distillation. The yields reported in Table I were ascertained by ^{13}C NMR and GLC analyses.

Acknowledgment. We are grateful to the Rohm & Haas Company for sponsoring the American Chemical Society's Organic Divisional Fellowship for J.W.K. (1985–1986). We also thank the National Research Council's Senior Postdoctoral Fellows Program (Ford Foundation), the Fulbright-Hays Scholar Program (to S.A.E.), and the Department of Energy for support of this research.

Registry No. 1, 84-11-7; 2, 604-84-2; TDP, 6546-78-7; $HO(CH_2)_4OH$, 110-63-4; $HOCH_2CH(OH)CH_3$, 57-55-6; $HO(CH_2)_5OH$, 111-30-8; $HOCH_2CH(NH_2)CH_2Ph$, 16088-07-6; $HO(CH_2)_2SH$, 60-24-2; $HOCH_2CH(CH_3)SH$, 3001-64-7; $HOCH_2CH(Ph)SH$, 60615-96-5; $HO(CH_2)_3SH$, 19721-22-3; $HO(CH_2)_4SH$, 14970-83-3; $HO(CH_2)_5SH$, 1633-79-0; PPh_3, 603-35-0; tetrahydrofuran, 109-99-9; propylene oxide, 75-56-9; tetrahydropyran, 142-68-7; *trans*-2-aminohexanol, 6982-39-4; 2-benzylaziridine, 13906-90-6; 7-azabicyclo[4.1.0]heptane, 286-18-0; thiirane, 420-12-2; phenylthiirane, 1498-99-3; methylthiirone, 1072-43-1; 7-thiabicyclo-[4.1.0]heptane, 286-28-2; thietane, 287-27-4; tetrahydrothiophene, 110-01-0; tetrahydro-2*H*-thiopyran, 1613-51-0; *trans*-2-mercaptocyclohexanol, 60861-06-5.

Asymmetric Synthesis. 6.[1] Practical Synthesis of (+)-Solenopsin A[2]

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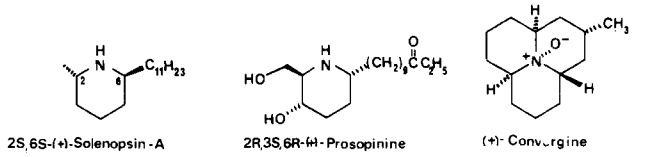
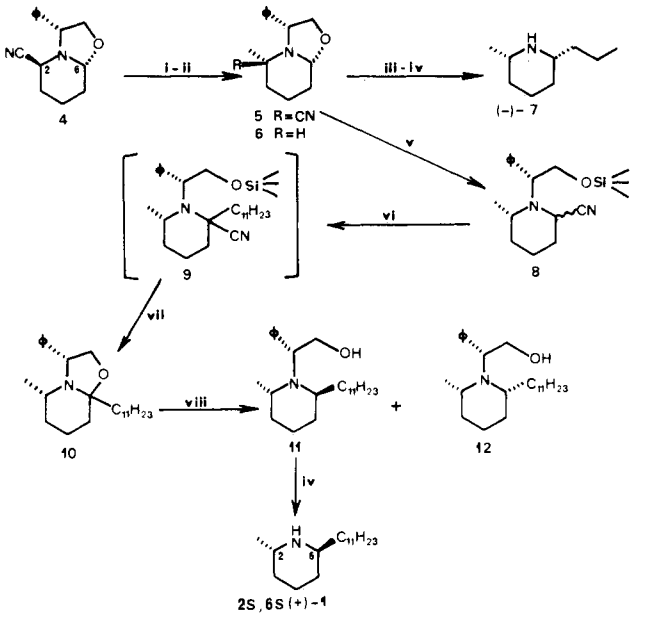
In a recent publication[3] we described the preparation of the (−)-2-cyano-6-oxazolopiperidine synthon **4**, a new chiral 1,4-dihydropyridine equivalent, and showed that selective functionalization of either the C-2 (α-amino nitrile) or C-6 (α-amino ether) centers could be achieved. In particular, it was shown that introduction of a second alkyl substituent at C-6 of intermediate **6** by reaction with PrMgBr was highly stereoselective producing the 2,6-cis substitution pattern typical to the piperidine alkaloid (−)-dihydropinidine (**7**) (Scheme I).

We have now extended our study of synthon **4** to the synthesis of the alternate and generally less accessible 2,6-trans relative configuration which is indigenous to piperidine alkaloids of both animal [i.e., solenopsin A (**1**) and the ladybug alkaloid convergine (**3**)] and plant [i.e., prosopinine (**2**)] origin (Chart I). Our strategy is based upon observations made during earlier work on the stereoselective reductive decyanation of 2-cyanopiperidines[4] and is illustrated by the first enantiospecific synthesis of the fire ant venom solenopsin A (**1**).[5]

Chart I



Scheme I[a]



[a] Reagents: (i) LDA, CH_3I, THF, −78 °C, 2.5 h; (ii) $Zn(BH_4)_2$, $AgBF_4$, THF, −78 °C, 1 h; (iii) PrMgBr, Et_2O, −60 °C, 20 h; (iv) H_2, Pd–C, MeOH; (v) Me_3SiCN, $ZnBr_2$ (catalyst), CH_2Cl_2, Δ, 15 h; (vi) LDA, THF–HMPA, $C_{11}H_{23}Br$, −20 °C, 15 h; (vii) 5% HFaq, CH_3CN; (viii) $NaBH_4$, MeOH, −10 °C, 2 h.

A key step (Scheme I) involved the reaction of intermediate **6** with trimethylsilyl cyanide in the presence of a catalytic amount of $ZnBr_2$ in refluxing CH_2Cl_2 (15 h). Under these conditions the oxazolidine ring was opened, which transformed the C-6 amino ether center to an α-amino nitrile system and converted the liberated hydroxyl group to its *O*-Me_3Si derivative. On rapid filtration of the crude reaction mixture through a short column of silica gel [hexane–ether (8/2)] compound **8** was obtained as a (7:3) mixture of epimers in nearly quantitative yield.

The possibility then existed to generate an anion at C-6 of **8**. Treatment of **8** with lithium diisopropylamide (LDA) in THF proved to be inefficient. However anion formation was readily achieved by reaction with 3 equiv of LDA in THF–HMPA (5 equiv) at −20 °C (30 min). Subsequent reaction of the orange anion solution with undecyl bromide (−20 °C, 15 h) gave **9**. As the crude product mixture invariably contained significant quantities of the recyclized compound **10** a solution of 5% aqueous HF in CH_3CN was generally added to the reaction before extractive workup in order to liberate the alcohol function and effect complete cyclization of **9** to **10**.[6] Compound **10** was isolated in 58% yield as a colorless low-melting crystalline solid after flash chromatography on silica gel.

Reductive cleavage of the oxazolidine ring of **10** was studied under a variety of conditions. In analogy with our earlier results[4] reaction of **10** with $NaBH_4$ in methanol (−10 °C, 2 h) led to formation of a 70:30 mixture of the trans

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0022-3263/86/1951-4475$01.50/0

compound **11** and its cis isomer **12** isolated in 84% combined yield after flash column chromatography [silica gel; hexane–ether (6/4)].

Surprisingly, however, a complete reversal in the trans/cis product ratio was observed when **10** was reacted with $Zn(BH_4)_2$ in THF (room temperature, 15 h) or with $NaBH_4$ in THF containing trifluoroacetic acid (room temperature, 5 min). In both instances a 5/95 mixture of *trans*-**11** and *cis*-**12** was obtained. With $Zn(BH_4)_2$ in ether, nearly equal amounts of both isomers were obtained. The precise influence of change of solvent and/or reducing agent on the reaction outcome has not been determined at the present time.

Final hydrogenolytic cleavage of the chiral appendage in the major product **11** derived from the reaction of **10** with $NaBH_4$–MeOH gave (2*S*,6*S*)-(+)-solenopsin A (**1**) isolated in 95% yield [**1**·HCl: mp 146 °C; $[\alpha]^{20}_D$ +7.5° ($CHCl_3$, *c* 1.3)]. To our knowledge this represents the first chiral synthesis of alkaloid **1**; the optical rotation and absolute sterochemistry of the natural isomer of which have not been reported.

Work is presently in progress toward the synthesis of more complicated 2,6-trans piperidine alkaloid convergine (**3**) (Chart I).

Experimental Section

Infrared spectra (IR) were recorded neat or in chloroform solution on a Perkin-Elmer 297 spectrophotometer. Peaks yielding structural information are reported. ^1H NMR spectra were recorded in $CDCl_3$ (tetramethylsilane as an internal standard, δ 0) on a Bruker WP 80 (80 MHz) and/or the I.E.F.[7] 400 MHz spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ (Me_4Si, δ 0) on a Bruker WP 200 (50 MHz) instrument. Mass spectrometry was performed on a AEI MS 50 by the Mass Spectrometry Service of the ICSN at Gif.

Preparation of 2-Methyl-2-cyano-6-oxazolo[*a*]piperidine (5). The anion of **4** was prepared by slow addition of **4** (1.37 g, 6 mmol) in THF (30 mL) to a cooled (−70 °C) solution of LDA [13.4 mmol; prepared from BuLi (8.4 mL, 1.6 M in hexane) and diisopropylamine (1.87 mL, 13.4 mmol)]. The resulting pale yellow solution was stirred from 15 min before addition of methyl iodide (1.5 mL, 24 mmol). Stirring was continued at −70 °C for 3 h, after which time the reaction was quenched by addition of phosphate buffer (pH 6.2). Once room temperature was reached the reaction mixture was diluted with additional buffer (30–50 mL) and extracted with CH_2Cl_2. The combined organic fractions were washed with H_2O, dried over Na_2SO_4, and concentrated, giving a yellow oil. The crude mixture was separated by flash chromatography on silica gel [hexane–ether (85/15)]. The methylated amino nitrile **5** was obtained as colorless crystals (1.1 g; 75% yield): mp 59 °C (ether–hexane); IR ($CHCl_3$) 2200 cm^{-1} (CN); MS, *m/z* (relative intensity) 242 ($M^{\bullet+}$, 2), 241 (20), 227 (8), 214 (45), 104 (100); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.05 (s, 3 H, CH_3), 1.4–2.1 (m, 6 H, CH_2), 3.72 (dd, J = 8.5, 5 Hz, 1 H, H-8a), 4.0 (dd, J = 8.5, 5 Hz, 1 H, H-9), 4.1 (dd, J = 10, 2 Hz, 1 H, H-6), 4.2 (t, J = 8.5 Hz, 1 H, H-8b), 7.3 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$, 15.08 MHz) δ 20.2 (C-4), 27.6 (CH_3), 29.6, 38.2 (C-3, C-5), 58.0 (C-2), 62.7 (C-9), 74.6 (C-8), 92.1 (C-6), 119.7 (CN), 127.3, 127.8, 128.8, 144.2 (Ar C). Anal. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56; O, 6.60. Found: C, 74.11; H, 7.51; N, 11.64; O, 6.60.

2-Methyl-6-oxazolo[*a*]piperidine (6). Silver tetrafluoroborate (1.02 g, 5.2 mmol) dissolved in dry THF (2 mL) was added under argon to a solution of **5** (0.99 g, 4.1 mmol) in THF (50 mL). A white precipitate formed immediately, and after 5 min at room temperature the mixture was cooled to −60 °C. A ~0.1 M etheral solution of $Zn(BH_4)_2$ (15 mL, 1.5 mmol) was then added slowly via syringe, and stirring was continued for 1.5 h. After this time, 1 mL of water was added slowly with vigorous stirring. The reaction mixture was allowed to rise to room temperature, and more water (~10 mL) was added. The black mixture was filtered through a Celite bed, and the clear solution was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated in vacuo. The residual oil was purified by filtration through a short column of silica gel (CH_2Cl_2 as eluant) to give **6** as a colorless oil (0.836 g, 94% yield). **6** (epimeric mixture ≃ 6:4; not observable on TLC): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.49 (d, J = 6.5 Hz, 0.6 × 3 H, CH_3), ($M^{\bullet+}$, (d, J = 6.5 Hz, 0.4 × 3 H, CH_3), 1–2.3 (m, 6 H, ring CH_2), 3.48 (t, J = 7 Hz, 0.6 H, H-8 or H-9), 3.51 (t, J = 7 Hz, 0.6 H, H-8 or H-9), 3.61 (dd, J = 9.5, 2.5 Hz, 0.4 H, H-6) 3.65 (m, partly overlapped, 0.4 H, H-8a), 4.0 (t, J = 7 Hz, 0.6 H, H-8 or H-9), 4.18 (t, J = 7.5 Hz, 0.4 H, H-9), 4.24 (dd, J = 7.5, 4 Hz, 0.4 H, H-8b), 4.33 (m, 0.4 H, H-6), 7.3 (m, 5 H, Ar); MS, *m/z* (relative intensity) 217 ($M^{\bullet+}$, 68), 216 (70), 202 (100), 148 (40), 117 (47), 104 (95).

Preparation of Amino Nitrile 8. A mixture of oxazolidine **6** (0.6 g, 2.76 mmol), trimethylsilyl cyanide (0.8 mL, 6 mmol), and zinc bromide (0.05 g) in CH_2Cl_2 (60 mL) was refluxed overnight under an argon atmosphere. The crude reaction mixture was then rapidly washed with water, dried over Na_2SO_4, and evaporated to dryness. The oily residue was purified by filtration through a short column of alumina [hexane–ether, (80/20)] to give **8** (0.804 g, 85% yield) as a 65:35 mixture of epimers. **8** (oil): MS, *m/z* (relative intensity) 316 ($M^{\bullet+}$, 1), 301 (3), 289 (4), 217 (3), 214 (15), 213 (100), 202 (3), 187 (7); ^1H NMR ($CDCl_3$, 400 MHz) [major epimer] δ 0.23 (s, 9 H, $SiMe_3$), 1.35 (d, J = 6 Hz, 3 H, CH_3), 1.5–2 (m, 6 H, piperidine ring CH_2), 3.36 (m, J = 12.0, 6.0, 2.0 Hz, 1 H, H-2), 3.57 (dd, J = 5, 2 Hz, 1 H, H-6), [minor epimer] 0.05 (s, 9 H, $SiMe_3$), 1.46 (d, J = 6 Hz, 3 Hz, 3H, CH_3), 1.5–2 (m, 6 H, piperidine ring CH_2), 3.75 (m, 1 H, H-2), 3.86 (m, partly overlapped, 1 H, H-6); ^{13}C NMR ($CDCl_3$, 50 MHz) [major epimer] δ 21.1 (CH_3) 21.3, 30.4, 35.7, 47.1 (C-2), 51.6 (C-6), 59.3, 61.8, 120.2 (CN), [minor epimer] δ 12.0 (CH_3), 15.8, 29.3, 31.2, 46.2 (C-2), 48.8 (C-6), 65.0, 66.6, 120.9 (CN). Anal. Calcd for $C_{18}H_{28}N_2OSi$: C, 68.30; H, 8.91; N, 8.85. Found: C, 68.98; H, 9.0; N, 9.0.

Alkylation of 8. Compound **8** (0.632 g, 2 mmol) in THF (4 mL) was added over 10 min via syringe to a cooled (−20 °C) solution of LDA (6 mmol) + HMPA (10 mmol) in THF (40 mL). The resultant bright orange anion solution was stirred for 1 h before addition of undecyl bromide (0.58 mL, 2.6 mmol). Stirring was continued at −20 °C for 15 h after which time the reaction was stopped by the addition of a solution of 5% aqueous HF in CH_3CN (20 mL). The resultant mixture was stirred for 15 min, neutralized with sodium bicarbonate, diluted with water, and extracted with ether. The combined ether layers were washed with brine, dried over Na_2SO_4, and concentrated to give a pale yellow liquid. Compound **10** was obtained pure as a colorless oil (0.438 g, 59% yield) which solidified in cooling after flash column chromatography on silica gel [hexane–ether (7/3)]: MS, *m/z* (relative intensity) 371 ($M^{\bullet+}$, 5), 356 (1), 279 (3), 244 (12), 217 (42), 216 (100); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, J = 7 Hz, 3 H, CH_3), 0.98 (t, J = 7 Hz, 3 H, CH_3), 1.2–1.8 (m, 26 H, piperidine and side chain CH_2), 2.88 (dq, J = 7, 11 Hz, 1 H, H-2), 3.67 (t, J = 7 Hz, 1 H, H-8 or H-9), 4.20 (ABX_2, J = 6.5 Hz, J = 7 Hz, 2 H, H-8/H-9), 7.2–7.4 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.2 (CH_3), 17.8, 22.3 (CH_3), 22.8, 24.2, 28.2, 29.4, 29.8, 30.1, 31.4, 32.0, 39.9 (piperidine and side chain CH_2), 51.9 (C-2), 67.8 (C-9), 71.5 (C-8), 96.4 (C-6), 127.1, 128.4, 143.1 (Ar).

Reduction of Oxazolidine 10. $NaBH_4$ (0.3 g, 7.9 mmol) was added in portions over 30 min to a cooled (−10 °C) solution of oxazolidine **10** (0.35 g, 0.96 mmol) in MeOH (75 mL). After being stirred for 2 h at −10 °C the reaction was diluted with water (50 mL) and extracted with CH_2Cl_2. The CH_2Cl_2 layers were washed with H_2O, dried over Na_2SO_4, and concentrated, giving a colorless oil (0.348 g) containing two compounds, which were separated by flash chromatography on silica gel [CH_2Cl_2–MeOH (95/5)]. The less polar component *trans*-**11** (0.203 g) was isolated as a colorless oil in 57% yield: MS (IC), *m/z* 374 (MH^+) 356, 254; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 t, J = 6.5 Hz, 3 H, CH_3), 1.12 (d, J = 6 Hz, 3 H, CH_3), 1.2–1.8 (m, 26 H, piperidine and side chain CH_2), 3.09 (m, 1 H, H-6), 3.38 (dq, J = 6, 3 Hz, 1 H, H-2), 3.47 (dd, J = 10, 5 Hz, 1 H, H-8a), 3.89 (t, J = 5 Hz, 1 H, H-9), 4.21 (J = 10, 5 Hz, 1 H, H-8b), 7.3 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1 (CH_3), 20.3, 20.6 (CH_3), 22.7, 26.5, 27.5, 29.4, 29.7, 29.9, 30.1, 32.0, 33.0 (piperidine and side chain CH_2), 48.8 (C-2), 52.9 (C-6), 59.5 (C-9), 60.7 (C-8), 127.6, 128.4, 129.4, 141.3 (Ar).

(7) Institut d'Electronique Fondamentale, Université Paris-Sud 91405 Orsay, France. We thank Dr. S. K. Kan for the use of his 400-MHz ^1H NMR spectrometer.

Anal. Calcd for $C_{25}H_{43}NO$: C, 80.36; H, 11.60; N, 3.75. Found: C, 80.13; H, 11.18; N, 3.94.

The more polar compound *cis*-**12** (0.093 g, 27% yield) was also obtained as a colorless oil: MS (IC), m/z 374 (MH^+); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, J = 6.5 Hz, 3 H, CH_3), 1.13 (d, J = 6 Hz, 3 H, CH_3), 1.1-1.7 (m, 26 H, piperidine and side chain CH_2), 2.75 (dq, J = 9, 6 Hz, 1 H, H-2), 3.16 (m, 1 H, H-6), 3.72 (dd, J = 6, 10 Hz, 1 H, H-8a), 3.85 (dd, J = 7, 10 Hz, 1 H, H-8b), 3.98 (dd, J = 6, 7 Hz, 1 H, H-9), 7.35 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.1 (CH_3), 16.0, 20.9 (CH_3), 22.8, 27.9, 28.4, 29.5, 29.7, 30.0, 30.7, 32.0, 33.8 (piperidine and side chain CH_2), 47.8 (C-2), 56.7 (C-6), 62.3 (C-8), 66.3 (C-9), 127.5, 128.4, 128.5, 140.8 (Ar). Anal. Calcd for $C_{25}H_{43}NO$: C, 80.36; H, 11.60; N, 3.75. Found: C, 80.37; H, 11.59; N, 4.16.

(2*S*,6*S*)-(+)-Solenopsin A (1). A solution of alcohol **11** (0.115 g, 0.3 mmol) in methanol (15 mL) was hydrogenated over 5% Pd/C at atmospheric pressure for 15 h. The reaction mixture was then filtered through a Celite bed and the filtrate concentrated after addition of a few drops of concentrated HCl. The resultant white residue was then dissolved in water (10-15 mL) and extracted with ether to remove phenylethanol. The aqueous solution was then made alkaline with sodium carbonate and extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were dried over Na_2SO_4 and concentrated to give a colorless oil.

The crude product was purified by filtration through a short column of silica gel [CH_2Cl_2-MeOH (95/5)]. By collection and acidification of the appropriate column fractions (+)-solenopsin A (**1**) was isolated as its HCl salt (0.072 g, colorless crystals, 81% yield): **1**·HCl: mp 146 °C (CH_2Cl_2-ether) (lit. mp 114 °C[8]); $[\alpha]^{20}_D$ +7.5° ($CHCl_3$, c 1.3), $[\alpha]^{20}_D$ -1° (MeOH, c 1.7). The ^1H and ^{13}C NMR spectra for **1** were identical with those reported in the literature.[8]

Registry No. **1**, 35285-25-7; **1**·HCl, 104713-87-3; **4**, 88056-92-2; **5**, 104713-83-9; **6** (isomer 1), 104713-84-0; **6** (isomer 2), 104713-88-4; **8** (isomer 1), 104642-00-4; **8** (isomer 2), 104713-85-1; **10**, 104642-01-5; **11**, 104642-02-6; **12**, 104713-86-2; $C_{11}H_{23}Br$, 693-67-4.

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Quenching of Singlet Oxygen by 4-[2-(*N*,*N*-Dimethylhydrazono)ethylidene]-2,6-diphenyl-4*H*-pyran

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It is well-known that singlet oxygen is an active oxygen species and it may be involved in photodegradation of cells by pigments, light, and oxygen in biological systems.[1] Efficient quenchers of $^1O_2$[2] might, therefore, have practical importance. Carotenes,[3] the most efficient quenchers, show protective action against photobleaching of chlorophyll *a* but are not very stable to oxidation. Several tertiary aliphatic amines are capable of inhibiting oxidations by $^1O_2$[4] and DABCO (1,4-diazabicyclo[2.2.2]octane)[5] is often used as convenient quencher in photosensitized oxygenations, but the quenching rates appear to be somewhat lower than with other quenchers. Recently, we found that 1,3,5-triaryl-2-pyrazolines with relatively low oxidation potential are not oxidized by $^1O_2$ but capable of quenching $^1O_2$ efficiently.[6] We now wish to report a novel $^1O_2$ quencher, 4-[2-(*N*,*N*-dimethylhydrazono)ethylidene]-2,6-diphenyl-4*H*-pyran (**1**, first oxidation potential; E_p(anodic) = +0.24 V and E_p(cathodic) = +0.13 V vs. SCE, reversible), which quenches $^1O_2$ efficiently. In preliminary quenching experiments, dye-sensitized photooxidation of 6.3 × 10^{-2} M of diethyl sulfide (k_r = 7 × 10^6 M^{-1} s^{-1}[7]) (rose bengal (RB)/CH_3COCH_3, tetraphenylporphine (TPP)/C_6H_6, and methylene blue (MB)/CH_2Cl_2) was carried out in the presence of 6.3 × 10^{-3} M of pyran **1** and their results obtained are shown in Figure 1.

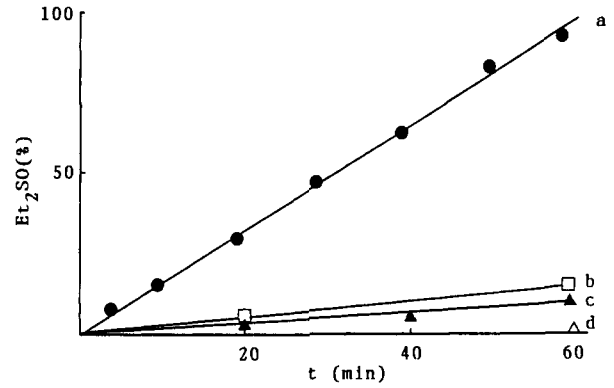
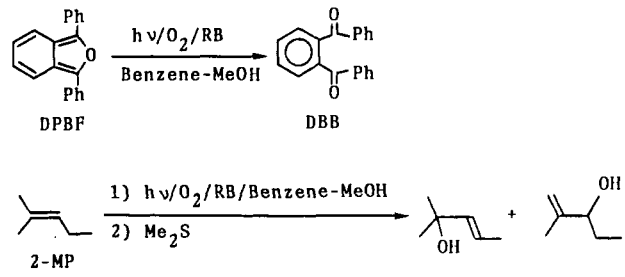
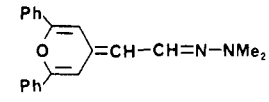


Figure 1. Photosensitized oxygenation of diethyl sulfide in the presence of **1**. Conditions: [Et_2S] = 6.3 × 10^{-2} M; [**1**] = 6.3 × 10^{-3} M; (a) MB/CH_2Cl_2; (b) **1**/RB/CH_3COCH_3; (c) **1**/TPP/C_6H_6; (d) **1**/MB/CH_2Cl_2.

Scheme I





1

The data indicate that the formation of diethyl sulfoxide was apparently suppressed by addition of pyran **1**. These findings encouraged us to carry out an exploratory quenching experiment of $^1O_2$. The quenching efficiency of pyran **1** was determined by measuring the inhibition rate for the oxidation of 1,3-diphenylisobenzofuran (DPBF)[8]

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