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°, $[\alpha]^{29}\text{D}$ $-39°$ (lit.[4] m.p. 204–206°, $[\alpha]^{20}\text{D}$ $-39.5°$).

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°, $[\alpha]^{25}\text{D}$ $-160°$. Two recrystallizations from methanol furnished the analytical sample, m.p. 155–157.5°, $[\alpha]^{25}\text{D}$ $-182°$, $\lambda_{\max}^{\text{Nujol}}$ 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°, $[\alpha]^{27}\text{D}$ $+109°$, $\lambda_{\max}^{\text{EtOH}}$ 254 (log ϵ 3.91) $\lambda_{\max}^{\text{Nujol}}$ 6.05 and 6.30 μ (lit.[9] m.p. 131.5–134°, $[\alpha]\text{D}$ $+110°$, $\lambda_{\max}^{\text{EtOH}}$ 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).

[3] E. L. Pace, D. J. Sasmor and E. L. Heric, THIS JOURNAL, **74**, 4413 (1952).

[4] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

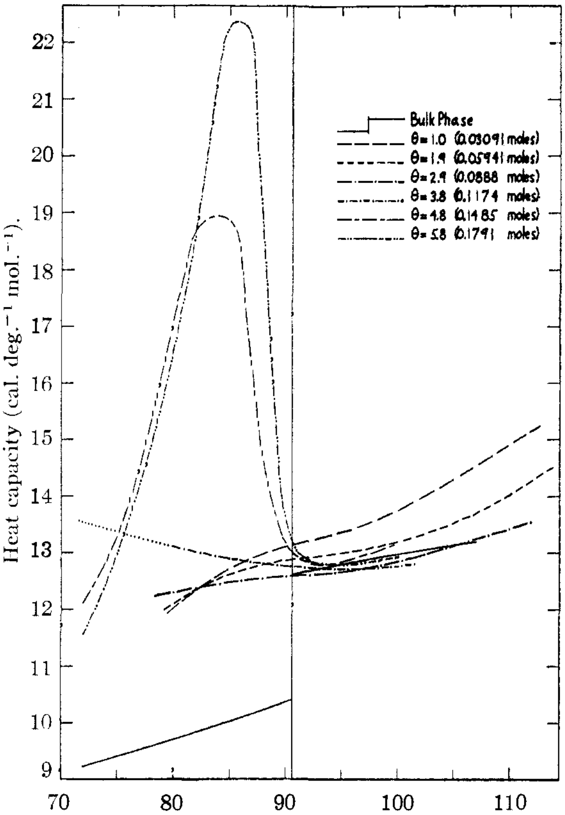

Fig. 1.—Multilayer heat capacities of methane adsorbed on rutile.

begin to exhibit bulk properties. The maxima are interpreted as indicating a rearrangement in the adsorbed film corresponding to melting in the bulk phase. Morrison[2] suggests that the melting point is lowered because a distortion of the normal lattice makes solidification more difficult, and that the spreading of the effect over a temperature range might be due to the small thickness of the absorbed films. The graphs show two noticeable differences between argon and methane. For argon, bulk properties begin between 1.6 and 2.9 monolayers; for methane they begin between about three and four monolayers. There is quite a difference in the shape of the 1.6 monolayer curve of argon and the one and two monolayer curves of methane. The argon curve is practically a straight line with only a small slope. The methane curves rise steeply to about 85°K., level off between 85 and 95°K., and then rise rather sharply again. The three monolayer curve of methane more closely approximates the argon curve in shape between 80 and 95°K. Mastrangelo[5] proposes that the shifts in the helium maxima are caused by pressure effects—high pressures at low coverages, and lower pressures at higher coverages. However, this will not explain the shifts for argon and methane, because their melting points are raised by increases in pressure. It is interesting to notice that the heat capacities of methane and argon adsorbed in the monolayer region are above or nearly the same as those of the liquid phases above the melting point; but one monolayer of nitrogen has heat capacities decidedly below those of the bulk liquid phase.[6]

If the differential heat capacities ($\overline{C_{N_s}}$) at 5.3 monolayers are plotted, using the data of 4.8 and 5.8 monolayers, the integral

$$\int_{72}^{90.6} (\overline{C_{N_s}} - C_{p_{\text{solid}}}) = 230 \text{ cal.}$$

which is very nearly equal to the heat of fusion of methane (*cf.* ref. 2).

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[5] S. V. R. Mastrangelo, *J. Chem. Phys.*, **18**, 896 (1950).

[6] J. A. Morrison and G. J. Szasz, *ibid.*, **16**, 280 (1948).

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Synthesis of Poly-N$^{\beta}$-benzyl-*dl*-asparagine

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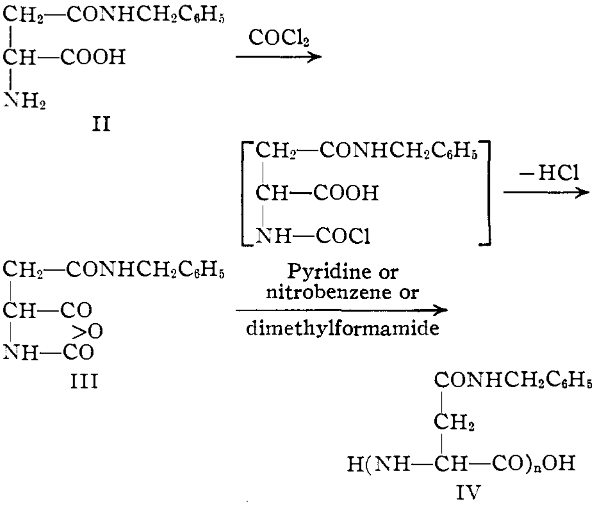
In continuation of previous work on syntheses of polyfunctional polyamino acids and derivatives,[1] the synthesis of poly-N$^{\beta}$-benzyl-*dl*-asparagine is reported in the present paper.

This polymer was prepared by the following series of reactions (Table I), starting from N$^{\alpha}$,N$^{\beta}$-dibenzylasparagine (I),[2,3] which was catalytically hydrogenolyzed to N$^{\beta}$-benzyl-*dl*-asparagine (II). This on being suspended in dioxane and treated with phosgene, yielded the N-carboxy anhydride (III), probably through N$^{\alpha}$-chloroformyl-N$^{\beta}$-benzylasparagine. III represented a white crystalline, comparatively stable compound, decomposing at 225°.

TABLE I



$$\underset{\text{II}}{\begin{array}{l}CH_2\text{—}CONHCH_2C_6H_5\\ |\\ CH\text{—}COOH\\ |\\ NH_2\end{array}} \xrightarrow{COCl_2} \left[\begin{array}{l}CH_2\text{—}CONHCH_2C_6H_5\\ |\\ CH\text{—}COOH\\ |\\ NH\text{—}COCl\end{array}\right] \xrightarrow{-HCl}$$

$$\underset{\text{III}}{\begin{array}{l}CH_2\text{—}CONHCH_2C_6H_5\\ |\\ CH\text{—}CO\\ |\quad\quad >O\\ NH\text{—}CO\end{array}} \xrightarrow[\text{dimethylformamide}]{\text{Pyridine or nitrobenzene or}} \underset{\text{IV}}{\begin{array}{c}CONHCH_2C_6H_5\\ |\\ CH_2\\ |\\ H(NH\text{—}CH\text{—}CO)_nOH\end{array}}$$

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[1] M. Frankel and A. Berger, *Nature*, **163**, 213 (1949); *J. Org. Chem.*, **16**, 1513 (1951); M. Frankel, M. Breuer and S. Cordova, *Experientia*, **VIII**, 299 (1952); M. Frankel and M. Halmann, *J. Chem. Soc.*, 2735 (1952); M. Frankel, M. Harnik and Y. Levin, *Experientia*, **VIII**, 98 (1952); E. Katchalski, I. Grossfeld and M. Frankel, THIS JOURNAL, **69**, 2564 (1947); **70**, 2094 (1948).

[2] F. H. McMillan and N. F. Albertson, *ibid.*, **70**, 3778 (1948).

[3] M. Frankel, Y. Liwschitz and Y. Amiel, *ibid.*, **75**, 330 (1953).