acid for 3 hr. as described above gave 59 mg. of pale yellow needles, which was shown by gas chromatography to be a 94:6 mixture of recovered hydroxy ketone **18** and an unidentified product. No evidence

for the formation of any of the hydroxy ketone **17** could be detected.

# Reactivity and Geometry in Allylic Systems. VI.[1] Stereospecific Conversion of Allylic Alcohols to α,β-Epoxy Ketones by Photosensitized Oxygenation[2]

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In pyridine with hematoporphyrin sensitization, Δ^4- and Δ^5-steroidal olefins with an allylic hydroxyl group at C-3 and C-7, respectively, underwent photooxygenation more slowly than the parent olefins. In those cases where the allylic hydrogen on the hydroxylated carbon had (or could attain) a quasi-axial orientation, the products were the corresponding α,β-unsaturated ketone and α,β-epoxy ketone. The configuration of the epoxide group was the same as that of the allylic hydrogen abstracted. The stereospecificity is interpreted in terms of known steric and conformational factors in photosensitized oxygenations. Acetate and benzoate esters of the allylic alcohols proved essentially inert, and this deactivation is attributed to electronic factors. The proportion of enone to epoxy ketone from cholest-4-en-3β-ol was found to depend on the sensitizer.

Photosensitized oxygenation of monoolefins is a useful way to introduce an allylic oxygen function with accompanying rearrangement of the double bond.[4] Studies with steroid systems indicated that the reaction proceeds by a cyclic abstraction mechanism with rather stringent geometric requirements.[5,6] The effects of polar functional groups are not known, and the object of the present study was to examine substrates with an oxygen function (*e.g.*, OH, OCOR) on the allylic carbon. The hydroxyl group seemed of special interest because successful abstraction of the allylic hydrogen in the normal *cis* manner could generate a transient enol as shown, which could collapse to products
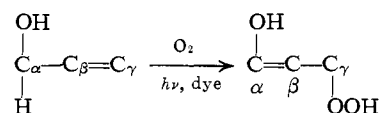
other than the usual allylic hydroperoxides. We now report the findings with some ring-A and ring-B allylic alcohols (and their derivatives) in the cholestane series.

Synthesis of Starting Compounds and Products

The ring-A epimeric allylic alcohols and their derivatives (partial structures **1** and **4**) were prepared as described elsewhere.[5c] We synthesized 4α,5-epoxy-5α-cholestan-3-one (**2**) from **4a** by treatment with perbenzoic acid in chloroform followed by oxidation with chromium trioxide in pyridine.[7] The epimeric epoxy ketone **5** was obtained from cholest-4-en-3-one (**3**) by treatment with alkaline hydrogen peroxide.[8] All the ring-B allylic alcohols and their esters (**8** and **9**), the related epoxy ketones (**10**), and the enones (**11**) were prepared by reported methods with the exception of cholest-5-en-7α-ol (**8b**), which was obtained conveniently from cholest-5-ene (**6a**) as follows. Photosensitized oxygenation converted **6a** to a hydroperoxide (**7a**), which was not purified but which was rearranged in chloroform to a second hydroperoxide (**8a**).[9] Reduction of the crude product with sodium iodide gave **8b** along with some cholest-5-en-7-one (**11c**), which was removed by chromatography.

Methods

Photooxygenations were conducted in pyridine solution with hematoporphyrin as sensitizer. The enone content in a crude reaction product was determined by ultraviolet spectroscopy, and the starting allylic alcohol was assayed by oxidation of an aliquot with manganese

(1) Part V: A. Nickon and W. L. Mendelson, *J. Org. Chem.*, 30, 2087 (1965).

(2) This work was supported by the National Institutes of Health (Grant GM 09693) and an early phase of it was aided by the Alfred P. Sloan Foundation and by a grant-in-aid from the Hynson, Westcott, and Dunning Fund of The Johns Hopkins University. A preliminary communication appeared in *J. Am. Chem. Soc.*, 85, 1894 (1963).

(3) (a) Alfred P. Sloan Foundation Fellow, 1957–1961. (b) Taken from the Ph.D. Dissertation of W. L. M., The Johns Hopkins University, 1963.

(4) G. O. Schenck, *Agnew. Chem.*, 69, 579 (1957).

(5) (a) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, 81, 6330 (1959); (b) *ibid.*, 83, 1498 (1961); (c) A. Nickon and W. L. Mendelson, *Can. J. Chem.* 43, 1419 (1965); (d) A. Nickon, N. Schwartz, J. B. DiGiorgio, and D. A. Widdowson, *J. Org. Chem.*, 30, 1711 (1965); (e) see ref. 1.
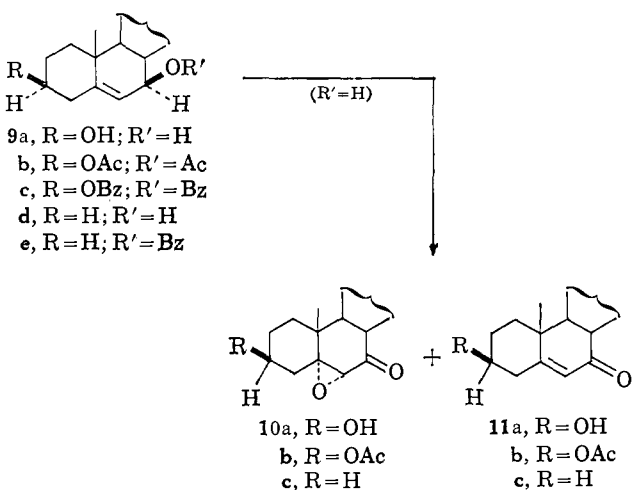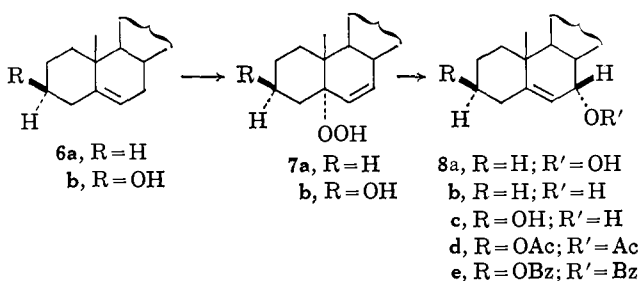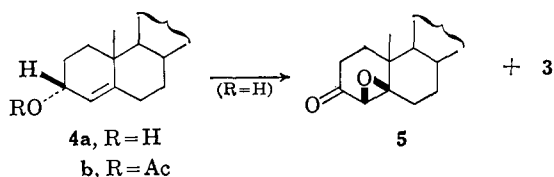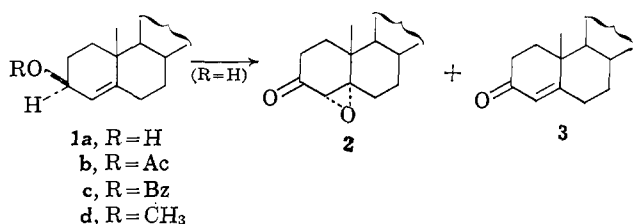
(6) For relevant stereochemical studies with monocyclic terpenes see (a) R. L. Kenney and G. S. Fisher, *J. Org. Chem.*, 28, 3509 (1963); (b) G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Ann.*, 674, 93 (1964).

(7) (a) α-Epoxidation was expected on the basis of stereochemical studies by H. B. Henbest and R. A. Wilson, *J. Chem. Soc.*, 1958 (1957) (b) Epoxy ketone 2 has been prepared by other routes: E. P. Oliveto, G. Gerold, and E. B. Hershberg, *J. Am. Chem. Soc.*, 79, 3596 (1957); D. J. Collings, *J. Chem. Soc.*, 3919 (1959).

(8) (a) P. A. Plattner, A. Furst, F. Koller, and W. Lang, *Helv. Chim. Acta*, 31, 1455 (1948); P. A. Plattner, H. Heusser, and A. B. Kulkarni, *ibid.*, 31, 1822 (1948); (b) H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963).

(9) For analogies see ref. 5c; G. O. Schenck, O. A. Neumuller, and W. Eisfeld, *Ann.*, 618, 202 (1958); B. Lythgoe and S. Trippett, *J. Chem. Soc.*, 471 (1959).

dioxide followed by ultraviolet determination of the increase in enone content. Suitable controls verified the completeness of the manganese dioxide oxidations. Exploratory oxygenations of 1a revealed the need for a higher light intensity than was used in previous studies with steroids.[5a,b] For example, irradiation conditions (30 w., 72 hr.) that converted cholesterol (6b) virtually completely to its hydroperoxide 7b left 1a largely unchanged.[10] In contrast, substantial conversion of 1a occurred within the same period when the light intensity was approximately doubled. Consequently, this higher light intensity was adopted for all the runs; the heat from the lamps kept the temperature of the solution at ca. 40°.

1a, R=H
b, R=Ac
c, R=Bz
d, R=CH₃

2

3

4a, R=H
b, R=Ac

5

+ 3

6a, R=H
b, R=OH

7a, R=H
b, R=OH

8a, R=H; R'=OH
b, R=H; R'=H
c, R=OH; R'=H
d, R=OAc; R'=Ac
e, R=OBz; R'=Bz

9a, R=OH; R'=H
b, R=OAc; R'=Ac
c, R=OBz; R'=Bz
d, R=H; R'=H
e, R=H; R'=Bz

(R'=H)

10a, R=OH
b, R=OAc
c, R=H

11a, R=OH
b, R=OAc
c, R=H

Results

The first striking observation with cholest-4-en-3β-ol (1a) was that the allylic hydroxyl group deactivates the olefin link. Under similar conditions 1a required

(10) That the lower reactivity is not uniquely associated with this particular solvent and sensitizer was shown by similar irradiation of 1a in methanol containing methylene blue, which produced little change even after 90 hr.

80–100 hr. for completion whereas the parent olefin, cholest-4-ene, was entirely consumed within 25–30 hr.[5c] Typically, the crude product from 1a gave a very weak or negative hydroperoxide test and contained ca. 65–75% of 4α,5-epoxy-5α-cholestan-3-one (2) and 15–16% of cholest-4-en-3-one (3), as determined by quantitative infrared and ultraviolet analyses, respectively. The products could be separated by column chromatography, and in a typical run (72-hr. irradiation) we isolated 2, 3, and the starting alcohol 1a in yields of 50, 13, and 25%, respectively. The epoxy ketone appeared to be stereochemically pure and in no run with 1a did we detect the presence of the epimeric epoxide 2. Control experiments showed that enone 3 and epoxy ketone 2 are individually stable to the irradiation conditions, and also that the starting allylic alcohol is unchanged on prolonged irradiation and oxygenation in the absence of the sensitizer. The alcohol was also unaffected on attempted photooxygenation with nonfluorescent dyes such as Janus green, orange II, and methyl orange, which are reported not to function as sensitizers.[11]

The epimeric allylic alcohol 4a underwent photosensitized oxygenation more slowly than did 1a.[12] The products from 4a were 4β,5-epoxy-5β-cholestan-3-one (5) and cholest-4-en-3-one (3), and in a typical 72-hr. run the mixture contained 50% of 5 (quantitative infrared) and 10% of 3 (ultraviolet analysis). Epoxy ketone 5 is partly decomposed on chromatography, but by using Florisil or deactivated alumina, we isolated pure 5 in 29% yield, along with ca. 10% of 3 and ca. 35% of starting alcohol 4a. Attempts were made to increase conversion by prolonged oxygenation (144 hr.), but ultraviolet inspection indicated that secondary reactions had set in, and the yields of epoxy ketone 5 were not significantly altered. Attempted photooxygenation of 4a in the absence of sensitizer gave material whose infrared spectrum was essentially the same as that of starting alcohol except for appearance of weak absorptions in the carbonyl region.

The deactivation of the Δ⁴-olefin bond by a hydroxyl group at C-3 prompted us to examine cholest-4-en-3β-ol acetate (1b) and benzoate 1c, 3β-methoxycholest-4-ene (1d), and cholest-4-en-3α-ol acetate (4b). The esters proved inert after prolonged oxygenation and irradiation in the presence of different sensitizers. The allylic ether 1d underwent some oxygenation as indicated by spectroscopic appearance of saturated carbonyl absorption (infrared) and enone absorption (ultraviolet). However, even after an 80 hr. run, 62% of starting ether was recovered by chromatography.

In the ring-B series, the behavior of cholest-5-ene-3β,7β-diol (9a) paralleled that of its ring-A analog. In typical runs (80–85 hr.) 9a gave 5,6α-epoxy-5α-cholestan-3β-ol-7-one (10a, 53–56%) and cholest-5-en-3β-ol-7-one (11a, 13–17%). The physical constants of 10a and its corresponding acetate 10b (obtained by acetylation) agreed satisfactorily with reported values.[13] Although enone 11a was isolated only in semicrystalline form its structure was established from its ultraviolet

(11) F. Millich and G. Oster, J. Am. Chem. Soc., 81, 1357 (1959); G. Oster, J. S. Bellin, R. W. Kimball, and M. E. Schrader, ibid., 81, 5095 (1959); B. Holmstrom and G. Oster, ibid., 83, 1867 (1961).
(12) For verification, we photooxygenated a 1:1 mixture of the epimeric alcohols and showed that after 40 hr. about twice as much of 1a had undergone conversion as had 4a.
(13) W. Bergmann and M. B. Meyers, Ann., 620, 46 (1959).

absorption (235 mμ)[14] and by infrared comparison with an authentic specimen. Similar oxygenation of a small sample of cholest-5-en-7β-ol (9d) gave a crude product whose infrared and ultraviolet spectra were consistent with the presence of an α,β-epoxy ketone (10c) and about 20% of cholest-5-en-7-one (11c). However in this case, product isolation was not attempted owing to paucity of material.[15]

In contrast, the 7α-alcohols 8b and 8c each reacted with oxygen only very slowly. Considerable proportions of starting material (e.g., ca. 60% recovered in one run from 8c) remained even after prolonged treatment (140 hr.), which also produced some of the corresponding enone (13-23%) and complex mixtures from which no other definite products were isolated on chromatography. The following ring-B esters were subjected to photosensitized oxygenation (96-144 hr.) and were recovered with virtually unchanged infrared absorption: 9b, 9c, 9e, 8d, and 8e.

In the course of our work with the ring-A alcohols, we observed that when hematoporphyrin was replaced by another dye the proportion of enone in the product was significantly altered. To explore the generality of this finding, we photooxygenated cholest-4-en-3β-ol (1a) in pyridine with a variety of sensitizers under standardized conditions (80 hr.). The enone 3 and the unconverted alcohol were assayed as before; the content of epoxy ketone 2 was calculated by difference and in some runs was independently checked by quantitative infrared analysis. The results are summarized in Table I, which also lists the principal fluorescence emission maximum for each dye.

Table I. Photooxygenation of Cholest-4-en-3β-ol

Sensitizer	Fluorescence maximum, mμ[a]	Total % conversion	Ratio of 3:2
Chlorine e₆	670	85	1:4.5 (1:4.4)[b]
Hematoporphyrin	630	80[c]	1:4.5 (1:4.6)
Methylene blue	690	52	1:3 (1:2.5)
Rose bengal	580	88	1:1.2 (1:1.4)
Erythrosin B	578	71	1.6:1
Sulforhodamin B	575	33	1.8:1
Acridine orange	520	34	2.8:1
Eosin Y	565	82	3.1:1
Fluorescein	525	30	3.1:1
Riboflavin[d]	510	61[d]	30:1

[a] Measured in pyridine on dye concentrations of 0.001-0.002 g./100 ml. [b] Values in parentheses obtained from quantitative infrared assays of epoxy ketone. [c] Average of three runs in which enone varied ±1% and epoxy ketone varied ±2%. [d] Owing to low solubility of the dye this run was in pyridine-methanol (4:1) for 100 hr. About the same product ratio was observed in pyridine alone but the total conversion was only 35% in 72 hr.

Discussion

The behavior of the alcohols and their derivatives shows that an allylic oxygen function deactivates a double bond. In fact, acetylation or benzoyation appears an effective way to protect an allyli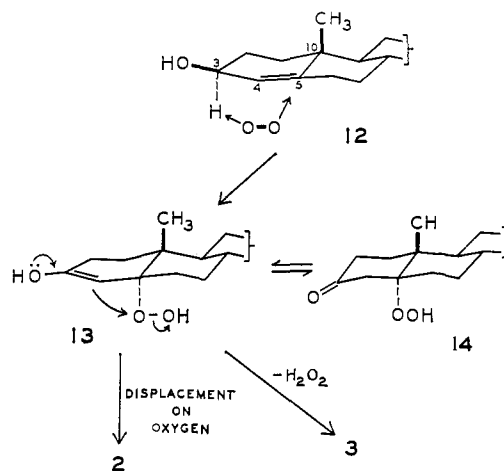c alcohol unit when selective oxygenation at another site is desired. Steric hindrance is probably not the prime factor responsible for the deactivation because the allylic substituent is on the side of the ring system opposite to that from which oxygenation occurs. Some steric shielding by the substituent could operate at the C–H bond but not at the remote site where the C–O bond is formed. Recent work with cholest-4-ene revealed that hindrance to the developing C–O bond is of greater importance than hindrance to the C–H bond.[5c]

Deactivation by electron withdrawal is probably a more critical factor, and the enhanced effect with the esters is in line with their greater electron-attracting ability.[16] Support is found in the work of Sharp[17] and of Schenck[18] who showed that attachment of alkyl groups to olefinic carbons increased the susceptibility of the double bond toward photosensitized oxygenation. The known greater reactivity of Δ⁴- and Δ⁵-steroids relative to Δ³- and Δ⁶-steroids also follows this same trend.[5,19] The combined evidence indicates that during reaction an electrophilic demand is made upon the substrate. This demand could result from a species (oxygen or a dye–oxygen complex) that has electrophilic character or that develops it by polarization during the reaction.[20]

The stereospecificity in the conversion of allylic alcohols to epoxy ketones is most simply interpreted as illustrated with cholest-4-en-3β-ol. In the preferred half-chair conformation of ring-A (see 12) the hydrogen at C-3 is quasi-axial, and α-oxygenation at C-5 with a cyclic (but not necessarily concerted)[20] abstraction of the hydrogen would lead to the enol hydroperoxide 13,

(14) C. W. Greenhalgh, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 2375 (1952).

(15) The time required (80-90 hr.) for oxygenation of the ring-B alcohols 9a and 9c was greater than that needed (ca. 25 hr.) for the parent olefin, cholest-5-ene (6a). This corroborates the finding in the ring-A series that an allylic OH deactivates.

(16) (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 421 (1958). (b) As an alternate explanation a referee has suggested that the hydroxyl group might have a deactivating effect on the reactive species, such as a singlet-state oxygen, whereas the ester group could have a stronger deactivating effect.

(17) D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960, p. 79P.

(18) G. O. Schenck, H. Mertens, W. Müller, E. Koch, and G. P. Schiemenz, *Angew. Chem.*, **68**, 303 (1956).

(19) One of the products from photosensitized oxygenation of cholest-4-ene is 4β-hydroperoxycholest-5-ene.[5c] That no β-attack at C-4 was detected with either of the ring-A allylic alcohols (or their esters) is understandable in terms of electronic, but not steric, factors because inductive electron withdrawal by the substituent at C-3 could be more pronounced at C-4 than at C-5, which is also more highly alkylated. Similar considerations explain why sensitized oxygenations of olefins in general stop largely after one OOH is introduced, even though the product may still have allylic hydrogens.

(20) For different views see references quoted in ref. 5b; also see ref. 6a and 17; C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964); E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964); K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

which could equilibrate with its keto form **14**. Collapse of **13** (or its anionic equivalent) by a displacement on oxygen at C-5 would give an epoxide (**2**) with the same configuration as that of the abstracted hydrogen; competitive elimination of hydrogen peroxide would lead to enone **3**.[21] A pathway to epoxy ketone involving subsequent addition of hydrogen peroxide to enone **3** is excluded by the stereospecificity from each allylic alcohol and because similar additions are known to give largely the β-epoxide **5**.[8]

The faster rate of photooxygenation of **1a** over **4a** is interpretable on steric and conformational grounds. Simple analysis of nonbonded interactions in a Δ^4-steroid suggests that of the two half-chair forms for ring-A the one shown in **12** is the more stable; this preference should be enhanced by a β-substituent at C-3. α-Oxygenation at C-5 meets no serious steric hindrance and the C-3 hydrogen has the necessary geometry for cyclic transfer to oxygen.[5,6] In epimer **4a** (shown in the two possible half-chair conformations **15** and **16**) oxygen attacks C-5 from the β-side, and cyclic hydrogen abstraction cannot readily occur from **15**, in which the hydrogen is quasi-equatorial, but only from **16** (or its equivalent), in which the hydrogen is quasi-axial. On the reasonable assumption that conformational equilibration is rapid in comparison to photooxygenation, the greater reactivity of **1a** lies in its having a higher relative proportion of the necessary conformation; in addition, any inherent preference for α-attack over β-attack would also favor **1a** over **4a**. Recent work with cholest-4-ene supports these views.[5c]
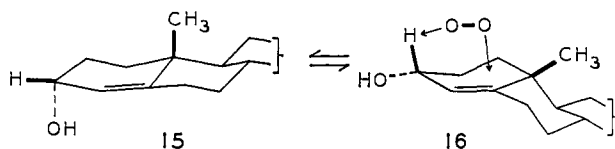
In the ring-B series the 5-en-7β-ols **9a** and **9d** have the appropriate geometric features and behaved as expected. The resistance of the epimeric 7α-ols **8b** and **8c** accords with conformational predictions because ring-B cannot adopt a half-chair form in which the 7β-hydrogen is quasi-axial.

Our finding (Table I) that the sensitizer can strongly effect the enone–epoxy ketone ratio has obvious practical utility in synthetic work. However, the mechanistic implications are presently not clear, especially as the nature of the attacking species is still not settled.[20,22] If both products arise from a common steroidal intermediate,[21] partitioning could very well be influenced by a dye molecule that is present at the time of reaction or that is encountered after the intermediate is formed. Various interpretations are possible but a discussion is not warranted at the present time. Interestingly, Marshall and Fanta[23] have recently photooxygenated 10β-methyl-1(9)-octalin-2β-ol in pyridine with hematoporphyrin and obtained the expected epoxy ketone

and enone in a ratio (*ca.* 3:1) comparable to that found with our steroid system. Table I shows that for cholest-4-en-3β-ol there is a rough correlation between the trend in product ratio and the trend in fluorescence emission maximum for the different sensitizers. Whether or not this correlation has any mechanistic significance must await further study.

Experimental[24]

General. Color tests for hydroperoxides and reductions with sodium iodide in methanol were conducted as reported in earlier papers.[5] Assays for cholest-4-en-3α- or -3β-ol after a reaction were effected by manganese dioxide oxidation,[26] followed by ultraviolet analysis of the derived cholest-4-en-3-one (λ 241 mμ). The sample (*ca.* 0.020 g.) in chloroform (10 ml.) was stirred with manganese dioxide[27] (0.03–0.04 g.) at room temperature for 60–70 hr. The solution was warmed on the steam bath and filtered, and the solid was washed repeatedly with hot chloroform and then with anhydrous ether. Solvents were evaporated and last traces were removed by thorough evacuation in a vacuum desiccator prior to ultraviolet analysis. Controls with pure samples showed that oxidation of the 3β-ol **1a** was 96% complete in *ca.* 20 hr., whereas the 3α-ol **4a** was *ca.* 90% oxidized in 40 hr.; product recovery in the controls ranged from 85 to 95%. Photosensitized oxygenations in reagent grade pyridine and work-up were conducted as detailed earlier[5] and, unless otherwise noted, irradiations involved the use of four 15-w. fluorescent tubes.

Ring-A Allylic Alcohols and Esters. Compounds **1a**, **1b**, **4a**, and **4b** were those used in previous work.[5c] Benzoate **1c**, prepared conventionally with benzoyl chloride in pyridine, had m.p. 125–126°, [α]D +1° (lit.[28] m.p. 125–128°, [α]D ±0°).

3β-Methoxycholest-4-ene (**1d**). Our product prepared as described[29] had m.p. 72–73°, [α]D +39° (lit. m.p. 68–70°, [α]D −37°). The reported rotation should be positive (see ref. 7a).

Cholest-4-en-3-one (**3**). The procedure of Eastham and Teranishi[30] gave **3** with m.p. 79–81°, [α]D

(21) Loss of hydrogen peroxide from 13 could conceivably be preceded by allylic rearrangement of the hydroperoxy group from C-5 to C-3. For analogies see ref. 5c. The possibility that some enone arises by an unrelated path (*e.g.*, autoxidation induced by hydroperoxides such as 14) cannot be entirely excluded.

(22) Sensitizer control of product composition has been observed in other photochemical reactions: G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.* **28**, 3297 (1963); G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(23) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

(24) Unless stated otherwise the following information applies. Elemental analyses were performed by Mr. J. Walter. Melting points were taken in a Hershberg-type apparatus and are corrected. Optical rotations refer to the sodium D-line and were taken at room temperature (21–25°) in chloroform solution. Fisher or Alcoa alumina (F-20, 80–200 mesh) and Fluorisil (60–200 mesh; Matheson Coleman and Bell) were used for chromatography. The term "deactivated alumina" refers to Fisher alumina that had previously been spread out and exposed to air for 6–8 hr. Petroleum ether (b.p. 30–50°) was extracted with sulfuric acid and distilled prior to use; hexane (b.p. 50–70°) was purified by passage through alumina. Anhydrous sodium sulfate was the drying agent for all ether layers. Ultraviolet spectra were taken in 95% ethanol on a Cary Model 11 M recording instrument, and infrared spectra were taken in carbon disulfide with a Perkin-Elmer Model 21 double-beam spectrophotometer. For quantitative infrared estimation of ketones, solutions (*ca.* 0.015 g./ml.) were prepared gravimetrically and examined in matched, 0.5-mm. sodium chloride cells. Apparent molar extinction coefficients (e^a) for the carbonyl absorption were determined[25] and used for assay of unknown solutions prepared in the same way.

(25) R. N. Jones and C. Sandorfy in "Techniques of Organic Chemistry," Vol. 9, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 279.

(26) F. Sondheimer, C. Amandolla, and G. Rosenkrantz, *J. Am. Chem. Soc.*, **75**, 5930 (1953).

(27) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jensen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(28) A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *ibid.*, 1969 (1957).

(29) D. D. Evans and C. W. Shoppee, *ibid.*, 540 (1953).

(30) J. F. Eastham and R. Teranishi, *Org. Syn.*, **35**, 39 (1955).

$+90°$, λ 241 mμ (ϵ 16,600), ν 1680 cm.$^{-1}$ (ϵ^a 705) (lit. m.p. 79.5–80.5°,[30] λ 240.5 (ϵ 18,000)).[31]

4α,5-Epoxy-5α-cholestan-3-one (**2**). Cholest-4-en-3α-ol (**4a**, 0.06 g.) was epoxidized[7a] with perbenzoic acid in chloroform (3 ml., 0.8 N).[32] Consumption was complete after 24 hr. at room temperature and the chloroform was washed with 10% potassium carbonate solution and with water, then dried. Evaporation under reduced pressure left a clear oil, which was dissolved in pyridine (10 ml.) and treated with 5 ml. of oxidation reagent, which we prepared separately by heating a mixture of chromium trioxide (10.0 g.) and pyridine (100 ml.) on a steam bath followed by filtration through glass wool to remove most of the undissolved solid. After 15 hr. at room temperature, the reaction mixture was poured into ether and washed in turn with dilute acetic acid, sodium carbonate solution, and water. Evaporation of the dried ether solution under reduced pressure gave a clear, hardened oil, which was dissolved in petroleum ether[24] and chromatographed on alumina (20 g.). Elution with benzene–petroleum ether (1:10) gave crude **2** (0.045 g., m.p. 110–115°), which was crystallized once from acetone–methanol, m.p. 123–124°, $[α]D$ $-42°$, ν 1710 cm.$^{-1}$ (ϵ^a 350). These constants agree with those reported.[7b]

4β,5-Epoxy-5β-cholestan-3-one (**5**). A reported[5c] modification of the procedure of Plattner, *et al.*,[8] gave **5** with m.p. 118–119°, $[α]D$ $+128°$, ν 1710 cm.$^{-1}$ (ϵ^a 350). Reported values are m.p. 116–117°, $[α]D$ $+136°$.[8]

Cholest-5-en-3β-ol-7-one Acetate (**11b**).[33] A mixture of cholesterol (10 g.) and anhydrous sodium acetate (5 g.) in acetic acid (30 ml.) and acetic anhydride (16 ml.) was heated on a steam bath and stirred vigorously for 1 hr. The resulting solution was cooled to 20°, sodium dichromate dihydrate (7.3 g.) and benzene (15–20 ml., to effect homogeneity) were added, and the mixture was stirred at 40 $\pm$ 2° (critical) for 48 hr. The dark mixture was treated with water (100 ml.), and the aqueous layer was separated and washed twice with benzene. The combined benzene layers were washed to neutrality with 1% potassium carbonate, then dried (magnesium sulfate) and evaporated. Crystallization of the solid residue from ligroin (b.p. 60–80°) gave fine needles, m.p. 152–154° (5–6 g.), which was raised to m.p. 157–158° by one recrystallization from ethyl acetate (lit.[33c] 156–158°). Saponification of **11b** with potassium carbonate in methanol gave cholest-5-en-3β-ol-7-one (**11a**), ν 3500 and 1665 cm.$^{-1}$.

Cholest-5-ene-3β,7β-diol (**9a**) *and Esters* **9c** *and* **9b**. A solution of the acetate **11b** (6.0 g.) in dry ether (50 ml., distilled from lithium aluminum hydride) was added to a solution of lithium aluminum hydride (5.0 g.) in dry ether (200 ml.). After 2.5 hr. at reflux the excess of hydride was destroyed by addition of wet ether followed by water (1 ml.). After further addition of 3 N sodium hydroxide (1 ml.) the mixture was stirred for 5 min., then filtered, and the solid was washed with more ether. The ether was dried and evaporated to leave a diol mixture (4.8 g., $[α]D$ $-32°$), which was conventionally benzoylated. The 3β,7β-dibenzoate **9c** was isolated by fractional crystallization[33c] from ethyl acetate–methanol (suitable for larger scale work) or by chromatography on alumina (suitable for small scale) followed by crystallization of appropriate fractions; m.p. 173–174.5°, $[α]D$ $+95°$ (lit.[33b] m.p. 171.5–172°, $[α]D$ $+94°$).

The corresponding diol **9a** was obtained by treatment of dibenzoate **9c** (2.1 g.) with lithium aluminum hydride (2.1 g.) in dry ether (125 ml.). After 3 hr. of reflux followed by normal work-up, the derived product was purified by chromatography on alumina (50 g.), 0.75 g., m.p. 175–178°, $[α]D$ $+5°$ (lit.[34] m.p. 177–178.5°, $[α]D$ $+7.2°$).

Acetylation of **9a** gave the corresponding diacetate **9b**, m.p. 106° (acetone–methanol) (lit.[34] m.p. 106–107°).

Cholest-5-en-7β-ol (**9d**) *and Benzoate* **9e**. A small sample of **9e** (m.p. 104–105°) available from an earlier study[5b] was reduced to alcohol **9d** (m.p. 88–90°) as reported.[5b]

Cholest-5-ene-3β,7α-diol (**8c**) *and Esters* **8d** *and* **8e**. Rearrangement in chloroform[35] of 3β-hydroxy-5-hydroperoxy-5α-cholest-6-ene (**7b**), prepared from cholesterol (**6b**),[5b] followed by reduction with sodium iodide, gave **8c**, m.p. 158–160° (acetone–methanol), $[α]D$ $-90°$. The melting point is known to depend on the degree of solvation by methanol.[5b,34]

Acetylation gave **8d**, m.p. 122–123° on crystallization from acetone–methanol (lit.[36] m.p. 121–122°). Benzoylation gave **8e** with m.p. 154–155° when crystallized from ethyl acetate–methanol (lit.[34] m.p. 151–152°).

Cholest-5-en-7α-ol (**8b**). Cholest-5-ene[37] (1.0 g., m.p. 95–95.5°, $[α]D$ $-53°$) and hematoporphyrin (0.006 g.) in pyridine (70 ml.) was photooxygenated at 15° in a cold room for 25 hr. The product, after normal work-up,[5] gave a strong hydroperoxide test, had no carbonyl absorption in the infrared, showed only one spot on thin layer chromatography with silica gel, and is presumably **7a**. Without purification the product in chloroform (100 ml.) was allowed to stand in the dark at room temperature for 24 hr. Removal of the chloroform on a rotary evaporator left crude **8a** whose infrared spectrum showed little or no enone absorption. Reduction with sodium iodide in methanol–ether–acetic acid gave allylic alcohol **8b**, whose infrared spectrum showed that 20–30% of enone **11c** was formed during the reduction. The product (0.8 g.) in hexane was chromatographed on alumina (25 g.) and eluted with varying proportions of benzene–hexane. Early fractions gave cholest-5-en-7-one (**11c**), m.p. 131° after crystallization from ether–methanol. Mixture with authentic **11c** (m.p. 130–

(31) P. Bladon, J. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2402 (1951).

(32) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(33) (a) This procedure was described by Dr. F. McCapra, Thesis, University of London, 1959, to whom we are grateful for the experimental details; (b) A. Windaus, H. Lettre, and F. Schenck, *Ann.*, **520**, 98 (1935); (c) L. F. Fieser, M. Fieser, and R. N. Chakravasti, *J. Am. Chem. Soc.*, **71**, 2226 (1949).

(34) O. Wintersteiner and W. L. Ruigh, *ibid.*, **64**, 2453 (1942).

(35) G. O. Schenck and O. A. Neumuller, *Ann.*, **618**, 194 (1958).

(36) T. Barr, I. M. Heilbron, E. G. Parry, and F. S. Spring, *J. Chem. Soc.*, 1437 (1936).

(37) Prepared from cholesteryl chloride: S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), by reduction with sodium in liquid ammonia: R.E. Ireland, T. I. Wrigley, and W. G. Young, *ibid.*, **80**, 4604 (1958).

131°)[5b] showed no depression. Later fractions (0.6 g. total) were rich in **8b** and were rechromatographed on alumina (15 g.). Elution followed by crystallization from ethyl acetate–methanol (*ca.* 1:4) gave cholest-5-en-7α-ol, 0.21 g., m.p. 62–64°, [α]D −107° (lit.[5a] m.p. 65–65.5°, [α]D −112°).

Photosensitized Oxygenation of Cholest-4-en-3β-ol (**9b**). *A. Identification of Products.* The following results were typical. The allylic alcohol (0.36 g.) in pyridine (75 ml.) containing hematoporphyrin (0.005 g.) was irradiated (with four 15-w. fluorescent tubes)[38] and oxygenated for 72 hr. Normal work-up gave a clear oil (0.340 g.), which gave a very weak or negative test for hydroperoxide and which was dissolved in petroleum ether and chromatographed on alumina (18 g.). Elution with benzene–petroleum ether (1:3) gave crude 4α,5-epoxy-5α-cholestan-3-one (**2**, 0.180 g., 49%, m.p. 105–110°). After one crystallization from ethanol or from acetone–methanol, it had m.p. 123°, [α]D −39°, ν 1710 and 858 cm.⁻¹, gave a satisfactory C and H analysis, and was identical (mixture melting point, infrared) with an authentic sample.

Elution with benzene–petroleum ether (2:1–3:1) gave 0.045 g. (13%) of solid (m.p. 70–75°), which had m.p. 78.5–79° (ν 1680 cm.⁻¹) after crystallization from acetone–methanol. Its identity with authentic cholest-4-en-3-one (**3**) was established by mixture melting point determination and superposability of infrared spectra.

Elution with benzene–ether (5:1) yielded a white solid (0.093 g., 26%, m.p. 120–126°) whose infrared spectrum showed traces of carbonyl absorption but otherwise was the same as that of starting alcohol **1a**. One crystallization from ethanol gave material that corresponded in all respects to authentic **1a**.

B. Spectroscopic Assays of Products. Alcohol **1a** (0.50 g.) was photooxygenated as in part A but the reaction was allowed to continue for 108 hr. After work-up the crude product contained 16% cholest-4-en-3-one as determined by the ultraviolet intensity at 241 mμ, and *ca.* 75% of epoxy ketone **2** as determined by a quantitative infrared analysis. Chromatography on Fluorisil (15 g.) and elution with benzene–petroleum ether (1:30) followed by crystallization of appropriate fractions from acetone–methanol gave **2** with m.p. 121–122° (48% yield; corrected for aliquot removal, etc.).

C. Control Reactions. A solution of **1a** in pyridine was irradiated and oxygenated for 72 hr. in the absence of sensitizer. The product had an infrared spectrum essentially superposable on that of starting material and also the correct melting point (130–131°) after one crystallization from acetone–water. Several photooxygenations of **1a** (0.05 g.) in pyridine (40 ml.) were attempted with nonfluorescent dyes[11] such as methyl orange, orange-II, and Janus green (*ca.* 0.005 of the dye). In each case there was no evident reaction (*via* infrared) after 72 hr., and the starting alcohol was recovered. Cholest-4-en-3-one (**3**) and epoxy ketone **2** were individually irradiated and

oxygenated in the usual way in pyridine containing hematoporphyrin. Each compound was recovered with unchanged infrared absorption except for the appearance of a weak shoulder near 1725 cm.⁻¹ in the case of **3**, and slight broadening of the 1710-carbonyl band in the case of **2**.

Photosensitized Oxygenation of Cholest-4-en-3α-ol (**4a**). *A. Identification of Products.* The 3α-alcohol **4a** (0.10 g.) was photooxygenated for 72 hr. in pyridine (50 ml.) with hematoporphyrin (0.005 g.). The product was dissolved in petroleum ether and chromatographed on alumina (8 g.). Elution with benzene–petroleum ether (1:20) gave 4β,5-epoxy-5β-cholestan-3-one (**5**; 0.01 g., m.p. 116–118°) identified by its infrared spectrum. Elution with benzene–petroleum ether (3:2) gave 0.015 g. of semisolid identified as cholest-4-en-3-one (**3**) from its infrared spectrum. On crystallization from acetone–methanol it had m.p. 79–81°, undepressed on mixture with authentic **3**. Elution with 1:1 benzene–petroleum ether gave the starting alcohol **4a** (*ca.* 0.030 g.) identified by its infrared spectrum. More polar solvents gave material that contained hydroxyl and carbonyl bands in the infrared spectrum. The poor recovery of the β-epoxide **5** was subsequently found to be due to its lability on active alumina (see part B).

B. Spectroscopic Assay of Products. The 3α-alcohol **4a** (0.10 g.) was photooxygenated for 72 hr. as in part A. In typical runs the crude product (0.09 g.) contained 9–10% of enone **3** (*via* ultraviolet analysis) and 48–50% of epoxy ketone **5** (*via* quantitative infrared analysis). Chromatography on deactivated alumina (8 g.) and elution with benzene–petroleum ether (1:10) gave solid **5**. After crystallization from acetone–methanol it had m.p. 119–119.5°, [α]D +129° (0.03 g., 29%), and was identical (infrared and mixture melting point determination) with authentic material.

After a prolonged photooxygenation (144 hr.) the infrared spectrum of the product indicated about 60% of material with saturated carbonyl absorption. The ultraviolet spectrum had λ 260–263 mμ (ε 2300) (based on a molecular weight of 384) as well as intense end absorption from 240 to 215 mμ, and suggested that some breakdown of epoxy ketone had resulted from the extended reaction period.

C. Control Reaction. Alcohol **4a** was photooxygenated for 80 hr. in the absence of sensitizer. The infrared spectrum of the product was essentially the same as that of starting alcohol except for the appearance of weak absorption in the carbonyl region (1750–1680 cm.⁻¹). From the ultraviolet intensity at 241 mμ the product contained less than 4% enone.

Competitive Photooxygenation of Cholest-4-en-3α- and -3β-ols (**1a** *and* **4a**). *Run A.* The 1:1 molecular compound[5c] of **1a** and **4a** (1.0 g., m.p. 142°, [α]D +83°) was photooxygenated 85 hr. in pyridine (70 ml.) with hematoporphyrin (0.007 g.). The product contained *ca.* 70–75% epoxy ketones and *ca.* 16% cholest-4-en-3-one, as determined by quantitative infrared on the ν 1710 and 1680 cm.⁻¹ carbonyl bands, respectively. Ultraviolet analysis corroborated the enone assay (15%). Oxidation of an aliquot with manganese dioxide (70 hr.) raised the enone content to 29%, which indicated the presence of 14% allylic alcohols.

(38) When only two 15-w. tubes were used, very little conversion occurred as indicated by the infrared spectrum. Under identical conditions (72 hr.) we converted cholesterol (**6b**) in good yield (75%) to its derived hydroperoxide **7b**, m.p. 152° (vacuum).[5b] These irradiation conditions also effected very little change when alcohol **1a** was oxygenated in absolute ethanol containing methylene blue as sensitizer.

A portion (0.490 g.) of the original reaction product was chromatographed on deactivated alumina. Fractions containing only epoxy ketones (0.264 g.) were combined and had [α]D +17°, corresponding to a 2:1 ratio of the α-epoxy ketone 2 to the β-epoxy ketone 5. Control chromatographic experiments with the same deactivated alumina established that, whereas isomer 2 was virtually completely recovered, isomer 5 was partly decomposed (80% recovery), and led to a corrected ratio of 1.6:1. These results were duplicated on chromatography of a second portion (0.456 g.) of the original photooxygenation product.

Run B. This run was conducted as in run A except that the reaction time was 40 hr. The crude product had *ca.* 39% epoxy ketones and 7% enone. Chromatography gave a mixture of epoxy ketones whose optical rotation indicated an α-epoxide–β-epoxide ratio of 2.5:1 (corrected 2:1). A rough independent check was obtained from the mixture of unchanged allylic alcohols isolated from the chromatography. The optical rotation indicated 1a and 4a in a ratio of 1:1.5. Because of the smaller difference in the optical rotations of the allylic alcohols and their less efficient chromatographic separation from other products, the epoxy ketone assay is a more reliable measure of the extent of reaction from each alcohol.

Photooxygenation of 3β-Methoxycholest-4-ene (1d). A solution of 1d (0.060 g., m.p. 72–73°) and hematoporphyrin (0.005 g.) in pyridine (40 ml.) was photooxygenated for 80 hr. After normal work-up the oily product gave a slight positive hydroperoxide test. The infrared spectrum indicated the presence of a large proportion of starting material along with additional absorption in the regions 1730–1700, 1260, 1015, and 780 cm.$^{-1}$. Ultraviolet inspection showed strong end absorption with an inflection at 240 mμ corresponding to a maximum of 6% enone. The product was chromatographed on alumina, and elution with hexane gave solid starting material (62%), identified by its infrared spectrum. More polar eluents gave unidentified mixtures that were not identified, but showed carbonyl absorption around 1700 cm.$^{-1}$.

Photooxygenation of Cholest-5-ene-3β,7β-diol (9a). In typical runs, diol 9a (0.290 g.) and hematoporphyrin (0.006 g.) in pyridine (40 ml.) were oxygenated and irradiated for 80–85 hr. The product gave a faint, positive hydroperoxide test and contained 13–17% cholest-5-en-3β-ol-7-one (ultraviolet intensity at 235 mμ[14]). Chromatography on silica gel (9 g., British Drug House) and elution with benzene (alone or with small proportion of ether) gave 5,6α-epoxy-5α-cholestan-3β-ol-7-one (10a; 53–56%, m.p. *ca.* 160–164°). One crystallization from methanol at −15° gave m.p. 165–166.5°, [α]D +94° (lit.[13] for 10a, m.p. 167.5–168.5°, [α]D +88.3°). Acetylation and one crystallization from methanol gave the corresponding acetate 10b, m.p. 128–129° (lit.[13] m.p. 130–131.5°).

Continued elution with benzene–ether (6:1) gave oily semisolid (*ca.* 17% by weight) that appeared from its infrared spectrum to be cholest-5-en-3β-ol-7-one (11a) containing starting diol. Further elution gave unidentified oils containing hydroxyl (3500 cm.$^{-1}$) and saturated carbonyl (1710 cm.$^{-1}$) bands. In one run with diol 9a (96 hr.) rose bengal was used as the sensitizer. The crude product was not rectified but its

ultraviolet intensity at 235–238 mμ indicated 22% enone.

Photooxygenation of Cholest-5-en-7β-ol (9d). The 7β-ol 9d (0.088 g.) and hematoporphyrin (0.005 g.) in pyridine (40 ml.) were oxygenated and irradiated. Aliquots were worked up after 24, 48, and 72 hr. Each gave a negative hydroperoxide test, and infrared spectra indicated progressive diminution of bands due to starting material and increase of bands in the carbonyl region (1710 with a shoulder at 1680 cm.$^{-1}$). The ultraviolet intensity at 235 mμ corresponded to *ca.* 20% enone but this value is undoubtedly high because strong end absorption precluded the appearance of a distinct maximum (lit.[39] for cholest-5-en-7-one, λ 234 mμ (ε 13,800)).

Photooxygenation of Cholest-5-ene-3β,7α-diol (8c). This diol (0.50 g., m.p. 180–181°, solvated[5b]) in pyridine (60 ml.) containing hematoporphyrin (0.005 g.) was oxygenated and irradiated for 140 hr. The product gave a positive hydroperoxide test and showed bands at 1710 and 1680 cm.$^{-1}$, but otherwise the infrared spectrum was similar to that of the starting material. The ultraviolet spectrum indicated less than 13% enone. Chromatography on deactivated alumina (17 g.) and elution with benzene and benzene–ether (10:1) gave oily material (*ca.* 10% by weight) whose infrared spectrum showed, in addition to hydroxyl absorption, carbonyl bands whose complexity exceeded that of the material prior to chromatography and suggested some breakdown may have occurred on the column. Benzene–ether (5:2) gave solid (*ca.* 60%) whose infrared absorption was identical with that of starting material. Further elution gave unidentified mixtures. In one run, rose bengal was tried as sensitizer. After 144 hr. the product contained enone (20% maximum) and in the infrared spectrum the unsaturated carbonyl band (1670 cm.$^{-1}$) was more intense than the saturated one (1710 cm.$^{-1}$). Both bands were relatively weak, and the entire spectrum was generally similar to that of starting material.

Photooxygenation of Cholest-5-en-7α-ol (8b). The alcohol 8b (0.60 g.) and hematoporphyrin (0.010 g.) in pyridine (50 ml.) were irradiated and oxygenated for 140 hr. The product showed a weak but positive hydroperoxide test, complex infrared absorption in the carbonyl region (1720–1680 cm.$^{-1}$), and absorption at 233 mμ corresponding to a maximum of *ca.* 23% enone. A portion (0.450 g.) of the product was dissolved in hexane and chromatographed on Fluorisil (20 g.).[40] Benzene–hexane (2:5) eluted an oily solid (37%) identified by infrared as starting alcohol 8b. Further elution with solvents of graded polarity gave some fractions clearly identified as cholest-5-en-7-one followed by unidentified mixtures that contained saturated and unsaturated carbonyl as well as hydroxyl absorption in the infrared. In one photooxygenation of 8b methyl orange (a nonsensitizing dye) was used in place of hematoporphyrin. After 140 hr. the infrared spectrum of the product was nearly identical with that

(39) K. Tsuda and R. Hayatsu, *J. Am. Chem. Soc.*, 77, 665 (1953).
(40) Despite the presence of hydroperoxidic material, we did not treat the product with sodium iodide to avoid possible destruction of any 5β,6β-epoxy ketone that might be present. In separate experiments we learned that the 4β,5β-epoxy ketone 5 decomposes under the acidic conditions of the iodide reduction (iodine liberated within several minutes).

of starting material except for the presence of weak carbonyl absorption at 1700 cm.$^{-1}$.

Attempted Photooxygenation of Esters. The following ring-A and ring-B esters were photooxygenated in the usual way in pyridine with hematoporphyrin for periods that ranged from 72 to 144 hr.: **1b, 1c, 4b, 8d, 8e, 9b, 9c,** and **9e**. In each case work-up gave material whose infrared spectrum was the same as that of the starting ester. Other dyes (methylene blue, eosin-Y, erythrosin-B) were tried with esters **1b** and **1c** with the same results.

Effect of Sensitizer on Product Ratio from Cholest-4-en-3β-ol (**1a**). The alcohol (0.05 g./40 ml. of pyridine) was photooxygenated for 80 hr. under a standardized set of conditions with various sensitizers. Initially 0.007 g. of the dye was used but more was added as needed during the reaction to compensate for bleaching. After normal work-up the enone content was determined directly from the absorption at 241 mμ. A portion of the product was oxidized with manganese dioxide to assay for remaining alcohol **1a**, and the epoxy ketone content was calculated by difference. In some cases the percentage of epoxy ketone was checked by the quantitative infrared technique. The correlation with the ultraviolet method was excellent when the enone proportion was small. An Aminco-Bowman spectrophotofluorometer (American Instrument Co.) was used to measure the fluorescence emission maxima of the dyes. Table I in the text summarizes the results.

Organic Peroxides. IV. Kinetics and Products of Decompositions of Cyclohexaneformyl and Isobutyryl Peroxides. BDPA as a Free-Radical Scavenger[1]

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The kinetics and free-radical efficiencies of the thermal decompositions of cyclohexaneformyl peroxide (*I*) and isobutyryl peroxide (*II*) in carbon tetrachloride were determined with excess α,γ-bis(diphenylene)-β-phenylallyl (*BDPA*) at temperatures between 30 and 85° in experiments in which initial BDPA concentrations were near 5 × 10^{-5} M. First-order rate constants obtained by this method differ by less than 10% from rate constants obtained by infrared and iodometric analysis in runs conducted at peroxide concentrations near 0.1 M. The rate constants and efficiencies obtained by the excess BDPA method are independent of the ratio of initial concentrations of BDPA to peroxide (Z_0/P_0). Product studies were performed (by g.l.c. and infrared analysis) on mixtures obtained from the decompositions of I and II in carbon tetrachloride, and in the same solvent containing excess BDPA. Evidence is presented which indicates that inversion compounds (*RCOOCOOR*)[3] are formed in the decompositions of both peroxides. While BDPA does not change the kinetics of decomposition of either peroxide significantly, the yields of some of the volatile products are changed drastically in its presence. Thus, alkyl chloride yields are reduced significantly in the presence of BDPA while the yields of carboxylic acid are increased substantially. The interpretation given to the latter effect is that acyloxy radicals are transformed into carboxylic acids by an unknown process by BDPA. Rate constants for decom-

positions of II in several other polar and nonpolar solvents at 40° were determined by iodometric assay. The solvent effects on the decomposition rate are similar to those reported recently by Pincock for the second-order reaction between pyridine and t-butyl peroxyformate.[4] Thus in nonpolar solvents, the rates increase with increasing solvent polarizabilities, while in polar solvents, the rates increase with increasing dielectric constants. In some of the nonpolar solvents in which the intermediate inversion compound is relatively stable, the yield of inversion compound increases significantly with increasing rate. These results suggest that the homolysis and the rearrangement of peroxide to inversion compound are two distinct modes of decomposition. Kinetics of decomposition of II in isooctane were also measured at various pressures between one and 3000 kg./cm.[2]. The negative activation volume thus determined is another indication that the peroxide undergoes rearrangement.

Introduction

In a recent paper, two of us presented experimental evidence which showed that stable radicals (galvinoxyl, BDPA, and DPPH) could be used to determine simultaneously the rates and efficiencies in the decompositions of cyclohexanecarbonyl peroxide in benzene.[5] The present paper is an extension of that work, namely, a report of similar experiments performed upon cyclohexaneformyl peroxide (I) and isobutyryl peroxide (II) in carbon tetrachloride.

(3) F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).
(4) R. E. Pincock, *ibid.*, **86**, 1820 (1964).
(5) Paper III in this series: R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).