lets: yield 65 mg (51%), mp 94–95°. A second recrystallization, from ether–petroleum ether (bp 30–60°) gave pure **9**: mp 95.0–95.5°, $[\alpha]^{18}D$ −6.2 ± 1° (*c* 0.2, chloroform) (lit.[5] mp 95–96°); λ_{max}^{KBr} 3.05 (NH), 5.70 (OAc), and 6.15 μm (C=N); nmr (chloroform-*d*) τ −1.08 (s, 1 H, disappears on deuteration in the presence of triethylamine, NH), 0.80 (d, 1 H, J_{meta} = 1 Hz, aryl H-3), 1.66 (q, 1 H, J_{ortho} = 5 Hz, aryl H-5), 2.06 (d, 1 H, aryl H-6), 2.39 (t, 1 H, $J_{1,2}$ = 2.5 Hz, H-1), 4.75–5.09 (m, 2 H, H-4,5), 7.36–7.60, 7.80–8.20 (both m, 4 H, H-2,2′,3,3′), 7.88, 7.93 (both s, 3 H, OAc), 8.73 (d, 3 H, $J_{5,6}$ = 3.5 Hz, H-6).

Registry No.—**2**, 16848-76-3; **3**, 18933-68-1; **5**, 21317-48-6; **6**, 21317-49-7; **7**, 21317-50-0.

Acknowledgment.—The authors thank J. H. Lauterach and J. D. Wander for nmr spectral measurements.

Reduction of 3β-*p*-Toluenesulfonoxycholest-5-en-4β-ol by Lithium Aluminum Hydride. Clarification of an Anomalous Reduction

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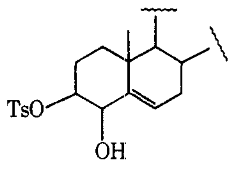
The products of lithium aluminum hydride reduction of 3β-*p*-toluenesulfonoxycholest-5-en-4β-ol (**1**) are shown to be cholest-4-ene (**3**), cholest-5-en-4α-ol (**4**), and 3β-hydroxymethyl-A-norcholest-5-ene (**8**). A mechanism for this unusual reduction is proposed and supported by the deuterium incorporation observed in the reduction of **1** with lithium aluminum deuteride, and the formation of cholest-5-en-4-one on treatment of **1** with sodium hydride.

Reductive cleavage of alkyl tosylates by lithium aluminum hydride has become a useful synthetic operation,[1,2] and it is therefore important to identify and elucidate examples which deviate from expected behavior.

In 1951 Karrer and coworkers[3] reported that lithium aluminum hydride reduction of 3β-*p*-toluenesulfonoxy-4β-hydroxycholest-5-ene (**1**) gave three products, referred to as A, B, and C. Product A (*ca.* 20%) was identified as cholest-5-en-4β-ol (**2**) on the strength of its catalytic reduction to a compound thought to be 5α-cholestan-4β-ol. Product B (*ca.* 4%) was not identified, but C (*ca.* 2%) was shown to be cholest-4-ene (**3**) by a mixture melting point with authentic material. The major product (A) was thus assumed to arise from a simple displacement of the 3β-tosylate group by hydride.



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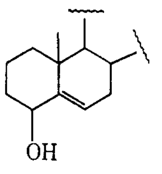

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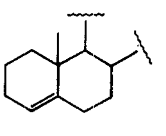

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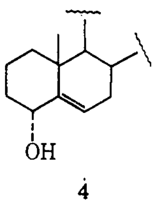
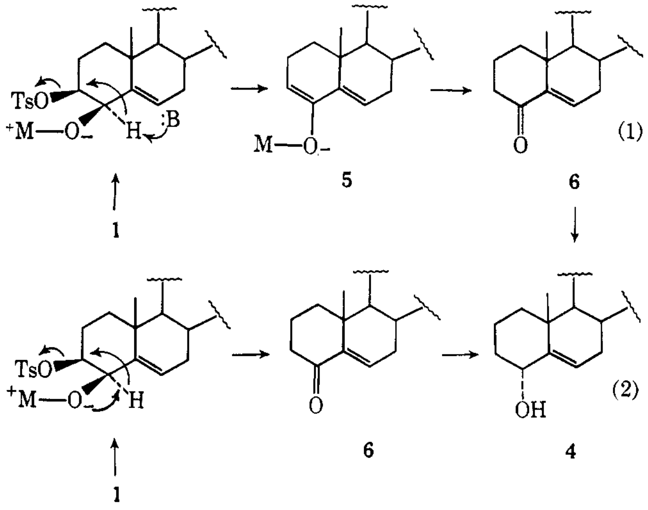


4

That same year, however, Barton and Rosenfelder[4] reported that the physical properties of the compound assumed to be cholestan-4β-ol by Karrer, *et al.*, actually corresponded to the 4α-hydroxy epimer. This fact apparently escaped notice until Jones, *et al.*,[5] demonstrated that compound A was cholest-5-en-4α-ol (**4**) rather than the 4β epimer **2**, an assignment subsequently confirmed by Becker and Wallis.[6] The reduction of **1** thus becomes anomalous, and it is to this subject that we address this paper.

We began by considering two mechanisms (outlined in eq 1 and 2) for the conversion of **1** into **4**. The free hydroxyl group in **1** will be rapidly converted into a salt (M = Li or Al), which can either suffer E2 elimination of toluenesulfonic acid (mechanism 1) or undergo an intramolecular displacement of arylsulfonate by the 4α-hydride (mechanism 2). Cholest-5-en-4-one (**6**) then becomes a key intermediate in both mechanisms, and it is gratifying to note that Jones, *et al.*,[5] report the reduction of **6** to **4** in excellent yield by the action of lithium aluminum hydride.



A consideration of mechanism 2 led us to propose 3β-hydroxymethyl-A-norcholest-5-ene (**8**) for compound B, since it could be formed by the closely related

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[1] L. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, New York, N. Y., 1967, p 588.

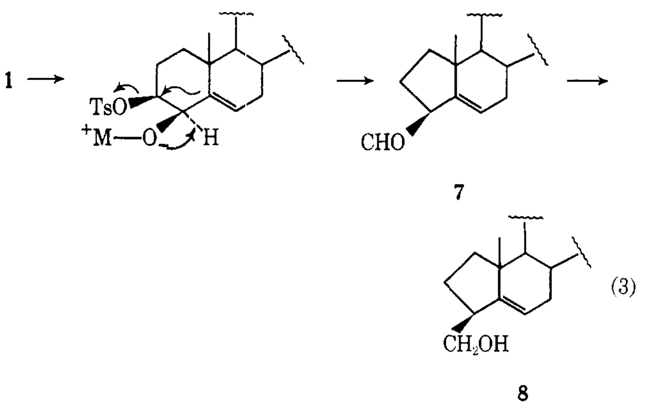
[2] G. Büchi, W. Hofheinz, and J. Paukstelis, *J. Amer. Chem. Soc.*, **88**, 4113 (1966), describe a particularly high yield example.

[3] P. Karrer, H. Asmis, K. Sareen, and R. Schwyzer, *Helv. Chim. Acta*, **34**, 1022 (1951).

[4] D. H. R. Barton and W. Rosenfelder, *J. Chem. Soc.*, 2875 (1951).

[5] D. N. Jones, J. R. Lewis, C. W. Shoppee, and G. Summers, *ibid.*, 2876 (1955).

[6] E. J. Becker and E. S. Wallis, *J. Org. Chem.*, **20**, 353 (1955).



reaction shown in eq 3. In fact we found that the properties of B reported by Karrer's group (mp 98° and $[\alpha]_D$ $-27.1°$) compared very favorably with properties determined by Whitham and Wickramasinghe[7] for **8** (mp 99–101° and $[\alpha]_D$ $-26°$). This assignment was then confirmed by a direct comparison with an authentic sample of **8** kindly provided by Dr. Whitham.

Our experiences with $LiAlH_4$ reduction of **1** in ether solution require brief elaboration. When the reduction is conducted in a normal fashion, crystallization of the crude product yields about 60% crystalline material, mp 123–124°. Although this substance was homogenous according to silica gel tlc, it proved to be a 1:1 molecular compound of **4** and **8**. Analysis by alumina tlc disclosed the two components, and a preparative separation was achieved by a modified ascending dry column chromatography technique[8,9] on alumina (described in the Experimental Section). Treatment of the crude reduction mixture in this manner yielded **4** (48%), **8** (33%), and **3** (3%).

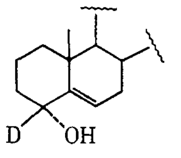
The intermediacy of enone **6** in the proposed routes to **4**, was confirmed by its preparation in 48% yield from **1**, through the action of sodium hydride, a nonreducing strongly basic metal hydride. It is not surprising that aldehyde **7**, the proposed intermediate in the formation of **8**, was not isolated, since under these strongly alkaline conditions this aldehyde could easily undergo further reactions.

Of the two routes proposed for the formation of **4**, the mechanism shown in eq 1 seems unlikely, since there are reports that enolate salts are not readily reduced by $LiAlH_4$.[10,11] Consequently, if the enolate salt (**5**) is an intermediate in the reduction one would expect to recover some cholest-5-en-4-one, but this ketone is not observed (ir, tlc). Furthermore, the conversion of enolate salt **5** to enone **6** requires a source for the second hydrogen at C-3. The only possible sources appear to be the metal hydride and the water employed in the work-up. Work-up of the $LiAlH_4$ reduction of **1** with D_2O in place of water gave **4** with no extra deuterium incorporation; and reduction of **1** with lithium aluminum deuteride ($LiAlD_4$) gave **9**, **10**, and **11**. It is apparent that **9** is the result of $LiAlD_4$ reduction of intermediate **6**, and that no deuterium has been incorporated at carbon 3, thus ruling out mechanism 1.

The hydride shift proposed in mechanism 2 is analogous to the deuterium rearrangement reported in the benzylic acid rearrangement of 1-deuteriophenylglyoxal.[12]

The formation of **10** from the $LiAlD_4$ reduction is consistent with the proposed intermediacy of aldehyde **7**. The deuterium was shown to be on the hydroxymethyl group by the relative area of the carbinol hydrogen signal in the nmr spectrum, and by the prominent *m/e* 355 fragment in the mass spectrum due to loss of CHDOH.

The mass spectrum of **11** revealed incorporation of two deuterium atoms. Since the nmr did not show a vinyl hydrogen signal, one of the deuteriums must be on carbon 4. The location of the second deuterium is predicted to be 6β from a consideration of reasonable pathways for the formation of this hydrocarbon.



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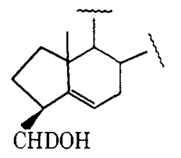

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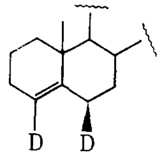

11

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer, using sodium chloride cells. A Unicam SP. 800 spectrophotometer was used for ultraviolet spectra. Nuclear magnetic resonance spectra were taken on a JEOL Co. C-60H high resolution spectrometer in deuterochloroform, using tetramethylsilane as an internal standard. Mass spectra were determined on a LKB type 9000 mass spectrometer with an ionizing voltage of 70 eV and an ion source temperature of 230°.

Melting points were determined on a Kofler hot stage, and are uncorrected. Specific rotations were obtained on a Perkin-Elmer Model 141 polarimeter.

Lithium Aluminum Hydride Reduction of 3β-*p*-Toluenesulfonoxycholest-5-en-4β-ol (1).—Tosylate **1** was prepared according to the method of Karrer[3]: mp 102–104° dec (lit. mp 111° dec); $\bar{\nu}_{max}^{CHCl_3}$ 3580, 3950, 2860, 1175 cm^{-1}; nmr ($CDCl_3$) methyl signals at δ 0.65, 0.80, 0.90, 1.25, 2.43 (Ar–CH_3), OH singlet at 2.16, multiplets for C-4 H and C-3 H at 4.24 and 4.45, C-6 H 5.65, four aromatic proton quartet at 7.6; one spot on tlc (silica gel G, $CHCl_3$). To a flask equipped with a reflux condenser and a magnetic stirrer, and containing 1.2 g (31 mmol) of lithium aluminum hydride in 200 ml of anhydrous ether was added 10.0 g (17.9 mmol) of **1** in 100 ml of dry benzene. The mixture was stirred for 1 hr at room temperature and then heated at reflux temperature for 20 hr. The mixture was cooled and 6.1 ml of ethyl acetate was added, followed by slow dropwise addition of water until a precipitate formed. After stirring overnight, the mixture was filtered and the filter cake washed with ether. The filtrate was washed twice with water, once with 5% sodium bicarbonate, once with brine, and then dried over sodium sulfate. Evaporation of the solvent gave 6.6 g of crude product.

Crystallization of the crude product from benzene afforded a solid: mp 123–124°; $[\alpha]^{25}_D$ $-38.6°$ (*c* 0.5, $CHCl_3$); tlc (silica gel G, $CHCl_3$) one spot, R_f 0.36. Recrystallization from acetone–hexane did not change the melting point.

Ascending Dry Column (ADC) Chromatography of the $LiAlH_4$ Reduction Products.—ADC chromatography is a modification of methods described by Loev and Goodman,[8] and Dev, *et al.*[9] A 0.5-g portion of the crude product, which had been preadsorbed on 2.5 g of alumina, was added to the top of 110 g of neutral alumina (Woelm, activity II, Brockman scale) dry packed in a 2.5 × 45 cm glass column. An additional 2.5 g of alumina was placed on top of the preadsorbed sample and the empty portion of the column was filled with cotton. The column was *inverted* into anhydrous ether and allowed to develop by the ascending solvent. The solvent front was kept just above the level of the solvent outside the column to ensure a fairly even development by capillary action. When the solvent had reached the top of the alumina

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[7] G. H. Whitham and J. Wichramasinghe, *J. Chem. Soc.*, 1655 (1964).

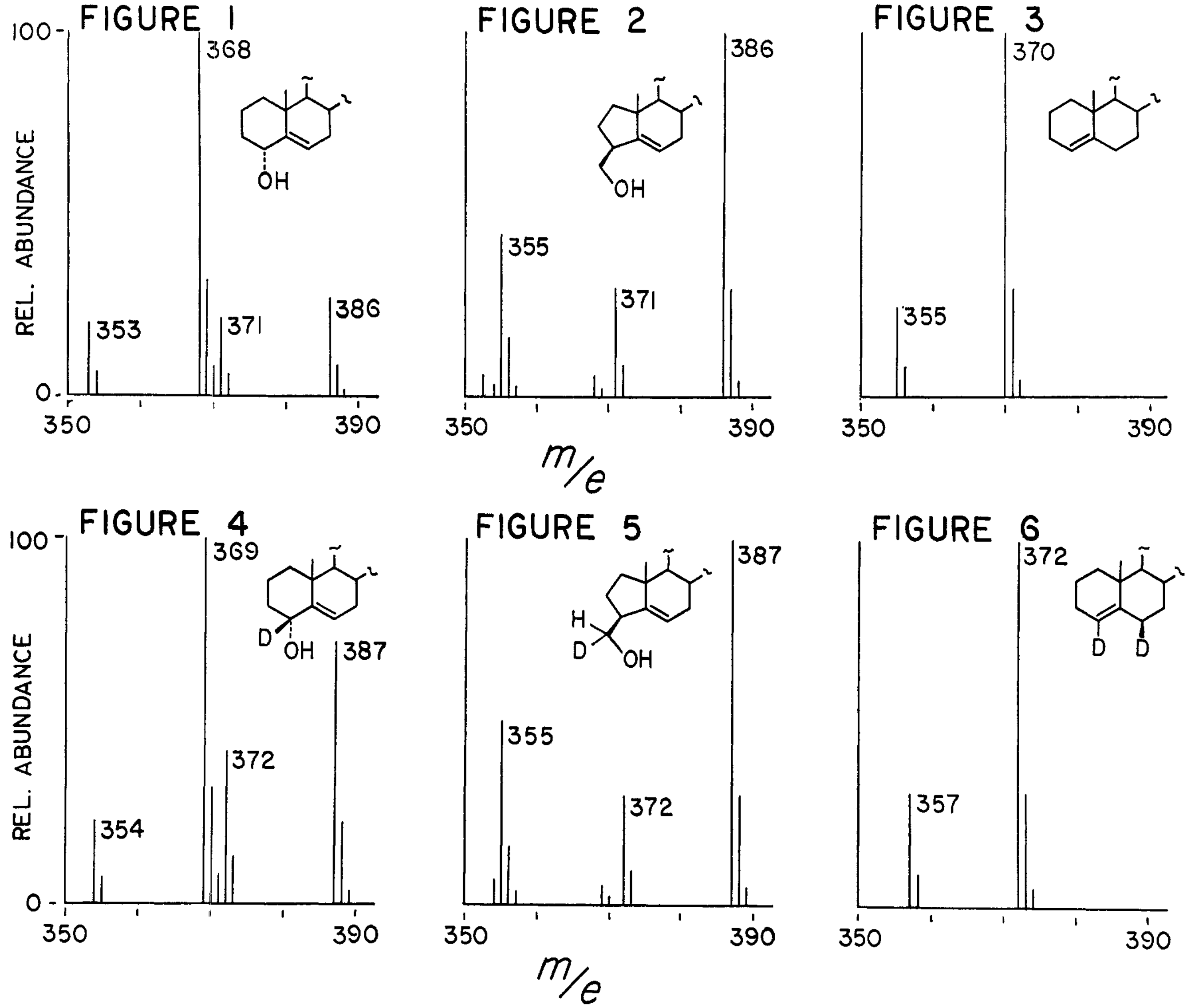
[8] B. Loev and M. Goodman, *Chem. Ind.* (London), 2026 (1967).

[9] V. K. Bhalla, U. R. Nayak, and S. Dev, *J. Chromatog.*, **26**, 54 (1967).

[10] F. A. Hochstein, *J. Amer. Chem. Soc.*, **71**, 305 (1949).

[11] W. G. Dauben and J. Eastham, *ibid.*, **73**, 3260 (1951).

[12] K. Heyns, W. Walter, and H. Scharmann, *Chem. Ber.*, **93**, 2057 (1960).



Figures 1–6.—Mass spectra of normal and deuterium-labeled steroids. High-mass region.

packing, the column was righted and, after removal of the cotton, eluted with anhydrous ether in a normal fashion. Fractions of 20 ml each were collected.

Isolation of 4 (Compound A).—Recrystallization of fractions 3 and 4 (250 mg, 48% yield) from hexane gave cholest-5-en-4α-ol (4): mp 141–142°; $[\alpha]^{25}\text{D}$ −53° (*c* 0.45, $CHCl_3$); [lit.[5,6] mp 144, 143°; $[\alpha]^{17.5}\text{D}$ −55.0 (*c* 1.49, $CHCl_3$), $[\alpha]\text{D}$ −54° (*c* 1.0, $CHCl_3$)]; R_f 0.43 (neutral alumina activity II, ether); $\bar{\nu}_{max}^{CHCl_3}$ 3600, 2940, 2860, 1470, 1375, and 1070 cm^{-1}; nmr ($CDCl_3$) δ 0.68 (18 CH_3), 0.80 (CH_3), 0.91 (CH_3), 0.98 (19 CH_3), 1.05–2.5 (methylene envelope), 2.05 (O–H), 4.25 (1 H, line width 21 cps, CH–OH), 5.8 (1 H, vinyl H); mass spectrum (70 eV, direct probe, ion source 230°) (Figure 1).

Isolation of 8 (Compound B).—Recrystallization of fractions 7–10 (175 mg 33% yield) from methanol gave 3β-hydroxymethyl-A-norcholest-5-ene (6): mp 99°; $[\alpha]^{25}\text{D}$ −24.4° (*c* 0.5, $CHCl_3$), [lit.[7] mp 99–101°; $[\alpha]\text{D}$ −26° (*c* 1.56, $CHCl_3$)]; R_f 0.32 (neutral alumina activity II, ether); $\bar{\nu}_{max}^{CHCl_3}$ 3600, 2950, 2860, 1465, 1380, and 1020 cm^{-1}; nmr ($CDCl_3$) δ 0.70 (18 CH_3), 0.82 (CH_3), 0.90 ($2CH_3$), 1.0–2.4 (methylene envelope), 2.05 (OH), 2.7 (1 H, C-3 H), 3.62 (doublet, 2 H, *J* = 7.2 cps, carbinol H), 5.5 (1 H, vinyl H); mass spectrum (70 eV, direct probe, ion source 230°) (Figure 2).

Isolation of 3 (Compound C).—Preparative thin layer chromatography of ADC chromatography fraction 1 (48 mg) on one 20 × 20 cm glass plate with a 1.5-mm layer of silica gel PF_{254}, using hexane as the developing solvent, showed a band of R_f 0.80. Elution of this band with ether and crystallization from acetone gave 15 mg (3% yield) of cholest-4-ene (3): mp 80–81°; $[\alpha]^{27}\text{D}$ +67° (*c* 0.6, $CHCl_3$) [lit.[13] mp 81°, $[\alpha]^{18}\text{D}$ +67° ($CHCl_3$)]; $\bar{\nu}_{max}^{CHCl_3}$ 2940, 2860, 1470, and 1375 cm^{-1}; nmr ($CDCl_3$) δ 0.67 (18 CH_3), 0.80 (CH_3), 0.90 (CH_3) 1.00 (19 CH_3), 1.05–2.4 (methylene envelope), 5.25 (vinyl H); mass spectrum (70 eV, glpc inlet, ion source 230°) (Figure 3).

Lithium Aluminum Deuteride Reduction of 3β-p-Toluenesulfonoxycholest-5-en-4β-ol (1).—The same procedure and work-up used in the lithium aluminum hydride reduction was employed for the lithium aluminum deuteride reduction of 1. Separation by ADC chromatography afforded the three products in yields similar to those obtained in the lithium aluminum hydride reduction of 1.

A.—4β-Deuteriocholest-5-en-4α-ol (9): mp 141–142° (from hexane); $\bar{\nu}_{max}^{CHCl_3}$ 2110 cm^{-1} (C–D); nmr ($CDCl_3$) identical with nmr spectrum of 4 except for the absence of the δ 4.25 (CH–OH) signal; mass spectrum (70 eV, direct probe, ion source 230°) (Figure 4).

B.—3β-Hydroxydeuteriomethyl-A-norcholest-5-ene (10): mp 99° (from methanol); $\bar{\nu}_{max}^{CHCl_3}$ 2140 cm^{-1} (C–D); nmr ($CDCl_3$) two doublets at δ 3.56 and 3.62 (combined area 1 H, *J* = 7.2 and 7.2 cps); mass spectrum (70 eV, direct probe, ion source 230°) (Figure 5).

C.—4,6β-Dideuteriocholest-4-ene (11): mp 99° (from acetone); $\bar{\nu}_{max}^{CHCl_3}$ 2220, 2100 cm^{-1} (C–D); nmr ($CDCl_3$) vinyl hydrogen signal present in the nmr spectrum of 3 at δ 5.25 is absent in

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[13] J. Broome, B. Brown, A. Roberts, and A. White, *J. Chem. Soc.*, 1406 (1960).

the spectrum of **11**; mass spectrum (70 eV, glpc inlet, ion source 230°) (Figure 6).

Jones Oxidation of Cholest-5-en-4*α*-ol (4).—Jones reagent[14] (8 *N*, 0.85 ml) was added dropwise to a solution of 1.125 g (2.92 mmol) of alcohol **4** in 100 ml of acetone at 20°. The solution was warmed to room temperature and then diluted with an equal volume of water. The ether extract of this solution was washed with water (twice), saturated sodium bicarbonate solution, and brine. Evaporation of the solvent and crystallization from acetone gave 0.9 g (81%) of pure cholest-5-en-4-one **6**: mp 111–112°; $\lambda_{\max}^{C_2H_5OH}$ 241 mμ (ϵ 6000) [lit.[15] mp 111–112°; $\lambda_{\max}^{C_2H_5OH}$ 241 mμ (ϵ 7200)]; $\nu_{\max}^{CHCl_3}$ 1675 and 1620 cm^{-1}.

Reaction of Sodium Hydride with 3*β*-*p*-Toluenesulfonoxycholest-5-en-4*β*-ol (1).—To a stirred solution of 500 mg (0.9 mmol) of tosylate **1** in 25 ml of tetrahydrofuran (thf) under a nitrogen atmosphere was added 41.0 g (0.9 mmol) of sodium hydride on mineral oil 52.8% NaH). The mixture was heated at reflux for 3 hr, cooled, and 1 equiv of water was added dropwise. The resulting solution was filtered and evaporated to dryness at reduced pressure. The brown residue which resulted was dissolved in ether and the ether solution was washed with water (twice), 5% sodium bicarbonate, and brine, and then dried over sodium sulfate. Evaporation of the solvent gave 0.45 g of crude product. Column chromatography on 20 g of silica gel (E. Merk), afforded 165 mg (48%) of cholest-5-en-4-one (**6**): mp 111–112° (from acetone); $\tilde{\nu}_{\max}^{CHCl_3}$ identical with that of the material obtained from Jones oxidation of cholest-5-en-4*α*-ol (**4**).

Lithium Aluminum Hydride Reduction of Cholest-5-en-4-one (6).—To a slurry of 380 mg (10 mmol) of lithium aluminum hydride in 5.8 ml of refluxing anhydrous ether was added 200 mg (0.52 mmol) of ketone **6** in 3.0 ml of dry benzene. The resulting slurry was heated at reflux for 24 hr. The usual work-up gave a crude product that tlc identified as cholest-5-en-4*α*-ol (**4**) but no cholest-4-ene (**3**). Crystallization of the crude product from hexane gave 190 mg (95%) of **4**: 140–151°; $\nu_{\max}^{CHCl_3}$ identical with that of the known **4**.

Registry No.—Lithium aluminum hydride, 16853-85-3; **1,** 5847-14-3; **3,** 16732-86-8; **4,** 20230-16-4; **8,** 21537-62-2; **9,** 21537-63-3; **10,** 21537-64-4; **11,** 21537-65-5.

Acknowledgments.—We wish to thank the National Institutes of Health for partial support of this work through research grant AM-10849, and for the award of a predoctoral fellowship to R. H. Starkey. We also thank Professor C. C. Sweeley of the biochemistry department for determining the mass spectra for us.

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Anomeric C-19-Steroid *N*-Acetylglucosaminides[1]

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The *α* and *β* anomers of C-19-steroid 2′-acetamido-2′-deoxy-D-glucopyranoside conjugated at C-3 or C-17 have been prepared from their corresponding 3′,4′,6′-tri-*O*-acetyl derivatives. The acetylated *β*-glucosaminides were synthesized from the steroid and 1*α*-chloro-2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose with mercuric salts; anomerization was achieved by treatement of the acetylated *β*-glucosaminides with titanium tetrachloride. The differences in the molecular rotation and ir and nmr spectra between the anomers were studied. The *α* anomer had a sharply defined intense band between 1110 and 1125 cm^{-1} whereas the *β* anomer lacked this strong absorption between 1100–1200 cm^{-1}. In addition to the difference of the splitting patterns of the anomeric H-1′ protons in the nmr spectra, a broad multiplet for the H-6′ methylene protons, $W_{1/2} \sim 8.5$ cps, in the *β* anomer and a narrow multiplet, $W_{1/2} \sim 4.0$ cps, in the *α* anomer at δ 4.1–4.2 ppm were observed. For comparison purposes the synthesis and physical properties of the anomers of cyclohexyl *N*-acetylglucosaminides were investigated.

Three steroids conjugated with *N*-acetylglucosamine have been recently isolated: 3-hydroxy-$\Delta^{1,3,5(10)}$-estratrien-17*α*-yl 2′-acetamido-2′-deoxy-*β*-D-glucopyranoside,[4] $\Delta^{1,3,5(10)}$-estratriene-3,16*α*,17*α*-triol 2′-acetamido-2′-deoxy-*β*-D-glucopyranoside conjugated at C-16 or -17,[5] from rabbit urine, and 3*β*-hydroxy-Δ^5-pregnen-20*α*-yl 2′-acetamido-2′-deoxy-*α*-D-glucopyranoside from human urine.[6] All were present as the double conjugate, the first two as the 3-glucosiduronate and the last as the 3-sulfate ester. In order to study the properties of steriod *N*-acetylglucosaminides to aid in the isolation of this type of conjugate, the synthesis of various C-19 steroids conjugated with *N*-acetylglucosamine at C-3 or at C-17 in both the *α*- and *β*-glycosidic linkage were investigated.

The Koenigs–Knorr reaction has been successfully employed for the preparation of alkyl *N*-acetyl-*β*-D-glucosaminides.[7] An application of this reaction to steroids has been reported by Hirschmann and coworkers[8] without experimental detail in the preparation of 11*β*,17-dihydroxy-3,20-diketo-$\Delta^{1,4}$-pregnadien-21-yl 2′-acetamido-2′-deoxy-*β*-D-glucopyranoside. Preliminary studies in the reaction of 1-*α*-chloro-2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose with various steroid alcohols in the presence of silver carbonate demonstrated that only the *β*-glycoside was isolated but in very poor yields. The yields were improved (10–25%) by carrying out the reaction with mercuric salts, mercuric chloride and mercuric cyanide, and the chloro sugar.[7a] In these cases, trace amounts of the *α*-glycosides were formed but were readily separated from the desired *β* epimer. Consequently the tetraacetyl *β*-glucosaminides conjugated at C-3 with 3*α*-hydroxy-5*α*-androstan-17-one, its 3*β* and 5*β* epimers, and 3*β*-hydroxy-Δ^5-androsten-17-one and those con-

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[1] This investigation was supported by a grant from the American Cancer Society and by grants CA-07304 from the National Cancer Institute, National Institutes of Health, USPHS.

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