case the ionic strength was 1.9 and in the second 2.9. The extinction coefficients were identical within 2% throughout the range from 250 to 270 mμ.

Effect of *p*H.—Two solutions of identical thiosulfate concentration (0.0106 *M*), sodium chloride concentration (2.0 *N*) and ionic strength (2.0) but with a *p*H of 4.6 in one case and 12.0 in the other were found to have identical molar extinction coefficients within 2% from 250 to 270 mμ.

Effect of Changing Cation Species.—A comparison of columns 2, 3 and 4 of Table I indicates that equal concentrations of lithium, sodium or potassium chloride have equal effect in reducing the thiosulfate extinction coefficient. Columns 5 and 6 show that magnesium sulfate exerts about the same effect (possibly slightly greater) as a solution of lithium chloride of the same normality. A similar result was obtained when a 1 *M* solution of magnesium sulfate was compared with a 2 *M* solution of sodium chloride.

TABLE I

EFFECT OF THE CATION SPECIES ON THE THIOSULFATE ABSORPTION SPECTRUM

	Molar extinction coefficients				
mμ	Li^{+a}	Na^{+b}	K^{+c}	Mg^{++d}	Li^{+e}
250		184.0	187.3	144.2	156.9
2	155.7	150.9	153.9	114.4	124.5
4	119.8	119.8	118.6	89.9	97.1
6	92.0	94.3	91.2	70.4	74.5
8	68.9	69.8	68.6	54.7	56.9
260	51.7	52.8	52.0	42.1	43.1
2	38.6	39.6	38.7	32.9	32.7
4	28.8	29.6	28.8	25.5	24.7
6	21.1	22.1	21.1	19.2	18.6
8	15.5	16.1	15.5	14.7	14.0
270	11.3	11.8	11.3	11.4	10.3

[a] $S_2O_3^{=}$ = 0.0106 *M*; LiCl = 1.91 *M*; *p*H = 12.5. [b] $S_2O_3^{=}$ = 0.0106 *M*; NaCl = 1.91 *M*; *p*H = 12.7. [c] $S_2O_3^{=}$ = 0.0102 *M*; KCl = 1.91 *M*; *p*H = 12.5. [d] $S_2O_3^{=}$ = 0.0104 *M*; $MgSO_4$ = 1.91 *M*. [e] $S_2O_3^{=}$ = 0.0102 *M*; LiCl = 3.82 *M*; *p*H = 12.5.

Effect of Sodium Salt Concentration on Sulfite Spectrum.—The molar extinction coefficient of sulfite is low in the wave length range above 260 mμ but rises rapidly below 250 mμ and depends on sodium salt concentration in a manner similar to that observed for thiosulfate. For example, a pure 0.010 *M* sulfite solution gave an extinction coefficient of 180 at 238 mμ. This was lowered to 110 when the solution was made 1 *M* in sodium chloride.

Effect of Temperature.—If the decrease in the extinction coefficients of thiosulfate and sulfite produced by increased salt concentration in solutions is due to ion pair formation, the coefficients might be expected to increase with increase in temperature. The effect of temperature has been tested qualitatively by determining the extinction coefficients of 0.010 *M* thiosulfite solutions in 2 *M* sodium chloride on a Cary recording spectrophotometer with the cell at room temperature and immediately after the cell was removed from a bath of boiling water. At 255 mμ the extinction coefficient increased from 111 to 145 and at 260 mμ from 54 to 76 at the elevated temperature. A spectrum taken after cooling was identical with that obtained before heating.

Acknowledgment.—We are indebted to Evalyn Ortelt Hornig of our laboratory for carrying out independent check determinations of the effects reported here, using a Cary recording spectrophotometer. This work was supported in part by the United States Atomic Energy Commission and in part by the University Research Committee with funds supplied by the Wisconsin Alumni Research Foundation.

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The Rearrangement of 9α,11α-Oxido-$\Delta^{7,22}$-ergostadiene-3β-ol Acetate with Magnesium Bromide

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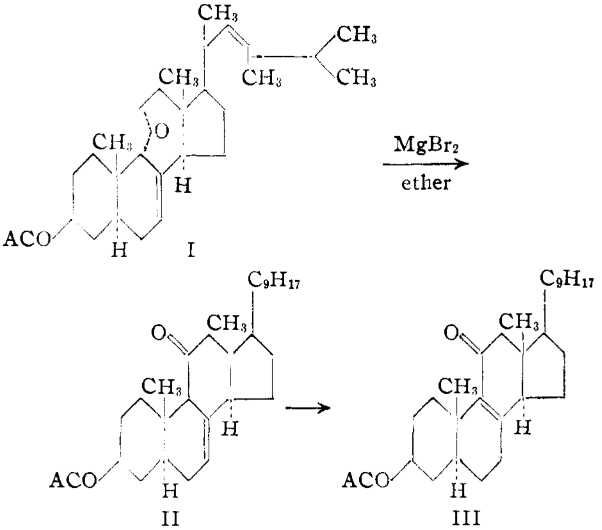
It has previously been reported that the monoepoxide derived from $\Delta^{7,9(11),22}$-ergostatriene-3β-ol acetate (ergosteryl D acetate) (I) may be rearranged to the corresponding α,β-unsaturated ketone III by the action of boron trifluoride etherate.[3] We have found that the rearrangement of I, as induced by magnesium bromide etherate, affords the non-conjugated ketone, $\Delta^{7,22}$-ergostadiene-3β-ol-11-one 3-acetate (II) in yields of 60–73%. On passing a benzene–petroleum ether solution of II over a column of activated alumina, the β,γ-unsaturated ketone II was isomerized to the known $\Delta^{8(9),22}$-ergostadiene-3β-ol-11-one acetate (III). In addition, it was found that the isomerization of the non-conjugated ketone II to the conjugated isomer III may be induced with a trace of hydrochloric acid in alcohol and it is possible to observe the transformation spectrophotometrically.



In the early stages of this investigation it became apparent that the methods available in the litera-

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[1] Deceased, March 22, 1951.

[2] Parke, Davis Postdoctoral Fellow, 1950–1951.

[3] H. Heusser, *et al.*, *Helv. Chim. Acta*, **34**, 2106 (1951).

ture for the selective reduction of ergosterol to 5,6-dihydroergosterol were of little synthetic value.[4] The importance of 5,6-dihydroergosterol, as an intermediate in the preparation of I, caused us to investigate a host of reducing agents. Accordingly, it was found that this selective reduction may conveniently be accomplished by refluxing an ethyl acetate solution of ergosteryl acetate in the presence of one-half to one equivalent of W-7 Raney nickel.[5,6] Furthermore, this method was successfully applied to the reduction of 7-dehydrocholesterol to Δ^7-cholesterol. The Δ^7-allosteroids were obtained in 55–65% yield.

Experimental[7]

5,6-Dihydroergosteryl Acetate.—Hydrogenation was accomplished with 40 g. of commercial ergosterol in 1600 cc. of reagent ethyl acetate in the presence of 8 level teaspoonfuls (approx. 20 g.) of W-7 Raney nickel. After one hour of reflux the mixture was filtered, and taken to dryness under reduced pressure. The white residue crystallized from 1 liter of 95% denatured alcohol to give 24 g. (60%) of 5,6-dihydroergosterol, m.p. 170–173° (lit.[5] 174°).

Δ^7-Cholesterol.—Hydrogenation was accomplished in the manner described for ergosteryl acetate with the substitution of absolute ethanol for ethyl acetate. Thus 19.2 g. of 7-dehydrocholesterol and 3 to 5 level teaspoonfuls of W-7 Raney nickel (approx. 10–15 g.) in 800 cc. of absolute ethanol gave 11.4 g. (59%) of Δ^7-cholesterol, in the form of fine white needles, after recrystallization from methanol, m.p. 120–122° (lit.[8] 122–123°).

9α,11α-Oxido-$\Delta^{7,22}$-ergostadiene-3β-ol acetate was prepared by the perphthalic acid epoxidation of $\Delta^{7,9(11),22}$-ergostatriene-3β-ol acetate in a manner essentially the same as that already described by Heusser and co-workers,[3] m.p. 204–206°, $[\alpha]^{29}\mathrm{D}$ −39° (lit.[4] m.p. 204–206°, $[\alpha]^{20}\mathrm{D}$ −39.5°).

Magnesium Bromide Etherate.—To a mixture of 60 cc. of anhydrous ether and 30 cc. of dry, reagent benzene was added 0.3 g. of magnesium dust (0.012 g. atom) followed by the addition of 2.16 g. of reagent grade mercuric bromide (0.006 mole). The mixture was then refluxed for two hours, filtered and used immediately in the rearrangement.

$\Delta^{7,22}$-Ergostadiene-3β-ol-11-one 3-Acetate (II).—To a solution of 1.23 g. of 9,11-epoxide described above (0.003 mole) in 140 cc. of dry ether was added 75 cc. of freshly prepared magnesium bromide etherate. After refluxing the mixture for two hours, an equal volume of water was added and the mixture shaken vigorously. The ether–benzene layer was drawn off, dried over anhydrous sodium sulfate and evaporated to dryness in a steam-bath in a stream of dry air. The residue crystallized from 100 cc. of methanol to give 0.9 g. (73% yield) of the non-conjugated ketone (II), m.p. 148–155°, $[\alpha]^{25}\mathrm{D}$ −160°. Two recrystallizations from methanol furnished the analytical sample, m.p. 155–157.5°, $[\alpha]^{25}\mathrm{D}$ −182°, $\lambda^{\mathrm{Nujol}}_{\mathrm{max}}$ 5.85 μ.

Anal. Calcd. for $C_{30}H_{46}O_3$: C, 79.29; H, 10.13. Found: C, 79.84; H, 10.47.

$\Delta^{8,22}$-Ergostadiene-3β-ol-11-one 3-Acetate.—A solution of 40 mg. of II, m.p. 150–155°, in 6 cc. of petroleum ether (60–75°), was put on a column of activated alumina (10 × 40 mm.). The solid was then eluted with 5-cc. mixtures of petroleum ether–benzene, the concentration of the latter being gradually increased until pure benzene was used. The fractions eluted from 40% benzene to pure benzene were combined and evaporated to dryness to give 33.6 mg. of white, crystalline material. This residue was crystallized from approximately 1 cc. of methanol to give 15 mg. of isomerized product, m.p. 129–131°, $[\alpha]^{27}\mathrm{D}$ +109°, $\lambda^{\mathrm{EtOH}}_{\mathrm{max}}$ 254 (log ε 3.91) $\lambda^{\mathrm{Nujol}}_{\mathrm{max}}$ 6.05 and 6.30 μ (lit.[9] m.p. 131.5–134°, $[\alpha]\mathrm{D}$ +110°, $\lambda^{\mathrm{EtOH}}_{\mathrm{max}}$ 254 (log ε 3.82)).

The appearance of the maximum 254 mμ was also observed spectrophotometrically by adding a drop of hydrochloric acid to a 10^{-5} *M* solution of II in alcohol.

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[4] A. Windaus and J. Brunken, *Ann.*, **460**, 225 (1923): A. Windaus and R. Langer, *ibid.*, **58**, 108 (1934); M. Heilbron and W. A. Sexton, *J. Chem. Soc.*, 921 (1929).

[5] H. Adkins and H. Billica, THIS JOURNAL, **70**, 695 (1948).

[6] After the present study had been completed, a general catalytic method was reported in which $\Delta^{5,7}$-steroids are reduced to Δ^7-allosteroids with Raney nickel in benzene: W. V. Ruyle, *et al.*, *ibid.*, **74**, 5929 (1952).

[7] All melting points are uncorrected. Analyses by Micro-Tech Laboratory, Skokie, Illinois. Rotations were determined in chloroform.

[8] Fr. Schenk, K. Buchholz and O. Wiese, *Ber.*, **69**, 2696 (1936).

[9] E. Schoenwaldt, *et al.*, THIS JOURNAL, **74**, 2697 (1952).

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Heat Capacities of Multimolecular Layers of Methane Adsorbed on Rutile

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Multilayer heat capacities of helium on jeweler's rouge and argon on rutile have been reported by Frederikse[1] and Morrison,[2] respectively. The heat capacities of the helium were for three to twelve monolayers and covering a range from 1 to 3°K.; those of the argon were for 1.6 to 4.6 monolayers covering a range from 65 to 86°K. In each case the heat capacity curves exhibited maxima near a transition point (the lambda-point for helium and the melting point for argon). These maxima became higher and the peaks moved nearer the transition point for each increase in the number of layers. The peaks at high coverages were less diffuse than those at lower coverages.

This Laboratory recently investigated the multilayer heat capacities of methane adsorbed on rutile. Coverages of 1.0 to 5.8 monolayers over a temperature range from 72 to 116°K. were used. The apparatus and procedure have been described.[3] The surface area of the adsorbent was determined from a BET plot,[4] and it was found that 0.03106 mole constituted a monolayer. At high coverages pressures were quite large after a series of measurements, and there was danger of condensing gas in the tube used for the introduction of the gaseous sample. This was remedied by continually heating the tube while the calorimeter was being cooled prior to beginning a set of measurements. During the measurements, all portions of the tube were as warm as or warmer than the calorimeter vessel containing the solid adsorbent.

The data are graphed in Fig. 1. Individual points are not shown because then the figure would be too crowded. The experimental points for the curves θ = 3.8, 4.8 and 5.8 fall exactly on the curves as drawn. The points for the curves θ = 1.0, 1.9, and 2.9 are scattered (each curve progressively more so). However, these latter three curves as shown do correctly indicate the trend of the data. This graph exhibits maxima, each one higher and closer to the transition, just as do Morrison's[2] and Frederikse's.[1] It is to be expected that above one monolayer the adsorbed gas will

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[1] H. P. R. Frederikse, *Physica*, **XV**, No. 10, 860 (1949).

[2] J. A. Morrison and L. E. Drain, *J. Chem. Phys.*, **19**, 1063 (1951).

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