SYNTHESIS AND SULFURATION OF 2’-ADAMANTYLIDENE-9-BENZONORBORNENYLIDENE†

Yoshiaki Sugihara,* Ayumi Kobiki, and Juzo Nakayama*

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan; e-mail; ysugi@chem.saitama-u.ac.jp

Abstract – A novel alkene, 2’-adamantylidene-9-benzonorbornene 6, was synthesized from 2-adamantanone 7 in three steps resulting in a good overall yield. The alkene 6 reacted with elemental sulfur in refluxing o-Cl₂C₆H₄ to give syn-thiirane 14, anti-thiirane 15, and 6. Almost the same ratio of the products was obtained when 14 or 15 was reacted with and without elemental sulfur under the same conditions. Sulfuration with Ph₃CSCl in CH₂Cl₂ at –78 °C afforded 14, and that at room temperature furnished a 3:1 mixture of 14 and 15. In contrast, although the sulfuration with Ph₃CSCl in CH₂Cl₂ at room temperature afforded 14 quantitatively, that at –78 °C gave 14 and 15 in 12 and 3% yields, respectively. Sulfuration by 1 molar equiv. of S₂Cl₂ or SCl₂ afforded 14 and vic-dichloride 28.

INTRODUCTION

Considerable attention has been paid to the study of the sulfuration of alkenes because sulfuration is important as a model reaction of the vulcanization of rubber, and is it easy to introduce sulfur atoms into their C=C bonds.¹ One of the goals of its study would be the control of the number of sulfur atoms introduced. The number was found to noticeably depend on the structure of the alkenes when elemental sulfur was used as the sulfurating agent.²³⁴⁵ Although, in most cases, sulfuration gives a complex mixture containing polymeric compounds, cyclic oligosulfanes are obtained as the principal component in some cases. Thus, the sulfuration of norbornene and dibenzobarrelene by elemental sulfur gave a mixture of the corresponding 1,2,3-trithiolane and 1,2,3,4,5-pentathiepane,⁶ and that of acenaphtho[1,2-α]-acenaphthylene afforded the corresponding pantathiepane as a sole product.⁴ On the other hand, sterically congested 2,2’-biadamantylidene reacted with elemental sulfur to furnish the corresponding thiirane exclusively.³ Sulfurations of anti- and syn-9,9’-bibenzonorbornenylidenes, 1 and 2,⁶ by elemental sulfur afforded the corresponding thiiranes, 3 and 4, respectively, with retention of the original stereochemistry,
whereas those by S₂Cl₂ afforded a mixture of 3, 4, and vic-dichloride 5. We have been interested in introducing one sulfur atom into alkenes, that is, directly synthesizing thiiranes from alkenes. Although some number of direct syntheses has been reported so far, most of the methods seem to be specific to the starting alkenes and present difficulties in synthesizing sulfuratting agents. Furthermore, most alkenes used in the study were hard to handle in laboratories, because the separation and analysis of the reaction mixture were difficult to achieve. We have designed a model alkene suitable for investigation into the reaction conditions for direct synthesis because of its ease in handling. Using 1 and 2 in the study would facilitate the analysis of the reaction mixture by ¹H NMR and, therefore, 1 and 2 were thought to be a good candidate for the alkene. However, their synthesis from a commercial compound is lengthy and an extra reaction step is required in order to separate the two alkenes. We have designed a novel alkene carrying a 9-benzonorbornenylidene group to overcome the faults of 1 and 2. Here, we report the synthesis of 2'-adamantylidene-9-benzonorbornenylidene and its sulfuration.

RESULTS AND DISCUSSION

Synthesis of 2'-Adamantylidene-9-benzonorbornene 6

2'-Adamantylidene-9-benzonorbornenylidene 6 was synthesized from commercially available 2-adamantanone 7 in three steps. The ketone 7 was treated with cyclopentadiene in the presence of pyrrolidine to give fulvene 8. Reaction of 8 with benzyne, generated by reaction of anthranilic acid with dioxygen and chloroform, afforded diene 9 in 96% yield together with bis-adduct 10 in 3% yield. The diene 9 was hydrogenated with HN=NH, generated by oxidation of H₂NNH₂ with NaIO₄, and 1,4-dioxane in reflux, afforded diene 9 in 96% yield and diene 10 in 3% yield. The diene 9 was hydrogenated with HN=NH, generated by oxidation of H₂NNH₂ with NaIO₄, or with HCO₂NH₄, Pd/C, or isomyl nitrite in CH₂Cl₂ and dioxane at reflux, afforded diene 9 in 96% yield together with bis-adduct 10 in 3% yield. The diene 9 was hydrogenated with HN=NH, generated by oxidation of H₂NNH₂ with NaIO₄, and 1,4-dioxane in reflux, afforded diene 9 in 96% yield and diene 10 in 3% yield. The diene 9 was hydrogenated with HN=NH, generated by oxidation of H₂NNH₂ with NaIO₄, and 1,4-dioxane in reflux, afforded diene 9 in 96% yield and diene 10 in 3% yield.
the presence of 5% Pd/C in MeOH/CHCl₃ (1:1) at reflux also afforded 6 in 87% yield. Neither 11 nor 12 was obtained in either reaction.

The alkene 6 showed five multiplets centered at δ 1.21 (2H), 1.76 (14H), 3.77 (2H), 7.04 (2H), and 7.14 (2H) and one broad singlet at δ 2.56 (2H) in the ¹H NMR spectrum. The bridgehead hydrogen signal of the 2-benzonorbornenylidene group (δ 3.77) appeared at a lower field than the corresponding signals of 1 (δ 3.65) and 2 (δ 3.66), whereas that of the 2-adamantylidene group (δ 2.56) appeared at a higher field than the corresponding signals of 2,2'-biadamantylidene 13 (δ 2.95). The ¹³C NMR spectrum showed a higher field shift of the sp² carbon signal of the 2-adamantylidene group (δ 126.9) and a lower field shift of the sp² carbon signal at the 9-position of the 9-benzonorbornenylidene group (δ 141.3) by comparison with the corresponding carbon signals of 1 (δ 134.1), 2 (δ 134.3), and 13 (δ 133.1). These sizable upfield or downfield shifts would be caused by the homoconjugation interaction between the central C=C bond and the benzene ring shown as 6".

The bis-adduct 10 was a product by cycloaddition reaction of 9 and benzyne. The structure of 10 was exo- or endo-adduct, 10a or 10b, with respect to the benzene ring of 9. Since no single crystals of 10 suitable for an X-ray analysis were obtained, the ¹H NMR spectrum of 10 was compared with the spectra of 10a and 10b calculated by Gaussian 98. Thus, 10 showed five multiplets centered at δ 0.75 (2H), 1.59 (10H), 3.24 (2H), 3.86 (2H), and 7.12 (8H) and one broad singlet at δ 2.39 (2H) in the ¹H NMR spectrum. The multiplet centered at δ 0.75, assigned to axial hydrogens (Hₐ) at the 4-position of the adamantylidene group, appeared at a higher field than the corresponding signals in 9 and 6, and that centered at δ 3.24, assigned to hydrogens (Hₖ) on the cyclobutene ring, developed newly when the further benzene ring was introduced into 6. The calculation of 10 at B3LYP/6-311+G(2d,p) level shows that the Hₐ and Hₖ signals appear at δ 0.96 and 3.13 for 10a and at δ 1.86 and 3.74 for 10b, respectively, revealing that the structure of 10 proves to be 10a. The ring current effect of the close benzene ring would result in the higher field shift of the signal of Hₖ.
Sulfuration of 2'-Adamantylidene-9-benzonorbornene 6 by Elemental Sulfur

The alkene 6 was sulfurated with elemental sulfur (1 molar equiv. as S\textsubscript{8}) in refluxing o-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4} to furnish anti- and syn-thiirane, 14 and 15, in 76 and 4% yields, respectively, together with 6 in 19% yield. The sulfuration in DMF at 135 °C afforded 14 and 15 in 54 and 6% yields, respectively, along with 6 in 40% yield. Prolonging the reaction time did not bring about the disappearance of 6 in spite of the presence of an excess of sulfur atoms. These observations suggest that sulfuration must be reversible.\textsuperscript{15}

Actually, 15 reacted with and without elemental sulfur in refluxing o-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4} to afford about 19:1:5 and 23:1:9 mixtures of 14, 15, and 6, respectively. The reactions of 14 gave almost same the product ratios as did that of 15. The calculations for 14 and 15 at the B3LYP/6-311+G(2d,p) level predict that 14 is thermally more stable by 3.2 kcal mol\textsuperscript{-1} than is 15.\textsuperscript{14} The energy difference means that the calculated equilibrium ratio of 14 to 15 at 180 °C, the boiling point of o-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4}, is 32:1. The solvent effect would make the calculated ratio slightly higher than the actual ratios. Two mechanisms of the reversible process might be possible. One includes direct decomposition of the thiiranes to 6 and elemental sulfur, followed by the resulfuration of 6. The other contains three consequent processes: 1) cleavage of the C—S bond close to the 9-benzonorbornenylidene group heterolytically or homolytically to give intermediates 16 and 17, or 18 and 19, 2) rotation about the central C—C bond, and 3) recombination of the C—S bond or elimination of sulfur from the intermediates.

<table>
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<th>conditions</th>
<th>14</th>
<th>15</th>
<th>6</th>
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<tr>
<td>o-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4}, refl., 2 d</td>
<td>76%</td>
<td>4%</td>
<td>19%</td>
</tr>
<tr>
<td>DMF, 135 °C, 2 d</td>
<td>54%</td>
<td>6%</td>
<td>40%</td>
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Structure of 14 and 15

A molecular structure of 14 is shown in Figure 1. Selected bond length and bond angle data are summarized in Table 1. The C(2)—C(3) bond length, 1.477(2) Å, is slightly shorter than that of the parent thiirane, 1.484 Å,\textsuperscript{16} and is slightly longer than those of 3 and 4, 1.464(3) and 1.455(4) Å,\textsuperscript{6} respectively. At the same time, the S(1)—C(2) bond length, 1.817(2) Å, is nearly equal to that of the parent thiirane, 1.815 Å, but the S(1)—C(3) bond length, 1.856(2) Å, is longer. The C(2)—S(1)—C(3)
and S(1)—C(3)—C(2) bond angles, 47.39(7) and 64.89(9)°, respectively, are smaller than those of the parent thiirane, 48.16 and 65.52°, respectively, but the S(1)—C(2)—C(3) bond angle, 67.72(9)° is larger. Deformation of the thiirane ring is probably due to steric repulsion among the S(1) atom and some hydrogen and carbon atoms in the substituents.

In the ¹H NMR spectra, the two hydrogen atoms of the methylenes of 14, which face the benzene ring and hence are placed under the influence of the ring current effect of the benzene ring, appeared as a multiplet centered at δ 1.07, which is a higher field than the multiplet centered at δ 2.00 assigned to the corresponding methylene hydrogens of 15. The bridgehead protons in the benzonorbornenylidene group of 14 and 15 appeared as a multiplet centered at δ 3.12 and 3.29, respectively, which are apart from the corresponding protons of 6 (δ 3.77), suggesting that, if a reaction mixture of the sulfuration of 6 contains only 14, 15, and 6 as compounds having protons that appeared in the range δ 3–4, a ratio of the mixture could easily be determined by ¹H NMR analysis.

**Table.** Bond Lengths and Bond Angles Data of 14

<table>
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<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
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<tr>
<td>S(1)-C(2) 1.617(2)</td>
<td>C(2)-S(1)-C(3) 47.39(7)</td>
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<tr>
<td>S(1)-C(3) 1.856(2)</td>
<td>S(1)-C(2)-C(3) 67.72(9)</td>
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<tr>
<td>C(2)-C(3) 1.477(2)</td>
<td>S(1)-C(3)-C(2) 64.89(9)</td>
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<tr>
<td>C(2)-C(5) 1.544(2)</td>
<td>C(2)-C(3)-C(4) 121.16(8)</td>
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<td>C(3)-C(4) 1.520(2)</td>
<td>C(3)-C(2)-C(5) 126.50(9)</td>
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<td>C(4)-C(3)-C(4') 110.87(13)</td>
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<tr>
<td>C(5)-C(2)-C(5') 95.28(12)</td>
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**Sulfurations of 6 by Ph₃CSCl and Ph₃CSSCl**

The alkene 6 reacted with 1 molar equiv. of Ph₃CSCl in CH₂Cl₂ at −78 °C to give 14 in 60% yield along with 6 in 40% yield. A mixture of 14, 15, and 6 was obtained when the reactions were performed above −18 °C, and the ratio of 14 to 15 decreased as the reaction temperature increased. The yield of 6 increased...
at rt because Ph₃CSCl decomposes into Ph₃CCl and elemental sulfur by the thiiranes prior to reacting with 6. In fact, Ph₃CSCl reacted with 14 in CH₂Cl₂ at rt to form Ph₃CCl, elemental sulfur, and 14 quantitatively. In contrast to these results, when 6 reacted with 1 molar equiv. of Ph₃CSSCl, the ratio of 14 to 15 increased as the reaction temperature increased. In particular, the reaction at rt furnished 14 exclusively. The possible mechanism of the sulfurations is as follows. The alkene 6 reacts with Ph₃CSCl to form thiiranium intermediates, 20 and 21. The intermediates liberate triphenylmethylcarbenium ions, which react with chloride ions to give Ph₃CCl, via an E1 process to form the thiiranes.

\[
\text{S}2\text{Cl}_2 + \text{Ph}_3\text{CSCl} \rightarrow \text{Ph}_3\text{CCl} + \text{Ph}_3\text{C}^+\text{S}^- + \text{Cl}^-
\]

On the other hand, 6 reacts with Ph₃CSSCl to afford thiiranium intermediates, 22 and 23. The intermediates have the less polar Ph₃C–S bond compared with 20 and 21, hence the liberation of triphenylmethylcarbenium ion from 22 and 23, which form thiirane sulfides, 26 and 27, and Ph₃CCl, becomes slower. The C—S bond of 22 and 23 that is close to their 9-benzonorbornenylidene group cleaves easily to form carbenium salts, 24 and 25, which are stabilized by neighboring group participation of their benzene ring. Rotation about the central C—C bond of the carbenium salts, followed by recombination of the C—S bond takes place to furnish 26 and 27. The equilibrium among 22—25 in which 22 must be most stable, occurs under the reaction conditions. Finally, 26 and 27 eliminate sulfur to give 14 and 15, respectively.

\[
\text{S}2\text{Cl}_2 + \text{Ph}_3\text{CSSCl} \rightarrow \text{Ph}_3\text{CSS}^+\text{Cl}^- + \text{Ph}_3\text{C}^+\text{S}^- + \text{Cl}^-
\]

**Sulfurations of 6 by S₂Cl₂ and SCl₂**

The alkene 6 was sulfurated with 1 molar equiv. of S₂Cl₂ in CH₂Cl₂ at –78 °C. After the sulfuration was quenched by the addition of water at the same temperature, a 68:32 mixture of 14 and vic-dichloride 28 was obtained. Purification of the mixture by silica gel column chromatography furnished 14 and ketone 29 in 68 and 32% yields, respectively. The ketone 29 is most likely formed by silica gel catalyzed
hydrolysis of 28 to chlorohydrin 32 through formation of the carbenium ion 30, which is in equilibrium with the epichloronium ion 31, followed by pinacol-type rearrangement of 32. The \textit{vic}-dichloride 28 was not obtained from the reaction mixture in pure form. Therefore, 28 was synthesized separately by chlorine addition of 6 to confirm its structure. Reaction of 6 with 1.0 molar equiv. of SO\textsubscript{2}Cl\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2} at −78 °C gave 28 whose spectral data were the same as those of the product that was formed by the sulfuration in quantitative yield.

Temperature-variable \textsuperscript{1}H NMR spectra of 28 showed that all signals broaden at rt and separate sharply as the temperature falls. The signal (δ 0.44) due to the H\textsubscript{c} atom at the 1-position of the adamantylidene group appeared at a higher field than that (δ 2.99) due to the H\textsubscript{d} atom at the 3-position at −50 °C, revealing that 28 adopts a gauche conformation like 28\textsuperscript{′} at low temperatures.\textsuperscript{21} Rotation about its central C—C bond occurs as the temperature gradually rises.

Sulfuration with 1.0 molar equiv. of SCl\textsubscript{2} furnished 14 and 28 in 42 and 57% yields, respectively. When 6 was sulfurated with 0.5 molar equiv. of S\textsubscript{2}Cl\textsubscript{2} at −78 °C, 14 and 15 were obtained in 71% and 7% yields, respectively, revealing that two sulfur atoms of S\textsubscript{2}Cl\textsubscript{2} are involved with the formation of thiiranes and, even if 15 is formed by the sulfuration, further reaction of 15 with S\textsubscript{2}Cl\textsubscript{2} would occur to form 14 and 28.

In fact, 15 reacted with S\textsubscript{2}Cl\textsubscript{2} under the same conditions as the sulfurations of 6 to afford 14 and 28 in 91% and 9% yields, respectively. The same reaction of 15 with SCl\textsubscript{2} and those of 14 with S\textsubscript{2}Cl\textsubscript{2} and SCl\textsubscript{2} occurred to give a mixture of 14 and 28.

The possible mechanism of the sulfuration with S\textsubscript{X}Cl\textsubscript{2} is as follows. The alkene 6 reacts with S\textsubscript{X}Cl\textsubscript{2} to form thiiranium salts, 33 and 34. Then, 14 and 15 are produced from the salts together with SCl\textsubscript{2} (X = 2)
or Cl₂ (X = 1). Cl₂ is also produced by equilibrium SCl₂ and S₂Cl₂, and reacts with 6 to give 28. After 33 and 34 come to equilibrium with the carbenium salts, 35 and 36, isomerization of 15 to 14 and formation of the sulfanyl chlorides, 37 and 38, proceed. The reason 14 is a main product having a sulfur atom seems to be its thermal stability compared with 15. The epichloronium salt 31 is formed by elimination of sulfur from 37 and 38, and then is finally transformed into 28.

CONCLUSION
We succeeded in synthesizing a novel alkene 6 from commercially available 2-adamantanone in three steps. The sulfuration of 6 with elemental sulfur proceeded to give a mixture of thiiranes 14 and 15. The syn-thiirane 15 was readily transformed into the alkene 6 and thermally more stable 14 under the sulfuration conditions, although no other products having sulfur atoms such as polymers and cyclic oligosulfanes were observed. The sulfuration with SCl₂ and S₂Cl₂ afforded 14 and vic-dichloride 28. A ratio of the sulfuration products could easily be determined by their ¹H NMR spectra. From these results, we believe that 6 is a good candidate for the model alkene for studying the reaction conditions of the direct synthesis of thiiranes from alkenes, and have been using 6 to investigate the reaction conditions of direct synthesis with general applicability.

EXPERIMENTAL
Solvents were dried and purified in the usual manner. All the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 60N (Kanto, 63—210 μm, spherical, neutral). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ¹H and ¹³C-NMR spectra were recorded on a Bruker DRX400, a Bruker ARX400, a Bruker AM 400 (400.4
MHz for $^1$H and 100.6 MHz for $^{13}$C), a Bruker AC300P (300.1 MHz for $^1$H and 75.5 MHz for $^{13}$C), or a Bruker AC200 (200.1 MHz for $^1$H and 50.3 MHz for $^{13}$C) spectrometer using CDCl$_3$ or CD$_2$Cl$_2$ as the solvent with TMS for $^1$H and with CDCl$_3$ or CD$_2$Cl$_2$ for $^{13}$C as the internal standard. IR spectra were recorded on a Hitachi FT-IR 660+ spectrophotometer. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode or using $m$-nitrobenzyl alcohol as a matrix in the FAB mode. Elemental analyses were performed by the molecular Analysis and Life Science Center of Saitama University.

**Reaction of Fulvene 8 with Benzyne.** To a solution of 8 (4.0 g, 20 mmol) and isoamyl nitrite (4.1 mL, 30 mmol) in CH$_2$Cl$_2$ (160 mL) was added dropwise a solution of anthranilic acid (4.15 g, 30 mmol) in dioxane (40 mL) at reflux for 1 h. After the addition was finished, the reaction mixture was cooled to rt and then evaporated. Hexane and aqueous NaHCO$_3$ solution were added to the residue and then the insoluble materials were collected by filtration. After the filtrate was separated, the organic layer was washed with H$_2$O, dried over K$_2$CO$_3$, and evaporated. The residue was chromatographed on a column of silica gel and the column was eluted with hexane to give 5.3 g (96%) of 9 and 0.21 g (3%) of 10 in this order. 2'-Adamantylidene-9-benzonorbornadienylidene 9: colorless crystals (from CH$_2$Cl$_2$ and hexane); mp 90—91 °C; $^1$H NMR (300.1 MHz, CDCl$_3$) $\delta$ 1.42—1.60 (m, 2H), 1.65—1.95 (m, 10H), 2.58 (br s, 2H), 4.30—4.40 (m, 2H), 6.80—7.00 (m, 4H), 7.11—7.28 (m, 2H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 28.3, 28.5, 32.7, 37.2, 38.3, 38.5, 49.7, 117.4, 120.5, 124.1, 143.2, 151.0, 155.3; IR (KBr) 3061, 3002, 2990, 2923, 2851, 1556, 1447, 784, 761, 749, 693, 552, 447 cm$^{-1}$. Anal. Calcd for C$_{21}$H$_{22}$: C, 91.92; H, 8.08. Found: C, 91.78; H, 8.23. 2'-Adamantylidene-9-(2,3-o-phenylenebenzonorbornadienylidene) 10: colorless powder (from benzene); mp 295—298 °C; $^1$H NMR (400.4 MHz, CD$_2$Cl$_2$) $\delta$ 0.69—0.77 (d-like, 2H), 1.43—1.57 (m, 5H), 1.60—1.68 (m, 4H), 1.72—1.77 (m, 1H), 2.38 (br s, 2H), 3.29 (s, 2H), 3.87 (s, 2H), 7.07—7.13 (m, 4H), 7.17—7.21 (m, 2H), 7.23—7.27 (m, 2H); $^{13}$C NMR (100.6 MHz, CD$_2$Cl$_2$) $\delta$ 27.9, 28.3, 33.7, 37.2, 38.5, 38.8, 45.6, 49.5, 120.8, 122.2, 125.5, 127.3, 133.5, 136.3, 145.6, 147.4; IR (KBr) 3067, 2994, 2951, 2916, 2894, 2841, 1456, 1445, 767, 752, 743, 686, 678, 439 cm$^{-1}$. Anal. Calcd for C$_{27}$H$_{26}$: C, 92.52; H, 7.48. Found: C, 92.26; H, 7.52.

**Reaction of 9 with Diimide.** To a mixture of 9 (1.60 g, 5.8 mmol), H$_2$NNH$_2$•H$_2$O (7.3 g, 140 mmol), and saturated CuSO$_4$ aqueous solution (2.0 mL) in CHCl$_3$ (10 mL) and MeOH (10 mL) was added dropwise a solution of NaIO$_4$ (6.2 g, 30 mmol) in water (60 mL) at rt for 1 h. After the addition was finished, the organic layer was separated, washed with H$_2$O, dried over MgSO$_4$, and evaporated. 2'-Adamantylidene-9-benzonorbornenylidene 6 was obtained in quantitative yield (1.61 g). 6: colorless crystals (from hexane); mp 115—116 °C; $^1$H NMR (300.1 MHz, CDCl$_3$) $\delta$ 1.18—1.24 (m, 2H), 1.55—1.97 (m, 14H), 2.56 (br s, 2H), 3.73—3.80 (m, 2H), 7.00—7.08 (m, 2H), 7.10—7.17 (m, 2H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 27.3, 28.4, 28.6, 34.0, 37.3, 38.5, 39.7, 42.8, 119.8, 125.2, 126.9, 141.3,
Hydrogenation of 9 by Ammonium Formate in the presence of Pd/C. Ammonium formate (1030 mg, 16.3 mmol) and 5% palladium on charcoal (47 mg) was added to a solution of 9 (447 mg, 1.6 mmol) in CHCl₃ (4.0 mL) and MeOH (4.0 mL). After being heated at reflux for 1 day, the insoluble material was removed by filtration on a pad of Celite. The filtrate was washed with H₂O, dried over MgSO₄, and evaporated. The compound 6 was obtained in 87% yield (392 mg).

Sulfuration of 6 by Elemental Sulfur in Refluxing o-Cl₂C₆H₄. A suspension of 6 (970 mg, 3.5 mmol) and elemental sulfur (898 mg, 3.5 mmol as S₈) in o-Cl₂C₆H₄ (10 mL) was heated under reflux for 48 h. The mixture was evaporated under reduced pressure. The residue was placed on a column of silica gel and the column was eluted with hexane to give 190 mg (20%) of 6 and with CHCl₃/hexane (1:4) to give 821 mg (76%) of 14 and 39 mg (4%) of 15. anti-Thiirane 14: colorless crystals (from CH₂Cl₂ and MeOH); mp 164—166 °C; ¹H NMR (400.4 MHz, CDCl₃) δ 1.02—1.12 (m, 2H), 1.31—1.40 (m, 2H), 1.40—1.46 (m, 1H), 1.50—1.60 (m, 2H), 1.63 (br s, 2H), 1.70—1.82 (m, 4H), 1.88—1.93 (m, 1H), 1.99—2.04 (m, 2H), 2.23—2.35 (m, 2H), 3.10—3.14 (m, 2H), 7.09—7.15 (m, 2H), 7.16—7.22 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 26.4, 27.2, 27.6, 36.8, 37.3, 37.4, 38.2, 47.3, 66.1, 79.7, 120.7, 126.1, 146.5; IR (KBr) 3043, 3025, 2983, 2959, 2920, 2903, 2858, 2842, 1451, 1441, 736, 586, 480 cm⁻¹; MS (EI) m/z 308 (M⁺, 100%), 309 (M⁺+1, 26%), 310 (M⁺+2, 8%). Anal. Calcd for C₂₁H₂₄S: C, 81.76; H, 7.84. Found: C, 81.72; H, 7.92. syn-Thiirane 15: colorless crystals (from CH₂Cl₂ and MeOH); mp 202—203 °C (decomp.); ¹H NMR (400.4 MHz, CDCl₃) δ 1.42—1.49 (m, 2H), 1.80—1.90 (m, 6H), 1.93—2.11 (m, 8H), 2.25—2.33 (m, 2H), 3.26—3.32 (m, 2H), 7.09—7.15 (m, 2H), 7.17—7.23 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 26.8, 27.0, 27.8, 37.2, 37.6, 38.4, 38.8, 49.0, 70.3, 83.0, 120.7, 125.7, 147.6; IR (KBr) 3048, 2998, 2987, 2972, 2918, 2845, 1456, 763, 743, 578, 498 cm⁻¹; MS (EI) m/z 308 (M⁺, 100%), 309 (M⁺+1, 26%), 310 (M⁺+2, 8%). Anal. Calcd for C₂₁H₂₄S: C, 81.76; H, 7.84. Found: C, 81.81; H, 7.93.

Sulfuration of 6 by Elemental Sulfur in DMF at 135 °C. A suspension of 6 (8.0 mg, 29 µmol) and elemental sulfur (7.4 mg, 29 µmol as S₈) in DMF (0.6 mL) was heated at 135 °C for 20 h. The mixture was evaporated under reduced pressure to give 15.4 mg of a mixture of 14 (54%), 15 (6%), and 5 (40%).

X-Ray Crystallographic Analysis of anti-Thiirane 14. A single crystal of 14 of suitable quality and size was obtained by crystallization from a mixture of CH₂Cl₂ and hexane. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the MAC DIP3000 diffractometer by using Mo-Kα radiation (λ = 0.71073 Å) and the data collection was made by the MAC DENZO program system. Absorption collection was made by multi-scan method (SORTAV). Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR97 in the maXus program system. The atomic coordinates and the
anisotropic thermal parameters of the non-H atoms were refined on \( F^2 \) by full matrix least squares using SHELXL-97 \{weighting scheme: \( w = 1/[(\sigma(F^2) + (0.0493P)^2)] \) where \( P = (F_O^2 + 2F_C^2)/3 \}. \( \text{C}_{21}\text{H}_{24}\text{S} \) (308.49), orthorhombic, space group \( Pnma \), \( a = 18.295(1) \, \text{Å}, \, b = 10.430(1) \, \text{Å}, \, c = 8.417(1) \, \text{Å}, \, V = 1606.11(10) \, \text{Å}^3, \, Z = 4, \, D_{\text{calc}} = 1.276 \, \text{Mg}^{-3}, \, \mu = 0.196 \, \text{mm}^{-1}, \) crystal dimension: \( 0.23 \times 0.19 \times 0.14 \, \text{mm}, \) \( \theta \) range: 0—27.07°, number of observed reflections: 1423 \[ I > 2\sigma(I) \], refined parameters: 159, \( R = 0.0499 \, I > 2\sigma(I) \), \( wR_2 = 0.0953 \) (all reflections), \( S = 0.972, \, \Delta/\sigma_{\text{max}} = <0.001, \, \Delta\rho_{\text{max}} = 0.185 \, \text{eÅ}^{-3}, \, \Delta\rho_{\text{min}} = -0.369 \, \text{eÅ}^{-3}. \)

**General Procedure for Sulfuration of 6 by \( \text{Ph}_3\text{CS}_x\text{Cl} \).** To a solution of 6 in \( \text{CH}_2\text{Cl}_2 \) was added dropwise a solution of \( \text{Ph}_3\text{CS}_x\text{Cl} \) (1.0 molar equiv.) in \( \text{CH}_2\text{Cl}_2 \) at \(-78^\circ\text{C}, \,-18^\circ\text{C} \) or rt. After being stirred for 2 h at the same temperature, the reaction was quenched by addition of a solution of NaOEt in MeOH. The organic layer was washed with \( \text{H}_2\text{O} \), dried over \( \text{K}_2\text{CO}_3 \), and evaporated. The residue was placed on a column of silica gel and the column was eluted with \( \text{CHCl}_3/\text{hexane} \) (1:4) to give a mixture of 14, 15, and 6.

**Sulfuration of 6 by 1.0 molar equiv. of \( S_2\text{Cl}_2 \) at \(-78^\circ\text{C}.** To a solution of 6 (100 mg, 360 \( \mu \text{mol} \)) in \( \text{CH}_2\text{Cl}_2 \) (10 mL) was added dropwise a solution of \( S_2\text{Cl}_2 \) (49 mg, 360 \( \mu \text{mol} \)) in \( \text{CH}_2\text{Cl}_2 \) (5 mL) at \(-78^\circ\text{C}.\) After being stirred for 30 min at same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with \( \text{H}_2\text{O} \), dried over \( \text{K}_2\text{CO}_3 \), and evaporated to give 131 mg of a 68:32 mixture of 14 and 28. The mixture was placed on a column of silica gel and the column was eluted with \( \text{CHCl}_3/\text{hexane} \) (1:4) to give 76 mg of 12 (68\%) and with \( \text{CHCl}_3 \) to give 34 mg of 29 (32\%).

**Ketone 29:** colorless crystals (from \( \text{CH}_2\text{Cl}_2 \) and hexane); mp 189—191 \( ^\circ\text{C}; \) \(^1\text{H NMR} \) (400.4 MHz, CDCl\(_3\)) \( \delta \) 0.88 (br s, 1H), 1.28—1.48 (m, 3H), 1.55—1.75 (m, 5H), 1.85 (br s, 1H), 1.91 (br s, 1H), 1.98—2.07 (m, 2H), 2.10—2.22 (m, 2H), 2.26—2.31 (m, 2H), 2.68—2.75 (m, 1H), 3.49—3.52 (m, 1H), 3.87—3.89 (m, 1H), 7.13—7.24 (m, 4H); \(^{13}\text{C NMR} \) (75.5 MHz, CDCl\(_3\)) \( \delta \) 19.3, 23.7, 26.9, 27.5, 31.4, 32.4, 32.8, 32.8, 33.2, 33.3, 39.3, 42.6, 51.5, 54.7, 124.7, 125.0, 126.7, 126.8, 136.3, 142.4, 214.5; IR (KBr) 3036, 2967, 2951, 2905, 2853, 1700, 760, 753, 490 cm\(^{-1}\); MS (FAB) \( m/z \) 293 (MH\(^+\)). Anal. Calcd for \( \text{C}_{21}\text{H}_{24}\text{O} \): C, 86.25; H, 8.27. Found: C, 85.97; H, 8.38.

**Synthesis of 28 by Reaction of 6 by \( \text{SO}_2\text{Cl}_2 \) at \(-78^\circ\text{C}.** To a solution of 6 (100 mg, 360 \( \mu \text{mol} \)) in \( \text{CH}_2\text{Cl}_2 \) (5.0 mL) was added dropwise a solution of \( \text{SO}_2\text{Cl}_2 \) (49 mg, 360 \( \mu \text{mol} \)) in \( \text{CH}_2\text{Cl}_2 \) (3.0 mL) at \(-78^\circ\text{C}.\) After being stirred for 15 h at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with \( \text{H}_2\text{O} \), dried over \( \text{K}_2\text{CO}_3 \), and evaporated to give 125 mg of 28 (quantitatively). The \(^1\text{H and }^{13}\text{C NMR spectra of 28 are consistent with those of the product by the reaction of 6 with \( S_2\text{Cl}_2 \).**

**vic-Dichloride 28:** colorless crystals (from \( \text{CH}_2\text{Cl}_2 \) and MeOH); mp 126—127 \( ^\circ\text{C}; \) \(^1\text{H NMR} \) (300.1 MHz, CDCl\(_3\), 25 \( ^\circ\text{C} \)) \( \delta \) 1.02—2.65 (m, 18H), 4.76—4.14 (br s, 2H), 6.98—7.22 (m, 4H); \(^1\text{H NMR} \) (400.4 MHz, CDCl\(_3\), \(-50^\circ\text{C} \)) \( \delta \) 0.43—0.44 (m, 1H), 1.01—1.07 (m, 1H),
1.19—1.23 (m, 2H), 1.30—1.36 (m, 1H), 1.52—1.66 (m, 4H), 1.77—1.81 (m, 2H), 1.98—2.02 (m, 1H), 2.16—2.23 (m, 2H), 2.41—2.47 (m, 2H), 2.56—2.61 (m, 1H), 2.98—2.99 (m, 1H), 3.80—3.87 (m, 1H), 4.14—4.16 (m, 1H), 7.14—7.20 (m, 4H); $^{13}$C NMR (100.6 MHz, CDCl$_3$, –50 °C) δ 25.5, 26.0, 27.0, 29.1, 33.5, 35.9, 36.0, 36.1, 38.0, 38.1, 40.3, 55.4, 57.3, 89.2, 97.8, 120.2, 121.6, 126.2, 126.6, 143.2, 144.2; IR (KBr) 3032, 3006, 2976, 2953, 2901, 2862, 1470, 1453, 1279, 1099, 862, 797, 763, 746, 582, 508 cm$^{-1}$; MS (EI) m/z 129 (100%), 346 (M$^+$, 94%), 348 (M$^+$+2, 61%), 350 (M$^+$+4, 12%). Anal. Calcd for C$_{21}$H$_{24}$Cl$_2$: C, 72.62; H, 6.97. Found: C, 72.57; H, 7.01.

**General Procedure for Sulfuration of 6 by S$_x$Cl$_2$ at –78 °C.** To a solution of 6 (100 mg, 360 μmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise a solution of S$_x$Cl$_2$ (1.0 or 0.5 molar equiv.) in CH$_2$Cl$_2$ (5.0 mL) at –78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H$_2$O, dried over K$_2$CO$_3$, and evaporated. A ratio of the the products was estimated by $^1$H NMR.

**General Procedure for Reactions of 14 or 15 with 1.0 molar equiv. of S$_x$Cl$_2$ at –78 °C.** To a solution of 14 or 15 in CH$_2$Cl$_2$ was added dropwise a solution of S$_x$Cl$_2$ (1.0 molar equiv.) in CH$_2$Cl$_2$ at –78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched by addition of ice water. The organic layer was separated, washed with H$_2$O, dried over K$_2$CO$_3$, and evaporated. A ratio of the the products was estimated by $^1$H NMR.

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**REFERENCES AND NOTES**

†Dedicated to Prof. Kunio Ogasawara on the occasion of his 70th birthday.