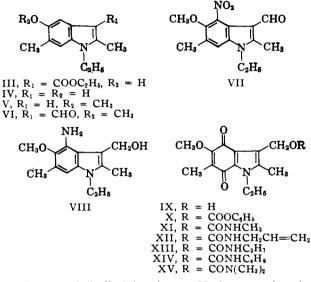
dium-on-charcoal catalyst resulted in the uptake of four molar equivalents of gas. Without isolation the presumed 4-amino-3-indolylmethanol (VIII) was treated with potassium nitrosodisulfonate to furnish the desired indoloquinonecarbinol IX [m.p. 85.5-86.5°, λ_{max} 231, 287, 350, and 460 m μ (ϵ 17,100, 13,900, 3160, and 1300)].⁹

The carbinol IX was converted into the carbamate II [m.p. 202-204°, λ_{max} 231, 286, 345, and 455 m μ (ϵ 18,400, 13,800, 3520, and 1290)] by ammonolysis of the derived phenylcarbonate X [m.p. 115-117°, λ_{max} 231, 285, 345, and 455 m μ (ϵ 17,700, 13,800, 3260, and 1150)].



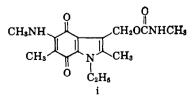
The 1,2-dialkylindoloquinone II has an *in vitro* antibacterial spectrum and *in vivo* activity comparable to that of 7-methoxymitosene (I).¹ It is approximately one-third as active as tetracycline when administered orally to mice infected with *Staphylococcus aureus* var. Smith. However, indoloquinone II is ineffective *in vivo* against *Streptococcus pyrogenes* C-203 and a tetracycline-resistant *Staphylococcus* species, despite its high activity *in vitro* against these organisms.

A variety of analogs of II has been prepared in this laboratory. For example, treatment of carbinol IX with the appropriate isocyanate gave XI-XIV (methyl¹⁰: m.p. 170-171°; allyl: m.p. '121-122°; propyl: m.p. 129-130°; butyl: m.p. 116-117°).¹¹ Reaction of phenylcarbonate X with dimethylamine gave XV (m.p. 119-120°).¹¹

More extensive reports on our efforts in this area will be published at a later date.

(9) The conversion of certain di- and trisubstituted anifines into the corresponding *p*-benzoquinones by potassium nitrosodisulfonate has been described [H. Teuber and M. Hassefback, *Ber.*, **92**, 674 (1959)].

(10) Treatment of the phenyl carbonate X with methylamine gave i [m.p. 213-215°; λ_{max} 249, 313, 342 (shoulder), and 550 m μ (ϵ 17,200, 10,800, 5750, and 1600)].



(11) The ultraviolet spectra of these compounds were essentially the same as that of the carbamate 11.

Acknowledgment.—The *in vivo* assays were carried out by Mr. G. S. Redin and his associates, and the *in vitro* antibacterial spectrum was determined by Mr. A. C. Dornbush and his staff. Microanalyses were furnished by Mr. L. Brancone and his staff, and spectral data were supplied by Mr. W. Fulmor and his associates. We are grateful to these groups for their kind cooperation.

ORGANIC CHEMICAL RESEARCH SECTION GEORGE R. ALLEN, JR-Lederle Laboratories Division John F. Poletto American Cyanamid Company Martin J. Weiss Pearl River, New York

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Olefin Oxidations with Excited Singlet Molecular Oxygen¹

Sir:

This communication describes a novel and useful synthetic method for the oxidation of olefins and dienoid compounds to give products identical with those of the well-studied dye-photosensitized autoxidations.² The active species appears to be molecular oxygen in an excited singlet state, formed *in situ* by the reaction of sodium hypochlorite and hydrogen peroxide.³⁻⁷

The significance of this reaction for the mechanism of the photosensitized autoxidations is discussed in the accompanying communication.⁸

The oxidations proceed exceptionally smoothly, and in preparatively useful yields. Examples of the conversions so far carried out are given below. As no attempt at optimization of conditions has been made, the yields given are minimal.

In methanol, 2,5-dimethylfuran (I) is converted to 2,5-dimethyl-2-hydroperoxy-5-methoxydihydrofuran (II) in 84% yield (based on sodium hypochlorite used; in this case, dimethylfuran was in excess). The same product is produced in the photosensitized autoxidation of I in 74% yield, presumably by reaction of methanol with the hypothetical ozonide-like peroxide III.⁹

(1) Supported by N.S.F. Grant G-25086.

(2) G. O. Schenck, Angew. Chem., 69, 579 (1957), and references therein cited; G. O. Schenck and E. Koch, Z. Elektrochem., 64, 170 (1960); W. Bergmann and M. J. McLean, Chem. Rev., 28, 367 (1941).

(3) The chemiluminescence⁴ of this reaction was originally assigned to emission from the ${}^{1}\Sigma_{g}{}^{+}$ state of molecular oxygen⁵; more recent studies, however, have shown that the visible luminescence is more probably derived mainly from a dimer of the ${}^{1}\Delta_{g}$ state^{4,7}; infrared emission from the monomeric ${}^{1}\Delta_{g}$ state is also observed.⁷

(4) H. H. Seliger, Anal. Biochem., 1, 60 (1960); L. Mullet, Compl. rend.,
 185, 352 (1927); G. Gattow and A. Schneider, Naturwiss., 41, 116 (1954).

- (5) A. U. Khan and M. Kasha, J. Chem. Phys., **39**, 2105 (1963).
- (6) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *ibid.*, **40**, 1769 (1964)
 (7) R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc.*, **117** (1964).
- (1) R. J. Blowne and E. A. Oglyzlo, 1760, Chem. Soc., 11 (1904)
 (8) C. S. Foote and S. Wexler, J. Am. Chem. Soc., 86, 3880 (1964)

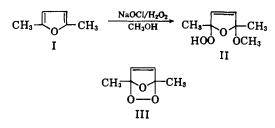
(9) Only polymeric peroxides had been previously isolated from the photosensitized autoxidation.¹⁰ The structure of 1f (m.p. 75-76°) follows from its chemical and physical properties: Anal. Found: C, 52.42, H.7.45: OCH₃, 18.83; mol. wt., 177.3 (osmometer); infrared (CC4, 0.005 M) 3512 cm.⁻¹ (OOH); n.m.r. (CDCla) τ 0.78, 3.98, 6.64, 8.42, and 8.47 (all sharp singlets, relative areas 1:2:3:3:3, assigned to OOH, oleinic H, OCH₃, C-CH₄, and C-CH₅, respectively). The *p*-nitrobenzoate (m.p. 91-92°) has an infrared band (CHCl₃) at 1775 cm.⁻⁷ (poester). Il gives the bis-2,4-dinitrophenylhydrazone of diacetylethylene, m.p. 286° dec. m.m.p with a sample (m.p. 284° dec.) prepared by the method of 1.evisalles¹¹ (reported m.p. 291-292°) was 284° dec. Schenck has also observed product 11.¹² The product formed from photosensitized autoxidation of metho-furan in methanol has an analogous structure (not the one originally assigned¹¹).¹²

(10) G. O. Schenck, Ann., 584, 165 (1953).

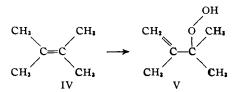
(11) J. Levisalles. Bull. soc. chim. France, 997 (1957)

(12) G. O. Schenck, private communication.

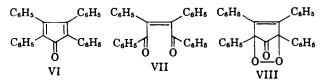
(13) G. O. Schenck and C. S. Foote, Angew. Chem., 70, 505 (1958).



The reaction of 2,3-dimethylbutene-2 (IV) gives 2,3dimethyl-3-hydroperoxybutene-1 (V), 63%, b.p. 54° (9 mm.), $n^{24.5}$ D 1.4408; the infrared and n.m.r. spectra are identical with those of the product of the photosensitized autoxidation (formed in 54% yield; lit.¹⁴: 82%, b.p. 55° (12 mm.), n^{20} D 1.4428).



Tetraphenylcyclopentadienone. (VI) gives *cis*-dibenzoylstilbene (VII, 50%, m.p. 215.9–216.3°, infrared spectrum identical with that reported¹⁶). The photosensitized autoxidation gave VII in 65%yield.¹⁶ The peroxide VIII is presumably intermediate.



Cyclohexadiene-1,3 (IX) gives 5,6-dioxabicyclo-[2.2.2]octene-2 ("norascaridol," X, 20%), with infrared and n.m.r. spectra identical with those of a sample prepared by the photosensitized autoxidation (35%yield; lit.¹⁷ 21%).



Preliminary indications are that rubrene and other aromatic hydrocarbons also form peroxides analogous to those formed photochemically.¹⁸

Sample Procedure.—To a solution of 5.05 g. (60 mmoles) of 2,3-dimethylbutene-2 (IV) in 300 ml. of methanol was added 19.2 ml. of 30% H₂O₂ [180 mmoles). The solution was stirred at 10° , and 145.5 ml. of 1.03 *M* NaOCl solution (150 mequiv.) was added in the course of 90 min. The solution was diluted with water and extracted with ether. Ether was distilled from the dried extracts through a column to prevent loss of the volatile product. The residue was

(15) D. R. Berger and R. K. Summerbell, J. Org. Chem., 24, 1881 (1959).
(16) C. F. Wilcox, Jr., and M. P. Stevens, J. Am. Chem. Soc., 84, 1258 (1962); G. O. Schenck, Z. Elektrochem., 56, 855 (1952).

(17) G. O. Schenck and W. Willmund, reported by R. Criegee in Houben-Wey, "Methoden der Organischen Chemie," Vol. VIII, 4th Ed., E. Mülfer, Ed., Georg Thieme Verlag, Stuttgart, 1952, p. 16. The yields referred to above are of distilled but unrecrystallized material.

(18) Corey has recently found that externally generated singlet O: is capable of oxidizing aromatic hydrocarbons: E. J. Corey and W. C. Taylor, J. Am. Chem. Soc., **86**, 3881 (1964).

distilled, giving 4.39 g. (37.8 mmoles, 63%) of V, with the physical constants described above.

The new reaction parallels the photosensitized autoxidations in every case so far studied; it appears to be a general and practical synthetic method for oxidization of olefins which give high quantum yields in the photosensitized autoxidation (for example, s-cis dienes, furans, and tri- and tetrasubstituted olefins). The products (when they are peroxides) are, of course, readily reduced to the corresponding alcohols. Where the parallel photosensitized autoxidation goes in low quantum yield, it is likely that the peroxide-hypochlorite reaction will be less useful, because of the large quantities of reagents which would be required: this suggestion is supported by preliminary studies. The quantities of oxidant are best adjusted so that nearly 1 mole of oxygen is actually taken up; the oxygen which evolves from the solution (small amounts with good acceptors such as dimethylfuran) is collected in a gas buret so that this loss can be compensated by further addition of reagents. The use of excess H_2O_2 appears to be of value in preventing further oxidation of the products.

The reaction is being extended to other acceptors and to other systems potentially capable of yielding singlet oxygen.

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Singlet Oxygen. A Probable Intermediate in Photosensitized Autoxidations¹

Sir:

Several mechanisms have been suggested for the dyephotosensitized autoxidations of dienes and olefins, studied in detail by Schenck,² and the analogous photooxidations of aromatic hydrocarbons, studied by many workers, particularly by Bowen.³ Of these mechanisms, all but two have been ruled out by careful kinetic studies and by other criteria such as product or energy considerations. The two mechanisms which are consistent with the kinetics differ only in steps 3 and 4 (see below). In mechanism a (originally proposed by

Sens
$$\xrightarrow{h_{\nu}}$$
 'Sens (1)

ⁱSens \longrightarrow ³Sens (2)

 $^{3}\text{Sens} + ^{3}\text{O}_{2} \longrightarrow \text{Sens-O-O}$ (3a)

$$Sens-O-O \cdot + A \longrightarrow AO_2 + Sens$$
 (4a)

$$\operatorname{Sens} + {}^{3}\operatorname{O}_{2} \longrightarrow \operatorname{Sens} + {}^{1}\operatorname{O}_{2}$$
(3b)

$$^{1}O_{2} + A \longrightarrow AO_{2}$$
 (4b)

Schönberg⁴), the postulated reactive intermediate (an adduct $(\cdot \text{SensOO} \cdot)$ of sensitizer (Sens) and oxygen) reacts with acceptor (A) to form the product peroxide (AO₂). Mechanism b was originally proposed by

⁽¹⁴⁾ G. O. Schenck and K. Schulte-Elte, Ann., 618, 185 (1958).

⁽¹⁾ Supported by N.S.F. Grant G-25086; we are pleased to acknowledge heipful discussions with Professor K. D. Bayes,

^{(2) (}a) G. O. Schenck, Angew. Chem., 69, 579 (1957); (b) Naturwiss.,
35, 28 (1948); (c) ibid. 40, 205, 229 (1953); (d) G. O. Schenck and E. Koch,
Z. Elektrochem., 64, 170 (1960)

⁽³⁾ E. J. Bowen in "Advances in Photochemistry," Vol. 1, W. A. Noyes, G. S. Hammond, and J. N. Pitts. In, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 23, and references therein cited.

⁽⁴⁾ A. Schönnerg, Ann, 518, 299 (1935).