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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RECEIVED OCTOBER 21, 1959

PHOTOSENSITIZED OXYGENATION OF MONO-OLEFINS

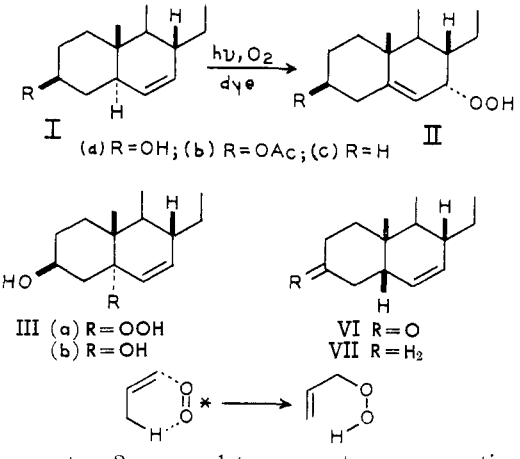
Sir:

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.

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°; α −137°; λ(chf) 3540, 3300 cm.$^{-1}$. IV m.p. 138.5–139°; α −59° λ 1684, 1621, 870 cm.$^{-1}$; λ (EtOH) 241 mμ (ϵ 12,010). V, m.p. 122–123°; α −46°; λ 1724, 892 cm.$^{-1}$. VI, m.p. 109–110°; α −52°; λ 1727; 1656 cm.$^{-1}$. VII, m.p. 44–45°; α −7°; λ 1647 cm.$^{-1}$.

(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.

(6) Alfred P. Sloan Foundation Fellow.

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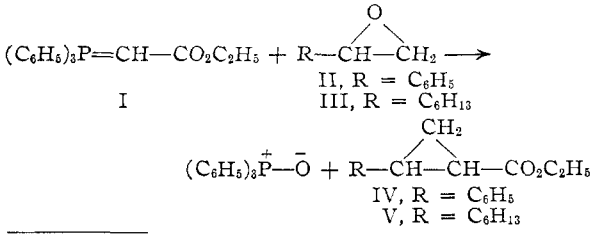
RECEIVED OCTOBER 7, 1959

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



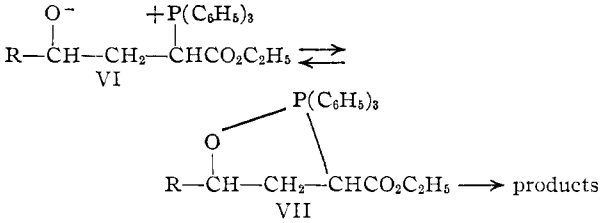
(1) Supported by the National Science Foundation.

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

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

acid was converted to the amide, m.p. 190.5–192° (reported[4] 187–188°). I also reacted with III at 210–220° under nitrogen to give triphenylphosphine oxide (97% of crude material) and 26% of the ester (V), b.p. 70–75° at 0.4 mm. (reported[5] 75–80° at 0.5 mm). The ester was converted to the amide, m.p. 109–110°. (reported[5] 107–107.5°). Under similar conditions, 180° for five hours, cyclohexene oxide and I gave only recovered I and cyclohexene oxide. No cyclopropane ester could be detected.

Although no definite information is available on the mechanism of this reaction, it seems reasonable to suggest that the initial step involves nucleophilic displacement by the phosphorane on the epoxide to give an intermediate zwitterion (VI) which is in equilibrium with the pentacovalent phosphorus compound (VII).



Several paths can be envisioned for the decomposition of VII. If VI is an intermediate, then the possibility exists of preparing cyclopropanes from compounds similar to VI. These compounds could be prepared by a variety of methods. This approach is now being investigated, as are the reactions of other phosphoranes with a variety of epoxides.

(4) E. Buchner and J. Geronimus, *Ber.*, **36**, 3784 (1903).

(5) K. Hofmann, O. Jucker, W. R. Miller, A. C. Young, Jr., and F. Tausig, THIS JOURNAL, **76**, 1799 (1954).

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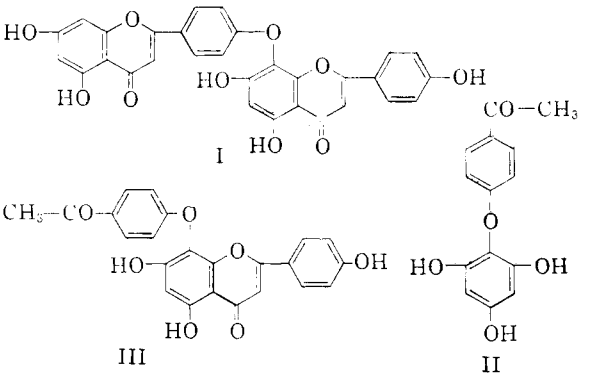
RECEIVED OCTOBER 26, 1959

THE STRUCTURE OF HINOKIFLAVONE, A NEW TYPE BISFLAVONOID

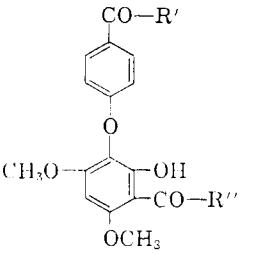
Sir:

Hinokiflavone, $C_{30}H_{18}O_{10}$, a bisflavonoid having a skeleton different from other bisflavonoids has been isolated.[1] The structures of ginkgetin and sciadopitysin recently were established as diflavonyls joined by a carbon–carbon linkage.[2,3] We now report that hinokiflavone is a diflavonyl ether represented by formula (I).

When treated with potassium hydroxide, hinokiflavone produces *p*-hydroxyacetophenone, a phenolic ketone (II), m.p. 201° (found: C, 64.83; H, 4.75. Calcd. for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65) and a ketoflavone $C_{23}H_{16}O_7$, m.p. 258° (III), which gave *p*-hydroxyacetophenone and II on further degradation. II has an acetyl and three hydroxyl groups. The trimethyl ether of II was oxidized to a carboxylic acid $C_{16}H_{16}O_6$, m.p. 192°, which was decarboxylated to 2,4,6-trimethoxydiphenyl ether m.p. 94.5°, which was newly synthesized from potassium phenoxide and bromophloroglucinol trimethyl ether. The infrared absorption spectra of II and its derivatives suggest *p*-substitution. This information, taken with that summarized below, allows the assignment of structures II and III.



Hinokiflavone has five hydroxyl groups. Its pentamethyl ether, treated with potassium hydroxide, gave anisic acid, *p*-methoxyacetophenone, 2,4-dimethoxy-6-hydroxyacetophenone, a phenolic acid (IV), m.p. 198° (found: C, 61.71; H, 4.75; OCH_3, 18.33. Calcd. for $C_{15}H_{16}O_5(OCH_3)_2$: C, 61.44; H, 4.85; OCH_3, 18.67) and a phenolic diketone (V), m.p. 147° (found: C, 65.28; H, 5.46; OCH_3, 18.30. Calcd. for $C_{16}H_{12}O_4(OCH_3)_2$: C, 65.44; H, 5.49; OCH_3, 18.77). The methyl ethers of IV and V were oxidized to the same



(IV) R′ = OH, R″ = CH_3
(V) R′ = R″ = CH_3
(VI) R′ = R″ = OH

dicarboxylic acid $C_{16}H_{14}O_8$ (VI methyl ether), m.p. *ca.* 110° (dec.), which was decarboxylated to 2,4,6-trimethoxydiphenyl ether. IV and V are positive to the Gibbs reagent and the infrared absorption spectra of IV and V also suggest *p*-substitution.

By boiling in methanolic barium hydroxide solution,[4] hinokiflavone pentamethyl ether produced 2,4-dimethoxy-6-hydroxyacetophenone (77% yield), IV (76% yield) and anisic acid (86% yield), and it can be deduced easily that hinokiflavone pentamethyl ether is constructed by condensation of these three fragments with loss of four molecules of water. Therefore, the structure of hinokiflavone must be represented by formula I. Now, it can be presumed that apigenin is a precursor in the biogenesis of hinokiflavone as well as in that of the other bisflavonoids such as ginkgetin and sciadopitysin.

Grateful acknowledgment is offered to Dr. T. Kariyone for his interest and encouragement.

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(1) T. Kariyone and T. Sawada, *Yakugaku Zasshi*, **78**, 1020, 1023 (1958); *Chem. Abstr.*, **53**, 3203, 3204 (1959).

(2) N. Kawano, *Chemistry & Industry*, 368, 852 (1959).

(3) W. Baker, A. C. M. Finch, W. D. Ollis and K. W. Robinson, *Proc. Chem. Soc.*, 91 (1959).

(4) T. Kariyone, N. Kawano and H. Miura, *Yakugaku Zasshi*, **79**, 1182 (1959).