heated at 80 °C with protection from moisture. At the time intervals shown in Figure 2, 0.2-mL samples were quickly taken out, diluted with 2 mL of water, and extracted with 2 mL of chloroform. One milliliter of the extract was evaporated to dryness, and the residue treated with 0.2 mL of ethereal diazomethane solution before injection into the gas chromatograph.

Preparation of 2 and 10. One gram of 1 or 9 was dissolved in 10 mL of 85% phosphoric acid and stirred under nitrogen at 80 °C for 20 min (30 min for 9). The mixture was poured onto ice and extracted with ether. The extract was washed with water and reextracted with 15 mL of 4% aqueous NaOH solution. The aqueous layer was neutralized with hydrochloric acid, and 2 or 10 separated as crystals.

2: yield 0.11 g (12%); mp 144-145 °C (2-propanol) (lit.[4] mp 154-155 °C).

10: yield 0.60 g (65%); mp 154-155 °C (2-propanol); IR (KBr) 3300-2550, 1695, 1680, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H), 2.00 (s, 3 H), 3.75 (s, 3 H), 4.17 (s, 2 H), 4.32 (q, 2 H), 7.59 (m, 4 H), 11.10 (br s, 1 H). Anal. Calcd for $C_{18}H_{18}NO_5Cl$: C, 59.43; H, 4.98; N, 3.85. Found: C, 59.22; H, 4.83; N, 4.00.

Preparation of 5 from 1 in 100% Phosphoric Acid. Compound 1 (2.0 g, 8.8 mmol) was dissolved in 100% phosphoric acid prepared by adding 29 mL of 85% phosphoric acid to 14.5 g of P_2O_5, and the solution was heated to 80 °C for 1 h under protection from moisture. The mixture was then poured onto ice and extracted with chloroform. The extract was dried over sodium sulfate and the chloroform evaporated under reduced pressure on a water bath at 20 °C. The residual reddish oil (1.23 g, 86%) was 95% pure (GC) and had a retention time of 4.72 min. Compound 5 is unstable and should be stored in a refrigerator.[20]

1,2,4-Trimethyl-3-(ethoxycarbonyl)-5-(*p*-chlorobenzoyl)-1*H*-pyrrole (11). One gram of 10 was decarboxylated by heating at 210-230 °C under nitrogen for 2 h. The resulting dark oil was crystallized from 2-propanol: pale yellow needles, 0.56 g (65%), mp 119-121 °C; IR (KBr) 3080, 2975, 1675, 1610, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H), 1.97 (s, 3 H), 2.56 (s, 3 H), 3.67 (s, 3 H), 4.28 (q, 2 H), 7.54 (m, 4 H). Anal. Calcd for $C_{17}H_{18}NO_3Cl$: C, 63.85; H, 5.67; N, 4.38. Found: C, 63.95; H, 5.68; N, 4.45.

Decarboxylation of 3 to 8. Diacid 3 was heated at 200-210 °C until evolution of CO_2 ceased. The resulting dark oil was quickly distilled by connecting the reaction flask to the distillation device and water pump: Colorless distillate, bp 160-165 °C,[21] ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H), 2.09 (s, 3 H), 3.31 (s, 3 H), 5.05 (s, 1 H), 6.19 (s, 1 H). Compound 8 is very unstable and turns red when applied to a TLC plate. It can be stored cool under Ar or N_2.

Kinetic Measurements. Solutions of 2 (0.044 M and 0.022 M) were prepared in 84.6% phosphoric acid, and 100 mg (0.44 mmol) of 2 and 0.052 mL (0.88 mmol) of absolute ethanol were mixed with phosphoric acid in a 10-mL volumetric flask. One milliliter of the first two solutions was pipetted into each of 12 test tubes, and 1 mL of the last solution into 8. The tubes were placed in a thermostated water bath at 61 ± 0.1 °C. At 15-min intervals (25 min in the case of 2 and ethanol) the tubes were removed from the bath, and the mixture was diluted with 5 mL of water and extracted with 5 mL of a chloroform solution of 1 (1.9 mg/mL), which served as an internal standard for GC analysis. Then 0.2 mL of the chloroform extract was pipetted out and mixed with 0.1 mL of ethereal diazomethane solution. When evolution of nitrogen ceased, the yellow solution was injected into the gas chromatograph. Values for k_{obsd} were calculated by the least-squares method. Correlation factors were >0.99 for each run.

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Registry No. 1, 33369-26-5; 2, 82875-55-6; 3, 33369-45-8; 4, 79673-54-4; 5, 33369-47-0; 6, 33369-46-9; 8, 931-25-9; 9, 33369-27-6; 10, 94324-21-7; 11, 94324-22-8.

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Photooxygenation of (*R*)-*p*-Mentha-3,8(9)-diene and 1-Isopropenyl-3,4-dihydronaphthalenes. Preparation of (*R*)-Menthofuran, (*R*)-Evodone, and (±)-Chromolaenin[1]

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As part of our study of the competition between "ene" reaction and the 1,4-cycloaddition reaction of singlet oxygen in a series of 1-vinylcycloalkenes **1a** and **1b**,[2] we decided to reinvestigate the photooxygenation of (*R*)-*p*-mentha-3,8(9)-diene (**2**) and to examine the behavior of 1-isopropenyl-3,4-dihydronaphthalenes of type **3** (Chart I).

As regards **2**, its conversion into (*R*)-*p*-menthofuran (**4**) via endoperoxide **5** has been reported,[3] but this intermediate, the sole product mentioned, was not characterized and no yield was given. In analogy with the photooxygenation of **1b** (n = 6),[2] the optically active diene **2** would be expected to give, after $P(OEt)_3$ treatment, not only a mixture of 1,4-cycloaddition products **5a,b** but also minor ene products such as **6a,b** as well as some or all of the compounds (**7a,b**, **8a,b**, **9a,b**, and **10a,b**) resulting from further reactions of **5a,b** and **6a,b** with $^1O_2$. Moreover, as the C-1 methyl group of **2** is presumably pseudoequatorial,[4] it should have little effect on the relative rates of attack (cis or trans) by $^1O_2$, and the proportions of the initial product **5a,b** or **6a,b** could presumably furnish additional information on the direction of $^1O_2$ approach to the reaction site for 1-vinylcycloalkenes.

As regards compounds of type **3a,b**, the only ene reactions which these substances can undergo would lead either to **3c** or to tertiary allylic hydroperoxides **11** in which the double bond is deconjugated. Formation of such products is not in accord with previous experiments in the 1-vinylcyclohexene series,[2] although in 1,2-dihydronaphthalenes of type **12** the ene reaction can compete successfully with 1,4-cycloaddition to the styrene system, the latter leading to compounds of type **13** and their transformation products.[5,6] It was of interest to ascertain whether such reactions could compete with 1,4-cycloaddition to the semicyclic diene system of **3**.

Photooxygenation of 2. (*R*)-3-Menthenol was prepared from (*R*)-(+)-pulegone by the literature method[7] and converted to **2** in 42% yield by dehydration with $POCl_3$-pyridine. Photooxygenation of **2** under our standard conditions[2] gave a 1:1 mixture of the 1,2-dioxin epimers **5a,b**, a 5:4 mixture of the dienols **6a,b**, and a mixture of polar substances in 58%, 10%, and approximately 15% yields, respectively.

The NMR spectra of the two 1,2-dioxin epimers exhibited superimposed signals for H-3, H-3', and the C-4 methyl group, but the signals of H-8a and the C-7 methyl appeared at different fields, δ 4.74 (J = 11 Hz) and δ 1.09

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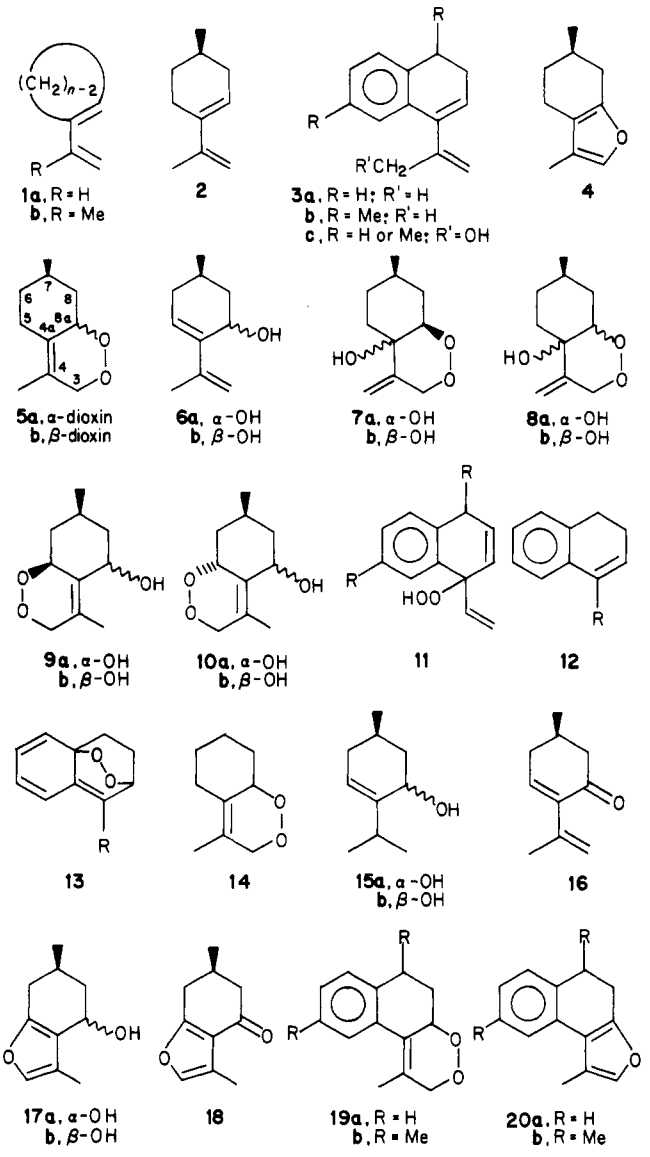
(7) Klein, E.; Ohloff, G. Tetrahedron **1963**, *30*, 2212.

0022-3263/85/1950-0700$01.50/0

Chart I



(J = 6.5 Hz) for isomer A and δ 4.54 and δ 0.96 for isomer B. Since the pseudoequatorial C-1 methyl group of **2** is far removed from the reaction site, the formation of equal amounts of **5a** and **5b** is not unexpected; $^1O_2$ attack on the π-system from the face cis to the C-1 methyl will give **5a** with the methyl group remaining equatorial, whereas attack from the opposite face will give **5b** with the methyl group axial so as to permit the cyclohexane ring to adopt the chair conformation. On this basis one would expect the NMR spectrum of **5a** to be similar to that of the dioxin **14** from 1-isopropenylcyclohexene,[2] hence, the resonance at δ 4.54 was assigned to **5a**. The upfield C-7 methyl resonance was also assigned to **5a** because the signal of an equatorial methyl group on a six-membered ring in the chair conformation usually appears upfield from that in its axial counterpart.

While each component of the **6a,b** mixture exhibited a separate set of NMR signals, the differences between the chemical shifts of each set were too small to permit correlation of either set with one of the pair of similarly constructed allylic alcohols **15a,b**.[9] Oxidation of the mixture furnished a single optically active α,β-unsaturated ketone, **16**. An attempt at cycloaddition of $^1O_2$ to this substance was not successful; this is not surprising as $^1O_2$ is a weak electrophile and the 1,3-diene system is strongly deactivated.

Attempts to separate the polar materials from the photooxygenation of **2** by column chromatography was not satisfactory, but examination of the various fractions by NMR spectrometry indicated that all eight possible further oxygenation products had been formed. Clarification of their constitution was achieved in part by photooxygenation of the **6a,b** mixture (5.5 h, 70% completion). This gave in 73% yield (based on recovered starting material) a mixture of the four diastereomers **9a,b** and **10a,b**, only one of which could be isolated in pure form from the first eluates of silica column chromatography. Its NMR spectrum was not sufficiently distinctive to permit assignment of one of the four possible diastereomeric formulas to this isomer. Treatment of the **9a,b/10a,b** mixture with $FeSO_4$ in aqueous THF achieved its transformation to a 1:1 mixture of the furan alcohols **17a,b** whose oxidation with pyridinium dichromate afforded (*R*)-evodone (**18**).[10] Racemic evodone has been synthesized previously by other routes.[11] Finally, (*R*)-menthofuran was prepared in 85% yield by $FeSO_4$ treatment of the **5a,b** mixture.

The behavior of (*R*)-*p*-mentha-3,8(9)-diene (**2**) in the reaction with $^1O_2$ thus duplicates very closely the behavior of other 1-vinylcyclohexenes, with 1,4-cycloaddition taking precedence over the ene reaction and tertiary allylic hydroperoxides absent from the ene products. Possible reasons for these observations have been discussed.[2]

Photooxygenation of 3a,b. Dienes **3a,b** were synthesized by addition of the appropriate tetralone to isopropylmagnesium bromide followed by dehydration with $POCl_3$–pyridine. Photooxygenation of **3a** at −78 °C in acetone[12] was somewhat sluggish; analytical TLC of the crude product revealed three spots which exhibited a positive test for peroxide. The least polar of these corresponded to **19a** which was isolated in 36% yield (based on recovered starting material); the two more polar fractions were mixtures of peroxides and nonaromatic by NMR criteria but decomposed too rapidly to permit adequate characterization. As **19a** resisted further photooxygenation, we assume that the polar fractions represented products resulting from competitive cycloaddition of $^1O_2$ to the styrene system. Analogously, photooxygenation of **3b** at 78 °C in acetone afforded 31% of **19b**, which was a mixture of diastereomers, and polar peroxide fractions which decomposed rapidly.

$FeSO_4$ treatment of **19a** and **19b** in aqueous THF afforded the corresponding furan derivatives **20a** and **20b** in 88% and 92% yields, respectively. Furan **20b** is (±)-chromolaenin (laevigatin), first isolated in optically active form of unknown absolute configuration from *Chromolaena laevigata* (Lam.) King and Robinson.[14,15] We have suggested[16] that the photooxygenation–Fe(II)-induced rearrangement route mimics the path by which terpenoid furans are formed in nature; a conventional synthesis of

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(±)-chromolaenin in six steps from 4,7-dimethyltetralone has been reported.[17]

Experimental Section[18]

Photooxygenation of (*R*)-Mentha-3,8(9)-diene. (*R*)-3-Menthen-8-ol was prepared from (*R*)-(+)-pulegone by the literature method:[7] bp 59–60 °C (0.6 mm); $[\alpha]^{24.5}_{D}$ +92.9° ($CHCl_3$); NMR δ 5.70 (br, H-3), 1.46 (OH), 1.32, 1.31 (C-8 methyls), 0.96 (d, *J* = 6.5 Hz, C-1 methyl). To a solution of 6.77 g of the allylic alcohol in 36 mL of pyridine was added at 0 °C with stirring 36 mL of $POCl_3$. Stirring was continued overnight at room temperature; the mixture was poured into ice water and worked up in the usual manner, affording 2.51 g (42%) of **2**: bp 89–90 (33 mm); $[\alpha]^{27}_{Hg}$ +185.1° ($CHCl_3$); NMR δ 5.84 (t, *J* = 2.5 H-2, H-3), 4.95 and 4.83 (both br, H-9), 1.90 (vinyl methyl), 1.29 (m, H-1), 0.98 (d, *J* = 6.5 Hz, C-1 methyl).

Reaction of 1.65 g of the diene with singlet oxygen, addition of 2 g of $P(OEt)_3$, and flash chromatography of the crude product gave 1.17 g (58%) of a 1:1 mixture of C-4a epimers **5a,b**, 0.18 g (9.9%) of a 5:4 mixture of C-3 epimers **6a,b**, and 0.35 g of a polar fraction containing **9a,b**/**10a,b**/(vide infra) and the tertiary alcohols **7a,b**/**8a,b** (NMR analysis) contaminated with triethyl phosphate. Isomer mixture **5a,b** (8a*R* and 8a*S*,7*R*)-3,5,6,7,8,8a-hexahydro-4,7-dimethyl-1,2-benzodioxin, was a gum: IR (neat) 1458, 1386, 1030, 1024, 960, 820, 738, cm^{-1}; NMR δ 4.74 (br d, *J* = 11 Hz, H-8a of **5b**), 4.64 and 4.11 (both d, *J* = 15 Hz, H-3 of both epimers), 4.54 (br d, *J* = 11 Hz, H-8a of **5a**), 1.63 (vinyl methyls of both epimers), 1.09 (d, *J* = 6.5 Hz, C-7 methyl of **5b**), 0.96 (d, *J* = 6.5 Hz, C-7 methyl of **5a**); MS, *m*/*z* (relative intensity) 168 (M^+, 18), 150 (11), 139 (17), 136 (45), 121 (32), 107 (50), 93 (42), 79 (56), 69 (60), 55 (100).

Isomer mixture **6a,b** (1*R*,3*R* and 3*S*)-mentha-4(5),8(9)-dien-3-ol, was also a gum: IR (neat) 3340, 1630, 1605, 1280, 1168, 1032, 898, 830 cm^{-1}; NMR δ 5.96 (dd, *J* = 5.5, 2.5 Hz, H-5 of major isomer), 5.87 (m, H-5 of minor isomer), 5.22 and 5.03 (H-9 of major and minor isomer), 4.99 (H-9′ of both isomers), 4.59 and 4.57 (both m, H-3 of major and minor isomer), 1.89 (vinyl methyl of both), 1.01 and 1.00 (both d, *J* = 6.5 Hz, C-1 methyl of minor and major isomer); MS, *m*/*z* (relative intensity) 152 (M^+, 44), 137 (23), 135 (37), 134 (29), 123 (78), 119 (42), 109 (69), 95 (83), 82 (92), 67 (100), 55 (76).

A solution of 50 mg of isomer mixture **6a,b** in 1 mL of CH_2Cl_2 was oxidized with 90 mg of pyridinium dichromate at 0 °C for 5 h. Workup in the usual fashion gave 37 mg (82%) of (*R*)-mentha-4(5),8(9)-dien-3-one (**16**), previously obtained only as part of a mixture:[19] $[\alpha]^{27}_{Hg}$ −89.6° ($CHCl_3$); IR (neat) 3070, 1672, 1630, 1220, 1132, 1024, 905 cm^{-1}; NMR δ 6.81 (dd, *J* = 5.5, 3 Hz, H-3), 5.11 and 5.01 (H-9), 1.90 (vinyl methyl), 1.06 (d, *J* = 6.5 Hz, C-1 methyl); MS, *m*/*z* (relative intensity) 150 (M^+, 100), 135 (57), 122 (14), 108 (28), 91 (28), 79 (95), 67 (33); M_r calcd for $C_{10}H_{14}O$ 150.1044, found (MS) 150.1036. This substance resisted further oxygenation.

(*R*)-Menthofuran (4). A solution of 200 mg of **5a,b** in 15 mL of THF and 400 mg of $FeSO_4 \cdot 7H_2O$ in 15 mL of H_2O was stirred for 5 h and worked up as described.[16] This furnished 153 mg of **4**: $[\alpha]^{24.5}_{D}$ +85°; NMR δ 7.02 (br, H-2), 2.64 (dd, *J* = 15.5, 5.5 Hz,), 2.34 m (2 H) and 2.15 (m, allylic protons), 1.85 (m, 2 H, H-5), 1.91 (d, *J* = 1.5 Hz, vinyl methyl), 1.35 (ddd, *J* = 13, 11, 6.5 Hz, H-6), 1.07 (d, *J* = 6.5 Hz, C-6 methyl).

(*R*)-Evodone (18). (a) Photooxygenation of 120 mg of isomer mixture **6a,b** in 20 mL of CH_2Cl_2–MeOH (19:1) containing 1×10^{-4} M rose bengal for 5.5 h, workup in the usual manner, and column chromatography gave 37 mg of starting material and 74 mg of a mixture (NMR analysis) of diastereomeric (7*S*)-3,5,6,7,8,8a-hexahydro-4-methyl-1,2-benzodioxin-5-ols **9a,b** and **10a,b**, which were also present in the polar fraction from photooxygenation of mentha-3,8(9)-diene (vide supra). A small amount (4 mg) of one of these could be isolated in pure form from the first few eluate fractions: IR (neat) 3310, 1680, 1115, 1060, 1036, 987, 978, 884 cm^{-1}; NMR δ 4.47 and 4.16 (both d, *J* = 16 Hz, H-3), 4.35 (c, H-5, H-8a), 1.92 (C-4 methyl), 1.52 (OH), 1.00 (d, *J* = 7 Hz, C-7 methyl); MS, *m*/*z* (relative intensity) 184 (M^+, 10), 166 (11), 152 (10), 137 (11), 123 (43), 109 (34), 99 (76), 95 (44), 81 (39), 69 (100), 55 (77); M_r calcd for $C_{10}H_{16}O_3$ 184.1098, found (MS) 184.1089.

A solution of 60 mg of the isomer mixture in 5 mL of THF and 135 mg of $FeSO_4 \cdot 7H_2O$ in 5 mL of water was stirred for 5 h at room temperature and worked up in the usual manner. This furnished 38 mg (76%) of a 1:1 mixture of epimeric furan derivatives **17a,b**: IR (neat) 3330, 1635, 1562, 1089, 1052, 994, 965, 842, 748 cm^{-1}; NMR of epimer A 7.03 (br, H-2), 4.79 (m, H-4), 2.07 (d, *J* = 1.8 Hz, C-3 methyl), 1.07 (d, *J* = 7 Hz, C-6 methyl); NMR of epimer B δ 7.04 (br, H-Z), 4.71 (t, *J* = 3 Hz, H-4), 2.04 (d, *J* = 1.8 Hz, C-3 methyl), 1.07 (d, *J* = 7 Hz, C-6 methyl); MS *m*/*z* (relative intensity) 166 (M^+, 64), 149 (19), 148 (9), 133 (7), 124 (100), 109 (6), 89 (31), 71 (57), 56 (40); M_r calcd for $C_{10}H_{14}O_2$ 166.0994, found (MS) 166.1008.

Oxidation of 20 mg of this mixture in 1 mL of CH_2Cl_2 with 38 mg of pyridinium dichromate at 0 °C for 5 h and workup in the usual fashion gave 12 mg of (*R*)-evodone (**18**) as a slightly colored solid: MS, *m*/*z* (relative intensity) 164 (M^+, 31), 149 (25), 137 (7), 122 (29), 110 (7), 97 (17), 83 (21), 73 (100). IR and NMR spectra of the product were identical with those of (±)-evodone synthesized by other methods.[11] Scarcity of pure material prevented accurate determination of melting point and rotation.

1-Isopropenyl-3,4-dihydronaphthalene (3a). To a 10% excess of isopropenylmagnesium bromide, prepared from 2-bromopropene and magnesium powder in dry THF, was added a solution of 7 g (47.9 mmol) of α-tetralone over a 15-min period in a nitrogen atmosphere. The mixture was heated at reflux for 2 h, cooled, poured into saturated NH_4Cl solution, and extracted with ether. To a solution of the crude alcohol in pyridine was added dropwise at 0–5 °C (N_2 atmosphere) a 10% excess of $POCl_3$ with stirring. After 24 h at room temperature, the mixture was poured into ice water and extracted with ether. Evaporation of the washed and dried extract followed by distillation at reduced pressure gave 4.1 g (51%) of **3a**; bp 45–46 °C (0.4); IR (neat) 3010–3050, 1630, 1600, 1450, 1407, 1020, 905, 835, 775, 775 cm^{-1}; NMR δ 7.2 (c, 4 Ar protons), 5.97 (t, *J* = 5 Hz, H-2), 5.08 and 5.02 (br, exocyclic vinyl H), 2.74 (t, *J* = 7.5 Hz, H-4a,b), 2.15 (m, H-3a,b), 1.96 (vinyl methyl); MS, *m*/*z* (relative intensity) 170 (M^+, 64), 155 (100), 141 (27), 129 (48), 115 (22). The elemental analyses remained unsatisfactory. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 89.89; H, 8.15.

4,7-Dimethyl-1-isopropenyl-3,4-dihydronaphthalene (3b). Freshly distilled 4,7-dimethyl-1-tetralone, 10.4 g, was transformed into 7.0 g (59% overall yield) of **3b** by the method described in the preceding paragraph: bp 53–55 °C (0.4 mm); IR (neat) 3020–3065, 1630, 1600, 1490, 1450, 1370, 1030, 900, 875, 820 cm^{-1}; NMR δ 7.05 (c, 4 Ar protons), 5.87 (t, *J* = 5 Hz, H-2), 5.07 and 5.00 (br, exocyclic vinyl H), 2.28 (C-7 methyl), 1.95 (vinyl methyl), 1.24 (d, *J* = 7 Hz, C-4 methyl). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.64; H, 9.12.

Photooxygenation of 3a. Reaction of 1.5 g of **3a** in 200 mL of acetone containing 20 mg of rose bengal with $^1O_2$ at −78 °C for 30 min followed by the usual workup and flash chromatography resulted in recovery of 624 mg of **3a** and isolation of 376 mg (36% based on recovered material) of **19a**: mp 76–77 °C; IR (KBr) 3020–3095, 1645 cm^{-1}; NMR δ 7.3 (c, 4 Ar protons), 4.92 (m, H-11), 4.81 and 4.35 (both d, *J* = 16.5 Hz, H-3, H-3′) 1.96 (C-4 methyl); M_r calcd for $C_{13}H_{14}O_2$ 202.0993, found (MS) 202.1004. The substance resisted further photooxygenation. Two other more polar fractions were obtained in 196- and 225-mg yields, respectively. After repurification by preparative TLC, the NMR spectra which contained no signals downfield of δ 6.5 still indicated the presence of mixtures which decomposed on standing.

Photooxygenation of **3a** (1 g) in 200 mL of acetone at 10 °C for 1 h afforded 568 mg (48%) of **19a**; photooxygenation of **3a** (1 g) in 200 mL of CH_2Cl_2–5% MeOH at 10 °C gave 555 mg (47%).

Photooxygenation of 3b. Reaction of 1 g of **3b** in 200 mL of CH_2Cl_2–5% MeOH containing 20 mg of rose bengal with $^1O_2$ for 1 h showed complete reaction, with one less polar spot and a more polar streak. After the usual workup the residue was chromatographed over 65 g of silica gel and yielded 298 mg (26%) of **19b**: IR (neat 3095, 1650 cm^{-1}, NMR δ 7.15 (c, 4 Ar protons), 4.76–5.08 (c, H-3, H-11), 4.76–5.08 (c, H-3, H-11), 4.35 (d, *J* = 16.5

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(18) For general methods, see ref 2.
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(20) Johnson, W. S.; Jones, A. R. *J. Am. Chem. Soc.* **1947**, *69*, 792.

Hz, H-31), 2.36 (C-6 methyl), 1.98 and 1.91 (C-4 methyl in two diastereomers), 1.32 (d, J = 7 Hz, C-9 methyl); M_r calcd for $C_{15}H_{18}O_2$ 230.1306, found (MS) 230.1289.

The polar fractions decomposed rapidly and could not be studied satisfactorily. Photooxygenation of 1 g of **3b** in acetone at 10 °C for 1 h gave 418 mg (36%) and photooxygenation of 1.5 g of **3b** in acetone at 78 °C gave 279 mg (31% based on recovered diene) at **19b**.

1-Methyl-4,5-dihydronaphtho[2,1-*b*]furan (20a). Reaction of 0.2 g of **19a** in 15 mL of THF with 0.4 g of $FeSO4{\cdot}7H_2O$ in 20 mL of H_2O at room temperature for 2 h followed by the usual workup and chromatography over 20 g of silica gel gave 0.16 g (88%) of **20a**: mp 37-38 °C; IR (KBr) 3010-3110, 1625, 1550, 1500, 1382, 1348, 1150, 1098, 993, 770, 750, 732 cm^{-1}; NMR δ 7.09-7.48 (c, 5 Ar protons), 3.04, (t, J = 8 Hz, H-5a,b) 2.84 (t, J = 8 Hz, H-4a,b), 2.30 (C-1 methyl); M_r calcd for $C_{13}H_{12}O$ 184.0887, found (MS) 184.0860.

(±)-Chromolaenin. Reaction of 0.2 g of **19b** with $FeSO_4{\cdot}7H_2O$ in the manner described above furnished 169 mg (92%) of **19b**. The spectra data (IR, ^1H and ^{13}C NMR, MS) of the synthetic material were identical with those reported for chromolaenin by Bohlmann and Zdero.[14]

Registry No. **2**, 62192-80-7; **3a**, 94348-46-6; **3b**, 94348-47-7; **4**, 17957-94-7; **5a**, 94425-39-5; **5b**, 94425-40-8; **6a**, 94348-40-0; **6b**, 94348-41-1; **7a**, 94348-43-3; **7b**, 94425-44-2; **8a**, 94425-45-3; **8b**, 94425-46-4; **9a**, 94348-42-2; **9b**, 94425-41-9; **10a**, 94425-42-0; **10b**, 94425-43-1; **16**, 74285-05-5; **17a**, 94348-44-4; **17b**, 94348-45-5; **18**, 529-63-5; **19a**, 94348-48-8; **19b**, 94348-49-9; **20a**, 94348-50-2; **20b**, 74111-42-5; (*R*)-3-menthen-8-ol, 24302-23-6; 4,7-dimethyl-1-tetralone, 28449-86-7.

Does a 1,4-Hydrogen Shift Occur in β-(Alkylthio)ethyl Radicals?

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It is well-known that radical rearrangements involving migrations from carbons in position 1 to carbons in position 4 are seldom observed.[1-3] Krusic and Kochi suggested,[4] however, that a 1,4-hydrogen shift might occur in the β-methoxyethyl radical; this rearrangement would in fact explain the observation of the ESR spectrum of $\dot{C}H_2OCH_2CH_3$ when cyclopropane solutions of β-methoxypropionyl peroxide are photolyzed within the cavity of an ESR spectrometer:

$$(CH_3OCH_2CH_2COO)_2 \xrightarrow{h\nu} 2CO_2 + 2CH_3OCH_2\dot{C}H_2$$

$$CH_3OCH_2\dot{C}H_2 \text{—}\bigcirc\text{—} \dot{C}H_2OCH_2CH_3$$

Subsequently we detected[5,6] ESR spectra that might conceivably arise from an analogous rearrangement occurring when thiyl radicals undergo addition to cyclic olefins. In these cases the spectra of the rearranged radicals were quite intense and in few circumstances[6] they turned out to be the only species detectable by ESR. On the other hand no such rearrangement was reported when the same addition occurs with linear ethylenic derivatives.[4] The present work was thus undertaken with the purpose of ascertaining as to whether the ESR spectra of these rearranged intermediates are also observable in the course of addition of thiyl radicals to ethylene. Even more important for assessing the occurrence of the migration is to verify that the rearranged radicals are formed even when the precursors are produced by a different, independent reaction. A number of experiments that apparently achieved this goal were carried out and the implications of these results are hereafter discussed.

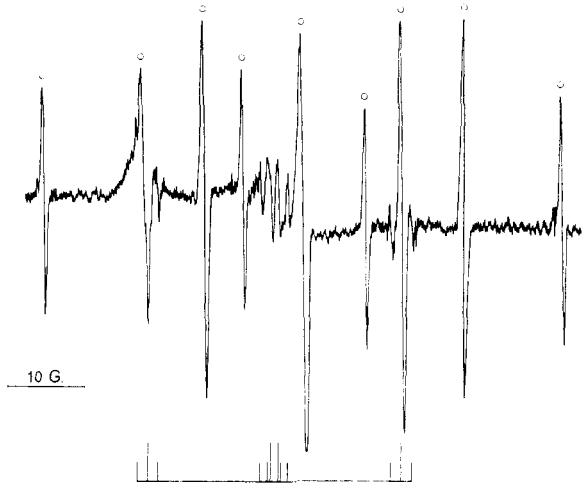

Figure 1. ESR spectrum obtained by photolyzing at -140 °C a cyclopropane solution of MeSSMe and $CH_2{=}CH_2$. The main signals (labeled with circles) are those of $\dot{C}H_3SCH_2CH_2$ (**1**); those of lower intensity belong to the radical $\dot{C}H_2SCH_2CH_3$ (**2**). The stick diagram reconstruction of the latter spectrum (two different α-hydrogens and two equivalent γ-hydrogens) is shown underneath.

Careful inspection of the ESR spectra obtained at -140 °C by photolysis of dimethyl disulfide (CH_3SSCH_3) and ethylene in cyclopropane (Figure 1) reveals that, besides the signals of the main radical due to addition of $CH_3\dot{S}$ to $CH_2{=}CH_2$ ($CH_3SCH_2\dot{C}H_2$, **1**), also those of a minor component are present. The a_H splittings (Table I) and the g factor (2.0049) of this second radical are consistent[7] with the structure $\dot{C}H_2SCH_2CH_3$ (**2**).

Actually we obtained the same spectrum from bromomethyl ethylsulfide according to the reaction

$$Me_3SnSnMe_3 \rightarrow 2Me_3\dot{S}n$$

$$Me_3\dot{S}n + BrCH_2SCH_2CH_3 \rightarrow \underset{\mathbf{2}}{\dot{C}H_2SCH_2CH_3}$$

Addition to ethylene of both $CH_3CH_2\dot{S}$ and n-Bu$\dot{S}$, obtained from the appropiate disulfides, confirms that the ESR spectra of the main radicals $RCH_2SCH_2\dot{C}H_2$ (**3**, R = Me, and **4**, R = n-Pr) are always accompanied by those of the radicals **5** ($Me\dot{C}HSCH_2CH_3$) and **6** (n-Pr$\dot{C}$HSCH_2CH_3), respectively. We checked again that radical **5** has the same spectrum[8] as that obtainable by H-abstraction with t-Bu$\dot{O}$ from diethyl sulfide (EtSEt) at a similar low temperature (Table I).

These observations seem to substantiate the hypothesis that once addition of $RCH_2\dot{S}$ (R = H, Me, n-Pr) to ethylene

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