9-Thiabarbaralane (9-Thiatricyclo[3,3,1,$0^{2,8}$]nona-3,6-diene)

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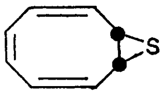
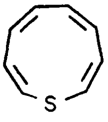
Summary Sensitized photolysis of 9-thiabicyclo[6,1,0]-nona-2,4,6-triene produces the title substance (**3a**) through what appears to be initial C–S-bond scission.

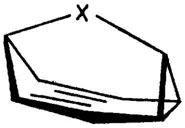
Recently[1] we described the synthesis of thiabicycles (**1**) and (**4**) and called attention to the potential of the former as a photoprecursor to thionin (**2**). We now report that sensitized excitation of either (**1**) or (**4**) leads to 9-thiabarbaralane (**3a**) instead.



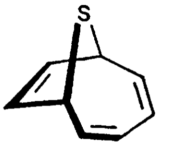
(1)



(2)



(3)
a; X = S
b; X = CO

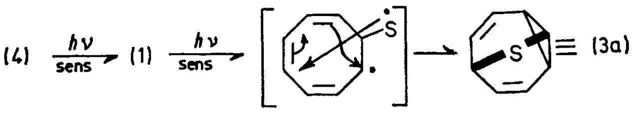


(4)

Irradiation of (**1**) (Pyrex-filtered; *ca.* −10°; in ether; *ca.* 0·5 h)† in the presence of benzophenone with a Hanovia 450-W lamp led, irreversibly and quantitatively, to a single crystalline isomer which was purified by low-temperature (*ca.* −15°) chromatography on alumina. The photoproduct is thermally labile [$t_{\frac{1}{2}}$ (34°) *ca.* 30 min.] and displays the following spectral characteristics, *m/e* 136 (M^+, 86%) and 91 ($C_7H_7^+$, 100%); ν_{max} (CS_2) 3050, 760, and 715 cm^{-1}, λ_{max} (C_6H_{14}) 199 nm (ϵ_{220} *ca.* 3350); τ [60 MHz; $(CD_3)_2CO$; −15°], 4·20 (2H, t, *J* 7 Hz), 5·60 (4H, t, *J* 7 Hz), and 6·33 (2H, t, *J* 7 Hz). The n.m.r. spectrum is uniquely consistent with the tricyclic arrangement (**3a**) in a state of rapid flux. Significantly, the spectrum is analogous to that described[2] for barbaralone in terms of both signal shape and temperature dependence whereby the 4-H triplet in the spectrum of (**3a**) loses all structural detail on cooling to *ca.* −30°.‡ The remaining spectral details are also readily accommodated by structure (**3a**).

Irradiation of (**4**) under similar conditions also leads to (**3a**) as the sole ultimate product. However, (**1**) appears to be an intermediate in this transformation since a control involving only brief (5 min) exposure of (**4**) to the same photolysis conditions produced a mixture consisting approximately (n.m.r.) of (**4**) (61%), (**1**) (31%) and (**3a**) (only 8%).

The Scheme depicts what we believe to be the major pathway leading to (**3a**) in the sensitized photolysis of either (**1**) or (**4**) but does not preclude the possibility that (**3a**) is produced, to a minor extent, directly from (**4**). The failure of (**1**) to yield thionin (**2**) on sensitized photolysis, *i.e.*, to behave similarly to *N*-ethoxycarbonyl-9-azabicyclo[6,1,0]nona-2,4,6-triene[3] and its oxa-analogue,[4] is no doubt due to the weakness of the C–S bond in (**1**). Nonetheless, we are continuing our efforts to locate thionin on the C_8H_8S energy surface.



Scheme

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† Direct, low-temperature (−78°), irradiation of (**1**) with a low-pressure source (2537 Å) for *ca.* 0·5 h led to considerable decomposition; unchanged (**1**) was the only substance observed (n.m.r.).

‡ The pronounced insolubility of (**3a**) in such media as acetone and CS_2 at temperatures below −30° frustrated all attempts at assessing the activation parameters of its degenerate bond-relocation.

[1] A. G. Anastassiou and B. Y.-H. Chao, *Chem. Comm.*, 1971, 979.
[2] J. B. Lambert, *Tetrahedron Letters*, 1963, 1901.
[3] A. G. Anastassiou and J. H. Gebrian, *J. Amer. Chem. Soc.*, 1969, **91**, 4011.
[4] A. G. Anastassiou and R. P. Cellura, *Chem. Comm.*, 1969, 903, 1521.