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Intramolecular Diels-Alder Reactions of Thio-Substituted Dienes with Enones

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Thio-substituted dienes bearing an enone moiety were readily prepared from 3-sulfolenes, and their intramolecular Diels-Alder (IMDA) reactions were studied. Octahydronaphthalenones were produced in good yield with high stereoselectivity. Hexahydroindenones were also obtained, but the stereoselectivity was lower.

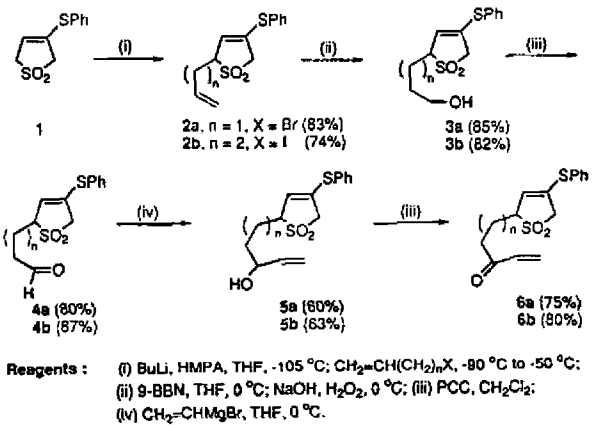
INTRODUCTION

The continuing importance of the intramolecular Diels-Alder (IMDA) reaction in modern organic synthesis may be attributed in large part to its unique utility for the construction of polycyclic frameworks from relatively simple precursors.[1] The problem of using the IMDA reaction is often the efficient and selective synthesis of the required diene and dienophile within the same molecule. It is well established that 3-sulfolenes are useful precursors to 1,3-dienes[2] and have often been used in the IMDA reaction.[3] We have been interested in the synthesis and reactions of sulfur-substituted dienes via 3-sulfolenes.[4] Although the use of sulfur-substituted dienes in the intermolecular Diels-Alder reaction has ample precedents,[5] examples of the corresponding intramolecular process are rare.[6] We recently reported that a sulfonyl group on the diene can facilitate its IMDA reaction with an alkenyl chain, but similar dienes bearing a phenylthio group resulted only in a 1,5-hydrogen shift without giving any cyclization product.[6a] We describe herein the synthesis and IMDA reactions of thio-substituted 3-sulfolenes bearing an enone as the dienophile.

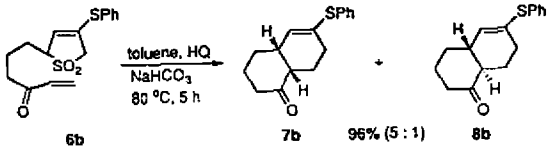
RESULTS AND DISCUSSION

3-Sulfolene derivatives **6a** and **6b** were synthesized in a straightforward manner as shown in Scheme I. Treatment of 3-phenylthio-3-sulfolene **1**[7] with BuLi (1 equiv) in THF at -105 °C in the presence of hexamethylphosphoric amide (HMPA, 4 equiv) followed by the addition of 3-bromopropene or 4-iodo-1-butene (2 equiv) gave the alkylated products **2** in good yield. Hydroboration of **2** with 9-BBN in THF followed by the oxidation with alkaline aqueous hydrogen peroxide produced the terminal alcohols **3** which were further oxidized with PCC to the aldehydes **4**. Addition of vinyl magnesium bromide at 0 °C afforded the allylic alcohols **5** which were subsequently oxidized to the enones **6**.

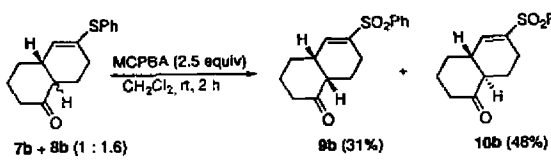
Scheme I



The 3-sulfolene derivatives **6** were directly used for the IMDA reaction. Thermolysis of **6b** in toluene at 80 °C for 5 h gave smoothly the Diels-Alder adducts **7b** and **8b** (5:1) almost in quantitative yield (Eq. 1). The ratio of **7b** and **8b** changed to 1:1.6 by treatment with NaOMe in MeOH. Since **7b** and **8b** could not be separated by column chromatography, they were further oxidized with MCPBA (2.5 equiv) in CH_2Cl_2 to give a separable mixture of **9b** and **10b** (Eq. 2). The *cis* ring structure of **9b** was confirmed by X-ray crystallography (Fig. 1).[8]

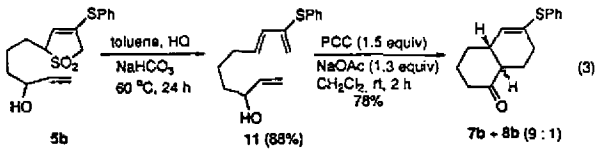


(1)



(2)

Since the stereoselectivity of IMDA reaction of **6b** was only moderate, we attempted to increase the stereoselectivity by carrying out the IMDA reaction at lower temperature. This requires the isolation of the triene precursor. Heating a solution of **5b** in toluene at 60 °C for 24 h gave the SO_2 extrusion product **11** in good yield. Further oxidation with PCC in the presence of NaOAc[9] at room temperature yielded directly the cycloaddition products **7b** and **8b** with good stereoselectivity (Eq. 3).



In contrast, thermolysis of **6a** in refluxing toluene for 30 min gave only the isomerized trienone as the result of a 1,5-hydrogen shift from the expected trienone.[6a] It was reasoned that the shorter chain length in **6a** (as compared to **6b**) made the desired IMDA reaction more difficult. To overcome this problem, a toluene solution of **6a** was heated in a sealed tube at 200 °C for 1 h in the presence of hydroquinone (HQ). This led successfully to the SO_2 extrusion and subsequent cycloaddition to afford a 6.6:1 mixture of products **7a** and **8a**, together with some of the isomerized trienone byproduct. Although **7a** and **8a** could not be separated, a single product **7a** was obtained when the mixture was treated with NaOMe in MeOH (Eq. 4). Oxidation of **7a** with MCPBA (2.5 equiv) in CH_2Cl_2 at room temperature for 2 h gave the sulfone **9a** whose structure was confirmed by comparing its spectra with those of **9b** (Eq. 5).

The stereoselectivity of the IMDA reaction can be explained by comparison of the various transition states involved in the cyclization. For the formation of octahydronaphthal-5-en-1-ones **7b** and **8b**, the *syn* transition state **A** is more favorable because the dienophile and the carbonyl group are in a coplanar arrangement so that the reaction proceeds through the preferred *endo*-orientation of the carbonyl

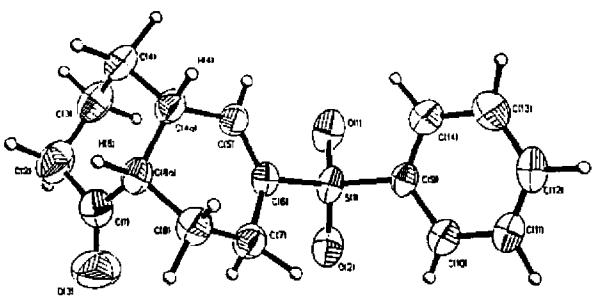
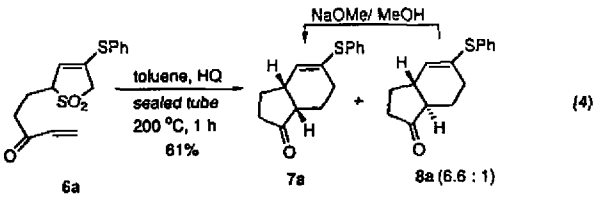
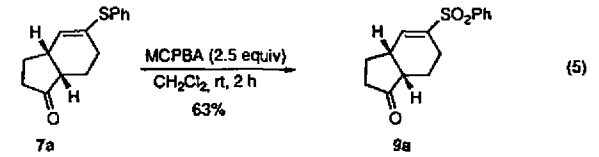
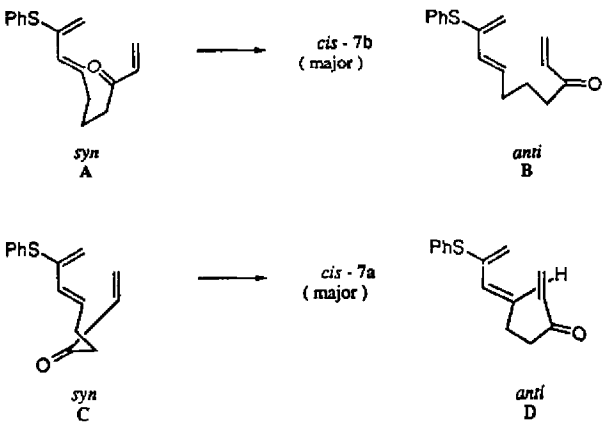


Fig. 1. Crystallographic structure of compound **9b**.





group. On the other hand, for the formation of hexahydroind-4-en-1-ones **7a** and **8a**, the required high reaction temperature for **6a** indicates that the IMDA proceeds through transition states of higher energy than for **6b**. Molecular models show that the carbonyl group is twisted out of the plane of the double bond in both the *syn* (**C**) and the *anti* (**D**) transition states. Thus, secondary orbital overlap of the carbonyl group with the diene in **C** is unlikely to contribute significantly in its stabilization. The preference for the transition state **C** is probably due to the disfavored interaction of the connecting chain with the vinylic hydrogen at C-4 in the transition state **D**.[10]



In summary, the thio-substituted dienes bearing an enone moiety can be readily prepared from the 3-sulfolene precursors, and undergo facile intramolecular Diels-Alder reactions. The presence of the carbonyl group increases the reactivity of the IMDA reaction. Without the carbonyl group, the thio-substituted dienes only undergo 1,5-hydrogen shift.[6a] The reactivity and stereoselectivity of the intramolecular Diels-Alder reaction of these dienes are also influenced by the chain length connecting the diene and the dienophile. The bicyclic products obtained from these reactions contain the functional group of ketone and vinyl sulfide or sulfone, which should be useful for further synthetic

transformations.[11]

EXPERIMENTAL SECTION

Infrared spectra were recorded with a FT-IR spectrometer Analect RFX-65. ^{1}H and ^{13}C NMR spectra were measured for samples in $CDCl_3$ with a FT-NMR spectrometer Bruker AC-300 at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. Mass spectra were recorded with a spectrometer JEOL JMS-D-100. High resolution mass spectra were measured with a mass spectrometer JEOL TMS-HX 110. Melting points were measured with an apparatus Mel-Temp and are uncorrected. The silica gel used for flash column chromatography was made by Merck (60 H). The sealed tube used for thermolysis was made by Ace Glass (catalog no. 8648-23). Compound **2a** was prepared by the literature procedure.[6a] All reagents were of reagent grade and were purified prior to use.[12]

2-(3-Butenyl)-4-phenylthio-3-sulfolene (2b)

To a solution of 3-(phenylthio)-3-sulfolene **1** (5.20 g, 23 mmol) in THF (90 mL) and HMPA (17.4 mL, 92 mmol) at -105 °C was added dropwise a solution of BuLi in hexane (19.1 mL, 1.2 M, 23 mmol). The solution was slowly warmed to -90 °C, and 4-iodo-1-butene (16.7 g, 92 mmol) was then added in one portion. The reaction mixture was poured into a saturated ammonium chloride solution (80 mL) at -50 °C. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (50 mL × 3). The organic solution was dried ($MgSO_4$) and evaporated. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:6) as eluent to give **2b** (4.8 g, 74% yield); IR (neat) 3074, 2976, 2927, 2852, 1440, 1313, 1219, 1128, 916, 749, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.63-1.78 (1H, m), 2.01-2.13 (1H, m), 2.20-2.28 (2H, m), 3.64-3.78 (2H, m), 3.82-3.87 (1H, m), 5.02-5.11 (2H, m), 5.69-5.83 (2H, m), 7.36-7.47 (5H, m); ^{13}C NMR ($CDCl_3$) δ 27.9, 30.7, 57.3, 66.1, 116.4, 125.3, 129.0, 129.6, 131.4, 133.1, 136.2, 136.2; MS (rel intensity) *m/z* 280 (M^+,2), 216 (100), 109 (66), 91 (80); exact mass calcd for $C_{14}H_{16}O_2S_2$ *m/z* 280.0593, found 280.0597.

2-(3-Hydroxypropyl)-4-phenylthio-3-sulfolene (3a)

To a solution of **2a** (2.15 g, 8.1 mmol) in dried THF (5 mL) at 0 °C was slowly added 9-BBN (17 mL, 8.5 mmol; 0.5 Min THF) under nitrogen, and the reaction mixture was allowed to warm to room temperature. The mixture was stirred for another 2.5 h. Residual hydride was decomposed by adding water (5 mL) followed by adding 3 N NaOH (3 mL) and 30% H_2O_2 (3 mL) at 0 °C. The mixture was warmed to room temperature, and stirred for 1 h. The solvent was removed under vacuum, and then the residue was extracted with CH_2Cl_2 (20 mL × 3). The organic solution was dried ($MgSO_4$) and evaporated. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:1) as eluent to give **3a** (1.95 g, 85% yield); IR (neat) 3491, 3057, 2931, 2874, 1440, 1308, 1219, 1126, 750, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64-1.77 (3H, m), 1.93-1.98 (1H, m), 2.62 (1H, br s), 3.59-3.75 (4H, m), 3.83-3.85 (1H, m), 5.71-5.73 (1H, m), 7.32-7.41 (5H, m); ^{13}C NMR ($CDCl_3$) δ 25.3, 29.4, 57.3, 61.5, 66.7, 125.4, 128.9, 129.4, 129.5, 131.1, 133.0; MS (rel intensity) *m/z* 284 (M^+, 2), 220 (14), 110 (100), 109 (40), 64 (39); exact mass calcd for $C_{13}H_{16}O_3S_2$ *m/z* 284.0545, found 284.0542.

2-(4-Hydroxybutyl)-4-phenylthio-3-sulfolene (3b)

To a solution of **2b** (3.60 g, 12.9 mmol) in dried THF (5 mL) at 0 °C was added 9-BBN (27 mL, 13.5 mmol; 0.5 M in THF) and then stirred at room temperature for 3 h. Residual hydride was decomposed by adding water (5 mL) followed by adding 3 N NaOH (4.7 mL) and 30% H_2O_2 (4.7 mL) at 0 °C. The workup procedure was the same as that for **3a** to give **3b** (3.14 g, 82% yield); IR (neat) 3450, 3080, 2950, 2880, 1440, 1311, 1218, 1130, 750, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51-1.71 (5H, m), 1.91-1.99 (2H, m), 3.61-3.81 (5H, m), 5.72-5.74 (1H, m), 7.36-7.43 (5H, m); ^{13}C NMR ($CDCl_3$) δ 23.2, 28.6, 32.1, 57.5, 62.1, 67.2, 125.5, 129.1, 129.6, 129.7, 131.5, 133.2; MS (rel intensity) *m/z* 298 (M^+, 1), 234 (11), 110 (100), 109 (32), 64 (39); exact mass calcd for $C_{14}H_{18}O_3S_2$ *m/z* 298.0698, found 298.0693.

2-(3-Oxopropyl)-4-phenylthio-3-sulfolene (4a)

To a stirred solution of pyridinium chlorochromate (680 mg, 3.10 mmol) in dried CH_2Cl_2 (20 mL) was added a solution of **3a** (440 mg, 1.55 mmol) in CH_2Cl_2 (10 mL) at room temperature under nitrogen. The reaction mixture was stirred at room temperature for 3 h and then diluted with dried ether (50 mL). The ether layer was filtered through Celite, dried ($MgSO_4$) and concentrated by a rotary evaporator. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:3) as eluent to give the pure product **4a** (348 g, 80% yield); IR (neat) 3057, 2975, 2929, 1721, 1440, 1310, 1221, 1126, 750, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05-2.14 (2H, m), 2.69-2.75 (2H, m), 3.65-3.73 (2H, m), 3.85-3.88 (1H, m), 5.61-5.63 (1H, m), 7.36-7.45 (5H, m), 9.75 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.3, 40.3, 57.5, 65.9, 124.1, 129.2, 129.2, 129.7, 132.3, 133.5, 199.9; MS (rel intensity) *m/z* 282 (M^+, 63), 218 (78), 173 (54), 109 (100), 65 (71); exact mass calcd for

$C_{13}H_{14}O_3S_2$ *m/z* 282.0385, found 282.0389.

2-(4-Oxobutyl)-4-phenylthio-3-sulfolene (4b)

To a stirred solution of PCC (1.20 g, 5.4 mmol) in dried CH_2Cl_2 (50 mL) was added a solution of **3b** (806 mg, 2.71 mmol) in CH_2Cl_2 (10 mL) at room temperature under nitrogen. After stirring for 2 h, the same workup procedure as that for **4a** gave **4b** (694 mg, 87% yield); IR (neat) 3070, 2950, 1715, 1440, 1310, 1220, 1130, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68-1.94 (4H, m), 2.50-2.55 (2H, t, *J* = 6.6 Hz), 3.65-3.81 (3H, m), 5.69-5.70 (1H, m), 7.37-7.45 (5H, m), 9.76 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 19.4, 28.4, 43.2, 57.6, 66.9, 124.6, 129.2, 129.4, 129.8, 132.1, 133.4, 201.1; MS (rel intensity) *m/z* 296 (M^+, 2), 232 (14), 218 (51), 110 (100), 109 (70), 77 (49), 64 (48); exact mass calcd for $C_{14}H_{16}O_3S_2$ *m/z* 296.0542, found 296.0542.

2-(3-Hydroxy-4-pentenyl)-4-phenylthio-3-sulfolene (5a)

To a solution of **4a** (1.21 g, 4.20 mmol) in dried THF (30 mL) was added vinyl magnesium bromide (5.5 mL, 5.50 mmol, 1.0 M in THF) dropwise at 0 °C under nitrogen, and was then stirred for 15 min. To the reaction mixture was added a saturated NH_4Cl solution (20 mL) at 0 °C. The solvent was removed by a rotary evaporator, and the residue was extracted with CH_2Cl_2 (20 mL × 3). The organic solution was dried ($MgSO_4$) and evaporated. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:3) as eluent to give an inseparable mixture of two diastereomers **5a** (798 mg, 60% yield); IR (neat) 3515, 3058, 2927, 1440, 1310, 1219, 1127, 1023, 925, 749, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66-1.79 (3H, m), 1.99-2.03 (2H, m), 3.69-3.72 (2H, m), 3.70-3.90 (1H, m), 4.12-4.16 (1H, m), 5.09-5.14 (1H, m), 5.23 (1H, d, *J* = 17.0 Hz), 5.71-5.74 (1H, m), 5.78-5.89 (1H, m), 7.36-7.44 (5H, m); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.0, 33.5, 33.8, 57.5, 66.8, 67.1, 72.1, 72.3, 115.2, 125.5, 129.0, 129.2, 129.7, 131.4, 133.2, 140.3; MS (rel intensity) *m/z* 310 (M^+-64, 0.2), 218 (100), 185 (11), 109 (74). These two isomers have some distinct ^{13}C NMR absorptions: the major isomer, δ 24.7, 33.5, 67.1, 72.3; the minor isomer, δ 25.0, 33.8, 66.8, 72.1 in a ratio of approximately 1:1.

2-(4-Hydroxy-5-hexenyl)-4-phenylthio-3-sulfolene (5b)

To a solution of **4b** (0.37 g, 1.25 mmol) in dried THF (10 mL) was added vinylmagnesium bromide (1.5 mL, 1.5 mmol, 1.0 M in THF) dropwise at 0 °C under nitrogen, and was then stirred for 15 min. The workup procedure was the same as that for **5a** to give an inseparable mixture of two diastereomers **5b** (0.26 g, 63% yield); IR (neat) 3512, 3059, 2929, 1440, 1309, 1219, 1127, 749, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54-1.71 (5H, m), 1.90-2.08 (2H, m), 3.62-3.80 (3H, m), 4.08-4.10 (1H, m), 5.08 (1H, d, *J* = 10.5 Hz), 5.20 (1H, d, *J* = 17.2 Hz), 5.73-5.88 (2H, m), 7.35-7.43 (5H, m); ^{13}C NMR ($CDCl_3$) δ 22.7, 22.7, 28.6, 28.7, 36.3, 36.4, 57.4, 67.0, 72.4, 114.8, 125.5, 129.0, 129.0, 129.6, 131.3, 133.1, 140.8; MS (rel intensity) *m/z* 324 (M^+ - 64,33), 150 (66), 110 (100), 109 (41), 64 (96). These two isomers have some distinct ^{13}C NMR absorptions: the major isomer, δ 22.6, 28.6, 36.3; the minor isomer, δ 22.7, 28.7, 36.4 in a ratio of approximately 1:1.

2-(3-Oxo-4-pentenyl)-4-phenylthio-3-sulfolene (6a)

To a stirred solution of PCC (38 mg, 0.174 mmol) in dried CH_2Cl_2 (3 mL) was added a solution of **5a** (27 mg, 0.087 mmol) in CH_2Cl_2 (2 mL) at room temperature under nitrogen, and was then stirred for 2 h. The workup procedure was the same as that for **4a** to give **6a** (20 mg, 75% yield); IR (neat) 2959, 2929, 1732, 1463, 1381, 1273,1123, 1072, 743, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09-2.19 (2H, m), 2.78-2.89 (2H, m), 3.17-3.74 (2H, m), 3.89-3.91 (1H, m), 5.64-5.67 (1H, m), 5.88 (1H, dd, *J* = 9.9, 1.6 Hz), 6.24 (1H, dd, *J* = 17.6, 1.6 Hz), 6.35 (1H, dd, *J* = 17.6, 9.9 Hz), 7.38-7.45 (5H, m); ^{13}C NMR ($CDCl_3$) δ 22.9, 35.8, 57.5, 66.2, 124.7, 124.8, 128.8, 129.3, 129.6, 131.8, 133.3, 136.0, 198.6; MS (rel intensity) *m/z* 308 (M^+, 3), 244 (76), 189 (93), 174 (52), 110 (89), 109 (76), 64 (100); exact mass calcd for $C_{15}H_{16}O_3S_2$ *m/z* 308.0542, found 308.0540.

2-(4-Oxo-5-hexenyl)-4-phenylthio-3-sulfolene (6b)

To a stirred solution of PCC (1.08 g, 4.89 mmol) in dried CH_2Cl_2 (30 mL) was added a solution of **5b** (792 mg, 2.4 mmol) in CH_2Cl_2 (10 mL) at room temperature under nitrogen, and was then stirred for 2 h. The workup procedure was the same as that for **6a** to give **6b** (0.63 g, 80% yield); IR (neat) 2928, 1697, 1440, 1311, 1219, 1125, 1023, 749, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66-1.93 (4H, m), 2.66 (2H, t, *J* = 6.3 Hz), 3.64-3.83 (3H, m), 5.71-5.74 (1H, m), 5.84 (1H, dd, *J* = 10.2, 1.4 Hz), 6.21 (1H, dd, *J* = 17.7, 1.4 Hz), 6.34 (1H, dd, *J* = 17.7, 10.2 Hz), 7.37-7.45 (5H, m); ^{13}C NMR ($CDCl_3$) δ 21.0, 28.3, 38.7, 57.5, 67.0, 125.0, 128.3, 129.1, 129.5, 129.7, 131.7, 133.3, 136.3, 199.5; MS (rel intensity) *m/z* 322 (M^+, 1), 258 (97), 149 (69), 131 (100), 109 (57), 77 (79); exact mass calcd for $C_{16}H_{18}O_3S_2$ *m/z* 322.0698, found 322.0698.

***cis*-5-Phenylthio-2,3,3a,6,7,7a-hexahydroinden-1-one (7a) and *trans*-5-Phenylthio-2,3,3a,6,7,7a-hexahydroinden-1-one (8a)**

A mixture of **6a** (35 mg, 0.114 mmol), hydroquinone (3 mg) and $NaHCO_3$ (9 mg, 0.114 mmol) in toluene (8 mL)

was heated in a sealed tube at 200 °C for 1 h. The solvent was removed under vacuum, and the crude product was purified by flash column chromatography using ethyl acetate/hexane (1:10) as eluent to give a 6.6:1 mixture of **7a** and **8a** (17 mg, 61% yield). These two isomers could not be separated by HPLC. The following spectral data were measured for the mixture: IR (neat) 3056, 2933, 1738, 1476, 1438, 743, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65-2.44 (m), 2.98-3.11 (m), 5.85-5.91 (m), 6.08-6.15 (m), 7.23-7.34 (m); MS (rel intensity) *m/z* 244 (M^+, 100), 135 (20), 109 (10), 91 (16), 77 (12); exact mass calcd for $C_{15}H_{16}OS$ *m/z* 244.0922, found 244.0928. The two isomers have different ^1H NMR absorptions for the vinylic proton: **7a**, δ 5.85-5.91; **8a**, δ 6.08-6.15. The ratio of these two isomers was determined by intergration of the vinylic proton. The ^{13}C NMR absorptions of these two isomers could be assigned due to the difference in peak intensities. **7a**: δ 21.4, 26.6, 27.4, 36.3, 38.0, 46.2, 127.0, 129.0, 131.2, 131.4, 133.7, 134.6, 220.0; **8a**: δ 21.7, 26.2, 30.9, 37.9, 42.3, 53.1, 127.2, 131.5, 131.6, 131.8, 133.8, 135.0, 215.3.

cis-6-Phenylthio-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-one (7b) and _trans_-6-Phenylthio-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-one (8b)

Method A: A mixture of **6b** (0.63 g, 1.96 mmol), hydroquinone (5 mg) and $NaHCO_3$ (166 mg, 1.96 mmol) in toluene (20 mL) was heated at 80 °C for 5 h. The solvent was removed under vacuum, and the crude product was purified by flash column chromatography using ethyl acetate/hexane (1:10) as eluent to give a 5:1 mixture of **7b** and **8b** (485 mg, 96% yield). These two isomers could not be separated by HPLC. The following spectral data were measured for the mixture: IR (neat) 3057, 2927, 2861, 1711, 1582, 1475, 1439, 742, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51-1.61 (m), 1.65-1.78 (m), 1.81-1.95 (m), 2.05-2.45 (m), 2.47-2.60 (m), 2.80-2.90 (m), 5.79-5.81 (m), 5.84-5.85 (m), 7.18-7.35 (m); MS (rel intensity) *m/z* 258 (M^+, 100), 218 (67), 109 (84), 91 (50), 77 (52); exact mass calcd for $C_{16}H_{18}OS$ *m/z* 258.1080, found 258.1080. The two isomers have different ^1H NMR absorptions for the vinylic proton: **7b**, δ 5.79-5.81; **8b**, δ 5.84-5.85. The ratio of these two isomers was determined by intergration of the vinylic proton. The ^{13}C NMR absorptions of these two isomers could be assigned due to the difference in peak intensities. **7b**: δ 23.3, 23.3, 27.6, 29.5, 39.0, 40.6, 47.2, 126.9, 128.9, 131.1, 133.0, 133.2, 134.0, 212.1; **8b**: δ 22.2, 26.2, 29.7, 31.8, 41.4, 44.3, 51.7, 127.0, 128.9, 131.2, 133.4, 134.0, 134.1, 211.1.

Method B: To a stirred solution of PCC (26 mg, 0.12 mmol) and NaOAc (9 mg, 0.10 mmol) in dried CH_2Cl_2 (5 mL) was added a solution of **11** (20 mg, 0.08 mmol) in CH_2Cl_2 (3 mL) at room temperature under nitrogen, and was then stirred for 2 h. The workup procedure was the same as that for **6a** to give a 9:1 mixture of **7b** and **8b** (16 mg, 78%).

cis-5-Phenylsulfonyl-2,3,3a,6,7,7a-hexahydroinden-1-one (9a)

To a solution of **7a** (65 mg, 0.266 mmol) in CH_2Cl_2 (5 mL) in an ice bath was added dropwise a solution of MCPBA (0.287 g, 0.666 mmol; 40% purity) in CH_2Cl_2 (5 mL). The mixture was stirred for 2 h, washed sequentially with saturated $NaHCO_3$ and $Na_2S_2O_3$, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:2) as eluent to give **9a** (46 mg, 63% yield); mp 135-136 °C; IR (KBr) 3062, 2942, 1737, 1446, 1304, 1150, 1091, 748, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65-1.75 (1H, m), 1.95-2.48 (8H, m), 3.08-3.20 (1H, m), 7.04-7.06 (1H, m), 7.45-7.64 (3H, m), 7.80-7.83 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.2, 20.2, 26.6, 36.3, 37.0, 45.6, 127.9, 129.2, 133.4, 138.6, 139.0, 141.7, 218.2; MS (rel intensity) *m/z* 276 (M^+, 100), 219 (14), 135 (51), 134 (28), 91 (27), 77 (51); exact mass calcd for $C_{15}H_{16}O_3S$ *m/z* 276.0820, found 276.0815. Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.83. Found: C, 65.23; H, 5.81.

cis-6-Phenylsulfonyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-one (9b) and _trans_-6-Phenylsulfonyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-1-one (10b)

To a solution of **7b** and **8b** (481 mg, 1.86 mmol, **7b**:**8b** = 1:1.6) in CH_2Cl_2 (5 mL) in an ice bath was added dropwise a solution of MCPBA (2.01 g, 4.66 mmol; 40% purity) in CH_2Cl_2 (5 mL). The mixture was stirred for 2 h, washed sequentially with saturated $NaHCO_3$ and $Na_2S_2O_3$, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using ethyl acetate/hexane (1:2) as eluent to give **9b** (0.26 g, 48% yield) and **10b** (0.17 g, 31% yield). **9b**: mp 112-113 °C; IR (KBr) 3062, 2935, 2864, 1711, 1446, 1304, 1151, 1086, 752, 717, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5-1.58 (1H, m), 1.61-1.76 (1H, m), 1.83-1.88 (2H, m), 1.95-2.08 (1H, m), 2.16-2.22 (2H, m), 2.25-2.32 (3H, m), 2.49-2.55 (1H, m), 2.91-3.01 (1H, m), 6.89-6.92 (1H, m), 7.49-7.55 (2H, m), 7.58-7.63 (1H, m), 7.79-7.82 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.9, 23.5, 28.8, 38.0, 40.5, 46.3, 127.9, 129.1, 133.3, 139.1, 139.6, 141.5, 210.4; MS (rel intensity) *m/z* 290 (M^+, 9), 149 (100), 125 (21), 77 (63); exact mass calcd for $C_{16}H_{18}O_3S$ *m/z* 290.0977, found 290.0971. Anal. Calcd for $C_{16}H_{18}O_3S_2$: C, 66.18; H, 6.25. Found: C, 66.13; H, 6.22. **10b**: a viscous liquid; IR (neat) 3062, 2935, 2864, 1714, 1446, 1304, 1151, 1085, 752, 717, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30-1.48 (1H, m),

1.52-1.81 (2H, m), 2.03-2.18 (5H, m), 2.25-2.42 (4H, m), 6.89-6.90 (1H, br s), 7.47-7.53 (2H, m), 7.56-7.62 (1H, m), 7.80-7.83 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.7, 22.8, 26.0, 30.7, 41.1, 42.9, 50.5, 128.0, 129.1, 133.3, 139.0, 140.2, 140.4, 209.5; MS (rel intensity) *m/z* 290 (M^+, 13), 165 (23), 149 (100), 148 (28), 131 (28), 91 (22), 77 (28); exact mass calcd for $C_{16}H_{18}O_3S$ *m/z* 290.0977, found 290.0979. Anal. Calcd for $C_{16}H_{18}O_3S_2$: C, 66.18; H, 6.25. Found: C, 66.11; H, 6.19.

(*E*)-9-Phenylthio-1,7,9-decatrien-3-ol (11)

A mixture of **5b** (47 mg, 0.145 mmol), hydroquinone (3 mg) and $NaHCO_3$ (13 mg, 0.145 mmol) in toluene (8 mL) was heated at 60 °C for 24 h. The solvent was removed under vacuum, and the crude product was purified by flash column chromatography using ethyl acetate/hexane (1:3) as eluent to give **11** (33 mg, 88% yield); IR (neat) 3374, 3073, 3008, 2925, 2851, 1478, 1439, 1303, 1222, 1125, 1090, 1024, 742, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35-1.48 (4H, m, H-4, H-5), 1.61 (1H, br s, OH), 2.13 (2H, q, *J* = 6.5 Hz, H-6), 4.05 (1H, q, *J* = 5.8 Hz, H-3), 5.08 (1H, s, H-10), 5.12 (1H, d, *J* = 11.4 Hz, H-1), 5.21 (1H, d, *J* = 17.1 Hz, H-1), 5.39 (1H, s, H-10), 5.82 (1H, m, H-2), 6.03 (1H, dt, *J* = 15.8, 6.5 Hz, H-7), 6.17 (1H, d, *J* = 15.8 Hz, H-8), 7.24-7.40 (5H, m); ^{13}C NMR ($CDCl_3$) δ 24.7, 32.2, 36.4, 73.0, 114.6, 117.5, 127.1, 129.0, 129.2, 131.7, 132.1, 134.0, 141.1, 141.4.

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Key Words

Intramolecular Diels-Alder reaction; 3-Sulfolene; Vinyl sulfides; Vinyl sulfones.

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8. Crystal data for **9b**: $C_{16}H_{18}O_3S$, fw = 290.4, monoclinic, $P2_1/n$, a = 11.747(2) Å, b = 8.6330(10) Å, c = 15.3740(10) Å, β = 110.170(0), V = 1463.6(3) Å^3, Z = 4, d_{calcd} = 1.318 Mg/m^3, λ (MoKα) = 0.71073 Å, μ = 0.225 mm^{-1}, F(000) = 616, T = 298 K. Sample was studied on an automatic diffractometer Siemens P4. Structure was solved with a Patterson map and refined by fullmatrix least-square techniques with the resulting R_f = 4.48%, $R\omega$ = 6.08%, $S\omega$ = 0.85% (residual $\Delta\rho < 0.23$ eÅ^{-3}).
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