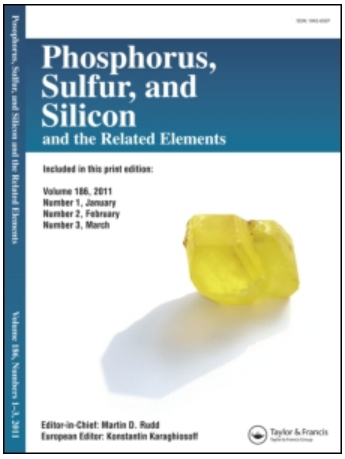

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Generation of New Reactive Cyclopentenethiones By Flash Vacuum Thermolysis

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GENERATION OF NEW REACTIVE CYCLOPENTENETHIONES BY FLASH VACUUM THERMOLYSIS

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The flash vacuum thermolysis (FVT) of the tricyclic sulfides **2** and **4** led, upon elimination of cyclopentadiene by retro-Diels-Alder reaction, to a mixture of isomeric allylthio- or propargylthiocyclopentadienes (**12, 13** and **16, 17**, respectively). Compounds **13** and **17** underwent in turn a thio-Claisen rearrangement giving the reactive 5-allyl- and 5-allenylcyclopentenethiones **11** and **15**. The possible retro-ene reaction eliminating propene or allene from the allylthio or propargylthio moiety has not been observed. Under FVT, the tricyclic thiol **3** led similarly to a mixture of cyclopentadienethiols **19** and **20**, the latter tautomerizing to cyclopentenethione **21** upon warming up in solution.

Precursors **7** and **8**, corresponding to **2** and **4** in the *cyclo*-C_6 series, behaved quite differently. No thio-Claisen rearrangement occurred, and the allylthio- and propargylthiocyclohexadienes **22** and **24** evoluted towards stable compounds resulting from competitive retro-ene reactions and β-eliminations. Upon FVT, the cyclobutanic precursor **10** gave quantitatively a mixture of cyclopentadiene, propene and thiophene, presumably *via* the cyclobutenic intermediate **26**.

Keywords: Flash vacuum thermolysis; Retro-Diels-Alder reaction; Thio-Claisen rearrangement; Thioketones; Cycloalkenethiones

We published recently[1] the synthesis and characterization of unstabilized cycloalkenethiones, using mainly the retro-ene cleavage of appropriate sulfides under flash vacuum thermolysis (FVT) conditions. Particularly,

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the unsubstituted, conjugated cyclopentene-, cyclohexene- and cycloheptenethiones were cleanly obtained in this way. We report now a novel and efficient way of access to 5-allyl- and 5-allenylcyclopent-2-enethiones by FVT involving retro-Diels-Alder cleavage and thio-Claisen rearrangement, as well as the tautomerization of cyclopenta-1,3-diene-2-thiol into the thermodynamically more stable, unsubstituted cyclopent-2-enethione. A tentative extension of these pathways in the *cyclo*-C_6 and C_4 series is also presented.

RESULTS AND DISCUSSION

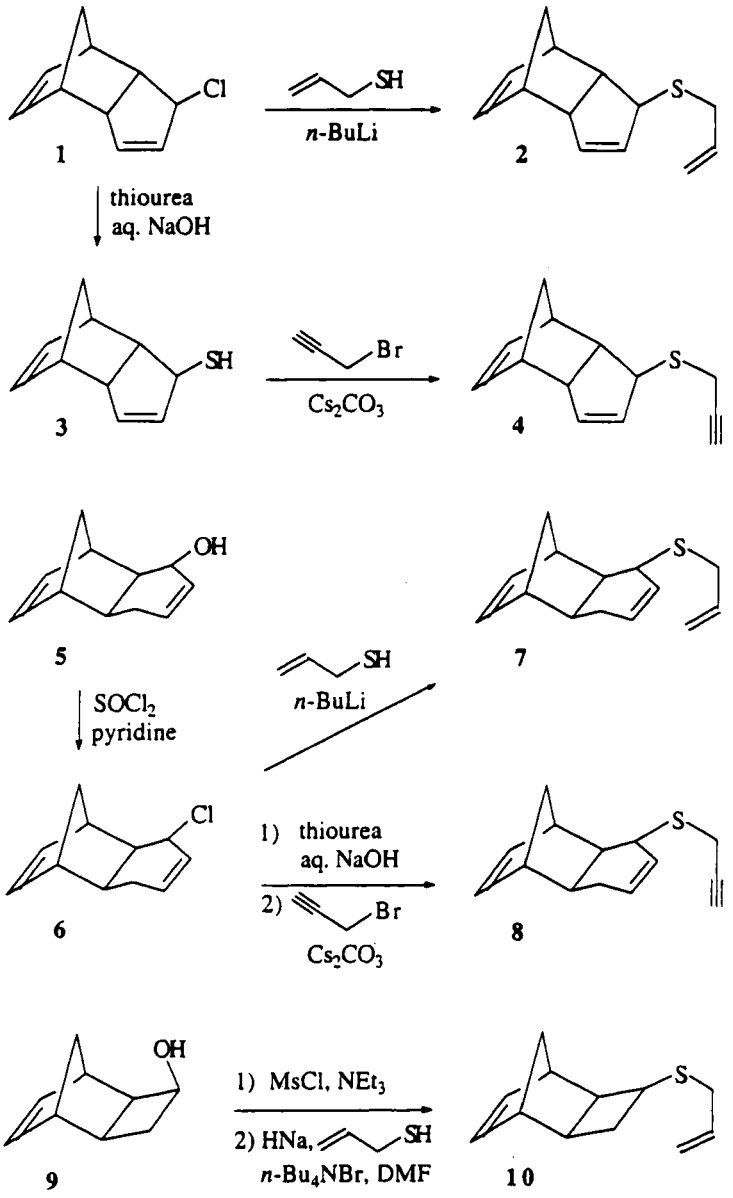
Synthesis of precursors

The tricyclic chloride **1**, obtained in two steps[2] from cyclopentadiene dimer, was treated by 2-propene-1-thiol and *n*-butyllithium to afford the allylic sulfide **2**. The reaction of **1** with thiourea followed by alkaline hydrolysis led to thiol **3**. This latter was converted into the propargylic sulfide **4** with propargyl bromide in the presence of cesium carbonate (Scheme 1).

Norbornadiene cycloadded to 1-trimethylsilyloxy-1,3-butadiene, affording thus, after desilylation by tetra-*n*-butylammonium fluoride, alcohol **5**, assumed to possess the *exo*-configuration.[3] The latter was converted into chloride **6** in the way used for the preparation of **1**.[2] Sulfides **7** and **8** were obtained from **6** as for compounds **2** and **4**. Cyclobutanol **9**[4] was transformed into its methanesulfonate which yielded in turn the expected sulfide **10** by action of sodium 2-propene-1-thiolate using a described general procedure.[5]

FVT of compounds 2 – 4

The thermolysis of sulfide **2** appeared to be extremely easy (50% of the starting material were already cleaved at the quite moderate FVT temperature of 400 °C). Whereas cyclopentadiene was quantitatively obtained, the absence of propene, unless traces, at any temperature between 400 and 800°C, ruled out the *a priori* possible pathway leading to cyclopentadi-

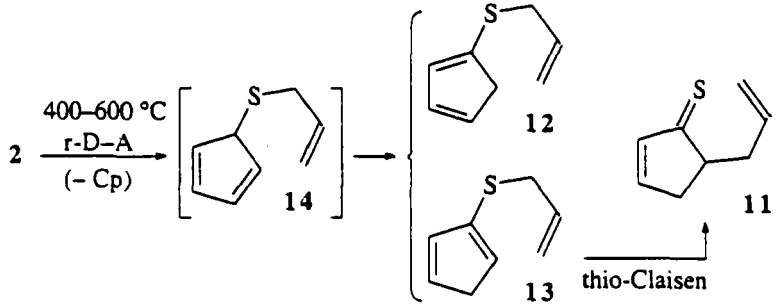


SCHEME 1

enethione[6] by retro-Diels-Alder and retro-ene reactions. An intense purple colour, fading rapidly upon warming, was observed when the FVT of **2** was performed between 400 and 600 °C. The corresponding product, fully characterized at low temperature by its spectra, was 5-allylcyclopent-2-enethione **11**. This structure was confirmed in the gas-phase by coupling the FVT with HRMS and B/E linked scan MS (Scheme 2, see the experimental section for the full spectral description of **11**).

Thioketone **11** was no more obtained when the FVT temperature was raised to 700 °C and only stable colourless products were isolated, mainly the isomeric allylthiocyclopentadienes **12** and **13**, accompanied by benzene, styrene, naphtalene, and hydrogen sulfide.

These results can be rationalized by the isomerization of the firstly formed sulfide **14** into its more stable isomers **12** and **13** (similar isomerizations have been reported for methylthio- and arylthiocyclopentadienes[7]). Compound **13** undergoes in turn a thio-Claisen rearrangement giving thioketone **11**. This latter does not enethiolize nor cyclize upon warming, but polymerizes similarly to the unsubstituted cyclopent-2-enethione.[1] At higher FVT temperatures, **11** was no more obtained, likely rearranging to styrene after loss of hydrogen sulfide, and the presence of its precursor **13** should result from the isomerization of **12** after trapping of the FVT products.

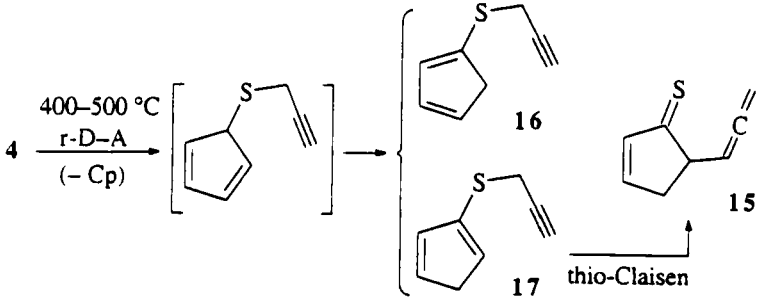


SCHEME 2

The propargylic sulfide **4** behaved similarly to the allylic one **2**. The retro-Diels-Alder cleavage of **4** was even easier (75% after FVT at 400° C) and the formation of allene has not been pointed out, showing the

absence of any retro-ene cleavage. The FVT of **4** was complete at 500 °C and 5-allenylcyclopent-2-enethione **15** has been thus obtained beside cyclopentadiene and fully characterized at low temperature. The deep purple colour of **15** vanished already at −130 °C in the pure state (IR, Visible), and at −70 °C in CD_2Cl_2-$CFCl_3$ solution (NMR) to give a polymeric material. The HRMS and B/E linked scan MS confirmed also its structure (Scheme 3, the spectra of **15** are fully described in the experimental section).

Thioketone **15** was no more obtained when the FVT temperature was raised to 600 °C, also, the intermediate sulfides **16** and **17** were too unstable to be isolated and definitely characterized.

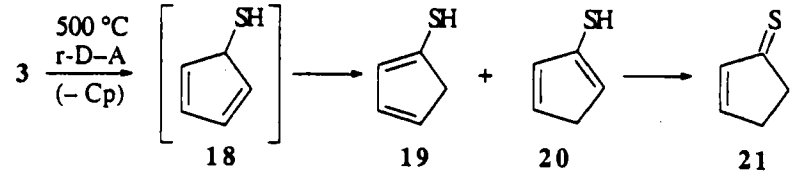


SCHEME 3

Thiol **3** underwent a total retro-Diels-Alder reaction at 500 °C and the nature and evolution of the FVT products have been investigated by low-temperature NMR. Cyclopentadienethiol **18**, directly resulting from the retro-Diels-Alder cleavage, was not observed, giving the more stable enethiolic isomers **19** and **20**, characterized beside cyclopentadiene, in a *ca* 50:50 ratio at −70 °C in $CDCl_3$-$CFCl_3$ solution. A small amount of cyclopentenethione **21**[1] was also visible in the spectrum at this temperature. The solution turned rapidly purple upon warming and at −30 °C enethiol **20** was no more present, whereas the concentration of **21** was maximum, showing the complete tautomerization of this enethiol into the corresponding, thermodynamically more stable thioketone. Above −30 °C, **21** polymerized rapidly as already described[1] and its colour vanished. In the mean time, the concentration of enethiol **19** (already obtained by tautomerization of the non-conjugated cyclopent-3-enethione[1]) remained

unchanged in the solution until room temperature, pointing out its stability and non-equilibrium with its isomer **20** under these conditions (Scheme 4).

In a CD_2Cl_2-$CFCl_3$ solution (shown to slow down, when compared to $CDCl_3$, the tautomerization of unstable enols[8]), the obtained mixture of enethiols **19** and **20** remained unchanged below room temperature, at which **20** tautomerized slowly to give polymeric **21**.



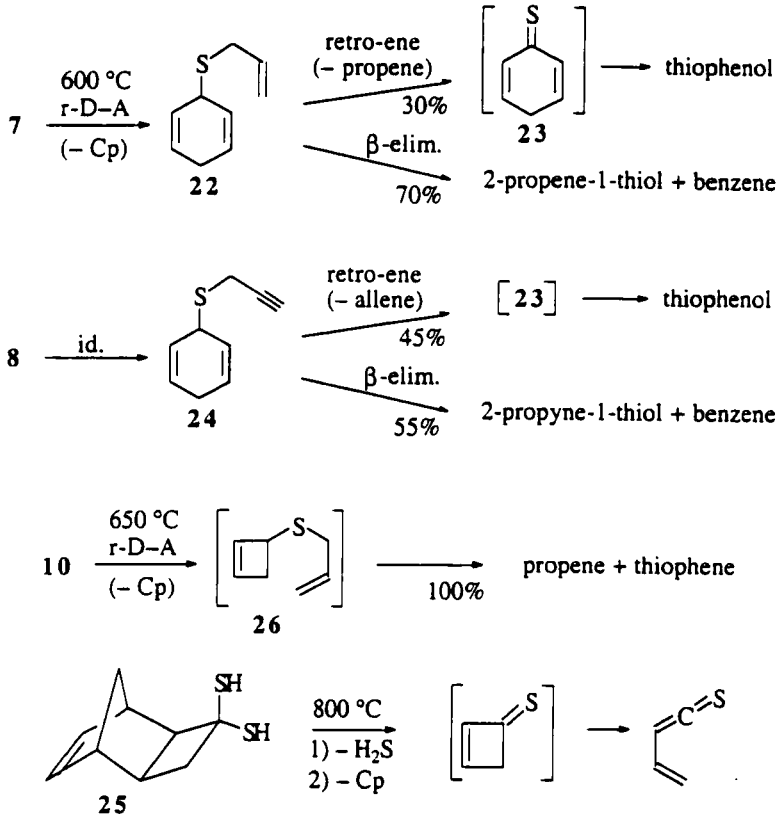
SCHEME 4

FVT of sulfides 7, 8 and 10

Sulfides **7** and **8** were potential precursors of the cyclohexenic counterparts of thioketones **11** and **15**, respectively, assuming their thermal behaviour to be the same as for **2** and **4**.

The FVT of sulfide **7** took place from *ca.* 500 °C with the quantitative elimination of cyclopentadiene and formation of the cyclohexadienic sulfide **22**, characterized only in the gas-phase by HRMS. At 600 °C, the decomposition of **7** was complete and two sets of stable compounds were obtained: benzene plus 2-propene-1-thiol (70%, β-elimination), and propene plus thiophenol (30%, retro-ene cleavage). Neither the intermediary cyclohexadienethione **23** (with the exception of a transient pink colour at -196 °C), nor the 6-allylcyclohex-2-enethione expected from a thio-Claisen rearrangement similar to that occuring in the FVT of **2**, could be detected (Scheme 5). Similar results were obtained when starting from the propargylic sulfide **8**, the presence of the propargylthio moiety favouring however the retro-ene reaction over the β-elimination (ratio 45:55), when compared to the FVT of sulfide **7**. The intermediary formation of compound **24** was pointed out by FVT/HRMS coupling.

Sulfide **10**, when thermolyzed at 650 °C, was transformed into equimolar amounts of cyclopentadiene, propene and thiophene. This result, quite different from that previously reported in the FVT of gemdithiol **25**,[1]



SCHEME 5

could be explained by the different pathway involved in each thermolysis: whereas, in the case of **25**, cyclobutenethione was a likely precursor of the product vinylthioketene, the thermolysis of **10** gave, presumably *via* the non-observed intermediate **26** by concomitant rearrangement and propene elimination, the stable molecule thiophene (Scheme 5).

To conclude, specific thermal pathways have been pointed out in the FVT of the cyclopentenic sulfides **2** and **4**, and thiol **3**. These pathways, quite different from those previously described[1] or reported here for the cyclohexenic sulfides **7** and **8**, result, after retro-Diels-Alder reaction, from the intermediary of rapidly isomerizing cyclopentadienic sulfides or thiols.

Particularly, sulfides **13** and **17** were thus obtained and underwent in turn a thio-Claisen rearrangement, providing an access to the new reactive 5-allyl- and 5-allenylcyclopentenethiones **11** and **15**.

EXPERIMENTAL

General

All reactions were carried out under nitrogen. Solvents and starting materials were distilled prior to use. The short-path bulb-to-bulb distillations of the thermally labile precursors were effected at 10^{-3} hPa, using a water bath heating. 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 ^{1}H, 62.89 and 100.62 MHz for ^{13}C, TMS as internal standard, solvents as indicated. MS: Jeol GCmate and AX 500.

FVT experiments

Typically, the precursors **2–4, 7, 8** and **10** (*ca* 25 mg) were thermolyzed between 400 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. 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, 50:50 $CDCl_3$-$CFCl_3$ or CD_2Cl_2-$CFCl_3$ mixtures).

Preparation of compounds 2 – 4

Compounds **2 – 4** have been synthesized according to the general procedures fully described in Ref.[1] and purified by fractionating bulb-to-bulb distillation.

Sulfide 2

Obtained by reaction of *endo, anti*-chloride **1**[2](1.60 g, 10 mmol) with 2-propene-1-thiol and *n*-butyllithium in ether. Yield 0.95 g (48%). ^{1}H

NMR ($CDCl_3$): δ = 1.33 and 1.52 (2 d AB, J = 8.1 Hz, 2 H), 2.78 (m, 2 H), 3.04 (m, 2 H), 3.17 (m, 2 H), 3.33 (m, 1 H), 5.10 (m, 2 H), 5.46 and 5.63 (2 d AB, J = 5.5 Hz, 2 H), 5.91 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ = 33.9, 45.0, 45.9, 50.4, 50.9, 51.9, 54.8, 116.6, 132.0, 132.7, 134.7, 135.0, 136.1. IR (liquid film): ν = 1633 cm^{-1} (-CH=CH_2). $C_{13}H_{16}S$ (204): calcd. S 15.69; found 15.55.

Thiol 3

Prepared from **1** (1.59 g, 9.55 mmol) by reaction with thiourea in 95% ethanol and hydrolysis by aq. sodium hydroxide. Yield 0.80 g (51%). **3** polymerized rapidly at room temperature in the pure state but could be kept several weeks below 0 °C in dichloromethane (5% solution). ^1H NMR ($CDCl_3$): δ = 1.33 and 1.54 (2 d AB, J = 8.2 Hz, 2 H), 1.70 (d, J = 8.4 Hz, 1 H, -SH), 2.80 (m, 2 H), 3.09 (m, 2 H), 3.40 (m, 1 H), 5.53 (m, 2 H), 5.95 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 44.9, 45.2, 45.5, 50.4, 54.6, 54.9, 131.9, 133.0, 136.1, 136.2. IR (liquid film): ν = 2540 cm^{-1} (-SH). $C_{10}H_{12}S$ (164): calcd. S 19.51; found 19.25.

Sulfide 4

Obtained from **3** (2.44 g, 14.9 mmol) using propargyl bromide and cesium carbonate in dimethyl formamide. Yield 1.89 g (63%). ^1H NMR ($CDCl_3$): δ = 1.34 and 1.53 (2 d AB, J = 8.1 Hz, 2 H), 2.23 (m, 1 H), 2.84 (m, 2 H), 3.06 (m, 1 H), 3.25 (m, 2 H), 3.34 (m, 2 H), 5.49 and 5.70 (2 d AB, J= 5.5 Hz, 2 H), 5.95 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 17.9, 45.0, 45.9, 50.3, 51.3, 51.8, 54.8, 70.6, 80.7, 132.0 (2 C), 135.5, 136.1. IR (liquid film): ν = 3286 and 2107 cm^{-1} (-C≡CH). $C_{13}H_{14}S$ (202): calcd. S 15.84; found 14.74.

Preparation of compounds 5 and 6

Alcohol 5

1-trimethylsilyloxybuta-1,3-diene (2.00 g, 14.0 mmol) and bicyclo[2.2.1]hepta-2,5-diene (13.0 g, 140 mmol) were heated 12 h at 140 °C in a sealed tube. The crude Diels-Alder monoadduct (2.60 g, 11.1 mmol, yield 79%), obtained after evaporation of the remaining starting materials, was dissolved in THF (25 mL) and tetra-*n*-butylammonium fluoride (3.51 g, 11.1 mmol) was added. After 2 h stirring at room temperature and

addition of an ether-pentane mixture (1:1) and of brine, the organic layer was washed with water, dried over magnesium sulfate and evaporated to give, after chromatography over neutral alumina (eluent: ether-pentane 50:50), alcohol **5** as a mixture of two isomers. Yield 1.69 g (93%). ^{1}H NMR ($CDCl_3$): δ = 1.1 – 2.0 (5 H), 2,1 – 2.4 (2 H), 2.50 and 2.85 (broad s, 2 H), 3.98 and 4.47 (m, 1 H), 5.6 – 6.2 (4 H). ^{13}C NMR ($CDCl_3$): δ = 28.8, 29.4, 38.3, 38.8, 43.6, 44.0, 44.8, 45.3, 46.0, 47.5, 47.6, 50.8, 66.4, 72.8, 128.4, 132.5, 133.2, 135.2, 136.8, 137.5, 138.2, 139.0. IR (liquid film): ν = 3335 cm^{-1}(-OH). HRMS; *m/z*: 162.1041 (M^+, calcd. $C_{11}H_{14}O$ 162.1045).

Chloride 6

A solution of alcohol **5** (1.3 g, 7.9 mmol) in anhydrous ether (20 mL) was treated by thionyl chloride (0.69 mL, 9.4 mmol) and pyridine (1.8 mL, 22.1 mmol), according to the procedure described[2] for the obtention of **1**. The crude product was purified by bulb-to-bulb distillation to give chloride **6** as a mixture of isomers. Yield 1.3 g (83%). ^{1}H NMR ($CDCl_3$): δ = 1.1 – 3.1 (8 H), 4.2 – 4.9 (1 H, ClCH), 5.4 – 6.2 (4 H). ^{13}C NMR ($CDCl_3$): δ = 28.4, 32.5, 37.0, 37.2, 38.6, 39.5, 43.3, 46.2, 46.9, 47.8, 48.1, 51.2, 54.4, 60.9, 122.0, 129.0, 133.1, 136.8, 136.9, 137.3, 137.6, 141.2. HRMS; *m/z*: 180.0702 and 182.0672 (M^+, calcd. $C_{11}H_{13}Cl$ 180.0706 and 182.0677). Due to its low stability, **6** should be used immediately in the following steps.

Preparation of sulfides 7 and 8

Sulfides **7** and **8** have been, as for **2** and **4**, obtained according to the procedures described in Ref.[1] and purified by bulb-to-bulb distillation. They were obtained as a mixture of isomers.

Sulfide 7

Obtained by reaction of chloride **6** (0.80 g, 4.0 mmol) with 2-propene-1-thiol and *n*-butyllithium in ether. Yield 0.46 g (53%). ^{1}H NMR ($CDCl_3$): δ = 1.0 – 2.1 (4 H), 2.2 – 2.9 (4 H), 3.20 (m, 2 H), 3.42 and 3.66 (m, 1 H), 5.10 (m, 2 H), 5.83 (m, 1 H), 5.9 - 6.2 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 33.6, 33.7, 36.9, 37.2, 37.8, 38.0, 38.7, 39.2, 39.6, 41.1, 43.6, 43.8, 47.4, 47.5, 47.7, 48.4, 116.9, 117.1, 131.2, 131.6, 132.5, 133.5,

134.8, 135.0, 136.0, 136.5, 137.3, 137.7. IR (liquid film): $\nu = 1631\ cm^{-1}$ (-CH=CH_2). $C_{14}H_{18}S$ (218): calcd. S 14.68; found 14.03.

Sulfide 8

Prepared from **6** (1.0 g, 5.2 mmol) by reaction with thiourea in 95% ethanol and hydrolysis by aq. sodium hydroxide to give the corresponding thiol, which was directly converted into **8** using propargyl bromide and cesium carbonate in dimethyl formamide. Yield 0.76 g (68%). ^1H NMR ($CDCl_3$): $\delta = 1.8 - 2.1$ (6 H), 2.23 (m, 1 H), 2.55 (m, 2 H), 3.26 and 3.33 (m, 2 H), 3.4 – 3.9 (1 H), 5.3 – 6.2 (4 H). ^{13}C NMR ($CDCl_3$): $\delta = 18.2$, 19.2, 33.1, 34.1, 36.7, 37.2, 37.9, 38.1, 38.5, 39.8, 40.4, 42.1, 43.7, 43.9, 47.4, 47.6, 47.8, 48.5, 55.4 (2 C), 131.7, 132.9, 133.8, 135.8, 136.1, 136.5, 137.3, 137.9. IR (liquid film): $\nu = 3288$ and $2106\ cm^{-1}$ (-C≡CH). HRMS; *m/z*: 216.0961 (M^+, calcd. $C_{14}H_{16}S$ 216.0973).

Preparation of sulfide 10

exo, *syn*-Alcohol **9** (0.89 g, 6.54 mmol, prepared by reduction of the corresponding ketone using sodium borohydride in ethanol[4]) and triethylamine (1.09 mL, 7.88 mmol) were cooled to −10 °C in dichloromethane (10 mL). Methanesulfonyl chloride (0.55 mL, 7.18 mmol) was added dropwise. After warming up and stirring at room temperature for 20 h, 1 *N* HCl (3 mL) was added and the organic layer separated, washed with aq. $NaHCO_3$ and dried over magnesium sulfate. The methanesulfonate of **9** was thus obtained in a practically pure state [oil, yield 1.17 g (84%). ^1H NMR ($CDCl_3$): $\delta = 1.2 - 2.7$ (8 H), 2.92 (s, 3 H), 5.11 (m, 1 H), 5.96 (m, 2 H). ^{13}C NMR ($CDCl_3$): $\delta = 29.8$, 32.4, 37.9, 41.3, 41.5, 44.2, 45.0, 72.2, 135.5, 136.4]. 2-Propene-1-thiol (1.40 mL of the 70% commercial compound, 12.3 mmol) was added dropwise at 0 °C under nitrogen to a stirred mixture of sodium hydride (0.24 g, 9.9 mmol) and tetra-*n*-butylammonium bromide (0.093 g, 0.29 mmol) in dry dimethyl formamide (8 mL). After 0.5 h at room temperature, a solution in the same solvent (2 mL) of the methanesulfonate obtained above (1.43 g, 6.6 mmol) was added and the mixture stirred at room temperature for 15 h. After addition of an ether-pentane mixture (50:50, 20 mL), successive washings with dilute sulfuric acid, sodium bicarbonate and water, drying and evaporation of solvents, the crude product was purified by bulb-to-bulb distillation followed by chromatography over neutral alumina. Elution by pentane

afforded 0.54 g of sulfide **10** (only one isomer likely *anti*, oil, 42%), unreacted methanesulfonate was then recovered upon elution by ether (0.53 g, 37%). **10**: ^{1}H NMR ($CDCl_3$): δ = 1.30 and 1.65 (2 d AB, J = 9.2 Hz, 2 H), 1.80 (m, 1 H), 1.95 (m, 1 H), 2.09 (m, 1 H), 2.57 (m, 1 H), 2.66 (m, 2 H), 2.78 (m, 1 H), 3.13 (m, 2 H), 5.07 (m, 2 H), 5.80 (m, 1 H), 5.97 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 28.7, 33.9, 34.4, 35.8, 40.5, 43.7, 44.1, 45.7, 116.4, 134.6, 134.7, 135.7. IR (liquid film): ν = 1632 cm^{-1}(-CH=CH_2). HRMS; *m/z*: 192.0963 (M^+, calcd. $C_{12}H_{16}S$ 192.0968).

FVT of sulfide 2 at 500 and 700 °C

FVT at 500 °C, *5-allylcyclopent-2-enethione* (**11**): Vis (-196 °C, solid film): λ = 536 and 564 nm. IR (-196 °C, solid film): ν = 1640 (allylic C=C); 1555 (ring C=C); 1235, 1198, 1080 cm^{-1} (related to C=S). ^{1}H NMR (-80 °C, CD_2Cl_2-$CFCl_3$): δ = 2.22 (dt, J = 13.5 and 8.2 Hz, 1 H^5); 2.49 and 2.83 (2 dm, J = 22.0 Hz, 2 H^4); 2.7–2.9 (m, 2 H, allyl); 5.05 (d, J = 9.8 Hz), 5.10 (d, J = 17.0 Hz) and 5.73 (m) (3 H, allyl); 6.68 (dt, J = 5.3 and 2.0 Hz, 1 H^2); 7.81 (dt, J = 5.3 and 2.9 Hz, 1 H^3). HRMS; *m/z*: 138.0498 (M^+, calcd. $C_8H_{10}S$ 138.0503). MS (B/E linked scan, daughter ions of M^+); *m/z* (%): 123 (100), 105 (43), 97 (32), 91 (26), 79 (15), 77 (24), 69 (10), 65 (13), 59 (13), 51 (9), 45 (15), 39 (12).

FVT at 700 °C, *allylcyclopentadienyl sulfides* **12** + **13**(*ca* 50:50, trapped on $CDCl_3$ and purified by GC at 100 °C on a SE30 column): IR (film): ν = 3062, 2910, 1635, 1604, 1425, 1360, 1320, 1255, 1025, 990, 920, 785 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.90 and 2.97 (2 m, 2 H); 3.15 (m, 2 H, allyl); 5.06 (m, 2 H, allyl); 5.93 (m, 1 H, allyl); 6.05, 6.18, 6.28 and 6.42 (4 m, 2 H); 6.43 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 32.3, 33.2, 39.3, 41.2, 113.3, 113.5, 124.7, 125.1, 129.1, 130.4, 131.8, 132.5, 134.4, 135.0, 142.8, 145.4.

FVT of sulfide 4 at 500 °C

5-allenylcyclopent-2-enethione (15)

Vis (-196°C, solid film): λ = 528 nm. IR (-196 °C, solid film): ν = 1958 (C=C=C); 1552 (ring C=C); 1220, 1182, 1084 cm^{-1}(related to C=S). ^{1}H NMR (-80 °C, CD_2Cl_2-$CFCl_3$): δ = 2.81 and 2.94 (2 dm, J = 20.5 Hz, 2 H^4); 3.39 (m, 1 H^5); 4.87 (m, 2 H) and 5.60 (dt ≈ q, J ≈ 6 Hz, 1 H) (alle-

nyl); 6.64 (≈ d, $J \approx 5$ Hz, 1 H^2); 7.81 (dt, $J = 5.1$ and 2.7 Hz, 1 H^3). HRMS: *m/z*: 136.0348 (M^+, calcd. C_8H_8S 136.0347). MS (B/E linked scan, daughter ions of M^+); *m/z* (%): 121 (15), 102 (14), 97 (6), 91 (100), 89 (20), 77 (10), 69 (15), 65 (9), 63 (10), 51 (10), 45 (7), 39 (6).

FVT of thiol 3 at 500 °C

^{1}H NMR (-40 °C, $CDCl_3$-$CFCl_3$): *enethiol* **19**: δ = 3.08 (1 H, SH), 3.29 (2 H), 6.30 (1 H), 6.38 (1 H), 6.43 (1 H); *enethiol* **20**: δ = 3.08 (1 H, SH), 3.21 (2 H), 6.21 (1 H), 6.34 (1 H), ≈ 6.5 (1 H, masked by cyclopentadiene); *thioketone* **21**: δ = 2.80 (2 H), 2.96 (2 H), 6.70 (1 H), 7.80 (1 H) [in agreement with the values already described[1] in CD_2Cl_2-$CFCl_3$ for **19** and **21**]. ^{1}H NMR (-40 °C, CD_2Cl_2-$CFCl_3$): *enethiols* **19** + **20** (*ca* 50:50): δ = 3.01 and 3.02 (SH), 3.03, 3.10, 6.12, 6.23, 6.27, 6.30, 6.36, 6.41. IR (25 °C, CCl_4): ν = 2570 cm^{-1} (SH).

FVT of sulfides 7, 8 and 10

The FVT of sulfides **7**, **8** and **10** were performed between 500 and 650 °C. The stable products obtained were characterized by ^{1}H and ^{13}C NMR spectrometry as well as, in the gas-phase, by FVT/MS coupling. The presence of the transient sulfides **22** and **24** (or isomers) was demonstrated, at the FVT temperature of 600 °C ensuring the complete decomposition of the precursors **7** and **8**, by FVT/HRMS:

Allylcyclohexadienyl sulfide 22

HRMS; m/z: 152.0654 (M^+, calcd. $C_9H_{12}S$ 152.0660);

Propargylcyclohexadienyl sulfide 24

HRMS; m/z: 150.0523 (M^+, calcd. $C_9H_{10}S$ 150.0503).

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