J. Org. Chem. **1997,** *62,* 8366−8371

Effective Precursors for Sulfur Monoxide Formation

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Received June 3, 1997[⊗]

When triphenylmethanesulfenyl chloride (**12**) (or its thio **13** or dithio homolog **14**) are treated with hindered olefins **15** and **16**, thiiranes **10** and **11** are produced in high isolated yields (*ca.* 94%). Treatment of **10** and **11** with *m*-chloroperoxybenzoic acid (*m*-CPBA) leads to the formation of thiirane 1-oxides **8** and **9** (99% isolated yields). The structures of **8**−**11** were established by ^{1}H and ^{13}C NMR, mass spectrometry as well as by X-ray. Thermal decomposition of either **8** or **9** smoothly delivers sulfur monoxide to various 1,3-dienes giving cyclic sulfoxides in good yield. A variety of conditions were employed to optimize the yield of the trapped adducts.

Introduction

There is a considerable interest in finding simple chemical methods to generate and examine the chemistry of reactive diatomic molecules such as singlet diatomic oxygen ($^1O_2$)[1] and singlet diatomic sulfur ($^1S_2$)[2] as well as related species such as RP=S,[3] RP=Se,[4] RN=S,[5] RN=O,[6] and RN=Se.[7] Relatively few studies have been carried out on the chemistry of sulfur monoxide (S=O).[8,9]

Up to now, the main method to generate S=O has been by the pyrolysis of ethylene episulfoxide (**1**) at *ca.* 100 °C.[10,11] Other less-used methods of S=O production have involved the thermal decomposition of sulfoxide **2**[12] and heterocycle **3**.[13]

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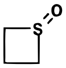

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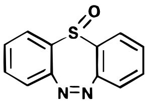

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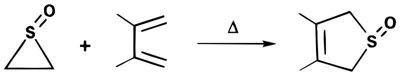
Diene and triene trapping experiments with S=O have been carried out by a number of workers;[14,15] the main product is Diels−Alder adduct **4** (eq 1) in yields generally in the 20−40% range.



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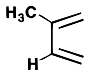
The work of Lemal focused primarily on the mechanistic features of this trapping process,[16,17] although he found that isoprene (**5**) can be trapped to give 2,5-dihydro-3-methylthiolene 1-oxide (**6**) in 72% isolated yield.[16] A recent, less direct route for the Diels−Alder trapping of S=O has been carried out *via* complex **7**.[18] Recently, the detailed photochemistry of **1** has been investigated for the first time.[19]



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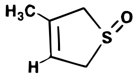

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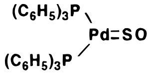

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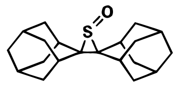
In order to further explore this chemistry, a more convenient source of sulfur monoxide (S=O) was needed. We recently reported our preliminary results which were achieved by the thermal decomposition of adamantylideneadamantanethiirane 1-oxide (**8**)[9] and bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonanethiirane 1-oxide (**9**).[20]



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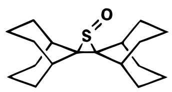

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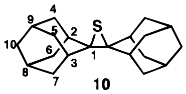
S0022-3263(97)00986-9 CCC: $14.00

Results and Discussion

Thiirane 1-oxides **8** and **9** can be prepared from the oxidation of the corresponding thiiranes **10** and **11** with *m*-CPBA in high isolated yield (99%). Episulfides **10** and **11** (stable at rt for months) can be synthesized from the reaction of triphenylmethanesulfenyl chloride **12** (or its thio **13** or dithio homolog **14**) with the corresponding olefins in high isolated yield (98%).[9]



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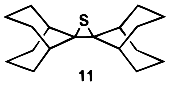

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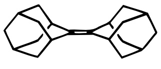
$(C_6H_5)_3C{-}S{-}Cl$ **12**

$(C_6H_5)_3C{-}S{-}S{-}Cl$ **13**

$(C_6H_5)_3C{-}S{-}S{-}S{-}Cl$ **14**

Thermal decomposition of episulfides **10** and **11** in refluxing ethyl acetate for 15 h under a nitrogen atmosphere affords the corresponding olefins **15** and **16**, respectively (98%), along with elemental sulfur (68%). In addition, **10** and **11** were completely decomposed when the mixture was refluxed for 2 h in toluene solution.



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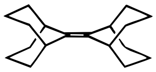

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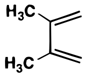

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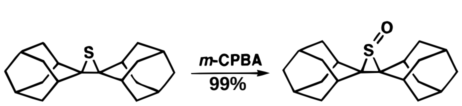
When the above reactions were carried out in the presence of 2,3-dimethyl-1,3-butadiene (**17**), the same products were obtained (elemental sulfur and olefin). No evidence was found for the trapping of diatomic sulfur by diene **17**. It would appear that the concatenation mechanism of sulfur loss from episulfides was operative.[21,22]

Episulfide **10** was previously prepared by Nakayama and co-workers[23] from the treatment of elemental sulfur with olefin **15**, but the yield was low. The authors[23] reported that episulfide **10** contained 10 peaks in the ^{13}C NMR spectra and the mp was 153−154 °C. In contrast, we found that thiirane **10** showed only seven peaks in ^{13}C NMR spectra. This can be explained by the fact, revealed by X-ray analysis, that there is a plane of symmetry passing through S, C_1, C_8, C_9, and C_{10}. This symmetry makes C_2 and C_3, C_4 and C_5, and C_6 and C_7 equivalent. In addition, we found that episulfide **10** has a lower melting point (142−143 °C) than previously reported by Nakayama.[23]

Thiirane 1-oxide **8** was prepared by *m*-CPBA oxidation of episulfide **10** in methylene chloride solution under a nitrogen atmosphere at −78 °C. Recrystallization from *n*-pentane gave a pure product of thiirane 1-oxide **8** in an isolated yield of 99% (eq 2).



10 **8**

The structure of thiirane 1-oxide **8** was established by ^{1}H and ^{13}C NMR, mass spectrometry, and X-ray analysis. In contrast to thiirane **10**, we found that thiirane 1-oxide **8** shows 10 carbon signals in ^{13}C NMR spectra. The tetrahedral geometry of the sulfur atom shows the chemical shifts for all of the carbon atoms in the adamantyl skeleton moiety to be different. The electron impact mass spectrum of thiirane 1-oxide **8** is straightforward, displaying both loss of O and SO from the parent ion radical.

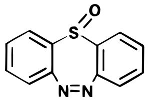
In simple episulfoxides, typical C−C bond lengths fall in the range 1.37−1.60 Å and C−S bonds range from 1.37 to 1.92 Å.[24] The C−C bond length in thiirane 1-oxide **8** is 1.505 Å, which suggests the presence of partial double bond character, since a typical sp^3−sp^3 C−C bond length is about 1.55 Å and a C=C bond length is 1.34 Å. The bond lengths of S−O, C−S; bond angles of C−S−C, C−C−S, and O−S−C in the three-membered ring moiety of episulfoxide **8** and ethylene episulfoxide (**1**) were found to be quite similar and are included in the Supporting Information (Table 1).[25]

Thiirane 1-oxide **9** was prepared in the same way as that of **8**. Thiirane **11** was reacted with *m*-CPBA in methylene chloride solution at −78 °C under a nitrogen atmosphere to give thiirane 1-oxide **9** in high isolated yield (98%). The structure of thiirane 1-oxide **9** was established as for **8**.

Trapping of Sulfur Monoxide (SO)

In the literature there are only three reaction systems reported which generate and trap sulfur monoxide in the presence of 1,3-dienes; the yields are low. Moreover, these methods have limitations. The major problem in the case of Dodson,[14,15] Lemal,[16] Anastassiou,[26] and Heyke[18] procedures is that ethylene episulfoxide (**1**) is unstable at room temperature, has a disagreeable odor, and causes skin burns.

In the case of the procedure of Chow[13] the important limitation is in the preparation of sulfoxide **3**. The authors could not isolate the corresponding episulfoxide **18** which they thought could have been resulted from the thermolysis of sulfoxide **3**. The yield of the trapped adduct was low in each case.



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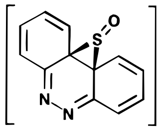

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It should be mentioned that *trans*-2,3-diphenylethene sulfoxide has been shown to transfer sulfur monoxide to ylides in low (11−19%) yield.[27]

In contrast, thiirane 1-oxides **8** and **9** are crystalline and stable even if they are exposed to the atmospheric moisture for several days. In addition, we found that sulfur monoxide can be easily generated and trapped in high, isolated yields to form substituted 2,5-dihydrothiophene 1-oxides through thermal decomposition of **8** and **9** in the presence of various 1,3-dienes.

The general procedure used for the reaction of **8** and **9** with 1,3-dienes is as follows: a solution of the diene and

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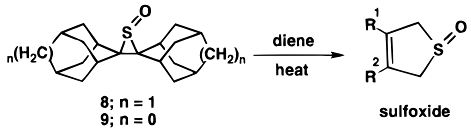
Table 1. Summary of Sulfur Monoxide Trapping Experiments of 1,3-Dienes (5, 17, 20, 22) with Thiirane 1-Oxide 8

entry no.	R[a]	solvent	temp (°C)	dienes (time (h))				sulfoxides (%)[b]			
								6	**19**	**21**	**23**
1	1:1	$CHCl_3$	61	all dienes (240)				NR			
2	1:1	EtOAc	77	all dienes (240)				NR			
3	1:1	CH_3CN	81	all dienes (240)				NR			
4	1:1	toluene	80	all dienes (240)				NR			
5	1:3	toluene	110	**5** (36)	**17** (12)	**20** (24)	**22** (16)	62	73	65	46
6	1:1	toluene	110	**5** (36)	**17** (12)	**20** (24)	**22** (16)	58	74	64	40
7	3:1	toluene	110	**5** (36)	**17** (12)	**20** (24)	**22** (16)	69	80	70	65
8	1:3	C_6H_5Cl	132	–	**17** (8)	–	–	–	30	–	–
9	1:1	C_6H_5Cl	132	**5** (20)	**17** (8)	**20** (15)	**22** (12)	30	30	25	23
10	3:1	C_6H_5Cl	132	**5** (20)	**17** (8)	**20** (15)	**22** (12)	35	33	27	27
11	1:3	xylene	138	–	**17** (8)	–	–	–	32	–	–
12	1:1	xylene	138	**5** (20)	**17** (8)	**20** (15)	**22** (12)	33	34	26	22
13	3:1	xylene	138	**5** (20)	**17** (8)	**20** (15)	**22** (12)	40	37	29	28
14	1:3	decane	135	–	**17** (8)	–	–	–	33	–	–
15	1:1	decane	135	–	**17** (8)	–	–	–	34	–	–
16	3:1	decane	135	**5** (20)	**17** (8)	–	**22** (12)	37	36	–	30
17	1:1	decane	174	**5** (20)	**17** (5)	–	**22** (8)	12	12	–	15
18	3:1	toluene	110	–	**17** (8)	**20** (72)	–	–	70	70	–
19	3:1	toluene	110	–	**17** (16)	–	–	–	76	–	–
20	3:1	xylene	110	**5** (36)	**17** (12)	–	**22** (16)	64	69	–	48
21	3:1	xylene	138	–	**17** (12)	–	–	–	35	–	–
22	3:1	xylene	138	–	**17** (20)	–	–	–	10	–	–
23	3:1	xylene	138	–	**17** (35)	–	–	–	0	–	–
24	3:1	decane	110	–	**17** (12)	–	–	–	67	–	–

[a] Refers to the molar ratio of thiirane 1-oxide **8** to 1,3-dienes (**5**, **17**, **20**, **22**). [b] Isolated yields after flash chromatography.

8 or **9** in an appropriate solvent was refluxed for a certain time under a nitrogen atmosphere (eq 3). The reaction was followed by thin layer chromatography using 15–25% ethyl acetate in hexane as eluent. The first fraction can be isolated in near quantitative yield by the same eluent and was identified (98%) as the corresponding olefin (**15** from **8**; **16** from **9**). By eluting with methanol, the second fraction was identified as the corresponding 2,5-dihydrothiophene 1-oxides as oily, pure product in the case of dienes **5**, **17**, **22**, and a solid product in the case of diene **20**; the yields are generally high (70–80% yield) compared to other SO sources.[12–18] The identity of sulfoxides **6**, **19**, **21**, and **23** was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



diene = 5 (isoprene); 17 (2,3-dimethyl-1,3-butadiene);

20 (2,3-diphenyl-1,3-butadiene); or 23 (myrcene).

sulfoxide = 6 ($R^1 = CH_3$, $R^2 = H$); 19 (R^1, $R^2 = CH_3$);
21 (R^1, $R^2 = C_6H_5$); or 23 ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 = H$

A variety of solvents, temperatures, times, and concentrations were employed to optimize the yields of the trapped adducts. A summary of the results are shown in Table 1 (episulfoxide **8**) and Table 2 (episulfoxide **9**); the yields with **9** are similar to those with episulfoxide **8** and are included in the Supporting Information.

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of 2,5-dihydrothiophene 1-oxide adducts are reported in the Supporting Information. As mentioned earlier, ethylene episulfoxide (**1**) has been shown to decompose at a temperature of 110 °C to give ethylene and sulfur monoxide;[10] the latter was trapped by dienes in yields of *ca.* 40%. In contrast, we found that thiirane 1-oxides **8** and **9** delivers sulfur monoxide to 1,3-dienes smoothly to give the corresponding 2,5-dihydrothiophene 1-oxide adducts in high, isolated yields. Ratios of thiirane 1-oxides **8** and **9** to diene were varied from 1:3 to 3:1 with relatively little change in yields (Tables 1 and 2). Interestingly, the choice of solvent temperature is critical; no decomposition either of **8** or of **9** took place over 10 days in refluxing chloroform, ethyl acetate, or acetonitrile ($T = 61$, 77, 81 °C, respectively).

The best conditions for the release of sulfur monoxide and its subsequent trapping (*ca.* 82% isolated yield) appear to be in refluxing toluene (110 °C) for 12 h in the case of 2,3-dimethyl-1,3-butadiene (**17**) with thiirane 1-oxide **8** (Table 1, entry 7) and 8 h in the case of thiirane 1-oxide **9** (Table 2, entry 7, Supporting Information). At 110 °C in xylene and decane, trapped yields of adduct **19** were *ca.* 68% (Table 1, entries 20, 24). In refluxing xylene (138 °C), the yield diminished to 35% (Table 1, entry 21). When a pure sample of **19** was heated in refluxing xylene for 20 h, only 10% remained. This confirms the retrochelotropic decomposition; diene adduct **19** decomposed completely in 35 h in refluxing xylene (138 °C) (Table 1, entry 23).

It is noteworthy to mention that Lemal[17] found when ethylene episulfoxide (**1**) reacted with each of the three 2,4-hexadiene isomers that mixtures of *cis*,*cis*-, *cis*,*trans*-, and *trans*,*trans*-2,5-dihydro-2,5-dimethylthiophene 1-oxides (**24**, **25**, and **26**, respectively) were formed. While there was significant stereoselectivity, Lemal concluded that because of the formation of multiple sulfoxide isomers in each reaction, the thermal decomposition of episulfoxide **1** proceeds *via* a biradical intermediate in the triplet state. This view is also supported by Baldwin[28] and Glass.[29]

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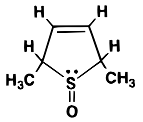
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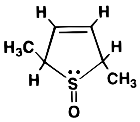
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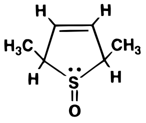
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Experimental Section

Preparation of Adamantylideneadamantane (15). Adamantylideneadamantane was prepared by the procedure of McMurry.[32] Potassium metal (3.84 g, 49 mmol) was added to a stirred slurry of titanium trichloride ($TiCl_3$) (4.30 g, 28 mmol) in 150 mL of dry tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature. After 40 min of reflux, the black mixture was cooled, a solution of adamantanone (1.05 g, 7.0 mmol) in 10 mL of THF was added, and the mixture was further refluxed for 16 h. The mixture was cooled to room temperature and filtered under an inert atmosphere. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with hexane afforded a solid product which upon crystallization from *n*-hexane gave 0.75 g, 80%, of adamantylideneadamantane (**15**): mp 184−186 °C (lit. mp 183−185 °C[32], 184−187 °C[33]); ^{1}H-NMR ($CDCl_3$) δ 1.58−1.98 (m, 24H) and 2.91 (br, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ 28.9, 32.2, 37.7, 40.0, and 133.5 ppm; MS (*m/z*, rel int, assignment) 268 (100, $M^{\bullet+}$).

Reaction of Adamantylideneadamantane (15) with Triphenylmethanesulfenyl Chloride (12). A solution of triphenylmethanesulfenyl chloride[34] (**12**) (0.116 g, 0.373 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantane (**15**) (0.10 g, 0.373 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 6 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 20% chloroform in hexane afforded a solid product which upon crystallization from *n*-hexane gave 0.101 g, 93%, of adamantylideneadamantanethiirane (**10**): mp 142−143 °C (lit. mp 153−154 °C[23], 131−132 °C[35]); ^{1}H-NMR ($CDCl_3$) δ 2.08−1.56 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ 27.1, 27.7, 35.0, 37.8, 38.4, 38.6, and 71.7 ppm; MS (*m/z*, rel int, assignment): 268, 100%, $M^{\bullet+}$-S; 300, 14%, $M^{\bullet+}$. Chlorotriphenylmethane was isolated in a yield of 58%. In addition, **15** reacted similarly with **13** and **14** to deliver thiirane **10** in excellent yield.

Thermal Chemistry of Thiirane 10 in the Presence of 2,3-Dimethyl-1,3-butadiene (17). 2,3-Dimethyl-1,3-butadiene (**17**) (0.073 g, 0.90 mmol) was added to a mixture of adamantylideneadamantanethiirane (**10**) (0.18 g, 0.60 mmol) in 15 mL of dry ethyl acetate. The solution was refluxed for 15 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% $CHCl_3$ in hexane as eluent. After the solvent was evaporated under reduced pressure, the products were separated by the same eluent (15% $CHCl_3$ in hexane), in which the first fraction was isolated and identified as adamantylideneadamantane (**15**) (0.15 g, 91%): mp 185−186 °C (lit. mp 183−185 °C[32], 184−187 °C[33]); ^{1}H-NMR ($CDCl_3$) δ 1.59−1.98 (m, 24H) and 2.91 (br, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ 28.9, 32.2, 37.7, 39.9, and 133.5 ppm; MS (*m/z*, rel int, assignment) 268 (100, $M^{\bullet+}$). The second fraction was isolated and identified as elemental sulfur (55%). The reaction was repeated in toluene using the above procedure. Adamantylideneadamantanethiirane (**10**) was completely decomposed when the solution was refluxed for 2 h in toluene solution (110 °C), giving adamantylideneadamantane (**15**) (98%) along with elemental sulfur (68%).

Oxidation of Adamantylideneadamantanethiirane (10) by *m*-Chloroperoxybenzoic Acid (*m*-CPBA). A solution of *m*-CPBA (0.172 g, 1.0 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantanethiirane (**10**) (0.30 g, 1.0 mmol) in 30 mL of dry methylene chloride under a nitrogen atmosphere at −78 °C . The mixture was stirred for 2 h. The solution was diluted with 5% NaOH solution and extracted three times with 20 mL portions of diethyl ether. The combined ethereal extracts were dried with $MgSO_4$, filtered, and evaporated to give the crude adamantylideneadamantanethiirane 1-oxide (**8**). Recrystallization from *n*-pentane gave 0.313 g, 99%, of the corresponding thiirane 1-oxide **8**: mp 129−130 °C; ^{1}H-NMR ($CDCl_3$) δ 1.53−2.38 (m) ppm; ^{13}C-NMR ($CDCl_3$) δ 27.0, 27.4, 27.6, 30.0, 36.2, 37.1, 37.2, 37.6, 37.6, and 72.9 ppm; MS (*m/z*, rel int, assignment) 316 (18, $M^{\bullet+}$), 300 (10, $M^{\bullet+}$ − O), 268 (100, $M^{\bullet+}$ − SO); HRMS *m/z* obsd 316.1864 (calcd for $C_{20}H_{28}OS$ 316.1861). Anal. Calcd for $C_{20}H_{28}OS$: C, 75.90; H, 8.92; S, 10.13. Found: C, 75.87; H, 9.44; S, 10.05.

Thermal Chemistry of Adamantylideneadamantanethiirane 1-Oxide (8). Adamantylideneadamantanethiirane 1-oxide (**8**) (0.25 g, 0.791 mmol) was dissolved in 25 mL of toluene, and the solution was refluxed for 2.5 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the mixture was adsorbed onto silica gel and chromatographed using the same eluent (20% EtOAc in hexane) to give adamantylideneadamantane (**15**) in a yield of 97%.

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 8 with 2,3-Dimethyl-1,3-butadiene (17). 2,3-Dimethyl-1,3-butadiene (**17**) (0.0513 g, 0.625 mmol) was added to a mixture of adamantylideneadamantanethiirane 1-oxide (**8**) (0.593 g, 1.875 mmol) in 30 mL of dry toluene. The solution was refluxed for 12 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (15% EtOAc in hexane) and was identified as adamantylideneadamantane (**15**) (99%). By eluting with methanol, the second fraction was isolated (0.065 g, 80%) as an oily product and identified as 2,5-dihydro-3,4-dimethylthiophene 1-oxide (**19**): ^{1}H-NMR ($CDCl_3$) δ 3.83 (d, 2H), 3.48 (d, 2H), and 1.77 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$) δ 14.5, 64.3, and 126.1 ppm; MS (*m/z*, rel int, assignment) 130 (100, $M^{\bullet+}$), 82 (30, $M^{\bullet+}$ − SO), 67 (61, $M^{\bullet+}$ − $SOCH_3$). The above reaction was repeated in a variety of solvents, varying temperature, time, and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in Table 1.

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 8 with 2,3-Diphenyl-1,3-butadiene (20). 2,3-Diphenyl-1,3-butadiene[36] (**20**) (0.129 g, 0.625 mmol) was added to a mixture of adamantylideneadamantanethiirane 1-oxide (**8**) (0.593 g, 1.875 mmol) in 30 mL of dry toluene. The solution was refluxed for 24 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (20% EtOAc in hexane) and was identified as adamantylideneadamantane (**15**) (98%). By eluting with methanol, the second fraction was isolated and identified as 2,5-dihydro-3,4-diphenylthiophene 1-oxide (**21**). Recrystallization from *n*-hexane gave 0.111 g, 70% of pure sulfoxide **21**: mp 134−135 °C; ^{1}H-NMR ($CDCl_3$) δ 4.05 (d, 2H), 4.41 (d, 2H), and 7.13−7.26 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ 64.5, 127.9, 128.5, 128.6, 132.0, and 135.6 ppm; MS (*m/z*, rel int, assignment) 254 (5, $M^{\bullet+}$), 236 (100, $M^{\bullet+}$ − H_2O), 205 (59, $M^{\bullet+}$ − SO), 191 (12, $M^{\bullet+}$ − $SOCH_2$). The above reaction was further investigated by varying the reaction conditions in a variety of ways. The

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[33] Geluk, H. W. *Synthesis* **1970**, 652.

[34] Williams, C. R.; Britten, J. F.; Harpp, D. N. *J. Org. Chem.* **1994**, *59*, 806.

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[36] For the preparation of 2,3-diphenyl-1,3-butadiene (**20**), see: Fulcher, B. C.; Hunter, M. L.; Welker, M. E. *Synth. Commun.* **1993**, *23* (2), 217. Newman, M. S. *J. Org. Chem.* **1961**, *26*, 582. Alder, K.; Haydn, J. *Justus Liebigs Ann. Chem.* **1950**, *570*, 201.

same products were isolated in each case but in varying yields as shown in Table 1.

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 8 with Isoprene (5). Isoprene (**5**) (0.014 g, 0.211 mmol) was added to a mixture of adamantylideneadamantanethiirane 1-oxide (**8**) (0.20 g, 0.633 mmol) in 25 mL of dry toluene. The solution was refluxed for 36 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (20% EtOAc in hexane) and was identified as adamantylideneadamantane (**15**) (97%). By eluting with methanol, the second fraction was isolated (0.0168 g, 69%) as an oily product and identified as 2,5-dihydro-3-methylthiolene 1-oxide (**6**): ^{1}H-NMR ($CDCl_3$) δ 5.58 (m, 1H), 3.69−3.90 (m, 2H), 3.34−3.58 (m, 2H), and 1.90 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$) δ 16.7, 60.0, 62.9, 119.1, and 125.0 ppm; MS (*m*/*z*, rel int, assignment) 116 (100, $M^{\bullet+}$), 68 (49, $M^{\bullet+} - SO$), 67 (86, $M^{\bullet+} - SOH$), 53 (46, $M^{\bullet+} - SOCH_3$). The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in Table 1.

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 8 with Myrcene (22). Myrcene (**22**) (0.069 g, 0.506 mmol) was added to a mixture of adamantylideneadamantanethiirane 1-oxide (**8**) (0.480 g, 1.519 mmol) in 20 mL of dry toluene. The solution was refluxed for 16 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 25% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (25% EtOAc in hexane) and was identified as adamantylideneadamantane (**15**) (98%). By eluting with methanol, the second fraction was isolated (0.06 g, 65%) as an oily product and identified as 3-(4′-methyl-3′-pentenyl)-2,5-dihydrothiophene 1-oxide (**23**): ^{1}H-NMR ($CDCl_3$) δ 1.60 (s, 3H), 1.68 (s, 3H), 2.12−2.31 (m, 4H), 3.35−3.59 (m, 2H), 3.70−3.89 (m, 2H), 5.07 (m, H), and 5.60 (m, H) ppm; ^{13}C-NMR ($CDCl_3$) δ 17.7, 25.6, 26.2, 31.3, 59.7, 61.6, 117.9, 123.9, 132.6, and 139.9 ppm; MS (*m*/*z*, rel int, assignment) 184 (39, $M^{\bullet+}$), 136 (27, $M^{\bullet+} - SO$), 135 (55, $M^{\bullet+} - SOH$), 116 (44, $M^{\bullet+} - C_5H_9$), 69 (100, $M^{\bullet+} - C_5H_7SO$). The above reaction was further investigated by varying the reaction conditions in a variety of ways. The same products were isolated in each case but in varying yields as shown in Table 1.

Preparation of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (16). Potassium metal (5.76 g, 147 mmol) was added to a stirred slurry of titanium trichloride ($TiCl_3$) (6.45 g, 42 mmol) in 250 mL of dry tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature. After 1.5 h of refluxing, the black mixture was cooled and a solution of bicyclo[3.3.1]nonan-9-one (1.45 g, 10.50 mmol) in 15 mL of THF was added. After the mixture was further refluxed for 24 h, the mixture was cooled to room temperature and filtered under an inert atmosphere. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with hexane afforded a solid product which upon crystallization from *n*-hexane gave 2.17 g, 85%, of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**): mp 144−145 °C (lit. mp 143−144 °C[37], 144−145 °C[38]); ^{1}H-NMR ($CDCl_3$) δ 1.40−2.12 (m, 24H) and 2.85 (br, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ 23.0, 32.5, 34.5, and 131.6 ppm; MS (*m*/*z*, rel int, assignment) 244 (72, $M^{\bullet+}$), 121 (100, $M^{\bullet+} - C_9H_{14}$).

Reaction of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (16) with Triphenylmethanesulfenyl Chloride (12). A solution of triphenylmethanesulfenyl chloride[34] (**12**) (0.152 g, 0.492 mmol) in 30 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) (0.12 g, 0.492 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 5 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane afforded a solid product which upon crystallization from *n*-hexane gave 0.116 g, 93%, of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane (**11**): mp 166−167 °C (lit.[39] mp 166.5−167 °C); ^{1}H-NMR ($CDCl_3$) δ 1.52−2.03 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ 20.7, 21.3, 31.9, 33.6, 34.8, and 70.4 ppm; MS (*m*/*z*, rel int, assignment) 276 (18, $M^{\bullet+}$), 244 (100, $M^{\bullet+} - S$), 121 (19, $M^{\bullet+} - C_9H_{14}S$). Chlorotriphenylmethane was isolated in a yield of 55%. In addition, **16** reacted similarly with **13** and **14** to deliver thiirane **11** in excellent yield.

Thermal Chemistry of Thiirane 11 in the Presence of 2,3-Dimethyl-1,3-butadiene (17). 2,3-Dimethyl-1,3-butadiene (**17**) (0.036 g, 0.435 mmol) was added to a mixture of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane (**11**) (0.12 g, 0.435 mmol) in 20 mL of dry ethyl acetate. The solution was refluxed for 8 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After the solvent was evaporated under reduced pressure, the products were separated by column chromatography using the same eluent (20% $CHCl_3$ in hexane) in which the first fraction was isolated and identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1] nonane (**16**) (0.10 g, 95%): mp 144−146 °C (lit. mp 143−144 °C[37], 144−145 °C[38]); ^{1}H-NMR ($CDCl_3$) δ 1.40−2.11 (m, 24H) and 2.86 (br, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ 23.0, 32.5, 34.5, and 131.6 ppm. The second fraction was isolated and identified as elemental sulfur (50%). The reaction was repeated in toluene using the above procedure. Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane (**11**) was completely decomposed after the solution was refluxed for 2.5 h in toluene (110 °C) under a nitrogen atmosphere giving bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) in a yield of 98%. In addition, elemental sulfur was isolated (58%).

Oxidation of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane (11) by *m*-Chloroperoxybenzoic Acid (*m*-CPBA). A solution of *m*-CPBA (0.0624 g, 0.362 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane (**11**) (0.10 g, 0.362 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at −78 °C. The mixture was stirred for 2.5 h. The solution was diluted with 5% NaOH solution and extracted three times with 20 mL portions of diethyl ether. The combined ethereal extracts were dried with $MgSO_4$, filtered, and evaporated to give the crude bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane 1-oxide (**9**). Recrystallization from *n*-hexane gave 0.104 g, 98%, of the corresponding thiirane 1-oxide **9**: mp 150−151 °C; ^{1}H-NMR ($CDCl_3$) δ 1.45−2.34 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ 21.3, 27.5, 30.1, 30.3, 30.8, 31.3, 32.3, and 71.5 ppm; MS (*m*/*z*, rel int, assignment) 292 (17, $M^{\bullet+}$), 276 (7, $M^{\bullet+} - O$), 244 (100, $M^{\bullet+} - SO$), 121 (81, $M^{\bullet+} - C_9H_{14}SO$); HRMS *m*/*z* obsd 292.1859 (calcd for $C_{18}H_{28}OS$ 292.1861).

Thermal Chemistry of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane 1-Oxide (9). A sample of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane 1-oxide (**9**) (0.20 g, 0.685 mmol) was dissolved in toluene, and the solution was refluxed for 4 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 30% EtOAc in hexane as eluent. After the solvent was evaporated under reduced pressure, the mixture was adsorbed onto silica gel and chromatographed using the same eluent (30% EtOAc in hexane) to give bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) in a yield of 98%.

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 9 with 2,3-Dimethyl-1,3-butadiene

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[40] The author has deposited atomic coordinates for structures **8** and **9** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(17). By using thiirane 1-oxide **9**, in a similar preparation, a 82% yield of **19** was obtained which had identical spectral properties as when prepared using 1-oxide **8**. ^{1}H- and ^{13}C-NMR and MS were completely consistent as in the preparation of **19** *via* **8**. In addition, bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) was isolated in a yield of 98%. A variety of solvents, temperatures, times, and concentrations were employed to optimize the yields of the trapped adducts (Table 2, Supporting Information).

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 9 with 2,3-Diphenyl-1,3-butadiene (20). By using thiirane 1-oxide **9**, in a similar preparation, a 73% yield of **21** was obtained which had identical spectral properties as when prepared using 1-oxide **8**. NMR and MS data were consistent with structure of **21** which was prepared *via* **8**. Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) was isolated in a yield of 98%. The above reaction was further investigated by varying the reaction conditions in a variety of ways. The same products were isolated in each case but in varying yields as shown in Table 2 (Supporting Information).

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 9 with Isoprene (5). By using thiirane 1-oxide **9**, in a similar preparation, a 72% yield of **6** was obtained which had identical spectral properties as when prepared using 1-oxide **8**. Spectral data were consistent with previous preparation of **6** *via* **8**. In addition, bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) was isolated in a yield of 99%. A variety of solvents, temperatures, times and concentrations, were used to optimize the yields of the trapped adducts (Table 2, Supporting Information).

Trapping of Sulfur Monoxide from the Decomposition of Thiirane 1-Oxide 9 with Myrcene (22). By using thiirane 1-oxide **9**, in a similar preparation, a 68% yield of **23** was obtained which had identical spectral properties as when prepared using 1-oxide **8**. ^{1}H- and ^{13}C-NMR and MS were completely consistent as in the preparation of **23** *via* **8**. Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**16**) was isolated in a yield of 98%. The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in Table 2 (Supporting Information).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and FCAR (Québec) for financial support of this work.

Supporting Information Available: ^{1}H- and ^{13}C-NMR spectra of compounds **6**, **8**−**11**, **19**, **21**, and **23** and Table 2 a summary of solvents, temperatures, times, and concentrations, employed to optimize the yields of the trapped adducts (episulfoxide **9**) (12 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9709864