2-Thiabicyclo[3.2.0]hepta-3,6-dienes. 2. Thermal and Photochemical Isomerization of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes. An Example of the Antarafacial–Antarafacial Cope Rearrangement

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Thermal rearrangement of 2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitriles 1–3 to their 4,5-dicarbonitrile isomers 4–6 takes place at 110–140 °C in yields of 82–84%. The reactions are first order with rates almost independent of the polarity of the solvent. Activation parameters (ΔH° = 120–140 kJ mol−1 and ΔS° = 0 J K−1 mol−1) are in agreement with a concerted symmetry-allowed antarafacial–antarafacial Cope rearrangement. Compounds 1–3 rearrange photochemically via cleavage of the C-1=S bond to the 1,7-dicarbonitrile isomers 7–9.

Isomer 9 rearranges further on prolonged irradiation to give 10. A tentative mechanism for this rearrangement is given.

The synthesis of 2-thiabicyclo[3.2.0]hepta-3,6-dienes (e.g., 1), potential precursors of thiiepins, has been described in the preceding paper.1 This paper deals with the thermal and photochemical isomerization of these compounds.2 The thermal isomerization of 1 is not only of importance as a possible route to thiiepins but also from a mechanistic point of view because the thermal isomerization of bicyclo[3.2.0]hepta-3,6-dienes has been the subject of controversy.

It has been suggested3 that the thermal rearrangement of bicyclo[3.2.0]hepta-3,6-dien-2-ones4 represents the first example of an antarafacial–antarafacial Cope rearrangement, a mode of rearrangement which usually will not take place for the less rigid analogous acyclic 1,6-hexadienes because of a highly strained transition state. However, the rearrangement of the bicyclo[3.2.0]hepta-3,6-dien-2-ones is unselective and is accompanied by formation of the analogous monocyclic tr~pones.5 Moreover, alternative mechanisms for this type of rearrangement have been advanced.6 Baldwin and Kaplan7 have proposed the intermediacy of cis,trans,cis-cycloheptatriene species which can subsequently recycle to give the isomeric bicyclo[3.2.0]hepta-3,6-diene-2-ones or isomerize to give tr~pones. Fräter et al.8 have put forward a further possibility, viz., two consecutive symmetry-allowed antarafacial–suprafacial [1,3] sigmatropic reactions and bicyclo[4.1.0]heptadienone intermediates, to account for the rearrangement.

Photochemical rearrangement of bicyclo[3.2.0]hepta-3,6-diene derivatives was reported by Eaton9 and by Chapman and Lassila.10 This type of rearrangement has also been described for 2a,7b-dihydrocyclobuta[b][1]benzothiophenes both in intermolecular photochemical [2 + 2] cycloaddition reactions of benzof[b]thiophenes and acetylenes11 and in intramolecular photochemical [2 + 2] cycloaddition reactions of 1-benzothiepins.12 Recently a similar rearrangement has been postulated to account for the desulfurated photoproducts of 3-benzoylthiophenes and dimethyl acetylenedicarboxylate (vide infra).13

### Results

#### Thermal Rearrangement

When 1,3,4,5-tetramethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitrile (1, Chart I) was heated in refluxing xylene (140 °C) for 18 h, a colorless crystalline compound was obtained in a yield of 82%. Elemental analysis (C12H12N2S) and mass spectrometry (M+, m/e 216.072) showed that it was an isomer of 1. When the compound was heated in refluxing tetraethyleneglycol dimethyl ether (275 °C) for 15 min, 3,4,5,6-tetramethyl-1,2-benzenedicarbonitrile3,18 was ob-

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3. The initial results of this work are partially also described in a thesis: Heider, R., Thesis, Groningen University, 1974.
16. The same kind of rearrangement has been postulated earlier by Kuhn and Gollnick,5 but it is possible that in their case the resulting phthalate esters are formed by sulfur elimination from 1,4-addition products. The 2-thiabicyclo[3.2.0]hepta-3,6-dienes described in the present paper do not undergo sulfur extrusion upon irradiation under the conditions described, except possibly to a limited extent.
2-Thiabicyclo[3.2.0]hepta-3,6-dienes

dicyano isomers
tained, indicating that the two carbonitrile groups were
methods. 'H NMR and HPLC
but less accurate (see Experimental Section).

sulfide a-donor and the dicyanoethylene σ*-acceptor
only possible structure for the isomer is 1,3,6,7-tetra-
methyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile
yield of 84% whereas

moieties in the compounds. This intramolecular
characterizations of
with consequent formation of a dimethylthiophenedi-

[(19) The isomerization of 1 to 4 was also measured by using two other
methods, 'H NMR and HPLC analyses. The results are almost the same
but less accurate (see Experimental Section).

Figure 1. UV spectra of compounds 1-6: 1, R1 = R2 = Me; 2,
R1 = CMe3, R2 = H; 3, R1 = H, R2 = CMe3; 4, R1 = R2 = Me; 5,
R1 = CMe3, R2 = H; 6, R1 = H, R2 = CMe3.

The rates of the isomerizations of 1 to 4, 2 to 5, and 3
to 6 were measured by monitoring the change in absorb-
cance, at the respective maxima, with time at various
temperatures. The rearrangement of 1 into 4 was found
to be first order for at least 3 half-lives in three different
solvents: 1,3,5-trimethylbenzene, pentachloroethane, and
dimethyl sulfoxide. Similarly, the rearrangements of 2 into
5 and 3 into 6 were found to be first order in penta-
chlorehane. A plot of log k vs. T-1 gave the activation
parameters of the isomerization reactions (Table II).
For comparison, the rate of conversion of 1 to 4 was also
measured by 'H NMR spectroscopy and HPLC analysis.
Both methods gave similar k values (±10%), but these
methods are less accurate. However, both methods have
the advantage that the formation of 4 could experimentally
be verified whereas the UV method only makes use of the
disappearance of 1.

Photochemical Reactions. When 1 was irradiated in ether
(N2, -20 °C, 8 h) with ultraviolet light, a colorless
crystalline compound was obtained in a yield of 67%.
Elemental analysis (C8H13NS8), mass spectrometry (M+, m/e 216.072), and its 13C NMR spectrum (four Csp3, two
carbonitrile, two Csp2, and four methyl carbon resonances)
showed that it was a second isomeric 2-thiabicyclo-
[3.2.0]hepta-3,6-diene. Again, when this isomer was heated in
refluxing tetramethylene glycol dimethyl ether (275 °C)
for 15 min, 3,4,5,6-tetramethyl-1,2-benzenedicarbonitrile
was obtained, indicating that the two carbonitrile
groups were adjacent in the isomer. Its 1H NMR spectrum
had four distinct methyl resonances, two of

<table>
<thead>
<tr>
<th>No.</th>
<th>mp, °C (pentane)</th>
<th>mass spectral data, m/e (relative intensity), fragment</th>
<th>IR, cm⁻¹ (assignment)</th>
<th>UV, (E=1, nm (c))</th>
<th>¹H NMR (CDCl₃), δ (assignment)</th>
<th>¹³C NMR (CDCl₃), δ (assignment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>98–99</td>
<td>216 (79), M⁺, 183 (37), MeC₆H₄ (C=N), 162 (100), M⁺ (MeCC=CCMe₃)</td>
<td>2245, 2210 (C=N), 1690, 1685 (C=C)</td>
<td>288</td>
<td>2.20 (3), 1.86 (6), 1.74 (1), 1.70 (7)</td>
<td>162.7 (3), 144.9 (7), 115.2 (1), 110.0 (5), 59.1 (1), 37.1 (3)</td>
</tr>
<tr>
<td>5</td>
<td>73–74</td>
<td>244 (61), M⁺, 162 (100), M⁺ (HC₆C=CCMe₃); 147 (33), MeC₆H₄ (C=N), 1600 (C=C)</td>
<td>2240, 2220 (C=N), 1620 (C=C)</td>
<td>288</td>
<td>6.02 (6), 2.21 (3), 1.88 (1)</td>
<td>164.9, 162.5 (3, 7), 124.6 (6), 98.5 (4)</td>
</tr>
<tr>
<td>6</td>
<td>81–82</td>
<td>244 (32), M⁺, 229 (32), MeC₆H₄ (C=N), 162 (100), M⁺ (HC₆C=CCMe₃)</td>
<td>2240, 2220 (C=N), 1625 (C=C)</td>
<td>288</td>
<td>6.06 (7), 2.24 (3), 1.74 (1)</td>
<td>163.6, 158.2 (3, 6), 133.3 (7), 97.8 (4)</td>
</tr>
<tr>
<td>7</td>
<td>103–104</td>
<td>216 (46), M⁺, 161 (100), M⁺ (NCC=CMe₃); 136 (89), MeC₆H₄ (C=N), 1650 (C=C)</td>
<td>2240, 2220 (C=N), 1650 (C=C)</td>
<td>250-325</td>
<td>2.01 (6), 1.85 (3), 1.70 (4), 1.54 (5)</td>
<td>169.6 (6), 129.0 (4), 121.9 (3), 106.6 (7)</td>
</tr>
<tr>
<td>8</td>
<td>93–94</td>
<td>244 (30), M⁺, 229 (42), MeC₆H₄ (C=N), 164 (100), M⁺ (NCC=CMe₃)</td>
<td>2250, 2230 (C=N), 1650 (C=C)</td>
<td>250-350</td>
<td>4.75 (5), 2.15 (6), 1.99 (3)</td>
<td>166.7 (6), 132.8 (4), 112.8 (7)</td>
</tr>
<tr>
<td>9</td>
<td>oil</td>
<td>244 (89), M⁺, 188 (100), M⁺ (C=C), 164 (100), M⁺ (NC₆C=CCMe₃)</td>
<td>2250, 2230 (C=N), 1640 (C=C)</td>
<td>250-325</td>
<td>5.41 (4), 2.09 (6), 1.99 (3)</td>
<td>169.1 (6), 139.5 (3), 115.1 (4), 106.1 (7)</td>
</tr>
<tr>
<td>10</td>
<td>59–60</td>
<td>244 (14), M⁺, 137 (100), M⁺ (NC₆C=CCMe₃); 122 (27), M⁺ (NCC=CMe₃)</td>
<td>2250, 2220 (C=C), 1640 (C=C)</td>
<td>250-325</td>
<td>5.20 (4), 1.95 (3), 1.62 (5)</td>
<td>180.9 (6), 138.3 (3), 118.0 (4), 103.5 (7)</td>
</tr>
</tbody>
</table>

* C, H, N, and S elemental analyses were done for all entries and agreed to ±0.2% of the theoretical values. *b* In a KBr disk. *c* Charge-transfer band. *d* Chemical shifts are given in parts per million relative to Me₄Si (6.0). *e* Singlet unless otherwise stated. *f* Long-range allylic and homoallylic coupling: J = 1.0–1.5 Hz. *g* Quartet on partial C-H decoupling. *h* Doublet on partial C-H decoupling.
transition state\textsuperscript{22} or whether the intermediate of the reaction is a 1,4-cyclohexylene biradical.\textsuperscript{23,24} Further, whereas the vast majority of Cope rearrangements, if concerted, are regarded to be suprafacial-suprafacial [3,3] sigmatropic processes with chairlike or, less commonly, boatlike transition states, Woodward and Hoffmann have predicted\textsuperscript{4} that the rearrangement can also proceed in an antarafacial-antarafacial mode via a twistlike transition state. However, such processes will not normally be competitive because of the steric strain involved\textsuperscript{4} and, to our knowledge, have never been unambiguously proven to occur. We believe that the results described here of the thermal rearrangement of 6,7-dicyano-2-thiabicyclo[3.2.0]hepta-3,6-dienes can be regarded as being the first unambiguously established example of a Cope rearrangement proceeding in such an antarafacial-antarafacial manner.

It can clearly be seen that the activation energy is nearly independent of the solvent polarity, as it should be in a concerted reaction, and that the activation energy values of 120–140 kJ mol\textsuperscript{-1} are comparable to those reported for the Cope rearrangements of simple 1,5-hexadienes.\textsuperscript{23,24,27} The faster rate of the rearrangement compared to the rate of rearrangement of simple 1,5-hexadienes is readily explained by the different activation entropies involved: +0.9 to +0.6 compared with −55 to −60 J K\textsuperscript{-1} mol\textsuperscript{-1}.\textsuperscript{26} The enhancement of the rate of isomerization of 3 to 6 compared to that of 2 to 5 must result from the presence of the tert-butyl group at the bridgehead (C-5) of 3. Presumably, the tert-butyl group in 3 weakens the C-1-C-5 bond and changes the conformation of the molecule. This change in conformation is reflected in the lower absorption maximum (377 nm) for the charge-transfer transition.

The low activation entropy of these rearrangements indicates that there is hardly any increase in strain in the transition state compared with that in the ground state (Scheme I, a). Alternative mechanisms that would also rationalize these isomerization reactions, which were proposed by Früster et al.\textsuperscript{7} and Baldwin and Kaplan\textsuperscript{8} for similar reactions of bicyclo[3.2.0]hepta-3,6-diene and -hepta-3,6-dien-2-ones, are two consecutive symmetry-allowed antarafacial-suprafacial [1,3] sigmatropic reactions via a thianorcaradiene intermediate (Scheme I, b) or a symmetry-allowed ring opening of the cyclobutene ring to give a cis,trans,cis-1-thiacycloheptatriene (Scheme I, c) that subsequently recyclizes.

### Table II. Rate Constants\textsuperscript{a} for Thermal Isomerization of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes under Various Conditions

<table>
<thead>
<tr>
<th>reaction solvent\textsuperscript{b}</th>
<th>70°C</th>
<th>80°C</th>
<th>90°C</th>
<th>140°C</th>
<th>150°C</th>
<th>160°C</th>
<th>$\Delta H^\ddagger$ (kJ mol\textsuperscript{-1})</th>
<th>$\Delta S^\ddagger$ (J K\textsuperscript{-1} mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\rightarrow$ 4</td>
<td>A</td>
<td>0.04</td>
<td>0.12</td>
<td>0.32</td>
<td>0.72</td>
<td>137 ± 0.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.06</td>
<td>0.16</td>
<td>0.38</td>
<td>1.07</td>
<td>134 ± 0.5</td>
<td>−0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.07</td>
<td>0.22</td>
<td>0.55</td>
<td>1.27</td>
<td>137 ± 0.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2 $\rightarrow$ 5</td>
<td>B</td>
<td>0.10</td>
<td>0.26</td>
<td>0.66</td>
<td>1.30 ± 0.5</td>
<td>117 ± 0.5</td>
<td>+0.9</td>
<td></td>
</tr>
<tr>
<td>3 $\rightarrow$ 6</td>
<td>B</td>
<td>0.06</td>
<td>0.17</td>
<td>0.64</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Obtained by UV spectrometry (see Experimental Section). \textsuperscript{b} A = 1,3,5-trimethylbenzene, B = pentachloroethane, and C = dimethyl sulfoxide.
must accelerate the ring opening of a fused cyclobutene enormously. To our knowledge such an effect is only known for dialkylamino substituents.10

On the other hand, Kuhn and Gollnick15,16 proposed that thiophene and 2,5-dimethylthiophene react photochemically with dimethyl acetylenedicarboxylate in a \([4 + 2]\) fashion via 7-thiabicyclo[3.2.0]hepta-2,5-dienes that spontaneously extrude sulfur at room temperature. The reactivity of 2-thiabicyclo[3.2.0]hepta-3,6-dienes at higher temperatures is the subject of the following paper.17

Experimental Section

See the preceding paper18 for general experimental information. A Karl Zeiss PMQ 11 spectrophotometer was used for the kinetic analyses by the ultraviolet method. Photochemical transformations were effected with a Hanau Hg medium-pressure TNN 15/32 lamp (254 nm).

Thermal Isomerizations. Compound 1 (1 mmol) was heated for 18 h at 25 mL of dry, refluxing xylene. Removal of the solvent and repeated recrystallization with toluene and then hexane gave a solid which on recrystallization (pentane) gave 4 as colorless crystals: 82%; mp 98–99 °C.

Compound 2 (1 mmol) was treated as described for 1 to give a solid which on recrystallization (pentane) gave 5 as colorless crystals: 84%; mp 73–74 °C.

Compound 3 (1 mmol) was heated for 4 h in 25 mL of dry, refluxing toluene. Removal of the solvent and repeated coevaporations with hexane gave a solid which on recrystallization (pentane) gave 6 as colorless crystals: 83%; mp 81–82 °C.

Kinetic Analysis by NMR Spectrometry. Method 1. Ten samples of 1 (40 mg) in 0.4 mL of pentachloroethane or hexadeuteriodimethyl sulfoxide in sealed NMR tubes were placed in a thermostatted bath. At regular intervals the samples were removed and immediately cooled. The samples were then analyzed by NMR spectrometry.

Method 2. Single samples of 1, 2, or 3 in the above solvents in sealed NMR tubes were placed in the heated probe of the NMR spectrometer. The spectra were recorded at regular intervals.

Kinetic Analysis by Ultraviolet Spectrometry. A solution of 1, 2, or 3 (30–40 mg) was freshly prepared with 25 mL freshly distilled solvent (pentachloroethane, dimethyl sulfoxide, or 1,3,5-trimethylbenzene). Twelve 1.0-mL samples were pipetted into 10-mL calibrated flasks. The 12 flasks were placed in a thermostatted bath and removed at regular intervals. On removal, each flask was immediately cooled, the sample diluted to 10 mL, and, as quickly as possible, the extinction coefficient measured at the absorption maximum for the charge-transfer transition of 1, 2, or 3. \(\lambda = 402 \text{ (1), 406 (2), and 377 nm (3)}\).

Kinetic Analysis by HPLC. Ten samples in sealed glass tubes, each containing 0.07 mmol of 1, 1.0 mL of pentachloroethane, and 0.81 mg of naphthalene (as the internal standard), were placed in an oil bath of constant temperature. In equal intervals of 5 min the samples were cooled to 25 °C and analyzed for their composition by HPLC (Lichrosorb Si 60-5 column) with benzene as the eluent. The rate constants were calculated from the standardized peak areas of 1, 4, and naphthalene.

Photochemical Isomerizations. A solution of 1 (1 mmol) in 400 mL of dry, deoxygenated ether \((\text{N}_{2})\) was irradiated with ultraviolet light at \(-20\) °C for 8 h. Removal of the solvent gave an oil which on multiple plate elution by high-layer plate chromatography (hexane/ethyl acetate, 9:1) gave a solid. Recrystallization (pentane) gave 7 as colorless crystals: 67%; mp 103–104 °C (lit.2 mp 103.5–104 °C).

Treatment of 2 (1 mmol) as described for 1 gave a solid which on recrystallization (pentane) gave 8 as colorless crystals: 71%; mp 93–94 °C.

Treatment of 3 (2 mmol) as described for 1 gave an oil which on column chromatography (hexane/ethyl acetate, 17:3) gave an oil which slowly solidified. Recrystallization (pentane) gave 10 as colorless crystals: 31%; mp 59–60 °C. Further elution gave 9 as a colorless oil, 42%.

Irradiation of 3, as described for 1, but for only 1 h gave 9, 74%. Irradiation of 9, as described for 1, for 8 h gave an approximately 1:1 mixture of 9 and 10 as shown by NMR spectroscopy. Further

References

(31) Reference 30, p 113.
Irradiation did not appear to affect this ratio substantially, but considerable darkening of the solution was observed.

Acknowledgment. We express our gratitude to Mr. T. W. Stevens, Mrs. J. L. M. Klop-Vrielink, and Miss J. M. Visser for recording spectral data.

Registry No. 1, 40221-00-4; 2, 80242-87-1; 3, 80242-88-2; 4, 37539-57-9; 5, 80242-89-3; 6, 80242-90-6; 7, 80242-91-7; 8, 80242-94-0; 9, 80242-92-8; 10, 80242-93-9.

2-Thiabicyclo[3.2.0]hepta-3,6-dienes. 3. Desulfuration and Sulfuration of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes and X-ray Crystal Structure of 3a,6,7,8,9,9a-Hexahydro-3a,5-dimethylthieno[3,2-b][2]benzothiophene-2,3-dicarbonitrile

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The 2-thiabicyclo[3.2.0]hepta-3,6-dienes 1-7 extrude sulfur in solution at 285 °C to give the 1,2-benzenedicarbonitriles 8-12 in yields of 42-56%, 5-(1,1-Dimethylpropyl)-3,6-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-1,7-dicarbonitrile (6) reacts at 140 °C to give a mixture of the Cope-rrearranged isomer 13, the 1,2-benzenedicarbonitrile 11, and possibly a 3a,6a-dihydrothieno[3,2-b]thiophene (14). Reaction of 2a,5,6,7,8a-hexahydro-2a,4-dimethylbenzo[c]cyclobuta[b]thiophene-1,2-dicarbonitrile (15) at 140 °C gives a mixture of desulfurized (16) and sulfurated (17) products in yields of 68% and 73%, respectively. Single-crystal X-ray analysis proved the 3a,6,7,8,9,9a-hexahydrothieno[3,2-b][2]benzothiophene structure (17). The possible mechanism of the insertion of sulfur in the carbon-carbon single bond of 15 is discussed.

The two preceding papers in this series describe the preparation of 2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitriles and their thermal (120-140 °C)2 and photochemical2 isomerization to the analogous 4,5- (1-8) and 1,7-dicarbonitriles (4-7), respectively. Since the two modes of isomerization did not lead to the desired thiepins,5 it was decided to investigate the effect of higher temperatures on the 4,5- and 1,7-dicarbonitriles as a possible route to thiepins.

Further, it was considered that the 1,2-dicarbonitrile (15),5 which cannot undergo photochemical isomerization by the described2 mechanism and which is unlikely, because of the bridging, to undergo the Cope rearrangement (16) (thermal isomerization at moderate temperature), would undergo facile C-2a,C-8a cleavage on heating and result in thiepin formation.

Two factors make it difficult to predict the temperatures required for ring opening of the cis-fused cyclobutene ring in 1-7 and 15. Comparison with the reactivity of other cis-fused cyclobutenes indicates that both increased strain and participation of the π electrons of the vinyl group will lower the activation energy.4,6 Frey et al.9 found that the isomerization of bicyclo[3.2.0]hept-6-ene to cyclohepta-1,3-diene has an activation energy of 190.4 kJ mol⁻¹ compared with a value of 143.9 kJ mol⁻¹ for cis-3,4-dimethylcyclobutene.5 However, the activation energy of the isomerization of bicyclo[3.2.0]hepta-3,6-diene to cycloheptatriene has an activation energy of only 185.3 kJ mol⁻¹.6 An allylic stabilization of an intermediate biradical or of a biradicaloid transition state in the symmetry-forbidden disrotatory ring opening has been postulated to account for this difference.6 To our knowledge, there is no information available as to how a sulfur or a thiovinyl substituent at the 3-position of cyclobutenes affects the rate of isomerization. Another unpredictable factor is the influence of cyano groups in compounds 1-7 and 15 below.

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