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A USEFUL PRECURSOR FOR SULFUR MONOXIDE TRANSFER

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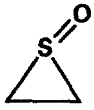
Abstract: *When triphenylmethanesulfenyl chloride* (**8**) *(or its thio* **9** *and dithio* **10** *homolog) is treated with adamantylideneadamantane* (**11**), *adamantylideneadamantane thiirane* (**12**) *is produced (92%). Compound* **12** *was treated with m-chloroperoxybenzoic acid (m-CPBA) forming adamantylideneadamantane thiirane 1-oxide* (**13**) *in 99% isolated yield. The structures of* **12** *and* **13** *were established by* ${}^1H$ *and* ${}^{13}C$ *NMR, mass spectrometry as well as by X-ray analysis. Sulfoxide* **13** *decomposes smoothly to deliver sulfur monoxide in good yield to various dienes.*

There is considerable interest in finding simple chemical methods to generate and frequently trap reactive diatomic molecules such as ${}^1O_2$,[1] ${}^1S_2$[2] as well as related species such as R-P=S,[3] R-P=Se,[4] R-N=S[5] and R-N=O.[6] Relatively little studied has been the chemistry of S=O.[7]

The main method of generation of S=O is by the pyrolysis of ethylene episulfoxide (**1**) at *ca.* 100 °C.[8] Other less-used modes of S=O production have involved the thermal decomposition of sulfoxide **2**[9] and heterocycle **3**.[10] Diene and triene trapping experiments with S=O have been carried out by a number of workers;[11] the main product is a Diels-Alder adduct **4** in yields generally in the 20-40% range.



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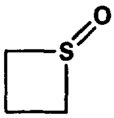

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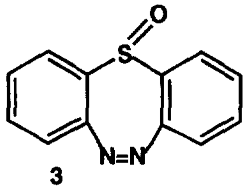

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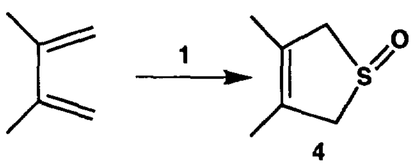
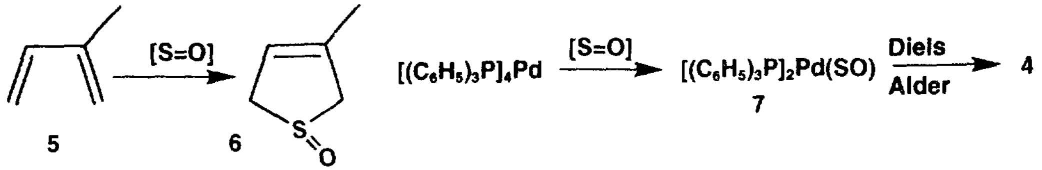
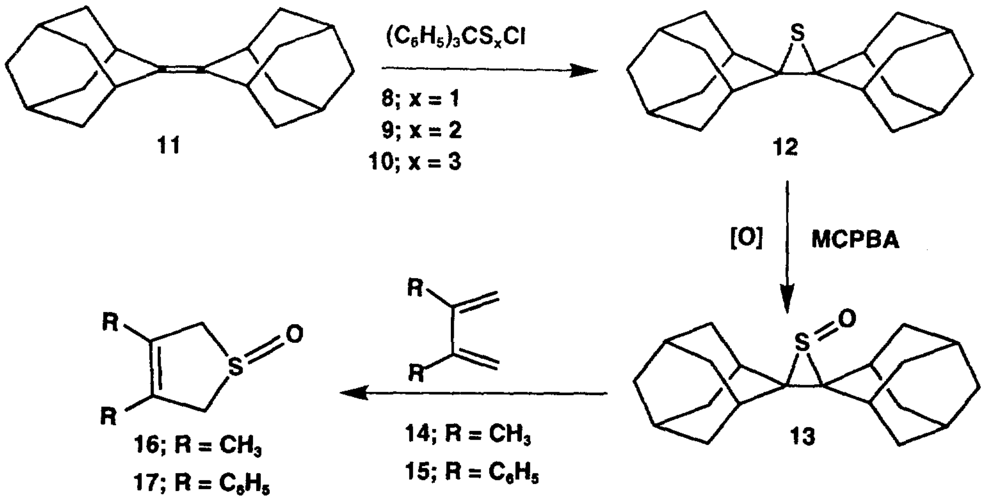


4

The work of Lemal focussed primarily on the mechanistic features of this trapping process,[12] although he indicated isoprene (**5**) can be trapped to give 3-methyl-3-thiolane oxide (**6**) in 72% isolated yield.[12a] A recent, less direct route for the Diels-Alder trapping of S=O has been carried out *via* complex **7**.[13]

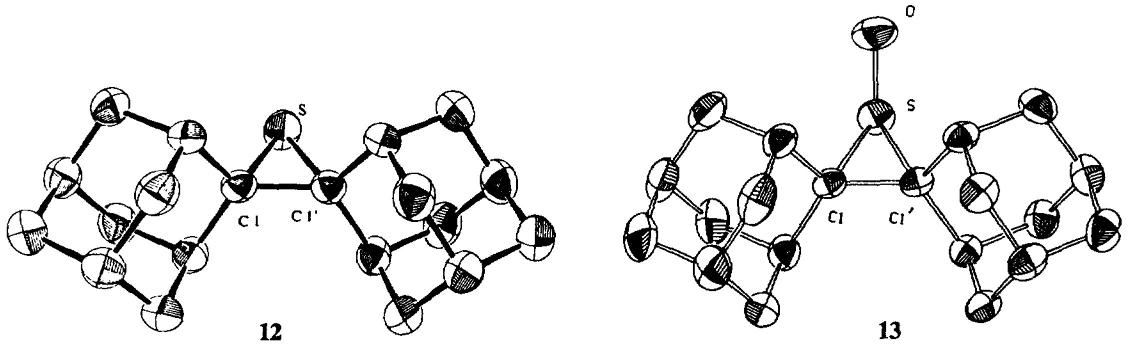


In order to explore this chemistry, a more convenient source of S=O was needed. We find that sulfenyl chlorides **8-10**[14] and adamantylideneadamantane **11** react to give thiirane **12** in 92% isolated yield.[15] Thiirane **12** in turn reacts with m-CPBA to give a 99% yield of stable sulfoxide **13**. The structures of **12** and **13** were established by ^{1}H, ^{13}C NMR; in addition, the X-ray structures are reported for the first time (Figure 1).[16]



Scheme 1

When thiirane 1-oxide 13 was heated in the presence of 2,3-dimethyl-1,3-butadiene (14) or 2,3-diphenyl-1,3-butadiene (15) in a variety of solvents, varying temperature, time and concentration, 2,5-dihydrothiophene 1-oxides (16 or 17)[17] were trapped and isolated in optimized yields of 70-78% (Scheme 1). In addition, adamantylideneadamantane (11) is also recovered near-quantitatively.[18]



12

13

Figure 1

Ratios of **13**/diene were varied from 1:3 to 3:1 with relatively little change in yields. Interestingly, the choice of solvent is critical; no decomposition of **13** took place over 10 days in refluxing $CHCl_3$, EtOAc or CH_3CN. The best conditions for the release of S=O and its subsequent trapping (*ca.* 77% isolated) appears to be in refluxing toluene (110 °C) for 14 h in the case of diene **14** and 24 h for diene **15**. At 110 °C in decane and xylene, yields were *ca.* 68%. In refluxing xylene (138 °C), the yield diminished to 35% implying decomposition of the diene adduct. When a pure sample of **16** was heated in refluxing xylene for 20 h, only 10% remained confirming the retro chelotropic decomposition; **16** decomposed completely in 35 h in refluxing xylene (*ca.* 138 °C).

Acknowledgments

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16. Spectral data for compound **12**: Recrystallizing solvent, *n*-pentane; yield, 92%; mp. 142-143 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.08-1.56 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 27.12, 27.69, 34.92, 37.75, 38.38, 38.58, and 71.62 ppm. MS (m/z, rel. int., assignment): 268, 100%, $M^{+\cdot}$ -S; 300, 14%, $M^{+\cdot}$; 135, 24%; spectral data for compound **13**: Recrystallizing solvent, *n*-pentane; yield, 100%; mp. 129-130 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.53-2.38 (m, 28H) ppm.; ^{13}C-NMR ($CDCl_3$) δ: 27.02, 27.39, 27.58, 30.02, 36.16, 37.12, 37.20, 37.56, 37.62, and 72.88 ppm. MS (m/z , rel. int., assignment): 316, 18.1%, $M^{+\cdot}$; 300, 0.3%, $M^{+\cdot}$ -O; 268, 100%, $M^{+\cdot}$ -SO; **X-Ray Data for 12.** Empirical Formula $C_{20}H_{28}S$, **M** = 300.50. Monoclinic, space group **P 2_1/a**, **a** = 12.7522 (19), **b** = 10.5600 (13), **c** = 13.441 (3) Å, β = 117.607 (12)°. **V** = 1604.0 (4) Å^3, **Z** = 4, **D$_c$** = 1.244 Mgm^{-3}, **mμ** = 1.65mm^{-1}, **F(000)** = 658.67. Data collected at 293 °K on a Rigaku diffractometer controlled by TEXRAY software and **$\theta/2\theta$** scans to a **2θ** max of 110°. Reflections measured: 2129; unique: 2018; number of reflections with **I** > 2.5σ (**I**): 1787. Solution by direct methods; hydrogens calculated. Last least-square with 49 atoms, 303 parameters and 1787 out of 2018 reflections gave **R_f** = 0.031, **R_w** = 0.035 and **GoF** = 2.06. **X-Ray Data for 13.** Empirical Formula $C_{20}H_{28}OS$, **M** = 316.50. Monoclinic, space group **P 2_1/n** (**#14**), **a** = 10.851 (2), **b** = 13.680 (2), **c** = 11.313 (2) Å, β = 105.64 (1)°. **V** = 1617.0 (8) Å^3, **Z** = 4, **D$_c$** = 1.300 Mgm^{-3}, **mμ** = 1.712 mm^{-1}, **F(000)** = 688. Data collected at 294 °K on a Rigaku AFC6S diffractometer with graphite monochromated Cu Kα radiation and **$\theta/2\theta$** scans to a **2θ** max of 140°. Reflections measured: 3151; unique: 2978; number of reflections with **I** > 3.00σ (**I**): 2033. Solution by direct methods; hydrogens calculated. Last least-square gave **R_f** = 0.041, **R_w** = 0.047 and **GoF** = 1.62.
17. Spectral data for a) compound **16**: Oil; yield, 78%; ^{1}H-NMR ($CDCl_3$) δ: 3.83 (d, 2H), 3.48 (d, 2H), 1.77 (s, 6H), ppm; ^{13}C-NMR ($CDCl_3$) δ: 14.46, 64.33, and 126.07 ppm. MS (m/z, rel. int., assignment): 130, 100%, $M^{+\cdot}$; 82, 30%, $M^{+\cdot}$ -SO; 67, 61%; 54, 9.4%; 43, 13%; b) compound **17**: Recrystallizing solvent, *n*-hexane; yield, 70%; mp. 134-135 °C; ^{1}H-NMR ($CDCl_3$) δ: 4.05 (d, 2H), 4.41 (d, 2H), 7.13-7.26 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 64.46, 127.92, 128.47, 128.60, 132.01, and 135.58 ppm. MS (m/z, rel. int., assignment): 254, 4.4%, $M^{+\cdot}$; 236, 100%; 205, 59%, $M^{+\cdot}$ -SO; 191, 12%.
18. Alkene **11** can easily be recycled for the regeneration of episulfide **12**. When either **12** or **13** are heated in toluene for *ca.* 1 h, **11** is isolated in near quantitative yield.

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