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# ORGANIC SYNTHESIS WITH ALLYLIC SULFUR COMPOUNDS: REACTIONS OF THE 13-THIABICYCLO[8.2.1]-5-TRIDECENE RING SYSTEM

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Ultraviolet irradiation of (*Z*)-2,9-bismethylene-13-thiabicyclo[8.2.1]-5-tridecene (**8**), prepared from (*Z*)-2,9-dichloro-13-thiabicyclo[8.2.1]-5-tridecene (**1**) by way of (*Z*)-2,9-dioxo-13-thiabicyclo[8.2.1]-5-tridecene (**7**), affords (*Z*)-3,10-bismethylene-1,6,11-dodecatriene (**15**) in trimethylphosphite and a 9:1 mixture of (*Z*)-2-methylenebicyclo[7.3.1]trideca-5(6),9(10)-diene (**16**) and (*Z,Z,Z*)-bicyclo[6.4.2]tetradeca-1(12),4(5),8(9)-triene (**17**) when irradiated in hexane. Similarly photolysis of 2,5-bis(3-methyl-1-buten-2-yl)thiolane (**18**) in hexane affords 2-isopropyl-4-(3-methyl-1-buten-2-yl)-cyclohexene (**19**). Mechanisms involving radicals are proposed.

## INTRODUCTION

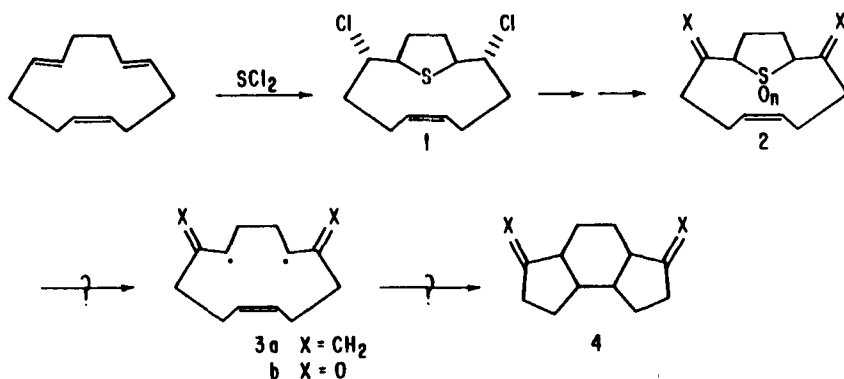
The readily available sulfur dichloride-(*E,E,Z*)-1,5,9-cyclododecatriene adduct (*Z*)-2,9-dichloro-13-thiabicyclo[8.2.1]-5-tridecene (**1**)<sup>1</sup> with its diversity of sterically proximate reactive centers is a potentially useful intermediate for the construction of polycyclic ring systems. For example conversion of **1** into derivatives **2** (*n* = 0 or 2) followed by thermal or photochemical desulfurization or extrusion of sulfur dioxide could give tricyclic compounds **4** via diradical **3** or related species (Scheme 1). We report the results of a study of transformations of **1**, and certain monocyclic analogues, leading to the formation of novel hydrocarbons.

## RESULTS AND DISCUSSION

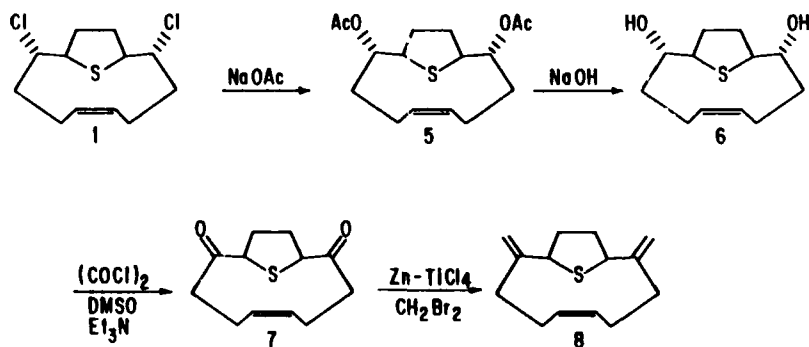
Following published procedures,<sup>1,2</sup> adduct **1** was converted to known<sup>2</sup> diol **6** by way of diacetate **5** (Scheme 2). Oxidation of **6** by the Swern procedure<sup>3</sup> gave nicely crystalline diketone (*Z*)-2,9-dioxo-13-thiabicyclo[8.2.1]-5-tridecene (**7**) in 97% yield. Attempts to prepare **7** directly from dichloride **1** with silver tetrafluoroborate/dimethyl sulfoxide<sup>4</sup> or tetrabutylammonium dichromate<sup>5</sup> met with only limited success. Conversion of **7** into bismethylene derivative (*Z*)-2,9-bismethylene-13-thiabicyclo[8.2.1]-5-tridecene (**8**) was best done using the useful procedure of Lombardo<sup>6</sup> involving zinc-titanium tetrachloride-methylene dibromide. In this manner **8** could be prepared in 89% yield (77% overall yield from **1**). Preparation of **8** using the

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SCHEME 1

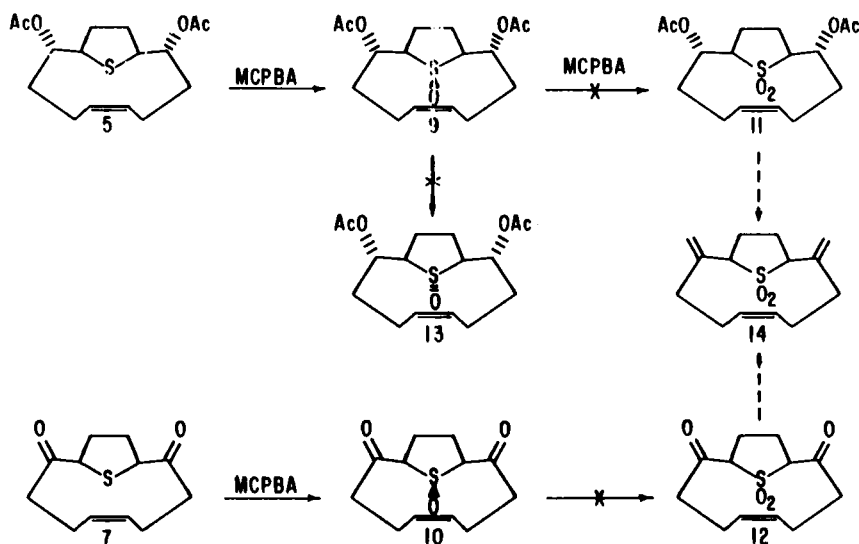


SCHEME 2

Wittig reagent triphenylphosphinemethylide was unsatisfactory due to low yields, incomplete methylenation and formation of diastereomers of **8**, perhaps via prior enolization of diketone **7**.<sup>7</sup> The lithiophosphine reagent developed by Corey<sup>8</sup> also was unsatisfactory for preparation of **8** from **7**.

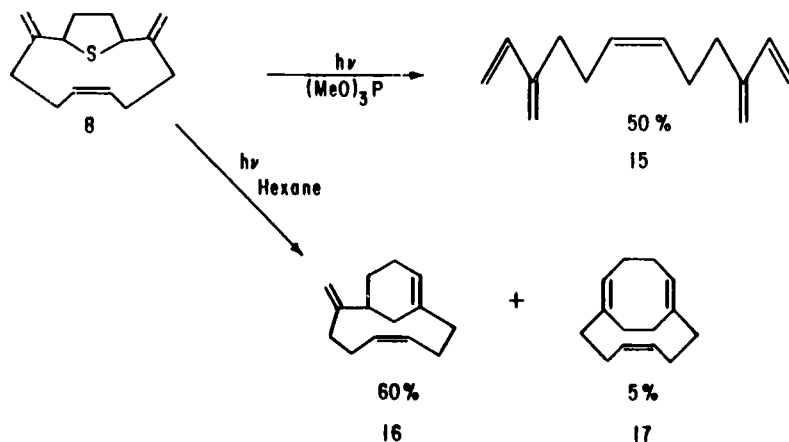
Diacetate **5** and diketone **7** could be oxidized with MCPBA to sulfoxides **9** and **10**, respectively (Scheme 3). However all efforts to convert **5** or **9** to sulfone **11** were unsuccessful as were attempts to oxidize diol **6** or diketone **7** directly to sulfone **12**. Efforts to invert sulfoxide **9** to sulfoxide **13**, which might undergo oxidation to sulfone **11** more easily than sulfoxide **9**, also were unsuccessful. Thus, we were not able to prepare bismethylenesulfone **14**. We conclude that substantial steric hindrance exists to the approach of reagents to the sulfur from the face containing the 12-membered ring so that only one (exo) oxygen can be attached.<sup>9</sup>

In order to test the proposal of Scheme 1, the photochemical extrusion of sulfur from sulfides **7** and **8** was explored. In particular it was hoped that diradical **3a** could be formed upon photolysis of allylic sulfide **8** in trimethyl phosphite, employing the useful procedure for allylic and benzylic coupling developed by one of us some years ago.<sup>10</sup> In the event, irradiation at 254 nm of a 1% solution of **8** in trimethyl phosphite for 4 h gave in 50% yield an oily liquid that could be

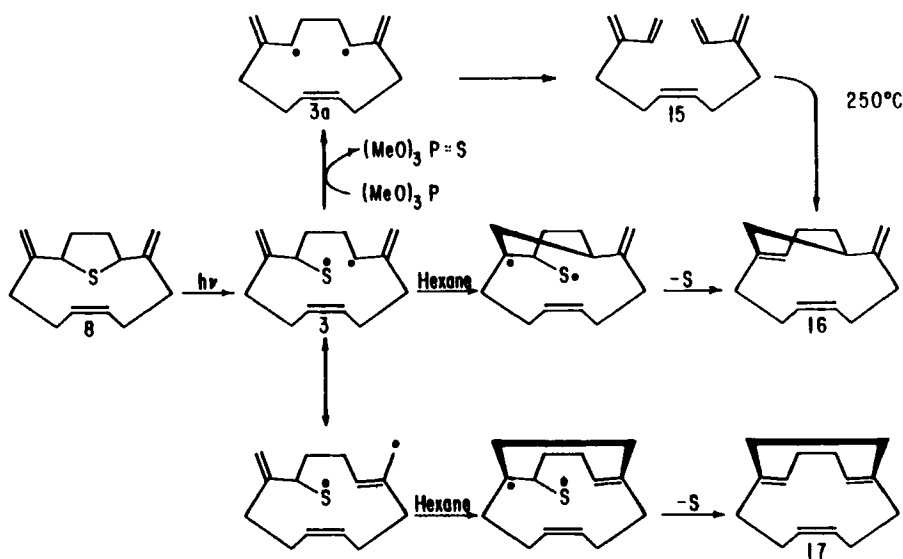


SCHEME 3

characterized by spectral methods (see Experimental) as (*Z*)-3,10-bismethylene-1,6,11-dodecatriene (**15**) (Scheme 4). The formation of **15** can be explained by 1,4-fragmentation of the intermediate diradical **3** (Scheme 5).<sup>11</sup> Photolysis of **8** in hexane at 254 nm was much slower than in trimethyl phosphite due to the build-up of a sulfur coating on the tube walls. This problem could be partially avoided by the addition of an equivalent of trimethyl phosphite. In this case photolysis for 25 h gave a 9 : 1 mixture of two hydrocarbon products which were separated by HPLC and characterized spectroscopically (see Experimental) as (*Z*)-2-methylenebicyclo[7.3.1]trideca-5(6),9(10)-diene (**16**) and (*Z,Z,Z*)-bicyclo[6.4.2]tetradeca-1(12),4(5),8(9)-triene (**17**). These products could arise via free-radical processes as



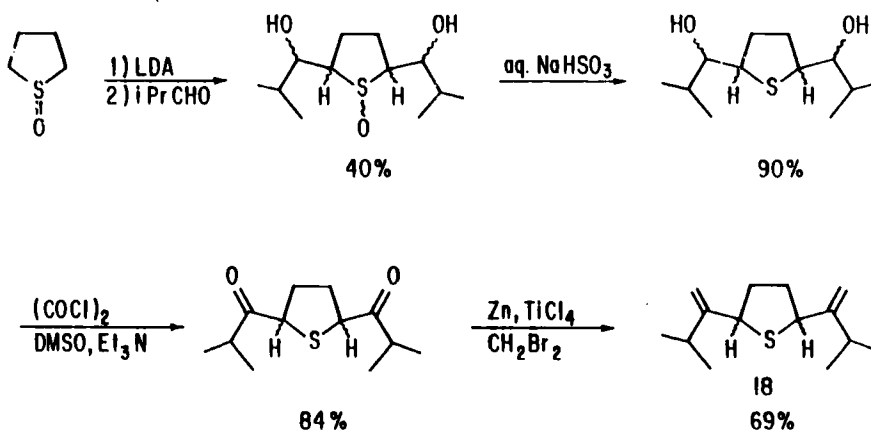
SCHEME 4



SCHEME 5

depicted in Scheme 5. Compound **16** might also arise via an intramolecular Diels-Alder reaction of pentaene **15** in accord with studies by Shea.<sup>12</sup> Indeed, a 10% yield of **16** (by GC) could be realized by heating **15** at  $250^\circ\text{C}$ . Irradiation of diketone **7** under a variety of conditions did not afford significant quantities of sulfur-free products.

We have examined the extension of these photochemical reactions to monocyclic diallylic sulfides. Thus we have prepared 2,5-bis(3-methyl-1-buten-2-yl)thiolane **18** from thiolane *S*-oxide in 21% overall yield as shown in Scheme 6. Irradiation of a hexane solution of **18** affords 2-isopropyl-4-(3-methyl-1-buten-2-yl)cyclohexene **19** in 25% yield (Scheme 7) by a mechanism presumably analogous to that shown in Scheme 5.



SCHEME 6



SCHEME 7

## EXPERIMENTAL

**General.** NMR spectra were recorded on a Bruker WH-90 or Varian EM360A or XL-300 spectrometers using tetramethylsilane as internal standard; abbreviations used are *s* (singlet), *d* (doublet), *t* (triplet), *m* (multiplet). Mass spectra were obtained on an AEI MS-902 mass spectrometer. Analytical gas chromatography (GC) was performed on a Perkin-Elmer Sigma 2B Gas Chromatograph interfaced to a Perkin-Elmer Sigma 10B Data Station. A 50 m OV-101 fused silica capillary column was used for all analyses. High pressure liquid chromatography (HPLC) was performed on a Perkin Elmer Series 3B liquid chromatograph with LC-85 spectrophotometric and LC-25 refractive index detectors. Melting points are corrected. Ultraviolet (UV) spectra were recorded on a Varian DMS 80 UV-visible spectrophotometer. Ultraviolet irradiation was conducted using a Rayonet Model RPR100 photochemical reactor equipped with 8 low pressure mercury lamps with maximum output at 254 or 300 nm. All samples were degassed with dry argon for 15 min prior to irradiation. Tetrahydrofuran and methylene chloride were dried by distillation from lithium aluminum hydride; dimethyl sulfoxide, trimethyl phosphite and triethylamine were distilled from calcium hydride prior to use.

(*Z*)-2,9-Dioxo-13-thiabicyclo[8.2.1]-5-tridecene (**7**). (*Z*)-2,9-Dihydroxy-13-thiabicyclo[8.2.1]-5-tridecene (**6**), mp 174–175°C (lit.<sup>2</sup> 176–178°C), was obtained in 96% yield from (*Z*)-2,9-diacetoxy-13-thiabicyclo[8.2.1]-5-tridecene (**5**) (85% yield, mp 146–147°C; lit.<sup>2</sup> 146–148°C) which was in turn prepared from (*Z*)-2,9-dichloro-13-thiabicyclo[8.2.1]-5-tridecene (**1**) (80% yield, mp 131–132°C; lit. 128–129°C<sup>2</sup>, 139.5–141.5°C<sup>1</sup>). To a solution of 11.3 g (88.6 mmol) of oxalyl chloride in 200 mL of anhydrous methylene chloride in a 3-necked 1 L round bottom flask equipped with a thermometer, a mechanical stirrer and a constant addition funnel was added a solution of 13.8 g (177.2 mmol) of anhydrous dimethyl sulfoxide in 45 mL of methylene chloride at –50 to –60°C. After stirring the reaction mixture for 10 min, a solution of 10 g (43.9 mmol) of **6** in the minimal quantity of dimethyl sulfoxide-methylene chloride was added during 10 min. The solution was stirred for 30 min and then treated over the course of 15 min with 60 mL of anhydrous triethylamine. The reaction mixture was warmed to room temperature, diluted with 150 mL of methylene chloride, washed with water (3 × 100 mL), 0.25% sulfuric acid (3 × 100 mL), 5% sodium bicarbonate (2 × 100 mL), and brine (100 mL), dried (magnesium sulfate), and concentrated *in vacuo* giving **7** (9.53g, 97% yield), mp 102–103°C (from ethanol), IR (CH<sub>2</sub>Cl<sub>2</sub>) 3005-2850, 1700 (C=O), 1450, 1220, 1100, 1055, 720 (Z-CH=CH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.4 (2 H, m, —CH=), 3.82 (2 H, m, C(O)—CH—S), 2.42 (12 H, m, 6 CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 205.9 (C=O), 129.5 (—CH=CH—), 57.2, 39.4, 30.9, 25.0; UV λ<sub>max</sub> 237, 302; MS 224 (100%, M<sup>+</sup>), 196, 191, 168, 163, 139, 137, 126, 113, 95.

Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>S: C, 64.25; H, 7.19. Found: C, 64.25; H, 7.30.

(*Z*)-2,9-Bismethylene-13-thiabicyclo[8.2.1]-5-tridecene (**8**). Titanium tetrachloride (23 mL; 0.21 mol) was added dropwise during the course of 30 min to a stirred suspension of zinc dust (57.5 g, 0.88 mol), methylene bromide (20.2 mL, 0.29 mol) and dry tetrahydrofuran (500 mL) at –40°C. The mixture was warmed to 5°C and was stirred at this temperature in a cold room for 3 days. The resultant thick grey slurry was added in portions to a solution of **7** (5.0 g, 22.3 mmol) in dry methylene chloride (750 mL) at 25°C, monitoring the reaction for starting material or monoketo intermediate by TLC or HPLC. When the reaction was complete, the product was poured into a stirred mixture of 15% sodium bicarbonate (500 mL) and ether (250 mL), and stirring was continued until effervescence ceased. The organic layer was separated, the aqueous layer extracted with ether (2 × 50 mL), the combined organic layers dried (magnesium sulfate) and concentrated *in vacuo* giving **8** as an oil (4.4 g; 89% yield), GC RT 9.28 min at 195°C; IR (neat) 3020-2850, 1630, 1460, 895, 705 cm<sup>-1</sup>; UV λ<sub>max</sub> 255 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.4 (2 H, m, —CH=), 4.76 (2 H, br s, =CH<sub>2</sub>), 4.60 (2 H, br s, =CH<sub>2</sub>), 3.98 (2 H, m, S—CH—), 2.1 (12 H, m) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 149.2 (C=CH<sub>2</sub>), 130.8 (—CH=CH—), 112.1 (=CH<sub>2</sub>), 55.4, 35.3, 35.0, 29.5 ppm; MS 220 (M<sup>+</sup>, 100%), 192, 188, 187, 173, 159, 151, 145, 139, 137, 133, 131, 120, 119, 117, 105.

Treatment of **7** with the ylide prepared from methyl triphenylphosphonium bromide and *n*-butyllithium led to a complex mixture of isomeric 2,9-bismethylene-13-thiabicyclo[8.2.1]-5-tridecenes and

2-methylene-9-oxo-13-thiabicyclo[8.2.1]-5-tridecenes as indicated by IR and  $^1\text{H}$  NMR spectroscopic analysis of chromatographic fractions.

**Photolysis of 8 in Trimethyl Phosphite. Preparation of (Z)-3,10-bismethylene-1,6,11-dodecatriene (15).** A degassed solution of **8** (0.300 g, 1.36 mmol) in 30 mL of freshly distilled trimethyl phosphite was irradiated at 254 nm in a sealed quartz tube for 4 h, monitoring the photolysis by GC (RT of **8** and **15**, 9.34 and 3.77 min, respectively, at 195°C). The photolysis was stopped short of completion to avoid formation of secondary products; irradiation at 300 nm gave more impurities compared to irradiation at 254 nm. The photolysis mixture was concentrated *in vacuo*, the residue dissolved in 25 mL of pentane, washed with 5% aqueous silver nitrate solution ( $2 \times 25$  mL), the pentane layer dried (magnesium sulfate), and concentrated *in vacuo* giving 0.256 g of oily residue which was purified by preparative TLC (silica gel/pentane) giving **15** (0.128 g, 50% yield), IR (neat) 3100-2850, 1630, 1592, 1440, 990, 890; UV ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  237;  $^1\text{H}$  NMR  $\delta$  6.39 (2 H, dd), 5.35-5.00 (8 H, m), 2.32 ppm (8 H, br s);  $^{13}\text{C}$  NMR  $\delta$  145.9, 138.9, 129.6, 115.8, 113.2, 31.5, 26.0 ppm; MS 188 ( $\text{M}^+$ ), 173, 159, 145, 133, 132, 131, 119, 105, 93 (100%), 92, 79.

**Photolysis of 8 in Hexane. Preparation of (Z)-2-Methylenebicyclo[7.3.1]trideca-5(6),9(10)-diene (16) and (Z,Z,Z)-bicyclo[6.4.2]tetradeca-1(12),4(5),8(9)-triene (17).** A degassed solution of **8** (1.00 g, 4.55 mmol) and trimethyl phosphite (0.57 g, 4.59 mmol) in 150 mL of hexane was irradiated for 25 h at 254 nm in a sealed quartz tube, monitoring the photolysis by GC (RT **8**, **16**, **17**, 9.28 min, 5.32 min and 5.87 min, respectively, at 195°C). Irradiation at 300 nm led to very slow disappearance of **8** with no significant change in the ratio of **16** to **17**. In the absence of trimethyl phosphite sulfur deposition significantly reduced the passage of light into the solution. The mixture was then filtered through alumina and concentrated *in vacuo* giving 0.8 g of an oily material containing mainly **17** and **18** in a 9:1 ratio. Preparative HPLC (silica gel, hexane) gave 0.512 g of **16** (60% yield) and 0.043 g of **17** (5% yield). Compound **16** showed IR (neat) 3005-2850, 1630, 1450, 890, 705  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.31 (3 H, m), 4.87 (1 H, br s), 4.69 (1 H, br s), 2.1 (15 H, br m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  152.4, 135.9, 131.5, 127.8, 122.6, 111.4, 38.4, 36.1, 36.0, 29.5, 27.2, 26.7, 25.1, 22.3; MS 188 ( $\text{M}^+$ ), 173, 159, 145, 131, 119, 117, 106, 105, 104, 93, 92, 91 (100%). Compound **17** showed IR (neat) 3005-2850, 1615, 1440, 880, 790  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.23 (4 H, m), 2.07 (16 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  132.2, 129.7, 125.4, 39.9, 29.5, 27.0, 25.0; MS 188 ( $\text{M}^+$ ), 173, 160, 159, 145, 131, 120, 119, 106, 105, 93, 92, 91 (100%).

**2,5-Bis(1-hydroxy-2-methylpropyl)thiolane S-Oxide.** *n*-Butyllithium (20 mL, 32 mmol; 1.6 M in hexane) was added to a solution of diisopropylamine (2.9 g, 28.7 mmol) in dry tetrahydrofuran (15 mL) at  $-78^\circ\text{C}$  under argon. The mixture was stirred for 15 min, a solution of thiolane S-oxide (1 g, 9.6 mmol) in dry tetrahydrofuran (15 mL) was added dropwise, the solution was stirred for 30 min, and then a solution of isobutyraldehyde (2.08 g, 28.8 mmol) in dry tetrahydrofuran (15 mL) was added dropwise with stirring during 25 min. at  $-78^\circ\text{C}$ . The reaction mixture was warmed to room temperature during 12 h and treated with saturated ammonium chloride solution (25 mL) followed by methylene chloride (50 mL). The organic layer was separated, washed with water ( $3 \times 50$  mL), dried (magnesium sulfate), and concentrated at  $50^\circ\text{C}/0.05$  mm giving 1.19 g (50% yield) of the title compound as a gummy product which is a mixture of diastereomers (GC showed a cluster of 4-5 broad peaks, RT 13.31-14.44 min,  $195^\circ\text{C}$ ); IR (neat) 3450 (OH), 2950-2850, 1475, 1390, 1370, 1010 ( $\text{S}=\text{O}$ , s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.35-3.47 (6 H, m), 2.45-1.43 (6 H, m), 1.1-0.7 (12 H, m). A portion of the mixture of diastereomers was subjected to preparative HPLC (12:88 *i*-propanol:hexane; silica gel) giving a major fraction which at  $40^\circ\text{C}/0.05$  mm gave a crystalline solid (mp  $91-93^\circ\text{C}$ ):  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  76.5, 76.5, 74.5, 62.2, 32.9, 32.5, 25.1, 24.3, 19.1, 19.0, 18.9 (2C).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{24}\text{O}_3\text{S}$ : C, 58.03; H, 9.74. Found: C, 57.59; H, 9.83.

**2,5-Bis(1-hydroxy-2-methylpropyl)thiolane.** A mixture of 2,5-bis(1-hydroxy-2-methylpropyl)thiolane S-oxide (2 g) and saturated sodium bisulfite solution (300 mL) was refluxed for 3 h while monitoring for disappearance of starting material by GC and then cooled and extracted with ether. ( $3 \times 50$  mL). The ether layer was dried (magnesium sulfate) and concentrated *in vacuo* giving the title compound (1.74 g, 93% yield) as an oil which was a mixture of diastereomers; IR (neat) 3430 (OH), 2950-2850, 1470, 1382, 1363, 1115, 995;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.57-2.04 (6 H, m), 2.2-1.3 (6 H, m), 1.0-0.7 (12 H, m). GC showed two major peaks at 7.29 and 7.45 min ( $195^\circ\text{C}$ ). A portion of the crude mixture of diastereomeric products was subjected to preparative HPLC (6:94 *i*-propanol:hexane, silica gel) to isolate the major diastereomer, a crystalline solid, mp  $88-89^\circ\text{C}$  (from hexane),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  77.6, 53.3, 32.0, 31.5, 19.3, 18.0.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$ : C, 62.03; H, 10.41. Found: C, 61.48; H, 10.55.

**2,5-Bis(2-methylpropionyl)thiolane.** 2,5-Bis(1-hydroxy-2-methylpropyl)thiolane (1.5 g, 6.46 mmol) was oxidized as in the preparation of **7** to give the title compound (1.41 g, 96% yield) as an oil which was a

mixture of two isomers (GC RT 5.6 min and 5.7 min at 195°C; 1:3 ratio); IR (neat) 2950–2850, 1710 (C=O), 1470, 1382, 1100–1020;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.08 (2 H, m, C(O)—CH—S), 3.0–1.8 (6 H, m), 1.12 (12 H, m); M S 228 ( $\text{M}^+$ ), 212, 196, 157, 141, 111, 107, 99, 95, 85 (100%).

**2,5-Bis(3-methyl-1-buten-2-yl)thiolane (18).** To a solution of 2,5-bis(2-methylpropionyl)thiolane (1.4 g, 6.14 mmol) in methylene chloride (75 mL) at 0°C was added the previously prepared zinc-titanium tetrachloride-methylene dibromide slurry (200 mL) in small portions. The reaction was monitored by GC. Workup as in the case of **8** gave the title compound as an oily mixture of two isomers (1 g, 72% yield); IR (Neat) 3075, 2950–2850, 1640 (C=C), 1460, 900  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.0 (2 H, s,  $=\text{CH}_a$ ), 5.82 (2 H, s,  $=\text{CH}_b$ ), 2.08 (8 H, m), 1.05 (12 H, m). Flash chromatography of the mixed product gave the major product (0.6 g from 1 g of mixed product; 43% yield), GC RT 4.94 min at 195°C; UV  $\lambda_{\text{max}}$  223 ( $\epsilon$  41260), 253 ( $\epsilon$  16590).

Exact mass. Calcd. for  $\text{C}_{14}\text{H}_{24}\text{S}$ : 224.4046. Found: 224.4045.

**Photolysis of 18 in hexane. 2-Isopropyl-4-(3-methyl-1-buten-2-yl)-cyclohexene (19).** A degassed solution of **18** (0.3 g, 1.34 mmol) in hexane (100 mL) was irradiated at 254 nm in a sealed quartz tube for 30 h, monitoring the progress of the photolysis by GC. The photolysis product was concentrated *in vacuo* and the residue was filtered through a short column of alumina (with hexane) and purified by preparative TLC (silica gel, pentane) giving **19** (0.051 g, 20% isolated yield, 25% GC yield), 300–2825, 1650, 1480, 1420, 1205, 800  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.31 (1 H, m), 4.69 (2 H, d,  $J = 3$  Hz), 2.00 (6 H, m), 1.05 (6 H, d,  $J = 7$  Hz), 1.00 (6 H, d,  $J = 7$  Hz).

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## REFERENCES AND NOTES

1. F. Lautenschlager, *J. Org. Chem.*, **33**, 2627 (1968).
2. N. N. Novitskaya, R. V. Kunakova, E. E. Zaev, G. A. Tolstikov and L. V. Spirikhin, *Zhur. Organ. Khim.*, **11**, 1434 (1975).
3. A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).
4. B. Ganem and R. Boeckman, *Tetrahedron Lett.*, 917 (1874).
5. D. Landini and F. Rolla, *Chem. Ind.*, 213 (1979).
6. L. Lombardo, *Tetrahedron Lett.*, **23**, 4293 (1982).
7. For examples of problems caused by the basicity of Wittig reagents, see reference 6 and C. H. Heathcock and R. Ratcliffe, *J. Amer. Chem. Soc.*, **93**, 1746 (1971); L. Lombardo, L. N. Mander, and J. V. Turner, *Ibid*, **102**, 6626 (1980), J. A. Marshall, M. T. Pike, and R. D. Carroll, *J. Org. Chem.*, **31**, 2933 (1966).
8. E. J. Corey and J. Kang, *J. Amer. Chem. Soc.*, **104**, 4724 (1982).
9. N. N. Novitskaya, R. V. Kunakova, L. K. Yuldasheva, E. E. Zaev, E. V. Dmitrieva, and G. A. Tolstikov, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 384 (1976).
10. E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969); E. Block, "Reactions of Organosulfur Compounds", Academic Press, NY, 1978, pp. 202–206.
11. See for example, P. S. Engel and D. E. Keys, *J. Amer. Chem. Soc.*, **104**, 6860 (1982).
12. K. J. Shea, S. Wise, L. D. Burke, P. D. Davis, J. W. Gilman, and A. C. Greeley, *J. Amer. Chem. Soc.*, **104**, 5708 (1982).