

commonly observed during isoprene metabolism. In addition, competition of hydride migration with elimination provides strong evidence that elimination is not concerted with electrophilic alkylation during cyclization of **6-PP** and **7-PP**.

Acknowledgments. We thank Dr. Ohloff for providing samples of **8-OH** and **9-OH** for comparison with our synthetic materials and Drs. T. Sharp and A. Sopchik for their assistance in obtaining spectral data. The VG Analytical Micromass 7070E mass spectrometer was supported by NSF Grants CHE-8100424 and CHE-8310031. This investigation was supported by Grant GM-25521 from the National Institutes of Health.

Trimethylsilyl Cyanide as a Trapping Agent for Dipolar Peroxide Intermediates¹

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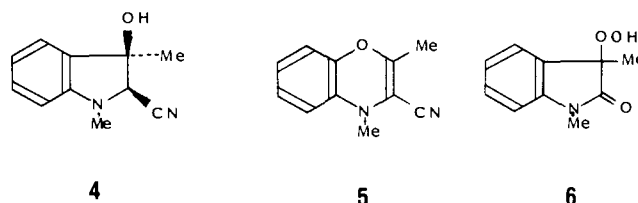
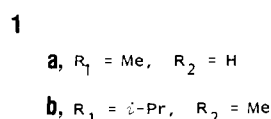
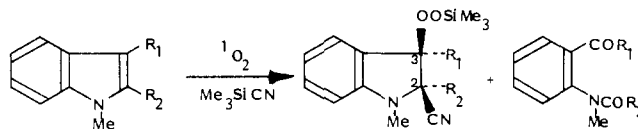
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The existence of dipolar peroxide intermediates has been proposed in singlet oxygen (¹O₂) reaction of a variety of electron-rich systems² such as enamines,³ enol ethers,⁴ dienes,⁵ heterocycles,⁶ indene,⁷ and sulfides.⁸ Transient zwitterionic peroxides have also been postulated in other oxidations⁹ and the decomposition processes of certain endoperoxides.^{6b,10} In many of these cases experimental support for zwitterionic peroxide intermediates has been based on the trapping reaction with nucleophilic solvents such as alcohols.^{2,11} The distinction between zwitterionic peroxide and

other polar intermediates such as perepoxides or charge-transfer complexes in ¹O₂ reaction of electron-rich olefins has not been made by trapping with such nucleophilic solvents.^{4,12,13} It is known that an electron-transfer-initiated photooxygenation also produces similar trapping products by interception of substrate radical cations with alcohols and oxygen without intervention of zwitterions.¹⁴ Accordingly, a reliable trapping agent that may serve as a diagnostic test for zwitterionic peroxide, usable in aprotic solvents, is clearly desirable for mechanistic studies of oxidation reaction. We now wish to report that trimethylsilyl cyanide (TMSCN) can serve as a superior reagent for trapping such dipolar peroxide intermediates.

We previously reported that singlet oxygenation of 3-substituted or 2,3-disubstituted *N*-methylindoles **1** in alcohols at low tem-



perature gives 2-alkoxy-3-hydroperoxyindolines in high yields which are explicable as arising from the interception of zwitterionic peroxides by alcohols.^{3c,15} Rose Bengal sensitized photooxygenation of 1,3-dimethylindole (**1a**, 10 mM) in the presence of TMSCN (5 equiv) in dry acetonitrile at -30 °C produced a similar trapping product, **2a** (70%), together with a minor amount of the ring cleavage product **3a** (17%).¹⁶ Product structures were assigned on the basis of spectroscopic data¹⁷ and confirmed by chemical transformations. For example, the adduct **2a** was reduced to **4** with dimethyl sulfide and converted directly to **5** by treatment of **2a** with silica gel. The *cis* relationship between the C-2 proton and the C-3 methyl was confirmed by means of NOE-FID difference experiments of the 400-MHz ¹H NMR of both **2a** and **4**.¹⁸ Similarly, tetraphenylporphyrin (TPP)-sensitized photooxygenation of 1,2-dimethyl-3-isopropylindole (**1b**, 17 mM) in the presence of TMSCN (5 equiv) in dichloromethane at -30 °C gave **2b** (45%) together with **6**^{15b} (40%). The products were separated by flash column chromatography over silica gel at 0 °C. The *cis* orientation of the two alkyl groups in **2b** was again confirmed by means of the NOE technique. In both cases ex-

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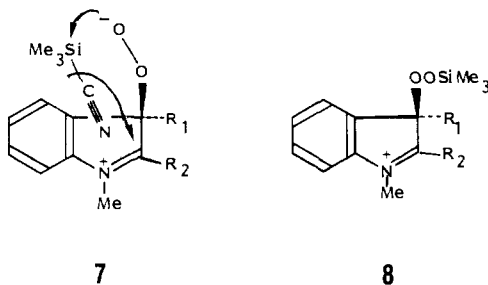
(16) Photooxygenation of **1a** in dichloromethane in the presence of TMSCN produced a different rearranged adduct together with **2a** and **3a**. Experimental details will be reported elsewhere.

(17) All new compounds gave consistent spectroscopic data (exact MS, IR, ¹H and ¹³C NMR).

(18) Saturation of the methine proton at C-2 (δ 4.09) of **2a** produced a positive NOE (25% enhancement) of the C-3 methyl group (δ 2.86).

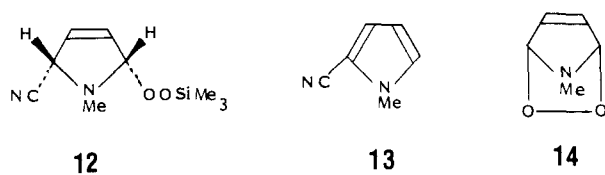
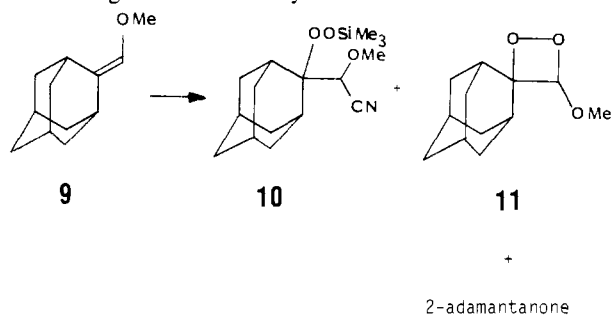
clusive formation of cis adducts was observed at least under the reaction conditions.¹⁹

The formation of cis adducts is significant as it constitutes evidence for the existence of a precursive peroxide intermediate. The results are most easily rationalized by assuming addition of TMSCN to a dipolar peroxide intermediate such as a zwitterion or perepoxide.²⁰ Thus the nucleophilic attack by peroxy anion on the silicon would give a pentacoordinated silicon which deposits directly the cyanide ion at the cationic site of the trapped dipolar species as illustrated as transition state 7 using an example of



zwitterion. However, the observed cis stereoselectivity cannot distinguish between the zwitterion and the alternative perepoxide formation.²¹

TMSCN was found to intercept the precursor of 1,2-dioxetanes formed in photooxygenation of unsymmetrical enol ethers. For example, TPP-sensitized photooxygenation of 2-(methoxymethylene)adamantane (**9**, 50 mM) in the presence of TMSCN (5 equiv) in dichloromethane at $-70\text{ }^{\circ}\text{C}$ produced the adducts **10** (35%), dioxetane **11** (30%), and 2-adamantanone (22%). Without TMSCN **9** gave **11** exclusively.²³ TMSCN did not react with



11 under the conditions of photooxygenation. It was reported that the precursor of **11** was captured by acetaldehyde as solvent at $-78\text{ }^{\circ}\text{C}$.¹² In contrast, photooxygenation of symmetrical enol ethers such as 1,4-dioxene²⁴ and 2,3-diphenyl-1,4-dioxene²⁵ in the presence of a large excess of TMSCN in dichloromethane or acetonitrile produced none of the trapping products but gave only the corresponding dioxetanes and their ring cleavage products.²⁶

(19) However, in the presence of a large excess of TMSCN (more than 10 equiv) at higher temperature, formation of trans adduct was detectable by ^1H NMR in case of **1a**.

(20) TMSCN-assisted ring opening of short-lived indole dioxetanes giving oxiranes by TMSCN is known to provide trans adducts exclusively.²² However, in that case a mixture of cis and trans adducts should be formed.

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Lastly, we demonstrate another example of photooxygenation of heterocycles in the presence of TMSCN. TPP-sensitized photooxygenation of *N*-methylpyrrole in the presence of TMSCN (5 equiv) in dichloromethane at $-70\text{ }^{\circ}\text{C}$ produced **12**²⁸ quantitatively as evidenced by ^1H NMR at $-70\text{ }^{\circ}\text{C}$. On warming to room temperature the adduct **12** was decomposed to afford **13** (90%) with 1,4-elimination of trimethylsilyl hydroperoxide. Addition of excess TMSCN to the solution of endoperoxide **14**,²⁹ prepared by photooxygenation of *N*-methylpyrrole in CDCl_3 at $-60\text{ }^{\circ}\text{C}$, also produced **12** (80%) presumably via trapping of the zwitterionic peroxide that may be in equilibrium with **14**.^{10a,30}

The results of our preliminary investigations demonstrate the potential use of trimethylsilyl cyanide as an excellent trapping agent for dipolar peroxide intermediates in aprotic solvents. The extension of the mechanistic principle and the synthetic applications are in progress.

(26) Recent ab initio MO calculations²⁷ have indicated that the concerted $[2_s + 2_a]$ mechanism is the most favorable for $^1\text{O}_2$ reaction of symmetrical enol ethers, whereas the two-step mechanism involving 1,4-zwitterion is the most probable for unsymmetrical enol ethers. For related recent papers, see ref 5c and 6d.

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36- to 40-Electron Complexes ($\text{C}_6\text{R}_6\text{FeCp}-\text{CpFeC}_6\text{R}_6$)^{n±} (R = H, Me; n = 0-2) and the First Delocalized Mixed Valence Complexes Containing Fe¹

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The electrochemistry and electron-transfer chemistry of binuclear delocalized transition-metal complexes has stimulated the study of mixed-valence systems.² These materials, some of which are biomimetic (e.g., ferredoxin models), have specific physical properties related to electron transfer.² We envisioned that coupling these properties with those of molecular electron reservoirs³ would give a novel class of compounds. For instance, an enhanced potential and efficiency in electron-transfer catalysis (electrocatalysis and redox catalysis)⁴ can be expected with two

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