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Synthesis of Bridged Steroids. IV.[1] Cholestane Derivatives with a 3,5-Iminomethano Bridge

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N-Sulfonylated 3-methoxycholestane (5→3)-lactams (Vc), (VIc) and (VId) were subjected to reductive fragmentation initiated with lithium aluminum hydride giving in good yields N-sulfonylated *cis*-amino alcohols (3α, 5α and 3β, 5β) (XIIIa), (XIVc), and (XIVa). These compounds were smoothly cyclized to 3α,5-iminomethano-5α- and 3β,-5-iminomethano-5β-cholestane derivatives, (Ia), (IIa), and (IIb), which were then desulfonylated to give 3α,5α- and 3β,5β-pyrrolidinocholestanes (Ib) and (IIc), respectively.

In the previous papers[1,3] of this series we reported syntheses of some steroid derivatives containing bridged carbocyclic rings on ring A. As a continuation of this work, synthesis of some cholestane derivatives containing bridged azacyclic rings was carried out with the same purpose described in the first paper.[3a] The present paper deals with a successful synthesis of bridged cholestane derivatives (Ib) and (IIc) with an iminomethano bridge at C_3 and C_5.

The only difficulty anticipated in the present synthesis was in placing the carbon bridge end at the angular C_5-position, just as in the case of the syntheses of the analogous carbocyclic bridged steroids.[1,3] However, this problem was already solved by the successful synthesis of 3-oxocholestane-5-carbonitriles, (III) and (IV),[4,5] and the related compounds, (V) and (VI)[4,6] from cholest-4-en-3-one by hydrocyanation[4,5] and the subsequent manipulation. Although several approaches starting from these compounds[7] are conceivable, the N-sulfonylated lactamol derivatives (Vc), (VIc), and (VId) were selected as the starting materials, since we were specially interested in the high susceptibility of these compounds to nucleophiles. Thus, as already reported,[6] compounds (Vc), (VIc), and (VId) are decomposed with alkali giving in good yields the corresponding 3-oxocholestane-5α- and 5β-carboxylic acids, (XI) and (XII), through the intermediates (IX) and (X), respectively, as illustrated in Chart 1. When lithium aluminum hydride is used as a nucleophilic reagent instead of alkali, one may expect a similar reaction sequence to give 3-sulfonylimino-5-formylcholestanes (XVIIc), (XVIIIc), and (XVIIId) as primary fragmentation products which are then transformed to an aminoalcohol derivatives (XIIIa), (XIVc), and (XIVa) by further reduction (Chart 2). Since no difficulty was expected in cyclization of these aminoalcohol derivatives to the desired

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[1] Part III: W, Nagata, M. Narisada, T. Sugasawa, and T. Wakabayashi, *Chem. Pharm. Bull.* (Tokyo), **16**, 885 (1968).

[2] Location: *Fukushima-ku, Osaka.*

[3] *a*) W. Nagata and M. Narisada, *Chem. Pharm. Bull.* (Tokyo), under contribution; *b*) W. Nagata, M. Narisada and T. Wakabayashi, *Chem. Pharm. Bull.* (Tokyo), under contribution.

[4] W. Nagata, S. Hirai, H. Itazaki, and K. Takeda, *J. Org. Chem.*, **26**, 2413 (1961).

[5] *a*) W. Nagata, M. Yoshioka, and S. Hirai, *Tetrahedron Letters*, **1962**, 461; *b*) W. Nagata and M. Yoshioka, *ibid* **1966**, 1913; *c*) W. Nagata and M. Yoshioka, Proceedings of the 2nd International Congress on Hormonal Steroids, Milan ,Italy, May 1966, Excerpta Medica Foundation, Amsterdam, 327 (1967).

[6] W. Nagata, S. Hirai, H. Itazaki, and K. Takeda, *Liebigs Ann. Chem.*, **641**, 184 (1961).

[7] An attempted lithium aluminum hydride reduction of the lactamol VIa was unsuccessful probably owing to low solubility of the metalated starting compound.

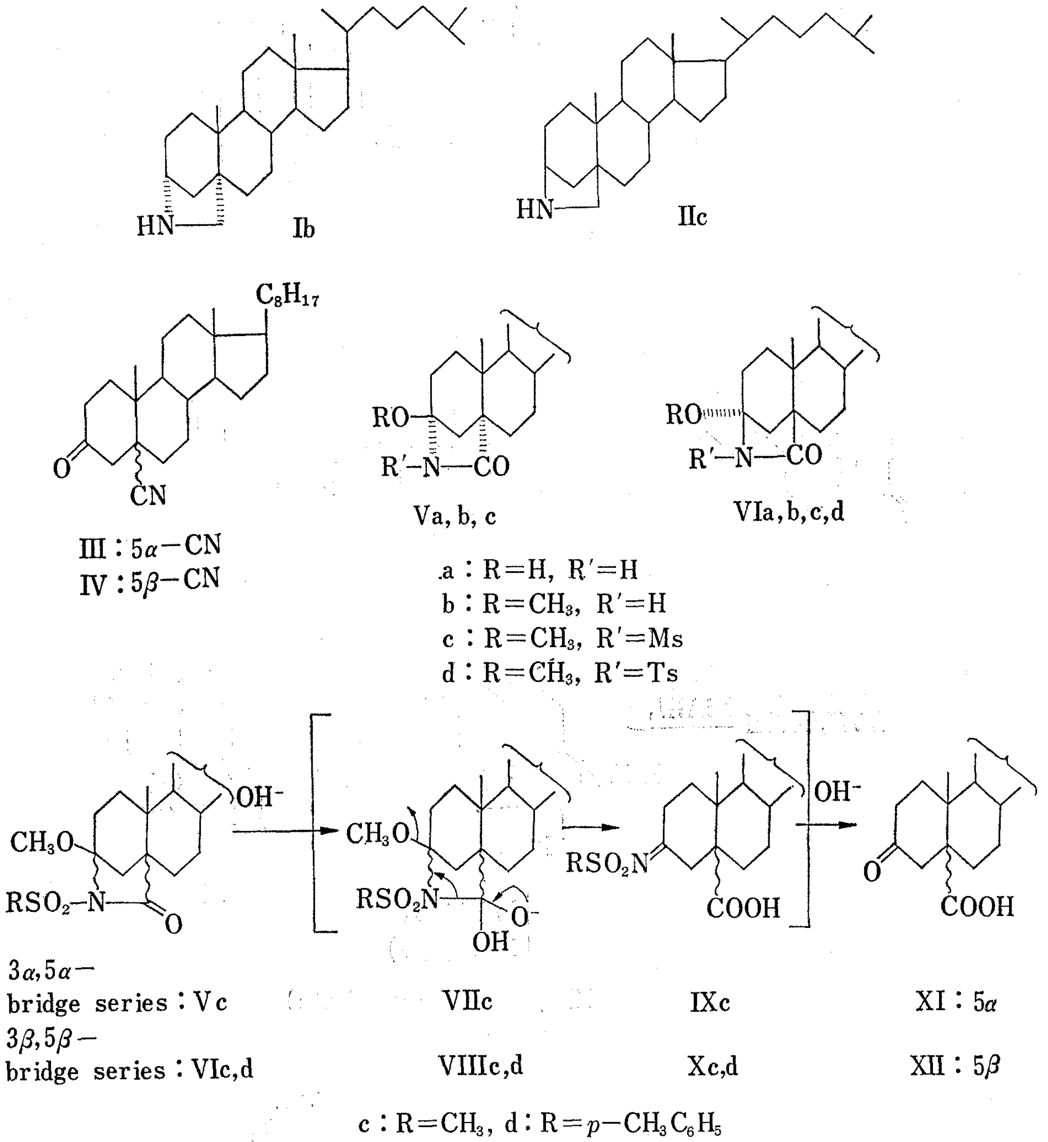

Chart 1

bridged compounds (I) and (II), the reductive degradation of the lactamol derivatives (Vc), (VIc), and (VId) appeared to provide a promising synthetic route.

The N–mesyl–*trans*–lactamol methyl ether (Vc) was subjected to lithium aluminum hydride reduction in refluxing tetrahydrofuran. As expected, the reduction proceeded smoothly giving the expected 3α–mesylamino–5–hydroxymethyl–5α–cholestane (XIIIa) as the sole product in 74.2% yield. The infrared spectrum of XIIIa supports the assigned structure.[8] The 3α–configuration assigned to the mesylamino group of this product was established by the successful ring closure as described later. Reduction of the *cis*–lactamols (VId) and (VIc) was likewise successful giving 3β–tosylamino– and 3β–mesylamino–5–hydroxymethyl–5β–cholestane (XIVa) and (XIVc) in 64 and 86% yields, respectively. Structural and configurational assignment for these products was based upon the spectral and the chemical evidence similar to that for the *trans*–isomer (Vc). These results support the predicted reaction course formulated in Chart 2. The almost exclusive formation of the 3–sulfonylamino group having an axial orientation *cis* to the 5–substituents observed in these three examples needs some discussion, since, as already reported, a similar reduction of 3–oxo–

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[8] See experimental.

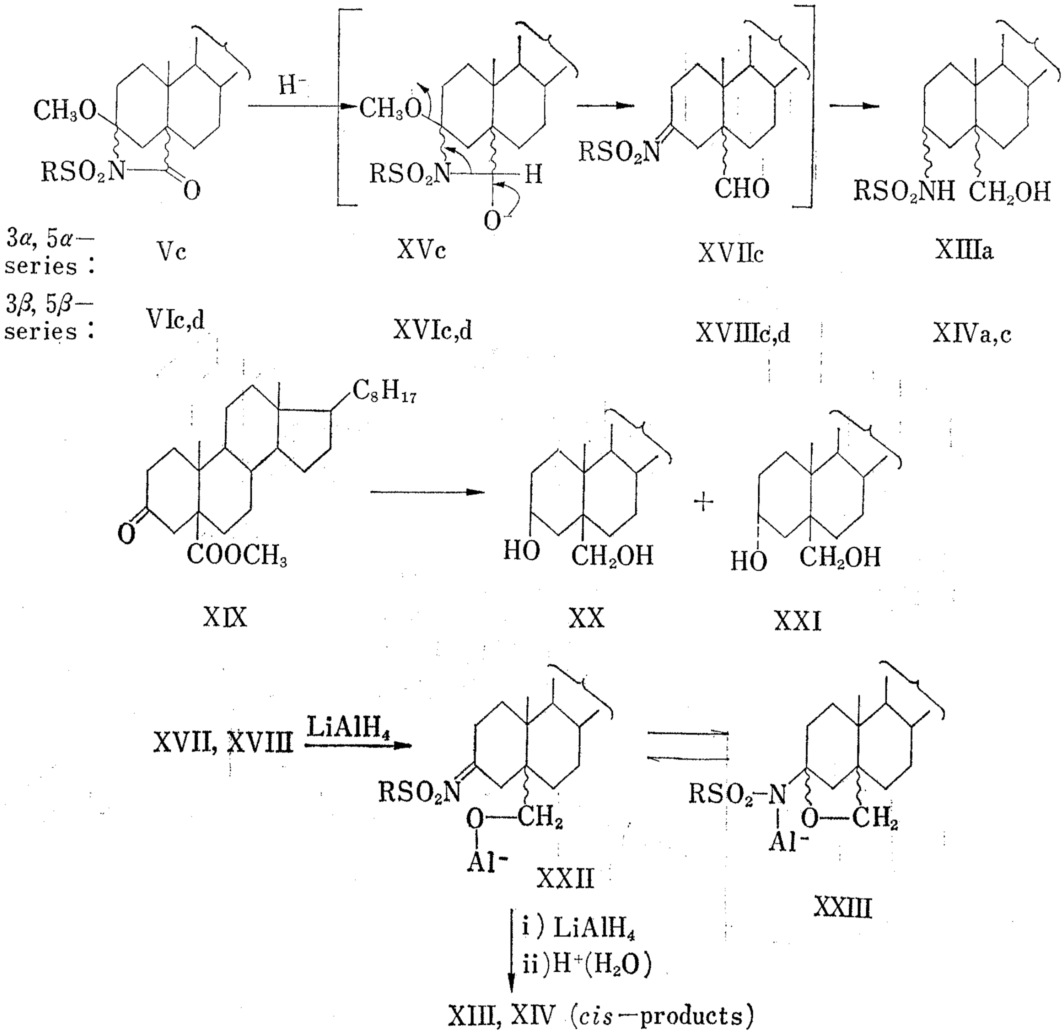
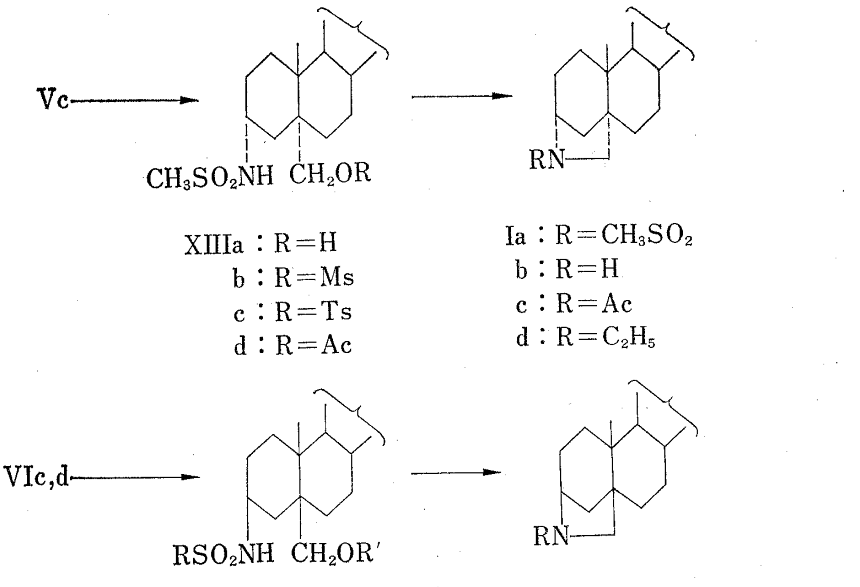


Chart 2



XIIIa : R=H
b : R=Ms
c : R=Ts
d : R=Ac

Ia : R=CH_3SO_2
b : R=H
c : R=Ac
d : R=C_2H_5

XIVa : R=p−$CH_3C_6H_4$,R′=H
b : R=p−$CH_3C_6H_4$,R′=Ac
c : R=CH_3,R′=H

IIa : R=CH_3SO_2
b : R=p−$CH_3C_6H_4$−SO_2
c : R=H
d : R=Ac

Chart 3

5β–cholestane–5–carboxylic acid ester (XIX) gave almost equal amounts of *cis*– and *trans*–diols (XX) and (XXI).[9] The marked contrast may be rationalized by assuming that initial attack of a hydride anion occurs at the angular formyl group rather than at the sterically less hindered 3–position yielding an O–aluminated intermediate (XXII). The negatively charged and voluminous 5–substituent of this intermediate probably existing in equilibrium with the bridged isomer (XXIII) may prevent approach of the reagent from the same side of the molecule resulting in predominant or exclusive formation of the *cis*–isomers.

Initial attempt to cyclize compound (XIIIa) or (XIVa) with conc. sulfuric acid in acetic acid was not quite satisfactory giving a mixture of the desired bridged compound (Ia) or (IIb) and the acetylated product (XIIId) or (XIVb) in variable ratios. However, more efficient cyclization was achieved by a two–step reaction sequence as follows. Compound (XIIIa) was sulfonylated with mesyl or tosyl chloride in pyridine giving in an excellent yield the corresponding mesylate or tosylate (XIIIb) or (XIIIc), which on treatment with potassium carbonate in dimethylformamide was cyclized to the bridged compound (Ia) in almost quantitative yield. A similar reaction sequence was applied to cyclization of the *cis*–isomer (XIVa). Compound (XIVa) was mesylated in the conventional manner and the resulting crude mesylate was treated with alumina affording the cyclized product (IIa) in 85% over–all yield. The infrared spectra of (Ia) and (IIa) showed no bands responsible for both O–tosyl or O–mesyl and imide (N–H), supporting the assigned structures. Demesylation of Ia and IIa was effected by means of lithium–ammonia reduction giving in good yields crystalline 3α,5–iminomethano–5α– and 3β,5–iminomethano–5β–cholestane (Ib) and (IIc). These final products were characterized also as their picrates and as N–acetates ,(Ic) and (IId).

Finally it is worthy to note that attempted fragmentation of Vc with methylmagnesium iodide failed and the demesylated lactamol methyl ether (Vb) was obtained as a major product. The failure is ascribable to the reagent bulkiness which makes the attack to the highly hindered carbonyl group at the angular C_5–position impossible.

Compounds (Ib) and (IIc) were tested for their antimicrobial activities. Both were found inactive against gram–negative bacteria but active against gram–positive bacteria and *Trichomonas vaginalis*: the compounds inhibited the growth of gram–positive bacteria at a minimum inhibitory concentration of 20—50 μg per ml. Against *Trichomonas vaginalis* (Ib) and (IIc) were effective at a concentration of 25 and 12.5 μg per ml respectively.

Experimental

All melting points were measured on a Kofler hot–stage apparatus and are corrected. Unless otherwise stated, infrared spectra were taken in chloroform by use of Koken DS–201B spectrophotometer and $[\alpha]_D$ in chloroform with Perkin–Elmer Polarimeter Type 141. Unless otherwise specified, the extracts were dried on anhydrous sodium sulfate and column chromatography was performed according to the method by Reichstein and Shoppee[10] using Woelm alumina (activity II).

3α-Mesylamino-5-hydroxymethyl-5α-cholestane (XIIIa)——To a suspension of $LiAlH_4$ (250 mg) in tetrahydrofuran (THF) (20 ml) was added dropwise a solution of Vc (250 mg) in THF (25 ml) with stirring. The reaction mixture was refluxed for 3 hr, cooled to 0°, and treated with water (10 ml) and 4N hydrochloric acid to dissolve the precipitated salts. After addition of ether (20 ml), the aqueous layer was separated and extracted with two 20 ml portions of ether. The extracts were washed with water, dried and concentrated *in vacuo* to give a residue (260.4 mg) which upon recrystallization from ether–methanol afforded XIIIa (156 mg) as needles: mp 236.5—238.5°. A second crop (20 mg, mp 230—238°) was obtained. The total yield is 176.0 mg (74.2%).

An analytical sample was recrystallized from ether–methanol to give the needles: mp 239—241°, $[\alpha]^{33}_D$ $-15.1°$ ($\pm 2°$) ($c=1.106$). IR ν^{Nujol}_{max} cm^{-1}: 3515, 3240, 1323, 1151, 1016. *Anal.* Calcd. for $C_{29}H_{53}O_3NS$: C, 70.26; H, 10.78; N, 2.83; S, 6.46. Found: C, 70.24; H, 10.69; N, 3.13; S, 5.97.

3β-Tosylamino-5-hydroxymethyl-5β-cholestane (XIVa)——To a suspension of $LiAlH_4$ (350 mg) in THF (20 ml) was added dropwise a solution of VId (250 mg) in THF with stirring. The reaction mixture was

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[9] W. Nagata, S. Hirai, T. Aoki, and K. Takeda, *Chem. Pharm. Bull.* (Tokyo),9, 845 (1961).

[10] *Disc. Trans. Farad. Soc.*, No. 7, 305 (1949).

then refluxed for 3 hr. The excess $LiAlH_4$ was decomposed by cautious addition of water (15 ml) and 2N hydrochloric acid (16 ml) and the mixture was diluted with ether (30 ml) and separated. The aqueous solution was extracted with ether twice. The combined organic layer was washed, dried and concentrated to give a residue which was chromatographed on Al_2O_3 (8 g). The fractions eluted with benzene and benzene–chloroform (3:1) gave the crude XIVa which was recrystallized from ether–pentane to give 151 mg (63.5%) of plates: mp 142—144°. After being dried at 80—90° (0.2 mg), they had mp 175—177°. Both samples of the different melting points showed identical solution infrared spectra (chloroform) and gave satisfactory analytical values for the same formula. $[\alpha]_D^{27}$ +40.3°(±3°) (c=0.78). IR ν_{max} cm^{-1}: 3612, 3544, 3274, 1602, 1500, 1329, 1154. *Anal.* Calcd. for $C_{35}H_{57}O_3NS$: C, 73.51; H, 10.05; N, 2.45; S, 5.60. Found: mp 175—177°. C, 73.43; H, 10.02; N, 2.40; S., 5.38; mp 142—144°. C, 73.30; H, 10.00; N, 2.41; S, 5.85.

3*β*-Mesylamino-5-hydroxymethyl-5*β*-cholestane (XIVc)——The lactam (VIc) (1.27 g) was heated under reflux in THF with an excess of $LiAlH_4$ for 3 hr. The product (1.036 g, 86%), isolated in the same manner as described above, had mp 163—166° after recrystallization from hexane.

An analytical sample of XIVc recrystallized from hexane had mp 170—172°. $[\alpha]_D^{24}$ +48.9° (±2°) (c=1.053). IR ν_{max}^{Nujol} cm^{-1}: 3520, 3195, 1164, 1142, 1035. *Anal.* Calcd. for $C_{29}H_{53}O_3NS$: C, 70.26; H, 10.78; N, 2.83; S, 6.46. Found: C, 70.37; H, 10.90; N, 2.72; S, 6.41.

3*α*-Mesylamino-5-tosyloxymethyl-5*α*-cholestane (XIIIc)——A solution of XIIIa (200 mg) in pyridine (2 ml) was treated with *p*–toluenesulfonyl chloride (TsCl) (500 mg) and allowed to stand at room temperature overnight. After decomposition of the excess TsCl by adding some water, the reaction mixture was poured into ice–water and extracted three times with each 20 ml of chloroform. The extracts were washed with water, dried and concentrated to dryness *in vacuo* to give a crystalline residue which upon recrystallization from chloroform–acetone gave XIIIc (155.4 mg) as needles: mp 168—169.5°. A second crop (42.9 mg, mp 160—162°) was obtained from the mother liquor. The total yield is 198.3 mg (70.3%). $[\alpha]_D^{23}$ −56.2° (±2°) (c=1.014). IR ν_{max}^{Nujol} cm^{-1}: 3280, 1602, 1328, 1296, 1193, 1184, 1150, 1142, 945, 788. *Anal.* Calcd. for $C_{36}H_{59}O_5NS_2$: C, 66.53; H, 9.15; N, 2.15; S, 9.85. Found: C, 66.54; H, 9.45; N, 2.08; S, 9.32.

3*α*-Mesylamino-5-mesyloxymethyl-5*α*-cholestane (XIIIb)——Compound (XIIIa) (300 mg) was mesylated with methanesulfonyl chloride (MsCl) (500 mg) and pyridine (2 ml) in a similar manner to that described above. The work–up as usual afforded 316.8 mg (91.5%) of the crystalline dimesylate (XIIIb). An analytical sample recrystallized from ether–methanol had mp 133.5—134.5°. $[\alpha]_D^{19}$ −18.1° (±2°) (c=1.063). IR ν_{max}^{Nujol} cm^{-1}: 3298, 1335, 1319, 1173, 1156, 979. *Anal.* Calcd. for $C_{30}H_{55}O_5NS_2$: C, 62.80; H, 9.66; N, 2.44; S, 11.16. Found: C, 63.37; H, 10.02; N, 2.50; S, 10.75.

N-Mesyl-3*α*,5-iminomethano-5*α*-cholestane (Ia), From (XIIIc)——A solution of XIIIc (394 mg) in dimethylformamide (DMF) (25 ml) was heated with 15% K_2CO_3 (1 ml) under reflux for 3 hr. After neutralization by addition of acetic acid, the reaction mixture was concentrated *in vacuo* to give a residue which was dissolved in chloroform and washed with water. The aqueous layer was extracted with two portions of chloroform. The organic layers were washed with water, dried and concentrated to dryness *in vacuo*. Recrystallization of the residue (338 mg) from acetone gave Ia as plates (190.6 mg): mp 185—188°. A second crop (86 mg) was obtained from the mother liquor. A total yield is 276.6 mg (95.2%). $[\alpha]_D^{25}$ +13.1° (±2°) (c=1.068). IR ν_{max}^{Nujol} cm^{-1}: 1332, 1314, 1144. *Anal.* Calcd. for $C_{29}H_{51}O_2NS$: C, 72.91; H, 10.76; N, 2.93; S, 6.67. Found: C, 73.30; H, 10.76; N, 3.22; S, 6.67.

From (XIIIb)——The same procedure for cyclization was carried out with XIIIb (190 mg). The product isolated (144.0 mg, 91%) in a similar manner to that described above had mp 185—187° after recrystallization from acetone. The sample was identical in every respect with the authentic sample of Ia obtained above.

N-Mesyl-3*β*,5-iminomethano-5*β*-cholestane (IIa)——A solution of XIVc (904 mg) and MsCl (1.4 g) in pyridine (2 ml) was allowed to stand at room temperature overnight. The reaction mixture was treated with a small amount of ice to decompose the excess MsCl. After one hour the solution was diluted with chloroform and water. The organic layer was separated and the aqueous layer was extracted with two portions of chloroform. The chloroform layers were washed successively with 2N sulfuric acid, water, 2N Na_2CO_3, and water, dried and concentrated to give a residue (973 mg) which was purified by chromatography on Al_2O_3 (30 g).

Elution with petr. ether–benzene (2:1), benzene and benzene–chloroform (4:1) gave after recrystallization from methanol IIa (742.7 mg, 85.3%) as plates: mp 128—129°. $[\alpha]_D^{25}$ +55.4° (±2°) (c=1.018). IR ν_{max}^{Nujol} cm^{-1}: 1333, 1185, 1165. *Anal.* Calcd. for $C_{29}H_{51}O_2NS$: C, 72.91; H, 10.76; N, 2.93; S, 6.70. Found: C, 72.82; H, 11.08; N, 3.01; S, 6.68.

Cyclization of (XIIIa) with conc. H_2SO_4 in AcOH——A solution of XIIIa (100 mg) in AcOH (7 ml) was treated with conc. H_2SO_4 (1 ml) with stirring under ice water cooling. The reaction mixture was then allowed to stand at room temperature overnight. The solution was poured into ice water and extracted three times with ether. The extracts, after being washed successively with 2N Na_2CO_3 and water, were dried and evaporated leaving 92.7 mg of an oily residue. This was chromatographed on Al_2O_3 (4 g) and the fractions eluted with petr. ether–benzene (1:1) and (1:2) were crystallized from methanol to give 5.0 mg of plates: mp 175—178°. Its infrared spectrum was superimposable on that of an authentic sample of Ia and a mixture melting point with a sample of Ia showed no depression.

Elution with benzene–chloroform (9:1) and (4:1) gave after recrystallization from ether–methanol the O–acetate XIIId (30.2 mg) as plates: mp 147—149°. $[\alpha]^{32}_{D}$ −29.0°(±2°) (c=1.062). IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 3306, 1742, 1726, 1245, 1316, 1158. *Anal.* Calcd. for $C_{31}H_{55}O_4NS$: C, 69.23; H, 10.31; N, 2.60; S, 5.95. Found: C, 68.91; H, 10.44; N, 2.81; S, 5.71.

3β-Tosylamino-5-acetoxymethyl-5β-cholestane (XIVb)——Compound (XIVa) was acetylated with acetic anhydride and pyridine in the usual manner. The product (XIVb) isolated in the conventional manner had mp 189—190° after recrystallization from ether. $[\alpha]^{26}_{D}$ +25.0° (±5°) (c=0.276). IR ν_{max} cm^{-1}: 3382, 1735, 1600, 1500, 1329, 1160, 1033. *Anal.* Calcd. for $C_{37}H_{59}O_4NS$: C, 72.39; H, 9.69; N, 2.28; S, 5.13. Found: C, 72.55; H, 9.66; N, 2.24; S, 5.38.

Cyclization of (XIVa) with conc. H_2SO_4 in AcOH——A solution of XIVa (100 mg) in acetic acid (4.5 ml) was treated with conc. H_2SO_4 (1 ml) and left at room temperature for 20.5 hr during which time fine needles precipitated. The precipitate (74.0 mg), collected, washed and dried, had mp 142—156°. After being made alkaline by KOH solution, the filtrate was extracted with ether. The extracts were washed, dried and concentrated *in vacuo* to give a crystalline residue (35 mg).

The residue and the precipitate were combined and chromatographed on Al_2O_3 (4 g) and the fractions eluted with petr. ether–ether (9:1) and (1:1) gave 43.3 mg (44.8%) of IIa as plates upon recrystallization from ether: mp 161.5—162°. $[\alpha]^{27}_{D}$ +47.5° (±2°) (c=0.995). IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1602, 1500, 1328, 1160. *Anal.* Calcd. for $C_{35}H_{55}O_2NS$: C, 75.90; H, 10.01; N, 2.53; S, 5.78. Found: C, 75.85; H, 10.10; N, 2.30; S, 5.75.

Elution with benzene—chloroform (9:1) and (3:1) gave 19.3 mg of needles after recrystallization from ether: mp 188—190°. A mixture melting point with an authentic sample of XIVb had no depression and the infrared spectrum was superimposable on that of the authentic specimen.

3α,5-Iminomethano-5α-cholestane (Ib)——In a 100 ml, threenecked flask, fitted with a sealed stirrer and a dry ice condenser, was placed liq. NH_3 (20 ml) and lithium (200 mg). To this solution, a solution of Ia (100 mg) in a mixture of abs. ethanol (1 ml) and ether (10 ml) was added dropwise with stirring. After 5 min, the excess lithium was decomposed by addition of ethanol, and NH_3 was evaporated at room temperature. The residue, after some water was added, was extracted with three portions of ether. After being washed and dried, the ether extracts were concentrated *in vacuo* to give a residue (92 mg) which was dissolved in 2N HCl (5 ml) and washed with ether to remove neutral substances. The aqueous layer, after being made alkaline by adding K_2CO_3, was extracted three times with ether. The ether extracts were washed with dil. K_2CO_3 and dried over K_2CO_3. Evaporation of the solvent left 70 mg of semisolid which was recrystallized from pentane to give 15 mg of Ib mp 98—103°. IR $\nu^{\text{CHCl}_3}_{\text{max}}$ cm^{-1}: 3330, 1605, 1024, 995, 837. $[\alpha]^{24}_{D}$ +26.4° (±1.0°) (c=0.637). *Anal.* Calcd. for $C_{28}H_{49}N \cdot H_2O$: C, 80.51; H, 12.31; N, 3.35. Found: C, 80.77; H, 11.88; N, 3.00. Picrate; mp 205.5—206.5°. *Anal.* Calcd. for $C_{34}H_{52}O_7N_4$: C, 64.94; H, 8.34; N, 8.91. Found: C, 64.80; H, 8.51; N, 8.86. N-acetate; mp 212—213°. IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1628. $[\alpha]^{19}_{D}$ −20.7° (±3°) (c=0.768). *Anal.* Calcd. for $C_{30}H_{51}ON$: C, 81.57; H, 11.64; N, 3.17. Found: C, 81.31; H, 11.70; N, 3.08.

3β,5-Iminomethano-5β-cholestane (IIc)——Compound (IIa) (150 mg) was reduced with Li and ethanol in liq. NH_3 in a similar manner to that described above to give a residue (136 mg) which upon recrystallization from pentane gave 30.0 mg of IIc: mp 73—76°. IR $\nu^{\text{CHCl}_3}_{\text{max}}$ cm^{-1}: 3320, 1603, 998, 835. $[\alpha]^{24}_{D}$ +38.0° (±0.8°) (c=1.030). *Anal.* Calcd. for $C_{28}H_{49}N$: C, 84.14; H, 12.36; N, 3.50. Found: C, 83.42; H, 12.13; N, 3.20. Picrate; mp 260—262°. $[\alpha]^{21}_{D}$ +29.4° (±2°) (c=1.046). *Anal.* Calcd. for $C_{34}H_{52}O_7N_4$: C, 64.94; H, 8.34; N, 8.91. Found: C, 64.97; H, 8.36; N, 9.05. N-acetate; mp 143—145°. $[\alpha]^{23}_{D}$ +61.7° (±2°) (c=1.010). IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 1665. *Anal.* Calcd. for $C_{30}H_{51}ON$: C, 81.57; H, 11.64; N, 3.17. Found: C, 81.46; H, 11.65; N, 3.43.

Grignard Reaction of Vc with Methylmagnesium Iodide——To an ethereal solution of methylmagnesium iodide (made from magnesium (58 mg) and methyl iodide (500 mg) in ether (15 ml)) was added dropwise a solution of Vc (250 mg) in THF (15 ml) at room temperature. The reaction mixture was then refluxed for 3 hr. The excess CH_3MgI was decomposed by addition of water (5 ml) and 2N hydrochloric acid, and the reaction mixture was extracted with three 30 ml portions of ether. The ether extracts were washed with water and dried. Evaporation of ether *in vacuo* gave a foam (278 mg) which was chromatographed on Al_2O_3 (8 g).

The fractions eluted with petr. ether—benzene (1:1) and benzene—chloroform (9:1) gave plates (68.6 mg) after recrystallization from ether—methanol; mp 188—190°. A mixed melting point with a sample of Vb showed no depression and the infrared spectrum was superimposable on that of the authentic specimen. Elution with benzene—chloroform (2:1) gave an unknown product (18.7 mg). A sample, crystallized from methanol–ether, had mp 207—210°. IR $\nu^{\text{Nujol}}_{\text{max}}$ cm^{-1}: 3270, 1738 (w), 1308, 1162, 1142, 756. *Anal.* Found: C, 64.50; H, 9.37; N, 2.31; S, 10.62. The structural elucidation of this compound was not carried out.