Roush,¹⁰ and those of the bicyclic diamine 5 studied by Alder, Gill, and Goode.¹² The ions of both 4 and 5 differ from those of 2 in that the former have a σ bonding interaction between the heteroatoms, while 2^+ and 2^{2+} are π ions.¹³



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Sensitized Photooxygenation of 1-Methyl-3-vinylindoles

Sir:

The oxidations of indoles with molecular oxygen, including singlet oxygen $({}^{1}O_{2})$, have been extensively studied.¹ Most of them involve C_2 - C_3 ring cleavage or the formation of 3-hydroperoxidic intermediates. In the sensitized photooxygenation of vinyl-substituted aromatics, ${}^{1}O_{2}$ attacks on the side chain to give carbonyl compounds (1,2-cycloaddition) and/or allylic hydroperoxides ("ene" reaction),² or adds to a diene system comprised of the side chain and an aromatic double bond (1,4-cycloaddition).³ In this communication, we wish to report on the results of the reaction of 1-methyl-3-vinylindoles with $^{1}O_{2}$. The characteristic features of our results are as follows: (a) ${}^{1}O_{2}$ can easily add to the vinylindoles with retention of stereochemistry to give dioxacarbazole-type 1,4-endoperoxides in aprotic solvents, while the photooxygenation in protic solvents yields 3-formyl-1-methylindole; (b) unusual fragmentation of the dioxacarbazole-type 1,4-endoperoxides occurs to afford two aldehydes through the supposed dioxetane intermediate. These observations suggest that the 1,4-endoperoxide might be an initial intermediate prior to the intermediary dioxetane in the oxidative double bond cleavage of the vinylindoles with ${}^{1}O_{2}$ in protic solvents.

When the sensitized photooxygenation⁴ of 1-methyltrans-3-styrylindole $(1a)^5$ was carried out in *n*-hexane containing 10% dichloromethane, a 1,4-endoperoxide 2a has precipitated as silky crystals in 96% yield, mp 99.0-100.5 °C. The NMR spectrum⁶ of **2a** displayed a singlet at δ 2.86 (3 H, N-CH₃), and four multiplets centered at 5.56 (1 H, Hd), 5.86 (1H, Ha or Hb) 5.92 (1 H, Hb, or Ha), and 7.0 (9 H, aromatic) ppm with their coupling constants: $J_{ab} = J_{ad} = J_{bd} = 2.6$ Hz. Other spectral characteristics of 2a were as follows: IR (KBr) 1605, 1060, 1040, and 1022 cm⁻¹; MS (m/e) 265 (M⁺, 25%), 160 (100). Anal. (C₁₇H₁₅NO₂): C, 76.99; H, 5.67; N, 5.17.

Similar photooxygenation of the cis-isomer 1b⁵ afforded the stereoisomer 2b^{7,8} as granules in 90% yield, mp 80-81 °C. The olefin 1a gave no 2b, whereas the isomer 1b gave no 2a. Consequently the 1,4-cycloaddition of ${}^{1}O_{2}$ to the vinylindoles 1 is a completely stereospecific process.

Similarly, 1-methyl-3-vinylindole (1c) was photooxygenated to give the corresponding peroxide $2c^9$ as flakes in 71% yield, mp 80-82 °C. The irradiation of 1-methyl-3-(2-methylpropen-1-yl)indole (1d) gave also the 1,4-endoperoxide $2d^{10}$ as an oil in quantitative yield.

Furthermore, a vinylindole bearing an electron-withdrawing substituent on the β -carbon of the side chain undergoes the 1,4-cycloaddition of ¹O₂. Thus 1-methyl-3-(2-pivaloylvinyl)indole (1e)¹¹ was photooxygenated¹² to give two oxindoles 3e¹³ and 4e¹⁴ in the yields of 43 and 24%, respectively. Under the reaction conditions, the corresponding 1,4-endoperoxide 2e could not be obtained because of its easy isomerization to the oxindole 3e (vide infra). The oxindole 4e might be formed through a further isomerization of 3e; in fact, 3e was converted to 4e quantitatively by prolonged treatment under the isolation conditions or in the presence of acid catalyst.



In contrast with the reaction in aprotic solvents, the sensitized photooxygenation of the vinylindoles 1 in protic solvents caused dramatic change of products.¹⁵ When the vinylindole 1a was irradiated in ethanol or methanol, not the corresponding peroxide 2a but 3-formyl-1-methylindole 5 was obtained together with benzaldehyde in more than 90% yield. The other vinylindoles 1b-d were also converted to the aldehyde 5 in protic solvents. It should be noted that, in all cases examined, the indole 1 gave no products derived from a 1,2-addition of $^{1}O_{2}$ onto the C₂-C₃ double bond or a 3-peroxidic intermediate.

The unexpected solvent effects on the sensitized photooxygenation of the vinylindole 1 could reasonably be interpreted by the following facts; the 1,4-endoperoxide 2a was quantitatively decomposed into the formylindole 5 and benzaldehyde in alcohol ($\tau_{1/2} \simeq 10$ min at room temperature) (path A), whereas, the peroxide 2a was fairly stable in aprotic solvents such as benzene, chloroform, acetonitrile, and *n*-octane. It was easily isomerized into an oxindole $3a^{16}$ when heated in solution



(path B).¹⁷ The oxindole **3a** was further isomerized into the alcohol 4a¹⁸ (80% yield based on 2a), which was finally transformed into the ketone $6a^{19}$ in quantitative yield. The ketone 6a was directly obtained from 2a by treatment with a catalytic amount of triethylamine at ambient temperature (97% yield). When the peroxide 2a was allowed to stand in chloroform containing a small amount of methanol, both the fragmentation (path A) and the isomerization (path B) occurred competitively to give a mixture of 3a, 5, and benzaldehyde. Thus, the fragmentation (path A) is catalyzed by alcohol and might occur through a dioxetane intermediate 7a. It is noteworthy that the weak chemiluminescence,²⁰ which may be due to the dioxetane intermediate, was observed in the course of fragmentation. This type of chemiluminescence has been scarcely reported so far, though several examples of the fragmentation of 1,4-endoperoxides into two carbonyls were known.21

From these facts, it may be concluded that in the sensitized photooxygenation of vinylindoles 1 in protic solvents, 1,4cycloaddition of ${}^{1}O_{2}$ initially takes place to afford a 1,4-endoperoxide, which is then isomerized to a dioxetane intermediate and finally cleft to two aldehydes under the reaction conditions. At this stage, however, the direct 1,2-cycloaddition of ${}^{1}O_{2}$ onto the vinly substituent cannot be excluded completely.

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 (4) Irradiation was carried out externally with eight 60-W low-pressure sodium vapor lamps (National SOI-60) at 5 °C; tetraphenylporphine (TPP) was used
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- The indoles 1a and 1b were prepared by a Wittig reaction of 1-methyl-3-(5)formylindole and benzyltriphenylphosphonium bromide followed by the separation with silica gel chromatography.
- The NMR spectra of all the compounds obtained here were measured in (6)
- CDCl₃, and tetramethylsilane was used as internal standard. NMR δ 2.87 (s, 3 H, N–CH₃), 5.82–5.98 (three m, 3 H, H_a, H_b, and H_c 6.5–7.5 (m, 9 H, aromatic) ppm; IR (KBr) 1603, 1060, and 1010 cm⁻ (*m/e*) 265 (M⁺, 16%) and 160 (M⁺ C₈H₅CO, 100). (7) and H_c), and 1: MS
- The configurations of 2a and 2b were assigned in accordance with the (8) configurations of the 1,4-endoperoxides of 1-vinyInaphthalenes^{3c} and 2-vinyIthiophenes.^{3d}
- (9) NMR δ 2.84 (s, 3 H, N–CH₃), 4.76 (q_{AB} of t, 2 H, J_{AB} = 1.5 Hz, H_c and H_o), 5.79 (t, 2 H, J = 1.5 Hz, H_a and H_b), and 6.5–7.3 (m, 4 H, aromatic) ppm; IR (KBr) 1608, 1060, 1040, and 1012 cm⁻¹; MS (m/e) 189 (M⁺, 47 %) and 160 (M⁺ - H₂CO, 100). (10) NMR δ 1.26, 1.41, and 2.81 (three s, three CH₃), 5.60 (broad s, 2 H, H_a and
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- (13) Colorless needles from a n-hexane-ether mixture, mp 86-87 °C; NMR δ 1.11 (s, 9 H, tert-butyl), 3.10 (s, 3 H, N–CH₃), 3.39 (d of d, J = 1.5 and 1.0 Hz, 1 H), 3.59 (d, J = 1.0 Hz, 1 H), 3.77 (d, J = 1.5 Hz, 1 H), and 6.6–7.3 (m, 4 H, aromatic) ppm; IR (KBr) 1710, 1685 cm⁻¹; MS (*m/e*) 273 (M⁺, 8%). 160 (100).
- Yellow needles from ether, mp 115-116 °C; NMR & 1.20 (s, 9 H), tert-buty (14)3.18 (s, 3 H, N–CH₃), 5.60 (d, *J* = 10.0 Hz, 1 H, –CHO–), 6.64 (d, *J* = 10.0 Hz, 1 H, olefinic CH), and 6.7–7.8 (m, 4 H, aromatic) ppm; IR (KBr) 3390, 1700, and 1685 cm⁻¹; MS (*m/e*) 273 (M⁺, 8%), and 160 (100).
- Irradiation was made at 5 °C and rose bengal was used as a sensitizer.
- (16) The structure of 3a was assigned by comparing the NMR spectrum of 3a with that of 3e, though 3a could not be further purified because of its instabilities.
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- (18) Pale yellow plates from ether, mp 134–135 °C; NMR δ 2.89 (s, 3 H, N–CH₃),
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- MS (m/e) 265 (M⁺, 42%) and 160 (100). (19) Coloriess plates, mp 136–137 °C, from ethanoi; NMR § 3.20 (s, 3 H, N– CH₃), 3.17–4.10 (m, 3 H), and 6.7–8.0 (m, 9 H) ppm; IR (KBr) 1721 and 1688 cm⁻¹; MS (m/e) 265 (M⁺, 27%) and 160 (100).
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