

**14 $\alpha$ - $\Delta^{5,7,9}$ -Anthracholestatrien-x-ol (IIm).**—The crystalline alcohol was obtained by boiling the *p*-chlorobenzoate IIo in 5% ethanolic potassium hydroxide solution for 50 minutes. After two crystallizations from methanol the compound melted constantly at 62–64°,  $[\alpha]_D -9.5^\circ$ .

*Anal.* Calcd. for  $C_{27}H_{42}O \cdot 1/2CH_3OH$ : C, 82.87; H, 11.13. Found: C, 83.26; H, 11.42.

After drying *in vacuo* at 60° for 3 hours, the m.p. rose to 82–82°,  $[\alpha]_D -9.7^\circ$ ;  $\lambda_{max}$  272.5, 277 and 282  $m\mu$  ( $\epsilon$  682, 575 and 708, respectively);  $\lambda_{max}^{CS_2}$  2.77 and 11.47  $\mu$ ;  $\lambda_{max}^{Nujol}$  3.02, 6.22, 6.35 and 11.43  $\mu$ .

*Anal.* Calcd. for  $C_{27}H_{42}O$ : C, 84.75; H, 11.07. Found: C, 84.61; H, 10.94.

The mixture of this alcohol IIm and its isomer Im melts unsharply at about 80°.

**14 $\alpha$ - $\Delta^{5,7,9}$ -Anthracholestatrien-x-ol Hexahydrobenzoate (IIn).**—A mixture of 20 mg. of the above alcohol IIm, 1.2 ml. of hexahydrobenzoyl chloride and 26 ml. of pyridine was allowed to stand at room temperature overnight. The first crystallization of the reaction product gave 200 mg. of an ester melting at 113–114°,  $[\alpha]_D -4.3^\circ$ . By a second crystallization from ethanol the m.p. rose to 114–115°,  $[\alpha]_D -4.7^\circ$ ;  $\lambda_{max}^{CS_2}$  272, 277 and 281.5  $m\mu$  ( $\epsilon$  690, 580 and 710, respectively);  $\lambda_{max}^{CS_2}$  5.77 and 11.45  $\mu$ ;  $\lambda_{max}^{Nujol}$  5.99, 6.21, 6.35 and 11.54  $\mu$ .

*Anal.* Calcd. for  $C_{31}H_{52}O_2$ : C, 82.87; H, 10.64. Found: C, 83.03; H, 10.90.

A mixture of this ester and its isomer In melted at 112–114°. **14 $\alpha$ - $\Delta^{5,7,9}$ -Anthracholestatrien-x-ol *o*-Chlorobenzoate (IIp).**—A mixture of 150 mg. of alcohol Ila, 0.7 ml. of *o*-chlorobenzoyl chloride and 10 ml. of pyridine was allowed to stand at room temperature overnight. The *o*-chlorobenzanhydride formed in the reaction was removed by passing a benzene–petroleum ether solution (1:1) of the reaction product through an alumina column (Grade I, almost neutral). By crystallization from acetone 130 mg. of crystalline material melting at 141–142° was obtained,  $[\alpha]_D -1.4^\circ$ . After a second crystallization, the derivative melted at 142°,  $[\alpha]_D -1.8^\circ$ ,  $\lambda_{max}^{CS_2}$  5.76  $\mu$ .

*Anal.* Calcd. for  $C_{31}H_{46}O_2Cl$ : C, 78.35; H, 8.70. Found: C, 78.57; H, 8.96.

**14 $\alpha$ - $\Delta^{5,7,9}$ -Anthracholestatriene (IIr) from Trienol IIm via 14 $\alpha$ - $\Delta^{(10r)3,5,7,9}$ -Anthracholestetraene (IIq).**—Alcohol IIm (300 mg.) was tosylated, and the crude tosylate was added to a boiling xylene–collidine mixture (10:1) as described in the analogous experiment in the 14 $\beta$ -series. By chromatography, 190 mg. of a colorless and apparently homogeneous oil was obtained,  $[\alpha]_D +6.5^\circ$ ;  $\lambda_{max}^{acetone}$  221.5, 227, 234, and 273  $m\mu$  ( $\epsilon$  25400, 28400, 19300 and 11400, respectively), *infl.* 306  $m\mu$  ( $\epsilon$  650). In the catalytic hydrogenation one mole equivalent of hydrogen was consumed rapidly. By crystallization from acetone–methanol 150 mg. of crystalline material melting at 78–79.5° was obtained. Additional crystallizations from the same solvent raised the m.p. to 80.82°,  $[\alpha]_D +28.7^\circ$ ;  $\lambda_{max}^{acetone}$  273, 278 and 283  $m\mu$  ( $\epsilon$  655, 553 and 701, respectively).

(12) Reference 8 reports  $[\alpha]_D +30^\circ$ , and m.p. 71–73°. The latter value is

*Anal.* Calcd. for  $C_{27}H_{42}$ : C, 88.45; H, 11.55. Found: C, 88.40; H, 11.86.

The compound proved to be identical, by direct comparison, with an authentic sample<sup>8,12</sup> obtained in the catalytic hydrogenation of  $\Delta^{5,7,9,14}$ -anthracholestetraene.

**Rearrangement of Dehydroergosteryl Acetate with Acetic Acid.**—A solution of 2.5 g. of dehydroergosteryl acetate in 60 ml. of acetic acid (reagent grade, minimum content 99.7%) was boiled under reflux for 4 hours. The resulting yellowish solution was evaporated to dryness *in vacuo* and the oily residue subjected to hydrolysis in 5% ethanolic potassium hydroxide. The oily hydrolysate dissolved in petroleum ether–benzene was absorbed on 85 g. of Florisil and the following eluates were collected: (a) 350 ml. of petroleum ether; (b) 350 ml. of petroleum ether–benzene, 10:1; (c) 350 ml. of benzene–petroleum ether, 1:1; (d) six 100-ml. portions of benzene; (e) 500 ml. of benzene–chloroform, 10:1; (f) 400 ml. of benzene–chloroform, 1:1.

The presence of minimal amounts of  $\Delta^{5,7,9,14,22}$ -anthraergosta-pentaene in fraction a became evident in the ultraviolet spectrum. The oily residue (800 mg.) obtained from the combined fractions e, f and g was treated with *p*-chlorobenzoyl chloride as described previously. The crude acylation product was recrystallized twice from acetone–ethanol and yielded 600 mg. of crystalline **14 $\alpha$ - $\Delta^{5,7,9,22}$ -ergostatetraen-x-ol *p*-chlorobenzoate (IIc)**, m.p. 121–123°,  $[\alpha]_D -13.9^\circ$ . Its identity was demonstrated by direct comparison with an authentic sample (m.p. of the mixture, ultraviolet and infrared spectra). **14 $\alpha$ - $\Delta^{5,7,9,22}$ -Ergostatetraen-x-ol (IIa)**, the crude alcohol obtained by hydrolysis of the above ester, was crystallized from methanol and then from ethanol. It melted at 126–127°,  $[\alpha]_D -28.2^\circ$ ;  $\lambda_{max}^{EtOH}$  273, 277 and 282  $m\mu$  ( $\epsilon$  687, 684 and 714, respectively). The compound was identical in every respect with an authentic sample. Fractions d<sub>1</sub> and d<sub>2</sub> gave 900 mg. of oily material which yielded on acylation 250 mg. of pure 14 $\alpha$ - $\Delta^{5,7,9,22}$ -ergostatetraen-x-ol *p*-chlorobenzoate. Fraction d<sub>4</sub> and the hydrolyzed mother liquors of the above *p*-chlorobenzoate were combined and rechromatographed on Florisil and yielded 50 mg. of the 14 $\alpha$ -*p*-chlorobenzoate and 100 mg. of a mixture of 14 $\alpha$ - and 14 $\beta$ - $\Delta^{5,7,9,22}$ -ergostatetraen-x-ol hexahydrobenzoates, m.p. 106–108°,  $[\alpha]_D +0.7^\circ$ .

**Rearrangement of  $\Delta^{5,7,9(11)}$ -Cholestatrien-3 $\beta$ -ol Acetate with Acetic Acid.**—A solution of 300 mg. of the above trienol acetate in 10 ml. of acetic acid was boiled under reflux for 4.5 hr. The yellow oily residue obtained by evaporation *in vacuo* was hydrolyzed with 5% ethanolic potassium hydroxide and the reaction product subjected to treatment with *o*-chlorobenzoyl chloride in pyridine in the manner described above. Thus, 120 mg. of an *o*-chlorobenzoate, twice recrystallized from acetone and melting at 130–133°, was obtained. This ester was hydrolyzed and the resulting alcohol treated with *p*-chlorobenzoyl chloride in pyridine. Two recrystallizations from acetone of the reaction product yielded 85 mg. of **14 $\alpha$ - $\Delta^{5,7,9}$ -anthracholestatrien-x-ol *p*-chlorobenzoate (IIo)** melting at 126–127°,  $[\alpha]_D +8.0^\circ$ . Direct comparison, ultraviolet and infrared spectra and melting points of the appropriate mixture demonstrated the identity with an authentic sample.

obviously an error, since the original laboratory notes and the samples indicate the m.p. as 77–79°.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, BETHESDA 14, MD.]

## The Anthrasteroid Rearrangement. IX. The Acid-catalyzed Rearrangement of $\Delta^{5,7,9(11),22}$ -Ergostatetraene and $\Delta^{5,8(14),9(11)}$ -Ergostatrien-3 $\beta$ -ol

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The acid-catalyzed rearrangement of  $\Delta^{5,7,9(11),22}$ -ergostatetraene (VII) leads to 14 $\alpha$ - $\Delta^{5,7,9,22}$ -anthraergostatetraene (VIII) in a yield of about 30% when *p*-toluenesulfonic acid monohydrate is used as catalyst and to the 14 $\beta$ -isomer IX in a yield of 8–10%, when hydrogen chloride is employed. When  $\Delta^{5,8(14),9(11),22}$ -ergostatetraene-3 $\beta$ -ol acetate was subjected to the customary conditions of the anthrasteroid rearrangement with either catalyst, the compound underwent rapid changes, but no anthrasteroid type product could be detected in the reaction mixture.

Mechanisms that have been proposed for the anthrasteroid rearrangement<sup>2,3</sup> leading, with loss of the oxygen function, from steroid  $\Delta^{5,7,9(11)}$ -trien-3 $\beta$ -ols or their

esters to anthrasteroid  $\Delta^{5,7,9,14}$ -tetraenes indicate a pathway through A, B, C and D (see Fig. 1). Of these suggested intermediates only type C has been isolated and characterized.<sup>3a</sup> We have demonstrated in the preceding paper<sup>4</sup> that under certain conditions the rearrangement can be conducted so as to lead to anthra-

(1) Visiting Scientist, National Institutes of Health. (b) Deceased, May 31, 1962.

(2) A. W. Burgstahler, *J. Am. Chem. Soc.*, **79**, 6047 (1957).

(3) (a) W. R. Nes, *ibid.*, **78**, 193 (1956); (b) W. R. Nes and J. A. Steele, *J. Org. Chem.*, **22**, 1457 (1957); (c) W. R. Nes, J. A. Steele and E. Mosettig, *J. Am. Chem. Soc.*, **80**, 5230 (1958).

(4) K. Tsuda, R. Hayatsu, J. A. Steele, O. Tanaka and E. Mosettig, *ibid.*, **85**, 1126 (1963).

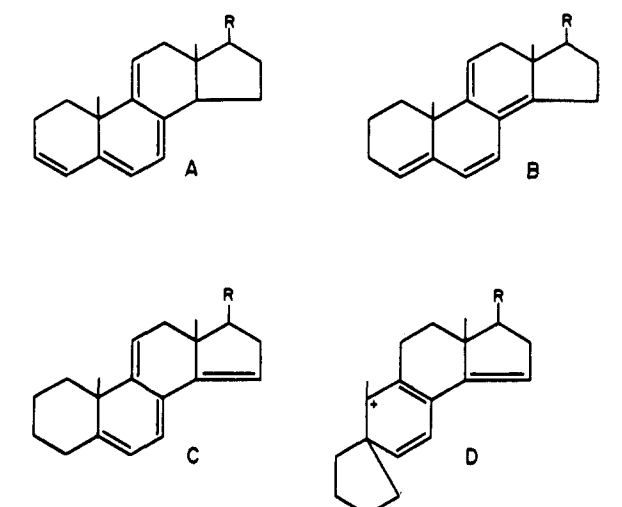


Figure 1.

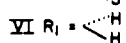
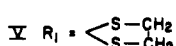
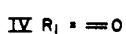
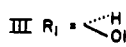
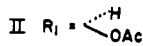
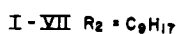
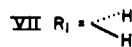
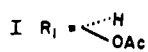
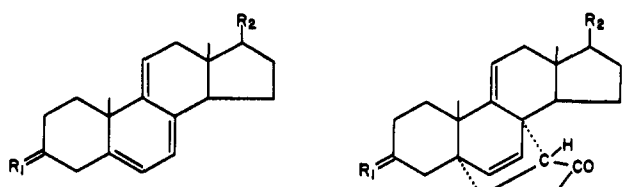


Figure 2.

steroid  $\Delta^{5,7,9}$ -trien-x-ols whereby no obvious elimination of the oxygen function takes place, and consequently no conjugated double bond ( $\Delta^{14}$ ) is created in addition to the aromatization of ring B. Thus it may appear that the 3-oxygen function or the 3,4-double bond in ring A of an intermediate A is not essential for the initiation of the rearrangement. In order to test such an assumption, we subjected  $\Delta^{5,7,9(11),22}$ -ergostatetraene (VII) (Fig. 2) to various conditions of the anthrasteroid rearrangement.

The preparation of the heretofore unknown "3-desoxydehydroergosterol" (VII) from I *via* the sequence II, III, IV, V, VI is shown in Fig. 2. The over-all yield from I was fair. The greatest losses were suffered in the hydrolysis of II to III. The conditions of this step must be chosen so as not to affect the acid anhydride function. Compound VII is very sensitive to air at room temperature, but can be stored reasonably long (2-3 months) at  $-20^\circ$ . It is considerably less stable than dehydroergosterol or its esters.

When VII was treated in chloroform with hydrogen chloride in small concentrations,<sup>5</sup> the course of the reaction being followed spectroscopically, an oily  $\Delta^{5,7,9,22}$ -anthraergostatetraene (IX) was formed in a rather low yield (8-10%). By catalytic hydrogenation of the side chain double bond a crystalline triene (XI) was obtained which proved to be identical with  $14\beta$ - $\Delta^{5,7,9}$ -anthraergostatetriene which, in turn, had previously<sup>4</sup> been obtained in two steps ( $\beta$ -elimination, catalytic hydrogenation) from XIII (R = tosyl). When, on the

(5) W. R. Nes and E. Mosettig, *J. Am. Chem. Soc.*, **76**, 3182 (1954).

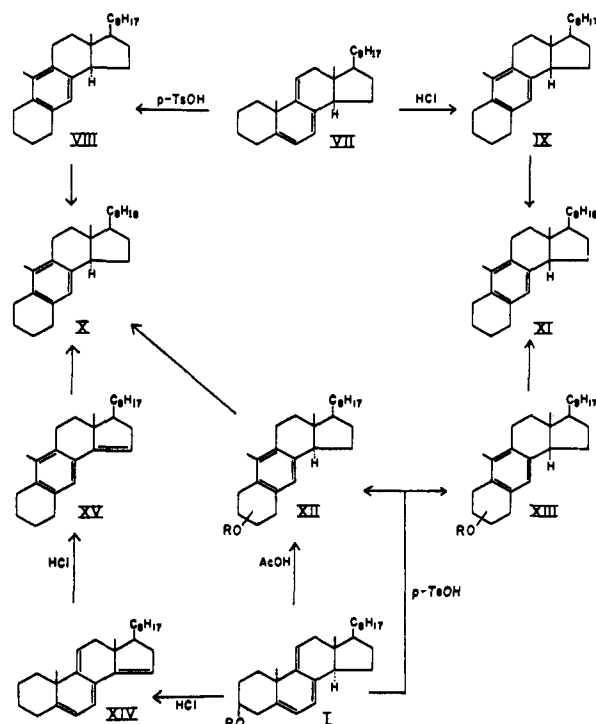


Figure 3.

other hand, the rearrangement of VII was effected with *p*-toluenesulfonic acid monohydrate, a crystalline  $\Delta^{5,7,9,22}$ -anthraergostatetraene (VIII) was obtained in yields of 25-30%. Catalytic reduction of VIII leads to  $14\alpha$ - $\Delta^{5,7,9}$ -anthraergostatetriene (X) which had been obtained previously from  $\Delta^{5,7,9,14}$ -anthraergostatetraene (XV)<sup>5</sup> as well as from XII (R = tosyl).<sup>4a</sup>

The rearrangement of desoxydehydroergosterol VII to IX ( $\text{CHCl}_3$ , HCl) proceeds apparently considerably more slowly than that of dehydroergosterol and its ester, the yields of anthrasteroid are much lower, and inversion at C<sub>14</sub> takes place. The rearrangement VII  $\rightarrow$  VIII, on the other hand, appears as a whole very similar to the rearrangement of dehydroergosterol acetate to the isomer pair XII ( $14\alpha$ ) and XIII ( $14\beta$ ), but no inversion takes place and only one isomer ( $14\alpha$ ) is obtained.

In view of the proposed structure B (Fig. 1) as an intermediate in the anthrasteroid rearrangement,<sup>2,3</sup>  $\Delta^{5,8(14),9(11),22}$ -ergostatetraen- $3\beta$ -ol acetate<sup>6</sup> was subjected to both types of rearrangement, *i.e.*, with hydrogen chloride and with *p*-toluenesulfonic acid monohydrate. In both sets of reactions the solutions turned dark green quickly, and spectroscopic examination revealed that the original trienol had disappeared in a short time. In none of the experiments could the formation of an anthrasteroid type be detected, chemically or spectroscopically, nor could starting material or any other characterizable product be isolated from the various reaction mixtures.

### Experimental<sup>7</sup>

**Maleic Anhydride Adduct of Dehydroergosterol (III).**—A solution of 25.0 g. of the maleic anhydride adduct of dehydroergos-

(6) G. D. Laubach, E. C. Schreiber, E. J. Agnello and K. J. Brunings, *ibid.*, **78**, 4743 (1956).

(7) All melting points were determined on a Kofler block and are uncorrected. Rotations were determined in chloroform in approx. 1% solution at  $20^\circ$ . Ultraviolet spectra were determined on a Cary recording spectrophotometer, model 11, in ethanol; infrared spectra on a Perkin-Elmer double beam spectrophotometer, model 21 (Mr. H. K. Miller and Mr. Richard T. Brown). Microanalyses are by the Analytical Service Laboratory of this Institute under the direction of Mr. Harold G. McCann. Woelm neutral alumina, Grades I and II, was used for chromatography. The Flori-

teryl acetate<sup>8</sup> in a mixture of 90 ml. of concd. sulfuric acid and 750 ml. of 95% ethanol was boiled under reflux for 2.5 hr., poured into water, and the precipitate extracted with ether. The residue left by evaporation of the washed and dried ethereal solution was crystallized from methanol yielding material (40%), m.p. 199–201°. Recrystallization from the same solvent raised the m.p. to 205°,  $[\alpha]_D +67.2^\circ$ ; the analytical sample was dried *in vacuo* at 110° for 12 hours, and melted at 213–215°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  2.28, 5.36 and 5.61  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{44}\text{O}_4$ : C, 78.01; H, 9.00. Found: C, 78.02; H, 9.22.

**Maleic Anhydride Adduct of  $\Delta^{5,7,9(11)}$ -Ergostatien-3-one (IV).**—To a solution of 9.3 g. of III in 150 ml. of acetone was added dropwise Kiliani reagent<sup>9</sup> (ca. 22 ml.) at room temperature until the orange color persisted. After 15 minutes a few drops of water were added, whereby the turbidity disappeared. The green precipitate was removed by filtration. The filtrate was poured into 500 ml. of water and the colorless precipitate collected and washed with water. By crystallization from 95% ethanol, a product melting at 181–183° was obtained in an average yield of 75%. The analytical sample obtained by another crystallization melted at 182–183°,  $[\alpha]_D +78.8^\circ$ ;  $\lambda_{\text{max}}^{\text{CS}_2}$  5.36, 5.60 and 5.80  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{42}\text{O}_4$ : C, 78.33; H, 8.63. Found: C, 78.08; H, 8.88.

**Ethylene Thioketal V.**—A mixture of 5.3 g. of ketone IV in 55 ml. of acetic acid, 4 ml. of ethylene dithiol and 4 ml. of boron fluoride etherate was allowed to stand for 1 hour. The reaction mixture was diluted with 100 ml. of methanol and kept at 0° for another hour. The crystalline precipitate was collected, washed with methanol and recrystallized from acetone-methanol or acetic acid. The product melted sharply at 182–183°, average yield 75%,  $[\alpha]_D +45.2^\circ$ ,  $\lambda_{\text{max}}^{\text{CS}_2}$  5.36 and 5.60  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{46}\text{O}_3\text{S}_2 \cdot 1/2\text{H}_2\text{O}$ : C, 70.94; H, 8.23; S, 11.18. Found: C, 70.71; H, 8.21; S, 11.56.

The water of crystallization could not be removed by drying the sample *in vacuo* at 110° for 12 hr. and an additional 2 hr. at 140°.

**Maleic Anhydride Adduct of  $\Delta^{5,7,9(11),22}$ -Ergostatetraene (VI).**—A suspension of Raney nickel (about 15 teaspoons) in 500 ml. of acetone was refluxed for 2 hours, a solution of 4.15 g. of V in 20 ml. of acetone was added and the mixture boiled under reflux for 15 hours. The decantate and the filtrate from the final removal of the catalyst were evaporated to dryness and the residue crystallized from ethanol, whereby colorless needles melting at 185–187° were obtained; yield 68%. The analytical sample melted at 188–189°,  $[\alpha]_D +103.5^\circ$ ,  $\lambda_{\text{max}}^{\text{CS}_2}$  5.36 and 5.60  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{44}\text{O}_3$ : C, 80.63; H, 9.30. Found: C, 80.79; H, 9.25.

**$\Delta^{5,7,9(11),22}$ -Ergostatetraene (Desoxydehydroergosterol) (VII).**—The maleic anhydride adduct VI (1.5 g.) was placed in a cold-finger distillation apparatus and heated to 235–240° at 12 mm. After ca. 15 minutes the sublimation was interrupted, and the sublimed maleic anhydride removed. Heating was continued at the above temperature at approximately 0.5 mm. After 30 minutes the pale yellow, partly crystalline distillate collected on the cold-finger was extracted with petroleum ether, the solution adsorbed on 45 g. of Florisil, and eluted with: (a) 500 ml. of petroleum ether, (b) 350 ml. of petroleum ether, (c) 500 ml. of

sil (60/100 mesh) was used as purchased from Floridin Co., Tallahassee, Fla. Petroleum ether refers to the solvent of b.p. 30–60°, purified in the conventional manner.

(8) W. Bergmann and P. G. Stevens, *J. Org. Chem.*, **13**, 10 (1948).

(9) Solution of: 53 g. of  $\text{CrO}_3$ , 80 g. of concd.  $\text{H}_2\text{SO}_4$  and 400 ml. of  $\text{H}_2\text{O}$ ; H. Kiliani, *Ber.*, **46**, 676 (1913).

benzene. From fraction c 150 mg. of the maleic anhydride adduct VI melting at 187–188° was recovered. Fraction b contained practically nothing. The residue from fraction a yielded after crystallization from methanol or acetone-methanol the colorless tetraene of m.p. 81–83° (60%). The analytical sample melted at 84–86°,  $[\alpha]_D +304^\circ$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  324  $\mu$  ( $\epsilon$  8700);  $\text{infl.}$  312 and 338  $\text{m}\mu$  ( $\epsilon$  7700 and 5500, respectively).<sup>10</sup>

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{44}$ : C, 88.35; H, 11.65. Found: C, 88.14; H, 11.51.

The compound turns yellow when exposed to air at room temperature, but is stable when sealed under a high vacuum, or at  $-20^\circ$ .

**Rearrangement of  $\Delta^{5,7,9(11),22}$ -Ergostatetraene (VII) with *p*-Toluenesulfonic Acid Monohydrate.**—To a stirred solution of 300 mg. of VII in 15 ml. of dichloromethane was added 150 mg. of *p*-toluenesulfonic acid monohydrate and the mixture was allowed to stand at room temperature overnight. The resulting dark colored reaction mixture was extracted with ether, the ethereal solution washed with 5% aqueous potassium carbonate and water, dried and evaporated to dryness. The residue dissolved in petroleum ether was adsorbed on 22 g. of neutral alumina (Grade I) and eluted with petroleum ether, petroleum ether-benzene (10:1) and petroleum ether-benzene (5:1). The course of the elution was checked spectroscopically, and the fractions showing the typical anthraeroid bands were combined. The crystalline material thus obtained in a yield of 25–30% had  $[\alpha]_D +10^\circ$ . Recrystallization from acetone-methanol gave a  $14\alpha$ - $\Delta^{5,7,9,22}$ -anthraergostatetraene (VIII) melting at 72–73°,  $[\alpha]_D +7.6^\circ$ ;  $\lambda_{\text{max}}^{\text{isooctane}}$  272, 277.5 and 282.5  $\text{m}\mu$  ( $\epsilon$  712, 588 and 753, respectively);  $\lambda_{\text{max}}^{\text{CS}_2}$  10.32 and 11.52  $\mu$  (aromatic B-ring).

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{42}$ : C, 88.82; H, 11.18. Found: C, 88.83; H, 11.44.

The sample holds moisture stubbornly and had to be dried *in vacuo* at about 70° for 2 days.

A solution of 55 mg. of VIII in a mixture of 7 ml. of ethyl acetate and 1.5 ml. of acetic acid was subjected to hydrogenation (15 mg. of  $\text{PtO}_2$ ). One mole equivalent of hydrogen was absorbed rapidly. The crude colorless oily triene had  $[\alpha]_D +19.4^\circ$ . By crystallization from acetone-methanol 38 mg. of X melting at 110–111° was obtained,  $[\alpha]_D +19.9^\circ$ ;  $\lambda_{\text{max}}^{\text{isooctane}}$  272, 278 and 282  $\text{m}\mu$  ( $\epsilon$  650, 521 and 691, respectively);  $\lambda_{\text{max}}^{\text{CS}_2}$  11.52  $\mu$ . It proved to be identical with authentic samples arrived at by different pathways.<sup>4,5</sup>

**Rearrangement of  $\Delta^{5,7,9(11),22}$ -Ergostatetraene (VII) with Hydrogen Chloride.**—A solution of 300 mg. of VII in 15 ml. of 0.033 *N* hydrogen chloride in chloroform was allowed to stand at room temperature, and the course of the reaction followed spectroscopically. After 3 hours the dark green solution was diluted with ether, washed with aqueous potassium bicarbonate solution and water, dried and evaporated to dryness. The residue was adsorbed on 50 g. of neutral alumina and eluted with petroleum ether (b.p. 38–44°) and the course of the elution followed spectroscopically. The fractions showing the expected ultraviolet spectrum were combined and yielded the  $14\beta$ - $\Delta^{5,7,9,22}$ -anthraergostatetraene (IX) as a colorless oil; yield 20.5 mg.,  $[\alpha]_D +51^\circ$ ;  $\lambda_{\text{max}}^{\text{isooctane}}$  273, 278 and 283  $\text{m}\mu$  ( $\epsilon$  795, 675 and 845, respectively);  $\lambda_{\text{max}}^{\text{CS}_2}$  10.28 and 11.54  $\mu$ .

A solution of 20 mg. of IX in ethyl acetate-acetic acid was subjected to catalytic hydrogenation in the manner described above for the tetraene VIII. The saturation of the side chain double bond proceeded rapidly. The oily reduction product ( $[\alpha]_D +72^\circ$ ) was crystallized from ethanol to give 14 mg. of  $14\beta$ - $\Delta^{5,7,9}$ -anthraergostatetriene (XI), m.p. 67–69°,  $[\alpha]_D +73^\circ$ ;  $\lambda_{\text{max}}^{\text{isooctane}}$  273, 278.5 and 284  $\text{m}\mu$  ( $\epsilon$  630, 530 and 697, respectively);  $\lambda_{\text{max}}^{\text{CS}_2}$  11.55  $\mu$ . It was found identical with an authentic sample obtained previously.<sup>4a</sup>

(10) *Cf.* ref. 3c.