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Deoxygenation of Dithiirane 1-Oxides with Lawesson's Reagent Leading to the Corresponding Dithiiranes

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Abstract: 3,3-Disubstituted dithiirane 1-oxides were efficiently reduced with Lawesson's reagent (LR) to give the corresponding dithiiranes. X-ray diffraction analysis of 3,3-di(1-adamantyl)dithiirane is reported. Reaction of ^{34}S-labeled 3,3-di(1-adamantyl)dithiirane 1-oxide with LR produced the corresponding dithiirane in which the ^{34}S atoms were retained quantitatively.

The chemistry of dithiiranes has been drawing much attention in view of the fundamental interest in organosulfur chemistry.[1−4] Recent progress in the chemistry includes the preparation of dithiirane derivatives by the reaction of thioketone *S*-oxides with Lawesson's reagent (LR), reported by Shimada and co-workers,[2] and the observation of the parent dithiirane under matrix conditions at 10 K by Mloston and co-workers.[3] In our study on the synthesis of isolable dithiiranes,[4] we recently reported two methods to prepare dithiirane 1-oxides **1**: thermal decomposition of tetrathiolane 2,3-dioxides **2**[5] and the reaction of diazoalkanes with an S_2O equivalent[6] (Scheme 1). As a variety of structurally diverse dithiiranes **3** are necessary to study the intrinsic chemical and physical properties of dithiiranes, we next investigated deoxygenation of **1** to lead it to the corresponding dithiiranes **3**. A reducing reagent that serves under mild conditions must be employed for this transformation because of the expected instability of **3** at high temperatures or under basic conditions.[1,2,4] Phosphorus sulfide reagents, such as LR,[7] P_2S_5,[8] and S=PBr$_3$,[8d,9] were reported to convert sulfoxides to sulfides under conditions appropriate for the present study. Indeed, LR reportedly converts thioketone *S*-oxides into dithiiranes as mentioned above.[2] Thus, we examined deoxygenation of **1** with LR and succeeded in removal of the oxygen atom from **1**.

SCHEME 1

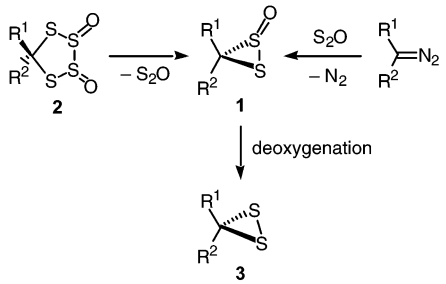
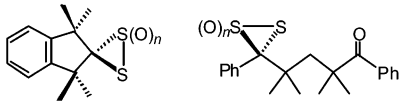


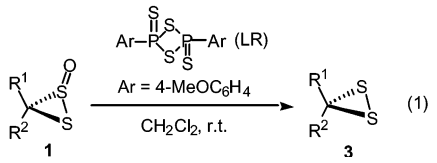
CHART 1



1e: n = 1
3e: n = 0

1f: n = 1
3f: n = 0

A typical procedure is as follows: equimolar amounts of dithiirane 1-oxide **1** and LR were dissolved in dichloromethane under argon, and the mixture was stirred at room temperature for 11 h (eq 1). After the solvent was



removed under reduced pressure, the residue was washed with hexane several times to leave a sparingly soluble residue derived from LR. The washings were combined and purified by column chromatography. The results are summarized in Table 1 with relevant spectroscopic data. (1-Adamantyl)-*tert*-butyldithiirane (**3a**) was obtained in high yields from stereoisomers, **1a** and **1b** (entries 1 and 2). The low yield of **3d** is attributed to its instability under the reaction conditions (entry 4). The reaction of spirodithiirane 1-oxide **1e** (Chart 1) with LR completed in a shorter reaction time (entry 5) in comparison to other cases. In all cases, the corresponding thioketone was obtained as a byproduct. A control experiment showed

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TABLE 1. Deoxygenation of Dithiirane 1-Oxides 1 to Dithiirane 3 with Lawesson's Reagent (LR)[a]

	dithiirane 1-oxide **1**				dithiirane **3**			
entry	R^1	R^2	compd no.	δ_C[b]	compd no.	yield (%)	δ_C[b]	λ_{max}/nm, (ϵ)[c]
1	1-Ad	*t*-Bu	**1a**	86.2	**3a**	59[d] (86)[e]	84.7	452 (78)
2	*t*-Bu	1-Ad	**1b**	87.7	**3a**	59[d] (63)[e]		
3	1-Ad	1-Ad	**1c**	87.4	**3c**	57[d]	86.2	454 (93)
4	Ph	*t*-Bu	**1d**	86.2	**3d**	20[f]	79.0	451 (50)
5			**1e**	89.0	**3e**	75[f]	88.4	455 (ca. 40)

[a] Conditions: CH_2Cl_2, rt, 11 h (entries 1−4) or 1.25 h (entry 5). [b] ^{13}C NMR chemical shifts of dithiirane carbons. [c] In CH_2Cl_2. [d] Isolated yields. [e] Determined by UV−vis. [f] Determined by ^1H NMR in $CDCl_3$.

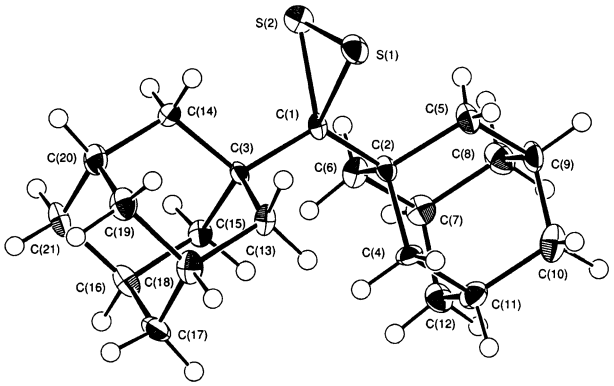


FIGURE 1. ORTEP drawing of 3,3-di(1-adamantyl)dithiirane (**3c**) (50% ellipsoid). Relevant bond lengths (Å) and angles (deg) data: S1−S2, 2.047(2); S1−C1, 1.826(5); S2−C1, 1.843(5); C1−C2, 1.575(6); C1−C3, 1.581(6); S1−S2−C1, 55.7(2); S2−S1−C1, 56.5(2); S1−C1−S2, 67.8(2); C2−C1−C3, 123.2(4).

that ca. 40% of dithiirane **3c** decomposed to the corresponding thioketone after 7 h by treatment with LR at room temperature. The reaction of dithiirane 1-oxide **1f**[4a] (Chart 1) did not yield the corresponding dithiirane **3f**[4b] under these conditions.

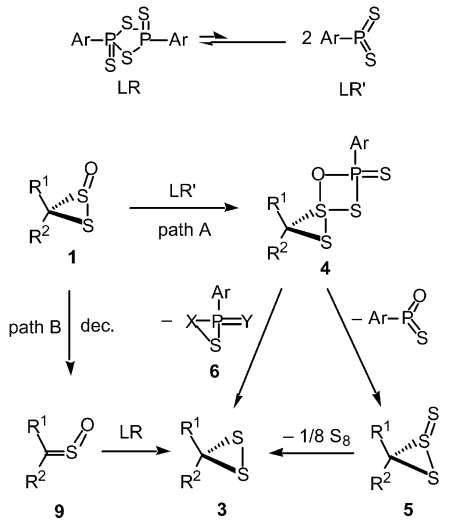
Dithiiranes **3** exhibited an absorption maximum due to the S−S bond in a range of 450−455 nm in UV−vis spectroscopy. In ^{13}C NMR spectroscopy, dithiirane carbons of 3,3-dialkyldithiiranes, **3a**, **3c**, and **3e**, resonated at around δ 86, and that of alkylaryldithiirane **3** at a little higher field (**3d**, δ 79.0; **3f**, δ 80.6[4b]), while the corresponding carbon of dithiirane 1-oxides **1** appeared in a relatively narrow range (δ 86−89) independent of the type of substituents.

Figure 1 depicts an ORTEP drawing of **3c** with the relevant bond lengths and angles data. The S−S bond length of 2.047(2) Å is shorter by 0.051 Å than that of the corresponding dithiirane 1-oxide **1c** [2.098(1) Å].[5a]

Two reaction pathways are considered for this deoxygenation reaction (Scheme 2). One (path A) is a mechanism analogous to that proposed for reduction of sulfoxides to sulfides with P_4S_{10}[8a,b] or S=PBr_3.[9] Dithiirane 1-oxide **1** would react with LR′[10] to form a sulfurane intermediate **4**, which gives dithiirane **3** through dithiirane 1-sulfide **5**, or directly by elimination of **6**.

Oxathiaphosphirane *P*-sulfides **6** (X = O, Y = S) or dithiaphosphirane *P*-oxides **6** (X = S, Y = O) are

SCHEME 2



unknown species as far as we know;[12] however, a stable dioxaphosphirane was recently reported.[13] Thiosulfoxides (RR′S=S) have been proposed as intermediates in deoxygenation of sulfoxides with phosphorus sulfide reagents.[8a,9,11] Steudel reported ab initio calculations on simple dialkyl thiosulfoxides that are less stable by 80 kJ mol^{-1} than the corresponding disulfides.[14] Flammang and co-workers recently showed by mass spectrometry methodology that thiosulfoxides are stable in the gas phase.[15] In a theoretical, mechanistic study on the thermal desulfurization of thiirane **7**,[16] thiirane 1-sulfide **8** was considered as a likely intermediate that lost sulfur atoms finally to yield ethylene with generation of S_2, S_3, or S_4 (Scheme 3). Chew and Harpp proposed an alternative, plausible mechanism on the basis of their experimental results that sterically hindered thiiranes lose of the sulfur atom by a concatenation process through the thiirane *S*-sulfide intermediate to give the corresponding alkenes and S_6 or S_8.[17] Taking this reactivity of thiirane *S*-sulfides into consideration, the intervention of dithiirane 1-sulfides **5** may be unlikely in the present reaction

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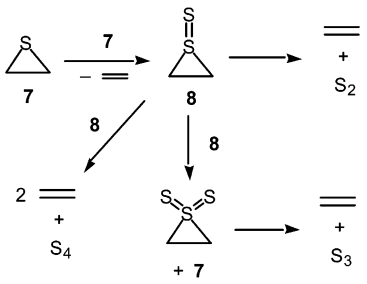
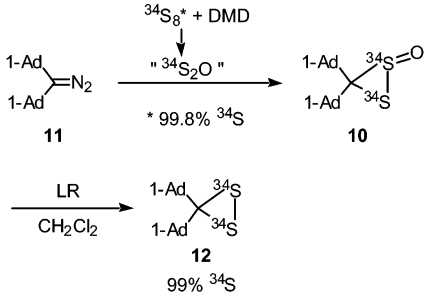
SCHEME 3



SCHEME 4



because it is barely believed that **5** gives only dithiirane **3** without formation of the corresponding thioketone, which was not a primary product as mentioned above.

Interestingly, the reaction of the parent thiolane 1-oxide with LR was reported to give not only thiolane but also the parent 1,2-dithiane, a ring expansion product.[7] If this is true of the present reaction, the formation of trithietanes would be expected. However, when the reactions of **1a** and **1b** with LR were monitored by UV−vis spectroscopy, no remarkable absorption due to other species appeared except for the absorption maximum (λ_{max} 450 nm) due to dithiirane **3a**. The reaction of **1c** with LR was traced with ^{31}P NMR spectroscopy to result in the observation of several signals in a range of δ 40−125 probably due to the decomposition products of LR.[18]

The other likely mechanism (Scheme 2, path B) is the reaction of thioketone *S*-oxide **9**, formed by decomposition of **1** in the reaction medium, with LR.[2] A control experiment showed that, for example, the reaction of thioketone *S*-oxide **9** (R^1 = Ph, R^2 = *t*-Bu) with LR gave dithiirane **3d** in a shorter reaction time (5 min) than that of **1d** with LR. To distinguish the two paths A and B, we prepared dithiirane 1-oxide **10** labeled with two ^{34}S atoms by reaction of diazoalkane **11** and $^{34}S_8O$[6] and subjected **10** to the reaction with LR. Mass spectra of the resulting **12** showed almost quantitative retention of the ^{34}S atoms to clearly rule out path B (Scheme 4).

Dithiirane **3c** and its ^{34}*S*-labeled dithiirane **12** in hand provided us with an opportunity to determine frequencies of the S−S stretching vibrations of the dithiirane rings by comparison of their Raman spectra. Thus, taking the results of DFT calculations into consideration, the frequencies of **3c** and **12** were determined to be 541 and 527 cm^{-1}, respectively.[19,20]

Experimental Section

General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz in $CDCl_3$, respectively. Dithiirane 1-oxides **1** and **10** were prepared by the reported method.[6]

3-(1-Adamantyl)-3-*tert*-butyldithiirane (3a): Dithiirane 1-oxide **1a** (10.0 mg, 0.0352 mmol) and LR (17.9 mg, 0.0443 mmol) were dissolved in dichloromethane (10 mL) and the mixture was stirred for 11 h at room temperature under argon. The solution was concentrated under reduced pressure until an oily material appeared, and then hexane was added to precipitate the decomposition products of LR. The precipitates were removed by filtration, and the filtrate was evaporated to dryness. Hexane was then added again to the residue and the above filtration−evaporation process was repeated two times. The resulting residue was subjected to column chromatography (SiO_2, hexane) to give dithiirane **3a** (5.6 mg, 59%): orange plates, mp 92−93 °C (hexane−CH_2Cl_2). ^{1}H NMR δ 1.31 (s, 9H), 1.63 (br s, 6H), 2.00 (br s, 9H); ^{13}C NMR δ 29.6, 32.5, 36.7, 42.5, 42.8, 43.5, 84.7; UV−vis (CH_2Cl_2, *c* 3.82 × 10^{-3} mol/dm^3) λ_{max} (ϵ) 452 (78) nm. Anal. Calcd for $C_{15}H_{24}S_2$: C, 67.10; H, 9.01. Found: C, 67.18; H, 9.10.

3,3-Di(1-adamantyl)dithiirane (3c): In a manner similar to the above, **3c** was obtained in 57% isolated yield (7.1 mg) together with di(1-adamantyl) thioketone (3.1 mg, 27%) from 13.2 mg (0.036 mol) of **1c** and 14.7 mg (0.036 mmol) of LR in dichloromethane (11.5 mL). **3c**: orange plates, mp 136−139 °C dec (pentane). ^{1}H NMR δ 1.58−1.69 (m, 12H), 1.98 (br s, 6H), 2.04 (br s, 12H); ^{13}C NMR δ 29.6, 36.7, 42.9, 44.1, 86.2; UV−vis (CH_2Cl_2, 4.15 × 10^{-3} mol/dm^3) λ_{max} (ϵ) 454 nm (93). Anal. Calcd for $C_{21}H_{30}S_2$: C, 72.77; H, 8.72. Found: C, 72.67; H, 8.81.

Crystal data for 3c: $C_{21}H_{30}S_2$, orthorhombic, *Pna*2$_1$, *a* = 21.887(1) Å, *b* = 11.037(1) Å, *c* = 7.1080(3) Å, *V* = 1717.1(2) Å^3, *Z* = 4, ρ_{calcd} = 1.341 g cm^{-3}, μ(Mo Kα) = 0.308 mm^{-1}. An orange plate with dimensions 0.26 × 0.16 × 0.05 mm^3 was mounted on a Mac Science DIP3000 diffractometer with a graphite monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo Kα radiation (λ = 0.71073 Å) at 153 K, and the data reduction was made by the MAC DENZO program system. Intensity data of 1893 independent reflections were collected in the range of $-27 \le h \le 27$, $0 \le k \le 13$, $0 \le l \le 7$. The structure was solved by direct methods using SIR[21] and refined with full-matrix least-squares (SHELXL-97[22]) using all independent reflections (1893 reflections) for 208 parameters. Absorption corrections were done by a multiscan method (SORTAV[23]). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. The final *R*1 = 0.0517 ($I > 2\sigma(I)$, 1420 reflections), *wR*2 = 0.1552 (for all), GOF = 1.059; max/min residual density = 1.366/−0.431 e Å^{-3}.

3-*tert*-Butyl-3-phenyldithiirane (3d): Dithiirane 1-oxide **1d** (13.6 mg, 0.060 mmol) and LR (24.3 mg, 0.060 mmol) were dissolved in dichloromethane (17 mL), and the solution was stirred for 11 h at room temperature under argon. Water was added and the resulting mixture was extracted with dichloromethane. The extract was washed with water, dried, and evaporated to dryness. The ^{1}H NMR spectrum of the residue was measured with dibenzyl (3.90 mg, 0.0214 mmol) as the

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internal standard to indicate the formation of **3d** (0.0121 mmol, 20%), thiopivalophenone (0.00577 mmol, 10%), and *cis*-3,5-di-*tert*-butyl-3,5-diphenyl-1,2,4-trithiolane[24] (0.00024 mmol, 0.4%).

An analytical sample of **3d** was obtained as follows. A solution of thiopivarophenone *S*-oxide (90 mg, 0.46 mmol) with LR (0.13 g, 0.32 mmol) in dichloromethane (15 mL) was stirred at room temperature.[2] Water was added and the resulting mixture was extracted with dichloromethane. The extract was dried and evaporated to dryness. Hexane was added to precipitate the decomposition products of LR and the resulting insoluble materials were removed by filtration. The filtrate was concentrated under reduced pressure to leave an orange oily residue. As dithiirane **3d** could not be purified by chromatography or distillation because of the occurrence of decomposition, the decomposition products of LR were removed as much as possible by repeating the above manipulations: orange oil; ^{1}H NMR δ 1.11 (s, 9H), 7.14−7.21 (m, 3H), 7.29−7.34 (m, 2H); ^{13}C NMR δ 28.7, 38.8, 79.0, 126.3, 127.6, 131.5, 141.2; UV−vis (CH_2Cl_2, c = 6.75 × 10^{-3} mol/dm^3) λ_{max} (ϵ) 451 nm (50). Anal. Calcd for $C_{11}H_{14}S_2$: C, 62.81; H, 6.71. Found: C, 63.32; H, 6.82.

1,1,3,3-Tetramethylindane-2-spiro-3′-dithiirane 1′-oxide (1e): To a solution of S_8 (64 mg, 0.25 mmol) in dichloromethane (7.5 mL) was added an acetone solution of dimethyldioxirane[25] (0.104 M, 2.4 mL, 0.25 mmol) at 0 °C, and the mixture was stirred for 1 h at 0 °C. To the mixture was added a solution of 1,1,3,3-tetramethyl-2-diazoindane[26] (10 mg, 0.050 mmol) in dichloromethane (2.5 mL). After being stirred for 2 h at room temperature, the mixture was evaporated to dryness. The residue was subjected to HPLC (SiO_2, hexane−CH_2Cl_2 1:1) to give **1e** (5.8 mg, 0.023 mmol, 46%) and 1,2,3,3-tetramethyl-1*H*-indene[27] (4.0 mg, 0.023 mmol, 47%). **1e**: colorless crystals, mp 103−104 °C dec (hexane−CH_2Cl_2). ^{1}H NMR δ 0.96 (s, 3H), 1.48 (s, 3H), 1.56 (s, 3H), 1.78 (s, 3H), 7.14−7.18 (m, 1H), 7.24−7.35 (m, 3H); ^{13}C NMR δ 26.6, 29.7, 29.8, 31.8, 48.6, 50.9, 89.0, 121.9, 122.4, 127.8, 128.1, 146.8, 149.1; IR (KBr) 1098 cm^{-1} (S=O). Anal. Calcd for $C_{13}H_{16}OS_2$: C, 61.87; H, 6.39. Found: C, 61.82; H, 6.45. The structure of **1e** was confirmed by X-ray crystallography, the details of which are given in the Supporting Information.

1,1,3,3-Tetramethylindane-2-spiro-3′-dithiirane (3e): Dithiirane 1-oxide **1e** (1.9 mg, 0.0077 mmol) and LR (3.0 mg, 0.0071 mmol) were dissolved in $CDCl_3$ (0.4 mL) in an NMR sample tube. Dibenzyl (1.5 mg, 0.0085 mmol) was added as an internal standard. The NMR sample tube was stood at room temperature, and the reaction was monitored by ^{1}H NMR spectroscopy. The starting dithiirane 1-oxide **1e** was consumed completely after 75 min. The yields of dithiirane **3e** and the corresponding thioketone[28] were estimated to be 75% and 9%, respectively.

In a larger scale experiment employing 10 mg (0.041 mmol) of **1e** and 16 mg (0.041 mmol) of LR in dichloromethane (6 mL) for 4.5 h, a 10:1 mixture of **3e** and the thioketone was obtained after removal of the decomposition products of LR by filtration. Despite much effort, pure **3e** could not be obtained by chromatographic methods or recrystallization because of the decomposition to the thioketone, which hampered elemental analysis. **3e**: ^{1}H NMR δ 1.37 (s, 12H), 7.22−7.25 (m, 4H); ^{13}C NMR δ 31.4, 48.5, 88.4, 122.6, 127.5, 148.2; UV−vis (CH_2Cl_2, c = ca. 6 × 10^{-3} mol/dm^3) λ_{max} (ϵ) 455 nm (ca. 40).

3,3-Di(1-adamantyl)-$^{34}S_2$-dithiirane 1-oxide (10): To a solution of $^{34}S_8$ (99.8%, 96 mg, 0.35 mmol) in CH_2Cl_2 (24 mL) was added an acetone solution of dimethyldioxirane[25] (0.083 M, 4.0 mL, 0.33 mmol) at 0 °C, and the mixture was stirred for 1 h at 0 °C. To the mixture was added a dichloromethane solution (5 mL) of di(1-adamantyl)diazomethane (**11**),[29] prepared by treatment of di(1-adamantyl) ketone hydrazone[29] (112 mg, 0.357 mmol) with nickel peroxide[30] (112 mg) in ether (20 mL). After the mixture was stirred for 1.5 h, the solvent was removed under reduced pressure, and the residue was passed through a short column of silica gel (hexane−CH_2Cl_2 1:1). The fraction containing **10** was subjected to HPLC [a reverse-phase column, MeCN, for removal of di(1-adamantyl) ketone and di(1-adamantyl) ^{34}S-thioketone] to give 33 mg of **10** (26%).

3,3-Di(1-adamantyl)-$^{34}S_2$-dithiirane (12): By a method similar to the case of **3a**, **12** was obtained in 65% isolated yield (6.2 mg) together with di(1-adamantyl) ^{34}S-thioketone (2.3 mg, 27%) from 10.0 mg (0.027 mol) of **10** and 11.0 mg (0.027 mmol) of LR in dichloromethane (8.5 mL). **12**: MS (EI, 70 eV) *m*/*z* 350 (M^+, 6.7%), 316 ($M^+ - {}^{34}S$, 99.7), 282 ($M^+ - {}^{34}S_2$, 23.5), 181 (58.5), 135 (100). The ^{34}S content in **12** was calculated to be 99% based on the average value of 10 scans.

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Supporting Information Available: Details of X-ray crystallographic analyses of **3c** and **1e**, ^{1}H NMR spectra of **3d**, **3e**, **10**, and **12**, and mass spectra of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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