Convenient synthesis of 1,3-dithiolane-2-thiones: cyclic trithiocarbonates as conformational locks[1]

Irina A. Dotsenko, Qinliang Zhao, Andreas H. Franz, Patrick Batoon, Nataliya M. Samoshina, and Vyacheslav V. Samoshin *

Department of Chemistry, College of the Pacific, University of the Pacific, Stockton, CA 95 211, USA
E-mail: vsamoshin@pacific.edu

DOI: http://dx.doi.org/10.3998/ark.5550190.p008.671

Abstract

A series of novel 1,3-dithiolane-2-thiones, or cyclic trithiocarbonates, has been prepared by a new simple procedure: a treatment of the corresponding epoxides with the commercially available potassium ethyl xanthogenate, KSC(S)OEt. The stereochemistry of the products was determined by ^{1}H NMR and in some cases by single-crystal X-ray data. Cyclohexane-based 1,3-dithiolane-2-thiones revealed a *trans*-fusion of the carbo- and hetero-cycles. The products obtained from the mono-substituted cyclohexene oxides demonstrated an *axial* position of the substituents. Thus the epoxide transformation into trithiocarbonate can be used as a method for locking cyclic compounds in unstable conformations.

Keywords: Conformational control, conformational lock, molecular switches, epoxides, 1,3-dithiolane-2-thiones, cyclic trithiocarbonates

Introduction

1,3-Dithiolane-2-thiones, or cyclic trithiocarbonates, attract much attention due to their variety of useful properties.[2,3] They are used as building blocks in the synthesis of new antibiotics, and as versatile ligands and polymers.[2-6] Trithiocarbonates are also of commercial importance in a wide variety of applications, for example as rubber stabilizers, ore flotation agents, and additives for lubricants and fuels.[7-9] Besides, they exhibit a remarkably high liver disorder suppressing effect, and hypocholesteremic, hypotriglyceridemic, radioprotective, and insecticidal activity.[9-12]

One of the most efficient methods for the synthesis of cyclic trithiocarbonates reported in literature is based on the reaction of epoxides with carbon disulfide (CS_2) in presence of a base and/or a catalyst.[2,5-8,10-14] However, these procedures often suffer from low yields and poor selectivity. Depending on the catalyst and reaction conditions, a variety of products can be

formed. In addition, use of the volatile, inflammable and toxic carbon disulfide is definitely a serious disadvantage.

Herein we report a new procedure for the synthesis of 1,3-dithiolane-2-thiones: a treatment of epoxides with commercially available potassium ethyl xanthogenate, KSC(S)OEt (for a preliminary communication see ref. 1) The procedure is simple, safe, inexpensive, and relatively fast. It does not require high pressure and catalyst, and often gives 1,3-dithiolane-2-thione as the only product in good to moderate yields. The mechanism and stereochemistry of the reaction are discussed.

When cyclohexene oxide was used as a starting material in catalytic reaction with CS_2, the newly formed five-membered cyclic trithiocarbonate was *trans*-fused to the cyclohexane ring.[2] Our modified procedure has the same stereochemical outcome. When it is applied to epoxides of substituted cyclic alkenes, the substituent(s) on the ring could be forced to adopt a sterically unfavourable axial position. Thus, the five-membered trithiocarbonate ring can serve as a lock for unfavourable conformations. We suggest this approach in addition to a set of other conformational locks (acetals, ortho-esters, urethanes, etc.) that have previously been used in various stereoselective syntheses.[15,16]

Results and Discussion

Synthesis of trithiocarbonates

In the course of our studies on the cleavage of epoxides with sulfur nucleophiles,[17,18] we found that treatment with potassium xanthogenate transformed epoxides into 1,3-dithiolane-2-thiones (cyclic trithiocarbonates) in good to moderate yields.[1] The procedures described previously for such a transformation used carbon disulfide in presence of a base and/or catalyst, and included an *in situ* formation of a xanthogenate or a similar intermediate, and then its reaction with an epoxide [2,5-8,10-14] (for a detailed critical consideration of the literature data see ref. 2). Thus, our modified procedure eliminates the most inconvenient step, which used the toxic, volatile and inflammable CS_2, by employing a safe commercially available reagent.

We carried out the reaction of cyclohexene oxide with KSC(S)OEt (Scheme 1) under various conditions as summarized in Table 1.

1a **2a**

Scheme 1. Synthesis of *trans*-hexahydro-1,3-benzodithiole-2-thione (**2a**)

Table 1. Reaction of cyclohexene oxide (**1a**) with potassium ethyl xanthogenate (Scheme 1)

Entry	KSC(S)OEt:epoxide mole ratio	Solvent	Temp (^{o}C)	Time (h)	Conversion (%)	Yield of **2a** (%)
1	1 : 1	EtOH	35	12	100	37
2	1 : 1	MeOH	35	12	100	39
3	*2 : 1*	*MeOH*	*35*	*3.5*	*100*	*73*
4	2 : 1	MeOH	35	12	100	51
5	2 : 1	MeOH	20	3.5	77	42
6	3 : 1	MeOH	35	3.5	100	54
7	5 : 1	MeOH	35	3.5	100	47

The isolated yield of the product was dependent on the molar ratio KSC(S)OEt to epoxide. The best result was achieved when the ratio was 2:1 (entry 3). Upon increase of the ratio to 3:1 and 5:1 the yield decreased, but no starting epoxide was recovered (entries 6, 7). Most likely the yield declined due to side reactions of epoxide such as an intermediate/product polymerization. Upon increase of the reaction time the yield decreased (experiment 4). Therefore it was important to monitor the reaction by TLC and to stop it immediately after the complete conversion of epoxide. A reaction temperature of 35-40 ^{o}C was found to be optimal, because a lowering of temperature reduced the yield of the product significantly (experiment 5).

Because the conditions of experiment 3 in Table 1 gave the best yield, they were used as standard conditions for the synthesis of a series of trithiocarbonates (Table 2). The starting epoxides were prepared by reaction of corresponding commercially available alkenes with *m*CPBA.

In some experiments, the reaction yielded intermediate products – thiiranes (see discussion of the mechanism below) or the products of polymerization.

We also explored the possibility of aromatization of the S-substituted cyclohexane rings by treatment of the compounds **2** with Br_2, NBS, or DDQ.[22-25] However, we obtained the products of oxidation (sulfur replacement) **3** (Scheme 2). Thus, these reagents may be added to the toolbox of other oxidizers used previously for the transformation of 1,3-dithiolane-2-thiones into 1,3-dithiolan-2-ones.[2,3,26-29]

Table 2. Reaction of various epoxides with potassium ethyl xanthogenate.[a]

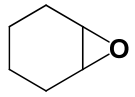
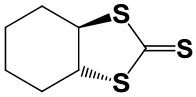
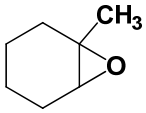
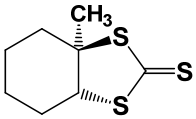
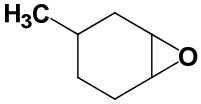
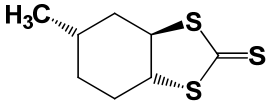
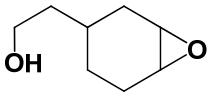
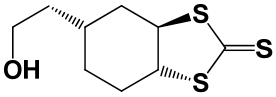
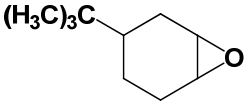
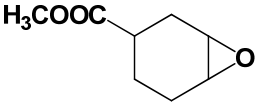
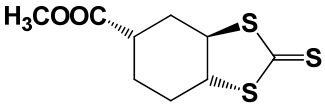
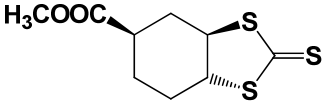
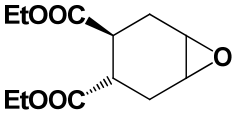
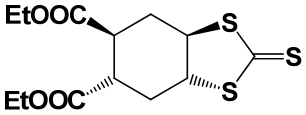
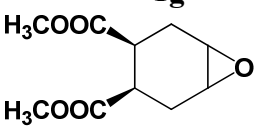
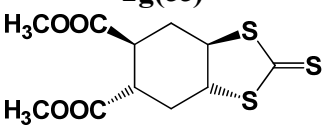
Entry	Epoxide	Isolated Product	Time (h)	Yield (%)
1	 **1a**	 **2a** [2]	3.5	73
2	 **1b**	 **2b**	24	37
3	 **1c** [b]	 **2c**	0.5	37
4	 **1d** [c]	 **2d**	0.5	59
5	 **1e** [d]	polymer [e]	20	0
6	 **1f** [f]	 **2f(*a*)** +  **2f(*e*)**	0.5	57 [g]
7	 **1g**	 **2g(*ee*)**	12	7 [h]
8	 **1h** [i]	 **2h(*ee*)**	3	55 [j]

Table 2. Continued

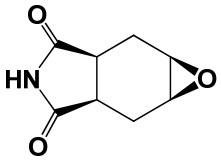
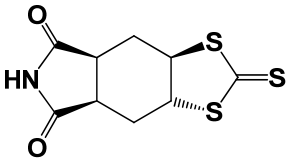
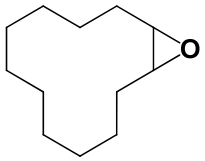
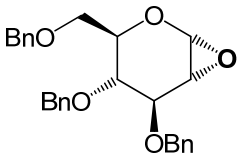
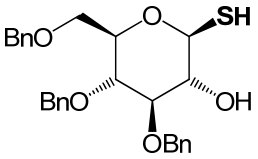
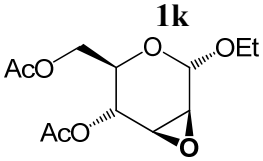
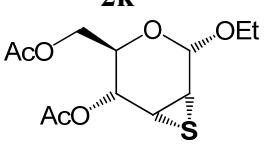
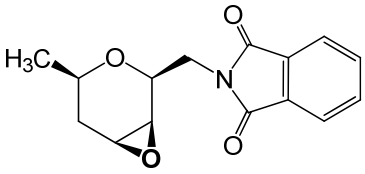
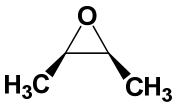
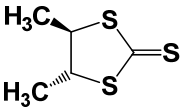
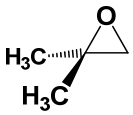
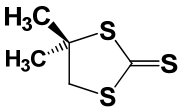
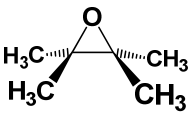
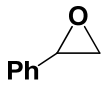
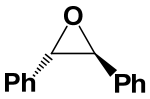
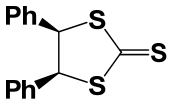
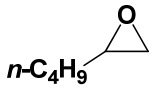
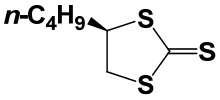
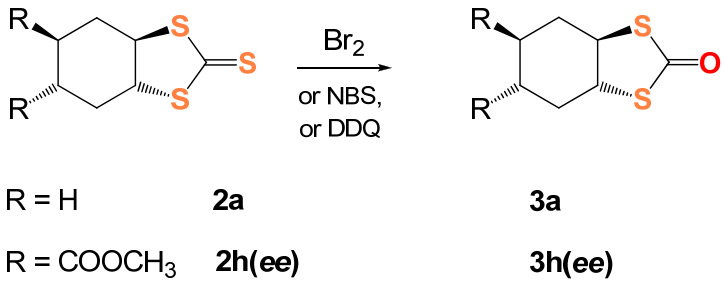
Entry	Epoxide	Isolated Product	Time (h)	Yield (%)
9	 **1i**	 **2i**	72	56 [k]
10	 **1j** [l]	**1j** recovered (97%)	60	0
11	 **1k**	 **2k** [19]	2	37
12	 **1l**	 **2l**	24	32 [m]
13	 **1m**	polymer [e]	24	0
14	 **1n**	 **2n** [13,20]	1	43
15	 **1o**	 **2o** [21]	1	30
16	 **1p**	polymer [e]	48	0

Table 2. Continued

Entry	Epoxide	Isolated Product	Time (h)	Yield (%)
17	 **1q**	polymer [e]	5	0
18	 **1r**	 **2r** [13]	72	25 [k]
19	 **1s**	 **2s**	0.5	52

[a] Epoxide-reagent ratio 1 : 2; solvent – methanol; 35-45 °C; yields are not optimized; the reactions were terminated after complete consumption of epoxide (by TLC); [b] *anti*:*syn* = 1.3:1; [c] *anti*:*syn* = 1:1; [d] *anti*:*syn* = 1:2; [e] Only polymeric products; no starting epoxide recovered; [f] Pure *anti* or *syn*-isomer, or the mixture *anti*:*syn* = 1:1; [g] After 0.5 h the ratio of products **2f(*a*)**:**2f(*e*)** was (2.2-3.3):1; after 2-3 h the ratio was 1:1.3; [h] In EtOH; the major product was a polymer; [i] Pure *anti* or *syn*-isomer (complete conversion in 2 h and 3 h, respectively); [j] Two diastereomers, **2h(*ee*)** and **2h(*ea*)**, in the ratio 10 : 1; [k]Reaction time 72 h; after 15 h thiirane was isolated as a major product; [l] A mixture of *cis* and *trans*-isomers; [m] After re-acetylation.



R = H **2a** **3a**

R = $COOCH_3$ **2h(*ee*)** **3h(*ee*)**

Scheme 2. Oxidation of trithiocarbonates **2.**

Stereochemistry of products

The structures of all compounds were determined by ^{1}H NMR, ^{13}C NMR and HRMS analysis. The vicinal coupling constants $^3J_{HH}$ between protons attached to the cyclohexane moiety are strongly conformation-dependent, which allows an assignment of the predominant conformation and an estimation of the position of conformational equilibrium.[30] For the products with non-symmetrical molecules, most coupling constants in ^{1}H NMR could be measured directly from the corresponding multiplets assuming the first order of spectra (for methodology see ref. 31). The

large vicinal coupling constants between the cyclohexane protons H3a and H7a geminal to the sulphur atoms (12.1-12.4 Hz) proved unambiguously the *trans*-diaxial position of these protons and, correspondingly, the *trans*-diequatorial position of the sulphur atoms in the cyclohexane derivatives **2c** – **2i** (Figure 1). This means a *trans*-fusion of two rings, which has also been shown recently by X-ray analysis for the compound **2a**.[2] The configuration of remote substituents was also established from the couplings of their geminal protons. Thus, the couplings of H5 in the product **2f(*e*)** (triplet of triplets with $^3J_{HH}$ of 12.3 Hz and 3.8 Hz) indicated an equatorial position of the methoxycarbonyl group, while all the couplings of H5 in the stereoisomer **2f(*a*)** were small ($^3J_{HH}$ ≈ 2.5 - 5.0 Hz) indicating an axial position of the substituent (Figure 1). The axial position of methyl group in the compound **2c** resulted in small couplings of H5, and was also confirmed by NOE with H3a (Figure 1).

The coupling constants in the half-chairs of epoxides and thiiranes are not characteristic, therefore we used ROESY and STEP-NOESY techniques [32,33] to establish or confirm the configuration of these compounds (Figure 2; for the details see Supplementary data). The STEP-NOESY technique makes use of optimized 1D-pfg-TOCSY magnetization transfer from a well-separated signal in the spectrum to a neighbouring proton in a crowded spectral region for a subsequent 1D-pfg-NOESY irradiation. When literature data were available, our results confirmed the assignments made previously (for instance, for epoxide **1l**). However, in case of a novel compound **1i** (the major *syn*-product of epoxidation) this approach was inefficient because of conformational peculiarities, and we had to transform **1i** into methoxycyclohexanol **4** in order to assign its configuration unambiguously (Scheme 3; see Supplementary data).

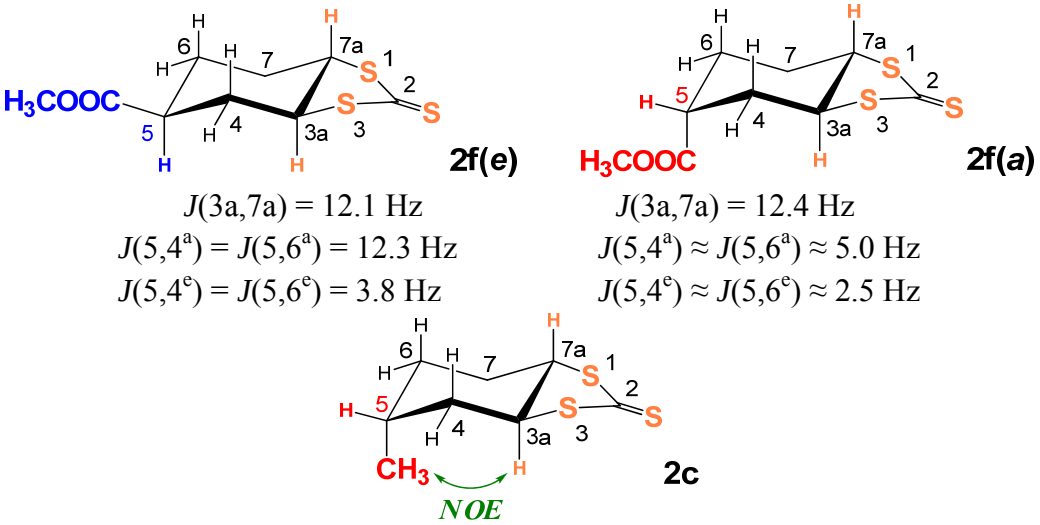


Figure 1. Examples of stereochemical assignment for cyclohexano-trithiocarbonates by ^{1}H NMR.

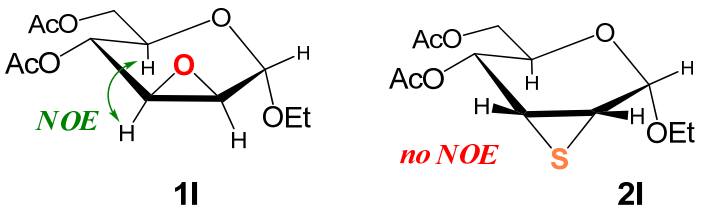
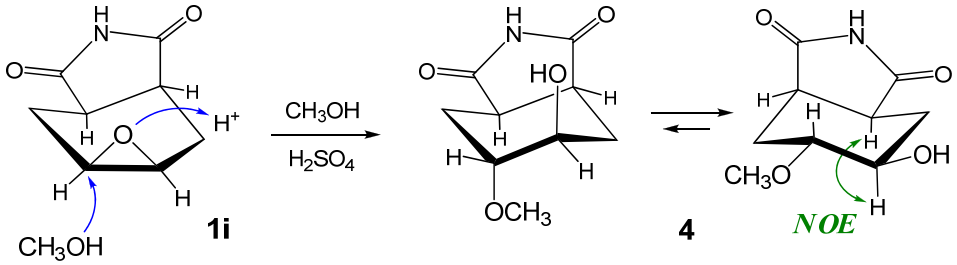


Figure 2. Examples of stereochemical assignment for epoxides and thiiranes by 1D-pfg-ROESY and 1D-pfg-STEP-NOESY experiments.



Scheme 3. Acid-catalyzed methanolic cleavage of epoxide **1i.**

The single-crystal X-ray analysis has been performed for the products **2f(*a*)**, **2f(*e*)**, **2h(*ee*)**, **2i**, and **3h** (Figures 3-7). Similar to the published research on compound **2a**,[2] the analysis was complicated by the extremely small size and fiber-like shape of the crystals, necessitating the use of synchrotron radiation.

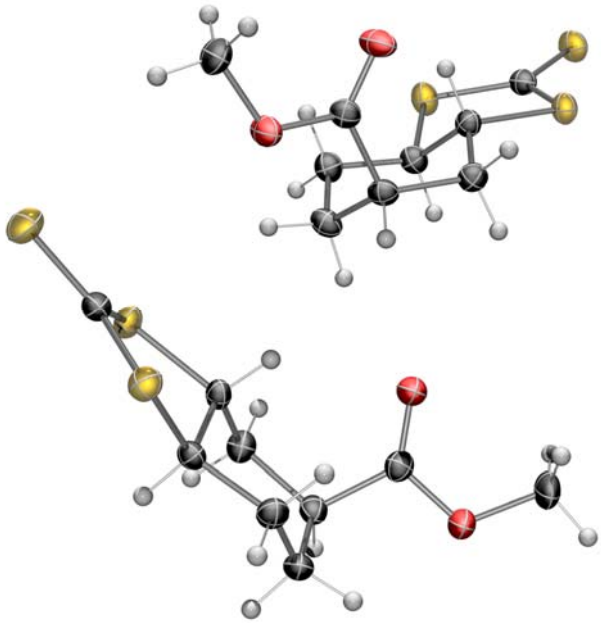


Figure 3. X-ray crystal structure of compound **2f(*a*)** with thermal ellipsoids set at the 50% probability level for non-H atoms (crystals were grown from MeOH). There are two molecules per asymmetric unit.

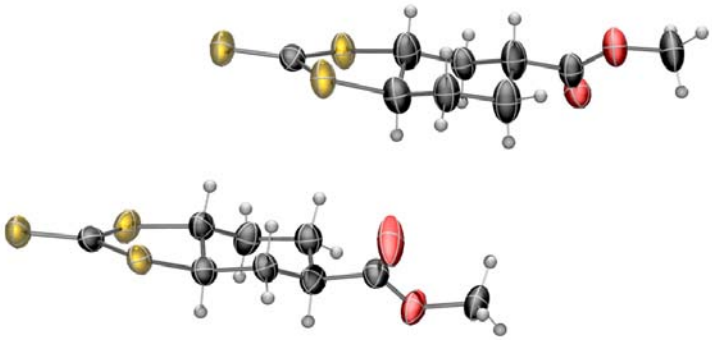


Figure 4. X-ray crystal structure of compound **2f(*e*)** with thermal ellipsoids set at the 50% probability level for non-H atoms (crystals were grown from MeOH). There are two molecules per asymmetric unit.

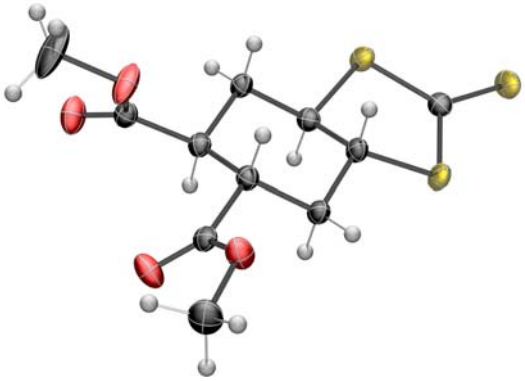


Figure 5. X-ray crystal structure of compound **2h(*ee*)** with thermal ellipsoids set at the 50% probability level for non-H atoms (crystals were grown from MeOH).

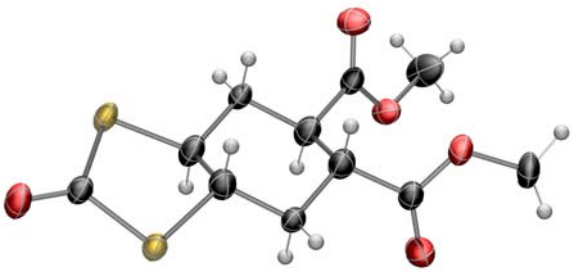


Figure 6. X-ray crystal structure of compound **3h**. Thermal ellipsoids set at the 50% probability level for non-H atoms (crystals were grown from MeOH).

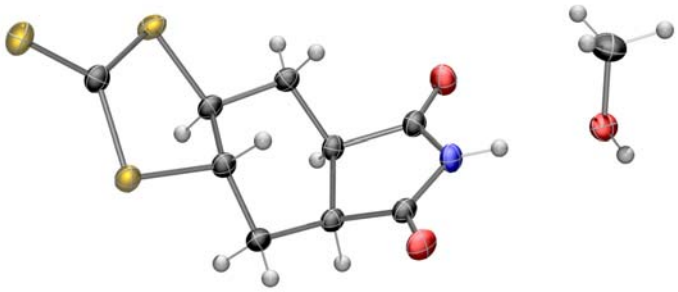


Figure 7. X-ray crystal structure of compound **2i**. Thermal ellipsoids set at the 50% probability level for non-H atoms (crystals were grown from MeOH).

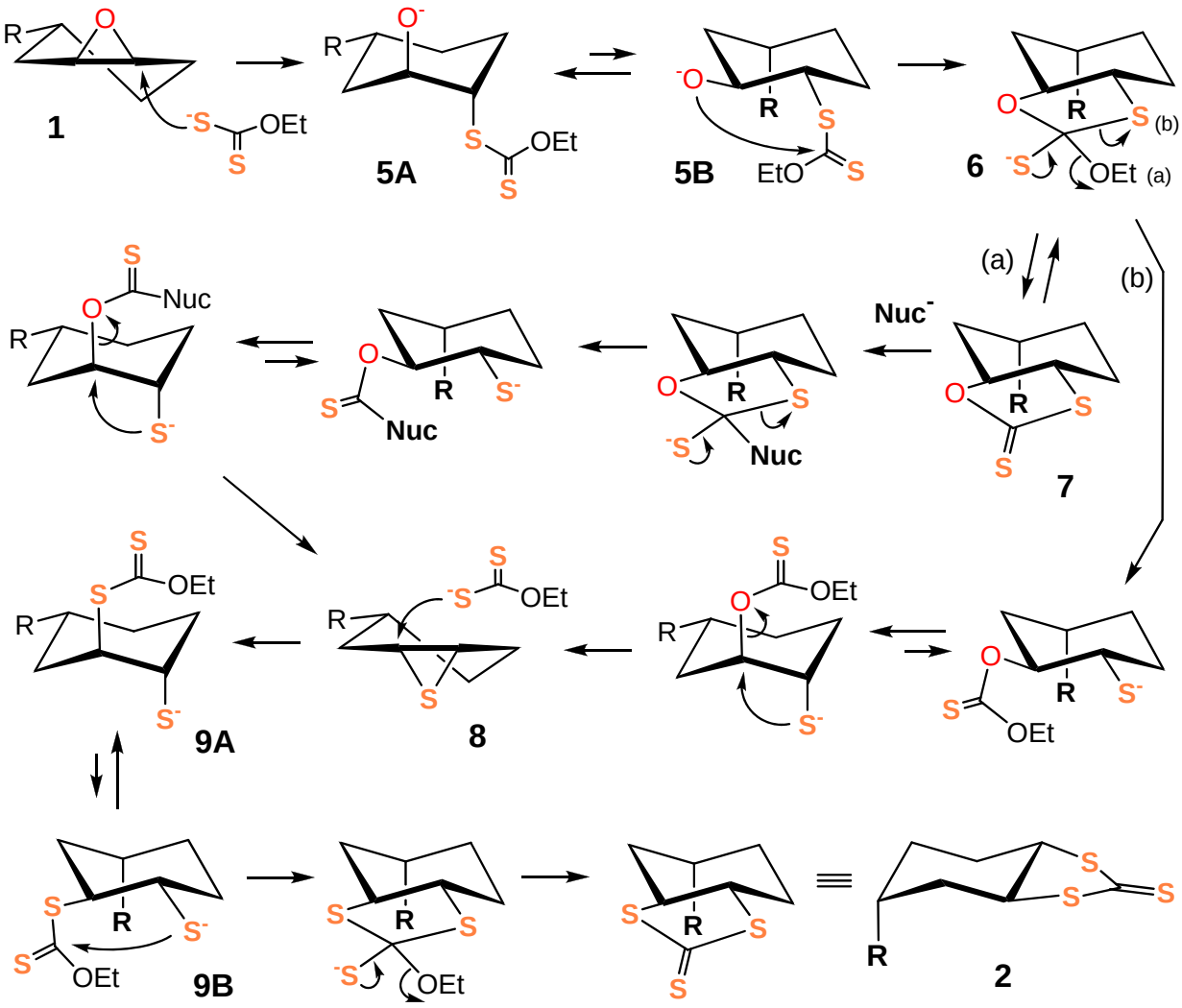
The X-ray data clearly demonstrate a chair conformation of the cyclohexane rings, a *trans* ring fusion, a nearly planar heterocycle, and in case of **2f(*a*)** an axial position of the substituent. Noteworthy, the molecules of racemic compound **2f(*a*)** are paired in asymmetric unit, and the components of the pair have the same configuration (Figure 3). The same kind of stereoselection occurs in case of compound **2f(*e*)** (Figure 4).

Mechanism and stereochemistry of the reaction

As described above, the ^{1}H NMR and X-ray data showed that all the obtained cyclohexano-trithiocarbonates were *trans*-isomers with equatorial position of both sulphur atoms. This requires an inversion of configuration at one of the epoxide carbons during the reaction. The configuration at the second epoxide carbon seems to remain the same as in the substrate, although the original oxygen is replaced by sulphur. This implies a double inversion at the second carbon. A plausible mechanism addressing these major peculiarities is presented in Scheme 4 for the case of mono-substituted cyclohexene epoxides. Similar, although less complete mechanistic considerations were published earlier for the formation of trithiocarbonates from the epoxides of non-cyclic alkenes using carbon disulfide in presence of a base.[2,13,14]

The key steps include the cleavage of epoxide **1** by xanthogenate anion, then cyclization of the intermediate **5** into the *trans*-fused bicyclic structure **6**, which requires a transfer of the substituent R into a sterically strained axial position (Scheme 4). Then **6** may eliminate ethoxide ion and give 1,3-oxathiolane-2-thione **7** (route *a*). We did not isolate these compounds, but the formation of some 1,3-oxathiolane-2-thiones in certain conditions was observed previously.[2,5,6,14] It is also known that these compounds react with excess carbon disulfide to give trithiocarbonates.[2,6] Apparently, in our case the subsequent addition of a nucleophile (Nuc = $EtOCS_2^-$, EtO^-, or MeO^- from the solvent) to probable intermediates **7** occurred quickly and caused cleavage of the heterocycle. An alternative detour (*b*) seems to be also possible.[13] Both ways include an intramolecular substitution leading to thiirane **8**, where the group R occupies again a more relaxed and stable equatorial position. We isolated thiirane **2l** as a major product in reaction of epoxide **1l** (entry 12 in Table 2). The epoxides **1i** and **1r** (entries 9 and 18 in Table 2)

produced mostly the corresponding thiiranes after 15-16 h, but finally gave trithiocarbonates when the time was extended to 72 h. Other researchers also reported isolation of thiiranes in certain conditions,[2,6,34] and the reaction of some thiiranes with carbon disulfide and base towards trithiocarbonates was described previously.[21,34,35] Noticeably, the configuration of the three-membered cycle in **8** is opposite to the configuration of the starting epoxide **1**.



Scheme 4. Plausible mechanism for the formation of cyclic trithiocarbonates.

The thiiranes **8** (Scheme 4) are in turn subjected to nucleophilic cleavage by xanthogenate anion, followed by yet another cyclization, which forces the group R again into the sterically strained axial position. Despite this strain, the resulting 1,3-dithiolane-2-thiones **2** must be much less susceptible to addition of nucleophiles than their analogues **7**, and they have been isolated in most cases as the major products of reaction. Thus, the monosubstituted cyclohexene oxides **1c**, **1d** and **1f** (entries 3, 4 and 6 in Table 2) yielded trithiocarbonates **2c**, **2d** and **2f(*a*)** respectively, with an axial substituent R (Figures 1, 3). According to the suggested mechanism, the

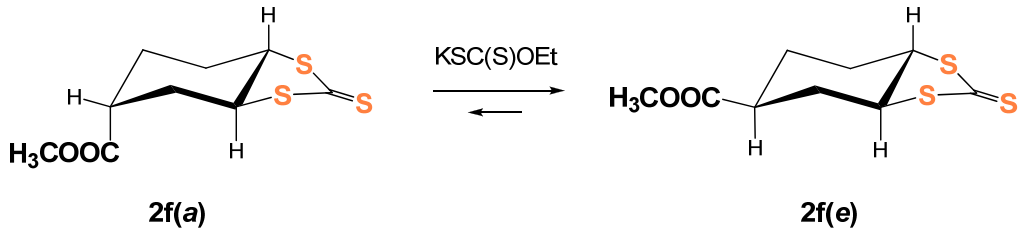
configuration of **2** does not depend on the configuration of the starting epoxide **1** (*syn*- or *anti*-position of R and O). Indeed, when a mixture of diastereomeric epoxides was used (entries 3, 4 in Table 2), only one product was isolated.

The transfer of substituent R into a sterically strained axial position is a barrier that occurs twice on the way of reaction in the case of epoxycyclohexanes and similar epoxides. It has to be overcome in conformational interconversions **5A** ⟶ **5B** and **9A** ⟶ **9B**. The second transition is more difficult, because the form **9B** must be additionally destabilized by a substantial *gauche*-repulsion between two equatorial atoms of sulfur as it was found in *trans*-1-RS-2-R′S-cyclohexanes.[36,37] This can explain why the reaction proceeds only up to thiirane in the case of sterically loaded epoxide **1l** (entry 12 in Table 2), or can be stopped at the thiirane step in the case of epoxides **1i** and **1r** (entries 9 and 18). Similarly, steric strain in reaction intermediates prevented transformation of steroid thiiranes into trithiocarbonates (with one questionable exception).[35] No trithiocarbonate or even thiirane was isolated in the reactions of 4-*t*-butylcylohexene oxide **1e** (mixture of stereoisomers; entry 5) and *cis*-2,6-disubstituted epoxytetrahydropyran **1m** (entry 13), which produced only polymeric side products. Obviously, it is very difficult to force the bulky *t*-butyl group or the *cis*-oriented substituents into axial/*syn*-diaxial positions already at the step of intermediate **5B**.

The studied reaction is sensitive to steric hindrance in general. Thus, no trithiocarbonate was obtained from the epoxycyclododecane **1j** (entry 10 in Table 2). The simple dimethyl oxiranes **1n** and **1o** (entries 14 and 15) produced the corresponding trithiocarbonates in moderate yields, while the yield from the bulkier diphenyl oxirane **1r** (entry 18) was much lower, and the tetramethyl oxirane **1p** (entry 16) gave no product at all. As described earlier, the *gem*-dimethyloxirane **1o** and trimethyloxirane gave no product in catalytic reaction with carbon disulfide.[2] However, the absence of steric hindrance may be also harmful because of fast side reactions: thus, styrene oxide **1q** (entry 17) produced only a polymer. Evidently, this polymerization is related to the benzylic moiety, because the structurally similar epoxide **1s** gave the expected product **2s** (entry 19).

Monosubstituted cyclohexene oxide **1f** with R = COOMe (entry 6, Table 2) did not produce a single product **2f(*a*)**, but yielded a mixture of diastereomers **2f(*a*)** and **2f(*e*)** with axial and equatorial positions of the ester group, respectively (Figures 1, 3, 4). The ratio of diastereomers was highly dependent on the time of reaction. After 0.5 h the ratio of products **2f(*a*)**:**2f(*e*)** in their mixture purified by column chromatography was (2.2-3.3):1 by ^{1}H NMR, while after 2-3 h the ratio almost inverted to 1:1.3. The longer time of reaction also decreased the overall yield from 57% (0.5 h) to 43-48% (2 h). This reaction was performed with pure *syn*- or *anti*-isomer of epoxide **1f**, or with their 1:1 mixture, and always produced approximately the same proportion of products regardless of the starting stereochemistry. Evidently, due to relative acidity of α-proton H5, a base-catalyzed epimerization of the expected ester **2f(*a*)** have occurred in the course of reaction, and the more stable diastereomer **2f(*e*)** was formed. This hypothesis was confirmed by conversion of pure **2f(*a*)** into a mixture of diastereomers **2f(*a*)** and **2f(*e*)** (1:1.3) after 72 h at 40 °C with one equivalent of KSC(S)OEt (Scheme 5). Assuming this is a ratio at equilibrium,

the equatorial form **2f(*e*)** is 0.7 kJ/mol more stable than the axial **2f(*a*)** in the conditions of reaction.



2f(*a*) **2f(*e*)**

Scheme 5. Base-induced epimerization of the product **2f(*a*)** with axial ester group.

We noticed that the epimerization of the final product **2f(*a*)** with KSC(S)OEt (Scheme 5) required a longer time than that observed in the reaction of starting epoxides under the same conditions (that is in presence of $EtOCS_2^-$, EtO^-, or MeO^- from the solvent). This may indicate that a faster α-deprotonation occurs intramolecularly within one or several intermediates of the reaction, when α-proton happens to be in a vicinity of an alcoholate or thiolate anion (Scheme 4).

The results obtained with the cyclohexene oxides **1g** and **1h** bearing two ester-groups also confirmed the proposed epimerization. Thus the *cis*-disubstituted epoxide **1h** (entry 8) yielded two diastereomers, **2h(*ee*)** and **2h(*ea*)**, in the ratio 10 : 1 (by ^{1}H NMR). The formation of the all-equatorial **2h(*ee*)** (Figure 5) can be explained by epimerization of the initially formed diastereomer **2h(*ea*)** containing one axial ester group. In the case of *trans*-disubstituted epoxide **1g** (entry 7, Table 2), a polymer was mostly obtained, and only small amount of the product **2g(*ee*)** was isolated. The configuration of both groups COOEt in the latter compound was opposite to what should have been expected. This can be explained by the relative instability of the expected product with both ester groups in axial positions, and by the base-catalyzed epimerization of these substituents.

Trithiocarbonate ring as a conformational lock

Control of molecular conformation is a powerful way to modulate the physical, chemical and biological properties of compounds. It can be achieved by a shift of conformational equilibrium towards unusual (relatively unstable) forms *via* modification of substituents or construction of bridged structures.[15,16] The synthesis of cyclic trithiocarbonates from epoxides is, in fact, a construction of a bridge that affixes one of possible conformations. Moreover, the stereochemical course of the reaction (the inversion of configuration at one of the former epoxide carbons and the double inversion at the second carbon) forces the structure to perform a flip into a conformation alternative to an original one. It was shown previously that the similar procedure with CS_2 as a reagent transformed the epoxides of *cis*-alkenes into trithiocarbonates with *trans*-arrangement of substituents.[13] We observed the same result in reactions of epoxides **1n** and **1r** (entries 14 and 18 in Table 2). When our procedure was applied to epoxides of substituted cyclic alkenes, these substituent(s) were forced to adopt a sterically unfavourable axial position (see

above). Thus, the five-membered ring of trithiocarbonate can serve as a lock for unfavourable conformations. This lock is powerful enough to make a methyl group axial, which requires 7.3 kJ/mol,[38] but fails to do the same with *t*-butyl (~20 kJ/mol[38]). The lock can be subsequently removed or cleaved by reduction [4,13,26,27] or hydrolysis [27] of trithiocarbonates to dithiols. We suggest this approach as a potentially useful addition to a set of other conformational locks (acetals, ortho-esters, urethanes, etc.) that have been used in various syntheses previously.[15,16] In particular, the results of our study clearly point to a possible application of the trithiocarbonate lock for a stereoselective epimerization of ester substituents in basic conditions.

Conclusions

A simple and convenient procedure for the selective synthesis of 1,3-dithiolane-2-thiones (cyclic trithiocarbonates) from epoxides has been developed. The mechanism and stereochemistry of the reaction have been studied. The formation of cyclic trithiocarbonates can be used to lock unstable conformations.

Experimental Section

General. The chemicals used in this study were purchased from commercial sources (Sigma-Aldrich, TCI) and used without additional purification. All solvents were purified by conventional techniques prior to use. Column chromatography was performed on silica gel (40-75 μm, Sorbent Technologies) and aluminum oxide (activated basic, 58Å, Aldrich). The reactions were monitored by TLC on silica gel 2.5 × 7.5 cm plates, J. T. Baker (visualization by staining with $KMnO_4$–sulfuric acid), or alumina 8 × 2 cm plates, Analtech Inc. (visualization by staining with I_2).

^{1}H NMR and ^{13}C NMR spectra were acquired on JEOL ECA-600 NMR-spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C) with spinning at rt. ^{1}H-^{1}H-COSY and ^{1}H-^{13}C-HMQC techniques were used to assign the signals. 1D-pfg-ROESY and 1D-pfg-STEP-NOESY experiments [32,33] were carried out non-spinning at rt with selective Gauss-shaped 180º-pulses and with 10 s recovery times between pulses. After initial gradient shimming, the spinner was turned off and the shims were manually touched up for best field homogeneity. The optimal mixing time for TOCSY magnetization transfer to a specific neighboring proton was established with an arrayed experiment of 5-10 mixing times between 20-200 ms in 20 ms increments. The ROESY and STEP-NOESY experiments were run for 1024 scans and the raw data were zero-filled four times prior to Fourier transformation.

High resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF time-of-flight mass spectrometer (Peabody, MA) coupled with an Ionsense DART open-air ionization source (Saugus, MA). The instrument was tuned to a resolving power of 7,000 with reserpine directly

infused into the electrospray ionization source; this provides a stable ion current to tune the time-of-flight parameters. Samples were introduced into the DART sample gap with a glass melting point capillary by first dipping the closed end of the capillary into the sample then immediately placing it into the helium metastable beam. The helium gas temperature was set to 250 ^{o}C to aid in the desorption of the analyte from the capillary. The samples were held in the sample gap for 10-15 seconds to acquire several mass spectra to average for an accurate *m/z* assignment.

Crystallographic Data for compounds **2f(*a*)**, **2f(*e*)**, **2h(*ee*)**, **3h** and **2i** were collected on Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab using monochromatic radiation (λ = 0.7749 Å) at 150(2) K. Data reduction and cell refinement for all compounds were performed with SAINT.[39] We used SADABS to obtain the absorption-corrected data.[40] Crystallographic data are given in Table S1 (Supplementary data). Selected bond distances, bond angles and torsion angles are given in Tables S2-S6. CCDC 972800 (**2f(*a*)**), 972796 (**2f(*e*)**), 972799 (**2h(*ee*)**), 972797 (**3h**) and 972798 (**2i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for epoxidation

Alkene (5 mmol) was dissolved in dry CH_2Cl_2 (30 mL), and *m*-CPBA (7 mmol; 70% tech. grade) was added in small portions at 0 ^{o}C while stirring. The mixture was allowed to warm to 20 ^{o}C and was stirred at r.t. for 12-48 h until complete conversion of the alkene as monitored by TLC. After addition of $CHCl_3$ (30 mL) and of satd. aqueous Na_2CO_3 (20 mL), the mixture was stirred for 30 min. Then the organic phase was separated, washed with satd. Na_2CO_3 (3 × 10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed on a rotary evaporator. The purification of product was done either by column chromatography or by crystallization.

1-Methylcyclohexene 1,2-oxide (**1b**) was isolated by column chromatography (Al_2O_3, CH_2Cl_2) as a colorless liquid (62%). R_f 0.61 (silica gel, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.16 (m, 1H; H4), 1.25 (m, 1H; H5), 1.28 (s, 3H; CH_3), 1.35-1.44 (m, 2H; H4+H5), 1.64 (ddd, *J* 14.8, 8.1, 5.6 Hz; $H6^{ax}$), 1.79-1.90 (m, 3H; 2H3+$H6^{eq}$), 2.94 (d, *J* 3.5 Hz; H2); ^{13}C NMR ($CDCl_3$): δ 19.72 (C4), 20.11 (C5), 24.06 (CH_3), 24.82 (C3), 29.94 (C6), 57.61 (C1), 59.64 (C2) (Lit.[41] ^{13}C NMR); HRMS: $C_7H_{12}O$ requires $[2M+H]^+$ *m/z* 225.1855, $[M+H]^+$ *m/z* 113.0966; observed *m/z* 225.1857, 113.0961.

3-Methyl-7-oxabicyclo[4.1.0]heptane (**1c**). Epoxides **1c-*anti*** and **1c-*syn*** were prepared in 1.3:1 ratio and were isolated by column chromatography (Al_2O_3, CH_2Cl_2) as a colorless liquid (80%). R_f 0.51 (silica gel, hexane/EtOAc 9:2). Epoxide **1c-*anti*** ^{1}H NMR ($CDCl_3$): δ 0.83 (d, *J* 6.8 Hz, 3H; CH_3), 0.86 (m, 1H; H4), 1.22-1.33 (m, 1H; H3), 1.40 (m, 1H; H4), 1.69 (dddd, *J* 14.8, 12.5, 5.2, 1.5 Hz, $H2^{ax}$), 1.82 (ddd, *J* 15.6, 11.4, 6.6 Hz, $H5^{ax}$), 1.93-2.01 (m, $H5^{eq}$), 2.07-2.13 (ddd, *J* 15.0, 4.3, 2.0 Hz, $H2^{eq}$), 3.08-3.11 (m, 2H; H1+H6); ^{13}C NMR ($CDCl_3$): δ 21.71 (CH_3), 23.47 (C5), 25.26 (C4), 29.04 (C3), 33.62 (C2), 51.56, 53.23 (C1, C6) (Lit.[42] ^{1}H NMR, ^{13}C NMR for a mixture of isomers); Epoxides **1c-*syn*** ^{1}H NMR ($CDCl_3$): δ 0.82 (d, *J* 6.6 Hz, 3H; CH_3), 1.05 (dd, *J* 14.4, 6.9 Hz, 1H; H4), 1.09 (dddd, *J* 12.5, 4.4 Hz, H3) 1.22-1.32 (m, 1H; H4), 1.38 (dd, *J* 15.0,

11.7 Hz, $H5^{ax}$), 1.55 (m, 1H; H2), 1.93-2.01 (m, 1H; $H5^{eq}$), 2.07-2.13 (m, 1H, H2); 3.11-3.14 (m, 2H; H1+H6); ^{13}C NMR ($CDCl_3$): δ 22.08 (CH_3), 24.33 (C5), 26.47 (C4), 27.67 (C3), 32.53 (C2), 51.95, 52.36 (C1, C6) (Lit.[42] ^1H NMR, ^{13}C NMR); HRMS for the mixture: $C_7H_{12}O$ requires $[2M+H]^+$ *m/z* 225.1855, $[M+H]^+$ *m/z* 113.0966; observed *m/z* 225.1858, 113.0970.

2-(7-Oxabicyclo[4.1.0]heptan-3-yl)ethanol (**1d**)**.** Epoxides **1d-*anti*** and **1d-*syn*** were prepared in 1:1 ratio as a colorless liquid (70%) and were used for further step without purification. R_f 0.13 (silica gel, hexane/EtOAc 7:4). Configuration was established based on the analogy of ^1H NMR spectra with the other 3-substituted epoxides. Epoxide **1d-*anti*** ^1H NMR ($CDCl_3$): δ 0.91 (m, 1H; H4), 1.29-1.50 (m, 4H; H3+H4+CH_2), 1.59 (m, 1H; H2), 1.83 (m, 1H; H5), 1.96 (m, 1H; H5), 2.13 (m, 1H; H2), 3.09-3.16 (m, 2H; H1+H6), 3.62 (t, *J* 6.7 Hz, 2H; CH_2O); ^{13}C NMR ($CDCl_3$): δ 23.51 (C5), 24.49 (C4), 27.23 (CH_2), 31.87 (C2), 39.14(C3), 51.96, 53.11 (C1, C6), 60.64 (CH_2O); Epoxide **1d-*syn*** ^1H NMR ($CDCl_3$): δ 1.12 (m, 1H; H4), 1.30-1.49 (m, 4H; H3+H4+CH_2), 1.70 (m, 1H; H5), 1.83 (m, 1H; H2); 2.04 (m, 1H; H5); 2.13 (m, 1H; H2), 3.09-3.16 (m, 2H; H1+H6), 3.62 (t, *J* 6.7 Hz, 2H; CH_2O); ^{13}C NMR ($CDCl_3$): δ 25.24 (C5), 26.34 (C4), 29.21 (CH_2), 30.67 (C2), 39.62(C3), 51.87, 52.71 (C1, C6), 60.34 (CH_2O); HRMS for the mixture: $C_8H_{14}O_2$ requires $[2M+H]^+$ *m/z* 285.3991, $[M+H]^+$ *m/z* 143.1072; observed *m/z* 285.2040, 143.1079.

3-*t*-Butyl-7-oxabicyclo[4.1.0]heptanes (**1e**). Epoxides **1e-*anti*** and **1e-*syn*** were prepared in 1:2 ratio (the ratio 1:1.5 is previously described[43]) and were isolated by column chromatography (Al_2O_3, CH_2Cl_2) as a colorless liquid (65%). R_f 0.73 (silica gel, CH_2Cl_2). Epoxide **1e-*syn*** ^1H NMR ($CDCl_3$): δ 0.78 (s, 9H; $C(CH_3)_3$), 0.97 (dtd, *J* 2.1, 12.2, 5.9 Hz, H4ax), 1.06 (dq, *J* 4.1, 12.6 Hz, H3), 1.36 (m, $H4^{eq}$), 1.57 (dd, *J* 12.1, 15.2 Hz, $H5^{ax}$), 1.65 (dddd, *J* 1.5, 4.8, 12.5, 14.6 Hz, $H2^{ax}$), 1.95 (dtd, *J* 2.2, 5.8, 15.3 Hz, $H5^{eq}$), 2.16 (m, $H2^{eq}$), 3.11 (m, H1), 3.14 (dd, *J* 5.5, 3.9 Hz, H6); Epoxide **1e-*anti*** ^1H NMR ($CDCl_3$): δ 0.80 (s, 9H; $C(CH_3)_3$), 0.85 (m, 1H; H4), 1.21 (dtd, *J* 2.0, 12.1, 3.9 Hz, H3), 1.37 (m, 1H; H4), 1.50 (m, 1H; H2), 1.75 (ddd, *J* 15.4, 12.9, 6.3 Hz, $H5^{ax}$), 2.04 (dtd, *J* 15.5, 5.9, 1.7 Hz, $H5^{eq}$), 2.16 (m, 1H; H2), 3.11 (m, 1H; H6), 3.21 (m, 1H; H1).

Methyl 7-oxabicyclo[4.1.0]heptane-3-carboxylates (**1f**). Epoxides **1f-*anti*** and **1f-*syn*** were prepared in 2:1 ratio (the same ratio as described previously[44]) and were separated by column chromatography (Al_2O_3, CH_2Cl_2). Epoxide **1f-*anti*** is a colorless liquid (51%). R_f 0.68 (Al_2O_3, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.39 (ddt, *J* 13.4, 10.1, 6.5 Hz, $H4^{ax}$), 1.74 (m, $H4^{eq}$), 1.85-1.99 (m, 3H; 2H5+$H2^{ax}$), 2.25 (dd, *J* 15.0, 4.9 Hz, $H2^{eq}$), 2.50 (ddd, *J* 9.5, 4.9, 3.0 Hz, H3), 3.12 (t, *J* 4.0 Hz, H6), 3.21 (m, H1), 3.65 (s, 3H; OCH_3); ^{13}C NMR ($CDCl_3$): δ 22.84, 22.96 (C4, C5), 27.23 (C2), 35.79 (C3), 51.46, 51.81, 52.28 (C1, C6, CH_3), 175.98 (C=O); HRMS: $C_8H_{12}O_3$ requires $[2M+H]^+$ *m/z* 313.1651, $[M+H]^+$ *m/z* 157.0865; observed *m/z* 313.1675, 157.0898. Epoxide **1f-*syn*** is a colorless liquid (25%). R_f 0.63 (Al_2O_3, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.52-1.64 (m, 2H4), 1.75 (dddd, *J* 15.0, 11.1, 5.6, 1.7 Hz, $H5^{ax}$), 2.08-2.27 (m, 4H; 2H2 +H3+$H5^{eq}$), 3.12-3.16 (m, 2H; H1+H6), 3.65 (s, 3H; OCH_3); ^{13}C NMR ($CDCl_3$): δ 21.11 (C4), 24.11(C5), 26.33 (C2), 37.89 (C3), 50.76, 51.81 (C1, C6, CH_3), 175.33 (C=O); HRMS: $C_8H_{12}O_3$ requires $[2M+H]^+$ *m/z* 313.1651, $[M+H]^+$ *m/z* 157.0865; observed *m/z* 313.1675, 157.0898.

Diethyl 7-oxabicyclo[4.1.0]heptane-*trans*-3,4-dicarboxylate (**1g**) was prepared as described[45] and isolated by column chromatography (Al_2O_3, hexane/EtOAc gradient washing 8:2 →7:3) as a colorless liquid (60%). R_f 0.74 (Al_2O_3, hexane/EtOAc 7:3). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, *J* 7.1 Hz, 3H; CH_3), 1.22 (t, *J* 7.1 Hz, 3H; CH_3), 1.87 (ddd, *J* 14.9, 10.8, 2.1 Hz, $H2^{ax}$), 2.04 (dd, *J* 15.5, 10.9 Hz, $H5^{ax}$), 2.30 (ddd, *J* 15.5, 6.6, 4.8 Hz, $H5^{eq}$), 2.45 (ddd, *J* 14.9, 4.8, 1.8 Hz, $H2^{eq}$), 2.58 (dt, *J* 10.7, 6.7 Hz, H4), 2.80 (dt, *J* 10.7, 4.9 Hz, H3), 3.17 (t, *J* 4.3 Hz, H6), 3.24 (m, H1), 4.11 (m, 4H, OCH_2); ^{13}C NMR ($CDCl_3$): δ 14.20 (CH_3), 26.44 (C5), 27.30 (C2), 37.80 (C3), 40.14 (C4), 50.40 (C6), 52.00 (C1), 60.84 (OCH_2), 173.76, 174.82 (C=O); HRMS: $C_{12}H_{18}O_5$ requires $[M+H]^+$ *m/z* 243.1233; observed *m/z* 243.1240.

Dimethyl 7-oxabicyclo[4.1.0]heptane-*cis*-3,4-dicarboxylates (**1h**). Epoxides **1h-*anti*** and **1h-*syn*** were prepared according to the synthetic procedure reported previously.[45] Epoxide **1h-*anti*** is a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 2.17–2.29 (m, 4H; 2H2+2H5), 2.88-2.92 (m, 2H; H3+H4), 3.20-3.23 (m, 2H; H1+H6), 3.67 (s, 6H; OCH_3); ^{13}C NMR ($CDCl_3$): δ 24.79 (C2, C5), 37.69 (C3, C4), 51.61 (C1, C6), 52.12 (OCH_3), 173.56 (C=O). Epoxide **1h-*syn*** is a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 2.08-2.14 (m, 2H; H2+H5), 2.63-2.68 (m, 2H; H2+H5) 2.71-2.75 (m, 2H; H3+H4), 3.14-3.16 (m, 2H; H1+H6), 3.66 (s, 6H; OCH_3); ^{13}C NMR ($CDCl_3$): δ 24.82 (C2, C5), 37.57 (C3, C4), 51.03 (C1, C6), 51.97 (OCH_3), 173.09 (C=O). The configurations were assigned according to ^{1}H and ^{13}C NMR data previously reported.[45]

7-Oxabicyclo[4.1.0]heptane-*cis*-3,4-dicarboxylic acid imides (**1i**). Epoxides **1i-*anti*** and **1i-*syn*** were prepared in 1:5.5 ratio. Configuration of the major **1i-*syn*** epoxide was established based on NOE analysis of the product **4** of epoxide cleavage with $MeOH/H^+$ (see Supplementary data). Epoxide **1i-*syn*** was isolated by recrystallization from MeOH as a white solid (84%). Mp 225-229 °C; R_f 0.55 (Al_2O_3, $CHCl_3$/MeOH 10:1). ^{1}H NMR (CD_3OD): δ 2.16-2.22 (m, 2H; H2+H5), 2.51-2.57 (m, 2H; H2+H5), 2.79-2.82 (m, 2H; H3+H4), 3.13-3.16 (m, 2H; H1+H6); ^{13}C NMR (CD_3OD): δ 21.63 (C2, C5), 36.51(C3, C4), 50.79 (C1, C6), 183.11 (C=O); HRMS: $C_8H_9NO_3$ requires $[2M+H]^+$ *m/z* 335.1243, $[M+H]^+$ *m/z* 168.0661; observed *m/z* 335.1226, 168.0681. Epoxide **1i-*anti*** was characterized by NMR in the mixture with the major epoxide. ^{1}H NMR (CD_3OD): δ 1.94-2.00 (m, 2H; H2+H5), 2.42-2.48 (m, 2H; H2+H5), 2.87-2.93 (m, 2H; H3+H4), 3.20-3.22 (m, 2H; H1+H6); ^{13}C NMR (CD_3OD): δ 22.56 (C2, C5), 36.56 (C3, C4), 49.08 (C1, C6), 182.84 (C=O).

1,2-Anhydro-3,4,6-tri-*O*-benzyl-α-D-glucopyranose (**1k**). Tri-*O*-benzyl-glucal (0.53 g, 1.27 mmol) was dissolved in the mixture of CH_2Cl_2 (5 mL), acetone (1 mL) and satd $NaHCO_3$ (10 mL). A solution of Oxone (1.6 g, 2.6 mmol) in H_2O (6 mL) was added dropwise over 15 min at 0 °C while stirring. The mixture was allowed to warm up to room temperature and was stirred for 16h. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2x20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The pure product was obtained by crystallization from MeOH as a white solid (0.40 g, 73%). ^{1}H NMR ($CDCl_3$): δ 3.06 (d, *J* 2.2 Hz, H2), 3.66-3.75 (m, 4H; H4+H5+2H6), 3.97 (d, *J* 7.8 Hz, H3), 4.53 (d, *J* 12.1 Hz, 1H; CH_2, benzyl), 4.58 (d, *J* 11.0 Hz, 1H; CH_2, benzyl), 4.62 (d, *J* 12.0 Hz, 1H; CH_2, benzyl), 4.69 (d, *J* 11.5 Hz, 1H; CH_2, benzyl), 4.81 (d, *J* 11.3 Hz, 2H; CH_2, benzyl),

4.99 (d, *J* 1.4 Hz, H1), 7.15-7.19 (m, 2H, aromatic), 7.25-7.38 (m, 13H, aromatic) (Lit.[46,47] ^{1}H NMR data). HRMS: $C_{27}H_{28}O_5$ requires $[2M+H]^+$ *m/z* 865.3952, $[M+H]^+$ *m/z* 433.2015; observed *m/z* 865.3988, 433.2002.

Ethyl 4,6-di-*O*-acetyl-2,3-anhydro-α-D-manno- (**1l**) and **allo-hexopyranosides** were prepared according to the procedure previously reported.[48] The diastereomeric epoxides were obtained in the ratio 10:1 (manno:allo) with the overall yield 45%. *Manno-hexopyranoside* (**1l**): was isolated by column chromatography, (silica gel, hexane/EtOAc gradient washing 5:1→5:2) as a colorless syrup. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, *J* 7.1 Hz, 3H; CH_3, ethyl), 2.06 (s, 3H; CH_3, acetyl), 2.11 (s, 3H; CH_3, acetyl), 3.08 (d, *J* 3.5 Hz, H3), 3.21 (d, *J* 3.5 Hz, H2), 3.60 (dq, *J* 9.7, 7.1 Hz, 1H; CH_2, ethyl), 3.83 (dq, *J* 9.7, 7.1 Hz, 1H; CH_2, ethyl), 3.90 (ddd, *J* 9.8, 5.5, 2.8 Hz, H5), 4.10 (m, 2H6), 4.86 (d, *J* 10.0 Hz, H4), 5.00 (s, H1) (Lit.[48] ^{1}H NMR data); ^{13}C NMR ($CDCl_3$): δ 15.12 (CH_3, ethyl), 20.84 (CH_3, acetyl), 20.90 (CH_3, acetyl), 49.38(C3), 53.34 (C2), 63.13 (C4 and C6), 64.24 (CH_2, ethyl), 64.73 (C5), 94.89 (C1), 169.69 (C=O), 170.82 (C=O); HRMS: $C_{12}H_{18}O_7$ requires $[C_{10}H_{13}O_6]^+$ *m/z* 229.0712; observed *m/z* 229.0722. The configuration of epoxide **1l** was confirmed by NOE analysis (see Supplementary data). *Allo-hexopyranoside* was characterized by ^{1}H NMR in mixture with the major stereoisomer. ^{1}H NMR ($CDCl_3$): δ 1.24 (t, *J* 7.2 Hz, 3H; CH_3, ethyl), 2.08 (s, 3H; CH_3, acetyl), 2.11 (s, 3H; CH_3, acetyl), 3.53 (dd, *J* 4.2, 3.0 Hz, H2), 3.55 (dd, *J* 4.1, 1.6 Hz, H3), 3.60 (dq, *J* 9.8, 7.1 Hz, 1H; CH_2, ethyl), 3.81 (dq, *J* 9.8, 7.1 Hz, 1H; CH_2, ethyl), 4.10 (m, 2H6), 4.20 (dd, *J* 12.4, 5.1 Hz, H5), 5.04 (d, *J* 3.0 Hz, H1), 5.00 (dd, *J* 10.0, 1.5 Hz, H4) (Lit.[48] ^{1}H NMR data).

(1*S,2*S**,4*R**,6*R**)-4-methyl-2-phthalimidomethyl-3,7-dioxabicyclo[4.1.0]heptane** (**1m**). Synthesis of this compound was reported previously.[49,50] ^{1}H NMR ($CDCl_3$): δ 1.08 (d, *J* 6.2 Hz, 3H; CH_3), 1.62 (ddd, *J* 14.6, 11.0, 1.8 Hz, $H5^{ax}$), 2.01 (dt, *J* 14.6, 2.2 Hz, $H5^{eq}$), 3.16 (d, *J* 4.3 Hz, H1), 3.33 (dt, *J* 4.2, 1.8 Hz, H6), 3.47 (m, *J* 6.2, 2.6 Hz, H4), 3.92 (m, 2H; CH_2N), 4.10 (t, *J* 7.02 Hz, H2), 7.72 (m, 2H, aromatic), 7.86 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$): δ 21.08(CH_3), 32.82 (C5), 40.11 (CH_2N), 51.68 (C6), 52.36 (C1), 65.95 (C4), 72.41 (C2), 123.53, 132.03, 134.22 (C, aromatic), 168.35 (C=O). HRMS: $C_{15}H_{15}NO_4$ requires $[M+H]^+$ *m/z* 274.1079; observed *m/z* 274.1072.

General procedure for the synthesis of trithiocarbonates. Potassium ethyl xanthogenate (2 mmol) was dissolved in MeOH (3 mL) under Ar atmosphere and a solution of epoxide (1 mmol) in MeOH (2 mL) was added at 35-45 ^{o}C while stirring. The mixture was stirred at this temperature until the complete conversion of the epoxide, as monitored by TLC (the time of reaction is shown in Table 2). The solvent was removed on a rotary evaporator. The purification of product was done either by column chromatography or by crystallization.

Hexahydro-1,3-benzodithiole-2-thione (2a) was prepared from cyclohexene epoxide **1a** and was isolated by column chromatography (silica gel, $CHCl_3$/hexane 9:2) as a yellow solid (73%). Mp 167-169 ^{o}C, (Lit.[2,34] Mp 164-169 ^{o}C); R_f 0.54 (silica gel, $CHCl_3$/hexane 9:2). ^{1}H NMR ($CDCl_3$): δ 1.42-1.50 (m, 2H; $H5^{ax}$+$H6^{ax}$), 1.67-1.77 (m, 2H; $H4^{ax}$+$H7^{ax}$), 1.91-1.99 (m, 2H; $H5^{eq}$+$H6^{eq}$), 2.18-2.23 (m, 2H; $H4^{eq}$+$H7^{eq}$), 4.05-4.11 (m, 2H; H3a+H7a); ^{13}C NMR ($CDCl_3$): δ

25.13 (C5, C6), 29.17(C4, C7), 64.59 (C3a, C7a), 227.21 (C=S), (Lit.[2] ^{1}H NMR, ^{13}C NMR); HRMS: $C_7H_{10}S_3$ requires $[M+H]^+$ *m/z* 191.0023; observed *m/z* 191.0040.

3a-Methyl-hexahydro-1,3-benzodithiole-2-thione (**2b**) was prepared from epoxide **1b** and was isolated by column chromatography (silica gel, CH_2Cl_2) as a yellow oil (37%). R_f 0.49 (silica gel, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.48 (m, H6^{ax}), 1.62 (m, H5^{ax}), 1.68 (s, 3H; CH_3), 1.71-1.79 (m, 2H; H5^{eq}+H7^{ax}), 1.93-1.98 (m, 2H; H6^{eq}+H7^{eq}), 2.01 (dt, *J* 4.3, 13.0 Hz, H4^{ax}); 2.13 (dddd, *J* 12.8, 3.9, 2.7, 1.1 Hz, H4^{eq}), 4.41 (dd, *J* 13.1, 3.4 Hz, H7a); ^{13}C NMR ($CDCl_3$): δ 18.91 (CH_3), 20.83 (C5), 23.78 (C7), 25.37 (C6), 35.69 (C4), 67.99 (C3a, C7a), 226.69 (C=S); HRMS: $C_8H_{12}S_3$ requires $[M+H]^+$ *m/z* 205.0179; observed *m/z* 205.0173.

(1*S,2*S**,5*R**)-5-Methylhexahydro-1,3-benzodithiole-2-thione** (**2c**) was prepared from epoxide **1c** and was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 10:3) as a yellow solid (37%). Mp 123-125 ^{o}C; R_f 0.62 (silica gel, CH_2Cl_2/hexane 10:3). ^{1}H NMR ($CDCl_3$): δ 1.09 (d, *J* 7.4 Hz, 3H; CH_3), 1.68-1.72 (m, 2H6), 1.86-2.03 (m, 4H; 2H4+2H7), 2.25 (m, H5), 4.03 (dt, *J* 12.2, 3.7 Hz, H7a), 4.32 (dt, *J* 12.2, 4.1 Hz, H3a); ^{13}C NMR ($CDCl_3$): δ 17.98 (CH_3), 23.98 (C7), 27.20 (C5), 30.51 (C6), 34.40(C4), 59.79 (C3a), 65.01 (C7a), 227.14 (C=S); HRMS: $C_8H_{12}S_3$ requires $[M+H]^+$ *m/z* 205.0179; observed *m/z* 205.0125.

(1*S,2*S**,5*S**)-5-(2-Hydroxyethyl)hexahydro-1,3-benzodithiole-2-thione** (**2d**) was prepared from epoxide **1d** and was isolated by column chromatography (silica gel, CH_2Cl_2/MeOH 10:0.5) as a yellow oil (59%). R_f 0.56 (silica gel, CH_2Cl_2/MeOH 10:0.5). ^{1}H NMR ($CDCl_3$): δ 1.66-1.77 (m, 3H; CH_2+H6), 1.81-1.88 (m, 2H; H6+H7^{ax}), 1.93 (dt, *J* 13.0, 4.7 Hz, H4^{ax}), 2.05 (dq, *J* 13.5, 3.6 Hz, H7^{eq}), 2.10 (m, H4eq), 2.22 (m, H5), 3.71 (dt, *J* 6.4, 2.2 Hz, 2H; CH_2O), 4.06 (dt, *J* 12.1, 3.7 Hz, H7a), 4.27 (dt, *J* 12.6, 3.5 Hz, H3a); ^{13}C NMR ($CDCl_3$): δ 24.50 (C7), 28.91 (C6), 29.34 (C5), 32.85 (C4), 34.21 (CH_2), 60.18 (C3a), 61.03 (CH_2OH), 64.92(C7a), 227.00 (C=S); HRMS: $C_9H_{14}OS_3$ requires $[M+H]^+$ *m/z* 235.0285; observed *m/z* 235.0273.

5-(Methoxycarbonyl)hexahydro-1,3-benzodithiole-2-thiones [**2f(*a*)** and **2f(*e*)**] were synthesized from individual **1f-*anti*** and **1f-*syn*** epoxides or from their mixture with overall yields 50-60%. The ratio of diastereomers was dependent on the time of the reaction: after 0.5 h the ratio of products **2f(*a*):2f(*e*)** was (2.2-3.3):1; after 2-3 h the ratio was 1:1.3.

(1*S,2*S**,5*R**)-5-(Methoxycarbonyl)-hexahydro-1,3-benzodithiole-2-thione** [**2f(*a*)**] was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 10:3) as a yellow solid. Mp 95-97 ^{o}C; R_f 0.39 (silica gel, CH_2Cl_2/hexane 10:3). ^{1}H NMR ($CDCl_3$): δ 1.69 (dddd, *J* 14.2, 13.5, 5.3, 4.0 Hz, H6^{ax}), 1.88 (dq, *J* 3.6, 13.1 Hz, H7^{ax}), 1.92 (dq, *J* 12.9, 5.0 Hz, H4^{ax}), 2.12 (dq, *J* 13.3, 3.5 Hz, H7^{eq}), 2.41 (m, H6^{eq}), 2.64 (ddd, *J* 13.3, 3.6, 2.1 Hz, H4^{eq}), 2.94 (tt, *J* ≈ 2.5, 5.0 Hz, H5), 3.74 (s, 3H; OCH_3), 4.07 (dt, *J* 12.2, 3.6 Hz, H7a), 4.29 (dt, *J* 12.4, 3.5 Hz, H3a); ^{13}C NMR ($CDCl_3$): δ 25.90, 26.44 (C6, C7), 29.89 (C4), 38.55 (C5), 52.27 (OCH_3), 60.55 (C3a), 63.88 (C7a), 173.67 (C=O), 226.03 (C=S); HRMS: $C_9H_{12}O_2S_3$ requires $[M+H]^+$ *m/z* 249.0078; observed *m/z* 249.0074.

(1*S,2*S**,5*S**)-5-(Methoxycarbonyl)hexahydro-1,3-benzodithiole-2-thione** [**2f(*e*)**] was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 10:3) as a yellow solid. Mp 64-66 ^{o}C; R_f 0.32 (silica gel, CH_2Cl_2/hexane 10:3). ^{1}H NMR ($CDCl_3$): δ 1.63 (dtd, *J* 13.1, 13.1, 3.6

Hz, $H6^{ax}$), 1.77 (dtd, *J* 11.6, 13.1, 3.6 Hz, $H7^{ax}$), 1.90 (q, *J* 12.2 Hz, $H4^{ax}$), 2.23 (ddq, *J* 13.6, 1.8, 3.5 Hz, $H6^{eq}$), 2.28 (dq, *J* 13.1, 3.4 Hz, $H7^{eq}$), 2.47 (dtd, *J* 12.9, 3.4, 1.8 Hz, $H4^{eq}$), 2.55 (tt, *J* 12.3, 3.8 Hz, H5), 3.68 (s, 3H; OCH_3), 4.06 (dt, *J* 3.5, 12.1 Hz, H3a), 4.10 (dt, *J* 3.4, 12.1 Hz, H7a); ^{13}C NMR ($CDCl_3$): δ 27.70, 27.90 (C6, C7), 31.02 (C4), 41.87 (C5), 52.12 (OCH_3), 62.90, 63.27 (C3a, C7a), 173.62 (C=O), 225.92 (C=S); HRMS: $C_9H_{12}O_2S_3$ requires $[M+H]^+$ *m/z* 249.0078; observed *m/z* 249.0074.

(1*S,2*S**,5*S**,6*S**)-5,6-Bis(ethoxycarbonyl)hexahydro-1,3-benzodithiole-2-thione** [**2g(*ee*)**] was prepared from epoxide **1g** and was isolated by column chromatography (silica gel, EtOAc/hexane 5:7) as a yellow liquid (7%). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, *J* 7.1 Hz, 6H; CH_3), 1.82-1.93 (m, 2H; H4+H7), 2.56-2.61 (m, 2H; H4+H7), 2.86-2.93 (m, 2H; H5+H6), 4.09-4.14 (m, 2H; H3a+H7a), 4.15 (q, *J* 7.1Hz, 2H; OCH_2), 4.16 (q, *J* 7.1 Hz, 2H; OCH_2); ^{13}C NMR ($CDCl_3$): δ 14.18 (CH_3), 30.84 (C4, C7), 43.83 (C5, C6), 61.47 (OCH_2), 62.29 (C3a, C7a), 172.51 (C=O), 225.10 (C=S); HRMS: $C_{13}H_{18}O_4S_3$ requires $[M+H]^+$ *m/z* 335.0446; observed *m/z* 335.0452.

5,6-Bis(methoxycarbonyl)hexahydro-1,3-benzodithiole-2-thiones [**2h(*ee*)** and **2h(*ea*)**] were obtained in 10:1 ratio from either **1h-*anti*** or **1h-*syn*** epoxide.

(1*S,2*S**,5*S**,6*S**)-5,6-Bis(methoxycarbonyl)hexahydro-1,3-benzodithiole-2-thione** [**2h(*ee*)**] was isolated by column chromatography (silica gel, EtOAc/hexane 3:7) as a yellow solid (50%). Alternatively, **2h(*ee*)** was purified by crystallization from MeOH (yield 46%). Mp 189-190 °C; R_f 0.48 (silica gel, EtOAc/hexane 3:7). ^{1}H NMR ($CDCl_3$): δ 1.83-1.93 (m, 2H; H4+H7), 2.56-2.61 (m, 2H; H4+H7), 2.88-2.95 (m, 2H; H5+H6), 3.71 (s, 6H; OCH_3), 4.10-4.17 (m, 2H; H3a+H7a); ^{13}C NMR ($CDCl_3$): δ 30.77 (C4, C7), 43.72 (C5, C6), 52.56 (OCH_3), 62.17 (C3a, C7a), 172.97 (C=O), 224.81 (C=S); HRMS: $C_{11}H_{14}O_4S_3$ requires $[M+H]^+$ *m/z* 307.0133; observed *m/z* 307.0116.

(1*S,2*S**,5*S**,6*R**)-5,6-Bis(methoxycarbonyl)hexahydro-1,3-benzodithiole-2-thione** [**2h(*ea*)**] was isolated by column chromatography (silica gel, EtOAc/hexane 3:7) as a yellow oil (5%). R_f 0.31 (silica gel, EtOAc/hexane 3:7). ^{1}H NMR ($CDCl_3$): δ 2.02 (ddd, *J* 13.6, 12.4, 5.1 Hz, $H4^{ax}$), 2.34 (dt, *J* 13.4, 12.4 Hz, $H7^{ax}$), 2.57 (dtd, *J* 3.5, 3.7, 0.9 Hz, $H7^{eq}$), 2.65-2.70 (m, 2H; $H4^{eq}$+H6), 3.50 (m, H5), 3.71 (s, 3H; OCH_3), 3.73 (s, 3H, OCH_3), 4.07-4.15 (m, 2H; H3a+H7a); ^{13}C NMR ($CDCl_3$): δ 27.28 (C7), 30.40 (C4), 41.11 (C5), 42.97 (C6), 52.48, 52.60 (OCH_3), 59.68, 63.16 (C3a, C7a), 171.88, 172.36 (C=O), 225.40 (C=S); HRMS: $C_{11}H_{14}O_4S_3$ requires $[M+H]^+$ *m/z* 307.0133; observed *m/z* 307.0125.

(1*S,2*S**,5*S**,6*R**)-2-Thioxohexahydro-1,3-benzodithiole-*cis*-5,6-dicarboximide** (**2i**) was prepared from epoxide **1i-*syn*** after 72 h at 40 °C and was isolated by column chromatography (silica gel, CH_2Cl_2/MeOH 9:1) as a yellow solid (56%). Mp 220-221 °C; R_f 0.32 (silica gel, CH_2Cl_2/MeOH 9:1). ^{1}H NMR (CD_3OD): δ 1.76 (q, *J* 12.5 Hz, $H4^{ax}$), 2.04 (ddd, *J* 13.7, 12.9, 7.5 Hz, $H7^{ax}$), 2.63 (ddd, *J* 13.4, 7.4, 3.3 Hz, $H4^{eq}$), 2.78 (ddd, *J* 13.8, 4.0, 1.3 Hz, $H7^{eq}$), 3.09 (dt, *J* 11.7, 7.6 Hz, H5), 3.34 (dt, *J* 7.7, 1.1 Hz, H6), 4.13 (dt, *J* 12.4, 4.1 Hz, H7a), 4.28 (dt, *J* 12.3, 3.1 Hz, H3a); ^{13}C NMR (CD_3OD): δ 24.09, 29.79 (C4, C7), 40.44 (C5, C6), 59.96, 60.45 (C3a,

C7a), 178.73, 179.51 (C=O), 225.76 (C=S); HRMS: $C_9H_9NO_2S_3$ requires $[M+H]^+$ *m/z* 259.9873; observed *m/z* 259.9867.

(1*S,3*R**,4*S**,6*R**)-7-Thiabicyclo[4.1.0]heptane-*cis*-3,4-dicarboximide** (**3,4-epithiohexahydrophthalimide**) was obtained in the reaction of epoxide **1i-*syn*** with potassium ethyl xanthogenate after 15 h at 40 °C and was isolated by column chromatography (silica gel, CH_2Cl_2/MeOH 9:1) as a yellow solid (52%). Mp 207-209 °C. Configuration was established based on the similarity of the ^{1}H NMR spectra of this thiirane and **1i-*anti*** epoxide. ^{1}H NMR (CD_3OD): δ 2.07-2.12 (m, 2H; H2+H6), 2.47-2.55 (m, 2H; H2+H5), 2.83-2.89 (m, 2H; H3+H4), 3.24-3.27 (m, 2H; H1+H6); ^{13}C NMR (CD_3OD): δ 23.73 (C2, C5), 32.90 (C3, C4), 36.79 (C1, C6), 182.04 (C=O); HRMS: $C_8H_9NO_2S$ requires $[M+H]^+$ *m/z* 184.0432; observed *m/z* 184.0420.

3,4,6-Tri-*O*-benzyl-1-thio-β-D-glucopyranose (**2k**) was obtained in the reaction of epoxide **1k** with potassium ethyl xanthogenate after 2h at 45 °C and was isolated by column chromatography (silica gel, CH_2Cl_2/EtOAc 10:0.5) as a colorless oil (37%). R_f 0.19 (silica gel, $CHCl_3$/EtOAc 10:1). ^{1}H NMR ($CDCl_3$): δ 2.19 (d, *J* 9.7 Hz, SH), 2.43 (d, *J* 2.1 Hz, OH), 3.40 (dt, *J* 9.0, 2.1 Hz, H2), 3.49 (ddd, *J* 9.8, 4.3, 2.0 Hz, H5), 3.53 (t, *J* 8.9 Hz, H3), 3.66 (dd, *J* 9.4 Hz, H4), 3.68-3.76 (m, 2H6), 4.33 (t, *J* 9.5 Hz, H1), 4.52 (d, *J* 10.7 Hz, 1H; CH_2, benzyl), 4.54 (d, *J* 12.2 Hz, 1H; CH_2, benzyl), 4.61 (d, *J* 12.2 Hz, 1H; CH_2, benzyl), 4.81 (d, *J* 10.7 Hz, 1H; CH_2, benzyl), 4.85 (d, *J* 11.3 Hz, 1H; CH_2, benzyl), 4.91 (d, *J* 11.3 Hz, 1H; CH_2, benzyl), 7.12-7.16 (m, 2H), 7.25-7.38 (m, 13H); ^{13}C NMR ($CDCl_3$): δ 68.73 (CH_2), 73.64, 75.17, 75.34 (CH_2, benzyl); 77.40 (C4), 77.67 (C2), 79.82 (C5), 81.02 (C1), 85.69 (C3), 127.83, 127.92, 127.94, 128.05, 128.50, 128.52, 128.64, 137.99, 138.02, 138.56 (C aromatic) (Lit. ^{1}H NMR and ^{13}C NMR for a mixture of α- and β-isomers see in SI for [19]); HRMS: $C_{27}H_{30}O_5S$ requires $[M+NH_4]^+$ *m/z* 484.2158, $[M+H]^+$ *m/z* 467.1892, $[M-H_2O+H]^+$ *m/z* 449.1787; observed *m/z* 484.2110, 467.1933, 449.1808.

***trans*-4,5-Dimethyl-1,3-dithiolane-2-thione** (**2n**) was prepared from *cis*-1,2-dimethyloxirane **1n** and was isolated by column chromatography (silica gel, EtOAc/hexane 3:7) as a yellow solid (43%). Mp 40-42 °C (Lit.[13] Mp 41.5-42.5 °C); R_f 0.56 (silica gel, EtOAc/hexane 3:7). ^{1}H NMR ($CDCl_3$): δ 1.58 (m, 6H, CH_3), 4.10 (m, 2H, H4+H5), (Lit.[20] ^{1}H NMR); ^{13}C NMR ($CDCl_3$): δ 18.58 (CH_3), 61.38 (C4, C5), 226.41 (C=S); HRMS: $C_5H_8S_3$ requires $[M+H]^+$ *m/z* 164.9866; observed *m/z* 164.9858.

4,4-Dimethyl-1,3-dithiolane-2-thione (**2o**) was prepared from 1,1-dimethyloxirane **1o** and was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 10:3) as a yellow liquid (30%). R_f 0.77 (silica gel, CH_2Cl_2/hexane 10:3). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 6H, CH_3), 3.74 (s, 2H, H5), (Lit.[21] ^{1}H NMR); ^{13}C NMR ($CDCl_3$): δ 27.58 (CH_3), 55.76 (C5), 66.22 (C4), 227.76 (C=S); HRMS: $C_5H_8S_3$ requires $[M+H]^+$ *m/z* 164.9866; observed *m/z* 164.9891.

***cis*-4,5-Diphenyl-1,3-dithiolane-2-thione** (**2r**) was prepared from *trans*-1,2-diphenyloxirane **1r** and was isolated by column chromatography (silica gel, EtOAc/hexane 3:7) as a yellow solid (25%). Mp 108-113 °C, (Lit.[13] Mp 115-120 °C); R_f 0.50 (EtOAc/hexane 3:7). ^{1}H NMR ($CDCl_3$): δ 5.75 (s, 2H; H4+H5), 6.97-7.00 (m, 4H; phenyl), 7.15 (t, *J* 7.6 Hz, 4H; phenyl), 7.22 (tt, *J* 7,4, 1.2 Hz; 2H, phenyl); ^{13}C NMR ($CDCl_3$): δ 67.92 (C4, C5), 128.35, 128.68, 128.83 133.06(C, phenyl), 227.52 (C=S); HRMS: $C_{15}H_{12}S_3$ requires $[M+H]^+$ *m/z* 289.0179; observed *m/z*

289.0171. ***trans*-2,3-Diphenylthiirane** was obtained in the reaction of *trans*-epoxide **1r** with potassium ethyl xanthogenate after 15 h at 40 °C and isolated by column chromatography (Al_2O_3, hexane) as a white solid (38%). Mp 52-54 °C (Lit.[51] Mp 53-54 °C); R_f 0.61 (Al_2O_3, hexane). ^{1}H NMR ($CDCl_3$): δ 3.97 (s, 2H; H2+H3), 7.27-7.30 (m, 2H; phenyl), 7.32-7.39 (m, 8H; phenyl) (Lit.[52] ^{1}H NMR); ^{13}C NMR ($CDCl_3$): δ 45.54 (C2, C3), 127.09, 127.89, 128.74, 138.77 (C, phenyl); HRMS: $C_{14}H_{12}S$ requires $[M+H]^+$ *m/z* 213.0738; observed *m/z* 213.0708.

4-*n*-Butyl-1,3-dithiolane-2-thione (**2s**) was prepared from 1,2-epoxyhexane **1s** and was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 2:1) as a yellow liquid (52%). R_f 0.52 (silica gel, CH_2Cl_2/hexane 1:1). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J* 7.1 Hz, 3H; CH_3), 1.38 (m, 4H; $2CH_2$), 1.92 (m, 2H; CH_2), 3.70 (dd, *J* 11.9, 7.9 Hz, 1H; CH_2S), 3.95 (dd, *J* 11.9, 5.5 Hz, 1H; CH_2S), 4.38 (tt, *J* 8.0, 5.5 Hz, 1H; CHS); ^{13}C NMR ($CDCl_3$): δ 13.92 (CH_3), 22.43 (CH_2), 30.48 (CH_2), 33.33 (CH_2), 48.29 (CH_2S), 61.07 (CHS), 228.06 (C=S) (Lit.[2] ^{1}H NMR, ^{13}C NMR); HRMS: $C_7H_{12}S_3$ requires $[M+H]^+$ *m/z* 193.0179; observed *m/z* 193.0163.

Ethyl 4,6-di-*O*-acetyl-2,3-epithio-2,3-dideoxy-α-D-allopyranoside (**2l**)

Potassium ethyl xanthogenate (130 mg, 0.8 mmol) was dissolved in 1 mL of MeOH under Ar atmosphere and solution of manno-epoxide **1l** (110 mg, 0.4 mmol) in 2 mL of MeOH was added at 40 °C while stirring. The mixture was stirred at this temperature for 24 h until complete conversion of the epoxide, as monitored by TLC. The reaction mixture was passed through a layer of silica gel and concentrated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 and acetic anhydride (0.5 mL) was added to the solution at 0 °C under stirring followed by pyridine (0.1 mL). The reaction mixture was allowed to warm up to room temperature and was stirred for 24 h. The solvent was removed on a rotary evaporator. The product was isolated by column chromatography (silica gel, hexane/EtOAc gradient washing 5:1→5:3) as a colorless oil (38 mg, 32%). R_f 0.24 (silica gel, hexane/EtOAc 4:1). ^{1}H NMR ($CDCl_3$): δ 1.22 (t, *J* 7.1 Hz, 3H; CH_3, ethyl), 2.05 (s, 3H; CH_3, acetyl), 2.08 (s, 3H; CH_3, acetyl), 3.54 (dd, *J* 6.7, 5.2 Hz, H2), 3.59 (dq, *J* 10.0, 7.1 Hz, 1H; CH_2, ethyl), 3.62 (dd, *J* 6.7, 4.1 Hz, H3), 3.76 (dq, *J* 10.0, 7.1 Hz, 1H; CH_2, ethyl), 4.03 (ddd, *J* 9.9, 5.1, 2.2 Hz, H5), 4.09 (dd, *J* 12.1, 2.2 Hz, H6), 4.18 (dd, *J* 12.1, 5.1 Hz, H6), 5.19 (dd, *J* 9.8, 4.1 Hz, H4), 5.27 (d, *J* 5.1 Hz, H1) (the spectrum is similar to the reported[48] ^{1}H NMR spectrum of the corresponding allo-epoxide); ^{13}C NMR ($CDCl_3$): δ 15.19 (CH_3, ethyl), 20.86 (CH_3, acetyl), 21.06 (CH_3, acetyl), 35.72 (C3), 38.72 (C2), 62.76 (C6), 63.18 (C5), 63.76 (CH_2, ethyl), 67.10 (C4), 92.37 (C1), 170.43 (C=O), 170.80 (C=O); HRMS: $C_{12}H_{18}O_6S$ requires $[M+H]^+$ *m/z* 291.0902, $[C_{10}H_{13}O_5S]^+$ *m/z* 245.0484; observed *m/z* 291.0912, 245.0493.

Oxidation of trithiocarbonates. Trithiocarbonate (0.5 mmol) was dissolved in 2 mL of dry $CHCl_3$, and solution of Br_2 (2 mmol) in 2 mL of $CHCl_3$ was added dropwise at 0 °C while stirring. The mixture was allowed to warm to room temperature (20 °C) and was stirred for 6-12 h until complete conversion of the starting material as monitored by TLC. After addition of 20 mL $CHCl_3$, an orange precipitate was removed by suction filtration. The filtrate was washed with dilute aqueous $NaHCO_3$ (10 mL) followed by saturated NaCl (10 mL) and dried over anhydrous

Na_2SO_4. The solvent was removed on a rotary evaporator. Purification of the product was achieved by column chromatography.

Hexahydro-1,3-benzodithiol-2-one (**3a**) was prepared by oxidation of trithiocarbonate **2a** with Br_2 and was isolated by column chromatography (silica gel, CH_2Cl_2/hexane 3:1) as a white solid (60%). Mp 106-108 ^oC; R_f 0.55 (silica gel, CH_2Cl_2/hexane 3:1). ^1H NMR ($CDCl_3$): δ 1.49-1.54 (m, 2H; H5+H6), 1.63-1.72 (m, 2H; H4+H7), 1.90-1.95(m, 2H; H5+H6), 2.14-2.19 (m, 2H; H4+H7), 3.79-3.85 (m, 2H; H3a+7a); ^{13}C NMR ($CDCl_3$): δ 25.63 (C5, C6), 29.51(C4, C7), 58.46 (C3a, C7a), 195.88 (C=S), (Lit.[14] ^1H NMR); HRMS: $C_7H_{10}OS_2$ requires $[2M+H]^+$ *m/z* 349.0424, $[M+H]^+$ *m/z* 175.0251; observed *m/z* 349.0403, 175.0253.

(1*S,2*S**,5*S**,6*S**)-5,6-Bis(methoxycarbonyl)-hexahydro-1,3-benzodithiol-2-one** [**3h(*ee*)**] was prepared by oxidation of trithiocarbonate **2h(*ee*)** with Br_2 and isolated by column chromatography (silica gel, CH_2Cl_2) as a white solid (75%). Mp 130-132 ^oC; R_f 0.23 (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.78-1.88 (m, 2H; H4+H7), 2.54-2.59 (m, 2H; H4+H7), 2.91-2.97 (m, 2H; H5+H6), 3.69 (s, 6H; OCH_3), 3.80-3.86 (m, 2H; H3a+H7a); ^{13}C NMR ($CDCl_3$): δ 31.19 (C4, C7), 44.00 (C5, C6), 52.51 (OCH_3), 56.15 (C3a, C7a), 172.96 (C=O), 194.15 (SSC=O); HRMS: $C_{11}H_{14}O_5S_2$ requires $[M+H]^+$ *m/z* 291.0361; observed *m/z* 291.0354. The same product was obtained in reactions of trithiocarbonate **2h(*ee*)** (1 equiv) with DDQ (4 equiv) in dry THF (yield 45%, and 32% recovered **2h(*ee*)**) and with NBS (4 equiv) in dry $CHCl_3$ (yield 23%).

Methanolysis of epoxide 1i

(1*S,2*R**,4*S**,5*S**)-4-Hydroxy-5-methoxycyclohexane-*cis*-1,2-dicarboximide** (**4**). Epoxide **1i-*syn*** (35 mg, 0.2 mmol) was dissolved in methanol (1 mL), and H_2SO_4 in methanol (1:3 v/v, 0.1 mL) was added at room temperature. The mixture was stirred for 14 h, then diluted with $CHCl_3$ (30 mL) and washed with saturated $NaHCO_3$ (5 mL). Organic phase was dried over Na_2SO_4, and solvent was removed on a rotary evaporator yielding 30 mg of white solid (75%). R_f 0.41 (silica gel, $CHCl_3$/MeOH 10:1). ^1H NMR ($CDCl_3$): δ 1.75 (ddd, *J* 14.2, 7.6, 6.4 Hz, 2H; $H3^{ax}$+$H6^{ax}$), 2.25 (ddd, *J* 14.3, 7.3, 3.6 Hz, $H6^{eq}$), 2.37 (ddd, *J* 14.2, 6.2, 4.1 Hz, $H3^{eq}$), 2.94 (q, *J* 7.6 Hz, H2), 3.04 (dt, *J* 7.7, 6.5 Hz, H1), 3.18 (ddd, *J* 7.8, 6.4, 4.0 Hz, H5), 3.41 (s, 3H; OCH_3), 3.73 (ddd, *J* 7.8, 6.4, 3.7 Hz, H4); ^{13}C NMR ($CDCl_3$): δ 24.17 (C6), 29.07 (C3), 39.15 (C2), 39.21 (C1), 56.91 (OCH_3), 68.74 (C4), 79.08 (C5), 179.04, 179.14 (C=O); HRMS: $C_9H_{13}NO_4$ requires $[2M+H]^+$ *m/z* 399.1767, $[M+H]^+$ *m/z* 200.0923; observed *m/z* 399.1866, 200.0924.

Acknowledgements

We thank Prof. O. David Sparkman and Dr. Matthew Curtis for the use of Pacific Mass-spectrometry Facility, and Dr. Simon Teat for the single crystal measurements. We gratefully acknowledge the support from the Department of Chemistry at University of the Pacific, the NSF Major Research Instrumentation Grant (CHE-0722654) for the funding of JEOL ECA-600 NMR spectrometer, and the general user proposal for beam time at the Advanced Light Source of Lawrence Berkeley National Lab. The Advanced Light Source is supported by the Director,

Office of Science, and Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supplementary data

Available information: X-ray crystallographic data and selected NMR spectra. Supplementary data associated with this article can be found with the online version.

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