). The first fraction (40 ml.) was discarded. The second fraction (50 ml.) yielded 0.086 g. of white crystalline material which was rechromatographed under identical conditions to give 0.060 g. (22%) of pure material. Recrystallization from absolute methanol gave white needles, m.p. 93–95°, $[\alpha]^{27}D$ +31.0° (*c* 0.84), $\nu_{max}$ 5.65 μ (cyclobutanone C=O).

*Anal.* Calcd. for $C_{25}H_{42}O$: C, 83.73; H, 11.81. Found: C, 83.95; H, 12.05.

***anti*-2-Oximinocholest-3-en-1-one (XXIV).**—Cholest-2-en-1-one (1.00 g., 2.67 mmoles) was dissolved in dry *t*-butyl alcohol (16 ml.) and added to a base solution prepared from potassium (0.40 g., 10.2 mg.-atoms) and dry *t*-butyl alcohol (10 ml.). *n*-Butyl nitrite (1.0 ml., 8.83 mmoles) was added, the reaction mixture was stirred under nitrogen for 1 hr., and an additional quantity of *n*-butyl nitrite (0.5 ml., 4.42 mmoles) was then added. After a total reaction time of 2.5 hr., the reaction mixture was worked up in the usual manner to give a yellow solid which was chromatographed on Davison silica gel (40 g.). Two fractions were obtained.

Fraction A (50 ml. of chloroform) was evaporated to dryness and the residue was crystallized from a mixture of tetrahydrofuran and 95% ethanol to give 0.033 g. (3%) of a compound isomeric with XXIV, white platelets: m.p. >300°; $[\alpha]^{28}D$ +277° (*c* 1.00); $\nu_{max}$ 3.05, 5.96, 6.17, and 10.52 μ; $\lambda_{max}^{neutral}$ 225 mμ (ε 4900) and 205 mμ (ε 3900), $\lambda_{max}^{basic}$ 225 mμ (ε 3800) and 295 mμ (ε 6950).

*Anal.* Calcd. for $C_{27}H_{47}NO_2$: C, 78.40; H, 10.48; N, 3.39. Found: C, 78.06; H, 10.76; N, 3.92.

No metal complexes were formed when the compound was treated with aqueous $Co^{+2}$ or $Cu^{+2}$ solutions.

Fraction B (440 ml. of 2:9 ethyl acetate–chloroform) was evaporated to dryness and the residue was recrystallized from ethyl acetate to give 0.51 g. (48%) of *anti*-2-oximinocholest-3-en-1-one as white needle clusters: m.p. 220–223° dec.; $[\alpha]^{28}D$ +157.3° (*c* 1.16); $\nu_{max}$ 3.12, 5.83, 6.17, 6.27, and 10.52 μ; $\lambda_{max}^{neutral}$ 260 mμ (ε 10.670), $\lambda_{max}^{basic}$ 308 mμ (ε 13,300).

*Anal.* Calcd. for $C_{27}H_{47}NO_2$: C, 78.40; H, 10.48; N, 3.39. Found: C, 78.58; H, 10.51; N, 3.37.

The compound (XXIV) gave a yellow complex with an aqueous $Co^{+2}$ solution and a green complex with an aqueous $Cu^{+2}$ solution.

**Monooxime of 1,4,4a,5,8,8a-Hexahydronaphthalene-1,4-dione (XXVII).**—Dienedione XXVII[18] (0.60 g., 3.70 mmoles) was dissolved in absolute ethanol (10 ml.) and treated with hydroxylamine hydrochloride (0.256 g., 3.71 mmoles) and sodium acetate (0.294 g., 3.58 mmoles). Water (1.5 ml.) was added and the solution was stirred in an ice bath for 2 hr. under nitrogen. The reaction mixture was diluted with cold water (100 ml.) and the precipitate (0.370 g., 56% yield) was dissolved in methanol, treated with charcoal, and reprecipitated with three volumes of water. The product had m.p. 152–154° dec.; $\lambda_{max}$ 3.01, 6.02, 6.19, 6.25, and 10.22 μ; $\lambda_{max}^{neutral}$ 220 mμ (ε 5950) and 282 mμ (ε 13,800); $\lambda_{max}^{basic}$ 235 mμ (ε 6720) and 346 mμ (ε 17,100).

The monooxime did not form complexes with aqueous $Co^{+2}$ or $Cu^{+2}$ solutions.

*Anal.* Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.59; H, 6.39; N, 7.88.

**2-Diazocholest-3-en-1-one (XXX).**—*anti*-2-Oximinocholest-3-en-1-one (0.50 g., 1.21 mmoles) was dissolved in a solution of tetrahydrofuran (1.5 ml.) and 5 *N* sodium hydroxide (1.2 ml.). Ether (55 ml.) was added, followed by concentrated ammonium hydroxide (2.5 ml.) and Clorox (2.5 ml.). The system was stirred under nitrogen in an ice bath for 1 hr. and then additional concentrated ammonium hydroxide (2.5 ml.) and Clorox (2.5 ml.) were added. The reaction mixture was stirred for 0.5 hr. longer at 0°, then for 2.5 hr. at room temperature. After the usual work-up, 0.36 g. (73%) of a red-orange solid was obtained: m.p. 81–83° (after recrystallization from pentane); $[\alpha]^{28}D$ +31.6° (*c* 1.24); $\nu_{max}$ 4.85, 6.08, and 6.21 μ; $\lambda_{max}^{dioxane}$ 260 mμ (ε 17,100) and 324 mμ (ε 5280).

*Anal.* Calcd. for $C_{27}H_{42}N_2O$: C, 78.97; H, 10.31; N, 6.82. Found: C, 79.35; H, 10.35; N, 6.29.

**1β-Carboxy-A-norcholest-2-ene (XXXI).**—2-Diazocholest-3-en-1-one (0.759 g., 1.90 mmoles) was photolyzed under the usual conditions to give, after the usual work-up, a yellow oil which was crystallized from acetone. The product, white prisms, m.p. 175–180°, weighed 0.351 g. (48%). It was dissolved in benzene and chromatographed on Baker silica gel (14 g.). The initial eluent (200 ml., benzene) was evaporated to dryness and the residue was recrystallized from acetone to provide the analytical sample, m.p. 178–180°. Further elution with benzene (200 ml.) and then with chloroform (200 ml.) provided the balance of the material which, after recrystallization from acetone, was found to have m.p. 177–180°, $[\alpha]^{28}D$ −8.7° (*c* 1.03), $\nu_{max}$ 3.0–4.0 and 5.86 μ.

*Anal.* Calcd. for $C_{25}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.03; H, 11.21.

**1β-Hydroxymethyl-A-norcholest-2-ene (XXXII).**—1β-Carboxy-A-norcholest-2-ene (0.100 g., 0.25 mmole) was stirred with lithium aluminum hydride (0.330 g., 6.09 mmoles) in tetrahydrofuran for 16 hr. under nitrogen. After the usual work-up, an oil was isolated which was chromatographed on Woelm neutral alumina (activity III, 1 × 12 cm. column), using a mixture of Skellysolve F–benzene (1:1) as eluent. The first fraction (40 ml.) was discarded. The second fraction (105 ml.) furnished 0.88 g. (91%) of crystalline material. The analytical sample, m.p. 95–97°, was obtained by recrystallization from methanol–acetone (3:1): $[\alpha]^{28}D$ +17.5° (*c* 1.03), $\nu_{max}$ 3.11 μ.

*Anal.* Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 84.12; H, 12.21.

**Hydrogenation of 1β-Carboxy-A-norcholest-2-ene (XXXI).**—The nor acid (0.100 g., 0.25 mmole) was dissolved in ethyl acetate (35 ml.) and hydrogenated for 3 hr. at atmospheric pressure in the presence of 0.033 g. of 10% palladium on charcoal. The solution was filtered and the solvent was removed. The crystalline product (0.085 g., 84% yield) was dissolved in benzene and chromatographed on Baker silica gel (4.0 g.). The first fraction (benzene, 50 ml.) furnished material identical in melting point (200–202°), recrystallized from acetone) and infrared spectrum with 1β-carboxy-A-norcholestane.

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