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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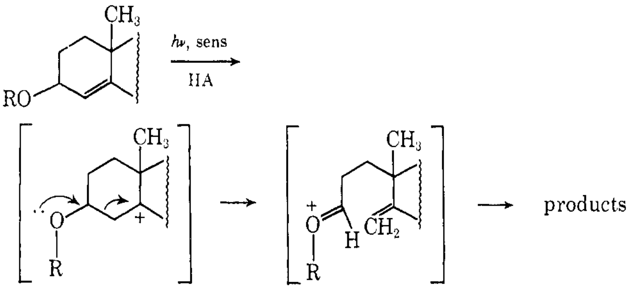
Several years ago we found that certain cyclic olefins undergo a photochemically initiated protonation reaction, thereby giving rise to products *via* carbonium ion pathways.[1] We have subsequently been engaged in studies aimed at the application of this novel finding to polyfunctional olefins wherein the initially formed cation, through interaction with a second functional group, could initiate further reactions. Scheme I shows a predicted reaction pathway for cyclohexenols[2,3] which constitutes the subject of this report.

Scheme I



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.

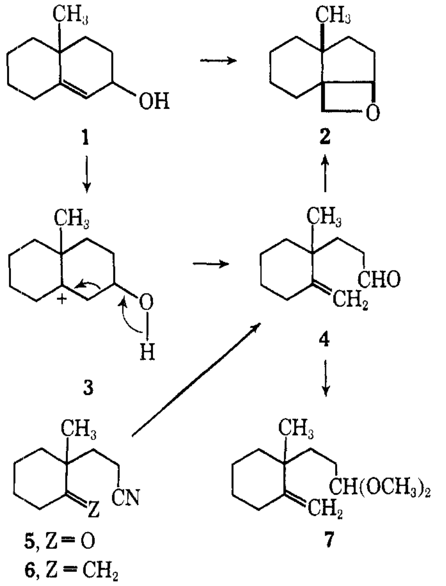
[4] R. L. Frank and R. C. Perle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).

[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).

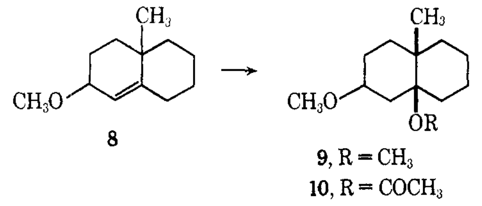
[7] For examples of carbonyl–olefin potochemical additions, see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York N. Y., 1965, pp 208–211.

SCHEME II



act with the exocyclic double bond without undue strain in the developing bicyclo[3.2.0] ring system.

An attempt to extend the concept depicted in Scheme I to the methyl ether **8** was unsuccessful. Irradiation in methanol–acetic acid–*p*-xylene led to the addition products **9** and **10**.[1] None of the acetal **7** could be detected.



From a synthetic standpoint, the photoinitiated fragmentation of cyclohexenols described above represents a convenient route to polycyclic oxetanes or to ring-cleaved products such as **4** and **7**. The widespread occurrence of steroidal 4-en-3-ones makes the corresponding alcohols likely candidates for future studies.[3,7a]

Experimental Section[8]

Photolysis of Unsaturated Alcohol 1. A. In Methanol Acetic Acid.—A solution of 1.40 g of alcohol **1**,[9] 5.0 ml of acetic acid, and 5.0 ml of *p*-xylene in 180 ml of methanol was irradiated[10] for 2 hr.[8a] The product was isolated with ether[8b] affording 1.3 g of a mixture shown by gas chromatography to contain, in order of increasing retention time, oxetane **2**, aldehyde **4**, acetal **7**, and alcohol **1** in the ratio 1:1:3:1. This mixture was separated *via* preparative gas chromatography to give the following pure components.

(1) **Oxetane 2** showed $\lambda_{\max}^{\text{film}}$ 9.78, 10.15, 11.00, 11.34, and 11.7 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.60 (multiplet, –OCH–), 4.09 (–OCH$_2$–, AB quartet, J_{AB} = 6 Hz, $\Delta\nu_{AB}$ = 34 Hz), and 0.90 ppm (CH$_3$).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.5; H, 10.9.

(2) **Aldehyde 4** showed $\lambda_{\max}^{\text{film}}$ 3.70, 5.80, 6.09, and 11.19 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 9.69 (CHO triplet, J = 1 Hz), 4.6 (C=CH$_2$ multiplet), and 0.97 ppm (CH$_3$).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46, H, 10.91. Found: C, 79.2; H, 10.9.

(3) **Acetal 7** showed $\lambda_{\max}^{\text{film}}$ 6.10, 8.91, 9.36, 9.50, and 11.19 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.65, 4.50 (C=CH$_2$), 4.18 (acetal α-H triplet, J = 6 Hz), 3.19 (CH$_3$O), and 1.0 ppm (CH$_3$).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.75; H, 11.2.

B. In Methanol.—A solution of 1.09 g of alcohol **1** and 5 ml of xylene in 175 ml of methanol was subjected to irradiation.[10] After 1 hr, gc analysis of aliquot indicated a 26:74 mixture of oxetane **2** and aldehyde **4**. After an additional 4 hr of irradiation, gc analysis showed that a 60:40 mixture of these two components was present.

C. In DME–Water–Acetic Acid.—A solution of 1.25 g of alcohol **1**, 5 ml of *p*-xylene, 5 ml of acetic acid, and 40 ml of water in 140 ml of DME was irradiated[10] for 4 hr.[8a] The product was isolated with ether[8b] aud distilled affording 0.75 g (60%) of oxetane **2** purified by preparative gas chromatography.

3-(2-Methylene-1-methylcyclohexyl)propanenitrile (**6**).—To a solution of methylenetriphenylphosphorane in DMSO[5] (50 ml of 2 *M*) was added 8.20 g (0.047 mol) of ketonitrile **5**[4] in 5 ml of DMSO dropwise.[8a] The mixture was stirred overnight and poured into 250 ml of ice–water, and the product was isolated with pentane[8b] and chromatographed on alumina. Elution with hexane afforded 2.77 g (33%) of unsaturated nitrile **6**: $\lambda_{\max}^{\text{film}}$ 4.45, 6.08, and 11.14 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.70, 4.59 (C=CH$_2$), and 1.02 ppm (CH$_3$). The analytical sample, bp 55–60° (0.05 mm), was obtained *via* short-path distillation.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.9; H, 10.4; N, 8.3.

3-(2-Methylene-1-methylcyclohexyl)propanecarboxaldehyde (**4**).—To a stirred solution of 900 mg (6.0 mmol) of nitrile **6** in 50 ml of hexane at −60° was added 10.0 ml of 0.9 *M* diisobutylaluminum hydride[6] in hexane.[8a] The solution was allowed to reach room temperature and, after 2 hr, 60 ml of saturated aqueous ammonium chloride was added. After 20 min, the mixture was poured into 20 ml of 5% aqueous sulfuric acid and the product was isolated with hexane[8b] and distilled affording 383 mg (42.5%) of aldehyde, bp 62–65° (0.07 mm). The infrared and nmr spectra exactly matched those of aldehyde **4** secured through photolysis of alcohol **1** as described above.

Photolysis of Aldehyde 4.—A solution of 315 mg (1.90 mmol) of aldehyde **4** and 3.0 ml of *p*-xylene in 105 ml of methanol was irradiated[10] for 2 hr.[9a] The product was isolated with ether[8b] and distilled affording 285 mg (90%) of a 9:1 mixture of oxetane **2** and aldehyde **4**. The material isolated by preparative gc exhibited infrared and nmr spectra which exactly matched those of the oxetane secured *via* photolysis of alcohol **1**.

3-(2-Methylene-1-methylcyclohexyl)propanecarboxaldehyde Dimethyl Acetal (**7**).—A solution of 80 mg (0.48 mmol) of aldehyde **4**, 0.5 ml of acetic acid, and 0.5 ml of trimethyl orthoformate in 6 ml of methanol was stirred at reflux for 18 hr. The product was isolated with ether[8b] and distilled (60°, 0.05 mm), to give 68 mg (66.7%) of acetal **7**, identical with the material described above.

Registry No.—**1**, 26675-10-5; **2**, 26675-09-2; **4**, 26675-11-6; **6**, 26731-50-0; **7**, 26675-12-7.

Acknowledgment.—We are indebted to the National Science Foundation for support of this work through a research grant.

[7a] NOTE ADDED IN PROOF.—Since submission of this note a study has appeared which likewise postulates the pathway depicted in Scheme I for steroidal allylic and homoallylic alcohol photolysis: D. Guénard and R. Beugelmans, *Tetrahedron Lett.*, 1705 (1970).

[8] (a) The apparatus described by W. S. Johnson and W. P. Schneider ("Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 132) was used to maintain a nitrogen atmosphere. (b) The isolation procedure consisted of thorough extraction with the specified solvent, washing the combined extracts with saturated brine solution, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a rotary evaporator. (c) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

[9] W. J. Vandenheuvel and E. S. Wallis, *J. Org. Chem.*, **27**, 1233 (1962).

[10] The irradiation was carried out with a 450-W Hanovia medium-pressure mercury arc (type L) in a water-jacketed Vycor immersion well. Mixing was effected by a fine stream of nitrogen introduced through a gas dispersion tube fitted in the bottom of the reaction vessel.