Flash Vacuum Thermolysis – Synthesis and Characterization of Unstabilized Cycloalkenethiones

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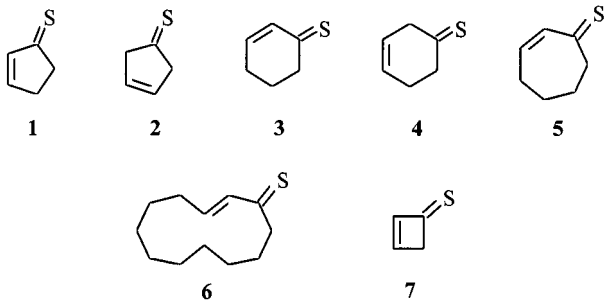
The flash vacuum thermolysis (FVT) of cycloalkenyl allyl (or propargyl) sulfides **8**, **9**, **12**, and **13** led, as the main thermal pathway, to the conjugated cycloalkenethiones **1**, **3**, and **5**, resulting from a retro-ene reaction. These reactive thioketones, thus obtained in ca. 70% yield, have been characterized in the gas phase by mass spectrometry, and at low temperature by IR, UV/Vis and NMR spectroscopy. The polymerization of **1**, **3**, and **5** upon warming is generally more rapid than the other attempted reactions and only the [2 + 3] dipolar cycloaddition with diazomethane led in low yield, besides polymeric materials, to isomeric 1,3-dithiolanes **20** from cyclopentenethione **1**. The obtention of the nonconjugated cycloalkenethiones **2** and **4**, expected in the FVT of sulfides **10** and **11**, has been confirmed only by UV/Vis spectroscopy at –196 °C, due to their rapid enethiolization. In the case of the large-ring sulfide **14**, the (*E*) geometry of the double bond favoured the competitive retro-ene reaction yielding cyclododecene and propynethial; on the other hand, the FVT of the tricyclic *gem*-dithiol **15**, a possible precursor of cyclobutenethione (**7**), led to vinyl thioketene (**18**), obtained by thermal ring opening of **7**.

The chemistry of thioketones and other thiocarbonyl compounds has been extensively investigated[1]. Also, the various routes to the most reactive terms in these series, using appropriate methods such as flash vacuum thermolysis (FVT), have been recently reviewed[2].

Among these compounds, α,β-unsaturated thioketones have been only scarcely studied[1a] and nothing reported, to our knowledge, about the obtention and properties of the simplest conjugated or nonconjugated cycloalkenethiones, i.e. those possessing no stabilizing substituent on the ring carbon atoms. However, by analogy with the stable β-substituted cyclopentene- and cyclohexenethiones[3], an interesting reactivity could be expected from these thioketones.

We report here our results concerning the synthesis by FVT, spectrometric identification, and thermal evolution of five unsubstituted, α,β- or β,γ-unsaturated thioketones in the *cyclo*-C_5−C_7 series (Scheme 1, compounds **1**−**5**; see ref.[4] for a preliminary report on **1** and **3**). This work has been also tentatively enlarged, with compounds **6** and **7**, to two unsaturated thioketones possessing large (C_{12}) and small (C_4) ring backbones.



Scheme 1

Synthesis of Precursors

The retro-ene reaction, when used under the conditions of FVT, is an efficient method for generating reactive, unsaturated species[5]. This thermal cleavage, reported to be easier and more concerted for allyl sulfides, relative to the corresponding ethers and amines[6], has already been applied to the synthesis of several reactive thiocarbonyl compounds[7]. In the absence of steric hindrance, the retro-ene reaction can be further facilitated when replacing the allylthio moiety by a propargylic one, due to the planar transition state involved in the last case only[8].

The above considerations, added to the simple syntheses of sulfides **8**−**14**, led us to retain these compounds as possible precursors of cycloalkenethiones **1**−**6**. Three general methods have been used for the preparation of **8**−**14** (Scheme 2). The corresponding allylic bromides can be converted into sulfides **8** and **9** by reaction with 2-propene-1-thiol and *n*-butyllithium in ether (method [A]). Sulfides **10** and **11** were obtained from the less reactive homoallylic mesylate or bromide by action of 2-propene-1-thiol and cesium carbonate in DMF[9] (method [B]). For the preparation of propargylic sulfides **12**−**14**, the need of 2-propyne-1-thiol has been avoided by transforming at first the bromides, via their isothiouronium salts, into the corresponding thiols[10],

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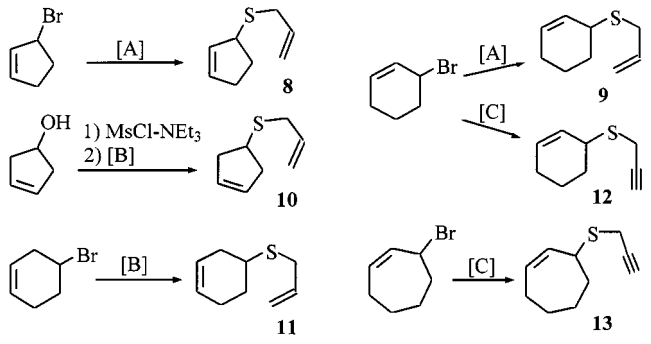
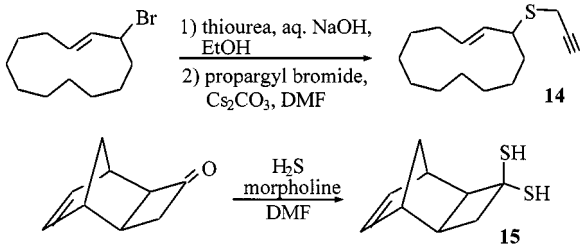
which in turn yield sulfides **12**−**14** when treated by propargyl bromide and cesium carbonate in DMF (method [C], modified for **14**, see Experimental Section).

Owing to the expected reactivity of the cyclobutene derivatives, we chose as a precursor of the elusive cyclobutenethione (**7**) the tricyclic *gem*-dithiol **15**. Compound **15**, obtained from the corresponding cyclobutanone[11] by action of hydrogen sulfide in the presence of morpholine[12], may give **7** directly upon FVT by retro-Diels−Alder reaction and β-elimination of hydrogen sulfide (a similar β-elimination has been successfully used for the generation of cyclobutanethione[13]).



[A] 2-propene-1-thiol, *n*-butyllithium, ether
[B] 2-propene-1-thiol, cesium carbonate, DMF
[C] 1) thiourea, tetraethylenepentamine, triethyleneglycol
2) propargyl bromide, cesium carbonate, DMF



Scheme 2

FVT of Compounds 8−15, Spectrometric Investigations

The FVT of precursors **8**−**15** have been performed under 10^{-5} hPa at temperatures ranging from 550 to 800°C (see Experimental Section, general conditions).

When starting from sulfides **8**, **9**, **12**, and **13**, the expected conjugated cycloalkenethiones **1**, **3**, and **5** were obtained as the major thermolysis products (yields ca. 70%, estimated by NMR as those of the co-formed propene or allene by comparison with a benzene quantitative standard), besides propene or allene, providing that the FVT temperature was maintained as low as possible, still allowing the complete decomposition of the precursor (600°C in the case of allylic sulfides **8** and **9**, 550°C for the propargylic sulfides **12** and **13**).

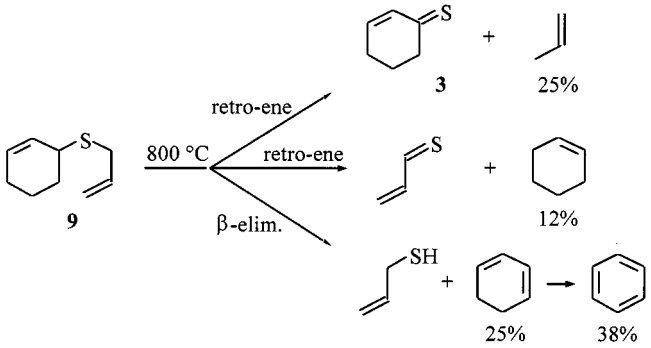
The purple-blue compounds **1**, **3**, and **5**, stable below −80°C, have been characterized in the gas phase by FVT-MS coupling, in the solid state at −196°C by UV/Vis and IR spectrometry, as well as by NMR at −80°C in CD_2Cl_2/$CFCl_3$ solution. The most characteristic features of these spectra, fully reported in the Experimental Section, are given in Table 1. The obtained values are in good agreement with those reported for stable substituted analogues[3a,14].

Table 1. Characteristic spectral data for the conjugated cycloalkenethiones **1**, **3**, and **5**

Compound	**1**	**3**	**5**
$M^{+\cdot}$	98.0163	112.0373	126.0506
$\delta_H{}^2$	6.74	6.72	6.80
$\delta_H{}^3$	7.94	6.89	6.71
JH^2H^3	5.2	9.6	11.2
JH^2H^4	2.0	1.9	[a]
JH^3H^4	2.9	4.2	6.1
$\lambda max_{n\rightarrow\pi^*}$(nm)	524	554	553
$\nu_{C=C}(cm^{-1})$	1553	1586	1582
IR absorptions related to C=S	1264, 1183, 1082	1252, 1151, 1126	1218, 1170, 1105

[a] Nonmeasurable *J*.

The specificity of the thermal decomposition of compounds **8**, **9**, **12**, and **13** decreases when increasing the FVT temperature, as shown in the case of allyl cyclohexenyl sulfide **9**, which gave upon FVT at 800°C a mixture of products resulting from competitive retro-ene reactions and, mainly, β-eliminations (Scheme 3).



Scheme 3

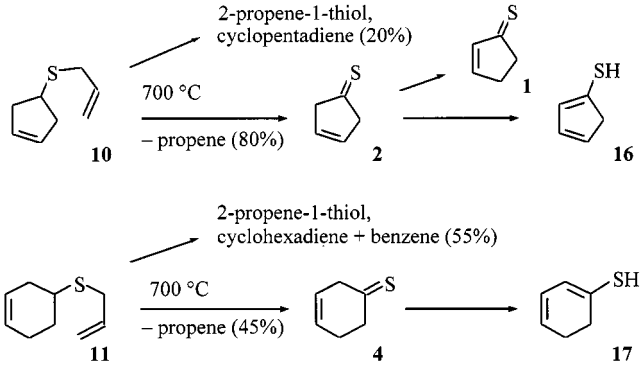
Less straightforward results were obtained in the thermolysis of sulfides **10** and **11**, precursors of the nonconjugated cycloalkenethiones **2** and **4**. The presence of compounds **2** and **4** is likely, between −196 and −90°C, from the orange colour of the thermolysis products and the corresponding n → π* transitions at 491 (**2**) and 475 nm (**4**), found at similar wavelengths to saturated thioketones[15]. Upon warming, the orange colour of **2** turns rapidly pink, indicating a possible partial reconjugation into **1**, then vanishes (Scheme 4).

The IR spectra are too complicated to attribute definitely the absorption bands of thioketones **2** and **4**. The most prominent feature in these spectra is the large amount, already present at −196°C, of cycloalkadienethiols **16** and **17** (ν_{SH} = 2460 and 2500 cm^{-1}, respectively).

The presence of cyclopentadienethiol **16** has been confirmed, besides cyclopentadiene (resulting from the compet-

ing β-elimination) and propene (20:80), in the NMR spectrum of the FVT products of **10**, showing four multiplets at δ = 6.31 (H^2), 6.44 (H^3), 6.37 (H^4), 3.10 (H^5), and a SH singlet at 2.89. This spectrum, recorded at −40°C in $CD_2Cl_2/CFCl_3$, is in good agreement with that described for the *S*-methylated analogue of **16**[16]. Small amounts of 2-propene-1-thiol and conjugated cyclopentenethione **1** were also visible in this spectrum. The β-elimination is more favoured in the FVT of **11** [(cyclohexadiene + benzene)/propene, 55:45] and, due to the large amounts of these by-products, the NMR spectrum of dienethiol **17** could not be definitely established. Also, the possible conjugation of **4** into **3** has not been pointed out.

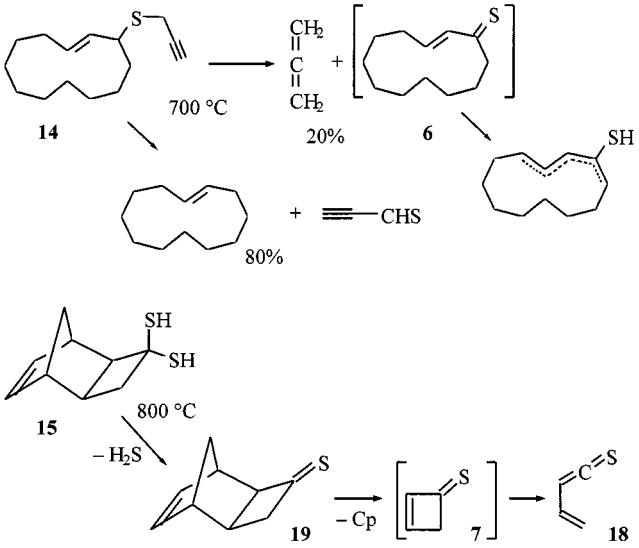
The molecular ions at *m/z* 98.0186 (calcd. C_5H_6S 98.0189) and 112.0343 (calcd. C_6H_8S 112.0347) have been obtained, in the FVT of **10** and **11**, respectively, by high resolution mass spectrometry (HRMS) under electron impact (EI) ionization. The fragmentation pattern of these molecular ions has been investigated by direct coupling with the mass spectrometer, using the B/E linked scan technique, and compared with the fragmentation of the molecular ions arising from the conjugated thioketones **1** and **3** in the FVT of **8** and **12**. Similar fragments are found as a rule, although with clearly different ion abundance (see Experimental Section for a full description). Noteworthy is the abundance discrepancy, confirming the presence of dienethiol **17** as the main compound, observed for the ion at *m/z* 79 (loss of SH) coming from the molecular ion at *m/z* 112 in the FVT product of **11** (100%) relative to that originating from **3** (88%), and mainly for the ion at *m/z* 84 (retro-Diels−Alder under EI, 28% in the FVT of **11**, 92% for **3**).



Scheme 4

In the FVT of cyclododecenyl sulfide **14** (700°C), the retro-ene reaction is mainly directed, probably due to the (*E*) geometry of the cyclic double bond, towards the formation of cyclododecene (cyclododecene/allene ratio 80:20) (Scheme 5). The presence of thioketone **6** has not been suggested by its colour or spectrometric data. Besides cyclododecene and allene, the IR spectrum at −196°C shows a transient band at 2070 cm^{-1}, possibly belonging to propynethial[17] co-formed with cyclododecene. The SH absorption at 2540 cm^{-1}, as well as the peak at *m/z* 196 ($M^{+\cdot}$, 13%) in the mass spectrum of the FVT products, are attributed to an enethiolic isomer of **6**. No β-elimination products were observed in this instance.

The FVT of *gem*-dithiol **15** (Scheme 5) was complete at 800°C, as shown in the NMR spectrum of the thermolysis products by the absence of **15** and the formation of cyclopentadiene and hydrogen sulfide. No evidence was found in the IR spectrum at −196°C supporting the presence of cyclobutenethione itself (**7**). On the other hand, that of its thermal ring opening product, vinyl thioketene (**18**), was clearly established by its absorptions at 1740 (strong, C=C=S) and 1600 cm^{-1} (medium, C=C), disappearing together at −130°C. A quite similar band (1738 cm^{-1}) has been previously described for the only reported α,β-ethylenic thioketene, isopropenyl thioketene[18]. Also, the presence of cyclobutanethione **19**, formed as an intermediate in the thermolysis of **15**, is obvious in the mass spectrum of the FVT products by its molecular peak at *m/z* 150 (72%).



Scheme 5

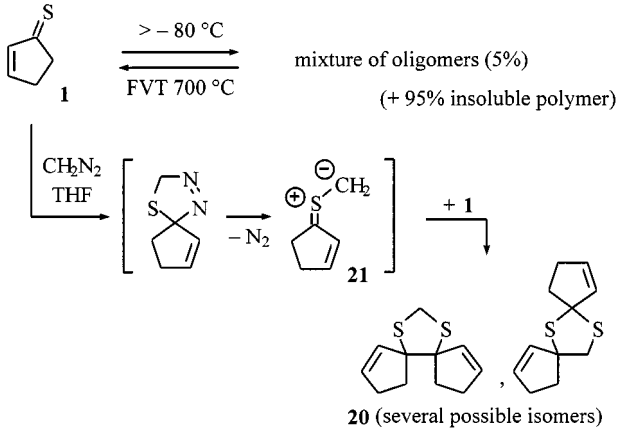
Cyclopentenethione 1, Thermal Evolution and Cycloaddition with Diazomethane

Cycloalkenethiones **1**, **3**, and **5** do not enethiolize upon warming but polymerize extremely rapidly, as shown here in the case of cyclopentenethione **1**.

The deep colour of **1** faded rapidly above −80°C and an insoluble white polymer was recovered at room temperature. A small amount of soluble oligomer could be extracted by ether and was shown to be mainly a dimer from its mass spectrum. This compound gave again monomeric **1** upon FVT (Scheme 6).

This extremely rapid polymerization overwhelmed the attempted reactions of **1** with ethylmagnesium bromide and with ketene. The [2 + 3] dipolar cycloaddition of thioketone **1** with diazomethane was just rapid enough to allow the formation of a cycloaddition product, obtained in low yield besides polymeric **1**. Its mass spectrum suggests, by analogy with the results reported on the cycloaddition of stable

thioketones with diazomethane[3d,19], the formation of one or several regio- and stereoisomeric 1,3-dithiolanes **20**, resulting from the reaction of excess **1** with the transiently formed thiocarbonyl ylide **21**. The possibility to obtain, according to the involved starting compounds and experimental conditions, various intermediates and products in such dipolar cycloadditions has, however, been pointed out more recently[20] and the structure of **20** could not be more precisely defined, due to the low amount obtained and the presence of oligomeric **1**.



Scheme 6

Experimental Section

General: All reactions were carried out under nitrogen. Solvents and starting materials were distilled prior to use. − IR: Perkin-Elmer 1420. − UV/Vis: Jobin-Yvon 201. − NMR: Bruker DPX 250 and DRX 400, operating at 250.13 and 400.13 MHz for ^1H, 62.89 and 100.62 MHz for ^{13}C, TMS as internal standard, solvents as indicated. − MS: Jeol GCmate and AX 500.

FVT of Compounds 8−15: Typically, the precursors **8**−**15** (ca. 25 mg) were thermolyzed between 550 and 800°C under 10^{-5} hPa in an empty quartz tube (dimensions: *l* = 10 cm, *i.d.* = 14 mm). As needed, the oven was coupled either to UV/Vis or IR cryostats, allowing direct recording of spectra under vacuum between −196 and +25°C, or to a high resolution mass spectrometer. In the UV/Vis spectra, (sh) refers to a shoulder. For NMR experiments, the products of thermolysis were trapped at −196°C on a cold finger coated with the appropriate solvent ($CDCl_3$ or, for the low temperature spectra, a 50:50 $CD_2Cl_2/CFCl_3$ mixture).

Preparation of Sulfides 8 and 9. − General Method A: *n*-Butyllithium (1.4 M in hexane, 10 mmol) was added dropwise to a solution of 2-propene-1-thiol (15 mmol), stirred at −30°C under nitrogen in anhydrous ether (10 mL). After warming up to room temperature, the mixture was cooled again to −50°C and the bromocycloalkene (10 mmol) was added slowly. The mixture was allowed to warm up and stirred 2 h at room temperature. After washing with aqueous ammonium chloride, drying on magnesium sulfate and removing solvents under vacuum, the residue was purified by bulb-to-bulb distillation under vacuum and finally gas-phase chromatography at 150°C on a SE30 column.

Sulfide 8: 0.91 g of **8** (yield 65%, after bulb-to-bulb distillation) was obtained according to method [A] from 3-bromocyclopentene (prepared following a literature procedure[21]). ^1H NMR ($CDCl_3$): δ = 1.8−2.6 (4 H), 3.17 (dm, *J* = 7.1 Hz, 2 H), 3.83 (m, 1 H), 5.07 (dm, *J* = 10.9 Hz, 1 H), 5.13 (dm, *J* = 17.7 Hz, 1 H), 5.80 (m, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 29.7, 31.0, 34.2, 50.0, 116.9, 131.8, 132.8, 134.5. − IR (liquid film): $\tilde{\nu}$ = 1635 cm^{-1} (−CH=CH_2). − $C_8H_{12}S$ (140): calcd. S 22.86; found S 23.18.

Sulfide 9: Obtained from commercial 3-bromocyclohexene. Yield 1.23 g (80%). ^1H NMR ($CDCl_3$): δ = 1.5−1.9 (4 H), 2.01 (m, 2 H), 3.17 (dm, *J* = 7.2 Hz, 2 H), 3.33 (m, 1 H), 5.06 (dm, *J* = 10.5 Hz, 1 H), 5.12 (dm, *J* = 17.1 Hz, 1 H), 5.78 (m, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 19.8, 25.1, 29.0, 34.2, 39.5, 116.8, 127.6, 129.8, 135.0. − IR (liquid film): $\tilde{\nu}$ = 1637 cm^{-1} (−CH=CH_2). − $C_9H_{14}S$ (154): calcd. S 20.78; found S 21.18.

Preparation of Sulfides 10 and 11

General Method [B]: Cesium carbonate (2 g, 6.17 mmol, 2 equiv.) was dissolved in anhydrous DMF (10 mL). The solution was degassed under vacuum, then stirred under nitrogen. 2-Propene-1-thiol (0.55 mL, 6.17 mmol) and the used mesylate or bromide (6.17 mmol) were added and the mixture stirred at 60°C for 9 h (mesylate) or 1 h (bromide). After addition of water, the solution was extracted with ether and the organic phase washed with brine and dried over magnesium sulfate. The crude sulfides were purified as in method [A].

Sulfide 10: Cyclopent-3-en-1-ol (1.68 g, 20.2 mmol, prepared according to the literature[22]) and triethylamine (3.36 mL, 24.3 mmol) were cooled to −20°C in dichloromethane (20 mL). Methanesulfonyl chloride (1.7 mL, 22.2 mmol) was added dropwise. After warming up to 0°C, 1 N HCl (3 mL) was added and the organic layer separated, washed with aq. $NaHCO_3$ and dried with magnesium sulfate. Cyclopent-3-en-1-yl methanesulfonate was thus obtained in a practically pure state [oil, yield 2.9 g, (89%); ^1H NMR ($CDCl_3$): δ = 2.57−2.91 (m, 4 H), 3.00 (s, 3 H), 5.37 (tt, *J* = 6.6 and 6.1 Hz, 1 H), 5.72−5.78 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ = 38.6, 40.4, 81.3, 127.8]. 1 g (6.17 mmol) of this methanesulfonate was directly treated by 2-propene-1-thiol according to the general method [B] to give sulfide **10**. Yield 0.51 g (59%) after bulb-to-bulb distillation. − ^1H NMR ($CDCl_3$): δ = 2.34 (≈ ddd, *J* = 15.0, 5.5 and <1 Hz, 2 H), 2.76 (≈ ddd, *J* = 15.0, 8.2 and <1 Hz, 2 H), 3.18 (d, *J* = 7.0, 2 H), 3.41 (tt, *J* = 8.2 and 5.5, 1 H), 5.07 (dd, *J* = 9.6 and 1.2 Hz, 1 H), 5.12 (dd, *J* = 17.0 and 1.2 Hz, 1 H), 5.71 (br. s, 2 H), 5.85 (ddt, *J* = 17.0, 9.6 and 6.9 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 35.1, 40.2, 40.9 (2 C), 117.0, 129.7 (2 C), 135.0. − IR (liquid film): $\tilde{\nu}$ = 1636 cm^{-1} (−CH=CH_2). − $C_8H_{12}S$ (140): calcd. S 22.86; found S 22.21.

Sulfide 11: 4-Bromocyclohexene, prepared following the described procedure[22] was converted into sulfide **11** using method [B]. Yield 0.51 g (54%). − ^1H NMR ($CDCl_3$): δ = 1.51−1.69 (m, 1 H), 1.87−2.18 (m, 4 H), 2.31−2.45 (m, 1 H), 2.82−2.96 (m, 1 H), 3.20 (d, *J* = 7.2 Hz, 2 H), 5.07 (dd, *J* = 9.4 and 1.3, 1 H), 5.12 (dd, *J* = 16.7 and 1.3 Hz, 1 H), 5.59−5.73 (m, 2 H), 5.84 (ddt, *J* = 16.7, 9.4, and 6.7 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 25.2, 29.3, 32.6, 33.8, 38.9, 116.9, 125.9, 127.2, 135.3. − IR (liquid film): $\tilde{\nu}$ = 1637 cm^{-1} (−CH=CH_2). − $C_9H_{14}S$ (154): calcd. S 20.78; found S 21.23.

Preparation of Sulfides 12−14

General Method [C]: The bromocycloalkenes (0.19 mol) were added dropwise to a solution of thiourea (15.6 g, 0.2 mol) in triethyleneglycol (50 mL), heated at 75°C. The temperature was controlled to remain below 130°C during the addition and the mixture stirred until homogeneous. The reflux condenser was then replaced by a cooled Dean−Stark collector and the system evacuated to 10^{-3}

hPa. Tetraethylenepentamine (35.3 g, 0.19 mol) was added dropwise and the obtained thiols, collected in the Dean−Stark apparatus (yields ca. 60%), were dried over magnesium sulfate. These thiols (6.17 mmol) were directly transformed into the corresponding propargyl sulfides by reaction of propargyl bromide and cesium carbonate (1 equiv.) following the experimental procedure described in the general method [B].

Sulfide 12: Obtained from 3-bromocyclohexene. Yield 0.80 g (85%). − ^{1}H NMR ($CDCl_3$): δ = 1.5−1.9 (4 H), 1.96 (m, 2 H), 2.17 (t, *J* = 2.7 Hz, 1 H), 3.21 (m, 2 H), 3.55, 5.66 and 5.76 (3 m, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 18.6, 19.9, 25.0, 28.8, 40.7, 70.9, 80.6, 126.9, 130.6. − IR (liquid film): $\tilde{\nu}$ = 2115 and 3295 cm^{-1} (−C≡CH). − $C_9H_{12}S$ (152): calcd. S 21.06, found S 21.18.

Sulfide 13: Obtained from 3-bromocycloheptene. Yield 55%. Spectra identical with those previously described[23].

Sulfide 14: The reaction of 3-bromocyclododecene [prepared from 80% (*E*)-cyclododecene and *N*-bromosuccinimide] with thiourea was performed, due to the low volatility of products, with ethanol and aq. sodium hydroxide as described for the preparation of *n*-dodecane-1-thiol[10b], and the resulting thiol (62% yield) treated as above by propargyl bromide and cesium carbonate. Sulfide **14** was purified by flash chromatography on silica (eluent: *n*-pentane). Yield 0.60 g (41%). − ^{1}H NMR ($CDCl_3$): δ = 1.0−1.8 (16 H), 2.03 (m, 1 H), 2.21 (t, *J* = 5.0 Hz, 1 H), 2.26 (m, 1 H), 3.09 and 3.19 (dd AB, *J* = 16.8 and 5.0 Hz, 2 H), 3.47 (m, 1 H), 5.17 (dd, *J* = 15.1 and 1.4 Hz, 1 H), 5.46 (dt, *J* = 15.1 and 4.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 20.1, 25.8, 26.4, 27.2, 27.3, 28.1, 28.3, 33.8, 33.9, 40.9, 49.2, 72.3, 82.7, 132.5, 135.9. − IR (liquid film): $\tilde{\nu}$ = 2108 and 3300 cm^{-1} (−C≡CH). − $C_{15}H_{24}S$ (236): calcd. S 13.56, found S 13.38.

Preparation of *gem*-Dithiol 15

exo-Tricyclo[4.2.1.0^{2,5}]non-7-en-3-one (0.25 g, 1.86 mmol, prepared following the literature[11]) and morpholine (75 mg, 0.86 mmol) were dissolved in DMF (5 mL) and cooled to −10°C. Hydrogen sulfide was bubbled through the solution for 6 h. The mixture was kept 40 h at 0°C, then poured on ice. After addition of dilute HCl, the solution was extracted with pentane, washed with water, and dried with magnesium sulfate. Compound **15** (0.31 g, 91%) was thus obtained in a practically pure state. − ^{1}H NMR ($CDCl_3$): δ = 1.40 (m, 2 H), 1.95 (m, 2 H), 2.32 (br. s, 1 H), 2.56 (m, 1 H), 2.62 (s, 1 H, SH), 2.69 (br. s, 1 H), 2.94 (br. s, 1 H), 3.09 (s, 1 H, SH), 6.02 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 33.0, 41.6, 42.9, 43.9, 44.1, 44.5, 56.5, 135.4, 137.0. − IR (liquid film): $\tilde{\nu}$ = 2530 cm^{-1} (SH). − $C_9H_{12}S_2$ (184): calcd. S 34.79, found S 32.19.

FVT of Sulfides 8, 9, 12, and 13: Generation of Cycloalkenethiones 1, 3, and 5

Thioketones **1**, **3**, and **5** were typically prepared by thermolysis at 600°C (from sulfides **8** and **9**) or 550°C (from **12** and **13**) and their spectra recorded as indicated in the general conditions. The given yields and ratios were determined by NMR, using when appropriate a quantitative standard of benzene or *p*-dioxane. Thioacrolein, obtained in the FVT of **9** at 800°C, was characterized at −196°C by comparison with its previously described IR spectrum[24].

Cyclopent-2-enethione (1): HRMS; *m*/*z*: 98.0163 ($M^{+\cdot}$, calcd. C_5H_6S 98.01892). − MS (B/E linked scan, daughter ions of $M^{+\cdot}$); *m*/*z* (%): 71 (54), 70 (47), 69 (100), 65 (43), 63 (37), 58 (56), 57 (32), 53 (65), 45 (96), 39 (63), 27 (31). − UV/Vis (−196°C): λ = 297, 502 (sh), 524, 552 nm (sh). − IR (−196°C): $\tilde{\nu}$ = 1553, 1427, 1372, 1264, 1183, 1082, 921 cm^{-1}. − ^{1}H NMR (−80°C, CD_2Cl_2/$CFCl_3$): δ = 2.86 (m, 2 H^4), 2.98 (m, 2 H^5), 6.74 (dt, *J* = 5.2 and 2.0 Hz, 1 H^2), 7.94 (dt, *J* = 5.2 and 2.9 Hz, 1 H^3).

Cyclohex-2-enethione (3): HRMS; *m*/*z*: 112.0373 ($M^{+\cdot}$, calcd. C_6H_8S 112.03468). − MS (B/E linked scan, daughter ions of $M^{+\cdot}$); *m*/*z* (%): 84 (92), 79 (88), 78 (30), 77 (65), 71 (100), 70 (39), 69 (71), 67 (32), 66 (63), 65 (36), 58 (39), 51 (26), 45 (65), 39 (56). − UV/Vis (−196°C): λ = 236, 287, 531 (sh), 554, 583 nm (sh). − IR (−196°C): $\tilde{\nu}$ = 1586, 1400, 1252, 1151, 1126, 973 cm^{-1}. − ^{1}H NMR (−80°C, CD_2Cl_2/$CFCl_3$): δ = 1.97 (m, 2 H^5), 2.32 (m, 2 H^4), 2.96 (dd ≈ t, *J* ≈ 6.4 Hz, 2 H^6), 6.72 (dt, *J* = 9.6 and 1.9 Hz, 1 H^2), 6.89 (dt, *J* = 9.6 and 4.2 Hz, 1 H^3).

Cyclohept-2-enethione (5): HRMS; *m*/*z*: 126.0506 ($M^{+\cdot}$, calcd. $C_7H_{10}S$ 126.05030). − UV/Vis (−196°C): λ = 244, 302, 523 (sh), 553, 580 nm (sh). − IR (−196°C): $\tilde{\nu}$ = 1582, 1447, 1398, 1218, 1170, 1105, 1037, 840 cm^{-1}. − ^{1}H NMR (−80°C, CD_2Cl_2/$CFCl_3$): δ = 1.89 (m, 2 H^6), 2.31 (m, 2 H^5), 2.42 (m, 2 H^4), 3.27 (dd ≈ t, *J* ≈ 6.0 Hz, 2 H^7), 6.71 (dt, *J* = 11.2 and 6.1 Hz, 1 H^3), 6.80 (dm, *J* = 11.2 Hz, 1 H^2).

FVT of Sulfides 10 and 11: Generation of Compounds 2, 4, 16, and 17

Sulfides **10** and **11** were thermolyzed at 700°C and the FVT products analyzed as above.

Cyclopent-3-enethione (2) + Cyclopenta-1,3-dienethiol (16): HRMS; *m*/*z*: 98.0186 ($M^{+\cdot}$, calcd. C_5H_6S 98.01892). − MS (B/E linked scan, daughter ions of $M^{+\cdot}$); *m*/*z* (%): 71 (46), 70 (42), 69 (53), 65 (45), 63 (45), 62 (25), 58 (32), 57 (23), 53 (71), 45 (100), 39 (61), 27 (27). − UV/Vis (−196°C): λ = 216, 491 nm. − IR (−196°C): $\tilde{\nu}$ = 2460, 1640, 1510, 1445, 1426, 1357, 1234, 1039, 990 cm^{-1}. − ^{1}H NMR (−40°C, CD_2Cl_2−$CFCl_3$, **16**): δ = 2.89 (s, 1 H, SH), 3.10 (m, 2 H^5), 6.31 (m, 1 H^2), 6.37 (m, 1 H^4), 6.44 (m, 1 H^3).

Cyclohex-3-enethione (4) + Cyclohexa-1,3-dienethiol (17): HRMS; *m*/*z*: 112.0343 ($M^{+\cdot}$, calcd. C_6H_8S 112.03468). − MS (B/E linked scan, daughter ions of $M^{+\cdot}$); *m*/*z* (%): 84 (28), 79 (100), 78 (17), 77 (43), 71 (8), 69 (11), 67 (12), 66 (29), 65 (14), 58 (15), 51 (8), 45 (6), 39 (5). − UV/Vis (−196°C): λ = 230, 475 nm. − IR (−196°C): $\tilde{\nu}$ = 2500, 1640, 1580, 1447, 1426, 1366, 1350, 1325, 1250, 1125, 980, 915 cm^{-1}.

FVT of Sulfide 14

30 mg of sulfide **14** was introduced, using a sliding spatula, into the FVT oven preheated at 700°C. The products were analyzed by MS [*m*/*z* (%): 196 (13), 166 (15), 123 (20), 111 (30), 97 (54), 91 (60), 81 (80), 79 (72), 67 (100), 56 (83)]; by IR at −196°C showing transient absorptions, disappearing between −120 and −80°C, at 2540, 2070, 1950, 1510 and 1250 cm^{-1}; and by NMR at room temperature indicating the presence of cyclododecene and allene in a 80:20 ratio.

FVT of *gem*-Dithiol 15: Vinylthioketene (18) and Cyclobutanethione 19

The products of FVT (800°C) of *gem*-dithiol **15**, introduced as above with a sliding spatula, were analyzed by MS [*m*/*z* (%): 150 (72, $M^{+\cdot}$ of **19**), 136 (43), 135 (86), 134 (100), 117 (41), 116 (58), 115 (76), 91 (100), 84 (41), 79 (44), 77 (48), 71 (49), 69 (43), 66 (82), 65 (48), 63 (47)], and by IR at −196°C pointing out the presence of the transient bands of **18** at 1740 and 1600 cm^{-1}. These two absorptions vanished together below −130°C while another set of bands, belonging possibly to **19**, remained present until −80°C [1610, 1585, 1435, 1405, 1355, 1285, 1235, 1170, 1080, 1025, 990, 960, 915, 885, 830, 805, 770, 720 cm^{-1}]. The NMR spectrum

showed only the presence of cyclopentadiene and H_2S (δ ^1H = 0.83).

Thermal Evolution of 1

Sulfide **8** (0.5 mmol) was thermolyzed at 650°C and the products were trapped at −196°C on frozen pentane (2 mL). After warming up to room temperature, the white polymer obtained was extracted by ether and the solution evaporated under vacuum to give a small amount (ca. 5%) of a viscous colourless oil. MS; *m*/*z* (%): 196 (2.5), 98 (77). This oil was thermolyzed again at 700°C. The products, analyzed by IR spectroscopy at −196°C, were essentially the same as those obtained by FVT of **8**, showing all the absorptions belonging to monomeric cyclopentenethione **1**.

Cycloaddition of 1 with Diazomethane

Diazomethane (1 mmol in THF, prepared from 1-methyl-3-nitro-1-nitrosoguanidine) was evaporated at the oven exit during the FVT of sulfide **8** (0.5 mmol) and the effluents condensed on a cold finger at −196°C. After warming up to room temperature, the FVT products were extracted as above to give ca. 10% of a 70:30 mixture of oligomers of **1** and a product of cycloaddition, possibly a mixture of isomeric dithiolanes **20**: MS; *m*/*z* (%): 209 [$M^{+\cdot}$ − H] (4), 195 (5), 163 (12), 162 (10), 161 (12), 113 (66), 112 (42), 98 (29), 97 (100). − ^1H NMR ($CDCl_3$): δ = 2.09 (m, 4 H), 2.44 (m, 4 H), 3.74 and 3.78 (2d AB, 3.9 Hz) + 3.83 (s) (2 H), 5.41 (m, 4 H).

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