

9-Thiabicyclo[6,1,0]nona-2,4,6-triene

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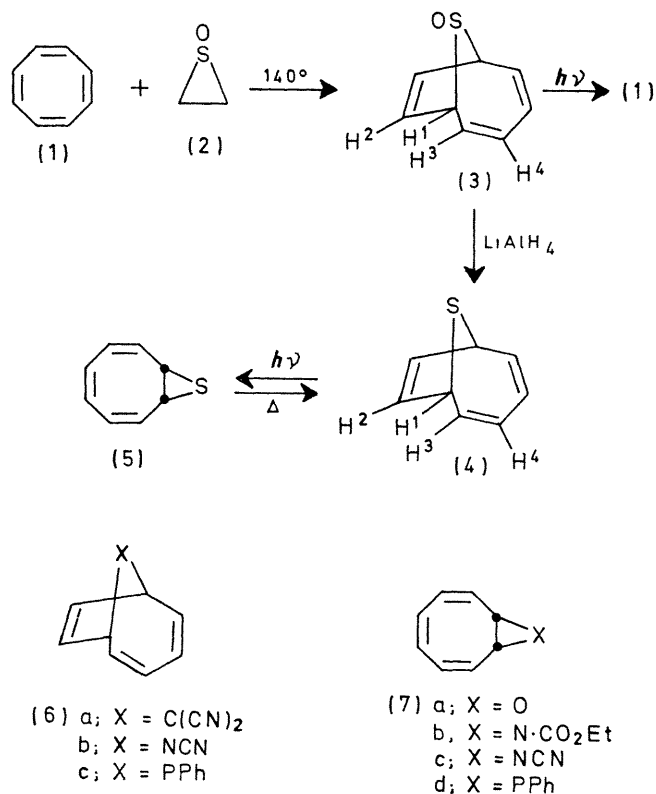
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Summary 9-Thiabicyclo[6,1,0]nona-2,4,6-triene (**5**) was synthesized by a two-step sequence via the novel thiabicyclo[4.2,1]nonatrienes (**3**) and (**4**).

THE epoxide of cyclo-octatetraene (**7a**) has been long available¹ whereas the corresponding epithio-compound (**5**) has not, to our knowledge, been described. We became interested in (**5**) in connection with work on the heteronins² and we report here the synthesis of this compound.

We have extended the reported³ simple 1,4-cycloaddition of sulphur monoxide on to cyclo-octa-1,3-diene to the thermal reaction with cyclo-octatetraene (**1**). Treatment of (**1**) with ethylene sulphoxide (**2**)⁴ in boiling xylene led to a white crystalline solid, † m.p. 120–121°, (ca. 30%), τ (60 MHz; CDCl₃) 3.40 (2H, dt, $J_{3,4}$ 12.5 Hz, 4-H), 3.8–4.3 (2H, m, 3-H), 4.50 (2H, d, $J_{1,2}$ 2.7 Hz, 2-H), and 5.75 (2H, dd, $J_{1,2}$ 2.7 Hz and $J_{1,3}$ 8.0 Hz, 1-H). This spectrum supports the formulation of the product as (**3**), by comparison with the n.m.r. spectrum of (**6a**).⁵ The presence of sulphur in (**3**) greatly enhances the resolution of its spectrum which, at 60 MHz, is almost identical with that of (**6a**) at 220 MHz. Further support for structure (**3**) derives from the u.v. spectrum λ_{\max} (MeCN) 220 (ϵ 4100) and 278 nm (2600), the mass spectrum, m/e 152 (M^+ , 97%), and the i.r. spectrum, ν_{\max} (KBr) 1075 (SO), 860, 742, and 683 cm⁻¹, of the cycloadduct.

Careful treatment of (**3**) with LiAlH₄ led to the colourless and odourless sulphide (**4**) (ca. 60%). m/e 136 (M^+ , 19%), ν_{\max} (neat) 2900, 1380, 1310, 943, 850, 798, and 726 cm⁻¹, τ (60 MHz; [²H₆]Me₂CO) 3.3–3.7 (2H, m, 3-H), 3.96 (2H,



† Correct elemental analysis was obtained for this compound.

dt J 12.5 Hz, 4-H), 4.60 (2H, d, J_{12} 2.0 Hz, 2-H), and 5.56 (2H, dd, J_{12} 2.0 Hz and J_{13} 7.0 Hz, 1-H). The four well resolved two proton patterns are almost identical with those in the spectrum of (3). Hence, the sulphide (4) must possess the same skeletal arrangement as its sulphoxide progenitor (3).

Conversion of (4) into (5) was accomplished photochemically, *cf.* a similar isomerization, (6b) \rightarrow (7c) described previously.⁶ Irradiation of (4) (Pyrex-filtered, at 0°, in light petroleum, for *ca.* 2 h) with a Hanovia high-pressure lamp gave (5), irreversibly and in high yield (*ca.* 80%).⁷ The pure sulphide (5), a colourless, intensely malodourous liquid, was isolated by low-temperature (*ca.* -12°) chromatography on neutral alumina and was characterized spectrally, m/e 136 (M^+ , 86%), ν_{\max} (neat) 1080, 798, 780, and 685 cm^{-1} , λ_{\max} (MeCN) *ca.* 250sh nm (ϵ 2400), τ (60

MHz; [$^2\text{H}_6$]Me₂CO) 3.87 (2H, m), 3.98 (2H, m), 4.07 (2H, m), and 6.34 (2H, s). Formulation of this compound as (5) is chiefly based on its u.v. and n.m.r. spectra which are very similar to those of the known heterobicyclic systems shown in (7).^{1,8-10} In addition, structure (5) draws strong support from the rapid,¹¹ irreversible thermal isomerization [$t_{1/2}$ (56°) *ca.* 60 min] to (4). The thermal behaviour of (5) is reminiscent of that of the phospho-analogue (7d), which produces (6c) on mild heating,¹⁰ but sharply contrasts with the tendency of compounds such as (7) to undergo thermal isomerization by scission of the cross-link rather than the C-X bond, when X is a first-row element. We are currently investigating the possible conversion of (5) into thionin.^{12,13}

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¹¹ Characterized through direct spectral comparison (i.r. and n.m.r.) with an authentic sample.

¹² Although parent thionin remains unknown, annelated derivatives were described recently (A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *J. Amer. Chem. Soc.*, 1968, **90**, 7372; P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *ibid.*, 1970, **92**, 4492).

¹³ At the request of a referee we point out that all our preliminary findings regarding the possible conversion of (5) into thionin by sensitized photolysis, *i.e.*, in a manner analogous to that we previously employed in the synthesis of oxonn and *N*-ethoxycarbonyl-azonine,³ indicate that the excessive weakness of the C-S bond in (5) may well complicate the situation here.