Enethiols. VIII.* 3-Mercapto-5,5-dimethyl-2-cyclohexen-1-one
(“Thiodimedone”) and Derivatives. Thermal and Photochemical
Rearrangements

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Reaction of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one with Na₂S gave 3-mercapto-5,5-dimethyl-
2-cyclohexen-1-one (RSH). Subsequent alkylation of RSH (Na⁺ salt) gave the sulfides RSR’
(R’=CH₂=, CH₃=CHCH₂=, CH₃CH=CHCH₂=, and CH₃COCH₃=). Similarly RSH
(Tl⁺ salt) yielded RSR’ (R’=H=CHCH₂=) while RSH (Bu₄N⁺ salt) gave (R’=H₄C=C=CH–)
by alkylation with H₂C=CHBr. Allylic sulfides (RSR’ undergthio-Claisen rear-
rangement and cyclization at about 140 °C in quinoline to 2,6,6-trimethyl-4-oxo-2,3,4,5,6,7-
hexahydrobenzo thiophene (when R’=CH₃=CHCH₂=) and 2,3,6,6-tetramethyl-4-oxo-
2,3,4,5,6,7-hexahydrobenzo thiophene (when R’=CH₃CH=CHCH₂=). Rearrangem
in acetic anhydride gave 3-acetythio-2-allyl-5,5-
dimethyl-2-cyclohexen-1-one (when R’=CH₃=CHCH₂=). Photolysis of RSR’ (R’=CH₃=CHCH₂=
CH₃CH=CHCH₂=, PhCH₂=CH₃CH=CHCH₂=, and H–) gave RSSR and a 1,3-
dithiole:

This product was obtained in 79% yield by photolysis of RSSR. Photolysis of RSR’
(R’=phenyl) gave 3,3-dimethyl-5-oxo-2,3,4,5-
tetrahydrodibenzothiophene.

In previous papers dealing with the thermal
1-4 and photochemical 1 behaviour (Z→E isomerization
1,2 and thio-Claisen rearrangements 1,2) of
α,β-unsaturated sulfides, open chain compounds

* Part VII. See Ref. 1.

with the appropriate thioles gave the sulfides 14' and 15' together with the thioacetal 16. When 14 was reacted with ethylthiostannane a 1,2-addition followed by elimination took place resulting in the formation of 17, while treatment of 14 with LiNH3/NH3 gave partly isomerization to 18 (see also Refs. 17, 18).

**Thermal rearrangements of allylic derivatives.** 3-Allyloxy-2-cyclohexen-1-one has been shown 29 to undergo Claisen rearrangement at 190–210 °C. Similarly the 3-allylthio analogues do undergo thio-Claissen rearrangement. Rearrangement in the presence of p-toluenesulfonic acid resulted in the formation of 2-allyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one 19, which cyclized partly during distillation. When the reaction was performed in boiling acetic anhydride, 3-acetylthio-2-allyl-5,5-dimethyl-2-cyclohexen-1-one 20 was isolated. Rearrangement in quinoline at 160 °C yielded the hexahydrobenzothiophene 20. The 2-butenyl derivative rearranged to 21 somewhat slower under similar conditions. Heating of the 2-propynyl (10) and the allenyl (11) sulfides in quinoline or pyridine resulted mostly in tarry material. However, the 2H-thiopyran 23 could be isolated in a reasonably pure state by rearrangement of 10.

**Photolysis of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and sulfide derivatives.** Photolysis of the compounds 5, 7, 8, 12, and 15 (Table 1) did not yield the expected 23–24 2+2 cycloadducts. Irradiation of the enethiol 5 gave the disulfide 13 which is an ordinary type of product in photolysis of thiols, 29 the 1,3-dithiole 24 and the 1,4-dithiane 25. The allyl 7, 2-butenyl 8, and the benzyl 15 derivatives gave 13 and 24 in variable ratios. In one experiment when 15 was irradiated traces of PhCHO arising from the benzyl group were detected along with 13. The acetyl derivative 12 yielded 13 and 24 together with EtOAc upon photolysis in EtOH. As might be expected the phenyl derivative 14 did not undergo cleavage reaction at the R—S bond, but instead an intramolecular cyclization-oxidation reaction (eqn. 1) took place, giving the tetrahydrodibenzothiophene 26 in poor yields. Similar reactions have been observed for other types of divinyl sulfides. 26 In

\[
\text{Scheme 1}
\]

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**Fig. 1.** Compounds 1-18. 1 (ROH), 2 (RCI), 3 (RS®), 4 (RSR), 5 (RSH), 6 (RSCH), 7 (RSCH₂CH = CH₂), 8 (RSCH₂CH = CHCH₃), 9 (RSCH₂COCH₃), 10 (RSCH₂C≡CH), 11 (RSCH = C = CH₂), 12 (RSCH₂CO₂), 13 (RSSR), 14 (RSPH), 15 (RSCH₂Ph).

**Fig. 2.** Compounds 19–23.
Table 1. Photolysis of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives. Conditions and product distribution.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Starting material (g (mmol))</th>
<th>Solvent (175-200 ml)</th>
<th>Reaction time (h)</th>
<th>Light source (nm)</th>
<th>Recovered 5, g (%)</th>
<th>Recovered 24, g (%)</th>
<th>Compound, g (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>H</td>
<td>1.52(0.75)</td>
<td>hexane</td>
<td>44</td>
<td>300 py.</td>
<td>0</td>
<td>0.624(41)</td>
<td>0.322(22)</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>5.00(16.0)</td>
<td>EtOH</td>
<td>18</td>
<td>254 qu.</td>
<td>0.26(5)</td>
<td>3.95(79)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH₃CH=CH₃</td>
<td>2.45(12.5)</td>
<td>cyclohexane</td>
<td>16</td>
<td>300 qu.</td>
<td>1.11(45)</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>CH₃CH=CH₂CH₃</td>
<td>0.75(3.57)</td>
<td>EtOH</td>
<td>19</td>
<td>300 qu.</td>
<td>1.49(61)</td>
<td>0.165(11)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Ac</td>
<td>4.97(25.2)</td>
<td>EtOH</td>
<td>33</td>
<td>254 qu.</td>
<td>0.248(28)</td>
<td>1.08(28)</td>
<td>2.3(59)</td>
</tr>
<tr>
<td>14</td>
<td>Ph</td>
<td>2.34(10.1)</td>
<td>acetone⁺</td>
<td>72</td>
<td>300 qu.</td>
<td>1.08(46)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Ph</td>
<td>4.56(19.7)</td>
<td>ether⁺</td>
<td>110</td>
<td>300 qu.</td>
<td>3.60(79)</td>
<td></td>
<td>26, 0.109(2.4)</td>
</tr>
<tr>
<td>14</td>
<td>Ph</td>
<td>3.70(16.0)</td>
<td>dioxan</td>
<td>67</td>
<td>300 py.</td>
<td>1.58(43)</td>
<td></td>
<td>26, 0.184(5)</td>
</tr>
<tr>
<td>15</td>
<td>PhCH₃</td>
<td>2.46(10.00)</td>
<td>ether</td>
<td>11</td>
<td>300 qu.</td>
<td>1.49(61)</td>
<td>0.165(11)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>PhCH₃</td>
<td>0.80(3.25)</td>
<td>hexane</td>
<td>36</td>
<td>300 py.</td>
<td>0.22(28)</td>
<td>0.10(20)</td>
<td></td>
</tr>
</tbody>
</table>

*λ*<sub>max</sub> of "Rayonet RS" mercury arcs. Reaction vessel: qu. = quartz, py. = pyrex.

⁺1 l.
order to find out if 24 could be formed from 13 this compound was irradiated at 254 nm in ethanol. It turned out* that 24 was produced in high yields (79%) and crystallized directly from the solvent. Also sunlight caused this conversion (13→24) in solution, while in the solid state 13 was quite stable. The possibility that the rearrangement was thermally induced was ruled out, as no conversion was observed when 13 was boiled in ethanol in the dark. More severe conditions (i.e. heating in HMPA in the presence of KHSO₄[29,30] which have brought about 3,3-sigmatropic rearrangements of other divinyl-disulfides[31,32] gave only tar.

Various methods were used in order to determine the mechanisms of the observed photochemical reactions. A hexane solution of the acetyl derivative 12 and 2-methyl-2-nitrosopropane was irradiated at 254–300 nm in the ESR spectrograph. The formation of N-acetyl-N-(t-butyl)nitroxide (an = 8 gauss) indicated that the primary photochemical process was a cleavage of 12 into acetyl and thyl radicals (eqn. 2). However, no well defined signal from the thyl radical or trapped thyl radical could be observed. Also attempts to trap radicals by photolysis of the disulfide 13 were fruitless. The conversion of 13 irradiated with monochromatic light (254 and 300 nm) was measured by the change of the UV spectrum. The change of the UV spectrum obtained in ethanol differed clearly from that obtained in CHCl₃. In both solvents the absorption at 277 nm disappeared with about equal rates. However, in ethanol an absorption at 350 nm appeared quickly, reached a maximum and then faded out. In CHCl₃ only comparatively weak absorption at 350 nm was found. It is believed that different tautomers (eqn. 3) of the same intermediate are formed when the solvent is changed, thus giving rise to different UV-spectra. For comparison, it should be pointed out that 5 showed a behaviour similar to the intermediate in eqn. 3 as 5 revealed absorption at 342 nm in ethanol and DMSO, while in CHCl₃ this band was comparatively weak. The suggested intermediate (M) represented by structure A, B, and C in eqn. 3 might be formed by a radical chain process initiated by light (eqn. 4). The propagation step (eqn. 5) consists of a thyl radical attack on C-2 of 13 (RSSR), giving M and another thyl radical. This means that the rate of disappearance of 13 is dependent on the concentration of 13. Measurement of the quantum yield (Φ = 0.1) for disappearance of 13 showed no such dependence on [RSSR], and it seems therefore reasonable to suggest another mechanism. The reaction could proceed through reactions in which two thyl radicals combine to give M either as free radicals or in a solvent cage (eqn. 7). Finally a concerted [1,3]-sigmatropic process could be suggested (eqn. 8). The conversion of M to 24 might be a thermal cyclisation reaction, but more likely a photochemical process, because it explains the change of the UV spectrum in EtOH. The absorption at 350 nm, ascribed to M, did not change on standing in the dark, while irradiation caused a change as described above.

Initiation:

\[ \text{RSSR} \rightarrow \text{RSSR}^* \rightarrow 2 \text{RS}^- \]  
(4)

Propagation:

\[ \text{RS}^- + \text{RSSR} \rightarrow \text{M} + \text{RS}^- \]  
(5)

\[ \Phi I = -\frac{dC}{dt} = k_1 [\text{RSSR}] [\text{RSSR}] \]  
(6)

\[ 2 \text{RS}^- \rightarrow \text{M} \]  
(7)

\[ \text{RSSR} \rightarrow \text{RSSR}^* \rightarrow \text{M} \]  
(8)

SPECTROSCOPY

Tautomerism of thiodimethone. In principle thiodimethone 5 can exist as the monomeric keto-enethiol (D), thioketo-enol (E), and the ketothioketo (F) structures (eqn. 10). In concentrated solutions or neat also dimer structures analogous to the findings for 1,3-cyclohexandione and dimesone should be considered likely.\textsuperscript{a6, a7} The IR spectrum of thiodimethone showed absorption at 2520 cm\(^{-1}\) and a broad band at 1680 cm\(^{-1}\) assigned, respectively, to the mercapto and the \(\alpha,\beta\)-unsaturated keto group of the keto-enethiol (D). This was the only tautomer detectable by NMR. The signal at \(\delta\) 6.05 was assigned to the vinyl proton, as an allylic coupling to the protons on C-4 was observed. The broad signal at \(\delta\) 4.23 could be attributed to a mercapto proton, excluding an enolic proton, which was expected to reveal a signal at lower field (\(\delta\) 9–13). The broadening of this signal was ascribed to proton exchange. Contrary to what is often found for enethiols, no coupling between the proton of the mercapto group on C-3 and the protons on C-4 was present. The structural requirement for a maximum coupling is that the bondings between the hydrogens obtain a planar zig-zag framework, as found for enethiols possessing an intramolecular chelated structure.\textsuperscript{a8} As only energetical less important intermolecular hydrogen bonding can occur in thiodimethone, the rotation about the C–S bond is less restricted, and the coupling decreases to zero. The UV spectrum of thiodimethone obtained in hexane showed absorption at 268 nm, ascribed to the \(\pi - \pi^*\) transition of the \(\alpha,\beta\)-unsaturated keto chromophore, present in the keto-enethiol (A). When the solvent was changed to EtOH or DMSO absorption maxima at 282 and 340 nm were observed. On going from an \(\alpha,\beta\)-unsaturated ketone to the thione the \(\pi - \pi^*\) absorption is shifted about 80 nm.\textsuperscript{a9–a11} The strong absorption of 340 nm must therefore arise from structure 5E. The structure 5F cannot be excluded because saturated thietoketones have only weak absorption above 300 nm and the observed one is strong.

Identification of other compounds. The spectroscopic data of 3-alkylthio derivatives of thiodimethone are shown in Table 3 (NMR) and Table 4 (IR and UV). These compounds gave rise to an IR absorption in the range of 1650–1680 cm\(^{-1}\) due to an \(\alpha,\beta\)-unsaturated carbonyl group and a band at 1570–1595 cm\(^{-1}\) corresponding to a carbon-carbon double bond. The UV spectra of compounds 7–10, 15 showed
Table 2. Rate of disappearance (−ΔC/Δt) of compound 13, measured by the change in UV absorbance (ΔAbs) for various concentrations (C) of 13.

<table>
<thead>
<tr>
<th>C × 10^5</th>
<th>ΔAbs</th>
<th>−ΔC × 10^4</th>
<th>Δt</th>
<th>−ΔC/Δt × 10^11</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/cm²</td>
<td>mol/cm²</td>
<td>(s)</td>
<td></td>
<td>mol/cm² s</td>
</tr>
<tr>
<td>0.645</td>
<td>0.29</td>
<td>1.45</td>
<td>180</td>
<td>8.06</td>
</tr>
<tr>
<td>1.30</td>
<td>0.23</td>
<td>2.30</td>
<td>300</td>
<td>7.67</td>
</tr>
<tr>
<td>1.94</td>
<td>0.25</td>
<td>3.45</td>
<td>420</td>
<td>8.23</td>
</tr>
<tr>
<td>3.23</td>
<td>0.21</td>
<td>5.25</td>
<td>720</td>
<td>7.23</td>
</tr>
<tr>
<td>3.87</td>
<td>0.23</td>
<td>6.90</td>
<td>900</td>
<td>7.67</td>
</tr>
<tr>
<td>6.45</td>
<td>0.29</td>
<td>14.50</td>
<td>1800</td>
<td>8.05</td>
</tr>
</tbody>
</table>

*a ΔC corresponds to 16–23% conversion of 13. ΔC = ΔAbs/Δt, where Δt is the difference between the molar absorbance of compound 13 (ε = 21 400) and that of compound 24 (ε = 1400) at 277 nm.

Table 3. 1H NMR chemical shift (δ values) and coupling constants (J Hz) of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives. The solvent is CDCl₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>δa</th>
<th>δb</th>
<th>δc</th>
<th>δd</th>
<th>δe</th>
<th>δf</th>
<th>Jcd</th>
<th>Jcf</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>H⁺</td>
<td>1.05(s)</td>
<td>2.13(s)</td>
<td>2.39(d)</td>
<td>6.05(t)</td>
<td>4.23(s)</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>1.06(s)</td>
<td>2.19(s)</td>
<td>2.39(d)</td>
<td>6.03(t)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH₃ = CH-CH₂⁺</td>
<td>1.05(s)</td>
<td>2.13(s)</td>
<td>2.26(d)</td>
<td>5.73(t)</td>
<td>5.1 – 6.2(m)</td>
<td>3.46(br,d)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>MeCH = CHCH₂⁺</td>
<td>1.05(s)</td>
<td>2.14(s)</td>
<td>2.25(d)</td>
<td>5.73(t)</td>
<td>5.2 – 9(m)</td>
<td>3.42(br,d)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>MeCOCH₂⁺</td>
<td>1.05(s)</td>
<td>2.24(s)</td>
<td>2.36(d)</td>
<td>5.78(t)</td>
<td>2.32(s)</td>
<td>3.76(s)</td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td>HCH = CH⁻</td>
<td>1.06(s)</td>
<td>2.17(s)</td>
<td>2.30(d)</td>
<td>5.82(t)</td>
<td>2.35(t)</td>
<td>3.60(d)</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>H₂C = C⁻</td>
<td>1.08(s)</td>
<td>2.15(s)</td>
<td>2.27(d)</td>
<td>6.18(t)</td>
<td>5.06</td>
<td>5.88</td>
<td>1.30</td>
<td>6.6c</td>
</tr>
<tr>
<td>12</td>
<td>MeCO⁻</td>
<td>1.10(s)</td>
<td>2.20(s)</td>
<td>2.50(d)</td>
<td>6.24(t)</td>
<td>2.37(s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Ph⁻</td>
<td>1.04(s)</td>
<td>2.12(s)</td>
<td>2.33(d)</td>
<td>5.42(t)</td>
<td>7.47(s)</td>
<td></td>
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<td></td>
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<tr>
<td>15</td>
<td>PhCH₂⁺</td>
<td>1.02(s)</td>
<td>2.12(s)</td>
<td>2.24(d)</td>
<td>5.82(t)</td>
<td>7.28(s)</td>
<td>3.94(s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a δf(Jcf Hz) = 1.74(5). b Solvent CDCl₃. c AB₃ spin system.

Table 4. IR and UV spectra of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR ν&lt;sub&gt;r&lt;/sub&gt;&lt;sup&gt;max&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;C=O&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;C=C&lt;/sub&gt;</th>
<th>Other</th>
<th>Conditions</th>
<th>UV,&lt;sup&gt;a&lt;/sup&gt; λ&lt;sub&gt;max&lt;/sub&gt; nm (log ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1680(br.s)</td>
<td>1595</td>
<td>2520(w,br.s)</td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>282(4.12), 340(3.74)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1660(s)</td>
<td>1580(s)</td>
<td></td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>228(3.96), 278(3.97), 313(3.50)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1650(s)</td>
<td>1580(s)</td>
<td></td>
<td>KBr</td>
<td>277(4.33)</td>
<td></td>
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<tr>
<td>7</td>
<td>1680(s)</td>
<td>1580(s)</td>
<td></td>
<td>film</td>
<td>288(4.24)</td>
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</tr>
<tr>
<td>8</td>
<td>1680(s)</td>
<td>1580(s)</td>
<td></td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>283(4.26)</td>
<td></td>
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<tr>
<td>9</td>
<td>1730(s)</td>
<td>1690(s)</td>
<td></td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>287(4.20)</td>
<td></td>
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<tr>
<td>10</td>
<td>1680(s)</td>
<td>1590(s)</td>
<td>3300(m)</td>
<td>film</td>
<td>287(4.22)</td>
<td></td>
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<tr>
<td>11</td>
<td>1660(s)</td>
<td>1590(s)</td>
<td>1930(w)</td>
<td>film</td>
<td>297(4.15)</td>
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<tr>
<td>12</td>
<td>1705(s)</td>
<td>1590(s)</td>
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<td>film</td>
<td>226(3.95), 277(3.96)</td>
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<tr>
<td>14</td>
<td>1680(s)</td>
<td>1580(s)</td>
<td></td>
<td>KBr</td>
<td>294(4.20)</td>
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</tr>
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<td>1680(s)</td>
<td>1570(s)</td>
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<td>KBr</td>
<td>282(4.30)</td>
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<tr>
<td>19</td>
<td>1655(s)</td>
<td>1600(s)</td>
<td>2530(m)</td>
<td>film</td>
<td>290, 350(shoulder)</td>
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</tr>
<tr>
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<td>1715(s)</td>
<td>1845(w)</td>
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<td>1605(s)</td>
<td></td>
<td>film</td>
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<tr>
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<td>1600(s)</td>
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<tr>
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<td>1650(s)</td>
<td>1550(m)</td>
<td></td>
<td>film</td>
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<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> The solvent is EtOH, unless otherwise stated. <sup>b</sup> Solvent: Hexane, <sup>c</sup> ether, <sup>d</sup> DMSO, <sup>e</sup> MeCN, <sup>f</sup> CHCl<sub>3</sub>.

Absorption at 287–292 nm which is ascribed to a π − π* transition of the conjugated system. The compounds 4, 11, 14 which were further conjugated with an additional carbon-carbon double bond showed a π − π* transition at somewhat longer wavelength i.e. in the range of 294–313 nm. The disulfide 13 and the acetyl 12 derivatives absorbed at shorter wavelength, namely at 277 nm, than the above mentioned compounds. The spectroscopic data of the products obtained by rearrangement of 3-allythio and 3-(2-butenyl) derivatives are shown in Table 5 (NMR) and Table 6 (IR and UV). The UV absorptions of the hexahydrobenzothiophenes were found at 312 nm which are about 25 nm higher than the corresponding bands of the starting materials. This is in agreement with the bathochromic effect exhibited by an α-substituent on α,β-unsaturated carbonyl chromophore.

The composition and the molecular weight of the 1,3-dithiole 24 were determined to be C<sub>12</sub>H<sub>12</sub>O<sub>5</sub>S<sub>2</sub> (M = 310) from the elemental analysis and the mass spectrum, respectively. The 1H NMR spectrum showed signals at δ 1.05–1.15 δ 2.25–2.48, and δ 3.02 with the relative intensity of 1:4:6, while the IR spectrum showed strong bands at 1705, 1660, and 1500 cm<sup>-1</sup>. Several structures, which were compatible with these data, could be drawn. Among the most plausible suggestions are those, which maintain the carbon skeleton and the positions of substituents of the starting material. However, an unambiguous choice could be made from the 13C-noise decoupled and the off resonance NMR spectra, which are shown in Table 6. The assignment of the signals was based on the data given for the chemical shifts and C–H coupling constants of cyclohexanone<sup>43</sup> and cyclohexenone.<sup>44</sup> Approximate values of the C–H coupling constants were determined from the residual splittings, using the expression given by Ernst,<sup>43</sup> and shown to be of the same size as for methylene groups of cyclohexane.<sup>43</sup>

Compound 25 was shown to have the composition C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>S<sub>2</sub> (molecular weight 312)
Table 5. $^1$H NMR chemical shift (δ values in ppm relative to TMS) and coupling constants of 2-alkyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one and derivatives.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>R</th>
<th>R'</th>
<th>δ&lt;sub&gt;a&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;b&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;c&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;d&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;e&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;f&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;g&lt;/sub&gt;</th>
<th>J&lt;sub&gt;de&lt;/sub&gt;</th>
<th>J&lt;sub&gt;ef&lt;/sub&gt;</th>
<th>J&lt;sub&gt;eg&lt;/sub&gt;</th>
<th>J&lt;sub&gt;fg&lt;/sub&gt;</th>
<th>J&lt;sub&gt;cf&lt;/sub&gt;</th>
<th>J&lt;sub&gt;cg&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>(CCl&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>H&lt;sup&gt;d&lt;/sup&gt; CH&lt;sub&gt;2&lt;/sub&gt;=CH − CH&lt;sub&gt;2&lt;/sub&gt; −</td>
<td>g</td>
<td>3.09</td>
<td>(br.d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>20</td>
<td>(CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>Ac&lt;sup&gt;d&lt;/sup&gt; CH&lt;sub&gt;3&lt;/sub&gt;=CH − CH&lt;sub&gt;2&lt;/sub&gt; −</td>
<td>e f g</td>
<td>1.09 (s)</td>
<td>2.36 (s)</td>
<td>2.69 (br.)</td>
<td>2.50 (s)</td>
<td>3.23 (br.d)</td>
<td>4.8 (m)</td>
<td>−6.05 (m)</td>
<td>6.75 (m)</td>
<td>8.92 (m)</td>
<td>5.74 (m)</td>
<td>−15.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.36</td>
<td>2.04</td>
</tr>
<tr>
<td>21</td>
<td>(CCl&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>R = −CH−CH&lt;sub&gt;2&lt;/sub&gt;− = R'</td>
<td>Me&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.33 (d)</td>
<td>1.38 (d)</td>
<td>3.83 (m)</td>
<td>3.08 (m)</td>
<td>2.66 (m)</td>
<td>6.75 (m)</td>
<td>8.92 (m)</td>
<td>5.74 (m)</td>
<td>−15.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.36</td>
<td>2.04</td>
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<tr>
<td>22</td>
<td>(CCl&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>R = −CH−CH− = R'</td>
<td>Me&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.78 (s)</td>
<td>2.05 (s)</td>
<td>1.97 (br.s)</td>
<td>1.11 (d)</td>
<td>1.19 (d)</td>
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</tr>
<tr>
<td>22&lt;sup&gt;'&lt;/sup&gt;</td>
<td></td>
<td>80 %&lt;sub&gt;(22)&lt;/sub&gt; + 20 %&lt;sub&gt;(22')&lt;/sub&gt;</td>
<td></td>
<td>0.78 (s)</td>
<td>2.05 (s)</td>
<td>1.97 (br.s)</td>
<td>1.07 (d)</td>
<td>1.05 (d)</td>
<td>2.5 (m)</td>
<td>3.5 (m)</td>
<td>7.0 (m)</td>
<td>7.0 (m)</td>
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<tr>
<td>22&lt;sup&gt;'&lt;/sup&gt;</td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;4&lt;/sub&gt;)</td>
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<tr>
<td>23&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>R = −CH−CH=CH− = R'</td>
<td></td>
<td>1.03 (s)</td>
<td>2.24 (br.s)</td>
<td>2.34 (br.s)</td>
<td>0.99 (d)</td>
<td>2.9 (m)</td>
<td>3.5 (m)</td>
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<td>0.9</td>
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</table>

<sup>a</sup> Rel. sign.  <sup>b</sup> J<sub>df</sub>=1.6 Hz.
Table 6. $^{13}$C NMR data of the noise and off resonance decoupled spectra of compound 24 (cf. p. 1081). Chemical shifts ($\delta$ values in ppm, relative to TMS) and approximate coupling constants ($J_{CH}$ Hz) evaluated from the expression $^{44}$

$$J_{CH}^{-1} = 2\pi A \nu J_{CH}/\gamma H_{2}$$

Relative intensities of lines ($I$). The solvent is CDCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Me</th>
<th>Me</th>
<th>Me</th>
<th>C5(11)</th>
<th>C11(5)</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH$_2$</th>
<th>CH$_2$</th>
<th>C9</th>
<th>C2</th>
<th>C3</th>
<th>C1</th>
<th>C7</th>
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<td>28.6</td>
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<td>53.2</td>
<td>57.4</td>
<td>66.9</td>
<td>128.9</td>
<td>152.5</td>
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<tr>
<td>$I$(rel)</td>
<td>206</td>
<td>185</td>
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<td>203</td>
<td>198</td>
<td>132</td>
<td>171</td>
<td>169</td>
<td>193</td>
<td>206</td>
<td>157</td>
<td>14.7</td>
<td>60</td>
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</tr>
<tr>
<td>$J$(Hz)</td>
<td>122±3</td>
<td>122±3</td>
<td>122±3</td>
<td>122±3</td>
<td>–</td>
<td>–</td>
<td>129±5</td>
<td>129±5</td>
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<td>129±5</td>
<td>129±5</td>
<td>–</td>
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<td>–</td>
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</tbody>
</table>
Table 7. $^{13}$C NMR data of the noise and off resonance decoupled spectrum of compound 25.

![Chemical structure](image)

Chemical shifts (δ values in ppm, relative to TMS) and relative intensities of lines (I). The solvent is CDCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Me</th>
<th>Me</th>
<th>C5</th>
<th>C3</th>
<th>C4</th>
<th>C2</th>
<th>C6</th>
<th>C1</th>
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<tbody>
<tr>
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<td>39.7</td>
<td>48.4</td>
<td>49.4</td>
<td>54.7</td>
<td>54.8</td>
<td>213</td>
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<tr>
<td>I</td>
<td>162</td>
<td>155</td>
<td>59</td>
<td>112</td>
<td>119</td>
<td>74</td>
<td>211</td>
<td>30</td>
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<tr>
<td>Multiplicity</td>
<td>q</td>
<td>q</td>
<td>s</td>
<td>d</td>
<td>t</td>
<td>d</td>
<td>t</td>
<td>s</td>
</tr>
</tbody>
</table>

![Possible structures](image)

Fig. 3. Possible structures for the photo-dimer 25.

as determined by the mass spectrum. The noise decoupled $^{13}$C NMR spectrum showed 8 signals (Table 7) from the 16 carbon atoms, indicating magnetic equivalent pairs of carbon atoms. The off resonance decoupled spectrum showed the presence of methyl methylene and methine carbon atoms. It was assumed that the carbon skeleton of thioldimedone δ was maintained in the photo-dimer 25, which might then have one of the 1,2- or 1,4-dithiane structures shown in Fig. 3. However, the 1,2-dithiane structure was unlikely, as it did not account for the $^1$H NMR multiplet signal at δ 3.6 – 4.1 assigned to a pair of equivalent methine protons. The signals due to the methine protons in the α-position to the carbonyl group of the 1,2-dithiane would be found at higher field, i.e. at about δ 3. The most probable structures are therefore those represented in Fig. 4, which could not be distinguished based on ground of the available data.

EXPERIMENTAL

$^1$H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. The temperature of the 15 – 20 % solutions (w/w) were 33 ± 1 °C. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values and are correct within ± 0.02 ppm. $^{13}$C spectra were recorded on a Varian XL-100-15 spectrometer operating in the c.w. mode at 25.2 MHz. Internal field-frequency lock was provided by the $^1$H resonance of CDCl$_3$ as solvent. Carbon line positions were measured relative to the carbon resonance of internal TMS. Noise-modulated and single-frequency proton decoupling experiments were performed by means of the Varian Gyrocode spin decoupler. The sample solution was contained in a 12 mm tube. 70 eV mass spectra were obtained on a Bell and Howell CEC 21 – 104 single focussing mass spectrometer. The IR spectra were recorded as 5 % solutions, film,

![Compound 25](image)

Fig. 4. Compound 25.
or as KBr pellets on a Perkin-Elmer infracord 137 and the UV spectra on a Bausch & Lomb Spectronic 20 spectrophotometer with EtOH as solvent. B. P.'s are uncorrected. Analyses were made by Novo Industri A/S, Copenhagen.

**General procedure for the preparation of the sodium salt of 3-mercapto-5,5-dimethyl-2-cyclohexen-1-one.** An amount of 16 g (0.1 mol) 3-chloro-5,5-dimethyl-2-cyclohexen-1-one, 2, was dropped to a solution of 25 g (0.1 mol) \( \text{Na}_2\text{S}_2\text{O}_3 \) in 25 ml water during 2 h. The mixture was kept at about 80 °C until it became homogeneous after further 2 h. This solution was then extracted with diethyl ether (2 × 10 ml), which after drying and evaporation gave small amounts of bis(5,5-dimethyl-2-cyclohexen-3-yl)-sulfide, 4. The water solution was then used for further reactions.

**3-Mercapto-5,5-dimethyl-2-cyclohexen-1-one, 5.** Acidification (0.1 mol) of the solution of the sodium salt of 5 with cold 4 M HCl, extraction with ether, drying and evaporation of the ether gave the crude product, which amounted to 14.8 g (95 %). The yield decreased considerably by distillation at 98 °C (0.1 mm Hg); \( n_\text{D}^26^q = 1.5690 \). (Found: \( C 61.49; H 7.79; S 19.47 \). \( C_{11}H_{15}O_S \) requires: \( C 61.52; H 7.75; S 20.49 \)).

**Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl)-sulfide, 4.** Ether extraction of the water solution of the sodium salt of 5 prepared by the general procedure gave after drying and evaporation 0.656 g (5 %) of m.p. 176 – 177 °C. (Found: \( C 68.84; H 7.98; S 11.46 \). \( C_{15}H_{16}O_S \) requires: \( C 69.04; H 7.97; S 11.50 \). MS, m/e (%): 280(9), 279(38), 278(61), 264(5), 263(23), 207(8), 196(5), 195(11), 194(57), 156(9), 155(47), 152(14), 151(16), 141(9), 139(9), 138(15), 137(24), 123(9), 112(11), 111(2), 110(77), 95(9), 93(8), 91(8), 79(23), 77(15), 71(17), 68(100), 58(8), 56(22), 53(22).)

**5,5-Dimethyl-2-cyclohexen-1-on-3-yl)-disulfide, 13.** To a water solution of 0.1 mol of the sodium salt of 5 prepared by the general method were added (excess) 20 g (0.079 mol) of iodine dissolved in 50 ml THF. After about 2 h at room temp. a saturated solution of \( \text{Na}_2\text{S}_2\text{O}_3 \) was added until the dark colour disappeared, and the mixture was extracted with \( \text{CH}_2\text{Cl}_2 \). This was then stripped off and the residue treated with ether and water. The ether was dried and evaporated giving 14.1 g (91 %) of crystalline product. M.p. 91 °C (ether). (Found: \( C 61.95; H 7.16; S 20.21 \). \( C_{15}H_{15}O_2S_2 \) requires: \( C 61.92; H 7.15; S 20.6 \). MS, m/e (%): 310(26), 295(9.2), 279(11), 278(37), 277(100), 255(9.2), 254(39), 253(56), 247(7.4), 246(45), 254(19), 220(11), 212(35), 156(26), 155(33), 100(50), 83(50), 71(32), 67(65), 55(37).)

**5,5-Dimethyl-2-thiacyclohexen-1-one, 6.** To the solution prepared by the general method were added 16 g (0.11 mol) MeI. The temp. was kept at about 30 °C. The mixture was then allowed to stand overnight. Extraction with ether, drying evaporation of the solvent yielded 15.1 g (89 %) of crystalline compound, m.p. 35 °C (lit. m.p. 34 – 37 °C).

**3-Allylthio-5,5-dimethyl-2-cyclohexen-1-one, 7.** An amount of 15 g (0.12 mol) allyl bromide in 25 ml DMSO was added to the water solution of the 0.1 mol sodium salt of 5. The temp. was allowed to rise to 45 °C. After 2 h the mixture was cooled and extracted with 15 ml ether, which was then evaporated. Extraction with water of the residue dissolved in light petroleum was repeated. Drying and evaporation and distillation gave 18 g (92 %); b.p. 65 °C/10 mmHg; \( n_\text{D}^26^q = 1.5520 \). (Found: \( C 67.34; H 8.21; S 16.11 \). \( C_{11}H_{14}O_S \) requires: C 67.32; H 8.22; S 16.31).

**3-(2-Butenylthio)-5,5-dimethyl-2-cyclohexen-1-one, 8.** An amount of 8 g (0.059 mol) of 2-butylthio bromide was added to 0.05 mol of the water solution of the sodium salt of 5. Stirring overnight, followed by extraction with ether, drying and evaporation of the ether gave 8.7 g (83 %); b.p. 114 – 116 °C/0.1 mm Hg; m.p. 33 – 34 °C. (Found: \( C 68.61; H 8.64; S 15.11 \). \( C_{11}H_{15}O_S \) requires: \( C 68.54; H 8.63; S 15.22 \)).

**5,5-Dimethyl-3-(3-propan-2-ol-1-thio)-2-cyclohexen-1-one, 9.** A water solution of 0.1 mol of the sodium salt of 5 was treated with 11 g (0.12 mol) chloroacetone. The exothermal process was finished within 0.5 h. Extraction with 50 ml of ether, drying, and evaporation of the solvent gave 14.5 g (88 %) of crystalline product; m.p. 65 °C (ether – light petroleum 1/1). (Found: \( C 62.47; H 7.74; S 15.21 \). \( C_{11}H_{14}O_S \) requires: \( C 62.25; H 7.60; S 15.08 \)).

**5,5-Dimethyl-3-(2-propynylthio)-2-cyclohexen-1-one, 10.** An amount of 1.80 g (11.5 mmol) of 5 was dropped to 3.0 g (12 mmol) of thallium(I) ethoxide dissolved in 25 ml benzene. The solid product was filtered off and washed with benzene and ether, giving an mount of 3.9 g (95 %). Then 3.59 g (10 mmol) of the salt were suspended in 15 ml HMPA and 1.5 g (12.6 mmol) of 2-propynyl bromide were added. The mixture was stirred overnight and extracted with ether and water. The ether was stripped off and extraction was repeated with light petroleum and water. Drying and evaporation of the solvent yielded 1.77 g (89 %) which were distilled quantitatively. B. p. 80 °C/10 mm Hg; \( n_\text{D}^25^q = 1.5608 \). (Found: \( C 68.23; H 7.04; S 16.23 \). \( C_{11}H_{14}O_S \) requires: \( C 68.02; H 7.27; S 16.5 \)).

**3-Allenylthio-5,5-dimethyl-2-cyclohexen-1-one, 11.** An amount of 4.62 g (29.5 mmol) of 5 dissolved in 30 ml \( \text{CH}_2\text{Cl}_2 \) was added to 10.5 g (31.0 mmol) of tetrabutylammonium hydrogensulfate and 3 g (75 mmol) of NaOH in 30 ml water. Then 4 g (34 mmol) of 2-propynyl bromide were added and the mixture stirred for 18 h. The \( \text{CH}_2\text{Cl}_2 \) phase was evaporated and the residue was treated with ether and water. Drying and evaporation yielded 4.9 g (86 %) of 11. However, the yield decreased considerably by distillation which gave 1.58 g of b.p. 70 °C/10 mm Hg; \( n_\text{D}^25^q = 1.5705 \). (Found: \( C 67.94 \);

3-Acetylthio-5,5-dimethyl-cyclohexen-1-one, 12. Acidification and work up (without distillation) of a solution prepared by the general method gave 5 which was then treated with 10 g pyridine and 100 ml ether. An amount of 9 g (0.115 mol) acetyl chloride was dropped to the mixture and after 1 h the pyridinium hydrochloride was filtered off and the residue washed with water. The ether was dried over NaHCO₃. Evaporation gave 19 g and distillation yielded 15.82 g (75 %); b.p. 96 °C/0.5 mm Hg; n₅ᵇ = 1.5314. (Found: C 60.79; H 7.13; S 15.80. C₃H₅O₅S requires: C 60.59; H 7.12; S 16.15).

1,5,3-Trinbenzylthio-5,5-dimethyl-1-cyclohexene, 16, and 3-benzylthio-5,5-dimethyl-2-cyclohexen-1-one, 17. Preparation by the method of Campagne. An amount of 14 g (0.1 mol) of dimedone, I, and 24.8 g (0.2 mol) of phenylmethylthiol were mixed in 200 ml ethanol. The solution was saturated with HCI gas. A precipitate of 1.16 g (3.6 %) of 16 was formed (theoretical yield 31.9 g). M.p. 77-82 °C. (Found: C 72.73; H 6.68; S 19.88. C₃H₅O₅S requires: C 73.09; H 6.77; S 20.14). NMR (ClCD): δ 0.96 (6 H, s), 1.83 (4 H, br.s), 3.53 (2 H, s), 3.70 (4 H, s), 5.18 (1 H, s), 7.22 (15 H, s). IR νmax(KBr) (cm⁻¹): 1590. UV (EtOH): λmax (log e): 212 (4.40), 252 nm (4.07). The alcohol solution was poured into 300 ml water in which 150 g Na₂CO₃ was dissolved. A precipitate was filtered, and then dissolved, dried and the solvent evaporated, giving 5.5 g (22 %) of 15. M.p. 84-85 °C. (Found: C 73.11; H 7.29; S 13.11. C₁₅H₃₀O₅S requires: C 73.14; H 7.37; S 12.99).

Treatment of 3-alkylthio-5,5-dimethyl-2-cyclohexen-1-ones with nucleophiles

3-Ethyliden-5,5-dimethyl-1-phenylthio-cyclohexene, 17. An amount of 11.6 g (0.05 mol) of 14 dissolved in 50 ml THF was treated with 0.05 mol EtLi in 50 ml THF solution at -10 °C. After about 1 h, 15 g (0.106 mol) MeI was added and the mixture allowed to stir for 1 h. The solvent was stripped off and extracted with ether and water. The ether phase was dried and evaporated, giving 12.0 g of a liquid. After a short time it became milky and separated into two layers. The mixture was treated with ether again, dried and the solvent evaporated. Distillation yielded 9.4 g (77 %) of b.p. 123-124 °C/0.2 mm Hg; n₅ᵇ = 1.5909. IR νmax(film) (cm⁻¹): 3050(m), 2900(s), 1570(m). NMR (ClCD): δ 0.89 and 0.92 (6 H, s), 1.70 (3 H, br. d, 7), 2.02 (4 H, br.s), 5.1-5.5 (1 H, m), 6.24 and 6.56 (1 H, br.s), 7.28 (5 H, br.s). (Found: C 78.24; H 8.00; S 13.17. C₁₅H₃₀O₅S requires: C 78.65; H 8.25; S 13.11).

5,5-Dimethyl-3-phenylthio-3-cyclohexen-1-one, 18. An amount of 2.32 g (0.01 mol) of 15 dissolved in 10 ml of dry ether was dropped to a suspension of LiNH₃ in liq. NH₃ (prepared from 100 mg Li). The NH₃ was evaporated and the residue acidified with H₂O and NH₄Cl. Extraction with ether drying and evaporation of the solvent gave 2.05 g of crude product, which was fractionated on a column, giving 1.85 g (80 %) of starting material and 0.19 g (8 %) of 19. IR νmax(film) (cm⁻¹): 1710(s). MS; m/e (%): 232(56), 219(6), 218(16), 217(100), 189(14), 176(6), 164(10), 156(6), 113(10), 111(12), 109(26), 107(56), 95(8), 93(8), 91(8), 81(15), 80(12), 79(68), 78(10), 77(45), 69(10), 67(17), 66(8), 65(15), 55(12), 53(19).

Rearrangement of 7

2-Alllyl-3-mercapto-5,5-dimethyl-2-cyclohexen-1-one, 19. Traces of p-toluenesulfonic acid were added to 5.3 g (27 mmol) of 7 and kept at 100 C for 4½ h in a Vigreaux distillation apparatus. Distillation gave 3 fractions, which were shown to consist of compounds 19 and 21, as shown by the NMR and IR spectra.

3-Acetylthio-2-allyl-5,5-dimethyl-1-cyclohexene, 20. An amount of 2.68 g (13.7 mmol) of 7 in 10 ml acetic anhydride was boiled at 140 °C for 2 h. The acetic anhydride was stripped off and the residue dissolved in ether, which was then extracted with 2 M aqueous Na₂CO₃. Drying and evaporation of the ether yielded 2.87 g crude product. 1.40 of this was purified with PLC yielding 0.5 g (36 %) of 20 and 0.26 g of an unidentified mixture. B.p. of 20 60° C/10⁻⁴ mmHg; n₅ᵇ = 1.5280. (Found: C 65.69; H 7.51; S 13.41. C₁₅H₃₀O₅S requires: C 65.53; H 7.61; S 13.41).

2,6,6-Trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene, 21. An amount of 2.05 g (10.4 mmol) of 7 in 5 ml quinoline was heated to 140 °C. After 3 h the starting material was converted. The mixture was extracted with ether and 4 M HCl. The ether layer was dried and evaporated. Crude product amounted to 1.78 g. Distillation gave 0.73 g (36 %) of b.p. 100 °C/0.01 mm Hg; n₅ᵇ = 1.5355. (Found: C 67.26; H 7.92; S 15.95. C₁₁H₁₄O₅S requires: C 67.32; H 8.22; S 16.31).

Rearrangement of 8

2,3,6,6-Tetramethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzothiophene, 22. An amount of 1.77 g (8.3 mmol) of 8 in 3 ml quinoline was heated for 5 h. Extraction with 4 M HCl and ether gave after drying and evaporation of the ether 1.40 g, which was distilled. B.p. 100 °C/0.01 mm Hg, giving 1.17 g of a mixture of 27 % starting material and 73 % product. The experiment was repeated with 0.585 g of this mixture at a temp. of 160 °C and a reaction time of 3 h. Work up as above gave 0.348 g (yield 39 %) of b.p.

100 °C/0.01 mmHg; n_D^20 = 1.5420; (Found: C 67.78; H 8.42; S 14.99. C_11H_8O_5S requires C 68.54; H 8.63; S 15.22).

Rearrangement of 10

7,7-Dimethyl-5-oxo-2,5,6,7,8-pentahydrobenzo-
thiopyran, 23. An amount of 1.19 g (6.2 mmol) of 10 was boiled in 4 ml pyridine for 3½ h. The solvent was evaporated and the residue distilled. B.p. 100 °C/0.01 mmHg; n_D^20 = 1.5796.

General procedure by photolysis of 3-alkylthio-
and 3-aryltthio-5,5-dimethyl-2-cyclohexen-1-ones. A solution of the compound was irradiated in a "Rayonet" RS photoreactor (see Table 1). A flow of dry and oxygen-free N_2 through the solution was maintained during the photolysis. The reaction was followed by UV spectroscopy and TLC. The solvent was evaporated and the residue was fractionated on a silica gel column or plate (about 100 g silica gel/g of product) with benzene—ethyl acetate = 4:1 (w/w) as eluent. However, the mixture obtained by photolysis of 14 was worked up using ether—light petroleum = 1:1 (w/w) as eluent.

The 1,3-dithiole, 24. M.p. 167—169 °C; (Found: C 61.90; H 7.12; S 20.63. C_4H_8O_2S requires: C 61.92; H 7.15; S 20.6). NMR (CDCl_3): δ 1.05—1.15 (12 H, 3 s); 2.25—2.46 (8 H, br. singlets and AB splittings); 3.02 (2 H, br. s). IR ν_MAX (CHCl_3) (cm⁻¹): 1710 (m-s); 1660 (s); 1560 (m-s).

UV (CHCl_3) λ_MAX (log e): 250 (3.71), 350 (3.71). MS, m/e (%): 310(33), 308(5), 277(5), 256(8), 255(21), 254(68), 253(100), 239(32), 214(8), 213(16), 212(72), 178(20), 156(11), 155(8), 83(48), 55(54).

The 1,4-dithiane, 25. M.p. 172—174 °C; NMR (CDCl_3): δ 0.93—1.12 (12 H, br.s); 1.7—2.7 (8 H, m); 3.1—3.32 (2 H, m); 3.6—4.1 (2 H, m). IR ν_MAX (CHCl_3) (cm⁻¹): 1710. MS, m/e (%): 312(2), 311(9), 310(4), 309(6), 308(8), 297(18), 282(12), 281(56), 280(40), 279(30), 278(10), 277(17), 263(16), 261(14), 260(75), 248(20), 247(100), 246(14), 245(10), 206(22), 195(40), 181(20), 157(25), 156(67), 155(8), 141(25), 140(5), 127(77), 97(38), 91(29), 83(56), 55(40), 43(26), 41(53).

3,3-Dimethyl-5-oxo-2,3,4,5-tetrahydrodibenzo-
thiophene, 26. M.p. 100—102 °C; (Found: C 73.88; H 6.16; S 13.86. C_11H_8O_5S requires: C 73.02; H 6.13; S 13.90). NMR (CDCl_3): δ 1.15 (6 H, s), 2.36 (2 H, s), 2.90 (2 H, s), 7.1 (3, H, m), 8.50—8.65 (1 H, m). IR ν_MAX (KBr) (cm⁻¹): 1650. UV (EtOH): λ_MAX (log e): 220 (4.08), 243 (3.70), 303 nm (3.48).

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