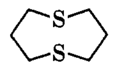
Roush,[10] and those of the bicyclic diamine **5** studied by Alder, Gill, and Goode.[12] The ions of both **4** and **5** differ from those of **2** in that the former have a σ bonding interaction between the heteroatoms, while $2^{+\bullet}$ and 2^{2+} are π ions.[13]



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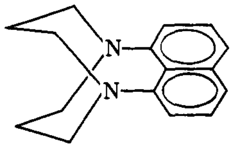

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(2) C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).
(3) G. R. Weisman and L. Echegoyen, unpublished results.
(4) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Am. Chem. Soc.*, **96**, 2916 (1974).
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(6) Isolated by TLC from photolysis of the tetrazine in cyclohexane. Purified by vacuum sublimation, 40%, mp 140–142 °C (sealed tube). Spectral properties in accordance with the proposed structure, and empirical formula established by high resolution mass spectroscopy.
(7) Prepared in 93% yield, mp 156–158 °C (pentane). Spectral properties in accordance with the proposed structure, and empirical formula established by high resolution mass spectroscopy.
(8) Using the method of J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3228 (1973).
(9) S. F. Nelsen, G. R. Weisman, E. L. Clennan, and V. Peacock, *J. Am. Chem. Soc.*, **98**, 6893 (1976).
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(11) Anal. Calcd for $C_{16}H_{28}N_2PF_6$: C, 48.85; H, 7.17; N, 7.12. Found: C, 48.79; H, 7.01, N, 7.18.
(12) R. W. Alder, R. Gill, and N. C. Goode, *J. Chem. Soc., Chem. Commun.*, 973 (1976).

(13) We thank the National Science Foundation for partial financial support of this work, and Professors Musker and Alder for communication of their results prior to publication.

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Sensitized Photooxygenation of 1-Methyl-3-vinylindoles

Sir:

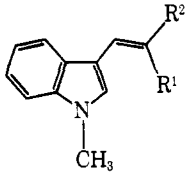
The oxidations of indoles with molecular oxygen, including singlet oxygen ($^1O_2$), have been extensively studied.[1] Most of them involve C_2–C_3 ring cleavage or the formation of 3-hydroperoxidic intermediates. In the sensitized photooxygenation of vinyl-substituted aromatics, $^1O_2$ attacks on the 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 $^1O_2$. The characteristic features of our results are as follows: (a) $^1O_2$ 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 $^1O_2$ in protic solvents.

When the sensitized photooxygenation[4] of 1-methyl-*trans*-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 spectrum[6] of **2a** displayed a singlet at δ 2.86 (3 H, N-CH_3), and four multiplets centered at 5.56 (1 H, Hd), 5.86 (1H, Ha or Hb) 5.92 (1 H, H_b, or H_a), 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. ($C_{17}H_{15}NO_2$): C, 76.99; H, 5.67; N, 5.17.

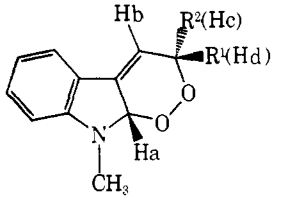
Similar photooxygenation of the cis-isomer **1b**[5] afforded the stereoisomer **2b**[7,8] as granules in 90% yield, mp 80–81 °C. The olefin **1a** gave no **2b**, whereas the isomer **1b** gave no **2a**. Consequently the 1,4-cycloaddition of $^1O_2$ to the vinylindoles **1** is a completely stereospecific 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.

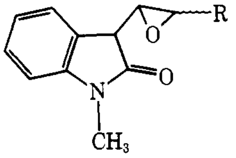
Furthermore, a vinylindole bearing an electron-withdrawing substituent on the β-carbon of the side chain undergoes the 1,4-cycloaddition of $^1O_2$. Thus 1-methyl-3-(2-pivaloylvinyl)-indole (**1e**)[11] was photooxygenated[12] to give two oxindoles **3e**[13] and **4e**[14] in the yields of 43 and 24%, 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.



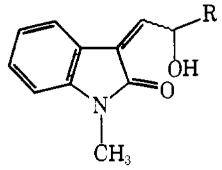
1a, R^1 = H; R^2 = C_6H_5
1b, R^1 = C_6H_5; R^2 = H
1c, R^1, R^2 = H
1d, R^1, R^2 = CH_3
1e, R^1 = H; R^2 = CO-*t*-C_4H_9



2a, R^1 = H; R^2 = C_6H_5
2b, R^1 = C_6H_5; R^2 = H
2c, R^1, R^2 = H
2d, R^1, R^2 = CH_3
2e, R^1 = H; R^2 = CO-*t*-C_4H_9



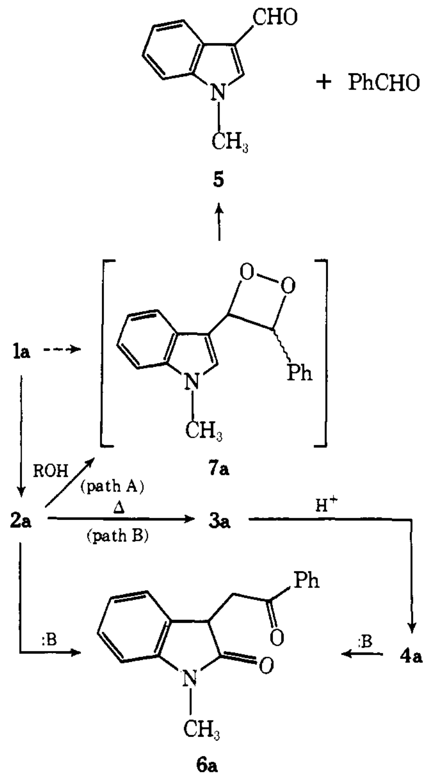
3a, R = C_6H_5
3e, R = CO-*t*-C_4H_9



4a, R = C_6H_5
4e, R = CO-*t*-C_4H_9

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 $^1O_2$ onto the C_2–C_3 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 **4a**[18] (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, 1,4-cycloaddition of ${}^1O_2$ 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 ${}^1O_2$ onto the vinly substituent cannot be excluded completely.

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(3) (a) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Am. Chem. Soc.*, **95**, 586 (1973); (b) G. Rio, D. Bricout, and L. Lacomb, *Tetrahedron*, **29**, 3553 (1973); (c) M. Matsumoto and K. Kondo, *Tetrahedron Lett.*, 3935 (1975); (d) M. Matsumoto, S. Dobashi, and K. Kondo, *ibid.*, 4471 (1975); (e) P. A. Burns, C. S. Foote, and S. Mazur, *J. Org. Chem.*, **41**, 899 (1976); (f) P. A. Burns and C. S. Foote, *ibid.*, **41**, 908 (1976).

(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 as a sensitizer, and consumed oxygen was measured by a gas buret.

(5) The indoles **1a** and **1b** were prepared by a Wittig reaction of 1-methyl-3-formylindole and benzyltriphenylphosphonium bromide followed by the separation with silica gel chromatography.

(6) The NMR spectra of all the compounds obtained here were measured in $CDCl_3$, and tetramethylsilane was used as internal standard.

(7) NMR δ 2.87 (s, 3 H, N-CH_3), 5.82–5.98 (three m, 3 H, H_a, H_b, and H_c), and 6.5–7.5 (m, 9 H, aromatic) ppm; IR (KBr) 1603, 1060, and 1010 cm^{-1}; MS (*m/e*) 265 (M^+, 16%) and 160 ($M^+ - C_6H_5CO$, 100).

(8) The configurations of **2a** and **2b** were assigned in accordance with the configurations of the 1,4-endoperoxides of 1-vinylnaphthalenes[3c] and 2-vinylthiophenes.[3d]

(9) NMR δ 2.84 (s, 3 H, N-CH_3), 4.76 (q_{AB} of t, 2 H, J_{AB} = 1.5 Hz, H_c and H_d), 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 ($M^+ - H_2CO$, 100).

(10) NMR δ 1.26, 1.41, and 2.81 (three s, three CH_3), 5.60 (broad s, 2 H, H_a and H_b), and 6.33–7.10 (m, 4 H, aromatic) ppm; IR (liquid film) 1606, 1060, and 1020 cm^{-1}; MS (*m/e*) 217 (M^+, 26%), 174 (100), and 158 (53).

(11) The indole **1e**, mp 133–134 °C, was prepared from 3-formyl-1-methylindole and *tert*-butylmethyl ketone by the modification of the literature; R. B. van Order and H. G. Lindwall, *J. Org. Chem.*, **10**, 128 (1945).

(12) Irradiation was made in benzene at 5 °C (TPP as a sensitizer). The NMR spectrum of the crude photolysate showed no peaks due to **4e** but peaks of **3e**, which was obtained by crystallization of the crude photolysate from ether at −20 °C and the residue gave no **3e** but **4e** after chromatographic purification on silica gel. The oxindole **3e** was easily isomerized into **4e** in protic solvent such as ethanol.

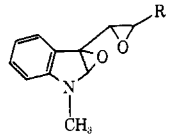
(13) Colorless needles from a *n*-hexane–ether mixture, mp 86–87 °C; NMR δ 1.11 (s, 9 H, *tert*-butyl), 3.10 (s, 3 H, N-CH_3), 3.39 (d of d, J = 1.5 and 1.0 Hz, 1 H), 3.59 (d, J = 1.0 Hz, 1 H), 3.77 (d, J = 1.5 Hz, 1 H), and 6.6–7.3 (m, 4 H, aromatic) ppm; IR (KBr) 1710, 1685 cm^{-1}; MS (*m/e*) 273 (M^+, 8%), 160 (100).

(14) Yellow needles from ether, mp 115–116 °C; NMR δ 1.20 (s, 9 H), *tert*-butyl), 3.18 (s, 3 H, N-CH_3), 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).

(15) 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.

(17) The oxindole **3** may be formed through a bisepoxide intermediate, **8**, which was suggested by a referee. A previous example of this type rearrangement is found in H. H. Wasserman and R. Kitzing, *Tetrahedron Lett.*, 5315 (1969).



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(18) Pale yellow plates from ether, mp 134–135 °C; NMR δ 2.89 (s, 3 H, N-CH_3), 4.2 (broad s, 1 H, OH), 5.95 (d, J = 9.0 Hz, -CHO-), 6.51 (d, J = 9.0 Hz, 1 H, olefinic CH), 6.8–7.6 (m, 9 H, aromatic); IR (KBr) 3380 and 1690 cm^{-1}; MS (*m/e*) 265 (M^+, 42%) and 160 (100).

(19) Colorless plates, mp 136–137 °C, from ethanol; NMR δ 3.20 (s, 3 H, N-CH_3), 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).

(20) The chemiluminescence was detected by means of a high sensitive photomultiplier for a liquid scintillation system (Beckman LS-250).

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