Work on these and related compounds is continuing. We wish to thank British Petroleum for a Fellowship (to P.M.M.) and D.S.I.R. for a studentship (to S.S.C.).

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PHOTOSENSITIZED OXYGENATION OF MONO-OLEFINS

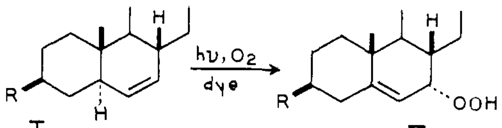
Sir:

Oxidations of olefins with molecular oxygen conducted photochemically in the presence of a sensitizing dye are proving most useful in synthetic work.[1] With mono-olefins Schenck, *et al.*, have established that the initial products are hydroperoxides and that the double bond always undergoes an allylic shift during the process.[1] We have studied the geometric requirements of photosensitized oxidations and have found that the reaction (a) is stereospecific, (b) is markedly subject to steric hindrance, (c) may have specific conformational (*i.e.*, stereoelectronic) requirements.

Photochemical oxygenation of various Δ^6-cholestenes (Ia,b,c,) in pyridine in the presence of hematoporphyrin gave the corresponding Δ^5-cholestene-7α-hydroperoxides (II), but no isolable amounts of the 7β-epimers.[2] For characterization the hydroperoxides were reduced without purification to the known allylic alcohols, which were identified as such and by conversion to known benzoates. As a typical result: Ia gave Δ^5-cholestene-3β,7α-diol (*ca.* 60% isolated), some $\Delta^{3,5}$-cholestadien-7-one (*ca.* 5–10%), and some starting material (*ca.* 5–10%). In one case (IIb) the hydroperoxide was isolated separately and purified. Similar oxygenation of cholesterol-7α-*d* gave us 3β-hydroxy-5α-hydroperoxy-Δ^6-cholestene[1] (IIIa) that retained only 8.5% of the original deuterium, whereas cholesterol-7β-*d* gave IIIa that retained 95% of the original deuterium.[3] We conclude that in hydroperoxide formation the new C–O bond bears a *cis* relationship to the C–H bond that suffers cleavage.

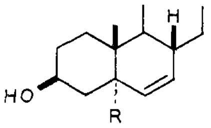
The effect of steric blocking is exemplified with 3β,5α-dihydroxy-Δ^6-cholestene (IIIb), which we find is largely unchanged even on prolonged photosensitized oxygenation.

The operation of a conformational factor is suggested by studies with Δ^6-coprosten-3-one (VI) and Δ^6-coprostene (VII), where the β-hydrogen at C-5 is *quasi*-equatorial on the (non-flexible) B ring. Peracid epoxidation of $\Delta^{4,6}$-cholestadien-3-one gave Δ^4-cholesten-3-one-6,7-epoxide (IV), hydrogenated at −27° (Pd/C) to coprostan-3-one-6,7-epoxide (V). Treatment with HBr, then acetylation and the action of zinc gave VI, which provided VII on Wolff–Kishner reduction. For characterization VI and VII were hydrogenated to coprostan-3-one and to coprostane, respectively. Both VI and VII proved inert to photosensitized oxygenation even on prolonged treatment.

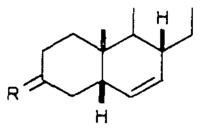


I II

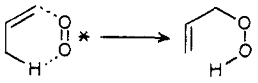
(a) R=OH; (b) R=OAc; (c) R=H



III (a) R=OOH
(b) R=OH



VI R=O
VII R=H₂



Our findings suggest a cyclic mechanism (concerted or not) for the olefin–oxygen combination, after the system has been suitably energized. The reaction is of special interest as a possible pathway for biological oxidations, particularly in plants, and may even represent a pathway for non-photochemical processes where the reactants can be activated enzymatically.

Constants[4] for the new compounds mentioned are: IIb m.p. 142–142.5°; $\alpha -137°$; λ(chf) 3540, 3300 cm.$^{-1}$. IV m.p. 138.5–139°; $\alpha -59°$ λ 1684, 1621, 870 cm.$^{-1}$; λ (EtOH) 241 mμ (ϵ 12,010). V, m.p. 122–123°; $\alpha -46°$; λ 1724, 892 cm.$^{-1}$. VI, m.p. 109–110°; $\alpha -52°$; λ 1727; 1656 cm.$^{-1}$. VII, m.p. 44–45°; $\alpha -7°$; λ 1647 cm.$^{-1}$.

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[1] See G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957), for a review and leading references.

[2] Mother liquors also were thoroughly investigated.

[3] The deuterated cholesterols were kindly provided by Dr. E. J. Corey.

[4] Optical rotations in chloroform; infrared spectra in CS_2. All compounds gave satisfactory C and H analyses.

[5] This work was supported by the National Science Foundation and by the Alfred P. Sloan Foundation.

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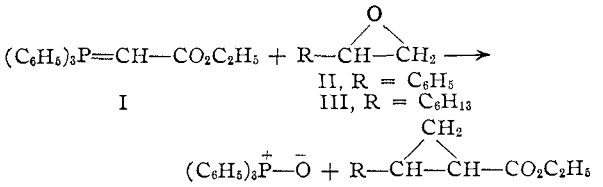
FORMATION OF CYCLOPROPANES FROM PHOSPHORANES AND EPOXIDES[1]

Sir:

The phosphorane (I) reacts with styrene oxide (II) at 190–200° to yield triphenylphosphine oxide (90%) and ethyl *trans*-2-phenylcyclopropane carboxylate (IV) (21%), b.p. 100–103° at 0.5 mm. (reported[2] 103–105° at 0.5–0.7 mm.). The ultraviolet absorption spectrum of IV agreed with that in the literature.[3] Alkaline hydrolysis afforded the *trans*-acid, m.p. 90–91° (reported[3] 92–93°). The



$$(C_6H_5)_3P{=}CH{-}CO_2C_2H_5 + R{-}\overset{\displaystyle O}{CH{-}CH_2} \longrightarrow$$

I   II, R = C_6H_5 III, R = C_6H_{13}

$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{O} + R{-}\overset{\displaystyle CH_2}{CH{-}CH}{-}CO_2C_2H_5$$

IV, R = C_6H_5
V, R = C_6H_{13}

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[1] Supported by the National Science Foundation.

[2] A. Burger and W. L. Yost, THIS JOURNAL, **70**, 2198 (1948).

[3] E. N. Trachtenberg and G. Odian, *ibid.*, **80**, 4015 (1958).