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REACTIONS IN HIGH BOILING SOLVENTS—I
EFFECT OF RANEY NICKEL ON STEROIDS

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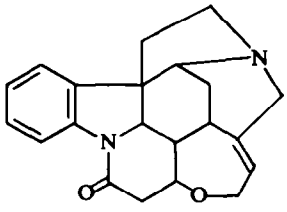
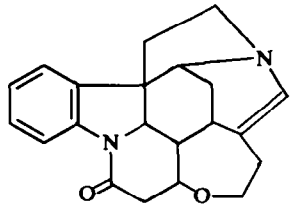
Abstract—The effect of Raney nickel on steroids in boiling *p*-cymene has been studied. The following four different types of reaction have been observed: (a) dehydrogenation (oxidation) of the 3-hydroxyl group, (b) hydrogenation of 5:6-double bond, (c) isomerization of the 5β-hydrogen to 5α, and (d) dimerization.

CHAKRAVARTI and Robinson[1] carried out an interesting conversion of the alkaloid strychnine (I) into an isomeric product, neostrychnine (II) by refluxing the former in xylene solution in presence of Raney Ni catalyst. This conversion involves shifting of the double bond of strychnine from the position 21(22) to 20, and may be visualized as a hydrogenation *cum* dehydrogenation process. This conversion is found to be quite a general one[2] as brucine, strychnidine etc may be converted in a similar manner to the corresponding neo-bases, neobrucine, neostrychnidine, etc. In the present instance an investigation was undertaken to study the effect of this catalyst on various steroid bodies at elevated temperatures.



I



II

Raney Ni was first used as a catalyst for hydrogenation, reduction, oxidation or isomerization by Bougault *et al.*[3] Ashida[4] observed that glucose in a saturated solution in cyclohexanol was reduced to *d*-sorbitol by heating at 130–135° in presence of Raney Ni. No reduction could be observed in absence of the catalyst. A report[5] on the work of Ruschig described the catalytic conversion of pregnenolone to progesterone in presence of Raney Ni with cyclohexanone as a hydrogen acceptor. Kleiderer and Kornfeld[6] determined the general applicability of this oxidation and also studied the possibility of using it in the reverse sense, i.e. as a reductive method in presence of a hydrogen donor, more or less similar to the use of aluminium alkoxides. Thus a number of secondary alcohols, e.g. cholesterol and cholestanol were oxidized to the related ketones, Δ^4-cholestenone and cholestanone respectively with Raney Ni in presence of cyclohexanone as a hydrogen acceptor. For catalytic reductions these workers used various types of hydrogen donors like ethanol, isopropanol and cyclo-

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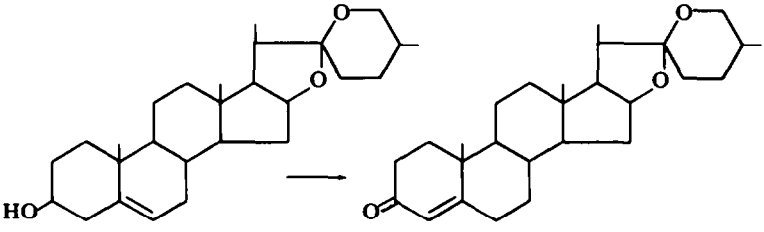
hexanol. Subsequently Romo[7] prepared a number of 3-keto-Δ^4-steroids by oxidation of 3-hydroxy-Δ^4-steroids with Raney Ni in presence of acetone or methyl ethyl ketone as the hydrogen acceptor. According to a patent taken out by Sondheimer *et al.*[8] steroids containing a double bond, α:β- to a secondary alcoholic group, on treatment with Raney Ni and a hydrogen acceptor like acetone are oxidized, the secondary alcoholic group being converted to a ketonic group.

In all the above cases involving oxidation/reduction with Raney Ni a hydrogen acceptor/donor is used. In the conversion of strychnine into neostrychnine[1] one part of the molecule acts as the donor while the other part acts as the acceptor. The present investigation[9–11] deals with the effect of Raney Ni on some steroids in the absence of a hydrogen acceptor/donor like acetone, methyl ethyl ketone, cyclohexanone, isopropanol, cyclohexanol. Most of these steroids were obtained in connection with

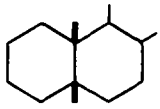


III IV

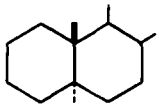
various investigations on Indian plants carried out in our laboratories. In the first instance diosgenin (III) was refluxed in xylene solution with Raney Ni when most of the diosgenin was recovered unchanged. As it appeared that the reaction was extremely slow at the temperature of boiling xylene, it was decided to use a higher boiling solvent in place of xylene. Accordingly, the above reaction was carried out in boiling *p*-cymene solution and the product isolated was Δ^4-tigogenone (IV). However, with an excess of the catalyst the major product obtained was the saturated ketone, tigogenone. The latter product was also obtained when tigogenin was heated with Raney Ni in boiling *p*-cymene solution. Hecogenin on similar treatment gave hecogenone. When cholesterol was heated with small amounts of Raney Ni the products isolated were cholestenone and cholestanone. With an excess of the catalyst, however, the product isolated was cholestanone. Stigmasterol on treatment with a small amount of the catalyst under similar experimental conditions afforded $\Delta^{4,22}$-stigmastadiene-3-one and Δ^{22}-stigmasten-3-one, whilst excess of the catalyst gave the latter product only. β-Sitosterol when refluxed with an excess of Raney Ni in *p*-cymene solution yielded sitostanone.

It was observed that in the above reactions, where there was a saturation of the 5:6 double bond, the configuration of A/B ring fusion of the products isolated was *trans*. To confirm the above finding regarding the sterospecificity of the effect of Raney Ni in high boiling solvents, steroids having *cis* configuration in A/B ring fusion were subjected to the above reaction with Raney Ni. Thus smilagenone, when heated under reflux condition with Raney Ni in *p*-cymene solution gave tigogenone, having A/B *trans* configuration. Tigogenone was also obtained when the reaction was carried out with epismilagenin. Under similar conditions coprostanone gave cholestanone and sarsasapogenin gave neotigogenone. The action of Raney Ni on cholic acid in boiling *p*-cymene appeared to be rather complex. Methyl cholate, however, gave a

small yield of methyl 7α,12α-dihydroxy-3-oxo-5α-cholanoate under similar experimental conditions.* In all these cases, it may be noted that a 5β-steroid (V) is transformed into a 5α-steroid (VI).



V



VI

The androgenic activity of 5β-androstanes are much weaker than those of the 5α-isomers.[12] It appeared to be interesting to examine the possibility for the conversion of the 5β-androsterones into the active 5α-isomers. In this respect, the inactive etiocholan-3:17-dione on heating with Raney Ni in boiling *p*-cymene solution gave androstan-3:17-dione having considerable androgenic activity. This latter product is also obtained from the inactive products, 3α-hydroxyetiocholan-17-one and 3β-hydroxyetiocholan-17-one. These observations with regard to the above isomerization of the A/B ring fusion of the steroids have recently been utilized in the partial synthesis of some biologically interesting steroids.[13–15]

It should be emphasized that this reaction with Raney Ni is very difficult to standardize. This is presumably due to the difference in activities of different preparations of Raney Ni catalysts. Moreover, there is a gradual decrease in activity of the catalysts on storage. No doubt any weakness in the activity of the catalyst may be compensated by using more of it but it becomes extremely difficult to decide as to the amount of the catalyst to be used. Same amounts of different preparations of the catalyst have been found to give varying yields of the products. The adsorbed hydrogen on the catalysts appears to have some influence in this reaction. When cholesterol was heated under reflux with Raney Ni in a solvent, having a b.p. somewhat lower than that of *p*-cymene, like *pseudo*-cumene (*pseudo*-cumene, b.p. 168°; *p*-cymene, b.p. 177°) the product isolated was cholestenone and not cholestanone. With the same or even much less amount of the catalyst of more or less the same activity the reaction in *p*-cymene gave cholestanone. Thus the reaction at lower temperatures makes it difficult for the catalyst to make hydrogen available for the reduction of the 5:6-double bond. At a still lower temperature, e.g. in xylene, no appreciable conversion takes place. Raney Ni, pre-heated in boiling *p*-cymene, has somewhat less activity. Nevertheless it is found to retain a considerable amount of the original activity and is still suitable for the above reaction.

It is stated above that when refluxed with excess of Raney Ni in *p*-cymene solution cholesterol yields cholestanone. With a further increase of the amount of the catalyst, however, a dimer having the molecular formula $C_{54}H_{90}O$ is also formed along with cholestanone. In the mass spectrum (Fig. 1) of the dimer *m/e* 754 is indeed the parent ion (by its persistence in intensity). A small peak is present at *m/e* 245 possibly due to a slight impurity. Very small ions at *m/e* 768 may also be observed in the spectrum. These are probably homologues of the product and one usually observes them in cholesterol samples as well. With a large excess of the catalyst, however, the dimer was the only product that could be isolated. This dimer was also formed when cholestanol

* Details of this particular case are not included in the experimental part of this report in view of similar records published by Mitra and Elliott.[15]

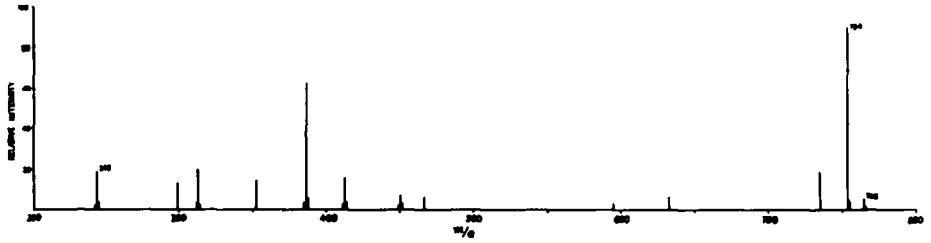


FIG. 1 Mass spectrum of the dimer (VII).

was heated with Raney Ni in *p*-cymene solution. It is perhaps not out of place to mention the polymerizing property of Raney Ni in the formation of bipyridyl and terpyridyl from pyridine.[16] The above dimer from cholesterol or cholestanol has no OH group as is evident by the inability to form an acetate as also by the lack of absorption in the region of 3μ in the IR spectrum. The dimer is an unsaturated non-conjugated ketone as is indicated by absorption at 1710 cm^{-1} in the IR spectrum (Fig. 2) and by the formation of a yellow colour with tetranitromethane. All attempts to reduce the product by catalytic hydrogenation, Clemmensen reduction or sodium/alcohol reduction were unsuccessful. The IR spectrum of the product (Fig. 2) is very much similar to that of cholestan-3-one (Fig. 3). The physical and chemical properties

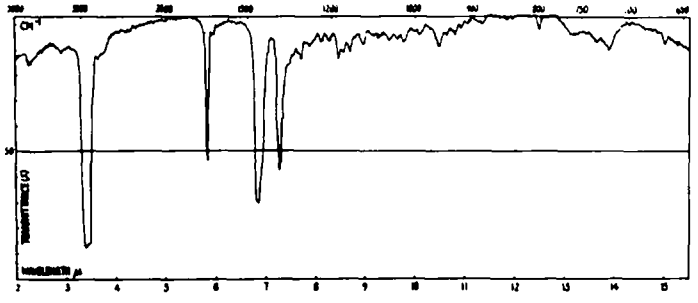


FIG. 2 IR curve of the dimer (VII) as Nujol mull.

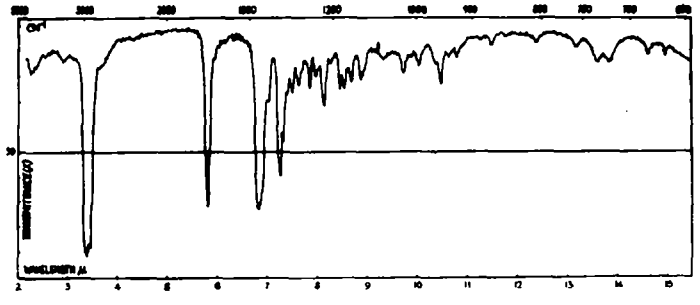
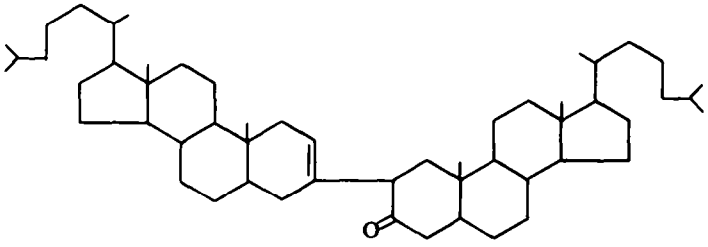


FIG. 3 IR curve of cholestan-3-one as Nujol mull.

of the dimer agree with those of the product (VII) obtained from cholestanone on treatment with hydrogen bromide in acetic acid-n-butyl ether.[17] The identity was established by a direct comparison. It appears that cholestanone is formed first,

from cholesterol or cholestanol, which then undergoes self condensation with the formation of the dimer (VII).



VII

In most of the above cases during heating of the steroid bodies with Raney Ni it has been observed that some high melting products are also formed in small amounts, particularly when an excess of the catalyst is taken. It was difficult to characterize these high melting products in view of the very low yields. It may be presumed that these high melting products are also dimers of the above type.

The effect of the Raney Ni on steroids in boiling *p*-cymene solution involving four different types of reactions may be summarized as follows:

Type A—dehydrogenation (oxidation) of the 3α- or 3β-OH group;
Type B—hydrogenation of 5:6- double bond;
Type C—isomerization of 5β- hydrogen to 5α-;
Type D—dimerization.

Type A reaction usually requires the use of a small amount of the catalyst whereas with excess of the catalyst the saturated ketone is obtained by a combination of type A and type B reactions. Type C requires a moderately large amount of the catalyst. Type D reaction is particularly favoured when a large excess of Raney Ni is used. If a steroid can undergo more than one possible type of reaction they may proceed simultaneously but in many cases an individual type of reaction, unassociated with any of the other types may be demonstrated.

EXPERIMENTAL

Preparation of Raney Ni *catalyst.* Raney Ni, W-2, was prepared by the action of NaOH aq on Raney Ni aluminium alloy according to the method of Mozingo.[18] The catalyst was generally used within a month of its preparation.

Purification of the solvent. p-Cymene used in this reaction was prepared by refluxing the technical *p*-cymene with Raney Ni ct for 2–3 hr followed by distillation. *pseudo*-Cumene and xylene were also purified similarly.

General procedure. The steroid taken in a ground joint flask was dissolved in *p*-cymene and to this was added Raney Ni ct previously washed with *p*-cymene. The flask was fitted with a distillation arrangement. The mixture was heated on a sand-bath and a few ml *p*-cymene was distilled so as to ensure complete removal of water and alcohol by azeotropic process. The mixture was then heated under reflux on the sand-bath for 10 hr. After the reaction the mixture was filtered hot and the filtrate distilled in steam to remove *p*-cymene. The residue obtained was taken up in ether and separated from the aqueous layer. The residue left after the removal of the solvent was chromatographed over a column of neutral Brockmann alumina using solvents successively in the order of increasing polarities (pet ether → pet ether–benzene mixtures → benzene → benzene–ether mixtures → ether → ethanol). The products obtained from different fractions were examined.

The pet ether used had b.p. 40–60°. Chromatographic separations were carried out over a column of neutral Brockmann alumina. The weights of the catalyst were taken after the reactions were over although the approximate amounts of the catalyst taken for a reaction were determined by taking the catalyst in a small spoon of known capacity. At times the catalyst is found to catch fire while kept for drying for the purpose of taking weight. For this purpose it is better to deactivate the catalyst after the reaction is over. All m.ps were taken in open capillary tubes and are uncorrected. Rotations were determined in chloroform solns at the room temp. UV absorption spectra refer to EtOH. IR spectra were recorded as Nujol mulls on a Perkin–Elmer 421 spectrophotometer. NMR spectra was determined with a Varian A-60 instrument, with TMS as internal standard (τ 10·00; Fig. 4). The mass spectrum was run at different ionizing voltages.

Action of Raney Ni *in diosgenin.* Diosgenin (3 g) in *p*-cymene (45 ml) and Raney Ni (1 g) were used and worked up as described above under "general procedure". The product from an ethereal extract was chromatographed over a column of alumina (80 g). The pet. ether–benzene (2:1) eluate yielded a residue which on crystallization from EtOH yielded diosgenone (1·6 g), m.p. 185–186° (undepressed on admixture with an authentic sample), $[\alpha]_D^{23}$ 0°, λ_{max} 243 mμ (log ε 4·28); IR spectrum was superimposable on that of an authentic sample of diosgenone (strong ketonic absorption at 1681 cm^{-1}). (Found: C, 78·41; H, 9·91; Calc. for $C_{27}H_{40}O_3$: C, 78·59; H, 9·77%); semicarbazone, m.p. 247° (dec); oxime, m.p. 224° (dec).

Diosgenin (1 g) in *p*-cymene (25 ml) and Raney Ni (2·5 g) were used and the product after chromatographic separation and purification by crystallization from EtOH afforded tigogenone, as needles (0·51 g), m.p. and mixed m.p. with authentic sample of tigogenone 205–206°, $[\alpha]_D^{32}$ −54·4°. (Found: C, 78·55; H, 10·26; Calc. for $C_{27}H_{42}O_3$: C, 78·21; H, 10·21%), semicarbazone, m.p. 263°. (Found: N, 8·69; Calc. for $C_{28}H_{45}O_3N_3$: N, 8·91%), oxime, m.p. 254–256° (dec).

Action of Raney Ni *on tigogenin.* Tigogenin (0·5 g) in *p*-cymene (15 ml) and Raney Ni (1 g) were used and the product isolated in the usual way was chromatographed on alumina (15 g). The material eluted with pet. ether–benzene (4:1) on crystallization from EtOH afforded tigogenone (0·22 g), m.p. 205–206°.

Action of Raney Ni on hecogenin. Hecogenin (1 g) in *p*-cymene (25 ml) and Raney Ni (2 g) were used and the ethereal extract of the residue after the steam distillation was chromatographed on alumina. Elution with benzene and crystallization from EtOH afforded hecogenone, as flakes (50% yield), m.p. and mixed m.p. with authentic sample 235–236°, $[\alpha]_D^{31}$ +30°. (Found: C, 76·42; H, 9·44; Calc. for $C_{27}H_{40}O_4$: C, 75·66; H, 9·41%); semicarbazone, m.p. 296°. (Found: N, 15·22. Calc. for $C_{29}H_{46}O_4N_6$: N, 15·49%). The identity was established by a comparison of the IR spectra.

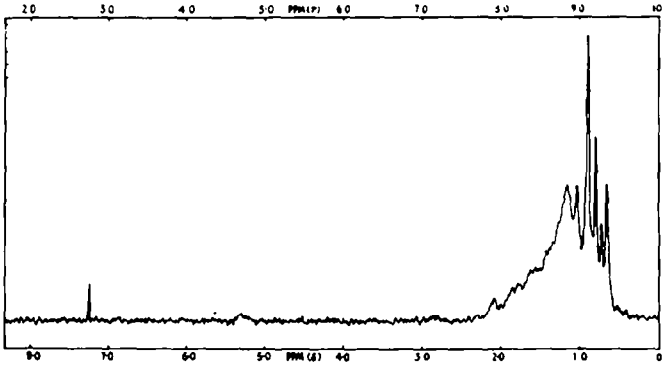


FIG. 4. NMR curve of the dimer (VII) in $CDCl_3$.

Action of Raney Ni *on cholesterol.* Cholesterol (1 g) in *p*-cymene (25 ml) and Raney Ni (50 mg) were used and the transparent sticky residue from the ethereal extract was chromatographed on alumina (40 g). The material eluted with pet. ether–benzene and benzene (0·69 g) was rechromatographed on alumina (40 g). The benzene eluate yielded a crystalline residue (m.p. around 80°) which is almost insoluble in alcohol. This on crystallization from acetone–MeOH afforded Δ^4-cholestenone, as long needles (0·15 g), m.p. 82°—undepressed on admixture with authentic sample, $[\alpha]_D^{22}$ +88·5°, λ_{max}^{EtOH} 241 mμ (log ε 4·2). (Found: C, 84·49; H, 11·62; Calc. for $C_{27}H_{44}O$: C, 84·31; H, 11·53%); semicarbazone, m.p. 226° (dec). Cholestanone and some unchanged cholesterol were also isolated in small amounts.

Cholesterol (2 g) in *p*-cymene (40 ml) and Raney Ni (1·4 g) yielded a pale yellow gummy material on extraction with ether after the steam distillation. It was subjected to chromatography over alumina (70 g). Pet. ether–benzene (4:1) and benzene eluted a material which on crystallization from EtOH yielded cholestanone (0·85 g), m.p. and mixed m.p. with authentic sample of cholestanone 129°, $[\alpha]_D^{23}$ +42°. (Found: C, 83·70; H, 11·94; Calc. for $C_{27}H_{46}O$: C, 83·87; H, 11·99%); the identity was confirmed by comparison of the IR curves. From later fractions a small amount of cholestenone (10 mg) was isolated.

Cholesterol (6 g) in *p*-cymene (100 ml) and Raney Ni (25 g) were used. The ether extract was chromatographed on alumina (180 g). Fractions were collected in 80 ml. The results are indicated below.

Fraction	*Eluate*
Pet. ether	
1–6	Colourless gum (0·71 g)
Pet ether–benzene (4:1)	
7–13	Cryst. (1·83 g)
14–23	Cryst. (1·5 g)
Benzene	
24–26	Gum (0·20 g)
Ether	Gum (0·33 g)
Ethanol	Gum (0·61 g)

Each of the fractions 7–13 was almost insoluble in EtOH. and crystallized from chloroform–EtOH in granular crystals (yield 1 g), m.p. 219–222°, $[\alpha]_D^{30}$ +39·1°, mol wt 754 in mass spectrum. (Found: C, 85·63; H, 11·97; Calc. for $C_{54}H_{90}O$: C, 85·87; H, 12·01%). The IR spectrum showed a strong ketonic absorption at 1710 cm^{-1}; this dimer in the Liebermann–Burchard test slowly develops a greenish yellow colour changing to light green on keeping. The m.p. of the dimer was undepressed on admixture with the product (VII) of Corey and Young.[17] The IR and mass spectra were also similar.

Fractions 14–23 (each fraction soluble in EtOH) on crystallization from EtOH afforded cholestanone (0·86 g), m.p. 128–129°.

Cholesterol (1·5 g) in *p*-cymene (35 ml) and Raney Ni (11·8 g) were used. The residue from the ether extract was chromatographed on alumina (45 g). Pet. ether–benzene (4:1) eluted a material which on crystallization from chloroform–EtOH mixture afforded the dimer (0·41 g), m.p. 217–220°. No crystalline product could be isolated from other chromatographic fractions.

Action of Raney Ni *on cholesterol in* pseudo-*cumene.* Cholesterol (1 g) in *pseudo*-cumene (25 ml) and Raney Ni (1 g) were used and worked up as described under "general procedure". The residue after the steam distillation was extracted with ether which on chromatography over alumina (30 g) yielded cholestenone (0·39 g), m.p. 82°.

Action of Raney Ni *on cholestanol.* Cholestanol (0·5 g) in *p*-cymene (15 ml) and Raney Ni (3 g) were used in the usual way. Chromatography of the material obtained after the steam distillation was carried out on alumina (15 g). Pet. ether–benzene (4:1) eluted successively the dimer (15–17% yield) and cholestanone (20–25% yield).

Action of Raney Ni *on stigmasterol.* Stigmasterol (1·5 g) in *p*-cymene (35 ml) and Raney Ni (1 g) were used. The ether extract yielded a residue which was chromatographed over alumina (50 g). Elution with pet. ether–benzene (4:1) gave a residue which on crystallization from EtOH afforded Δ^{22}-stigmasten-3-one (0·28 g), m.p. 164–165°, $[\alpha]_D^{30}$ +21°; the IR spectrum showed strong absorption peaks at 1709 cm^{-1} (CO), 1379 cm^{-1}, and 971 cm^{-1}. (Found: C, 84·09; H, 11·66; Calc. for $C_{29}H_{48}O$: C, 84·40; H, 11·72%). Pet. ether–benzene (1:1) eluted a material which on crystallization from 90% EtOH afforded stigmasta-4: 22-dienone (0·41 g), m.p. 124–125°, $[\alpha]_D^{23}$ +58°, λ_{max}^{EtOH} 241 (log ε 4·2). (Found: C, 84·62; H, 11·36; Calc. for $C_{29}H_{46}O$: C, 84·81; H, 11·29%); semicarbazone, m.p. 241° (dec). (Found: N, 8·63; Calc. for $C_{30}H_{48}ON_3$: N, 8·98%).

Stigmasterol (1 g) in *p*-cymene (25 ml) and Raney Ni (2 g) were used. The reaction product was worked up in the usual way and chomatographed when Δ^{22}-stigmasten-3-one (0·5 g), m.p. 165° was obtained.

Action of Raney Ni on β-*sitosterol.* β-Sitosterol (0·2 g) in *p*-cymene (10 ml) and Raney Ni (0·8 g) were used and worked up in the usual way. The etheral extract after removal of the solvent and chromatographic purification followed by crystallization from EtOH afforded sitostanone (0·08 g), m.p. 159–160°, $[\alpha]_D^{32}$ +14°. (Found: C, 84·13; H, 12·11; Calc. for $C_{29}H_{50}O$: C, 83·99; H, 12·15%).

Action of Raney Ni on smilagenone. Smilagenone (2 g) in *p*-cymene (40 ml) and Raney Ni (3 g) were used. The residue after the steam distillation was taken up in ether and the solvent removed. This was chromato-

graphed on alumina (60 g). Pet. ether–benzene (1:1) eluted a material which on crystallization from 90% EtOH afforded tigogenone (0·51 g), m.p. and mixed m.p. with authentic tigogenone, 205–206°, $[\alpha]_D^{32}$ −56°. (Found: C, 77·98; H, 10·12; Calc. for $C_{27}H_{42}O_3$: C, 78·21; H, 10·21%).

Action of Raney Ni *on epismilagenin.* Epismilagenin (0·5 g) in *p*-cymene (15 ml) and Raney Ni (0·8 g) were used. The product was worked up as in previous cases. Chromatography over alumina (15 g) followed by crystallization from 90% EtOH yielded tigogenone (25–30% yield), m.p. 206–207°, $[\alpha]_D^{32}$ −55·2°. (Found: C, 78·39; H, 10·26; Calc. for $C_{27}H_{42}O_3$: C, 78·21; H, 10·21%).

Action of Raney Ni *on sarsasapogenin.* Sarsasapogenin (1 g) in *p*-cymene (25 ml) and Raney Ni (2 g) were used. After working up in the usual way the product was chromatographed on alumina (30 g). Pet. ether–benzene (1:1) eluted a material which on crystallization from EtOH afforded neotigogenone as plates (0·22 g), m.p. 216–218°, $[\alpha]_D^{30}$ −62°. (Found: C, 78·13; H, 10·23; Calc. for $C_{27}H_{42}O_3$: C, 78·21; H, 10·21%); semicarbazone, m.p. 212–213° (dec). (Found: N, 8·78; Calc. for $C_{28}H_{45}O_3N_3$: N, 8·91%); oxime, m.p. 166–168°; the identity of neotigogenone was established by converting it to tigogenone, m.p. 207° by refluxing with ethanolic hydrochloric acid.

Action of Raney Ni *on coprostanone.* Coprostanone (0·75 g) in *p*-cymene (20 ml) and Raney Ni (1·5 g) were used and the gummy residue mixed up with crystals obtained from the ethereal extract was chromatographed over alumina (30 g). The material (0·19 g) eluted with pet. ether–benzene (4:1) was crystallized from EtOH when cholestanone (0·11 g), m.p. 128–129° was obtained. No other product could be isolated in the pure form from other fractions.

Action of Raney Ni *on etiocholan-3:17-dione.* Etiocholan-3:17-dione (0·25 g) in *p*-cymene (10 ml) and Raney Ni (1 g) were used. The ether extracted matter was thoroughly dried and chromatographed on alumina (15 g). Pet. ether eluted a material which on crystallization from 90% EtOH afforded a product, m.p. 140–146°. This was not purified further. The material (63 mg) eluted with benzene on crystallization from aqueous EtOH yielded 5α-androstan-3:17-dione, m.p. 133–134° undepressed on admixture with an authentic sample, $[\alpha]_D^{30}$ +108°. This product had considerable androgenic activity.

Action of Raney Ni *on* 3α-*hydroxyetiocholan*-17-*one.* Starting with 3α-hydroxyetiocholan-17-one (0·25 g) in *p*-cymene (10 ml) and Raney Ni (1 g) and proceeding in the usual way two crystalline residues were obtained, one from the pet. ether eluate and the other from benzene eluate. The residue (72 mg) from benzene eluate was rechromatographed. The benzene eluted material on crystallization from aqueous EtOH afforded 5α- androstan-3:17-dione (30 mg), m.p. 132–134°.

Action of Raney Ni *on* 3β-*hydroxyetiocholan*-17-*one.* 3β-hydroxyetiocholan-17-one (0·25 g) in *p*-cymene (10 ml) and Raney Ni (1 g) were used. After working up as above 5α-androstan-3:17-dione was obtained (32 mg), m.p. 133·134°.

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