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Liquid sulfur as a reagent: synthesis of polysulfanes with 20 or more sulfur atoms with characterization by UPLC-

(Ag⁺)-coordination ion spray-MS

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Liquid sulfur as a reagent: synthesis of polysulfanes with 20 or more sulfur atoms with characterization by UPLC-(Ag⁺)-coordination ion spray-MS

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Diallyl disulfide reacts within minutes with liquid sulfur at 120° C giving a family of diallyl polysulfanes, All₂S_n (n = 3-22), characterized by ultra-performance liquid chromatography-(Ag⁺)-coordination ion spray-mass spectrometry (UPLC-(Ag⁺)CIS-MS). Similarly, garlic oil (GO), bis-(2-methyl-2-propenyl), bis-(2-chloro-2-propenyl), bis-(3-methyl-2-butenyl), and bis-(2-cyclohexen-1-yl) disulfides all give families of polysulfanes with up to 22 sequential sulfur atoms. New members of families of silver chelators with up to 10 sulfur atoms were found in GO using UPLC-(Ag⁺)CIS-MS.



Keywords: elemental sulfur; UPLC-CIS-MS; diallyl polysulfides; garlic oil; thiosulfoxide

1. Introduction

While liquid sulfur occurs naturally (1) and is produced worldwide in excess of 35×10^6 tons/year by the Frasch and Claus processes (2), surprisingly little work has appeared on its use as a reagent for synthesis of monomeric organosulfur compounds (or other compounds) under mild conditions (3–6). At 120°C sulfur melts to a honey-yellow, low-viscosity liquid consisting of >95% S₈ and remains liquid down to its triple point of 115°C. In liquid form, sulfur is transported worldwide by ship, rail, and heated pipeline (2). We examined the use of liquid sulfur, without added solvents or catalysts, in transforming diallyl disulfide (1a; Scheme 1) into a mixture of higher linear polysulfanes (CH₂=CHCH₂)₂S_n (2a). This method was applied to diallylic disulfides 1b–1e and to garlic oil (GO), containing 1a as a major component. Polysulfanes 2 are of interest in our Allium chemistry research (7), particularly for use as environmentally benign nematicides (portions of the

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material covered in this paper are the subject of patents based on joint discoveries made by E.B. and M.G. at ECOspray Ltd in the UK: (7*a*) and earlier filings cited therein) (7*b*) and bird repellants (7*c*). While polysulfane biological activity increases with the number of sulfur atoms (8), diallylic polysulfanes with nine or more sulfur atoms are currently unavailable. We describe here a simple approach, using liquid sulfur as a reagent, to the synthesis of families of allylic and diallylic polysulfanes containing chains of up to 22 sulfur atoms, unavailable by other means (5) (polysulfane synthesis: with S₈ and Rh catalyst (9*a*), with methyl triflate (9*b*), and from sulfenyl halides (9*c*)). We also describe the use of ultra-performance liquid chromatography-(Ag⁺)-coordination ion spray-mass spectrometry (UPLC-[Ag⁺]CIS-MS) to characterize the complex mixtures of sulfur compounds involved in this work, including those in GO.



Scheme 1. Diallylic polysulfane synthesis.

2. Results and discussion

Diallyl disulfide (1a) and molten S_8 in a 1:1 molar ratio (calculated for sulfur as S_8) was stirred at 120°C. The initially heterogeneous mixture became homogeneous within 3 min (Figure 1). C18-HPLC analysis of reaction mixtures showed a series of evenly spaced peaks, eluting over the course of 3 h, corresponding to (CH₂=CHCH₂)₂ S_n (2a), n = 3-22, along with unreacted S_8 . The reaction was terminated after 1 h (Figure 2), after which time darkening occurred. Diode array UV spectra of each peak supported the "family" relationship of members of the mixture (see Supporting Information). Prior HPLC studies of dialkyl polysulfanes revealed linear relationships between the number of sulfur atoms in the chain and the natural logarithm of the capacity factor, calculated from the retention time (5, 10). Similar linear relationships for the relative UV detector response (*e.g.* higher sensitivity to higher polysulfanes) were also found (9b).

While mixtures of **2a** can be characterized by ¹H NMR spectroscopy, since the SCH₂ signal moves downfield as the number of sulfur atoms increase, for example, δ 3.11, 3.36, 3.52, 3.60, and 3.63, for **2a**, n = 1-5, respectively (*6a*, *7c*), the SCH₂ doublet for **2a**, $n \ge 6$ (in CDCl₃; insoluble in EtOH, which dissolves **2a**, $n \le 8$), also appears at δ 3.63, limiting the utility of ¹H NMR for analysis of higher polysulfanes (see Supporting Information for spectra).

The usual LC-MS technique using electrospray ionization mass spectrometry (MS) does not work with polysulfanes because the sulfane sulfurs are very weak bases and therefore do not undergo protonation. We find that UPLC-(Ag⁺)CIS-MS is particularly appropriate for product characterization in view of the very mild MS conditions and the high affinity of silver ions for divalent sulfur. While HPLC-(Ag⁺)CIS-MS has proven useful, for example, for analysis of nonpolar and poorly ionized substances such as polyolefins (*11a*), lipid peroxidation products (*11b*), and glycosides (*11c*), application of this powerful technique to organosulfur compounds has been very limited (*12*). Ultra-performance liquid chromatography (UPLC) has an advantage over HPLC in significantly reducing the elution times with a resultant sharpening of peaks, important for MS analysis of late-eluting trace components (*13*). Through the use of UPLC, the 3 h HPLC separation time for **2a** was reduced to ~20 min. The CIS-MS total ion chromatogram (TIC) showed **2a**, n = 2-16. Each polysulfane has isotopic molecular ions for the silver complexes whose ratios are in excellent agreement with those calculated for ¹⁰⁷Ag/¹⁰⁹Ag/³²S/³⁴S (Figure 3) (*14*). Higher polysulfanes **2a** (by preparative-HPLC) are stable in MeOH–H₂O in the dark and can be characterized by NMR (Supporting Information); storage at -78° C prevents disproportionation into mixtures of higher and lower polysulfanes found with light at 25°C.

We examined the effect of changing the $1a:S_8$ ratio and the temperature and found the reaction to be fastest using a 1:1 molar ratio (8:1, 4:1, 2:1 and 1:1 ratios required 18, 8, 2, and 1 h, respectively, at 120°C; very slow at 100°C and decomposition with red color at 150°C). We also examined the reactions of liquid S_8 at 120°C with known disulfides **1b–1f** (*15*), prepared from commercially available halides. All disulfides except **1f** reacted smoothly in high yield giving families of polysulfanes as shown by HPLC (chains of up to 22 sulfurs), UPLC-(Ag⁺)CIS-MS



Figure 1. Diallyl disulfide (1a; upper layer) and liquid S_8 (lower layer) (left), and homogeneous product diallyl polysulfane (2a) after 3 min at 120°C (right).



Figure 2. HPLC trace of reaction product of liquid S_8 and diallyl polysulfane (**2a**). The vertical axis corresponds to the approximate relative abundance of each peak based on UV absorbance. The number of sulfur atoms is listed following "DAS" in each case.



Figure 3. UPLC-(Ag⁺)CIS-MS TIC of diallyl polysulfane (**2a**). Inserts show $C_6H_{10}S_{16}$ •Ag⁺ molecular ion cluster with Ag and S isotopes. The vertical axis represents the signal intensity, approximating the relative abundance of each peak.

(chains of up to 15 sulfurs), and ¹H NMR spectroscopy. In summary, reaction of 1 with liquid S_8 provides a simple route to otherwise unavailable higher diallylic polysulfanes.

From prior work (7*c*, 16), we suggest (Scheme 2) that thiosulfoxide **3a** (17), in equilibrium with **1a**, is sufficiently nucleophilic¹ (18) to ring-open S_8 giving thiosulfonium ion **4a**. Nucleophilic

transfer of allyl groups between two **4a** species could give diallyl decasulfide, one of the major products seen after only 5 min. Alternatively, **4a** could attack S₈ prior to allyl transfer giving an S₁₈ homolog of **4a**. Both **4a** and its S₁₈ homolog could split out sulfur (S_n) prior to allyl transfer, giving the observed family of polysulfanes **2a**. Further scrambling could occur through nucleophilic attack on **4a** by the allyl polysulfane anion formed from mono-deallylation of **4a**. Similar mechanisms can be written involving thiosulfoxides AllS(S)S_{n-2}All from diallyl polysulfanes; indeed, diallyl trisulfide **2a**, n = 3, as well as **1a** reacted with liquid S₈. Equilibration of the **2a** mixture by radical processes is also likely. Disulfides **1b–1e** can undergo similar processes. After 2 h at 120°C, **1f** failed to react. The unreactivity of **1f** is understandable, since the formation of thiosulfoxide **3f** should be disfavored due to the loss of conjugation.



Scheme 2. Proposed mechanism for polysulfane formation involving nucleophilic attack of thiosulfoxide sulfur on cyclooctasulfur.

To contrast this mechanism with the proposal of Mislow (*16b*) that both diallyl sulfide and diallyl disulfide attack S_8 in the same manner, without initial involvement of **3a**, we followed by NMR the progress of the reaction of an equimolar mixture of diallyl sulfide and disulfide with an excess of S_8 in the presence of an internal standard. *Diallyl disulfide disappears more than five times faster than the monosulfide*, consistent with our favored mechanism, since diallyl sulfide would be expected to be a stronger S nucleophile than diallyl disulfide (**1a**) in Mislow's mechanism.

The much slower reaction of saturated disulfides with liquid sulfur is also consistent with our proposal. When dibenzyl disulfide is stirred with liquid S_8 under the above conditions, in contrast to **1a**, only 20% reaction occurs after 3 h. Saturated disulfides are presumed to react with sulfur via free radical processes, with higher activation energies than the processes proposed for diallyl disulfides. While α -toluenethiol reacts rapidly with liquid S_8 , giving H₂S and dibenzyl polysulfanes, 2-propenethiol reacts with S_8 in the presence of catalytic diethylamine at 50°C giving a polymer, through addition of sulfur to the double bond, precluding the use of this approach to polysulfanes **2a** (*19*).

GO is a ~4:1 mixture of **2a** and allyl methyl polysulfanes, $MeS_nCH_2CH=CH_2$ (**5**), and various minor products including dimethyl polysulfanes, Me_2S_n (7). UPLC-(Ag⁺)CIS-MS analysis of GO showed it to contain Me_2S_n , **2a**, n = 3-8, and **5**, n = 3-8, as well as families of isomeric compounds $C_9H_{14}S_n$, n = 2-10 (**6**, 7), $C_5H_{12}S_n$, n = 2-7 (**8a**), $C_7H_{14}S_n$, n = 2-8 (**8b** and **8c**)



Scheme 3. Formation of silver chelators in liquid sulfur-treated GO.



Figure 4. UPLC-(Ag⁺)CIS-MS TIC of diallyl polysulfane (2a) in GO before (2a, n = 3-9; left) and after (2a, n = 4-17; right) liquid S₈ treatment. The vertical axis in each trace represents the signal intensity, approximating the relative abundance of each peak.

and $C_9H_{16}S_n$, n = 2-10 (8d) (Scheme 3). Many of the compounds found are new, although they were not individually isolated. The enhanced sensitivity seen for 7 and 8 using (Ag⁺)CIS-MS compared with the earlier GC–MS studies (7d) reflects the good Ag⁺ chelating ability of 7 and 8 (Scheme 3, boxes). X-ray structures of Ag⁺ and Cu(I)⁺ complexes of 2a, n = 1-4, show that the Group Ia metals coordinate to both S as well as C=C (20, 21). However, using synthetic 8a (m = n = 2), we find (Ag⁺)CIS-MS to be ~100 times more sensitive to 8a than 2a (n = 1 or 2). Individual families of polysulfanes are seen by MS by extracting selected ions (Figures 4 and 5).

The mechanism for the formation of **6–8** follows from our prior work (7*d*) showing that: (1) C–S bond cleavage in **1a** is energetically favored over S–S bond cleavage. (2) Radical addition, giving a primary carbon radical (**B**), is followed by H• abstraction/thioacrolein-forming fragmentation and Diels–Alder addition of thioacrolein giving dihydrothiopyrans **6** and **7** along with the formation and trapping of thiyl radical **B**' giving **8**. The alternative process, radical addition giving



Figure 5. UPLC-(Ag⁺)CIS-MS TIC of GO components. $C_5H_{12}S_n$ polysulfanes **8a**, n = 2-7 (left) and $C_9H_{16}S_n$ polysulfanes **8d**, n = 2-10 (right) (x + y = n; different x, y combinations for the same value of n result in multiple or split peaks). The vertical axis represents signal intensity, approximating the relative abundance of each peak.

a secondary carbon radical (A), followed by H• abstraction/thioacrolein-forming fragmentation and the Diels–Alder formation of 6, 7 as above, along with the formation and trapping of thiyl radical A' giving 9, is clearly much less favorable, given that only trace amounts of 9 are found. (3) The process is completed by scrambling of the R/R' groups (methyl or allyl) and the number of sulfur atoms in each separate chain. The presence in GO of 8, previously demonstrated by GC–MS through comparison with authentic standards, also follows from the presence of characteristic ¹H NMR methyl group doublets from 1.34 (8, m = n = 1) to 1.37 ppm (8, m = n = 2) as well as ¹³C NMR methyl signals in the expected region (7c) for 8. When liquid sulfur and GO were kept at 120°C for 30 min, UPLC-(Ag⁺)CIS-MS showed that, while families of higher polysulfanes 2a, n = 3-17 (Figure 4), and 5, n = 6-14, were formed, other families of compounds lacking allyl groups, or having isolated allyl groups, such as Me₂S_n and 6–8, were unchanged, or diminished in concentration. Notably, allyl methyl sulfur also reacted giving polysulfanes with up to 14 contiguous sulfur atoms.

Our polysulfane synthesis is attractive in that it is fast and solvent free and, for **1a** and GO, uses only naturally occurring materials, in atom-economical one-step, one-pot processes, well suited for scale-up. Our method is tolerant of functionality, providing access to new materials of varying solubility and other properties. The higher polysulfanes, now very easily synthesized by our route, should show very interesting biological activity by analogy to that of the well-studied **2a**, n = 2-5 (8). As demonstrated by our work with GO, UPLC-(Ag⁺)CIS-MS represents a powerful technique for analysis of complex mixtures of non-polar sulfur compounds, particularly those with multiple sulfur atoms which can chelate silver (or other metal ions). Finally, in view of the natural occurrence of liquid sulfur in proximity to thermophilic microorganisms, it would be of interest to search for sulfur-rich natural products formed by the processes described here.

3. Experimental

3.1. General

Reagents were obtained from commercial sources and used without further purification. Dry diethyl ether and THF were distilled from sodium–benzophenone under argon. All other dried solvents were obtained by storage over 3 or 4 Å molecular sieves overnight. ¹H (400 MHz) and ¹³C (100.5 MHz) NMR spectra were obtained on a Bruker Avance 400 NMR spectrometer. Chemical shifts were referenced to residual ¹H and ¹³C signals of the deuterated chloroform (¹H 7.26 ppm and ¹³C 77.36 ppm). UV–VIS spectra were obtained on a Varian Prostar 330 photodiode array

detector. Analytical TLC was performed on Merck silica gel 60 F254 TLC plates and visualized by UV or I₂/silica. Flash chromatography was carried out with Adedge 32-63 D 60Å silica gel. Analytical HPLC analysis was performed on Varian Prostar 210 with Microsorb-MV 100-5 C18 250 \times 4.6 mm column and Varian Prostar 330 photodiode array detector. Preparative HPLC isolations were performed on Varian Prostar 218 with Rainin Dynamax[®] 60Å C18 250 \times 21.4 mm column and Varian Prostar 325 UV–VIS detector. UPLC-(Ag⁺)CIS-MS analysis was carried out by Dr. Robert Sheridan on a Waters Acquity UPLC with Waters Quattro Premier XE triple quadrupole mass spectrometer. Detailed UPLC-(Ag⁺)CIS-MS data for the various polysulfane mixtures is provided in the Supporting Information.

3.2. Bis-(2-propenyl) polysulfane mixture (2a)

Cautionary note: when working on a much larger scale than described below (e.g. \geq 100 larger), it is important to avoid heating significantly above 120°C by providing quick removal of the heating source as well as external cooling as needed, together with adequate stirring. Overheating can result in an exothermic reaction with darkening and gas evolution. A 10 ml round-bottomed flask containing sublimed sulfur (S₈, 0.640 g, 2.50 mmol) was placed in an oil bath pre-heated to 120°C. When all of the sulfur had melted into a clear, straw-colored liquid, **1a** (0.365 g, 2.50 mmol) was added all at once to the magnetically stirred liquid (1.1:1 S_8 :1a ratio). Within 3 min, the initial cloudy two-layer liquid mixture became clear and homogeneous. Samples were withdrawn for analysis at 5 min, 30 min, 1 h, 1.5 h, and 2 h. These samples were dissolved in CDCl₃ permitting both NMR and reversed phase HPLC analysis to be performed simultaneously. HPLC traces are given in the Supporting Information. For the 30 min sample, disulfide 1a eluted at 3.8 min, S_8 eluted between the heptasulfide and octasulfide at 23.8 min, and the highest polysulfane seen, eluting at 149 min, had a chain of 21 sulfur atoms. Similar results were obtained using diallyl trisulfide instead of 1a. When the reaction of 1a and S_8 is sampled after 1 h, less sulfur remains and the strongest polysulfane peak shifts to a higher number of sulfur atoms than for the 30 min sample. Individual pure polysulfanes can be isolated by preparative HPLC (85:15 MeOH:H₂O) on a reversed phase column, with concentration under reduced pressure, extraction into pentane, drying (Na₂SO₄), and re-concentration. Higher polysulfanes, for example, diallyl hexasulfide, are sensitive to light and traces of ammonia or amines and should be refrigerated. Purity after preparative HPLC was established by analytical HPLC as well as by ¹H NMR, as illustrated for diallyl trisulfide (2a, n = 3) and diallyl hexasulfide (2a, n = 6), as representative examples (see Supporting Information for ¹H NMR spectra and UPLC-(Ag⁺)CIS-MS data). Ethanol and methanol only partially dissolved 2a. The soluble and insoluble portions of 2a in EtOH and MeOH, after concentration, were separately redissolved in CDCl₃ and analyzed (¹H NMR). In MeOH/EtOH insoluble portions, only one δ 3.64 doublet signal corresponding to SCH₂ for **2a** (n > 5) appeared, whereas in MeOH/EtOH soluble portions, four doublets δ 3.10–3.62 corresponding to SCH₂ for **2a** (n = 2, 3, 4, 5) appeared. A smaller δ 3.64 doublet (SCH₂ for **2a**, $n \ge 5$) was found in the soluble portion in MeOH compared with EtOH, suggesting that higher polysulfanes 2a ($n \ge 5$) have less solubility in MeOH than in EtOH.

3.3. Ethanethioic acid, S-(2-methyl-2-propenyl) ester

Potassium thioacetate (2.50 g, 22 mmol) was added to a solution of 3-chloro-2-methylprop-1-ene (1.81 g, 20 mmol) in THF (50 ml). The mixture was stirred overnight giving an orange-yellow solution with a colorless precipitate. The solution was passed through a silica gel pad and then concentrated *in vacuo* to give a yellow oil (1.50 g, 58%) which was directly used for the next step; ¹H NMR (400 MHz, CDCl₃) δ 1.73 (s, 3H), 2.32 (s, 3H), 3.52 (s, 2H), 4.81 (s, 1H), 4.92 (s, 1H); ¹³C NMR δ 21.16, 30.43, 35.98, 114.00, 140.73, 195.24 ppm.

3.4. Bis-(2-methyl-2-propenyl) disulfide (1b)

Sodium chips (0.24 g, 10.0 mmol) were added to dry MeOH (50 ml) at 0°C. The mixture was stirred until the sodium was consumed. Ethanethioic acid, *S*-(2-methyl-2-propenyl) ester (1.30 g, 10.0 mmol) was added to the above solution at 0°C followed by I₂ (1.26 g, 5.0 mmol) after 2 h. The mixture was stirred for 30 min and then concentrated and purified by silica gel column chromatography (hexane) giving the known (22) **1b** as a light yellow liquid (0.68 g, 67%); ¹H NMR (400 MHz, CDCl₃) δ 1.81 (s, 6H), 3.27 (s, 4H), 4.87 (s, 2H), 4.90 (s, 2H); ¹³C NMR δ 20.83, 46.45, 114.93, 140.72 ppm.

3.5. Bis-(2-methyl-2-propenyl) polysulfane mixture (2b)

See above cautionary note for 2a. Sublimed sulfur (S_8 , 0.640 g, 2.50 mmol) was liquefied as for 2a. When all of the sulfur had melted, a solution of 4, 4'-di-*tert*-butylbiphenyl (0.0308 g, 0.116 mmol) in 1b (0.415 g, 2.38 mmol) was added all at once to the magnetically stirred liquid (1.1:1 S_8 :1b ratio). Within 3 min, the initial cloudy two-layer liquid mixture became a clear and homogeneous solution with a single liquid layer. Samples were withdrawn for NMR/HPLC analysis at intervals as for 2a (see Supporting Information for HPLC and UPLC-(Ag⁺)CIS-MS data). For the 30 min sample, disulfide 1b eluted at 6 min, S_8 eluted at 24 min overlapping with the hexasulfide, the internal standard eluted at 37.5 min, and the highest polysulfane seen, eluting at 179 min, had a chain of 21 sulfur atoms.

3.6. Ethanethioic acid, S-(2-chloro-2-propenyl) ester

Potassium thioacetate (2.50 g, 22 mmol) was added to a solution of 3-chloro-2-chloroprop-1-ene (2.22 g, 1.83 ml, 20 mmol) in THF (50 ml). The mixture was stirred overnight to give an orange yellow solution with white precipitate. Workup as above gave a red liquid (2.31 g, 77% yield), used for the next step: ¹H NMR (400 MHz, CDCl₃) δ 2.37(s, 3H), 3.78 (s, 2H), 5.25 (s, 1H), 5.42 (s, 1H); ¹³C NMR δ 30.35, 36.81, 115.16, 137.45, 193.84 ppm.

3.7. Bis-(2-chloro-2-propenyl) disulfide (1c)

As for **1b**, to NaOMe from Na (0.24 g, 10.0 mmol) and MeOH (50 ml), ethanethioic acid, *S*-(2-chloro-2-propenyl) ester (1.50 g, 10.0 mmol) was added at 0°C followed by I₂ (1.26 g, 5.0 mmol). Workup gave the known (23) **1c** as a light yellow liquid (0.81 g, 75%); ¹H NMR (400 MHz, CDCl₃) δ 3.52 (s, 4H), 5.31 (s, 2H), 5.42 (s, 2H); ¹³C NMR δ 47.27, 116.39, 137.37 ppm.

3.8. Bis-(2-chloro-2-propenyl) polysulfane mixture (2c)

See above cautionary note for 2a. Sublimed sulfur (S₈, 0.256 g, 1.0 mmol) was liquefied as for 2a. When the sulfur had melted, 1c (0.215 g, 1.0 mmol) was added. Within 3 min the initial twolayer liquid mixture became clear and homogeneous. Samples were withdrawn for NMR/HPLC analysis at intervals as for 2a (see Supporting Information for HPLC and UPLC-(Ag⁺)CIS-MS data). For the 30 min sample, disulfide 1c eluted at 4 min, S₈ eluted between the heptasulfide and octasulfide at 23.7 min, and the highest polysulfane seen, eluting at 159 min, had a chain of 23 sulfur atoms.

3.9. Ethanethioic acid, S-(3-methyl-2-butenyl) ester

Potassium thioacetate (2.50 g, 22 mmol) was added to a solution of 1-bromo-3-methylbut-2-ene (2.98 g, 2.33 ml, 20 mmol) in THF (50 ml). After overnight stirring, workup gave a yellow oil (2.86 g, 99%), used for the next step; ¹H NMR (400 MHz, CDCl₃) δ 1.66 (s, 3H), 1.69 (s, 3H), 2.29 (s, 3H), 3.49, 3.51 (d, 2H), 5.18 (t, 1H); ¹³C NMR δ 17.75, 25.61, 27.39, 30.41, 118.60, 136.59, 196.04 ppm.

3.10. Bis-(3-methyl-2-buten-1-yl) disulfide (1d)

As for **1b**, to NaOMe from Na (0.12 g, 5.0 mmol) and MeOH (25 ml) at 0°C, ethanethioic acid, *S*-(3-methyl-2-butenyl) ester (0.72 g, 5.0 mmol) was added to the above solution at 0°C followed by I₂ (0.63 g, 2.50 mmol). Workup gave the known (23) **1d** as a light yellow liquid (0.36 g, 71%); ¹H NMR (400 MHz, CDCl₃) δ 1.69 (s, 6H), 1.76 (s, 6H), 3.37, 3.39 (d, 4H), 5.27 (t, 2H); ¹³C NMR (CDCl₃) δ 17.94, 25.80, 37.58, 119.44, 137.14 ppm.

3.11. Bis-(3-methyl-2-buten-1-yl) polysulfane mixture (2d)

See above cautionary note for 2a. Sublimed sulfur (S_8 , 0.256 g, 1.0 mmol) was liquefied as for 2a. When the sulfur had melted, 1d (0.202 g, 1.0 mmol) was added. After 35 min, the initial two-layer liquid mixture turned red and became homogeneous. Samples were withdrawn for NMR/HPLC analysis at intervals as for 2a (see Supporting Information for HPLC and UPLC-(Ag⁺)CIS-MS data). For the 6 h sample, disulfide 1d eluted at 9.4 min, S_8 eluted between the tetrasulfide and pentasulfide at 22.7 min, and the highest polysulfane seen, eluting at 187 min, had a chain of 20 sulfur atoms.

3.12. Ethanethioic acid, S-2-cyclohexen-1-yl ester

Potassium thioacetate (1.25 g, 11 mmol) was added to a solution of 3-bromocyclohex-1-ene (1.61 g, 10.0 mmol) in THF (25 ml). The mixture was stirred overnight to give a brown solution with white precipitate. Workup as above gave the known (24) title compound as a brown liquid (1.35 g, 87% yield), used for the next step; ¹H NMR (400 MHz, CDCl₃) δ 1.64–2.02 (m, 6H), 2.28 (s, 3H), 3.72 (m, 1H), 5.60 (m, 1H), 5.80 (m, 1H); ¹³C NMR δ 19.97, 24.64, 29.48, 30.45, 39.82, 126.14, 130.78, 195.72 ppm.

3.13. Bis-(2-cyclohexen-1-yl) disulfide (1e)

As for **1b**, to NaOMe from Na (0.12 g, 5.0 mmol) and MeOH (25 ml) at 0°C, ethanethioic acid, *S*-2-cyclohexen-1-yl ester (0.78 g, 5.0 mmol) was added at 0°C followed by I₂ (0.63 g, 2.5 mmol). Workup gave the known (23) **1e** as a light yellow liquid (0.44 g, 78%); ¹H NMR (400 MHz, CDCl₃) δ 1.78–1.99 (m,12H), 3.47–3.51 (m, 2H), 5.72 (m, 2H), 5.84 (m, 2H); ¹³C NMR δ 18.86, 25.14, 28.31, 47.98, 126.30, 131.39 ppm.

3.14. Bis-(2-cyclohexen-1-yl) polysulfane mixture (2e)

See above cautionary note for 2a. Sublimed sulfur (S₈, 0.256 g, 1.0 mmol) was liquefied as for 2a. When the sulfur had melted, 1e (0.226 g, 1.0 mmol) was added. Within 3 min, the initial two-layer liquid mixture became a clear, homogeneous solution. Samples were withdrawn for NMR/HPLC analysis at intervals as for 2a (see Supporting Information for HPLC and UPLC-(Ag⁺)CIS-MS

data). For the 2 h run, disulfide **1e** eluted at 14.5 min, S_8 overlapped with the trisulfide at 23.7 min, and the highest polysulfane seen, eluting at 226 min, had a chain of 19 sulfur atoms.

3.15. 1,2-Bis(methylthio)propane (8a)

Sodium metal (0.46 g, 10 mmol) was added to MeOH (10 ml) at 0°C. After the Na disappeared, 1,2-propanedithiol (1.0 g, 9 mmol) was added and the mixture was stirred at rt for 1 h. Methyl iodide (2.84 g, 10 mmol) was added and the mixture was refluxed for 2 h. Water was added and the mixture was extracted with pentane. The combined, dried (Na₂SO₄) extracts were concentrated *in vacuo*, giving the known (25) **8a** as a colorless oil (1.13 g, 93% yield); ¹H NMR (400 MHz, CDCl₃) δ 1.35 (d, J = 6.6 Hz, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.53 (m, 1H), 2.81 (m, 2H).

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Supporting Information

NMR and UV spectra, HPLC, UPLC- (Ag^+) CIS-MS TIC and Ag-complex data for 1a-1e and 2a-2e and GO components are provided as Supporting Information.

Note

1. This sulfaxides are typically drawn with an S=S double bond (17), but the π -bond is calculated to be polarized, with the terminal sulfur being negatively charged (18), and capable of functioning as a nucleophile (7d).

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