

## 2,5-Diphenyl-3-thiabicyclo[4.4.1]undeca-1,5,7,9-tetraene-4-one, an Eleven- $\pi$ -electron Hetero[10]annulenone, from a Mesoionic Dithiolone

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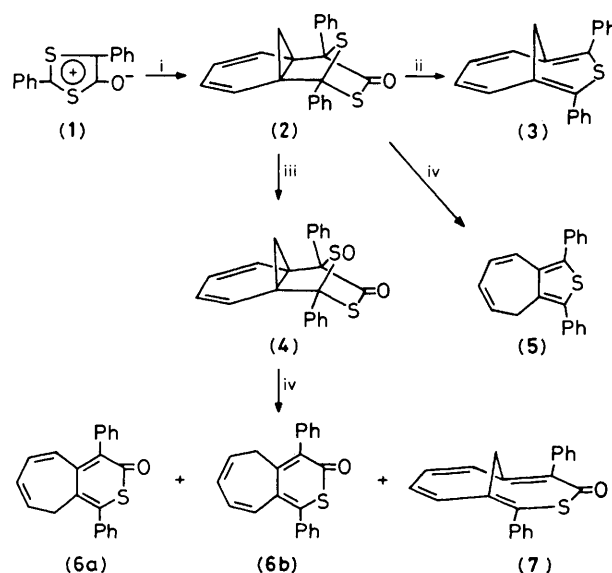
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The title compound (7), a potentially aromatic heterocyclic system, has been prepared from the cycloadduct of the mesoionic dithiolone (1) with benzocyclopropene.

The preparation of compound (3), a ten- $\pi$ -electron bridged hetero[9]annulene, has been achieved by pyrolysis of the cycloadduct (2) of the mesoionic dithiolone (1) with benzocyclopropene.<sup>1</sup> If the sulphur atom could be extruded from the adduct (2), the reaction would permit easy access to 2,5-diphenyl-3-thiabicyclo[4.4.1]undeca-1,5,7,9-tetraene-4-one (7). Such an eleven- $\pi$ -electron hetero[10]annulenone has not been reported, and the possibility of delocalisation of the ten  $\pi$ -electrons within the ring by polarisation of the ring carbonyl group is of interest. We report the synthesis of (7) from the adduct (2).

Attempted preparation of (7) by photochemical extrusion of sulphur<sup>2</sup> from the adduct (2) resulted in elimination of carbonyl sulphide accompanied by rearrangement to afford (5).<sup>†</sup> Peracid oxidation of the adduct (2) gave a quantitative yield of the corresponding sulfoxide (4). In accord with our earlier findings,<sup>3</sup> irradiation (high-pressure mercury lamp; Pyrex filter) of a benzene solution of the sulfoxide (4) resulted in extrusion of sulphur monoxide, and the formation of a mixture of products. The major product (39% yield) was a mixture of the isomers (6a) and (6b) (1:2.9, respectively) which are the products of Berson–Wilcott rearrangement of the sulfoxide (4) or the bicycle (7). The minor product (6%) was the desired title compound (7). The minor product (6% yield; m.p. 157–158.5 °C) was the desired title compound (7).

The <sup>1</sup>H n.m.r. signals for the protons of the methylene bridge in (7) appear at relatively low field, and the olefinic protons are not strongly deshielded.<sup>‡</sup> These data suggest only moderate delocalisation of electrons in (7). This view is further supported by comparison of the i.r. carbonyl band of (7) (1635 cm<sup>-1</sup>) with that of (6) (1595 cm<sup>-1</sup>). This shows that the carbonyl group of the former is less polarised than that of the



Scheme 1. Reagents and conditions: i, benzocyclopropene; ii, heat; iii, *m*-chloroperbenzoic acid; iv, *h* $\nu$ .

latter, and hence, a high degree of delocalisation of the ten  $\pi$ -electrons within the annulenone ring of (7) would not be expected.

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<sup>†</sup> All compounds gave satisfactory elemental analyses, and were adequately identified by i.r., <sup>1</sup>H and <sup>13</sup>C n.m.r., and mass spectral analyses.

<sup>‡</sup> N.m.r. data for (7):  $\delta_{\text{H}}$  2.16 (1H, d, *J* 11.2 Hz, *syn*-11-H), 2.61 (1H, dt, *J* 11.2 and 1.6 Hz, *anti*-11-H), 6.19–6.51 (2H, m, 8- and 9-H), 6.76–7.22 (2H, m, 7- and 10-H), and 7.32 and 7.36 (10H, each s, Ph);  $\delta_{\text{C}}$  37.5 (dd, *J* 136 and 138 Hz, CH<sub>2</sub>) and 190.5 p.p.m. (s, C=O); *syn* and *anti* for the C(11) protons refer to their position with respect to the carbocycle.