Photochemical and Thermal Rearrangement of *exo*-2,3-Epithionorborn-5-ene

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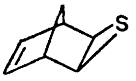
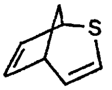
Summary 2-Thiabicyclo[3,2,1]octa-3,6-diene (**2**) is obtained by either photochemical or thermal rearrangement of *exo*-2,3-epithionorborn-5-ene (**1**), by a stepwise process.

Evidence favouring concerted rather than stepwise mechanisms has recently been reported in the photochemical and thermal rearrangement of olefinic three-membered heterocycles. Oxiran or aziridine fused to a norbornene unit undergo ready rearrangement to give ring-expanded valence isomer by a thermal ${}_{\pi}2_{a} + {}_{\sigma}2_{s} + {}_{s}2_{a}$ concerted processes[1] while their photochemical isomerization giving tetracyclic derivatives proceeds by a ${}_{\pi}2_{s} + {}_{\sigma}2_{s}$ concerted pathway.[2] We now report on the photochemical and thermal rearrangement of thiiran analogue with norbornene unit which involves a stepwise process.



(1)



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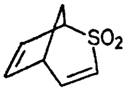

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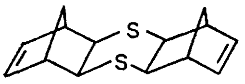

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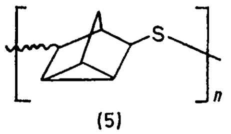
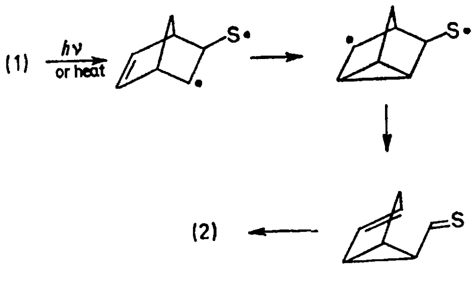


(5)

Irradiation of *exo*-2,3-epithionorborn-5-ene (**1**)[3] in O_2-free MeCN (room temperature; 1·0 g in 10 ml; 48 h) with Pyrex-filtered light from a high-pressure Hg vapour lamp (450 W) gave an isomerization product (84%), b.p. 63—64° at 19 mmHg; *m/e* 124 (M^+, 100%), purified by chromatography on silica gel, whose spectral characteristics were consistent with the thiabicyclo-octadiene structure (**2**). [δ (100 MHz; $CDCl_3$) 5·84 (2H, m), 5·77 (1H, q†), 5·63 (1H, q), 3·55 (1H, m), 2·34 (1H, m), 2·13 (1H, quintet), and 1·94 (1H, d) p.p.m.]. Its n.m.r. splitting patterns resemble those of the nitrogen[4] and oxygen[5] analogues, and indicate a bicyclic arrangement with characteristic bridgehead methine proton signals at δ 3·55 and 2·34 p.p.m. In addition, oxidation of (**2**) with *m*-chloroperoxybenzoic acid gave the corresponding sulphone (**3**)‡. With a higher concentration of (**1**), a considerable amount of the dimer (**4**)‡ was formed simultaneously.



Thiiran (**1**) was also converted into its isomer (**2**) (71%) when (**1**) (1·0 g) was heated at 160–170° for 19 h in

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† Half of the quartet peaks was obscured by the multiplet at δ 5·84 p.p.m.

‡ Structure confirmed by n.m.r., i.r., and/or mass spectra.

benzonitrile (10 ml) under nitrogen. When (**1**) was heated without solvent or with a catalytic amount of proton or Lewis acid, a nortricyclene type of sulphide polymer (**5**)‡ was obtained along with a small amount of (**2**). That dimer (**4**) was also formed in the thermal reaction was confirmed by use of diphenyl ether as a solvent.

Although the rearrangement seems similar to thermal rearrangements for oxiran and aziridine analogues, there is no symmetry-allowed $_{\pi}2_a + {}_{\sigma}2_s + {}_{\sigma}2_a$ process in photochemically excited states. Accordingly, these photochemical and thermal rearrangements do not proceed by the concerted pathway, but by a stepwise process initiated by a homolytic fission of the thiiran ring. The formation of by-products (**4**) and (**5**) supports this pathway.

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