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TETRAHEDRON

Rearrangement of the Carbanion Generated from a Tied-back 1,2,4-Trithiolane Oxide (6,7,8-Trithiabicyclo[3.2.1]octane 6-Oxide)

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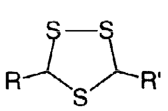
Abstract: Treatment of 2,2,4,4-tetramethyl-6,7,8-trithiabicyclo[3.2.1]octane 6-*exo*-oxide (**3**) with LDA, followed by treatment with D_2O, RI (R = Me, Et), and 2-PrBr, yielded the deuterated starting compound (**3-d**), bicyclic 1,3-dithietane oxides (**12**, **13**), and (2-propyldithio)thiolactone (**14**), respectively. The initially- formed bridgehead lithium salt (**11**) opens the bicyclic skeleton to give the lithium δ-thioxoperoxydithiocarboxylate (**15**), which finally isomerizes to the lithium [3-oxo(2-thianyl)]disulfide (**19**) via the peroxydithiocarboxylate-α-oxodisulfide rearrangement. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Dithioacetals have great synthetic utility, in particular, as an acyl anion equivalent.[1] Whereas six-membered cyclic dithioacetals, for example 1,3-dithianes, have been investigated extensively in this viewpoint,[1] the use of carbanions of five-membered cyclic dithioacetals, for example 1,3-dithiolanes, in organic synthesis is limited to a few cases[2a,b] because of the strong tendency toward fragmentation to alkenes and dithiocarboxylates.[2b,c] 1,2,4-Trithiolanes **1**, a sulfur analog of ozonides, are expected to have acidic hydrogens at the 3 and 5 positions as well, but there are few reports on their anions as far as we know.[3] We prepared a 6,7,8-trithiabicyclo[3.2.1]octane **2** and its 6-oxide **3**, tied-back 1,2,4-trithiolanes, as precursors for 6,7-dithiabicyclo[3.1.1]heptanes **4**, which could be converted to isolable dithiiranes **5** under oxidative hydrolysis conditions.[4] Generation of the bridgehead carbanion from **3**, followed by treatment with electrophiles, was now found to lead to unexpected reactions, in which products are strongly dependent on the electrophiles added (Eq. 1). We report here structure elucidation of the products and the mechanistic consideration on the reactions.



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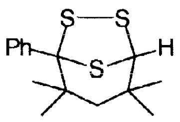

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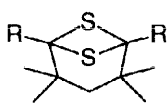

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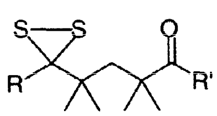

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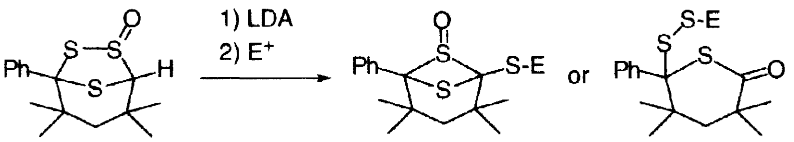

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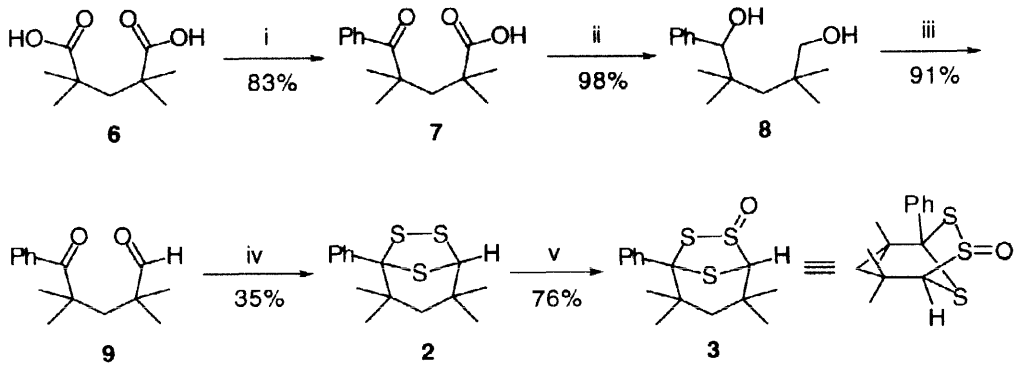
(1)

PII: S0040-4020(99)00589-X

RESULTS AND DISCUSSION

The 1,2,4-trithiolane **2** was prepared by reactions shown in Scheme 1. Treatment of the dicarboxylic acid **6**[5] with 3 molar amounts of PhLi gave the keto acid **7**, the reduction of which with $LiAlH_4$ yielded the diol **8**. A Swern oxidation of **8** followed by sulfurization of the resulting keto aldehyde **9** with Lawesson's reagent (LR)[6] furnished **2**. Such trithiolane formation by sulfurization of dicarbonyl compounds was observed in our previous study.[4,7] Since **2** resisted lithiation with LDA,[8] it was oxidized for increasing acidity of the bridgehead hydrogen. Oxidation of **2** with MCPBA proceeded regio- and stereoselectively to give the 1,2,4-trithiolane 1-*exo*-oxide **3**. The regio- and stereochemistry of **3** was determined by X-ray crystallography unambiguously (Figure 1). The present regioselectivity is contrast to the previous reports where the oxidation of the unsubstituted 1,2,4-trithiolane with $NaIO_4$[9] or H_2O_2-V_2O_5[10] gave an almost 1:1 mixture of the 1- and 4-oxides or the 4-oxide solely, respectively.

Scheme 1



i: PhLi (3 molar amounts), PhH, Et_2O, refl., 14 h; ii: $LiAlH_4$ (3 molar amounts), Et_2O, r.t., 3.5 h; iii: CF_3CO_2H (3 molar amounts), DMSO (4 molar amounts), CH_2Cl_2, −65 °C and then Et_3N (excess), r.t.; iv: LR (2 molar amounts), xylene, refl., 49 h; v: MCPBA (1.3 molar amounts), CH_2Cl_2, 0 °C, 3 h.

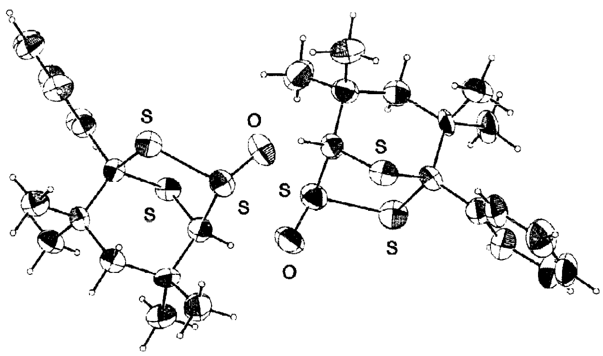
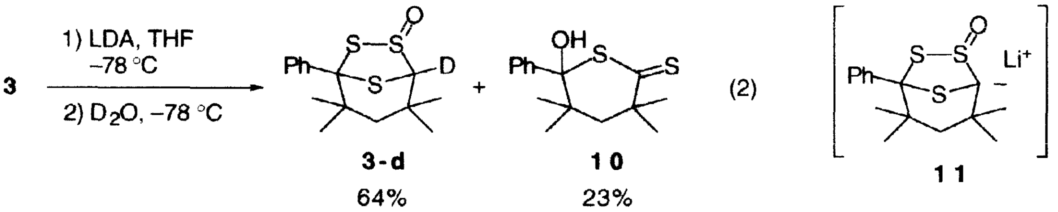
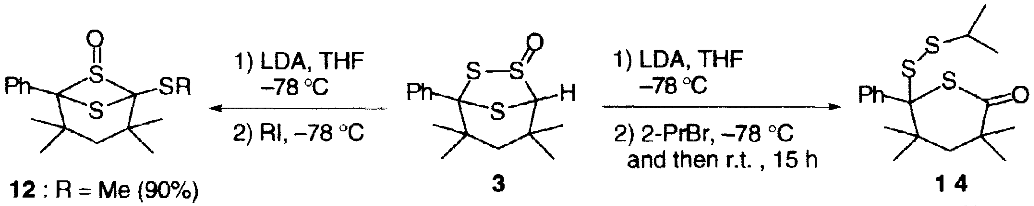


Figure 1. ORTEP drawing of the 1,2,4-trithiolane oxide **3** (50% probability ellipsoids)

Treatment of **3** with LDA in THF at –78 °C, followed by quenching with D_2O, yielded the deuterated trithiolane oxide **3-d** and the hydroxydithiolactone **10** (Eq. 2). The successful deuteration of **3**, apart from the formation of **10**, indicates the generation of the bridgehead carbanion **11**. It is worth noting here that, when LDA was added to a solution of **3**, the color of the reaction mixture turned from colorless to deep purple immediately, suggesting the presence of another intermediate with a strong chromophor. The purple color disappeared quickly when D_2O was added.



When the purple solution was treated with MeI and EtI, the color disappeared quickly. Purification of the mixture furnished 6,7-dithiabicyclo[3.1.1]heptane 6-oxides (tied-back 1,3-dithietane oxides) **12** and **13**, instead of expected substituted trithiolanes. The structures of **12** and **13** were determined by their spectroscopic data and the *endo* stereochemistry of the S=O group was confirmed by X-ray crystallography on **12** (Figure 2). On the other hand, the reaction with 2-PrBr did not proceed at low temperatures probably because of steric hindrance of the reagent, and the purple color remained up to room temperature. The product was the (2-propyldithio)thiolactone **14**. The structure of **14** was determined by X-ray crystallography (Figure 3).



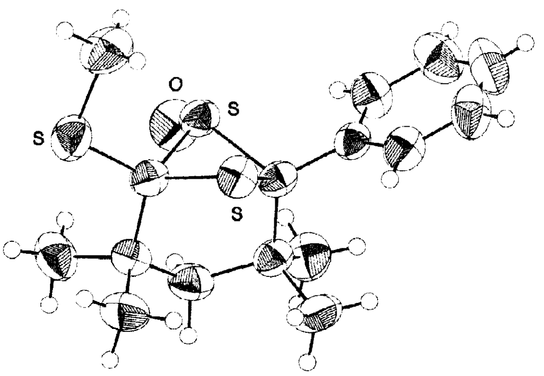


Figure 2. ORTEP drawing of **12**.
(50% probability ellipsoids)

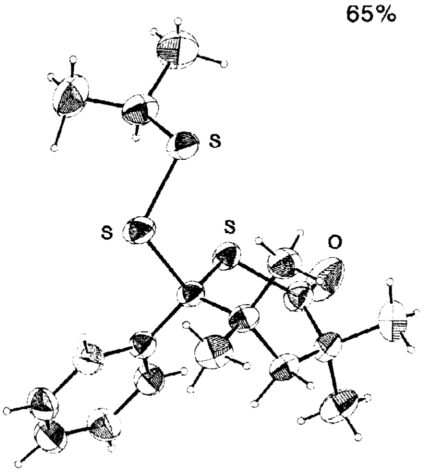
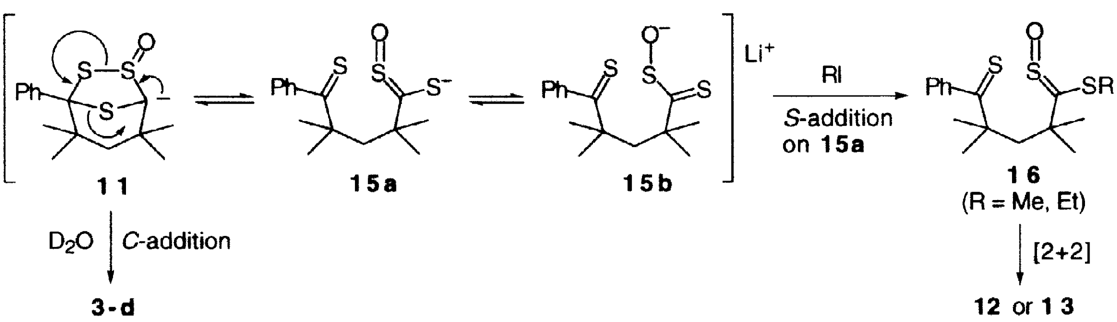


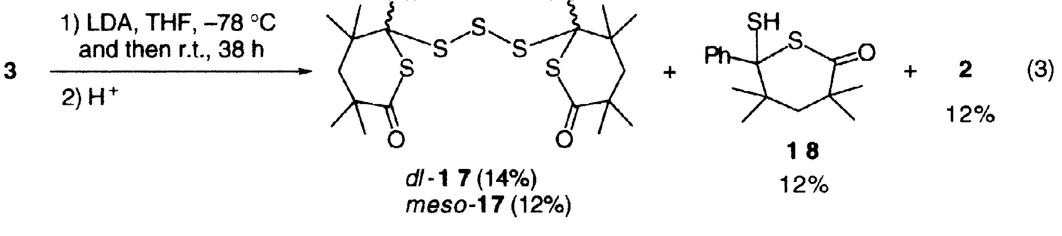
Figure 3. ORTEP drawing of **14**.
(50% probability ellipsoids)

It is hard to explain the formation of **12**—**14** in terms of simple reactions of the carbanion **11** with the alkyl halides, implying the existence of other anionic precursors for each product. A reaction mechanism to interpret the above results is considered as follows on the basis of additional two experiments. The first one is the UV-Vis spectrum of the purple solution (THF) that exhibited the longest absorption maximum at 563 nm (ε > 94). The position of the absorption is very similar to the $n \rightarrow \pi^*$ absorption of an alkyl aryl thioketone, PhC(=S)CMe$_2$CH$_2$CMe$_2$C(=O)Ph [λ_{max} 569 nm (ε 71)].[7] Therefore, it is possible to assume the ring-opening intermediates **15** with a thiocarbonyl group as the origin of the purple color. A similar ring-opening of ozonides is known.[3,11] Thus, the anionic intermediates **11** and **15** coexist at equilibrium at low temperatures. The formation of the dithietane oxides **12** and **13** is explained in terms of *S*-addition by MeI and EtI on **15a** to lead to the δ-thioxodithioester oxides **16**, which yield **12** and **13** by an intramolecular [2+2]-cyclization. An attempt to trap another tautomer **15b** with a silyl chloride failed to give a complex mixture.

Scheme 2



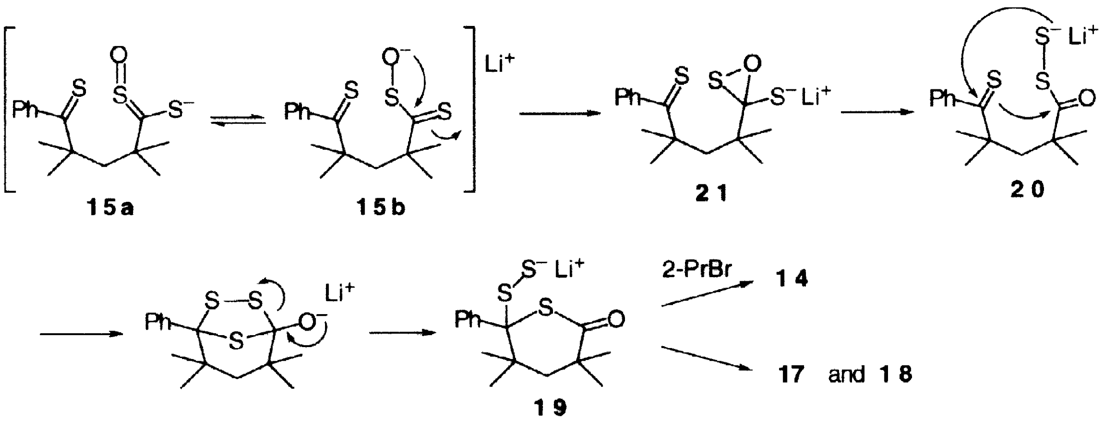
The second experiment is to allow the intermediate anions to decompose thoroughly. Thus, the purple-colored mixture was warmed to room temperature. After the disappearance of the color (38 h), the reaction was quenched with water to give *dl*- and *meso*-trisulfides **17** in 14 and 12% yields, respectively, along with the thiol **18** (12%) and **2** (Eq. 3). The structures of *dl*- and *meso*-**17** were elucidated by their spectroscopic data and results of elemental analysis. The one isomer of **17**, which gives two peaks on HPLC analysis using a chiral column, was assigned to the *dl*-isomer and the other, giving only one peak on the analysis, to the *meso*-one.

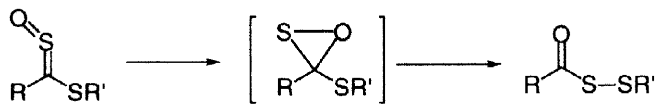


The formation of the trisulfides **17** and the thiol **18** is in harmony with that of the (2-propyldithio)thiolactone **14**, and is indicative of the disulfide salt **19** as their common precursor (Scheme 3). There is a precedent of the decomposition of disulfide salts (RS$_2^-$X$^+$) under basic conditions that leads to the formation of the corresponding trisulfides and thiols.[12] Metzner et al. observed the isomerization of dithioester oxides **22** to dithioperoxyesters **23** at room temperature, where they proposed a rearrangement via oxathiirane intermediates **23** (Eq. 4).[13] This would be also true for the present case: the rearrangement of **15** to **20** takes place via the oxathiirane intermediate **21** and then ring-closure and re-ring-opening would produce **19**.

Species produced by desulfurization of **20** or **21** or their protonated compounds may be responsible for the formation of hydroxydithiolactone **10** shown in Eq. 2. The mechanism for the formation of the reduction product **2** in Eq. 3 is not clear.

Scheme 3





(4)

In summary, we found characteristic reactivities of the carbanion generated from the tied-back 1,2,4-trithiolane oxide **3**, where the bridgehead carbanion **11** is in equilibrium with the δ-thioxoperoxydithiocarboxylate (**15**) at low temperatures. The peroxydithiocarboxylate **15** undergoes a rare type of oxygen-sulfur exchange at higher temperatures to give the α-oxodisulfide **20** which isomerizes to the [3-oxo(2-thianyl]disulfide **19** finally.

ACKNOWLEDGMENT

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EXPERIMENTAL

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on Bruker AM400 (400 and 100.6 MHz, respectively), AC300P (300 MHz for ^{1}H), or AC200 (200 and 50 MHz, respectively) spectrometers using $CDCl_3$ as the solvent. IR spectra were taken on a Hitachi 270-50 spectrometer. UV-Vis spectra were measured using a JASCO V-560 spectrophotometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analysis was performed by the Chemical Analysis Center of Saitama University. Throughout this work, the organic layer of the reaction mixture was dried over anhydrous magnesium sulfate. Column chromatography was performed with silica gel and the eluent is shown in parentheses.

2,2,4,4-Tetramethyl-5-oxo-5-phenylvaleric Acid (7): To a solution of 2,2,4,4-tetramethylglutaric acid (**6**)[5] (3.22 g, 17.1 mmol) in THF (3 mL) was added benzene (250 mL) and then PhLi in ether (1.04 M, 49.6 ml, 51.3 mmol) slowly with ice-water cooling. After having been heated under reflux for 14 h, the mixture was diluted with conc. HCl (50 mL) and extracted with benzene twice. The combined extracts were washed with water, dried, and evaporated to dryness. The residue was recrystallized from hexane to give **7** as colorless crystals (3.54 g, 83%): m.p. 122—123 °C. ^{1}H NMR (200 MHz) δ 1.14 (s, 6H), 1.32 (s, 6H), 2.34 (s, 2H), 7.33—7.66 (m, 5H); ^{13}C NMR (50 MHz) δ 26.6, 27.0, 41.7, 47.5, 48.9, 127.98, 128.03, 130.7, 139.0, 185.2, 209.3; IR (KBr) 3300—2300 (CO_2H), 1698 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.11. Found: C, 72.48; H, 8.23.

2,2,4,4,-Tetramethyl-1-phenylpentane-1,5-diol (8): A solution of **7** (3.54 g, 14.2 mmol) in ether (120 mL) was added to a suspension of $LiAlH_4$ (1.62 g, 42.7 mmol) in ether (20 mL) over a period of 1.3 h at room temperature. The mixture was stirred for 3.5 h and then diluted with aq. NH_4Cl. The mixture was filtered through a pad of Celite placed on a Büchner funnel and the filtrate was extracted with ether twice. The combined extracts were washed with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2-Et_2O 1:1) to give **8** as a colorless oil (3.30 g, 98%): b.p. 135.0—135.5 °C/2.5 mmHg (bulb-to-bulb distillation). ^{1}H NMR (400 MHz) δ 0.82 (s, 3H), 0.90 (s, 3H), 0.95 (s, 3H), 1.00 (s, 3H), 1.09 (d, J = 15.1 Hz, 1H), 1.86 (d, J = 15.1 Hz, 1H), 3.20 (d, J = 11.0 Hz, 1H), 3.48 (br s, 2H, OH×2), 3.57 (d, J = 11.0 Hz, 1H), 4.63 (s, 1H), 7.21—7.27 (m, 5H); ^{13}C NMR (100.6 MHz) δ 25.0 (CH_3), 25.6 (CH_3), 26.4 (CH_3), 29.7 (CH_3), 37.0 (C), 39.7 (C), 45.7 (CH_2), 72.1 (CH_2), 80.7 (CH), 127.2 (CH), 127.4 (CH), 128.0 (CH), 141.7 (C). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.19; H, 10.23.

2,2,4,4-Tetramethyl-5-oxo-5-phenylpentanal (9): To a solution of dimethyl sulfoxide (1.7 mL, 23.8 mmol) in CH_2Cl_2 (13 mL) cooled at –65 °C was added a solution of trifluoroacetic anhydride (2.5 mL, 17.8 mmol) in CH_2Cl_2 (7.5 mL) over a period of 20 min. To the mixture was added a solution of the diol **8** (1.40 g, 5.94 mmol) in CH_2Cl_2 (13 mL) over a period of 20 min and the mixture was stirred for 35 min at –65 °C. After having been warmed to room temperature and stirred for 40 min, the mixture was cooled on an ice-water bath and treated with triethylamine (5 mL) and then water. The mixture was extracted with ether twice. The combined extracts were washed with dil. HCl, aq. $NaCO_3$, and water in this order, dried, and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2-CCl_4 1:1) to give **9** as a pale yellow oil (1.25 g, 91%): additional chromatographic purification (at least twice with CH_2Cl_2) made it pure analytically: ^{1}H NMR (400 MHz) δ 1.00 (s, 6H), 1.30 (s, 6H), 2.23 (s, 2H), 7.37—7.46 (m, 3H), 7.61—7.64 (m, 2H), 9.48 (s, 1H); ^{13}C NMR (100.6 MHz) δ 23.0 (CH_3), 28.2 (CH_3), 46.2 (C), 47.3 (C), 47.7

(CH_2), 127.9 (CH), 128.1 (CH), 130.9 (CH), 138.8 (C), 206.1 (CH), 209.1 (C); IR (neat) 1728, 1676 cm^{-1}; MS *m/z* 232 (M^+). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.47; H, 8.76.

2,2,4,4-Tetramethyl-1-phenyl-6,7,8-trithiabicyclo[3.2.1]octane (2): A mixture of **9** (1.07 g, 4.62 mmol) and Lawesson's reagent[6] (3.74 g, 9.24 mmol) in xylene (50 mL) was heated under reflux for 49 h. The mixture was cooled to room temperature, washed with aq. $NaHCO_3$ and water, and dried, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CCl_4) to give a crude product of **2**. The crude material was recrystallized from hexane to give pure **2** as yellow needles (477 mg, 35%): m.p. 145.3—145.7 °C (hexane). ^1H NMR (300 MHz) δ 1.06 (s, 3H), 1.15 (dd, J = 14.6, 1.5 Hz, 1H), 1.14 (s, 3H), 1.16 (s, 3H), 1.41 (s, 3H), 1.89 (d, J = 14.7 Hz, 1H), 4.95 (d, J = 1.5 Hz, 1H), 7.28—7.32 (m, 3H), 7.46—7.51 (m, 2H); ^{13}C NMR (50 MHz) δ 26.5 (CH_3), 27.9 (CH_3), 29.7 (CH_3), 32.2 (CH_3), 39.3 (C), 43.8 (C), 48.2 (CH_2), 72.6 (CH), 90.0 (C), 127.3 (CH), 127.9 (CH), 129.7 (CH), 138.2 (C); MS *m/z* 296 (M^+). Anal. Calcd for $C_{15}H_{20}S_3$: C, 60.76; H, 6.80. Found: C, 60.96; H, 6.82.

2,2,4,4-Tetramethyl-1-phenyl-6,7,8-trithiabicyclo[3.2.1]octane 6-*exo*-Oxide (3): To a solution of **2** (540 mg, 1.82 mmol) in CH_2Cl_2 (15 mL) was added a solution of MCPBA (87%, 468 mg, 2.36 mmol) in CH_2Cl_2 (15 mL) at 0 °C. After having been stirred for 3 h, the mixture was diluted with aq. $NaHSO_3$. The organic layer was separated, washed with aq. $NaHCO_3$ and water, dried, and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2-Et_2O 96:4) to give **3** (432 mg, 76%): colorless needles, m.p. 162.0—166.0 °C (hexane). ^1H NMR (400 MHz) δ 0.89 (s, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 1.32 (dd, J = 14.8, 1.0 Hz, 1H), 1.44 (s, 3H), 1.59 (d, J = 15.0 Hz, 1H), 4.74 (d, J = 1.0 Hz, 1H), 7.30—7.34 (m, 3H), 7.43—7.47 (m, 2H); ^{13}C NMR (100.6 MHz) δ 26.1 (CH_3), 28.9 (CH_3), 30.2 (CH_3), 31.8 (CH_3), 35.1 (C), 41.6 (C), 49.8 (CH_2), 95.17 (C), 95.29 (CH), 127.5 (CH), 128.3 (CH), 129.9 (CH), 137.2 (C); IR (KBr) 1090 (S=O) cm^{-1}; MS *m/z* 312 (M^+). Anal. Calcd for $C_{15}H_{20}OS_3$: C, 57.65 ; H, 6.45. Found: C, 57.36 ; H, 6.40.

X-Ray Crystal Structure Determination of 3. M_w 312.50. 0.26 × 0.20 × 0.02 mm^3, monoclinic, space group $P2_1/n$, a = 30.26(1), b = 15.920(4), c = 6.475(2) Å, β = 95.84(3)°, V = 3100.0(2) $Å^3$, D_c = 1.339 g cm^{-3}, Z = 8, $\mu(Mo_{K\alpha})$ = 4.492 mm^{-1}. Mac Science MXC18KHF diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), $\theta/2\theta$ scans method in the range $3° < 2\theta < 48.5°$ ($0 < h < 35$, $-18 < k < 0$, $-7 < l < 7$), 5981 reflections measured, 4710 unique reflections. The structure was solved by direct methods and refined by a full-matrix least-squares method using 3079 reflections [$I \geq 2.5\sigma(I)$] for 348 parameters. The non-hydrogen atoms were refined anisotropically. The final R (R_w) = 0.075 (0.077) and GOF = 3.426; max/min residual electron density = 0.49/–0.48 e $Å^{-3}$.

General Procedure for Treatment of 1,2,4-Trithiolane Oxide (3) with LDA and then an Electrophile: D_2O: To a solution of **3** (63 mg, 0.20 mmol) in THF (10 mL) was added LDA (0.14 M solution in THF, 1.7 mL, 0.24 mmol) at –78 °C under argon. The color of the solution turned from colorless to deep purple immediately. The solution was stirred for 1 h at –78 °C and then D_2O (0.5 mL) was added. The color disappeared immediately. The mixture was warmed to room temperature and diluted with aq. NH_4Cl, and extracted with ether three times. The combined extracts were washed with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (Et_2O-hexane 1:1) to give the deuterated trithiolane oxide **3-d** (40 mg, 64%) and the dithiolactone **10** (13 mg, 23%). When D_2O was added at 0 °C, **3-d** and **10** were obtained in 55 and 19% yields, respectively.

3,3,5,5-Tetramethyl-2-phenyl-6-thioxothian-2-ol (**10**): yellow needles, m.p. 106.0—109.0 °C (hexane). ^{1}H NMR (400 MHz) δ 0.97 (s, 3H), 1.15 (s, 3H), 1.51 (s, 3H), 1.58 (s, 3H), 1.69 (d, J = 14.6 Hz, 1H), 2.68 (d, J = 14.6 Hz, 1H), 2.98 (s, 1H, OH), 7.31—7.40 (m, 3H), 7.57—7.62 (m, 2H); ^{13}C NMR (100.6 MHz) δ 25.2 (CH_3), 25.8 (CH_3), 35.3 (CH_3), 35.5 (CH_3), 40.4 (C), 49.0 (CH_2), 52.2 (C), 95.9 (C), 127.8 (CH), 128.0 (CH), 128.5 (CH), 139.6 (C), 252.2 (C); MS m/z 280 (M^+). Anal. Calcd for $C_{15}H_{20}OS_2$: C, 64.24; H, 7.19. Found: C, 64.34; H, 7.28.

MeI: the oxide **3** (209 mg, 0.67 mmol) was treated with LDA (0.80 mmol) and then with MeI (0.2 mL) to give 2,2,4,4-tetramethyl-1-methylthio-5-phenyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*-oxide (**12**) (40 mg, 90%): colorless crystals, m.p. 121.0—122.0 °C (hexane). ^{1}H NMR (200 MHz) δ 1.05 (s, 3H), 1.34 (s, 3H), 1.38 (s, 3H), 1.50 (s, 3H), 1.67 (d, J = 14.5 Hz, 1H), 2.24 (s, 3H), 2.87 (d, J = 14.4 Hz, 1H), 7.22—7.35 (m, 5H); ^{13}C NMR (50 MHz) δ 12.6 (CH_3), 28.6 (CH_3), 29.0 (CH_3), 29.3 (CH_3), 29.7 (CH_3), 38.6 (C), 40.2 (C), 49.6 (CH_2), 85.4 (C), 94.4 (C), 127.2 (CH), 127.8 (CH), 128.1 (CH), 139.4 (C); IR (KBr) 1096 (S=O) cm^{-1}; MS m/z 326 (M^+). Anal. Calcd for $C_{16}H_{22}OS_3$: C, 58.85; H, 6.79. Found: C, 58.94; H, 6.78.

X-Ray Crystal Structure Determination of 12. M_w 326.53. 0.30 × 0.24 × 0.10 mm^3, monoclinic, space group $P2_1/a$, a = 17.666(3), b = 11.310(2), c = 8.431(1) Å, β = 94.65(1)°, V = 1678.9(5) Å^3, D_c = 1.291 g cm^{-3}, Z = 4, $\mu(Mo_{K\alpha})$ = 39.154 mm^{-1}. Mac Science MXC3KHF diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation (λ = 1.54178 Å), $\theta/2\theta$ scans method in the range $3° < 2\theta < 140°$ ($0 < h < 21$, $0 < k < 13$, $-10 < l < 10$), 3571 reflections measured, 2366 unique reflections. The structure was solved by direct methods and refined by a full-matrix least-squares method using 2366 reflections [$I \geq 3\sigma(I)$] for 257 parameters. The non-hydrogen atoms were refined anisotropically. The final R (R_w) = 0.057 (0.056) and GOF = 2.168; max/min residual electron density = 0.68/–0.48 e Å^{-3}.

EtI: the oxide **3** (122 mg, 0.39 mmol) was treated with LDA (0.47 mmol) and then EtI (0.3 mL) to give 1-ethylthio-2,2,4,4-tetramethyl-5-phenyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*-oxide (**13**) (106 mg, 79%): colorless crystals, m.p. 92.0—92.1 °C (hexane). ^{1}H NMR (400 MHz) δ 1.04 (s, 3H), 1.25 (t, J = 7.5 Hz, 3H), 1.34 (s, 3H), 2.37 (s, 3H), 1.50 (s, 3H), 1.66 (t, J = 14.5 Hz, 1H), 2.75 (dq, J = 12.4, 7.5 Hz, 1H), 2.86 (d, J = 14.2 Hz, 1H), 2.88 (dq, J = 12.3, 7.3 Hz, 1H), 7.23—7.27 (m, 2H), 7.31—7.35 (m, 3H); ^{13}C NMR (100.6 MHz) δ 14.8 (CH_3), 24.0 (CH_2), 28.6 (CH_3), 29.0 (CH_3), 29.4 (CH_3), 29.8 (CH_3), 38.4 (C), 40.2(C), 49.5 (CH_2), 85.2 (C), 94.5(C), 127.2 (CH), 127.8 (CH), 128.1 (CH), 139.5 (C); IR (KBr) 1092 (S=O) cm^{-1}; MS m/z 340 (M^+). Anal. Calcd for $C_{17}H_{24}OS_3$: C, 59.95; H, 7.10. Found: C, 60.11; H, 7.16.

2-PrBr: the oxide **3** (126 mg, 0.40 mmol) was treated with LDA (0.48 mmol) and then 2-PrBr (0.5 mL) to give 3,3,5,5-tetramethyl-6-[(methylethyl)dithio]-6-phenylthian-2-one (**14**): colorless crystals, m.p. 101.8—102.0 °C (MeOH-CH_2Cl_2); ^{1}H NMR (400 MHz) δ 1.12 (s, 3H), 1.14 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 6.6 Hz, 3H), 1.29 (s, 3H), 1.36 (s, 3H), 1.37 (s, 3H), 1.65 (d, J = 15.1 Hz, 1H), 2.40 (d, J = 15.1 Hz, 1H), 3.21 (sept, J = 6.7 Hz, 1H), 7.27—7.32 (m, 1H), 7.33—7.38 (m, 2H), 7.74 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 21.9 (CH_3), 22.7 (CH_3), 26.93 (CH_3), 26.97 (CH_3), 30.0 (CH_3), 30.3 (CH_3), 40.8 (C), 41.6

(CH), 46.8 (C), 50.5 (CH_2), 84.1(C), 127.4 (CH), 127.7 (CH), 130.9 (CH), 138.7(C), 207.5 (C); IR (KBr) 1652 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{26}OS_3$: C, 60.97; H, 7.39. Found: C, 60.96; H, 7.40.

X-Ray Crystal Structure Determination of 14. M_w 354.58. 0.30 × 0.30 × 0.14 mm^3, triclinic, space group $P\bar{1}$, $a = 7.974(1)$, $b = 9.614(2)$, $c = 12.767(3)$ Å, $\alpha = 107.42(2)$, $\beta = 95.84(3)$, $\gamma = 96.15(2)°$, $V = 925.1(3)$ Å^3, $D_c = 1.273$ g cm^{-3}, $Z = 2$, $\mu(Cu_{K\alpha}) = 36.532$ mm^{-1}. Mac Science MXC3KHF diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $\theta/2\theta$ scans method in the range $3° < 2\theta < 140°$ ($0 < h < 9$, $-11 < k < 11$, $-15 < l < 15$), 3898 reflections measured, 3477 unique reflections. The structure was solved by direct methods and refined by a full-matrix least-squares method using 3373 reflections [$I \geq 2\sigma(I)$] for 300 parameters. The non-hydrogen atoms were refined anisotropically. The final R (R_w) = 0.0465 (0.0578) and GOF = 2.550; max/min residual electron density = 0.62/–0.72 e Å^{-3}.

H_2O at Room Temperature after Stirring for 38 h: the oxide **3** (62 mg, 0.20 mmol) was treated with LDA (0.24 mmol) at –78 °C. The purple-colored mixture was warmed to room temperature, stirred for 38 h at room temperature, and diluted with water. Column chromatography (CH_2Cl_2-hexane 1:1), followed by further purification with HPLC [INERTSIL PREP-SIL (GL Science Inc), CH_2Cl_2-hexane 1:1], gave the trithiolane **2** (7.2 mg, 12%), the thiol **18** (6.9 mg, 12%), *meso*-**17** (6.2 mg, 12%), and *dl*-**17** (8.3 mg, 14%). The compound *dl*-**17** gave two peaks on an HPLC analysis using a chiral column [CHIRALPAK AD (Daicel Chemical Industries, Ltd.)].

3,3,5,5-Tetramethyl-6-phenyl-6-sulfanylthian-2-one (**18**): colorless crystals, m.p. 77.0—77.6 °C. ^1H NMR (400 MHz) δ 1.09 (s, 3H), 1.31 (s, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.71 (d, J = 15.2 Hz, 1H), 1.91 (d, J = 15.2 Hz, 1H), 2.80 (s, 1H, SH, disappeared by shaking with CD_3OD), 7.26—7.35 (m, 3H), 7.75—7.77 (m, 2H); ^{13}C NMR (100.6 MHz) δ 26.0, 26.7, 30.0, 30.1, 40.0, 47.0, 49.0, 72.6, 127.3, 127.8, 129.7, 141.0, 207.7; IR (KBr) 2576 (S-H), 1648 (C=O) cm^{-1}; MS m/z 280 (M^+). HRMS calcd for $C_{15}H_{20}OS_2$: M, 280.0956. Found: m/z 280.0983.

meso-3,3,5,5-Tetramethyl-6-phenyl-6-[{4,4,6,6-tetramethyl-3-oxo-1-phenyl(2-thianyl)}trisulfanyl]thian-2-one (*meso*-**17**): colorless crystals, m.p. 199.0—200.0 °C. ^1H NMR (400 MHz) δ 1.08 (s, 3H), 1.21 (s, 3H), 1.34 (s, 6H), 1.64 (d, J = 15.2 Hz, 1H), 2.24 (d, J = 15.1 Hz, 1H), 7.28—7.37 (m, 3H), 7.67 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 26.8 (CH_3×2), 29.9 (CH_3), 30.3 (CH_3), 40.8 (C), 46.7 (C), 50.4 (CH_2), 84.4 (C), 127.4 (CH), 127.9 (CH), 131.5 (CH), 137.4 (C), 206.8 (C); IR (KBr) 1668 (C=O) cm^{-1}. Anal. Calcd for $C_{30}H_{38}O_2S_5$: C, 60.97; H, 6.48. Found: C, 60.45; H, 6.47.

dl-3,3,5,5-Tetramethyl-6-phenyl-6-[{4,4,6,6-tetramethyl-3-oxo-1-phenyl(2-thianyl)}trisulfanyl]thian-2-one (*meso*-**17**): colorless crystals, m.p. 190.0—191.0 °C. ^1H NMR (400 MHz) δ 1.06 (s, 3H), 1.17 (s, 3H), 1.35 (s, 3H), 1.36 (s, 3H), 1.65 (d, J = 15.2 Hz, 1H), 2.37 (d, J = 15.2 Hz, 1H), 7.24—7.32 (m, 3H), 7.61 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 26.78 (CH_3), 26.84 (CH_3), 30.0 (CH_3), 30.4 (CH_3), 40.7 (C), 46.9 (C), 50.6 (CH_2), 84.9 (C), 127.6 (CH), 127.7 (CH), 131.1 (CH), 138.1 (C), 206.8 (C); IR (KBr) 1658 (C=O) cm^{-1}. Anal. Calcd for $C_{30}H_{38}O_2S_5$: C, 60.97; H, 6.48. Found: C, 60.88; H, 6.49.

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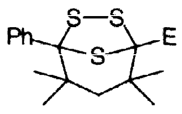
8. Our initial plan was to prepare unsymmetrically substituted 1,2,4-trithiolanes **25**, which are precursors for the corresponding 6,7-dithiabicyclo[3.1.1]heptanes **4**, by the reaction of the bridgehead carbanion generated from **2** with electrophiles (E^+). Meanwhile, desulfurization of **2** with $P(NMe_2)_3$ gave the 6,7-dithiabicyclo[3.1.1]heptane **26** whose reactivity is a subject of an alternative project.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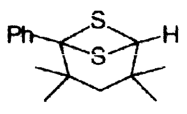
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