torr through a 17 cm × 1.2 cm quartz pyrolysis tube fitted with a 0.06-mm capillary leak between the reaction zone and the source of a Hewlett-Packard HP 5930 A quadrupole mass spectrometer. The mass spectral fragmentation pattern (electron impact, 5-eV nominal bombarding voltage) of the flow material below 160 °C showed fragments at m/z 286, 258, 230, 202, and 174 in ratios that were insensitive to temperature change. The intensities of the fragments of **1**, in ratio to the parent, were summed and divided by total ion current to give the fractional ion current (Fi) of the starting material which begins to decrease at oven temperatures above 160 °C. At 260 °C, ions indicative of starting material **1** have disappeared almost entirely and those of bibenzyl are not yet present. A metastable manganese tricarbonyl intermediate (m/z 230) is clearly suggested.

In experiments where the furnace temperature was held at 260 °C a yellow substance collected in a cold (liquid N_2) trap located between the furnace and pumping system. This material polymerized[9] on warming but could be dissolved in cold (−78 °C) acetone or methylene chloride. The ^1H and ^{13}C NMR spectral data[10] (−78 °C, deuterioacetone) are consistent with the ($\eta^5 \rightleftarrows \eta^6$-benzyl)-manganese tricarbonyl structure shown (**3**). This structure is also indicated by the isolation (35% yield) of the known[11] (η^6-toluene)tricarbonylmanganese(+1) cation (**4**) after treatment of an acetone solution of **3** with trifluoroacetic acid at −78 °C followed by metathesis with PF_6^-.

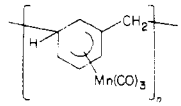
Finally, when a second pyrolysis oven was placed immediately downstream from a first oeven set at 260 °C, the m/z 230 (**3**) ions were replaced by those of bibenzyl (m/z 182) as the temperature of the second oven was raised to 350 °C. These observations suggest **3** is an intermediate in the formation of bibenzyl from **1** and not the product of an unconnected separate reaction. A CO dissociative σ–π rearrangement[12] to **3** is faster than the simpler C–Mn homolysis route to bibenzyl.

The mass spectral temperature profile for bis(manganese) compound **2** showed that the decrease in fractional ion current for starting material (m/z 494, 354, 299, 214, 159), beginning above 190 °C, is compensated principally by the appearance of a C_8H_8 compound (m/z 104) and dimanganese decacarbonyl (m/z 390). The latter compound was found, in independent experiments, to be unstable with respect to metallic manganese and CO in the present fvp system above 250 °C. The identity of the C_8H_8 species as *p*-xylylene was confirmed by the polymeric film that was isolated (40% yield based on Mn)[13] after warming the cold trap. This isolated hydrocarbon polymer showed infrared bands identical with those of poly(*p*-xylylene).[14] The results for **2** are consistent with a single C–Mn bond homolysis if the second $CH_2Mn(CO)_5$ group stabilizes the corresponding transition state relative to that for the unsubstituted case (**1**). Concerted possibilities also can explain the low-temperature formation of **5**.

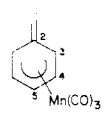
In summary, our results show that the bis(manganese) compound **2** undergoes a relatively rapid cleavage of the C–Mn bonds providing a low-temperature gas-phase source of *p*-xylylene **5**. Reduced temperatures for generating reactive intermediates can be an important requirement for their direct observation, as has recently been demonstrated by Schweig's recent success[4b] in the case of the *o*-xylylene. The fvp route has provided an entry into the new [($\eta^5 \rightleftarrows \eta^6$)-benzyl]tricarbonylmanganese (**3**) which is shown to undergo a fairly clean self-initiated polymerization and to be reactive with electrophiles. This species appears to be on the reaction surface between **1** and bibenzyl, indicating that a CO dissociative rearrangement is faster than the simpler C–Mn homolysis which could rationalize the ultimate bibenzyl product. The present results are suggestive as to a means (fvp) of characterizing the related $CpFeC_7H_7$ complexes which are not kinetically stabilized[15] by methylation[10] or delocalization.[16] The self-initiated polymerization of **3** suggests a new type of organometallic polymer which could be expected to show a number of interesting properties. Fvp studies of other examples of this type of compound are currently in progress.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to Dr. John Austin and J. R. Nunnelley and NASA for the polymer analysis and a summer fellowship (T.K.).

(9) The infrared spectrum of this insoluble polymer (ν_{CO} 2018, 1940 cm^{-1}) strongly suggests an interesting (η^5-cyclohexadienyl)manganese tricarbonyl system though the details of the structure are not available.



(10) ^1H NMR spectrum



(360 MHz $(CD_3)_2CO$, −60 °C) δ 366 (s, 2 = H, H_1), 4.43 (d, J = 7.4 Hz, 2 H, H_3), 5.50 (d, d, J = 7.4, 5.6 Hz, 2 H, H_4), 6.01 (t, J = 5.6 Hz, 1 H, H_5); ^{13}C NMR (90.8 MHz $(CD_3)_2CO$, −60 °C) 86.24 (C_1, J_{CH} = 158.5 Hz), 137.15 (C_2), 73.65 (C_3, J_{CH} = 167.6 Hz); 100.57 (C_4, J_{CH} = 170.3 Hz), 76.29 ppm (C, J_{CH} = 179.15 Hz). A closely related iron analogue is described by: Astruc, D.; Hamon, J.-R.; Román, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502–7514; **1979**, *101*, 2240. Astruc, D.; Enrique, R. E.; Hamon, J. R.; Batail, P. *Ibid.* **1979**, *101*, 2240.

(11) Brill, T. B.; Kotlar, A. J. *Inorg. Chem.* **1974**, *13*, 470. Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807.

(12) Druz, N. N.; Klepikova, V. I.; Lobach, M. I.; Kormer, V. A. *J. Organomet. Chem.* **1978**, *162*, 343. King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709–712.

(13) The volatility of **2** is such that some solid-phase decomposition competes with sublimation so that the titrated amount of Mn, depositing in the reaction zone, is used as a basis of yield.

(14) Gorham, W. "Encyclopedia of Polymer Technology"; Interscience Publishers: New York, 1971; Vol. 15, pp 98–113. Hunmmel, D. O.; Scholl, F. "Atlas der Kunstoff-Analyse"; Carl Hanser Velag: Munich, 1968; Band I, Teil 2. Thermal gravimetric analysis of the polymer obtained from **2** showed it to be thermally less stable in air than samples from [2.2]paracyclophane pyrolysis.

(15) Lee, C. C.; Steele, B. R.; Demchuk, K. J.; Sutherland, R. G. *Can. J. Chem.* **1979**, *57*, 946–948. Sutherland, R. G.; Steele, B. R.; Demchuk, K. J.; Lee, C. C. *J. Organomet. Chem.* **1979**, *181*, 411–412.

(16) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749–753.

Farnesylpyrophosphate Synthetase. A Case for Common Electrophilic Mechanisms for Prenyltransferases and Terpene Cyclases

V. Jo Davisson, Timothy R. Neal, and C. Dale Poulter*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received March 25, 1985

The isoprene biosynthetic pathway is truly unique in the diversity of metabolites it produces. Carbon–carbon bonds are formed in the major building steps by intermolecular prenyl transfer reactions or by intramolecular cyclizations,[1,2] and there is evidence the reactions occur by attack of electrophilic carbocations on neighboring π-electron functional groups.[1-11] Farnesyl-PP[12]

(1) Poulter, C. D.; Rilling, H. C. "Biosynthesis of Isoprenoid Compounds"; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; Vol. 1, pp 162–224.

(2) Cane, D. E. *Tetrahedron* **1980**, *36*, 1109–1159.

(3) Poulter, C. D.; Rilling, H. C. *Acc. Chem. Res.* **1978**, *11*, 307–313.

(4) Poulter, C. D.; Wiggins, P. L.; Le, A. T. *J. Am. Chem. Soc.* **1981**, *103*, 3926–3927.

(5) Mash, E. A.; Gurria, G. M.; Poulter, C. D. *J. Am. Chem. Soc.* **1981**, *103*, 3927–3929.

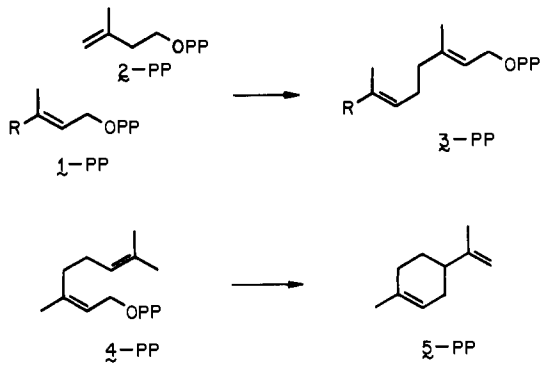
(6) Poulter, C. D.; Argyle, J. C.; Mash, E. A. *J. Biol. Chem.* **1978**, *253*, 7227–7233.

(7) Poulter, C. D.; Satterwhite, D. M. *Biochemistry* **1977**, *16*, 5470–5478.

(8) Cane, D. E.; Iyengar, R.; Shiao, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 914–931.

0002-7863/85/1507-5277$01.50/0

synthetase (EC 2.5.1.1), a prototypic prenyltransferase, catalyzes the conversion of dimethylallyl-PP (**1**-PP, R = CH_3) to geranyl-PP (**3**-PP, R = CH_3) and ultimately to farnseyl-PP (**3**-PP, R = C_6H_{11})

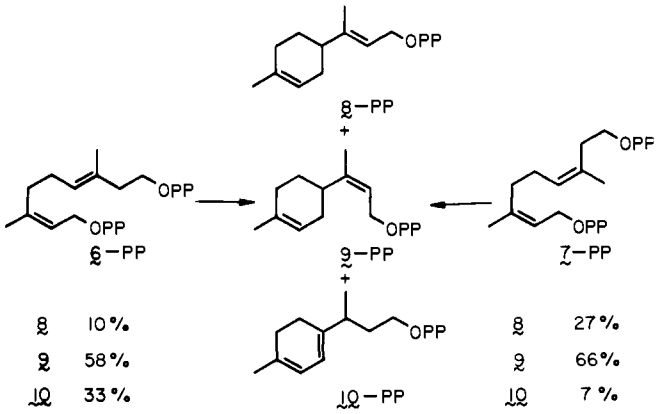


by an electrophilic condensation which links C1 in the allylic substrate with C4 in isopentenyl-PP (**2**-PP)[2,4] by a 1′-4 condensation.[13] Identical *changes* in bonding occur during the conversion of neryl-PP (**4**-PP) to limonene (**5**-PP) catalyzed by cyclases from plant sources,[14] and several groups have commented that the mechanisms may be similar.[2,10,11,14-16] In this paper we report experiments with farnsyl-PP synthetase which demonstrate that the enzyme can catalyze cyclization as well as prenyl transfer.

Bisubstrate analogues[17] **6**-PP and **7**-PP were synthesized[18] as part of a study to determine the topology of substrates in the E·S complex for farnsyl-PP synthetase. The compounds were initially tested as alternate substrates by using derivatives labeled with tritium at the allylic hydroxymethylene in the acid-lability assay normally employed to monitor condensation of **2**-PP with an allylic partner.[1,3] Both produced acid-labile material[19] upon incubation with avian liver farnsyl-PP synthetase.[20] Kinetic constants[21] were obtained for the normal 1′-4 condensation[22] ($K_M^{2\text{-PP}}$ 130 nM, $K_M^{3\text{-PP}}$ 500 nM, V_{max} 1.1 μmol m^{-1} mg^{-1}) and for cyclization of **6**-PP ($K_M^{6\text{-PP}}$ 9 nM, V_{max} 0.135 μmol m^{-1} mg^{-1}) and **7**-PP ($K_M^{7\text{-PP}}$ 17 nM, V_{max} 0.033 μmol m^{-1} mg^{-1}) with the same preparation of enzyme. Maximal velocities for cyclization were substantially slower than 1′-4 condensation. However, the catalytic efficiencies (V/K) for prenyl transfer and both cyclizations were similar due to the very low values of K_M for the bisubstrate analogues.

Product studies were conducted by incubation of 10–20 mM solutions of **6**-PP or **7**-PP at 37 °C for 12–15 h with 0.3 mg of farnesyl-PP synthetase in 4 mL of 20 mM BHDA buffer, pH 7.2, containing 2 mM magnesium chloride. The reaction was terminated by addition of 1 mL of 0.2 M lysine buffer, pH 10.5. The

Scheme I. Products from Incubation of Bisubstrate Analogues 6-PP and 7-PP with Avian Liver Farnesyl-PP Synthetase



pyrophosphate moieties of the products were hydrolyzed by addition of 0.3 mg of *E. coli* alkaline phosphatase (EC 3.1.3.1, Sigma) followed by incubation at 37 °C for 17 h. The resulting alcohols were extracted with methylene chloride and converted to the corresponding naphthoate esters using a modification of the Steglich procedure.[23] Alcohols and naphthoates were analyzed by GLPC and HPLC, respectively, and both procedures[24] indicated the presence of three products, **8**–**10**, in the percentages given in Scheme I.[25] Products **8**-PP and **9**-PP were shown to be substituted cyclohexenes with structures analogous to *p*-menthane monoterpenes by comparison of the corresponding alcohols and naphthoates with authentic materials.[26] Naphthoates **8**-Np, **9**-Np, and **10**-Np were separated by preparative thin-layer chromatography on silica gel impregnated with silver nitrate upon elution with a 6:4 (v/v) mixture of hexane and methylene chloride. The structure for the third product was assigned from the spectra of **10**-Np.[27] The ester had a molecular ion at m/z 320.1778 ($C_{22}H_{24}O_2$), an UV absorption at 266 nm (ϵ 6500) when contributions from the naphthoate moiety were substracted, and a linear connectivity for carbons C1–C4 in the side chain as established by sequential decoupling of ^1H resonances at 4.33 (C1), 1.81 and 1.92 (C2), 2.42 (C3), and 1.10 (C4) ppm.

Clearly the catalytic machinery which promotes the electrophilic alkylation of isopentenyl-PP during prenyl transfer also promotes cyclization of **6**-PP and **7**-PP. Thus, farnesyl-PP synthetase is the first example of an enzyme that catalyzes both of the fundamental bond-forming reactions in the isoprene biosynthetic pathway.[28] Formation of **10**-PP is also noteworthy. Not only does farnesyl-PP synthetase catalyze cyclization, the enzyme provides an environment that permits hydride migration, a reaction

(9) Cane, D. E.; Saito, A.; Croteau, R.; Shaskus, J.; Felton, M. *J. Am. Chem. Soc.* **1982**, *104*, 5831–5833.
(10) Croteau, R. "Biosynthesis of Isoprenoid Compounds"; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; Vol. 1, pp 225–282.
(11) Cane, D. E. "Biosynthesis of Isoprenoid Compounds"; Porter J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; Vol. 1, pp 283–374.
(12) Abbreviations: BHDA, *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid; GLPC, gas liquid partition chromatography; HPLC, high-pressure liquid chromatography; PP, pyrophosphate; WCOT, wall-coated open tubular.
(13) Poulter, C. D.; Marsh, L. L.; Hughes, J. M.; Argyle, J. C.; Satterwhite, D. M.; Goodfellow, R. J.; Moesinger, S. G. *J. Am. Chem. Soc.* **1977**, *99*, 3816–3823.
(14) Rojas, M. C.; Chayet, L.; Portilla, G.; Cori, O. *Arch. Biochem. Biophys.* **1983**, *222*, 389–396.
(15) Croteau, R.; Gundy, A. *Arch. Biochem. Biophys.* **1984**, *233*, 838–841.
(16) Cori, O.; Portilla, G.; Chayet, L. *Arch. Biol. med. Exp.* **1982**, *15*, 357–364.
(17) This term refers to a single molecule that contains the properties of both substrates for a bisubstrate enzyme.
(18) The synthesis of **6**-PP and **7**-PP will be described elsewhere.
(19) Allylic isomers **8**-PP and **9**-PP are detected by the acid lability assay. Infinity points for the enzyme-catalyzed reactions are less than theoretical in agreement with the amounts of **10**-PP found in the product studies.
(20) Bartlett, D. L.; King, C. H. R.; Poulter, C. D. *Methods Enzymol.* **1984**, *110*, 171–184.
(21) Laskovics, F. M.; Krafcik, J. M.; Poulter, C. D. *J. Biol. Chem.* **1979**, *254*, 9458–9463.
(22) This is the more efficient of the two steps catalyzed by farnesyl-PP synthetase.
(23) Boden, E. P.; Keck, G. E. *J. Org. Chem.* **1985**, *50*, 2394–2395.
(24) Methylene chloride extracts were analyzed on a 0.25 mm × 30 m SE 54 WCOT fused silica column. Separations for GCMS were performed on a 0.36 mm × 30 m bonded-phase DB-5 WCOT fused silica column. Normal-phase HPLC separations were performed on a Waters RCM-100 radial compression module with a 98:2 (v/v) mixture of hexane and *tert*-butylmethyl ether as the eluent.
(25) In control experiments without farnesyl-PP synthetase, **6**-PP and **7**-PP gave less than 4% of **8**-PP. The other two products were not detected. All products were stable to the conditions of analysis.
(26) All new materials gave satisfactory IR, MS, NMR, UV, and elemental compositions. Alcohols **8**-OH and **9**-OH were prepared by DIBAL reduction of the corresponding methyl esters. Delay, F.; Ohloff, G. *Helv. Chim. Acta* **1979**, *62*, 369–377.
(27) 300 MHz ^1H NMR ($CDCl_3$) δ 8.6 (s, 1 H), 8.06 (m, 1 H), 7.96 (m, 1 H), 7.86 (d, 2 H), 7.54 (m, 2 H), 5.65 (d, J = 5.2 Hz, 1 H), 5.60 (dt, J = 5.2, 1.2 Hz, 1 H), 4.33 (m, 2 H), 2.42 (d,d,d,J = 6.6, 5.9, 8.3 Hz, 1 H), 2.10 (m, 4 H), 1.92 (dddd, J = 14, 8.3, 6.8, 7.2 Hz, 1 H), 1.81 (dddd, J = 14, 5.9, 6.8, 8 Hz, 1 H), 1.74 (d, J = 1.2 Hz, 3 H), 1.10 (d, J = 6.6 Hz, 3 H); IR (neat) 3058–2835 (s), 1717 (s), 1286 (m), 1196 (s), 1014 (s), 962 (s), 865 (s), 825 (m) cm^{-1}; UV (CH_3CN) difference 266 nm (ϵ 6500); MS (70 eV), m/z (relative intensity) 320 (19), 173 (3), 155 (33), 133 (100), 127 (40), 119 (28), 105 (32), 91 (22); HRMS M^+ $C_{22}H_{24}O_2$ calcd 320.1776, found 320.1778.
(28) An inefficient cyclization of farnesyl-PP to an unknown mixture of hydrocarbons has been reported. Saito, A.; Rilling, H. C. *Arch. Biochem. Biophys.* **1981**, *208*, 508–511.

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 Intermediates[1]

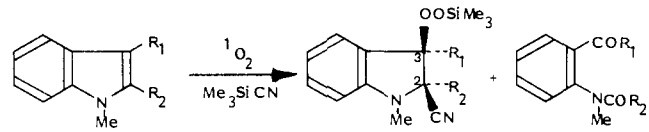
Isao Saito,* Hideki Nakagawa, Yueh-Hsiung Kuo, Keiichi Obata, and Teruo Matsuura

Department of Synthetic Chemistry Faculty of Engineering, Kyoto University Kyoto 606, Japan

Received February 26, 1985

The existence of dipolar peroxide intermediates has been proposed in singlet oxygen ($^1O_2$) reaction of a variety of electron-rich systems[2] 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 oxidations[9] 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 $^1O_2$ 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.

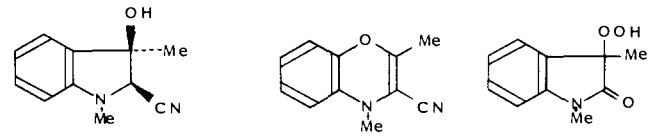
We previously reported that singlet oxygenation of 3-substituted or 2,3-disubstituted *N*-methylindoles **1** in alcohols at low temperature gives 2-alkoxy-3-hydroperoxyindolines in high yields which are explicable as arising from the interception of zwitterionic peroxides by alcohols.[3c,15] Rose Bengal 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 data[17] 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, tetraphenylporphine (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-



1 **2a,b** **3a**

a, R_1 = Me, R_2 = H

b, R_1 = *i*-Pr, R_2 = Me



4 **5** **6**

(1) Photoinduced reactions. 163.

(2) (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Schaap, A. P.; Zaklika, K. A. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 173. (c) Stephenson, L. H.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (d) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554. (e) Dewar, M. J. S.; Thiel, W. *Ibid.* **1975**, *97*, 3978. (f) Harding, L. B.; Goddard, W. A. III *Ibid.* **1977**, *99*, 4520.

(3) (a) Matsuura, T.; Saito, I. *Tetrahedron Lett.* **1968**, 3273. (b) Foote, C. S.; Lin, J. W.-P. *Ibid.* **1968**, 3267. (c) Saito, I.; Matsuura, T.; Nakagawa, M.; Hino, T. *Acc. Chem. Res.* **1975**, *97*, 3978.

(4) (a) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1977**, 2375. (b) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 295, 6437, 6615. (c) Rousseau, G.; Lechvallier, F.; Heut, F.; Conia, T. M. *Tetrahedron Lett.* **1978**, 3287. (d) Jefford, C. W.; Kohmoto, S. *Helv. Chim. Acta* **1982**, *65*, 133. (e) Asveld, E. M. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644. (f) Gorman, A. A.; Gould, I. R.; Hamblett, I. *Ibid.* **1982**, *104*, 7098. (g) Wilson, S. L.; Schuster, G. B. *Ibid.* **1983**, *105*, 679.

(5) (a) Hasty, N. M.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380. (b) Manring, L. E.; Foote, C. S. *Ibid.* **1983**, *105*, 4710. (c) Gollnick, K.; Griesbeck, A. *Tetrahedron* **1984**, *40*, 3235.

(6) (a) Wasserman, H. H. *Ann. N. Y. Acad. Sci.* **1970**, *171*, 108. (b) Wasserman, H. H.; Lipshutz, B. H., ref 2b, p 430. (c) Albini, A.; Betlinetti, G. F.; Minoli, G. *J. Org. Chem.* **1983**, *48*, 1080. (d) Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7112.

(7) (a) Hatsui, T.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2655. (b) Manring, L. E.; Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

(8) (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (b) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (c) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947. (d) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *Ibid.* **1983**, *105*, 4717 and references therein.

(9) (a) Turro, N. J.; Chow, M.-F.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5580. (b) Turro, N. J.; Ramamurthy, V.; Krebs, K. C.; Kemper, R. *Ibid.* **1976**, *98*, 6758.

(10) (a) Gollnick, K.; Griesbeck, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 726. (b) Saito, I.; Nittala, S. In "Peroxides; The Chemistry of Functional Groups"; Patai, S., Ed.; Wiley: New York, 1983; p 311.

(11) Recent reports have demonstrated the capture of dipolar peroxide intermediates by a carbonyl function.[4g,12]

(12) Jefford, C. W.; Kohmoto, S.; Boukouvalas, J.; Burger, U. *J. Am. Chem. Soc.* **1983**, *105*, 6498.

(13) For trapping of a perepoxide intermediate derived from adamantylideneadamantane with methyl phenyl sulfoxide, see: Schaap, A. P.; Recher, S. R.; Faler, G. R.; Villasenor, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 1691.

(14) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1982**, *104*, 1454. (b) Manring, L. E.; Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 4275.

(15) (a) Saito, I.; Imuta, M.; Takahashi, Y.; Matsugo, S.; Matsuura, T. *J. Am. Chem. Soc.* **1977**, *99*, 2005. (b) Saito, I.; Matsugo, S.; Matsuura, T. *Ibid.* **1979**, *101*, 7332.

(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 ^{13}C 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).

0002-7863/85/1507-5279$01.50/0