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 FeSO4·7H_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 $FeSO_4·7H_2O$ 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:

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

$$CH_3OCH_2\dot{C}H_2 \xrightarrow[\circlearrowright]{} \dot{C}H_2OCH_2CH_3$$

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.

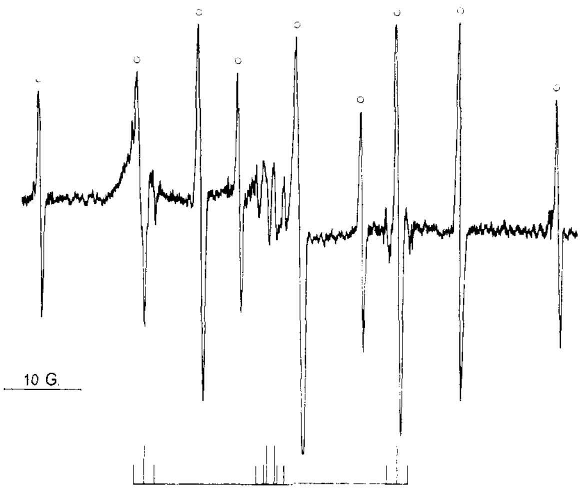

Figure 1. ESR spectrum obtained by photolyzing at −140 °C a cyclopropane solution of MeSSMe and $CH_2{=}CH_2$. The main signals (labeled with circles) are those of $CH_3SCH_2\dot{C}H_2$ (1); those of lower intensity belong to the radical $\dot{C}H_2SCH_2CH_3$ (2). The stick diagram reconstruction of 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

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

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

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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Table I. Hyperfine Spliting Constants (Gauss) of Radicals 1-7 Obtained in Cyclopropane by means of the Various Reactions Described in the Text (*g* Factors: for 1, 3, 4, and 7, 2.0026 ± 0.0001; for 2, 5, and 6, 2.0049 ± 0.0001)

no.	radical	T, °C	$a_{H\alpha}$	$a_{H\beta}$	$a_{H\gamma}$	ref
1	$CH_3SCH_2\dot{C}H_2$	−130	20.3 (2 H)	12.9 (2 H)		4
		−90	20.2 (2 H)	13.5 (2 H)		
2	$CH_3CH_2S\dot{C}H_2$	−140	16.25 (1 H) 17.25 (1 H)		1.4 (2 H)	7
3	$CH_3CH_2SCH_2\dot{C}H_2$	−145	21.1 (2 H)	13.4 (2 H)		
		−115	21.5 (2 H)	14.4 (2 H)		
4	n-$PrCH_2SCH_2\dot{C}H_2$	−115	21.2 (2 H)	14.2 (2 H)		
5	$CH_3\dot{C}HSCH_2CH_3$	−145	16.5 (1 H)	20.25 (3 H)	0.9 (2 H)	
		−115	16.75 (1 H)	20.5 (3 H)	0.9 (2 H)	8
6	n-$Pr\dot{C}HSCH_2CH_3$	−115	16.8 (1 H)	16.8 (2 H)		
7	t-$BuSCH_2\dot{C}H_2$	−115	21.4 (2 H)	15.9 (2 H)		4

has generated the major radicals $\dot{C}H_2CH_2SCH_2R$ (**1**, **3**, **4**) they may rearrange (1,4-hydrogen shift) to give also the radicals $CH_3CH_2S\dot{C}HR$ (**2**, **5**, **6**), according to the sequence

$$RCH_2SSCH_2R \rightarrow 2RCH_2\dot{S}$$

$$RCH_2\dot{S} + CH_2{=}CH_2 \rightarrow \dot{C}H_2CH_2SCH_2R$$

$$R = H, Me, n\text{-}Pr$$

$$\dot{C}H_2CH_2SCH_2R \xrightarrow[\circlearrowleft]{} CH_3CH_2S\dot{C}HR$$

$$R = H, Me, n\text{-}Pr$$

The driving force for this process could be the greater stability of the rearranged radicals with respect to their precursors, owing to the possibility for the unpaired electron on the α-carbon to conjugate with the adjacent sulfur atom. Contrary to what we found[9] in the case of the $MeSS\dot{C}H_2$ radical, the spectra of these minor species appear simultaneously with those of the major radical; it seems therefore unrealistic to propose that they are generated from byproducts accumulated during the photolytic process.

As already mentioned, the signals of the rearranged radicals are better detected at very low temperatures (below −120 °C). This behavior can be understood considering that addition of thiyl radicals to double bonds is an exothermic, reversible process.

$$RCH_2\dot{S} + CH_2{=}CH_2 \rightleftarrows RCH_2SCH_2\dot{C}H_2$$

The equilibrium is thus shifted to the right when the temperature is lowered,[10,11] and, as a consequence, also the amount of the rearranged radical increases along with that of its precursor.

If the radicals $R\dot{C}HSCH_2CH_3$ (**2**, **5**, **6**) actually derive from $RCH_2SCH_2\dot{C}H_2$ (**1**, **3**, **4**), they should be detectable even when the precursors are produced by reactions other than addition. Accordingly we produced radicals **3** and **4** by the following reaction sequence, starting from the appropriate bromine derivatives.

$$Me_3SnSnMe_3 \xrightarrow{h\nu} 2Me_3\dot{Sn}$$

$$Me_3\dot{Sn} + BrCH_2CH_2SCH_2R \rightarrow \dot{C}H_2CH_2SCH_2R$$

$$\mathbf{3}, R = Me; \mathbf{4}, R = n\text{-}Pr$$

In both cases the spectra of radicals **5** and **6** appeared simultaneously with those of **3** and **4**. On the other hand when $BrCH_2CH_2SBu$-t undergoes the same reaction, only the radical $\dot{C}H_2CH_2SBu$-t (**7**) is observed.[12] This can be explained by the absence of hydrogens in position 4 to the carbon bearing the unpaired electron which prevents the rearrangement to occur.

It seems thus safe to conclude that intermediates of general structure $CH_3CH_2S\dot{C}HR$ accompany at low temperatures the radicals $\dot{C}H_2CH_2SCH_2R$, whichever reaction is used to generate the latter. The intensity of these minor radicals is however much lower than in the cyclic derivatives,[5,6] thus suggesting that conformational preferences are important factors in this rearrangement. As to whether this is a genuine intramolecular rearrangement or an intermolecular reaction involving the $\dot{C}H_2CH_2SCH_2R$ radicals has yet to be unambiguously proved. We wish to mention, however, that the spectral intensity of the rearranged radicals is independent of the initial concentration of the reactants either in the addition or in the bromine abstraction reactions. This could be taken as an indication that an intramolecular mechanism is more likely than an intermolecular one.

Experimental Section

Materials. Bromomethyl ethyl sulfide ($BrCH_2SCH_2CH_3$) was obtained from trihydroxymethyl (trimer of formaldehyde) and ethyl mercaptan according to the method of Böhme[13] by substituting hydrochloric acid with gaseous HBr: bp 144 °C; ^1H NMR (CCl_4) δ 1.33 (3 H, t, J = 7.3 Hz), 2.68 (2 H, q, J = 7.3 Hz), 4.6 (2 H, s).

Bromoethyl ethyl sulfide ($BrCH_2CH_2SCH_2CH_3$) was obtained according to the literature.[14]

Bromoethyl *tert*-butyl sulfide ($BrCH_2CH_2SBu$-t) was prepared by mixing a benzene solution (40 ml) of *tert*-butyl mercaptan (2.8 mL, 0.025 mol) and 1,2-dibromoethane (2.15 mL, 0.025 mol) with an aqueous solution (40 mL) of sodium hydroxide 10 N (4 mL, 0.04 mol).

A few drops of tricaprilmethylammonium chloride (Aliquat 336) were subsequently added and the system was vigorously stirred at room temperature for 3 h. The organic layer was separated, washed with water up to neutrality, and dried (Na_2SO_4). After eliminating the solvent under vacuum, the residue (3.2 g) was distilled (73 °C at 8 mmHg): ^1H NMR (CCl_4) δ 1.3 (9 H, s), 2.9 (2 H, m), 3.3 (2 H, m).

Bromoethyl butyl sulfide ($BrCH_2CH_2SBu$-n) was obtained from 1,2-dibromoethane, n-butyl mercaptan, and MeONa in methanol: bp 83 °C at 4.5 mmHg; ^{13}C NMR ($CDCl_3$) δ 34.1 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 30.5 (CH_2), 21.8 (CH_2), 13.5 (CH_3).

Ethyl disulfide (bp 45 at 15 mmHg) was obtained from ethyl mercaptan, NaOH, and iodine.[15]

Spectral Measurements. The samples were prepared mixing the reactants in Suprasil quartz tubes connected to a vacuum line and condensing the gaseous materials with liquid nitrogen by the usual freeze–thaw technique. The samples, sealed under vacuum, were subsequently introduced in the precooled cavity of the ESR spectrometer (Varian E-4). Photolysis was accomplished with a 500-W high-pressure mercury lamp carefully focused into the ESR cavity.

Acknowledgment. Thanks are due to Prof. J. K. Kochi (Houston) for helpful comments. This work has been

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carried out with the financial support of the ministry of Public Education (Rome).

Registry No. 1, 31452-21-8; 2, 40921-46-8; 3, 94500-16-0; 4, 94500-17-1; 5, 16648-23-0; 6, 94500-18-2; 7, 31452-22-9; CH_3SSCH_3, 624-92-0; $Me_3Sn\cdot$, 17272-57-0; $CH_3S\cdot$, 7175-75-9; $MeCH_2S\cdot$, 14836-22-7; $PrCH_2S\cdot$, 16812-18-3; $BrCH_2SCH_2CH_3$, 36056-14-1; $BrCH_2CH_2SCH_2CH_3$, 35420-95-2; $BrCH_2CH_2SBu$-*t*, 5755-60-2; $BrCH_2CH_2SBu$-*n*, 94500-19-3; ethyl disulfide, 110-81-6; ethylene, 74-85-1; cyclopropane, 75-19-4.

The Decomposition of Cumyl Peracetate on Silica

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The decomposition of cumyl peracetate follows heterolytic (Criegee), homolytic, or mixed heterolytic–homolytic pathways, depending on the polarity of the solvent and the presence of acid catalysts.[1,2] In acetic acid the rate (moderately fast at room temperature) and products (phenol, acetone, and 2-phenoxypropene) are characteristic of the heterolytic mode.[1] In nonpolar or moderately polar solvents such as toluene, the low rate (conveniently measured at 70 to 90 °C) and the products (mainly carbon dioxide, methane, and acetophenone, with lesser amounts of phenol, acetone, and 2–phenoxypropene) correspond to a mixed homolytic–heterolytic reaction.[2] The yield of 2-phenoxypropene is increased to 83% in the presence of trichloroacetic acid catalyst.[2]

In nonpolar solvents the decomposition rates are often erratic and difficult to reproduce, possibly because of reactions on the wall of the reaction vessel. The rate of the reaction in toluene in a Pyrex container is 40% greater when freshly crushed Pyrex is added.[2] It is also well-known that a number of reactions subject to homogeneous acid catalysis in solution are fast even on neutral silica. These observations impelled us to examine the perester decomposition on silica surfaces, with the object of identifying the heterogeneous part of the reaction.

Results

The rates of decomposition of the perester in silica slurries were too high to permit the removal of the solvent to confine the reaction to the adsorbed phase. With P_0 silica[3] the rate constant in a stirred chloroform slurry was $8.6 \times 10^{-4}\ s^{-1}$ at 26 °C, which is faster than the extrapolated rate in toluene by 6 orders of magnitude and faster than the rate[1] in acetic acid by a factor of 30. The products from the reaction in a chloroform slurry of this silica were phenol (98% and 94%), acetic acid (89% and 92%), and acetone (88%). An IR band at 1763 cm^{-1}, probably due to the Criegee rearrangement product, 2-acetoxy-2-phenoxypropane, vanishes when the solution of reaction products is washed with water.

Similar experiments were carried out with slurries of P_1 silica.[3] Although the properties of P_1 silica as a medium for reactions confined to the surface, i.e., in the absence of liquid solvent, are often somewhat different from those of P_0 silica under the same solvent-free conditions,[4] the results from the two silicas appear to be the same in the present experiments.[8] The rate constant in a stirred chloroform slurry of P_1 silica at 26 °C was $9.6 \times 10^{-4}\ s^{-1}$. The products from the reaction in a pentane[5] slurry of P_1 silica were phenol (96%), acetic acid (89%), and acetone (91%).

Experimental Section

The chloroform slurry rates were determined from the carbonyl IR band of the perester in the supernatant liquid of samples of the slurry. The slurry was prepared from 50 mL of $CHCl_3$, 10.0 g of the silica, and 0.010 mol of the perester.

In a typical product determination, a solution of about 1 g of the perester in 25 mL of the solvent was added, with stirring, to a slurry of 25 g of the silica and 50 mL of the solvent. The slurry was filtered, products were removed from the silica by extraction with ether, and the ether combined with the filtrate. Phenol was determined by GLC using 4-methyl-2,6-di-*tert*-butylphenol as the internal standard and confirmed by isolation and weighing of the tribromophenol derivative. Acetic acid was determined by titration with alkali. Acetone was separated from the reaction mixture by distillation after neutralization of the acetic acid. The acetone in the distillate was determined gravimetrically as iodoform.

The perester was made from cumyl hydroperoxide and acetyl chloride as in ref 2. Iodimetric titration of this compound is not quantitative, but the preparation appeared to be pure as judged by its IR (carbonyl at 1785 cm^{-1}) and NMR: δ 1.65 (s, 6 H), 1.90 (s, 3 H), 7.40 (m, 5 H).

The Silicas.[4-7] The silicas were dried in an oven and stored over Drierite before use. Silica P_1 is the purer of the two and has 0.018% calcium as CaO, 0.005% iron as Fe_2O_3, 0.058% titanium as TiO_2, and 0.030% zirconium as ZrO_2. The percentages for P_0 silica are 0.02, 0.03, 0.09, and 0.03.[5] The surface areas (N_2) are 700 m^2/g for P_1 and 750 m^2/g for P_0. Silica P_1 has a greater H-bond donating ability, in the absence of solvent, as measured by its solvatochromic α value.[4] Both silicas have solvatochromic π^* values of about 2.0, greatly exceeding those reported for any fluid solvent.[4]

Registry No. Cumyl peracetate, 34236-39-0; silica, 7631-86-9.

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(8) The lack of dependence on the silica, P_0 vs. P_1, could be a result characteristic of this perester or it could be due to the presence of solvent. The fact that the products are the same in chloroform as in pentane supports the former interpretation.

Hydrogen–Deuterium Exchanges in a Friedel–Crafts Reaction

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Isotopic scramblings during Friedel–Crafts alkylations have been investigated with ^{14}C-labeled 2-arylethyl halides.[1] For example, scramblings in the 2-phenylethyl

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