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Formation of Allyl-Substituted Allene Episulfide S-Oxides and Their Thermal and Acid-Catalyzed Rearrangements

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ABSTRACT

Oxidation of allyl-substituted allene episulfides with a peracid gave the corresponding allene episulfide S-oxides which were found to undergo ready isomerization to bicyclo[2.1.1]thiahexane S-oxide derivatives on thermolysis or under acid-catalyzed reaction conditions.

INTRODUCTION

The chemistry of thiirane S-oxide has been widely explored [1]. Recently, we have investigated thermal, photochemical, and acid-catalyzed isomerization of allene episulfides [2] which are methylene homologues of thiiranes. Isomerization of allene episulfide S-oxides proceeded under milder conditions than isomerization of allene episulfides (Equation 1) [3]. We present here the peracid oxidation of allyl-substituted allene episulfides **1a** and **b** and the facile formation of bicyclo[2.1.1]-thiahexane S-oxides by the thermal and acid-catalyzed reactions of the resulting allene episulfide S-oxides.

RESULTS AND DISCUSSION

Each allyl-substituted allene episulfide (**1a** and **b**) was treated with an equimolar amount of m-chloroperbenzoic acid (m-CPBA) in dichloromethane at −50°C during 2 hours. Flushing of NH_3 over the surface of the mixture resulted in precipitation of ammonium benzoate [4]. The precipitate was filtered off and each S-oxide (**4a**, 35%; **4b**, 40%) was isolated along with each bicyclo[2.1.1]thiahexane S-oxide (**5a**, 42%; **5b**, 22%) by high-performance liquid chromatography. The structure of **5a** was determined by ^1H and ^{13}C NMR spectral data and the results of a deoxygenation reaction. The compound **5a** was treated with an equimolar amount of hexamethylphosphorous triamide to yield the corresponding bicyclo[2.1.1]thiahexane **6a** [2c]. Each S-oxide **3** could not be isolated, probably due to the ready isomerization into the respective **4** under the reaction conditions. When we used a half amount of m-CPBA in the oxidation of **1a**, S-oxides **4a** and **5a** were obtained in 22 and 23% yield, respectively, together with recovered **1a** in 35% yield. Furthermore, when **1a** was treated with m-chlorobenzoic acid (m-CBA) in dichloromethane at −50°C for 2 hours, no reaction was observed. Therefore, we concluded that in each case the S-oxide **4** was not formed via the oxidation of isomerized episulfide **2** by m-CPBA but was derived from the oxide **3** by the action of m-CBA (Scheme

Dedicated with admiration to Prof. A. Fava on the occasion of his seventieth birthday.

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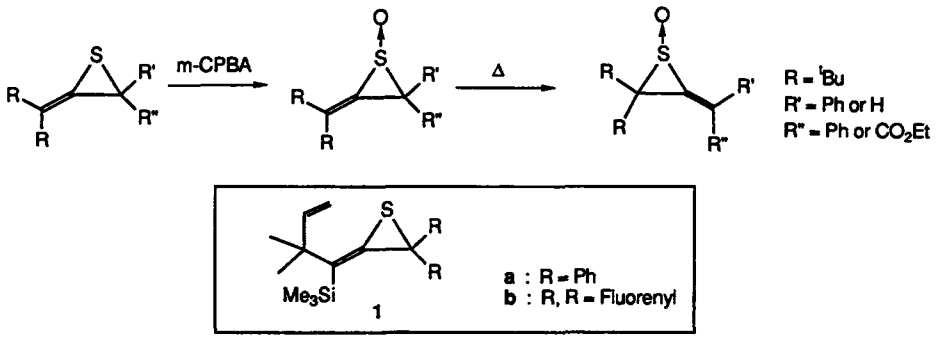
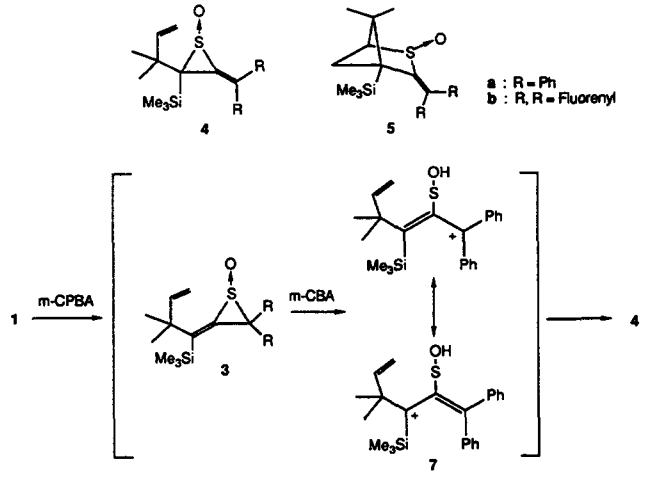
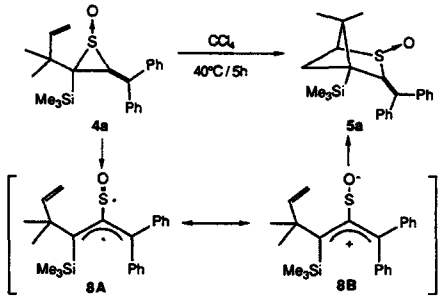


(1)



SCHEME 1



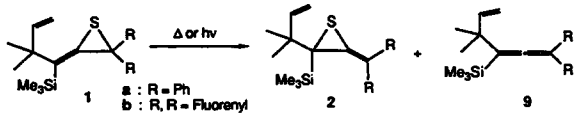
SCHEME 2

1). Each S-oxide **4** was formed kinetically in preference to the respective **5** via an intermediate of type **7** in the oxidation of each allene episulfide **1** with m-CPBA at −50°C. The addition of a catalytic amount of trifluoroacetic acid in benzene to **4a** also yielded **5a** (85% yield) which was thermodynamically more stable than **4a**, via the thioallyl cation type of intermediate **7** (Equation 2).

$$\mathbf{4a} \xrightarrow[\text{r.t. / 8h}]{\text{cat. } CF_3CO_2H} \mathbf{5a} \qquad (2)$$

We have investigated the thermal, photochemical, and acid-catalyzed reactions of allene episulfide S-oxide (**4a**) in order to compare the nature of the intermediate species, the thioallyl S-oxide, with that of the thioallyl formed in the isomerization of the allene episulfide.

Thermolysis of the S-oxide (**4a**) at 40°C in carbon tetrachloride for 5 hours, which was monitored by ^1H NMR, afforded **5a** quantitatively (Scheme 2). We have already reported that a Lewis acid which promotes cyclization of **1a** affords the corresponding cyclopentenethione along with bicyclo[2.1.1]thiahexane and bicyclo[3.1.0]thiahexane via a thioallyl cation intermediate [3c]. Thermolysis or photolysis of **1a** and **1b** did not give bicyclo[2.1.1]thiahexane derivatives but gave isomers **2a** and **2b** via thioallyl intermediates, which had diradical character, along with allenes **9a** and **9b**, respectively (Equation 3).



(3)

The oxidation of allylallene using a peracid gave the allene oxide without oxidation of the allyl moiety. The allylallene oxide could not be isolated under acidic conditions, and a ready intramolecular cyclization occurred to yield bicyclo[3.1.0]hexanone via an oxyallyl intermediate [5]. The facile conversion of **4a** to **5a** under milder conditions than those required for the isomerization of allene episulfide **1a** to **2a** seems to result from the increased nucleophilicity of the sulfur atom of **8**. Allene episulfide **2a** did not give bicyclo[2.1.1]thiahexane on thermolysis but afforded the corresponding allene **9a**. These results suggest that the intermediate produced on thermolysis of **4a**, i.e., thioallyl S-oxide, has a zwitterionic character, as depicted in the contributing resonance structure **8B**.

Furthermore, we have investigated the photolysis of an allene episulfide S-oxide. When the benzene solution of S-oxide **4a** was irradiated at room

temperature for 10 minutes by a high pressure mercury lamp, the corresponding allene **9a** was obtained quantitatively (Equation 4). Therefore, a cheletropic elimination of sulfur oxide is apparently an allowed process for photolysis of **4a** [6].

$$\mathbf{4a} \xrightarrow[\text{benzene / 10 min.}]{h\nu\ (>300\text{nm})} \mathbf{9a} \qquad (4)$$

This system provides us with an important account of the intrinsic character of a thioallyl S-oxide intermediate. Thus, the mechanism of the thermolysis of an allene episulfide S-oxide **4** seems to have a closer resemblance to an acid-catalyzed cyclization reaction than to the thermal valence isomerization mechanism of a nonoxidized allene episulfide.

EXPERIMENTAL SECTION

General Data

Reagent-grade solvents were distilled over CaH_2 before use. The compounds 2-[2′,2′-dimethyl-1′-(trimethylsilyl)-3′-butenylidene]-3,3-diphenylthiirane **1a** [2c] and spiro[fluorene-9,3′-[2′-[2″,2″-dimethyl-1″-(trimethylsilyl)-3″-butenylidene]thiirane]] **1b** [2c] were prepared by the published procedures. All reactions were performed under an argon atmosphere unless specified otherwise. Infrared spectra were recorded on a JASCO FT-IR-5000 instrument. NMR spectra were run on either a Bruker AM500 or a Bruker AC400 spectrometer operating at 500 and 400 MHz, respectively. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer.

Oxidation of Allene Episulfide **1a**

(a) To a solution of allene episulfide **1a** (128 mg, 0.34 mmol) in dichloromethane (10 mL) was added a dichloromethane solution (5 mL) of m-CPBA (70% assay, 84 mg, 0.34 mmol) at −78°C under an argon atmosphere. After the mixture had been stirred for 2 hours at −50°C, flushing of NH_3 over its surface resulted in precipitation of ammonium benzoate. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residual oil was separated by HPLC (eluent; chloroform) to yield 2-(1′,1′-dimethylallyl)-3-(diphenylmethylene)-2-(trimethylsilyl)thiirane S-oxide (**4a**) (46 mg, 35%) and 3-(diphenylmethylene)-4-(trimethylsilyl)-5,5-dimethyl-2-thiabicyclo[2.1.1]hexane S-oxide (**5a**) (56 mg, 42%).

For **4a**: a pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (9H, s), 1.13 (3H, s), 1.35 (3H, s), 4.86 (1H, d, J = 10.0 Hz), 4.89 (1H, d, J = 17.0 Hz), 5.89 (1H, dd, J = 10.0, 17.0 Hz), 7.2–7.6 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.2 (q), 25.9 (q), 27.8 (q), 46.5 (s), 65.8 (s), 111.3 (t), 128.43 (d), 128.47 (d), 128.68 (d), 128.69 (d), 129.0 (d), 129.7 (d), 139.2 (s), 139.5 (s), 139.7 (s), 142.4 (s), 146.5 (d); IR (CCl_4) ν 1055 cm^{-1} (m); HRMS calcd for $C_{23}H_{28}OSSi$ 380.1628. Found 380.1625. For **5a**: a pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.27 (9H, s), 1.28 (3H, s), 1.57 (3H, s), 1.56 (1H, dd, J = 2.9, 7.8 Hz), 2.64 (1H, dd, J = 2.9, 13.0 Hz), 3.73 (1H, dd, J = 7.8, 13.0 Hz), 7.2–7.3 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.5 (q), 21.4 (q), 24.3 (q), 32.3 (d), 33.2 (s), 43.6 (s), 50.7 (t), 127.7 (d), 128.21 (d), 128.28 (d), 128.3 (d), 129.3 (d), 129.4 (d), 141.2 (s), 142.3 (s), 146.5 (s), 150.7 (s); IR (CCl_4) ν 1045 cm^{-1} (m). HRMS calcd for $C_{23}H_{28}OSSi$ 380.1628. Found 380.1620.

(b) To a solution of allene episulfide **1a** (128 mg, 0.34 mmol) in dichloromethane (10 mL) was added a dichloromethane solution (5 mL) of m-CPBA (70% assay, 42 mg, 0.17 mmol) at −78°C under an argon atmosphere. After the mixture had been stirred for 2 hours at −50°C, flushing of NH_3 over its surface resulted in precipitation of ammonium benzoate. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residual oil was separated by HPLC (eluent; chloroform) to yield **4a** (29 mg, 22%) and **5a** (31 mg, 23%) along with recovered **1a** (45 mg, 35%).

Oxidation of Allene Episulfide **1b**

To a solution of allene episulfide **1b** (120 mg, 0.32 mmol) in dichloromethane (10 mL) was added a dichloromethane solution (5 mL) of m-CPBA (70% assay, 81 mg, 0.32 mmol) at −78°C under an argon atmosphere. After the mixture had been stirred for 2 hours at −50°C, flushing of NH_3 over its surface resulted in precipitation of ammonium benzoate. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residual oil was separated by HPLC (eluent; toluene) to yield 2-(1′,1′-dimethylallyl)-3-(fluorenylidene)-2-(trimethylsilyl)thiirane S-oxide (**4b**) (48 mg, 40%) and 3-(fluorenylidene)-4-(trimethylsilyl)-5,5-dimethyl-2-thiabicyclo[2.1.1]hexane S-oxide (**5b**) (27 mg, 22%).

For **4b**: a yellow solid; ^{1}H NMR (400 MHz, C_6D_6) δ −0.09 (9H, s), 1.50 (3H, s), 1.64 (3H, s), 5.02 (1H, d, J = 10.6 Hz), 5.08 (1H, d, J = 17.3 Hz), 6.52 (1H, dd, J = 10.6, 17.3 Hz), 7.0–8.6 (8H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 1.4 (q), 26.8 (q), 27.5 (q), 46.8 (s), 66.5 (s), 112.5 (t), 120.3 (d), 120.8 (d), 123.4 (d), 124.6 (d), 127.1 (d), 129.3 (d), 129.6 (d), 129.8 (d), 131.4 (s), 136.9 (s), 137.4 (s), 138.0 (s), 139.8 (s), 142.2 (s), 146.4 (d); IR (KBr) ν 1058 cm^{-1} (s). HRMS calcd for $C_{23}H_{26}OSSi$ 378.1474. Found 378.1477.

For **5b**: a pale yellow solid; ^{1}H NMR (400 MHz, C_6D_6) δ −0.15 (9H, s), 1.07 (1H, dd, J = 3.5, 7.5 Hz), 1.12 (3H, s), 1.17 (3H, s), 2.56 (1H, dd, J = 3.5, 12.7 Hz), 3.34 (1H, dd, J = 7.5, 12.7 Hz), 7.0–8.7 (8H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 1.4 (q), 18.8 (q), 25.1 (q), 32.2 (d), 34.9 (s), 36.3 (s), 50.5 (t), 119.5

(d), 119.8 (d), 125.2 (d), 126.4 (d), 127.8 (d), 128.4 (d), 129.1 (d), 129.9 (d), 136.4 (sx2), 138.4 (s), 140.6 (s), 140.7 (s), 141.3 (s); IR (KBr) ν 1048 cm^{-1} (m). HRMS calcd for $C_{23}H_{26}OSSi$ 378.1474. Found 378.1483.

Deoxygenation of **5a**

Hexamethylphosphorous triamide (116 μL, 0.65 mmol) was added dropwise at room temperature to a solution of **5a** (25 mg, 0.065 mmol) in 350 μL of $CDCl_3$. The mixture was heated at 60°C. The reaction was monitored by ^1H NMR. After 3 hours, **5a** was completely consumed and ^1H NMR showed the spectrum of 3-(diphenylmethylene)-4-(trimethylsilyl)-5,5-dimethyl-2-thiabicyclo[2.1.1]hexane **6a** [3c]. After removal of the solvent in vacuo, the residue was chromatographed by TLC. Elution with dichloromethane yielded **6a** (20 mg, 85%).

Reaction of **4a** *with m-CBA*

To a solution of **4a** (30 mg, 0.079 mmol) in 3 mL of dichloromethane a solution of m-CBA (10 mg, 0.063 mmol) in 0.5 mL of CH_2Cl_2 was added at −78°C. After the mixture had been stirred for 3 hours at −50°C, NH_3 was flushed over its surface, and the resulting precipitate was filtered off. After removal of the solvent in vacuo, the ^1H NMR spectrum of the residue was taken and found to be identical with that of the starting material **4a**.

Thermal Rearrangement of **4a**

A solution of **4a** (10 mg, 0.026 mmol) in 300 μL of CCl_4 was heated at 40°C. The reaction was monitored by ^1H NMR. After 5 hours, **4a** had been consumed completely and the product showed an identical ^1H NMR spectrum with that of **5a**.

Acid-Catalyzed Reaction of **4a**

To a solution of **4a** (10 mg, 0.026 mmol) in 300 μL of $CDCl_3$ was added 1 μL of a solution of CF_3CO_2H in $CDCl_3$ ($CF_3CO_2H/CDCl_3$ = 1 μL/1 mL) at room temperature. The reaction was monitored by ^1H NMR. After 8 hours, **4a** had been consumed completely and the product showed an identical ^1H NMR spectrum with that of **5a**.

Photolysis of **4a**

A benzene solution (10 mL) of **4a** (20 mg, 0.052 mmol) was irradiated with a high pressure mercury lamp (Riken, 400 W) for 10 minutes at room temperature. After removal of solvent, separation of the residue by preparative TLC (eluent; hexane) gave the corresponding allene **9a** (17 mg, 98%).

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