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Generation by Retro-ene Reaction of Cyclohex-2-enethione and Cyclopent-2-enethione

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Abstract: The reactive unsubstituted cyclohex-2-enethione (**1**) and cyclopent-2-enethione (**2**) have been synthesized in two steps (yields *ca* 70%) from the corresponding cycloalkenyl bromides. The key step is a retro-ene reaction under FVT conditions. The purple-blue thioketones **1** and **2**, polymerizing rapidly above -80°C in the condensed phase, have been characterized by UV-visible and IR spectroscopy at -196°C, as well as, in the gas phase, by direct FVT/HRMS coupling. The reaction of **2** with diazomethane in THF led to 1,3-dithiolane **9**. © 1997 Published by Elsevier Science Ltd.

The chemistry of thioaldehydes and thioketones is now well-documented[1-3] and the generation by flash vacuum thermolysis (FVT) of the most reactive terms in these series has been also reviewed.[4]

Among these compounds, the simple, conjugated cycloalkenethiones have been little investigated.[2] Cyclohexene- and cyclopentenethiones, stabilized by the presence of a methyl group in the β-position, have been obtained.[5] More recently, the reactive cyclopentadienethione[6] and 6-methylenecyclohexadienethione[7] have been generated by FVT or photolysis and characterized spectroscopically in the gas-phase or in argon matrix.

We report herein a rapid synthesis, by retro-ene reaction, of the unsubstituted thioketones **1** and **2**. These unstabilized conjugated cycloalkenethiones should be very reactive but, contrarily to the acyclic α,β-unsaturated thioketones,[8] they are fixed in the *s*-trans conformation and cannot dimerize in the usual [4+2] fashion.

The retro-ene reaction under FVT conditions allows to accede efficiently to reactive unsaturated species.[9] A kinetic investigation has pointed out the high rate and concertedness of this thermal decomposition in the case of allyl sulfides[10] and several reactive thiocarbonyl compounds have been generated in this way.[11]

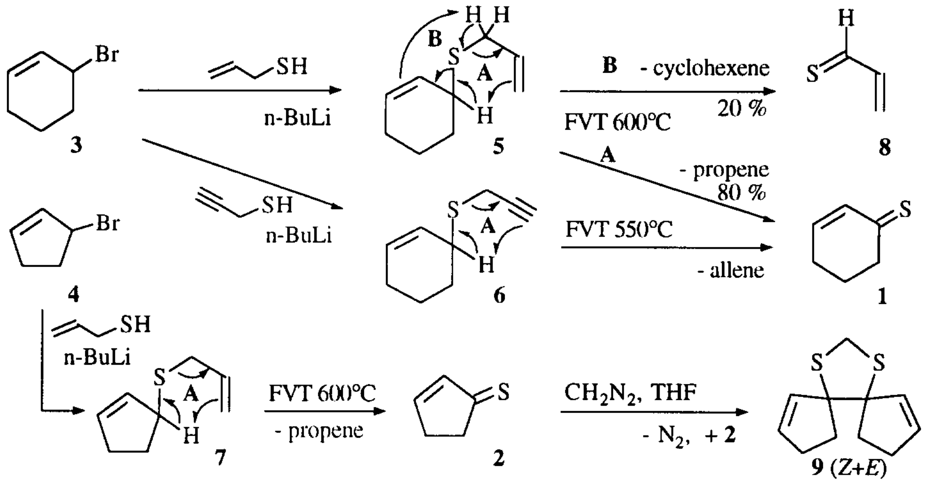
The allylic bromides **3** (commercial), and **4** (prepared[12]) were converted in a classic way into the sulfides **5-7** by reaction with allyl or propargyl mercaptan and n-butyl lithium in ether. Compounds **5-7**, obtained after bulb-to-bulb distillation in 80, 30 and 65% yield, respectively, were purified by GC on a SE30 column.[13]

The FVT of the allylic sulfide **5** (p = 10^{-5} hPa, oven 12 x 1.6 cm), complete at 600°C, led to two competitive retro-ene cleavages in a *ca* 80:20 ratio (Scheme). The major pathway (**A**) led to propene and the expected cyclohexenethione **1**, accompanied by cyclohexene and thioacroleine **8** resulting from the minor retro-ene cleavage (**B**). Compound **8** was characterized by IR at -196°C, in agreement with the reported spectrum.[14]

The replacement of the allylthio moiety by a propargylthio one is known[15] to facilitate the retro-ene reaction and, in fact, cleavage (**A**) became the only one observed when the propargylic sulfide **6** was submitted to FVT at 550°C. Compound **1**, obtained as sole FVT product with allene, was characterized by direct coupling of the FVT with HRMS and by low temperature UV-visible and IR spectroscopy.[16]

In the case of cyclopentenyl sulfide **7**, cleavage (**B**) is more disfavoured than for **5**, likely due to the geometry of the C_5 ring, and pathway (**A**) was again the only one observed, giving exclusively, by elimination of propene, the expected cyclopentenethione **2**, characterized by HRMS, UV-visible and IR.[16] The intense purple-blue colour of thioketones **1** and **2**, thus obtained in *ca* 70% yield,[17] vanished quickly above -80°C. No evolution products were identified, except polymeric materials, upon warming to room temperature.

The [2+3] dipolar cycloaddition of **2** with a 2-fold excess of diazomethane vaporized in THF at the oven exit led, beside polymeric **2**, to 1,3-dithiolane **9**,[18] in agreement with relevant prior results.[19,20] Further investigations concerning the chemical reactivity of thioketones **1** and **2** are presently in progress.



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13. Sulfides 5-7 (NMR in $CDCl_3$). **5**: S% calcd. $C_9H_{14}S$ 20.78, found 21.18; δ^1H: 1.5-1.9 (4H), 2.01 (m, 2H), 3.17 (dm, 2H, 7.2 Hz), 3.33 (m, 1H), 5.06 (dm, 1H, 10.5 Hz), 5.12 (dm, 1H, 17.1 Hz), 5.78 ppm (m, 3H); $\delta^{13}C$: 19.8, 25.1, 29.0, 34.2, 39.5, 116.8, 127.6, 129.8, 135.0 ppm. **6**: S% calcd. $C_9H_{12}S$ 21.06, found 21.18; δ^1H: 1.5-1.9 (4H), 1.96 (m, 2H), 2.17 (t, 1H, 2.7 Hz), 3.21 (m, 2H), 3.55, 5.66 and 5.76 ppm (3 m, 3H), $\delta^{13}C$: 18.6, 19.9, 25.0, 28.8, 40.7, 70.9, 80.6, 126.9, 130.6 ppm. **7**: S% calcd. $C_8H_{12}S$ 22.86, found 23.18; δ^1H: 1.8-2.6 (4H), 3.17 (dm, 2H, 7.1 Hz), 3.83 (m, 1H), 5.07 (dm, 1H, 10.9 Hz), 5.13 (dm, 1H, 17.7 Hz), 5.80 ppm (m, 3H); $\delta^{13}C$: 29.7, 31.0, 34.2, 50.0, 116.9, 131.8, 132.8, 134.5 ppm.
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16. Cyclohex-2-enethione (**1**): HRMS: m/z 112.0373 ($M^{+\cdot}$, calcd. C_6H_8S 112.03468); UV-visible (-196°C): 236, 287, 531 (i), 554, 583 nm (i); IR (-196°C): 1586, 1400, 1252, 1151, 1126, 973 cm^{-1}.
Cyclopent-2-enethione (**2**): HRMS: m/z 98.0163 ($M^{+\cdot}$, calcd. C_5H_6S 98.01892); UV-visible (-196°C): 297, 502 (i), 524 , 552 nm (i); IR (-196°C): 1553, 1427, 1372, 1264, 1183, 1082, 921 cm^{-1}.
17. Yields were estimated by NMR (benzene quantitative standard) as those of the co-formed allene or propene.
18. 1,3-Dithiolane 9 (oil, *Z+E* ratio *ca* 50:50, yield *ca* 30%): MS: m/z 209 ($M^{+\cdot}$ - H), 195, 163, 162, 161, 113, 112, 98, 97; δ^1H ($CDCl_3$): 2.09 (m, 4H), 2.44 (m, 4H), 3.74 and 3.78 (2d AB, 3.9 Hz, 2H, SCH_2S of *Z* isomer), 3.83 (s, 2H, SCH_2S of *E* isomer), 5.41 ppm (m, 4H).
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