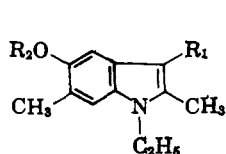
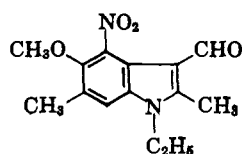


dium-on-charcoal catalyst resulted in the uptake of four molar equivalents of gas. Without isolation the presumed 4-amino-3-indolymethanol (VIII) was treated with potassium nitrosodisulfonate to furnish the desired indoloquinonecarbinol IX [m.p. 85.5–86.5°, λ_{\max} 231, 287, 350, and 460 m μ (ϵ 17,100,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

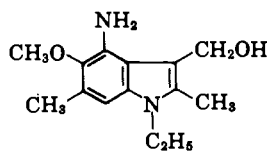
The carbinol IX was converted into the carbamate II [m.p. 202–204°, λ_{\max} 231, 286, 345, and 455 m μ (ϵ 18,400, 13,800, 3520, and 1290)] by ammonolysis of the derived phenylcarbonate X [m.p. 115–117°, λ_{\max} 231, 285, 345, and 455 m μ (ϵ 17,700, 13,800, 3260, and 1150)].



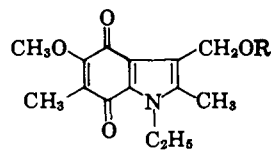
III, R₁ = COOC₂H₅, R₂ = H
IV, R₁ = R₂ = H
V, R₁ = H, R₂ = CH₃
VI, R₁ = CHO, R₂ = CH₃



VII



VIII



IX, R = H
X, R = COOC₂H₅
XI, R = CONHCH₃
XII, R = CONHCH₂CH=CH₂
XIII, R = CONHC₃H₇
XIV, R = CONHC₄H₉
XV, R = CON(CH₃)₂

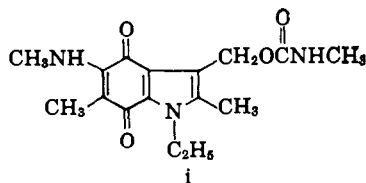
The 1,2-dialkylindoloquinone II has an *in vitro* antibacterial spectrum and *in vivo* activity comparable to that of 7-methoxymitosene (I).¹ It is approximately one-third as active as tetracycline when administered orally to mice infected with *Staphylococcus aureus* var. Smith. However, indoloquinone 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 anilines into the corresponding *p*-benzoquinones by potassium nitrosodisulfonate has been described [H. Teuber and M. Hasseback, *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.

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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 ¹Σ_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 ¹Δ_g state^{6,7}; infrared emission from the monomeric ¹Δ_g state is also observed.⁷

(4) H. H. Seliger, *Anal. Biochem.*, **1**, 60 (1960); I. Mallet, *Compt. 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).

(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 II (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 (CCl₄, 0.005 M): 3512 cm⁻¹ (OOH); n.m.r. (CDCl₃) 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, olefinic H, OCH₃, C-CH₃, and C-CH₃, respectively). The *p*-nitrobenzoate (m.p. 91–92°) has an infrared band (CHCl₃) at 1775 cm⁻¹ (ester). II gives the bis-2,4-dinitrophenylhydrazone of diacetylene. m.p. 286° dec. m m p with a sample (m.p. 284° dec.) prepared by the method of Levisalles¹¹ (reported m.p. 291–292°) was 284° dec. Schenck has also observed product II.¹² The product formed from photosensitized autoxidation of menthofuran in methanol has an analogous structure (not the one originally assigned¹³).

(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).

