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Regeneration of Steroid Alcohols from Their Methyl Ethers*,[1]

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A mixture of boron trifluoride etherate and acetic anhydride at 0° or below has been found to cleave different types of steroidal methyl ethers. Allylic and homoallylic ethers give the corresponding acetates in yields of over 90%. Completely saturated ethers give the acetate with retention of configuration as the main substitution product, but the epimeric acetate and elimination products are also obtained.

In work on the chemistry of natural products, it is often necessary to protect aliphatic hydroxyl groups before attacking other sensitive centers of the molecule. Esterification of the hydroxyl group is not always useful, since it may not give any protection even under mild alkaline conditions. Methylation does give the necessary protection under alkaline and mild acidic conditions, but there is no simple way to demethylate and regain the hydroxyl group from the methoxyl. The methods available at present[2] either use too drastic conditions, which might break up sensitive parts of the molecule, or may not lead to the desired alcohol.

Following the recent use[3] of boron trifluoride etherate and acetic anhydride at room temperature to cleave a steroid 18,20-epoxide to the 18,20-diacetate, we tried those reagents at 0° to cleave different types of steroid methyl ethers. The progress of the reaction was followed by isolating the total reaction product at intervals and scanning its p.m.r. spectra to see whether the signal due to the methoxyl group had disappeared. (The methyl ethers were prepared in high yields from the corresponding alcohols by using potassium metal and methyl iodide.[4])

It was found that cholesteryl methyl ether gave, after 15 hr. at 0°, cholesteryl acetate in about 93% yield, but, with 4-cholesten-7β-ol methyl ether, it took 50 hr. at 0° to complete the reaction. The extended time for the latter was not unexpected since the double bond assists in the cleavage of the ethers in both cases, and there is evidence[5] which might mean that the participation of the Δ^4 bond in the departure of a 7β-equatorial group is less than that of the Δ^5 bond in the departure of a 3β-equatorial group.

When the reaction was tried on an allylic ether, 4-cholesten-3β-ol methyl ether, it was observed that a large amount of 3,5-cholestadiene was obtained. As this was ascertained to be due to the elimination of the initially formed allylic acetate under the acidic conditions of the reaction, we found out the minimum conditions under which 4-cholesten-3β-ol acetate survives the reagents. Under these conditions, *i.e.*, −18° for 3 min., 4-cholesten-3β-ol methyl ether gave 4-cholesten-3β-ol acetate in about 90% yield.

Methyl ethers whose cleavage had no such assistance from π electrons gave both the epimeric acetates and elimination products. Thus, cholestanyl methyl ether gave cholestanyl acetate (33%), cholestan-3α-ol acetate (25%), and 2-cholestene (25%). Similarly from cholestan-3α-ol methyl ether, we obtained cholestan-3α-ol acetate (14%), cholestanyl acetate (8%), and 2-cholestene (50%).

That both boron trifluoride etherate and acetic anhydride are necessary for this cleavage and that the products, once formed, generally do not undergo further changes has been shown by treating cholestanyl methyl ether with (i) acetic anhydride alone and (ii) with boron trifluoride etherate and benzene, and also by treating cholesteryl and cholestanyl acetates with boron trifluoride etherate and acetic anhydride, and recovering in each case only the starting materials.

The cleavage thus appears to involve the initial formation of an oxonium ion by the addition of boron trifluoride etherate to the ether oxygen and cleavage of the carbon–oxygen bond from (a) the secondary carbon to give the elimination and epimeric products and (b) from the methoxy methyl to give the product with retention of configuration by the nucleophilic attack of the acetate moiety of the acetic anhydride. The boron trifluoride complex of the steroid is subsequently replaced by the acetylium moiety of the acetic anhydride. It is interesting to note that the acetate with retention of configuration predominates in both the cases. The larger amount of elimination with cholestan-3α-ol methyl ether is easily explicable as the axial methoxyl group is very favorably set for acid-catalyzed eliminations. When the allylic and homoallylic ethers are cleaved from the steroid nucleus, the double bond assists[6] in stabilizing the carbonium ion and gives the more stable equatorial acetate. Under the acidic conditions, even if a 3,5-cyclopropane-6β-ol acetate is formed, it will be readily rearranged into the Δ^5-3β-ol acetate.[6,7] These equatorial ethers, when cleaved from the methoxy

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methyl side, will also naturally give the equatorial acetates, thus giving only a single reaction product in the case of the homoallylic and allylic ethers.

In the 4,4-dimethyl terpenoids, cleavage of a 3β-equatorial group is known to be assisted and followed by the migration of the parallel C-4–C-5 bond.[8] When a reaction with such a compound, *viz.* 3β-methoxylupane, was tried, A-nor-$\Delta^{3(5)}$-lupene[9] was obtained in high yield, showing thereby that, wherever there is assistance for cleavage from the nucleus, that will take place to give the predominant product. To obtain the A-nor-$\Delta^{3(5)}$-lupene, the exocyclic $\Delta^{3(4)}$ bond that is first formed must be isomerizing into the A ring under the acid conditions, as is well known.[9]

It may look anomalous that cholestanyl and cholesteryl tosylates, under our reaction conditions, give back starting materials almost quantitatively. In these cases, the boron trifluoride might be complexing with the electron-rich sulfoxyl oxygen which may not lead to the cleavage of the ether oxygen bond. This must also be the case with cholesteryl and cholestanyl acetates (boron trifluoride etherate complexing with carbonyl oxygen in these cases) which also give back only starting material.

Youssefyeh and Mazur have also recently published results on some similar work.[10] They state that no ether cleavage is observed with boron trifluoride etherate and acetic anhydride alone, a lithium halide being essential for the cleavage, and that cholestanyl methyl ether gives under their conditions 2-cholestene (I) and cholestanyl acetate (II) only. With lithium chloride, lithium bromide, and lithium iodide they obtained I and II in the ratios 1:1.5, 1:3, and 1:10, respectively. Our findings as detailed above did not agree with these. Using lithium halides, we found that the cleavage was slowed down and that elimination was not decreased very much, as was reported. Lithium iodide however, increased to a small extent, but not very much, the proportion of the acetate with retention of configuration. Repeating the reaction with cholestanyl methyl ether under the described conditions,[10] we obtained a mixture of all three products in almost the same proportion as we had obtained under our conditions, as evidenced by the p.m.r. spectra of the total product and by isolation and identification of the individual components.

Experimental[11]

Methylation.—The general procedure given below gives high yields of the methyl ethers. The yields given are corrected for recovered starting material. To a solution of cholesterol (1 g.) in dry benzene (47 ml.), potassium metal (0.535 g.) was added and the mixture was refluxed for 1 hr. with vigorous shaking at intervals to disperse the molten potassium into small globulets. Methyl iodide (18 ml.) was added and the refluxing was continued for 3 hr. during which time potassium iodide gradually separated out. Methanol was added to the cooled reaction mixture, the solvents were removed *in vacuo*, and the residue was extracted with petroleum ether. The petroleum ether extracts were filtered through a column of alumina (30 g.). The petroleum ether eluates, after crystallization from methanol, gave **cholesteryl methyl ether**[13] (0.742 g.): m.p. 84°; ν_{max} 1195 and 1108 cm.$^{-1}$; p.m.r. τ 4.75 (C-6 vinyl proton), 6.75 (C-3 β-methyl ether), and 7.00–7.3 (C-3, α-H).

Elution of the column with alcohol gave cholesterol, 0.202 g., m.p. 146–147°, $[\alpha]_D$ −37.5°. The yield of cholesteryl methyl ether was 88%.

Cholestanyl methyl ether,[14] m.p. 82–83°, $[\alpha]_D$ +21.5°, was prepared similarly in a yield of 87%: ν_{max} 1171, 1144, 1135, and 1104 cm.$^{-1}$; p.m.r. τ 6.8 (C-3 β-methyl ether), 6.9–7.2 (C-3 α-H).

4-Cholesten-3-β-ol Methyl Ether.—This compound has not been obtained pure before.[15] There was considerable difficulty in getting this pure, since, under the above conditions of methylation, a large amount of 4-cholesten-3-one was formed, probably by the oxidation of the allylic alcohol by the alkoxide radical or ion produced during the reaction. It was also contaminated with 3,5-cholestadiene. The pure product was, however, obtained by the following procedure. A solution of 4-cholesten-3β-ol[16] (0.5 g.) in dry benzene (22 ml.) was treated with potassium metal (0.22 g.) and refluxed for 0.5 hr. as before under nitrogen. Methyl iodide (10 ml.) was added and refluxing was continued under nitrogen for 1 hr. The product was worked up as before and chromatographed on a column of alumina (15 g.). The first petroleum ether fraction (10 ml.) gave an oily product whose ultraviolet spectrum showed it to be 3,5-cholestadiene. Subsequent petroleum ether fractions afforded 4-cholesten-3β-ol methyl ether (0.122 g., crystals), m.p. 75–76°, $[\alpha]_D$ +29.6°. Thin layer chromatography on silica gel with petroleum ether–ethyl acetate (80:20) showed a single spot on spraying with concentrated H_2SO_4. It showed only end absorption in the ultraviolet; ν_{max} 1654, 1190, and 1094 cm.$^{-1}$; p.m.r. τ 4.77 (C-4 vinyl proton), 6.78 (C-3 β-methyl ether), and 6.3–6.6 (C-3 α-H).

Anal. Calcd. for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 83.45; H, 11.92.

Further elution of the column with alcohol gave 4-cholesten-3β-ol (0.321 g.), m.p. 129–130°, $[\alpha]_D$ +42°.

4-Cholesten-7β-ol Methyl Ether.[17]—This was prepared from 4-cholesten-7β-ol[18] in 75% yield by the usual procedure. It was obtained as an oil: $[\alpha]_D$ +64.5°; ν_{max} 1183 and 1099 cm.$^{-1}$; p.m.r. τ 4.76 (C-4 vinyl proton), 6.81 (C-7 β-methyl ether), and 7.2 to 7.4 (C-7 α-H).

Lupanol Methyl Ether.—The modified procedure given below gave a yield of 82% of the methyl ether compared to the very low yields (20–25%) obtained before in the case of the methyl ethers of triterpenoids prepared[19] by other procedures. Lupanol (0.3 g.) was dissolved in dry benzene (15 ml.) and treated with potassium metal (0.25 g.) as usual. This was refluxed for 3 hr. Methyl iodide (8 ml.) was added, and refluxing was continued for another 3 hr. Usual work-up gave lupanol methyl ether as colorless needles (0.194 g.) from acetone–methanol: m.p. 227–228°, $[\alpha]_D$ +2.33°, ν_{max} 1182 and 1103 cm.$^{-1}$, p.m.r. τ 6.75 (C-3 β-methyl ether) and 7.3–7.5 (C-3 α-H).

Anal. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.29; OCH_3, 7. Found: C, 84.5; H, 12.5; OCH_3, 7.36.

The alcohol eluates gave 59 mg. of crystals (m.p. 203–204°) of lupanol.

Cholestan-3α-ol methyl ether, m.p. 61°, $[\alpha]_D$ +18°, was prepared as described in literature[20]: ν_{max} 1174, 1165, and 1089 cm.$^{-1}$; p.m.r. τ 6.8 (3α-methyl ether) and 6.71 (3β-H).

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Cleavage of Methyl Ethers. General Procedure.—A solution of the steroid methyl ether (200 mg.) in acetic anhydride (8 ml.) and dry ether (2–3 ml. to dissolve the compound) was cooled to 0° and, to this, freshly redistilled boron trifluoride etherate (1.4 ml.) which had also been previously cooled to 0° was added. After 15 hr. at 0°, the mixture was poured into ice-cold water and, after a few hours, extracted with ether. The ether extract was washed with sodium bicarbonate solution and water, dried over sodium sulfate, and further processed. (The time of 15 hr. was arrived at by trial runs and by following the end of the reaction by the absence of the methoxyl signal in the p.m.r. spectra of the isolated products from cholesteryl and cholestanyl methyl ethers.) In most cases, the experiments were repeated several times and it was found that almost the same results were obtained.

Cholesteryl Methyl Ether.—After work-up, this product readily crystallized to give cholesteryl acetate (93% yield), identified by melting point, mixture melting point (110–111°), $[\alpha]D$ (−45°), and infrared and p.m.r. spectra. No other product was obtained from the reaction mixture.

4-Cholesten-7β-ol Methyl Ether.—It took 50 hr. to complete the reaction. The reagents were added in the same proportions, and conditions were the same as described above. Thus, 100 mg. of the ether gave 91 mg. of an oil (strong bands in the infrared spectrum at 1735 and 1245 cm.$^{-1}$ indicating the formation of the acetate) which did not crystallize nicely. It was hydrolyzed by refluxing for 2 hr. with 5% alcoholic potassium hydroxide, to give a first crop of 54 mg. of 4-cholesten-7β-ol, characterized by melting point, mixture melting point (115–116°), $[\alpha]D$ (+63.5°), and infrared spectra.

4-Cholesten-3β-ol Methyl Ether.—This compound, under the usual conditions, gave 3,5-cholestadiene[21] as the major product. When the boron trifluoride etherate–acetic anhydride reaction was conducted on 4-cholesten-3β-ol acetate,[22] 3,5-cholestadiene was still the predominant product. Hence by trial experiments it was found that the acetate could be completely recovered unchanged only at −18° for a maximum reaction time of 3 min. Hence the methyl ether (90 mg.) in dry ether (2 ml.) and acetic anhydride (4 ml.) was cooled at −18° for 1 hr. and to this cold (−18°) boron trifluoride etherate (0.25 ml.) was added. The mixture was kept at −18° for 3 min. and then worked up as usual. It gave a colorless oil (85 mg.) whose ultraviolet spectrum showed the presence of 5–6% of 3,5-cholestadiene. The p.m.r. spectrum showed signals at τ 4.67, 4.85 (C-3, C-4, and C-6 vinyl protons), 5.00 (C-3 α-proton on the carbon bearing the acetate), 6.77 (C-3β-methyl ether), and 8.06 (C-3 β-acetate, this position was identical with that in the spectrum of a separately prepared sample of pure 4-cholesten-3β-ol acetate). The intensity of the methyl ether signal showed that it formed about 12–15% and that of the acetate methyl 75–80% of the total mixture. Allowing for the unreacted material, the acetate forms about 90% of the reacted ether. After hydrolysis and chromatography, the pure 4-cholesten-3β-ol obtained was identified by its melting point, mixture melting point (128–129°), $[\alpha]D$ (+40°), and infrared spectra.

Cholestanyl Methyl Ether.—Reaction of 201 mg. of this ether, as described for cholesteryl methyl ether, for 15 hr. at 0° gave a pale yellow oil (198 mg.). The infrared spectrum of this oil showed strong bands at 1729 and 1250 cm.$^{-1}$ showing the formation of the acetate. The p.m.r. spectrum showed signals at τ 4.5 (C-2, C-3 vinyl protons), 8.04 (C-3 axial acetate), 8.09 (C-3 equatorial acetate), 5.1 (C-3 equatorial proton on the carbon bearing the axial acetate), and 5.3–5.7 (C-3 axial proton on the carbon bearing the equatorial acetate). After hydrolysis (10% alcoholic potassium hydroxide, overnight at room temperature) and chromatography on neutral alumina (7 g.), the petroleum ether eluates gave 44 mg. (25%) of long needles, identified by melting point, mixture melting point (70–71°), and infrared and p.m.r. spectra as 2-cholestene.[23] The petroleum ether benzene eluates crystallized from alcohol to give 47 mg. (25%) of fine needles, identified by melting point (183–184°), $[\alpha]D$ (+23°), and infrared spectra as cholestan-3α-ol.[24] The benzene–ether eluates gave a colorless solid, crystallized from alcohol (61 mg., 33%), which was identified as cholestanol (m.p. and m.m.p. 137–138°, $[\alpha]D$ +21°).

Cholestan-3α-ol Methyl Ether.—Reaction and work-up were the same as in the case of cholestanyl methyl ether. The p.m.r. spectrum of the reaction product showed the presence of 2-cholestene, cholestan-3α-ol acetate,[25] and cholestanyl acetate.[26] On hydrolysis and chromatography the product gave 2-cholestene (50%, m.p. 70–71°), cholestan-3α-ol (14%, m.p. 183–184°), and cholestanol (8%). The last product was too small a quantity on a 200-mg. run to obtain crystalline but was identified by thin layer chromatography and infrared spectrum as cholestanol with a very slight impurity.

Lupanol Methyl Ether.—From the reaction at 0° for 15 hr. or longer, only starting material was recovered. Hence the mixture was kept for 15 hr. at room temperature, and worked up and chromatographed as usual. The petroleum ether eluates crystallized from alcohol to give A-nor-$\Delta^{3(5)}$-lupene in 63% yield, m.p. 135–136°, $[\alpha]D$ +13°. The yield reported for a recent preparation of this compound[27] by the usual method, *i.e.*, by treating lupanol with phosphorus pentachloride and further treatment with acid, is much lower. The compound shows a positive tetranitromethane test. The p.m.r. spectrum [τ 8.9, 8.99, 9.05, 9.1, 9.16, 9.25, and 9.32 (methyl groups)] shows no vinyl proton or any methyl on a double bond.

The Effect of the Reagents Individually on the Starting Materials and Together on the Reaction Products.—Cholestanyl acetate, cholesteryl acetate, cholesteryl tosylate,[28] and cholestanyl tosylate[20] after reaction with boron trifluoride etherate and acetic anhydride in the usual way at 0° for 15 hr. gave back 90–97% of the starting material in each case, identified by melting point, mixture melting point, and infrared and p.m.r. spectra.

Similarly, cholestanyl methyl ether in a solution of dry benzene and boron trifluoride etherate, or in dry benzene and acetic anhydride, or cholestan-3α-ol methyl ether in dry benzene and acetic anhydride after 15 hr. at 0° gave back only starting materials in 93–97% yield.

Reactions with Lithium Halides.—Cholestanyl methyl ether (200 mg.) in dry ether (3 ml.) and acetic anhydride (8 ml.) was cooled to 0° for 0.5 hr., and to this cold boron trifluoride etherate (1.2 ml.) and lithium bromide (1 g.) were added, and the mixture was kept at 0° for 15 hr. Usual work-up and filtration through a column of alumina (7 g.) gave a colorless oil (196 mg.). The p.m.r. spectrum of the product showed signals at τ 4.41 (C-2, C-3 vinyl protons), 6.73 (C-3 β-methyl ether), 8.03 (C-3 axial acetate), and 8.08 (C-3 equatorial acetate). The integrated relative intensity of the signal at τ 6.73 showed that 55% of the starting material remained unreacted.

Hence the reaction with cholestanyl methyl ether (200 mg.) was carried out using the conditions[10] of Youssefyeh and Mazur (30 hr. at room temperature). Usual work-up gave an oil (192 mg.) whose p.m.r. spectrum was almost identical with that obtained under the conditions described here. After hydrolysis and chromatography the oil gave 2-cholestene (37 mg., 20%; m.p. 71°), cholestan-3α-ol (41 mg., 22%; m.p. 182–183°), and cholestanol (57 mg., 31%; m.p. 138–139°).

The reaction of cholestanyl methyl ether (200 mg.) and lithium iodide was then repeated at room temperature as above. The p.m.r. spectrum of the total product (185 mg.) showed the presence of all the above products with approximate relative intensities of the signals of 2-cholestene (19%), cholestanyl acetate (39%), and cholestan-3α-ol acetate (20%). After hydrolysis and chromatography the mixture gave 2-cholestene (16%, m.p. 70°), cholestanol (42%, m.p. 138–139°), and cholestan-3α-ol (20%, m.p. 181–183°).

The reaction with lithium iodide was then repeated with cholestan-3α-ol methyl ether and after the usual work-up it gave 2-cholestene (45%), cholestanol (5%), and cholestan-3α-ol (16%).

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