Nmr spectra were determined on a Varian Associates Model A-60 high-resolution spectrometer. Chemical shifts are recorded in parts per million (δ) downfield from internal TMS. Elemental analyses were performed by either Alfred Berhardt Laboratories, Mullheim, Germany, or Micro-Tech Laboratories, Skokie, Ill. Preparative scale irradiations were conducted in a RPR-100 Rayonet photochemical apparatus employing the 3500-Å range lamps and fitted with a merry-go-round attachment.

Preparative Irradiation of 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (3).—Three Pyrex tubes were each charged with 40 mg of nitroxide **3**[4] and 10 ml of toluene. The solutions were vacuum-degassed three times, sealed in the tubes, and then irradiated for 96 hr at 30–40°. Removal of the toluene under reduced pressure afforded a residue which was triturated with benzene. The crystalline solid which remained, 69 mg (~50% crude yield), mp 144–150°, was recrystallized from hexane–ether to give 40 mg (30% yield) of pure diol **5**, mp 156–158° (lit.[5] mp 158°), no melting point depression upon admixture with authentic **5**.[5]

Immediate chromatography of the benzene-soluble fraction over basic alumina and elution with pentane afforded 109 mg (~50% crude yield) of a colorless oil which crystallized upon scratching. Recrystallization from pentane afforded 16 mg (8% yield) of 1-benzyloxy-4-hydroxy-2,2,6,6-tetramethylpiperidine (**6**) as white needles: mp 87–87.5°; nmr (CCl_4) 1.21 (s, 6, pair of methyl groups), 1.28 (s, 6, pair of methyl groups), 1.7 (m, 4, ring protons), 3.9 (m, 1, H-4), 4.78 (s, 2, benzylic protons), 7.24 (s, 5, aromatic protons); ir (CCl_4) 3350 (m), 3000 (s), 1450 (m), 1380 (s), 1250 (s), 1190 (m), 1045 (s), 1025 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{25}NO_2$: C, 73.00; H, 9.51; N, 5.32. Found: C, 72.78; H, 9.57; N, 5.40.

Irradiation of Steroid Nitroxide 4.—Six Pyrex tubes were each charged with 40 mg of nitroxide **4**[7] and 10 ml of toluene. The solutions were vacuum-degassed three times, sealed in the tubes, and then irradiated for 144 hr at 30–40°. It could be estimated by esr spectroscopy that less than 2% of starting nitroxide **4** remained after the photolysis. Dried oxygen was then bubbled through the near colorless solutions for 24 hr. Removal of the toluene under reduced pressure afforded a pale yellow solid which was chromatographed over silica gel. Elution with 5:1 hexane–benzene afforded 113 mg (39% yield) of a white solid, mp 55–62°. Recrystallization from ether–methanol gave *N*-benzyloxy derivative **10** as white needles: mp 74–76°; nmr (CCl_4) 0.6–2.1 (m, 52), 3.43 (s, 2, oxazolidine ring protons), 4.65 (s, 2, benzylic protons), 7.28 (s, 5, aromatic protons).

Anal. Calcd for $C_{38}H_{61}NO_2$: C, 80.99; H, 10.83; N, 2.48. Found: C, 80.94; H, 10.80; N, 2.79.

Elution with benzene afforded 133 mg (57% yield) of a pale yellow solid which was recrystallized from ether–methanol and shown to be identical with starting **4** by ir and melting point comparisons.

Determination of Relative Rates of Photolysis of 3 in Various Solvents.—Rates of photolysis were determined on a Varian 4502 esr spectrometer equipped with a 50% transmittance cavity. The light source was a 100-W PEK high-pressure mercury lamp mounted on an optical bench about 50 cm from the cavity. The light was focused with quartz optics and passed through a Pyrex filter. Reagent grade cumene, toluene, cyclohexane, and benzene were carefully purified prior to use. Irradiations were conducted in stoppered quartz tubes and nitrogen was passed through the solutions immediately prior to irradiation. The photolysis exhibited cleanly first-order kinetics in each instance.

Registry No.—**3**, 2226-96-2; **4**, 78353-76-9; **6**, 26460-91-3; **10**, 26460-92-4.

Acknowledgment.—The authors wish to express their thanks to the National Science Foundation (GP10736), the National Institutes of Health (1-RO3 MH-17209-01), and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant GF 674), for generous financial support. Thanks are also due Professors O. H. Griffith, W. T. Simpson, and W. L. Peticolas for use of some of their equipment.

α-Ketols from Hydride Reduction of a Steroidal Enamino Ketone and the Corresponding α Diketone[1]

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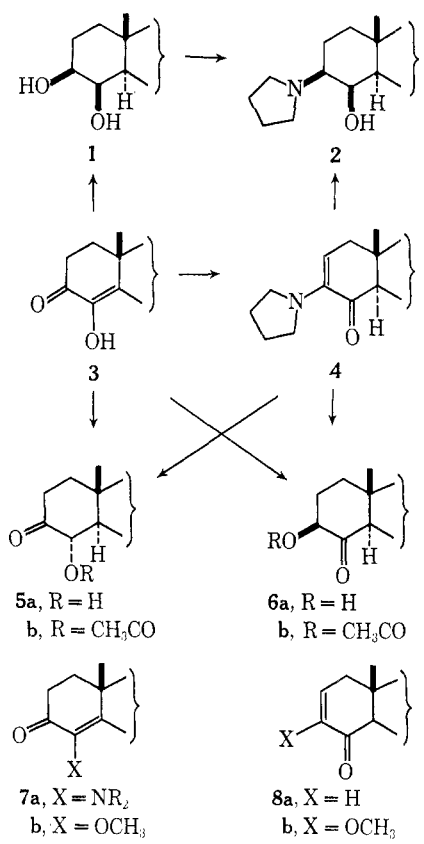
We describe here the reduction of the steroidal α diketone **3** and its derived enamine **4** with sodium borohydride, lithium aluminum hydride, and other reducing systems. Our interest in the reduction of the enamine **4** arose from the need to generate 3-amino-4-hydroxy steroids, both as precursors of steroidal heterocycles and as synthetic intermediates for naturally occurring steroid alkaloids. The pyrrolidyl enamine **4** seemed a convenient model compound for these studies, and the initial reduction results dictated additional experiments with the α diketone[2] **3**. The ultraviolet (λ_{max}^{MeOH} 277 nm, ϵ 12,500) and infrared ($\nu_{max}^{CHCl_3}$ 3484, 1672, and 1645 cm^{-1}) spectra of **3** testify to the enolized system and the nmr spectrum (no vinyl hydrogen) rules out the alternative 3-hydroxy-Δ^2-4-oxo system.[3] Reaction of **3** with pyrrolidine[4] gave, in high yield, the enamine-ketone **4**



* To whom correspondence should be addressed.

(1) This work was supported, in part, by U. S. Public Health Service Grant HE-08913 and GM 16492.

(2) A. Butenandt, G. Schramm, A. Wolff, and H. Kudszus, *Chem. Ber.*, **69**, 2779 (1936).

(3) *Cf.* D. P. Strike, D. Herbst, and H. Smith, *J. Med. Chem.*, **10**, 446 (1967).

(4) *Cf.* B. Camerino, D. Cattepan, U. Valcavi, and B. Patelli, *Gazz. Chim. Ital.*, **89**, 674 (1959).

which showed λ_{max}^{MeOH} 308 nm (ϵ 8700) and infrared absorptions at 1692 and 1626 cm^{-1}. A single vinyl hydrogen appeared at δ 5.4 in the nmr spectrum, supporting the 3-pyrrolidyl-Δ^2-4-oxo formulation for **4**. The C-19 hydrogens appeared at δ 0.85 supporting[5] the assignment of 5α configuration at the AB ring junction.

The ultraviolet spectrum of **4** (λ_{max}^{MeOH} 308 nm, ϵ 8700) deserves brief comment. The bathochromic effect of the α-dialkylamino group in the conjugated ketone **8a** (λ_{max} 226 nm) is +82 nm, while the effect of an α-methoxyl group[6] in the same system (**8b**) is +37 nm. In contrast, the bathochromic shifts caused by α-dialkylamino[7] and methoxyl[6] groups in a Δ^4-3 ketone (**7a** and **7b**, respectively) are +3 to +6 nm and +12 nm, respectively.

The small bathochromic effect of an α-methoxyl group in the Δ^4-3-ketone system relative to its effect in the Δ^2-4-ketone grouping has already been commented on.[6] Thus, Reusch suggested that for maximum bathochromic effect the bonding plane of the methoxyl oxygen should be parallel to the enone chromophore and pointed out that this condition is met in those α-methoxylenones (as **8**) which lack a β-alkyl substituent cis to the methoxyl group. He further noted that this condition *cannot* be met in the 4-methoxyl-Δ^4-3-ketone system, due to steric crowding of the methoxyl group by the C-6 methylene group and the carbonyl oxygen, which substantially prevents coplanarity.

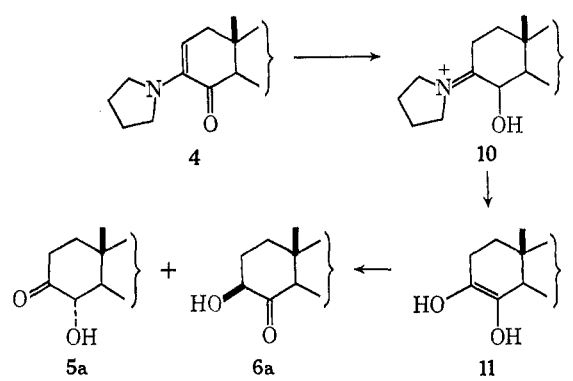
We note here that the very small bathochromic shifts of α-dialkylamino substituents (+3 to +6 nm) in the Δ^4-3-ketone grouping are consistent with even greater steric crowding of the large dialkylamino group by the C-6 methylene group, preventing efficient overlap of the nitrogen p electrons with the π system of the enone. On the other hand, the large (+82 nm) bathochromic shift shown by the α-dialkylamino substituent in the Δ^2-4-ketone system can presumably be taken as a maximal effect, as here the dialkylamino substituent can readily assume an unhindered conformation, permitting efficient overlap of the nitrogen p electrons with the enone π electrons.

We now turn to reduction experiments with the enamine **4** and the parent diosphenol **3**. Reductions of other steroidal enamines to amines using sodium borohydride[8] have been described, as have reductions of enamine salts with lithium aluminum hydride.[9] Repeated attempts to reduce the pyrrolidyl enamino ketone **4** with sodium borohydride under a variety of conditions proved disappointing. By using a large excess of sodium borohydride at room temperature, modest yields (*ca.* 16%) of the 3β-pyrrolidino-4β-ol, **2**, could be obtained. On some occasions, inexplicably, no reduction occurred under conditions which appeared to be identical with those in successful reductions. The gross constitution of **2** followed from elemental analysis, and the stereochemistry at C-3 and C-4 was assigned on the basis of nmr and infrared data. Thus, the nmr spectrum showed, in addition to the pyrrolidine–CH_2–N– resonances, a singlet at δ 1.04 (C-19 CH_3) and a multiplet centered on δ 3.75 ($W_{1/2}$ = 5.5 Hz, C-4 H). The C-19 methyl resonance at δ 1.04 is consistent with A/B trans stereochemistry and the presence of a 4β-hydroxyl group, while the width at half height (5.5 Hz) of the C-4 hydrogen testifies to its equatorial nature and hence to the axial (4β) configuration for the hydroxyl on the same carbon.

One must, then, be dealing with either a 3α,4β- or 3β,4β-disubstituted compound. Conclusive support for the 3β-pyrrolidyl-4β-hydroxy structure, **2**, came from infrared studies. At concentrations between 10^{-1} and 10^{-3} *M*, only associated hydroxyl absorption at 3462 cm^{-1} could be observed. Using 4β-hydroxycholestane as reference (ν_{OH} = 3631 cm^{-1}), the $\Delta\nu$ value in this system is 169 cm^{-1}, in good accord with literature data[10] for –OH --- N– bonding. For example, the $\Delta\nu$ for intramolecular hydrogen bonding in diethylaminoethanol is 170 cm^{-1}. Such bonding is clearly favored in the 3β-pyrrolidino-4β-hydroxy system (equatorial–axial) but ruled out in the alternative 3α,4β (diaxial) system.

Attempts to oxidize **2** to the amino ketone using chromium trioxide–acetic acid–hydrochloric acid gave material showing saturated carbonyl absorption in the infrared, but pure crystalline ketone could not be obtained.

In contrast to the sodium borohydride reduction of the enamino ketone **4**, reduction with lithium aluminum hydride in ether gave, after column and thick layer chromatography on silica gel, the two isomeric α-ketols, **5a** and **6a**. The structures of these hitherto undescribed and previously inaccessible ketols followed from the analytical and spectroscopic data, and from conversion of **5a** and **6a**, respectively, to the known[11,12] α-ketol acetates, **5b** and **6b**, with pyridine–acetic anhydride. A possible explanation for the formation of the 5α-cholestane-3,4-ketols from enamine **4** is shown below.



1,2 (or 1,4) addition of hydride to **4** might be expected to generate the iminium salt **10** on work-up. Decomposition of this salt could give rise to the α-ketols **5a** and **6a**, *via* protonation of the intermediate enediol **11**.

Attempts to reduce the enamino ketone **4** with other hydrides, *e.g.*, lithium aluminum tri-*tert*-butoxyhydride or trimethylamine borane were unsuccessful,

(5) Calculations from the Zürcher tables [R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963)], neglecting the effect of the nitrogen substituent at C-3, give δ values for the C-19 hydrogens as follows: 0.74 for a 5α-Δ^2-4-oxocholestane *vs.* 1.11 for the 5β-Δ^2-4-oxocholestane. The 5α-3-alkoxy-Δ^2-4-oxo compound[6] **8b** shows a value of 0.83 for the C-19 methyl hydrogens.

(6) W. Reusch and R. LeMahieu, *J. Amer. Chem. Soc.*, **85**, 1669 (1963).

(7) K. Irmscher, *Tetrahedron Lett.*, 2707 (1964).

(8) *Cf.* J. A. Marshall and W. S. Johnson, *J. Org. Chem.*, **28**, 421 (1963).

(9) *Cf.* G. Opitz and A. Griesinger, *Justus Liebigs Ann. Chem.*, **665**, 101 (1963).

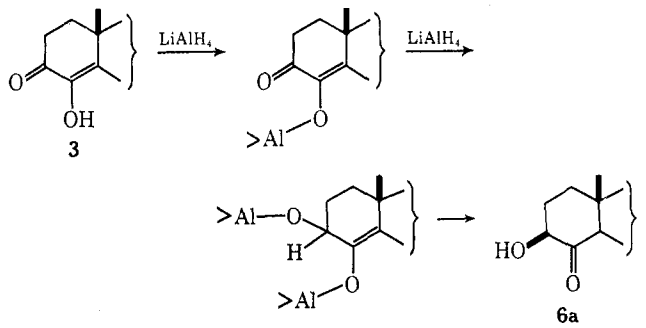
(10) See L. P. Kuhn, R. A. Wires, W. Ruoff, and H. Kwart, *J. Amer. Chem. Soc.*, **91**, 4790 (1969), for tabulation of amino alcohol frequency shifts and for prior references to hydrogen bonding in amino alcohols.

(11) K. L. Williamson and W. S. Johnson, *J. Org. Chem.*, **26**, 4563 (1961).

(12) S. Lieberman and D. K. Fukushima, *J. Amer. Chem. Soc.*, **72**, 5211 (1950).

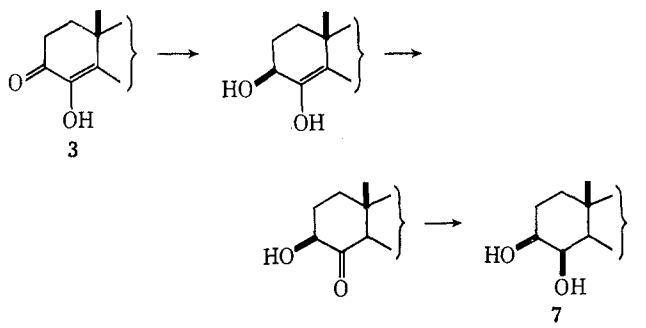
while the use of formic acid or Raney nickel gave unidentified polar products.

Work on another project involving the diosphenol **3** led us to study the reduction of the compound with lithium aluminum hydride and sodium borohydride and compare the results with those noted above for the enamine **4**. In the event reduction of compound **3** with lithium aluminum hydride in ether gave predominantly the 4-oxo-3β-ol, **6a**, this reduction possibly involving the path shown below.[13]



Thus, reaction of lithium aluminum hydride with the enol to give aluminum enolate may be followed by reduction at C-3 with lithium aluminum hydride, and the resulting intermediate could suffer cleavage of the O–Al bonds during work-up to give the observed product.

In contrast, sodium borohydride reduction of **3** in methanol gave, predominantly, the known 3β,4β-diol, **1**, characterized further as the 3,4-acetonide. This result is consistent with reduction of **3** first at C-3 to give 3β-ol, with subsequent ketonization of the resulting Δ^4-3β,4-diol in the protic medium and then reduction of the 3β-hydroxy-4 ketone so formed.[14]



The 3β,4β-diol **1** showed at high dilution, in CCl_4, OH stretching frequencies at 3587 (bonded OH) and 3631 cm^{-1} (free OH). These data giving a $\Delta\nu$ value of 44 cm^{-1} ($\Delta\nu$ = frequency of free OH − frequency of hydrogen-bonded OH) compare well with the value reported by Kuhn[15] for cyclohexane-1,2-diol ($\Delta\nu$ = 39 cm^{-1}).

Experimental Section[16]

3-*N*-Pyrrolidinocholest-2-en-4-one (4).—To a boiling solution of **3** (1.0 g) in methanol (100 ml) was added pyrrolidine (2.0 ml). The solution was heated for 30 min under reflux and then concentrated *in vacuo* to about 75 ml. The resulting suspension was filtered giving 873 mg of the enamine **4**. Two recrystallizations from methanol gave the analytical sample: mp 138–141°; $[\alpha]_D$ +80°; λ_{max} 308 nm (ε 8700); $\nu_{max}^{CHCl_3}$ 1692, 1626 cm^{-1}; nmr ($CDCl_3$) 0.66 (18-methyl), 1.09 (19-methyl), and 5.40 (q, 1, vinyl H).

Anal. Calcd for $C_{31}H_{51}NO$: C, 82.06; H, 11.33; N, 3.09. Found: C, 82.31; H, 11.33; N, 3.30.

3β-*N*-Pyrrolidino-5α-cholestan-4β-ol (2).—To the enamine **4** (615 mg) in methanol (250 ml) was added sodium borohydride (250 mg). After the mixture was stirred at room temperature for 15 min a further 250-mg portion of sodium borohydride was added, followed at 15-min intervals by two more 250-mg portions. After it was stirred for 18 hr more (total reaction time 19 hr), the solution was diluted with water and extracted with ether. The ethereal extract was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The crude product was chromatographed on silica gel (30 g), when elution with chloroform gave the diosphenol **3** (238 mg). Elution with chloroform–methanol–ammonia (132:12:0.9) mixture gave crude amino alcohol (**2**, 100 mg) which was recrystallized from methanol to give analytically pure **2**: mp 177–179°; $[\alpha]_D$ +41°; $\nu_{max}^{CCl_4}$ 3462 cm^{-1}; nmr ($CDCl_3$) δ 0.65 (s, 3, C-18 methyl), 1.04 (s, 3, C-19 methyl), 3.75 (m, 1, C-4 CHOH, $W_{1/2}$ = 5.5 Hz).

Anal. Calcd for $C_{31}H_{55}NO$: C, 81.33; H, 12.11; N, 3.06. Found: C, 81.03; H, 12.05; N, 3.42.

5α-Cholestane-3β,4β-diol (1) by Reduction of 4-Hydroxycholest-4-en-3-one (3) with Sodium Borohydride.—To a stirred solution of the diosphenol **3** (3.0 g) in methanol (800 ml) was added sodium borohydride (3.0 g) portionwise over 5 min. Stirring was continued at room temperature for 30 min, and the reaction mixture was neutralized with acid, concentrated *in vacuo* to about 100 ml, and diluted with water. The mixture was extracted with ether and the ethereal extract washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. Crystallization of the product from benzene gave the 3β,4β-diol, **1** (952 mg): mp 201–204°; $[\alpha]_D$ +18° (lit. mp 202–203°; $[\alpha]_D$ +19°); nmr ($CDCl_3$ δ 0.66 (s, 3, C-18 methyl), 1.03 (s, 3, C-19 methyl), 3.75 (m, 1, C-4 CHOH, $W_{1/2}$ = 6.5 Hz).

The diol (**1**, 73 mg) was converted to the 3,4-acetonide derivative by treatment with perchloric acid (0.15 ml, 70%) in acetone (25 ml) for 1.5 hr with stirring. The mixture was neutralized (solid $NaHCO_3$) and evaporated *in vacuo* to about 10 ml. Dilution with water and filtration gave 81 mg of crude product which was filtered, in benzene, through a short column of silica gel. The benzene eluates gave 5α-cholestane-3β,4β-diol acetonide: mp 150–151° (from acetone); $[\alpha]_D$ 0°; nmr ($CDCl_3$) δ 0.67 (s, 3, C-18 methyl), 1.05 (s, 3, C-19 methyl), 1.35 and 1.51 (s, 3 each, acetonide methyls), 4.0 (m, 1, C-4 CHO–, $W_{1/2}$ = 6 Hz).

Anal. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.06; H, 11.53.

Lithium Aluminum Hydride Reduction of 3-*N*-Pyrrolidinocholest-2-en-4-one (4), giving 5α-Cholestan-4α-ol-3-one (5a) and 5α-Cholestan-3β-ol-4-one (6a).—To a stirred solution of the enamine **4** (1.535 g) in ether (200 ml) was added lithium aluminum hydride (250 mg). After 4 hr the reaction mixture was cooled in ice and water was added cautiously. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to give 1.47 g of crude product. Chromatography on silica gel failed to separate the mixture. However, preparative tlc (petroleum ether–ethyl acetate, 4:1) of a 420-mg portion of the crude reaction product gave 5α-cholestan-4α-ol-3-one (**5a**, 94 mg): mp 162–170° (from benzene–methanol); $[\alpha]_D$ +50°; $\nu_{max}^{CHCl_3}$ 3521, 1718 cm^{-1}; nmr ($CDCl_3$) 0.67 (s, 3, C-18 methyl), 1.10 (s, 3, C-19 methyl), 3.97 (d, 1, C-4 CHOH, J = 11 Hz); mass spectrum, M^+ 402, and m/e 387, 384, 369.

Anal. Calcd for $C_{27}H_{46}O_2$: C, 80.54; H, 11.52. Found: C, 80.44; H, 11.22.

Acetylation of **5a** (pyridine–acetic anhydride, room temperature, 18 hr) gave 5α-cholestan-4α-ol-3-one acetate (**5b**): mp 139–144° (from ethanol) undepressed on admixture with an authentic

(13) *Cf.* C. H. Snyder, *J. Org. Chem.*, **31**, 4220 (1966), who comments on possible mechanisms for the lithium aluminum hydride reduction of 1,2-cyclohexanedione to 2-hydroxycyclohexanone.

(14) *Cf.* reduction of the steroidal 2-hydroxy-Δ^1-3-oxo system: H. Mori, K. Shibata, K. Tsuneda, and M. Sawai, *Chem. Pharm. Bull.*, **15**, 460 (1967).

(15) L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952).

(16) Melting points were determined on the Kofler block. Optical rotations were measured in chloroform solution by Janssen Pharmaceutica, Beerse, Belgium. Nmr spectra were recorded for deuteriochloroform solutions using Varian A-60 and HA-100 spectrometers, and chemical shifts were given in parts per million on the δ scale (tetramethylsilane = 0). Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer using carbon tetrachloride solutions or potassium bromide disks, and on a Perkin-Elmer Infracord using chloroform solutions. Unless otherwise specified, infrared data refer to chloroform solutions. For thin layer chromatography (tlc) silica gel GF254 was used in 0.25-mm layers for analytical purposes and in 2-mm layers for preparative work.

sample[11,17] of **5b**; infrared spectrum (KBr) identical with that of the authentic sample and showing same R_f on tlc (petroleum ether–ethyl acetate, 9:1); ORD [methanol–dioxane (2:1)], 298–259 mμ, a = +39; nmr ($CDCl_3$) δ 0.66 (s, 3, C-18 methyl), 1.11 (s, 3, C-19 methyl), 2.11 (s, 3, acetate methyl), and 5.0 (d, 1, C-4 CHOAc, J = 12 Hz). The chemical shifts for the C-19 methyl and the C-4 hydrogen are considerably different from those reported, presumably because of solvent differences ($CDCl_3$ *vs.* CS_2).

There was also isolated from the above preparative tlc 5α-cholestan-3β-ol-4-one (**6a**, 64 mg): double mp 106–109° and 113–115° (from benzene–methanol); $[\alpha]D$ ±0°; $\nu_{max}^{CHCl_3}$ 3521, 1715 cm^{-1}; nmr ($CDCl_3$) δ 0.67 (s, 3, C-18 methyl), 1.10 (s, 3, C-19 methyl), 4.08 (m, 1, C-3 CHOH).

Anal. Calcd for $C_{27}H_{46}O_2$: C, 80.54; H, 11.52. Found: C, 80.19; H, 11.37.

Acetylation of **6a** (pyridine–acetic anhydride, room temperature, 18 hr) gave 5α-cholestan-3β-ol-4-one acetate (**6b**): mp 120–121° (from acetone) undepressed on admixture with an authentic sample;[12,18] infrared spectrum (KBr) identical with that of the authentic material, showing the same R_f on tlc (petroleum ether–ethyl acetate, 9:1); the expected ORD [methanol–dioxane (2:1)] 305–265 mμ, a = −105; nmr spectrum ($CDCl_3$) δ 0.64 (s, 3, C-18 methyl), 0.73 (s, 3, C-19 methyl), 2.10 (s, 3, acetate methyl), and 5.10 (d, 1, C-3 CHOAc, J_{app} = 7 and 11.5 Hz).

Reduction of 4-Hydroxycholest-4-en-3-one (3) with Lithium Aluminum Hydride to Give 5α-Cholestan-3β-ol-4-one.—To a stirred solution of the diosphenol **3** (1.005 g) in ether (120 ml) was added lithium aluminum hydride (163 mg). After 4 hr, water was added cautiously to the cooled mixture and the ethereal phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to give 450 mg of crude product. Reextraction of the aqueous phases with chloroform gave a further 457 mg of crude product, total yield 907 mg.

A 450-mg portion of the crude material was acetylated (pyridine–acetic anhydride, room temperature for 18 hr) and chromatographed on silica gel (20 g). Elution with benzene and benzene–chloroform (95:5) gave mixtures (71 mg) rich in 5α-cholestan-3β-ol-4-one acetate **6b**, as judged by tlc. Further elution, with benzene–chloroform (1:1), gave pure **6b** (161 mg) identical in all respects with authentic material.

Although tlc revealed the presence of more **6b**, as well as minor amounts of the isomeric 4α-acetoxy-3 ketone (**5b**) and unidentified products in the other chromatogram fractions, further chromatography (both column and thick layer) gave only additional small quantities of **6b** in pure form.

Registry No.—**1**, 20834-99-5; **1** (acetonide), 26460-83-3; **2**, 26460-84-4; **4**, 26460-85-5; **5a**, 1105-27-7; **5b**, 16963-22-7; **6a**, 18897-84-2; **6b**, 1256-67-3.

Acknowledgments.—We thank Dr. D. P. Hollis for the 100-Hz nmr spectra, and Dr. H. Fales for the mass spectrum.

(17) We thank Professor W. S. Johnson (Stanford University) for kindly supplying us with an authentic specimen of the ketol **5b**.

(18) We thank Professor S. Lieberman (Columbia University) for kindly supplying us with an authentic sample of **6b**.

Photoinitiated Fragmentation of Cyclohexenols

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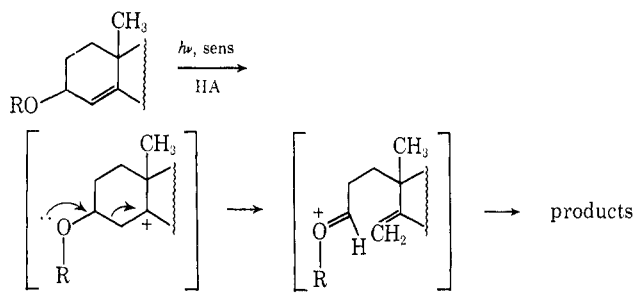
Several years ago we found that certain cyclic olefins undergo a photochemically initiated protonation reaction, thereby giving rise to products *via* carbonium ion pathways.[1] We have subsequently been engaged in studies aimed at the application of this novel finding to polyfunctional olefins wherein the initially formed cation, through interaction with a second functional group, could initiate further reactions. Scheme I shows

SCHEME I



a predicted reaction pathway for cyclohexenols[2,3] which constitutes the subject of this report.

Irradiation of the allylic alcohol **1** in aqueous acetic acid–1,2-dimethoxyethane (DME)–*p*-xylene afforded the oxetane **2** as the only observable product. In methanol–*p*-xylene, the aldehyde **4** was initially produced but this gradually gave way to oxetane **2** upon prolonged irradiation. When this latter irradiation was conducted in methanol which had not been freshly distilled from sodium carbonate, the acetal **7** was also observed. We therefore conclude that the acetal **7** arises *via* an acid-catalyzed ground-state reaction and that irradiation of undistilled methanol produces a strongly acidic substance which catalyzes this reaction. In fact, even acetic acid was found to promote the ground-state conversion of aldehyde **4** to acetal **7** in methanol, albeit somewhat inefficiently. In methanol–acetic acid–*p*-xylene, photolysis of the allylic alcohol **1** afforded a mixture of oxetane **2**, aldehyde **4**, and the dimethyl acetal **7**. Here again, prolonged irradiation produced increased amounts of the oxetane **2** at the expense of aldehyde **4**.

Aldehyde **4** was identified through its spectral properties and by independent synthesis from the known cyano ketone **5**[4] *via* condensation with triphenylmethylenephosphorane in dimethyl sulfoxide (DMSO)[5] followed by reduction with diisobutylaluminum hydride nad hydrolysis.[6] Irradiation of the aldehyde thus obtained afforded the oxetane **2**[7] (Scheme II). The stereochemistry of oxetane **2** has not been rigorously established, but steric considerations tend to favor the indicated structure wherein the propionaldehyde side chain of the unsaturated aldehyde precursor **4** can inter-

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(1) *Cf.* J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969); P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969), and references therein.

(2) For an example of a related homoallylic alcohol cleavage, see P. J. Kropp and H. J. Krauss, *ibid.*, **91**, 7466 (1969).

(3) Recently, J. A. Waters and B. Witkop [*J. Org. Chem.*, **34**, 3774 (1969)] reported on the conversion of cholesterol and 4-cholesten-3-ol to the steroidal counterpart of oxetane **2**. These authors suggested a mechanism involving C–C bond migration in the presumed intermediate tertiary cation leading to an *A*-nor primary cation which then underwent cyclization to the aforementioned oxetane.

(4) R. L. Frank and R. C. Perle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).

(5) *Cf.* E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).

(6) *Cf.* L. I. Zakharkin and I. M. Khorlina, *Dokl. Akad. Nauk SSSR*, **116**, 422 (1967); *Chem. Abstr.*, **52**, 8040*f* (1958).

(7) For examples of carbonyl–olefin potochemical additions, see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York N. Y., 1965, pp 208–211.