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Supporting Information (29 pages)

The Direct Episulfidation of Alkenes and Allenes with Elemental Sulfur and Thiiranes as Sulfur Sources, Catalyzed by Molybdenum Oxo Complexes

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Experimental Data

Experimental Section

General Remarks. All solvents were dried and distilled under argon gas prior to use.^{S1} The reactions with catalysts **1** were also carried out under an argon-gas atmosphere. For flash chromatography, Woelm silica gel (0.032–0.063 mm) was used. TLC was performed on Polygram SIL/UV 254 plates from Macherey-Nagel. The episulfide and allene spots were visualized by means of elemental iodine, alkene spots by means of potassium permanganate. The bulb-to-bulb distillations were conducted on a Büchi GKR-50 apparatus; the boiling points refer to oven temperatures. Melting points are uncorrected. For quantitative NMR analysis, a relaxation delay for T_1 of 23 s was applied and dimethyl isophthalate was used as internal standard. GC analysis was carried out on a HP-5 (15 m) column at 180 °C injector temperature and 200 °C detector temperature. The products were identified by comparison of the retention times with the authentic materials. For the GC analysis of the product ratios, calibration curves were prepared from defined mixtures of authentic materials by using *n*-decane as an internal GC standard. The IR spectra were run on KBr pellets. Elemental analyses were carried out by the Microanalytical Division of the Institut für Anorganische Chemie, Universität Würzburg.

Materials. Sodium molybdate dihydrate, *E*-cyclodecene (**E-4c**), methylthiirane (**Iα**), sodium diethyldithiocarbamate trihydrate, *O,O'*-diethyldithiophosphate, $\text{Mo}(\text{CO})_6$, and $\text{MoO}_2(\text{acac})_2$ were commercially available. The molybdenum complexes **1a,b**¹², **2a**¹³, $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ ^{S2}, $\text{MoO}_2[\text{PhC}(\text{O})\text{N}(\text{Ph})\text{O}]_2$ ^{S3}, $\text{Mo}_2\text{O}_3(\text{acac})_4$ ¹², $\text{Mo}_2\text{O}_3(\text{oxin})_4$ ¹², and $\text{Mo}_2\text{O}_3[\text{S}_2\text{P}(\text{OEt})_2]_4$ ¹² were synthesized according to the literature procedures.

E-Cyclooctene (**E-4b**)^{S4} and the cyclononenes^{S5} **E-4b** and **Z-4b** were prepared according to known procedures. Bicyclopropylidene (**4h**) was gratefully provided by Prof. A. de Meijere. The allenes **6a**^{S6} and **6b-d**^{S7} were freshly prepared as reported and stored at –50 °C. Phenylthiirane (**Iβ**) was obtained from styrene oxide by a literature-known method.^{S8}

Catalytic Episulfidation of the Alkenes

GP-1: General Screening Procedure of the Molybdenum Oxo Complexes for the Catalytic Episulfidation of *Z*-Cyclooctene (**Z-4a**) by Elemental Sulfur

A 5-mL Schlenck tube was charged with a solution of 0.50 mmol of the molybdenum complex, 100 mg (3.12 mmol) of elemental sulfur, 65.0 μ L (0.50 mmol) of *Z*-cyclooctene, and 50.0 μ L (0.25 mmol) of *n*-decane (internal GC standard) in 4.0 mL of dichloroethane. The tube was sealed with a rubber septum and Parafilm[®] and heated to 100 °C in an oil bath for 60 min. After cooling of the tube to room temperature (ca. 20 °C), the tube was opened, the content was poured into 60 mL of pentane, the suspended material removed by filtration over Celite, and a 0.5- μ L aliquot of the clear filtrate was submitted to GC analysis. The results are given in Table S1.

Table S1. Molybdenum-Catalyzed Sulfur Transfer to *cis*-Cyclooctene (**Z-4a**)

entry		convn (%) ^{a)}	yield (%) ^{a)}	m.b. (%) ^{a)}
	Molybdenum Catalyst	Z-4a	<i>cis</i> - 5a	Z-4a
1	Mo ₂ O ₃ (acac) ₄	0	0	>99
2	MoO ₂ (acac) ₂	0	0	>99
3	MoO ₂ (S ₂ CNEt ₂) ₂	5	4	99
4	Mo ₂ O ₃ (oxin) ₄	<1	<1	>99
5	Mo ₂ O ₃ [S ₂ P(OEt) ₂] ₄	0	0	>99
6	Mo(CO) ₆	18	0 ^{b)}	82
7	MoO ₂ [PhC(O)N(Ph)O] ₂	10	0	90
8	MoO[S ₂ CNEt ₂] ₂ (1a)	9	9	>99
9	MoO[S ₂ P(OEt) ₂] ₂ (1b)	14	7 ^{c)}	94

^{a)} Determined by GC analysis with *n*-decane as internal standard (error $\pm$ 1% of the stated values); reactions were carried out in a sealed Schlenck tube. ^{b)} Reaction was carried out under aerobic conditions. ^{c)} Dithiophosphorane disulfide was identified by means of an authentic sample, but not quantified.

Time Profile of the Desulfuration of Methylthiirane (**Iα**) and Phenylthiirane (**Iβ**)

In a NMR tube was placed a solution of 0.100 mmol of thiirane **Iα** or **Iβ** and 0.79 mg (1.63 μmol) of the molybdenum oxo complex **1b** in 0.7 mL of deuterobenzene. The NMR tube was sealed with a rubber septum and Parafilm® and quantitative NMR analysis was conducted after 10, 31.5, 40, 50, 60, 70.5, 80, 120, 160, 201 min, against dimethyl isophthalate as internal standard. The pseudo-first-order kinetics are plotted in Figure S1. The rate constants of the consumption of methylthiirane (**Iα**) and

Figure S1. Time profile of the desulfuration of thiiranes **Iα** and **Iβ** by the **1b** catalyst.

phenylthiirane (**Iβ**) were determined to be $k = (4.88 \pm 0.24) \times 10^{-5} \text{ s}^{-1}$ and $(6.25 \pm 0.31) \times 10^{-4} \text{ s}^{-1}$.

Treatment of the Thermolysate of Methylthiirane (**Iα**) or Phenylthiirane (**Iβ**) and Molybdenum Oxo Complex **1b** with Trianisylphosphine

In a NMR tube was placed a solution of 0.94–1.00 mg (1.95–2.07 μmol) of molybdenum oxo complex **1b** and 0.260 mmol of episulfide **Iα** or **Iβ** in 0.7 mL of deuterobenzene. The NMR tube was sealed with a rubber septum and Parafilm® and submitted to quantitative NMR analysis with dimethyl isophthalate as internal standard. The tubes were then heated for 30 min to 80 °C, allowed to cool to

room temperature (ca. 20 °C), and again submitted to ¹H-NMR analysis. To the solution were added 99.8 mg (0.283 mmol) of trianisylphosphine and allowed to stand for 2 h at room temperature (ca. 20 °C). Quantitative ¹H-NMR analysis revealed that in the case of methylthiirane (**Iα**) about 34% of the episulfide were converted and about 39% phosphine sulfide were formed, whereas ca. 83% of the episulfide were consumed in the case of phenylthiirane (**Iβ**) and ca. 84% of phosphine sulfide were obtained.

GP-2: General Catalytic Procedure for the Episulfidation of the Cycloalkenes **4** by the Molybdenum Oxo Complex **1b** with Phenylthiirane (**Iβ**) as Sulfur Donor

Analytical Scale: Analogous to the above procedure, 0.085–0.282 mmol of the alkene **4**, 0.132–0.293 mmol phenylthiirane (**Iβ**), and 0.74–2.00 mg (1.54–4.15 μmol) of the molybdenum oxo complex **1b** were used. The known episulfides *cis*-9-thiabicyclo[6.1.0]-nonane (*cis*-**5a**)^{S9}, *trans*-11-thiabicyclo[8.1.0]undecane (*trans*-**5c**)^{6f}, *exo*-3-thiatricyclo-[3.2.1.0^{2,4}]octane (**5d**)^{S9}, 6-thiabicyclo[3.1.0]-hexane (**5f**)^{S9}, 8-thiabicyclo[5.1.0]-octane (**5g**)^{S10}, and 7-thiadispiro[2.0.2.1]-heptane (**5h**), of which the spectral data are listed below, were identified by means of their characteristic ¹H-NMR and ¹³C-NMR signals directly on the crude reaction mixture and quantified by ¹H-NMR spectroscopy against dimethyl isophthalate as an internal standard.

Preparative Scale: A solution of 2.00 mmol alkene, 9.65 mg (20.0 μmol) of molybdenum oxo complex **1b**, and 312 μL (2.00 mmol) of phenylthiirane (**Iβ**) in 15 mL of solvent was placed into a Schlenck tube. After sealing the tube, the solution was magnetically stirred and heated to 60 °C in an oil bath. The tube was allowed to cool to room temperature (ca. 20 °C), opened, and the solvent was removed.

10-Thiabicyclo[7.1.0]decanes (5b**)**

According to the general procedure GP-2, a solution of 287 μL (2.00 mmol) of cyclononene in 15 mL of toluene was allowed to react for 2 h at 60 $^{\circ}\text{C}$. The toluene was removed (40 $^{\circ}\text{C}$ /20 mbar) and silica-gel chromatography (5:1 petroleum ether/ CH_2Cl_2) of the residue yielded 156 mg (1.00 mmol, 50%) of cyclononene episulfide **5b** (colorless oil) as a mixture of the two chromatographically inseparable diastereomers *cis-5b* and *trans-5b* (dr 77:23). The analytical data of the *trans* isomer has been reported¹⁰ and the *cis* isomer was spectrally characterized directly in the mixture of diastereomers: R_f (5:1 petroleum ether/ CH_2Cl_2) = 0.45; IR (KBr) 2927, 2851, 1472, 1445; ^1H NMR (CDCl_3 , 250 MHz) δ 1.24–1.82 (m, 12 H), 2.28–2.45 (m, 2 H), 2.92–3.04 (m, 2 H); ^{13}C NMR (CDCl_3 , 63 MHz) δ 23.7 (t), 25.1 (t), 25.9 (t), 29.0 (t), 43.3 (d); Anal. Calc. for $\text{C}_9\text{H}_{16}\text{S}$ (156.3): C, 69.17; H, 10.32; S, 20.51. Found: C, 68.84; H, 10.69; S, 20.37. The *Z/E* diastereomer ratio of the stilbenes could only be determined in CDCl_3 due to signal overlap in C_6D_6 ; therefore, all isomerization experiments were conducted in CDCl_3 .

Attempted Isomerization of *Z*-Cyclononene (*Z*-4b) in the Catalytic Episulfidation by Catalyst **1b and Phenylthiirane as Sulfur Donor.**

In a NMR tube was placed a solution of 42.0 μL (0.154 mmol) of *Z*-cyclononene, 0.74 mg (1.54 μmol) of oxo complex **1b**, and 22.6 mg (0.166 mmol) of phenylthiirane in 0.7 mL of CDCl_3 . The tube was sealed with a rubber septum and Parafilm[®], transferred to an oil bath, and heated at 60 $^{\circ}\text{C}$ for 3 h. The tube was opened under an argon-gas atmosphere, charged with an additional 21.0 μL

(0.077 mmol) of *Z*-cyclononene, and heated for another 2 h. A ^1H -NMR spectrum of the solution showed that no *E*-cyclononene had been formed.

Isomerization of *Z*-Stilbene in the Catalytic Episulfidation of *Z*-Cyclononene (*Z*-4b) by Catalyst 1b and Phenylthiirane as Sulfur Source.

In a NMR tube was placed a solution of 27.2 μL (0.154 mmol) of *Z*-stilbene, 0.74 mg (1.54 μmol) of oxo complex **1b**, and 22.6 mg (0.166 mmol) of phenylthiirane in 0.7 mL of CDCl_3 . The tube was sealed with a rubber septum and Parafilm[®], and heated in an oil bath at 60 $^\circ\text{C}$ for 2 h. A ^1H -NMR spectrum showed that a 82:18 mixture of the diastereomers *Z*-stilbene/*E*-stilbene had been formed, but no stilbene episulfide was detected. When in a second experiment an equal portion of *Z*-stilbene was added after the total conversion of phenylthiirane (**1b**), no isomerization of the *Z*-stilbene was observed.

Competition Experiment between *Z*- and *E*-Cyclononene in the Catalytic Episulfidation by Complex 1b

In a NMR tube were dissolved 33.0 μL (0.120 mmol) *Z*-cyclononene and 23.0 μL (0.113 mmol) *E*-cyclononene in 0.7 mL of deuterobenzene. To this solution were added 24.5 mg (0.180 mmol) of phenylthiirane (**1b**), 0.74 mg (1.54 μmol) of complex **1b**, and 13.1 mg (0.0675 mmol) of dimethyl isophthalate (internal ^1H -NMR standard). After sealing the NMR tube as described above, immediately a ^1H -NMR spectrum was recorded. The tube was set aside for 20 min at 20–25 $^\circ\text{C}$ and ^1H -NMR analysis revealed that after 20 min the initial *Z/E* ratio of 51.5 : 48.5 increased to 59 : 41.

Comparative Episulfidation of *E*-Cyclononene (*E*-4b) with Styrene Episulfide, Catalyzed by the Molybdenum Oxo Complexes 1a,b.

The general procedure GP-2 was applied. In a NMR tube was placed a solution of 22.2 μL (0.141 mmol) of olefin *E*-4b, 23.7 mg (0.174 mmol) of phenylthiirane (**1b**), and 0.62 mg (1.53 μmol) of molybdenum oxo complexes **1a** or 0.74 mg (1.53 μmol) of oxo complex **1b** in 0.7 mL of deuteriochloroform. The tubes were sealed with a rubber septum and Parafilm[®], and kept at 20–25 °C for 2 h, and submitted to quantitative NMR analysis with dimethyl isophthalate as internal standard. The results are listed in Table 2 (see main text).

Variation of the *Z*-Cyclooctene/Phenylthiirane (**1b**) Ratio at a Constant *Z*-Cyclooctene Quantity in the Episulfidation of *Z*-Cyclooctene

The general procedure GP-2 for the experiments at the analytical scale was followed, for which 20.0 μL (0.154 mmol) of *Z*-cyclooctene, 0.74 mg (1.54 μmol) of oxo complex **1b**, 2.68–24.0 mg (0.0196–0.176 mmol) phenylthiirane (**1b**), and ca. 0.080 mmol of dimethyl isophthalate (internal standard) were used. Results are depicted in Table S2.

Catalytic Episulfidation of the Allenes

GP-3: General Catalytic Procedure for the Episulfidation of the Allenes 6 by the Molybdenum Oxo Complex 1a

Analytical Scale: In a NMR tube were placed 28.6 mg (70.0 μmol) of molybdenum oxo complex **1a**, 19.4 mmol (0.100 mmol) of dimethylisophthalate as internal ¹H-NMR standard, and as sulfur donors 12.6 mg (0.393 mmol) of elemental sulfur, 51.5 mg (0.296 mmol) of Na₂S₄, or 30.8 μL (0.393 mmol) of methylthiirane (**1a**) in 0.7 mL of oxygen-free deuterioacetone. To this solution was added 0.196 mmol of allene **6** and the tube was sealed with a rubber septum and Parafilm. After recording a ¹H-NMR

Table S2. Catalyzed Episulfidation of Z-Cyclooctene under Variation of the Z-Cyclooctene/Phenylthiirane (**1B**) Ratio at a Constant Z-Cyclooctene Quantity

entry	equiv. 1B	time [min]	convn (%) ^{a)}	rel. yield
			Z- 4a	cis- 5a (%) ^{a)}
1	1.14	30	57	77 ^{b)}
2	1.14	90	52	53 ^{b)}
3	0.65	30	35	60
4	0.27	30	29	67
5	0.13	30	7	85

^{a)} Determined by comparison of characteristic ¹H-NMR signals of the crude reaction mixture with those of an internal standard (dimethyl isophthalate); error $\pm$ 5% of the stated values; the yield is based on converted thiirane **1B**, convn (**1B**) >95%. ^{b)} Yields are based on converted olefin Z-**4a**.

spectrum, the tube was then heated for 15 h in an oil bath to 56 °C. After cooling to room temperature (ca. 20 °C) again a ¹H-NMR spectrum was recorded and the content of thiiranes determined quantitatively against the dimethyl isophthalate as internal standard. Results are depicted in Table 3.

Preparative Scale: A 30-mL Schlenck tube was charged with a mixture of 7.5–14.7 mmol allene, 0.75–1.47 mmol of molybdenum oxo complex **1a**, 1.17–2.30 mL (14.9–29.4 mmol) of methylthiirane and 550 mg (3.98 mmol) of potassium carbonate in 10 mL of dichloromethane. The Schlenck tube was sealed and heated to 60 °C for 4 h, cooled to room temperature (ca. 20 °C), cautiously opened (to vent the propene gas), and the solid material removed by filtration. The dichloromethane was evaporated (40 °C/500 mbar), and the residue was dissolved in 10 mL of dimethylformamide. This solution was extracted with pentane (5 $\times$ 10 mL) and the pentane extracts were washed twice with brine (2 $\times$ 5 mL). The combined organic extracts were dried over MgSO₄, the pentane was removed (40 °C/800 mbar), and the oily residue consisted mainly of the allene episulfide. The latter was purified by either distillation (episulfide **7b**) or silica-gel chromatography with petroleum ether as eluent (episulfides **7a**

and

7c).

10-Thiabicyclo[7.1.0]dec-1-ene (7a)

According to the general procedure GP-3, 2.00 mL (14.7 mmol) of cyclonona-1,2-diene (**6a**), 395 mg (0.967 mmol) molybdenum oxo complex **1a**, and 2.30 mL (29.4 mmol) of methylthiirane (**1a**) were allowed to react as described. The solvent and methylthiirane were evaporated (20 °C/20 mbar) and silica-gel chromatography yielded 1.66 g (10.8 mmol, 73%) of a colorless oil; IR (KBr) 2932, 2867, 1722, 1464, 1443, 1336, 964, 811; MS (DCI, isobutane, 120–150 eV) [*m/z*] (rel. intensities in %) 211 (*M*+57, 7), 155 (*M*+1, 60), 121 (*M*+1-H₂S, 100); ¹H NMR (CDCl₃, 600 MHz) δ 1.25-1.34 (m, 1 H, 3-H_β), 1.36-1.44 (m, 1 H, 5-H), 1.45-1.52 (m, 2 H, 6-H), 1.52-1.59 (m, 1 H, 7-H_α), 1.59-1.67 (m, 2 H, H-5, H-4_β), 1.67-1.75 (m, 1 H, 7-H_β), 1.81-1.89 (m, 1 H, 4-H_α), 2.07-2.15 (m, 1 H, 8-H_α), 2.45-2.52 (m, 1 H, 8-H_β), 2.53-2.59 (m, 1 H, 3-H_α), 3.26-3.30 (m, 1 H, 2-H_β), 5.61 (dt, ³*J* = 4.81 Hz, ⁴*J* = 1.08 Hz, 1 H, H-9); ¹³C NMR (CDCl₃, 151 MHz) δ 21.2 (t, ¹*J* = 126.2 Hz, 7-C), 24.0 (t, ¹*J* = 129.2 Hz, 6-C), 24.1 (t, ¹*J* = 129.2 Hz, 4-C), 25.0 (t, ¹*J* = 136.0 Hz, 5-C), 29.4 (t, ¹*J* = 126.3 Hz, 8-C), 34.6 (t, ¹*J* = 129.8 Hz, 3-C), 37.8 (d, ¹*J* = 167.7 Hz, 2-C), 113.8 (d, ¹*J* = 160.3, 9-C), 128.7 (s, 1-C); signals and configuration were assigned with help of 2D-NMR spectra [HMQC, HMBC, NOESY, INADEQUATE] and NOE spectra; Anal. Calc. for C₉H₁₄S (154.3): C, 70.07; H, 9.15; S, 20.78. Found: C, 70.11; H, 9.05; S, 20.45.

The molecular weight of episulfide **7a** was determined by ebullioscopy.^{S11} Two stock solutions were prepared (Table S3) by dissolving the episulfide **7a** in 500 mg of *n*-decane. Aliquots of these solutions were transferred to boiling point capillaries and heated from 170 to 180 °C at a heating rate of 0.2 °C/min in a melting point apparatus. The results are given in Table S3.

Table S3. Determination of the Molecular Weight of Allene Episulfide **7a** by Ebullioscopy

Stock solution	M [mol•kg ⁻¹]	ΔT [K] ^{a)}	M _r [g•mol ⁻¹] ^{b)}
S1	0.264	1.61±0.5	138±38
S2	0.538	3.28±0.5	181±32

^{a)} Average values and standard deviation of three independent measurements. ^{b)} Ebullioscopic constant K_{eb} (*n*-decane)= 6.10 K•(kg•mol)⁻¹ (ref S12).

Desulfuration of Episulfide **7a** to the Allene **6a** by Methyloxothiorhenium

6a

The monomeric structure of the episulfide **7a** was also established by chemical means. For this purpose, 156 mg (1.01 mmol) of the allene episulfide (**7a**) were treated with 10 mol% of methyloxothiorhenium (prepared according to a known procedure^{S13}) at 4 °C in acetonitrile. After 5 d of standing at 4 °C, the reaction was worked up as described in literature.^{S13} After silica-gel chromatography (petroleum ether as eluent), 107 mg (0.694 mmol, 69%) of the episulfide **7a** were recovered and 13.5 mg (0.088 mmol, 9%) of the allene **6a** were isolated; R_f = 0.65; ¹H NMR (C₆D₆, 200 MHz) δ 1.20–1.78 (m, 10 H), 2.05–2.28 (m, 2H), 5.14–5.25 (m, 2H); ¹³C NMR (C₆D₆, 50 MHz) δ 24.9 (t), 27.0 (t), 27.6 (t), 92.6 (d), 206.3 (s).

2,2-Dimethyl-3-(1-methylethylidene)thiirane (**7b**)^{S14}

7b

The general procedure GP-3 was slightly modified, because due to the high volatility of episulfide **7b**, ethylene sulfide had to be used instead of methylthiirane and DMF instead of dichloromethane. A

solution of 724 mg (7.53 mmol) of tetramethylallene (**6b**), 296 mg (0.725 mmol) of molybdenum oxo complex **1a**, and 896 μL (15.1 mmol) of ethylene sulfide in 10 mL of DMF was allowed to react as described. After aqueous work-up, the product was distilled at low temperature (25 $^{\circ}\text{C}$ /10 mbar) to avoid dimerization of the allene episulfide **7b**, to yield 772 mg (6.02 mmol, 80%) of the episulfide **7b** as a colorless liquid; ^1H NMR (C_6D_6 , 200 MHz) δ 1.53 (s, 6 H), 1.67 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR (C_6D_6 , 50 MHz) δ 20.4 (t), 27.6 (t), 45.5 (s), 113.6 (s), 132.0 (s).

10-Thiabicyclo[7.1.0]dec-1,5-diene (**7c**)

According to general procedure GP-3, 1.00 mL (7.88 mmol) of allene **6c**, 1.17 mL (14.9 mmol) methylthiirane, 304 mg (0.744 mmol) of molybdenum oxo complex **1a**, and 550 mg (3.98 mmol) potassium carbonate were allowed to react as described. After silica-gel chromatography, 438 mg (2.88 mmol, 37%) of the allene episulfide **7c** were obtained as colorless needles, mp 54–55 $^{\circ}\text{C}$; R_f (petroleum ether) = 0.30; IR (KBr) 3005, 2945, 2912, 2898, 2881, 2851, 1721, 1658, 1452, 1438; ^1H NMR (CDCl_3 , 200 MHz) δ 1.14 (qq, $J = 12.13$ Hz, $J = 1.37$ Hz, 1 H, 3-H), 2.03–2.79 (m, 7 H, H-3,4,7,8), 3.30–3.42 (m, 1 H, 2-H), 5.39 (ddt, 1 H, $J = 11.14$ Hz, $J = 4.12$ Hz, $J = 0.76$ Hz, 9-H), 5.50–5.68 (m, 2 H, 5-H, 6-H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 23.2 (t), 24.1 (t), 29.8 (t), 36.8 (t), 36.9 (d), 114.3 (s), 127.6 (s), 128.2 (d), 131.3 (d); Anal. Calc. for $\text{C}_9\text{H}_{12}\text{S}$ (152.3): C, 71.00; H, 7.94; S, 21.06. Found: C, 71.12; H, 8.11; S, 21.09.

GP-4: General Catalytic Procedure for the Episulfidation of the Allenes **6** by the Molybdenum Oxo Complex **1b**

Analytical Scale: In a NMR tube was placed a solution of 0.74 mg (1.54 μmol) of molybdenum oxo complex **1b**, ca. 0.060 mmol of dimethylisophthalate as internal ^1H -NMR standard, and 21.0 mg (0.154 mmol) phenylthiirane (**1b**) in 0.7 mL deuterobenzene. To this solution was added 0.154 mmol of allene **6**. The tube was sealed with a rubber septum and Parafilm, and after recording a ^1H -NMR spectrum, the tube was then heated for 30 min in an oil bath to 80 $^{\circ}\text{C}$. The tube was cooled to room temperature (ca. 20 $^{\circ}\text{C}$), again a ^1H -NMR spectrum was recorded, and the amount of thiiranes determined quantitatively against the dimethyl isophthalate as internal standard. Results are depicted in Table 3 (see main text).

11-Thiabicyclo[8.1.0]undec-1-ene (**7d**) by Episulfidation of the Allene **6d** with the Molybdenum Oxo Complex **1b**

A 30-mL Schlenck tube was charged with a solution of 1.00 g (7.34 mmol) of cyclodeca-1,2-diene, 35.6 mg (0.073 mmol) of molybdenum oxo complex **1b**, 1.00 g (7.34 mmol) of phenylthiirane (**1b**) in 10 mL of toluene. The Schlenck tube was sealed and heated to 80 $^{\circ}\text{C}$ for 40 min, subsequently cooled to room temperature (ca. 20 $^{\circ}\text{C}$), opened, and the toluene was removed (40 $^{\circ}\text{C}$ /20 mbar). Silica-gel chromatography of the residue with petroleum ether as eluent afforded 410 mg (2.44 mmol, 33%) of a colorless oil, R_f (petroleum ether) = 0.40; IR (KBr) = 2933, 2849, 2666, 1723, 1463, 1442, 1373, 952, 854, 816, 803; ^1H NMR (CDCl_3 , 600 MHz) δ 1.08-1.26 (m, 7 H), 1.26-1.43 (m, 3 H), 1.61-1.67 (m, 1 H), 1.91-1.99 (m, 1 H), 2.00-2.06 (m, 1 H), 2.26-2.34 (m, 1 H), 3.15-3.18 (m, 1 H, H-2), 5.29 (ddd, J = 11.43 Hz, J = 5.16 Hz, J = 1.57 Hz, 1 H, H-10); ^{13}C NMR (CDCl_3 , 151 MHz) δ 17.3 (t), 21.3 (t), 22.1

(t), 26.2 (t), 27.5 (t), 28.7 (t), 29.3 (t), 37.3 (d), 115.3 (d), 129.0 (s); Anal. Calc. for C₁₀H₁₆S (168.3): C, 71.37; H, 9.58; S, 19.05. Found: C, 71.24; H, 9.26; S, 19.34.

Reversibility in the Episulfidation of Allene **6b**

6a

7b

A solution of 27.0 μ L (0.200 mmol) of tetramethylallene (**6b**), 62.8 mg (0.407 mmol) of allene episulfide **7a**, 8.17 mg (0.020 mmol) of molybdenum oxo complex **1a**, and 11.7 mg (0.060 mmol) of dimethyl isophthalate as internal ¹H NMR standard in 0.7 mL of CDCl₃ was placed into an NMR tube and processed according to GP-4. Before and after 12 h of heating at 65 °C, a NMR spectrum was recorded, which showed that 14% of allene **6a**, 31% of episulfide **7b** and 37% of 2,4-dimethylpenta-1,3-diene^{S15} had been formed. This demonstrates that the sulfur transfer is reversible.

Acid-Catalyzed Isomerization of Allene **6b**

To a solution of 27.0 mL (0.200 mmol) allene **6b** in 0.7 mL of CDCl₃ was added 50 μ L of a 5% DCl solution in D₂O. The solution was transferred to a NMR tube and heated in an oil bath at 65 °C for 3 h. ¹H-NMR spectrum showed that 31% of the allene **6b** were converted to 2,4-dimethylpenta-1,3-diene;^{S15} ¹H NMR (CDCl₃, 250 MHz) δ 1.76 (d, J = 1.22 Hz, 3 H), 1.80 (d, J = 1.06 Hz, 3 H), 1.82 (t, J < 1.00 Hz, 3 H), 4.72 (m, 1H), 4.89 (m, 1 H), 5.63 (m, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 19.4 (q), 23.6 (q), 26.9 (q), 113.5 (d), 127.0 (d), 134.0 (s), 142.2 (s).

Spectral Studies for the Determination of Intermediary Molybdenum Complexes

Low Temperature ^{31}P -NMR Spectroscopy of the Molybdenum Oxo Complex **1b**

In a NMR tube was placed a solution of 135 mg (0.280 mmol) of molybdenum oxo complex **1b** in 0.7 mL of deuterodichloromethane. The tube was cooled to $-50\text{ }^{\circ}\text{C}$ and a ^{31}P -NMR spectrum was recorded, which showed one singlet at δ 137.9 ppm. The spectrum is displayed in Figure S2.

Reaction of the Molybdenum Oxo Complex **1b** with Methylthiirane (**Ia**) and Phenylthiirane (**Ib**)

In a NMR tube kept at $-50\text{ }^{\circ}\text{C}$ was placed a solution of 15.5 mg (0.0321 mmol) of molybdenum oxo complex **1b** in 0.5 mL of methylthiirane (**Ia**) or phenylthiirane (**Ib**) and 0.3 mL of oxygen-free deuterodichloromethane were added slowly. The tube was sealed and immediately the ^{31}P - and ^{13}C -NMR spectra were recorded at $-50\text{ }^{\circ}\text{C}$. Besides the absorption of the molybdenum oxo complex **1b**, one new ^{31}P -NMR signal was observed at δ 107.6 ppm. ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 15.1 (q), 15.2 (q), 63.1 (t), 64.8 (t). The spectra are shown in Figures S3 and S4.

Reaction of the Molybdenum Oxo Complex **1b** with Thietane

In a NMR tube at ca. $20\text{ }^{\circ}\text{C}$ was placed a solution of 386 mg (0.800 mmol) of molybdenum oxo complex **1b** in 0.5 mL of thietane and 0.3 mL of oxygen-free deuterodichloromethane. The tubes were sealed and the ^{31}P -NMR spectrum was recorded at $-50\text{ }^{\circ}\text{C}$. One new ^{31}P -NMR signal was observed at δ 92.8 ppm. ^1H NMR (CD_2Cl_2 , 200 MHz) δ 1.71–1.80 (m, 12 H), 2.31–2.41 (m, 2H), 2.41–2.50 (t, J = 3.38 Hz, 2 H); the missing signal of 8 H of the ethoxy group could not be determined due to signal overlap; ^{13}C NMR (CD_2Cl_2 , 50 MHz) δ 14.1 (q), 15.1 (q), 29.6 (t), 31.8 (t), 63.5 (t), 63.6 (t). The ^{31}P -NMR spectrum is displayed in Figure S5.

Figure S2. ^{31}P -NMR Spectrum of Molybdenum Oxo Complex **1b**

Figure S3. ^{31}P -NMR Spectrum of Molybdenum Oxo Complex **1b** with the Thiirane **1a**

Figure S4. ^{31}P -NMR Spectrum of Molybdenum Oxo Complex **1b** with the Thiirane **1b**

Figure S5. ^{31}P -NMR Spectrum of Molybdenum Oxo Complex **1b** with the Thietane

Stoichiometric Episulfidation of the Alkenes

Reaction of the Molybdenum Disulfur Complex **2a** with *E*-Cyclooctene, the Isolation of the Bis(diethylcabamodithioato-κS,κS')oxomolybdenum (**1a**)¹²

In a 2-mL Schlenk tube under an argon-gas atmosphere were placed 20.2 mg (0.043 mmol) of molybdenum oxo-disulfur complex **2a** and 13.0 μ L (0.100 mmol) of *E*-cyclooctene in 1.0 mL of dichloromethane. The tube was sealed and the contents magnetically stirred for 4 h. About 0.5 mL of the solvent were evaporated (40 °C / 500 mbar), 1.0 mL of ethanol was added, and the tube stored at –20 °C. After two days, the red precipitate was collected by filtration, and dried under an oil-pump vacuum (10^{-2} mbar) at 20–25 °C to afford 7.40 mg (0.018 mmol, 42%) of the known molybdenum oxo complex **1a**^{S16} as red cubes.

Reaction of Molybdenum Disulfur Complex **2a** with *Z*-Cyclooctene, the Isolation of the Bis(diethylcarbamodithioato-κS,κS')dioxodi-μ-thioxodimolybdenum (**3a**)^{S17} and Tetraethylthiuram Disulfide.^{S18}

3a

Into a NMR tube were placed under an argon-gas atmosphere 123 mg (0.254 mmol) molybdenum oxo-disulfur complex **2a** and 68.0 μ L (0.523 mmol) of *Z*-cyclooctene in 1.0 mL of freshly distilled deuteriochloroform. The tube was sealed by means of a rubber stopper and Parafilm, immersed in an oil bath, and heated for 6 d to 60 °C in the dark. The solution was cooled to room temperature (ca. 20 °C) and the contents transferred to a 10-mL, round-bottomed flask. After evaporation of the dichloromethane

(40 °C/500 mbar), the residue was submitted to neutral-alumina chromatography (2:1 ethyl ether/methanol as eluent). First 92.5 mg of a mixture of complexes **2a** and **3a** were eluted. On repeated extraction with cold (ca. 0 °C) ethyl ether (5 × 1 mL), 33.2 mg (70.3 μmol, 28%) of the unreacted molybdenum oxo disulfur complex **2a** was recovered from the combined extracts after evaporation of the solvent (40 °C/800 mbar); complex **2a** was characterized by comparison with an authentic sample. The yellow amorphous residue [59.3 mg (101 μmol, 80%)] consisted of the dimeric complex **3a**^{S17}, mp 300–301 °C (from methanol); *R*_f (2:1 ethyl ether/methanol) = 0.80; IR (KBr) 1540 (C=N), 967 (Mo=O), 952 (Mo=O), 477 (MoSMo), 375 (MoSMo); ¹H NMR (CD₂Cl₂, 600 MHz) δ 1.38–1.45 (m, 12 H, CH₃), 3.92–4.07 (m, 8 H, CH₂); ¹³C NMR (CD₂Cl₂, 150 MHz) δ 12.5 (3 × q, CH₃), 12.6 (q, CH₃), 46.7 (2 × t, CH₂), 46.9 (t, CH₂), 47.4 (t, CH₂), 204.1 (s, S₂CN), 206.4 (s, S₂CN). Also 27.0 mg (0.091 mmol, 72%) of tetraethylthiuram disulfide^{S18}, purified by recrystallization (2:1 Et₂O/MeOH), was obtained as a white amorphous solid, mp 71–72 °C from methanol (lit.^{S18} mp 69–70 °C from ethanol); *R*_f (2:1 ethyl ether/methanol) = 0.55; ¹H NMR (CDCl₃, 200 MHz) δ 1.29 (t, *J* = 5.6 Hz, 3 H, CH₃), 1.47 (t, *J* = 5.6 Hz, 3 H, CH₃), 4.01 (q, 5.4 Hz, 4 H, 2 × CH₂); ¹³C NMR (CDCl₃, 50 MHz) δ 11.4 (q), 13.4 (q), 47.6 (t), 52.0 (t), 192.6 (s).

Reaction of the Molybdenum Oxo Complex 1a with *cis*-Cyclooctene Episulfide (*cis*-5a), the Isolation of the Bis(diethylcarbamdithioato-κS,κS')(dithio)oxomolybdenum (2a).¹³

A NMR tube was charged with a solution of 24.8 mg (60.7 μmol) molybdenum oxo complex **1a** and 9.30 mg (65.4 μmol) of *cis*-cyclooctene episulfide (*cis*-**5a**) in 0.7 mL of freshly distilled deuteriochloroform. The tube was sealed and kept for 15 min at 60 °C in an oil bath. Quantitative

¹H-NMR analysis revealed that 96% of the *cis*-cyclooctene episulfide (*cis*-**5a**) had been converted to the corresponding olefin *Z*-**4a**. The tube was opened and after evaporation of the solvent (40 °C/ 100 mbar), silica-gel chromatography (2:1 petroleum ether/CH₂Cl₂) of the residue afforded 28.5 mg (0.060 mmol, 99%) of the molybdenum oxo-disulfur complex **2a** as dark green cubes, mp 163–165 °C (dec.) [lit.¹³ 165 °C (dec.)] ; R_f (2:1 ethyl ether/methanol) = 0.80; IR (KBr) 1528 (C=N), 1503 (C=N), 913 (Mo=O), 550 (S-S); ¹H NMR (CDCl₃, 250 MHz) δ 1.10 (t, *J* = 7.18 Hz, 3 H), 1.38 (t, 3 H), 1.42 (t, 3 H), 1.43 (t, 3 H), 3.46 (dq, *J* = 14.34 Hz, *J* = 7.33 Hz, 2 H), 3.59 (dq, *J* = 14.34 Hz, *J* = 7.33 Hz, 2 H), 3.75–4.07 (m, 4 H); ¹³C NMR (CDCl₃, 63 MHz) δ 12.0 (q), 12.4 (q), 12.6 (q), 12.9 (q), 44.3 (t), 45.1 (t), 46.0 (t), 46.6 (t), 201.4 (s), 203.9 (s).

GP-5: General Procedure for the Stoichiometric Episulfidation of Cycloalkenes with the Molybdenum Oxo Disulfur Complex **2a**

Analytical Scale: A NMR tube was charged with a solution of 23.6 mg (0.050 mmol) of the molybdenum oxo-disulfur complex **2a** and 0.100 mmol of the particular olefin in 0.7 mL of CDCl₃. The tube was sealed by means of a rubber stopper and Parafilm and a NMR spectrum was taken. The tube was placed into a thermostated oil bath and kept at the required temperature and time as indicated in Table S1. The known episulfides¹⁰ *trans*-9-thiabicyclo[6.1.0]nonane (*trans*-**5a**), *cis*-9-thiabicyclo[6.1.0]nonane (*cis*-**5a**), *exo*-3-thiatricyclo[3.2.1.0^{2,4}]octane (**5d**), and 6-thiabicyclo[3.1.0]hexane (**5f**) were identified by means of the characteristic signals in their ¹H NMR and ¹³C NMR spectra directly in the crude reaction mixture, and quantified by ¹H-NMR analysis against dimethyl isophthalate as internal standard.

Preparative Scale: In a 25-mL, round-bottomed flask were placed 945 mg (2.00 mmol) of the molybdenum oxo-disulfur complex **2a** in 10 mL of dichloromethane. To this solution were added 378–540 µl (3.45–4.00 mmol) of the alkene **4e** or **4h** and the mixture heated at 40 °C in an oil bath under

reflux for 12 h. After evaporation of the solvent, silica-gel chromatography (petroleum ether as eluent) yielded the episulfides **5e** or **5h** as colorless oils.

***exo*-1a,2a,3,5a,6,6a-Hexahydro-2,6-methano-2*H*-indeno[5,6-*b*]thiirene (**5e**).**^{S19}

According to the general procedure GP-5, from 540 μ L (4.00 mmol) of dicyclopentadiene were isolated 92.1 mg (0.561 mmol, 28%) of the episulfide **5e**; R_f (petroleum ether) = 0.39; MS (EI, 70 eV): $[m/z]$ (rel intensities in %) 164 (18, M^+), 132.1 (9, $M^+ - S$), 66.0 (100, $M^+ - C_3H_4S$), 39.0 (22, $C_3H_3^+$); 1H NMR ($CDCl_3$, 250 MHz) δ 0.81–0.92 (m, 1H, 7- H^{anti}), 1.62–1.75 (m, 1 H, 7- H^{syn}), 2.19–2.81 (m, 5 H, H-1a or H-2a, H-2, H-3, H-6), 2.87–2.93 (d, $J = 4.16$ Hz, 2 H, H-1a or H-2a, H-6a), 3.22–3.33 (m, 1 H, H-5a), 5.56–5.72 (m, 2 H, H-4, H-5); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 30.9 (d, C-7), 31.0 (t, C-3), 34.5 (d, C-6a), 37.5 (d, C-1a), 39.6 (d, C-6), 41.2 (d, C-2), 42.5 (d, C-2a), 54.3 (d, C-5a), 130.1 (d, C-5), 132.2 (d, C-4); the signals were assigned with the help of 2D-NMR spectra [H,H -COSY, CH -COSY (HMBC, HMQC) and NOESY].

7-Thiadispiro[2.0.2.1]heptane (5h**)**

According to the procedure GP-5, from 378 μ L (3.45 mmol) of bicyclopentadiene were obtained 210 mg (1.87 mmol, 54%) of episulfide **5h**, bp 40 $^{\circ}C/11$ mbar; IR (KBr) 2921, 2852, 1637, 1055.; MS (EI, 70 eV) 112 (100, M^+), 84 (81, $M^+ - C_2H_4$), 58 (52, $C_2H_3S^+$), 39 (43, $C_3H_3^+$); 1H NMR ($CDCl_3$, 200 MHz)

δ 0.94–1.00 (m, 4 H), 1.37–1.56 (m, 4 H); ^{13}C NMR (CDCl_3 , 63 MHz) δ 7.5 (t), 37.6 (s) $\text{C}_6\text{H}_8\text{S}$ (112.2)

HRMS (ED): $[\text{M}^+]$ calcd 112.0347, found 112.0346.

Table S4: Stoichiometric Sulfur Transfer by the Disulfur Complex **2a** to the Alkenes **4**

entry	alkene 4	temp. [°C]	time [h]	convn 4 (%) ^{a)}	yield 5 (%) ^{a,b)}
1	(<i>E</i>)- 4a	20-25	3	65	65 ^{c)}
2	"	20-25	24	61 ^{d)}	85 ^{c)}
3	(<i>Z</i>)- 4a	60	6	19	20
4	"	60	20	32	16
5	"	60	>100	12	0
6	4d	20-25	18	59	50 ^{e)}
7	"	60	10	59	50 ^{e)}
8	4e	40	12	-	28 ^{f)}
9	4f	20-25	264	16	14
10	"	40	12	19	16
11	4h	40	12	-	54 ^{f)}

^{a)} Determined by ^1H -NMR analysis on the crude product mixture with dimethyl isophthalate as internal standard (error $\pm$ 5% of the stated values); the yield is based on complex **2a**. ^{b)} Material balance > 80%. ^{c)} Both sulfur atoms of complex **2a** are transferred; therefore, the yield is divided by the stoichiometric factor of 2. ^{d)} After addition of 0.5 equiv. of *trans*-cyclooctene. ^{e)} Additionally, 10% of the trithiolane was detected. ^{f)} Yield of isolated material.

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