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

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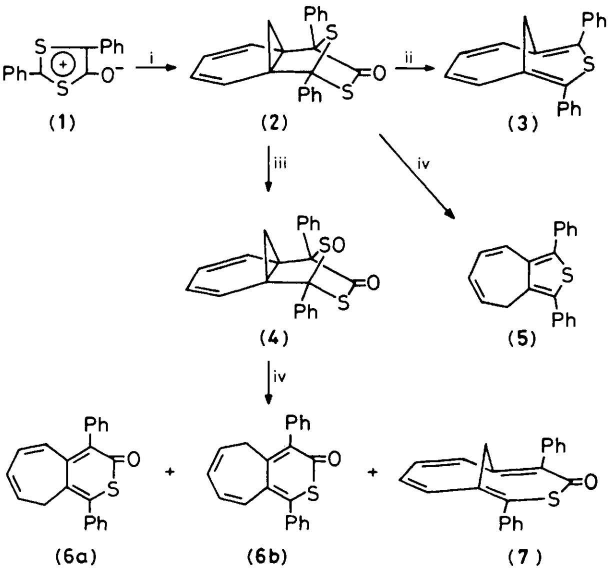
The title compound (**7**), a potentially aromatic heterocyclic system, has been prepared from the cycloadduct of the mesoionic dithiolone (**1**) with benzocyclopropene.

The preparation of compound (**3**), a ten-π-electron bridged hetero[9]annulene, has been achieved by pyrolysis of the cycloadduct (**2**) of the mesoionic dithiolone (**1**) with benzocyclopropene.[1] 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-π-electron hetero[10]annulenone has not been reported, and the possibility of delocalisation of the ten π-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[2] from the adduct (**2**) resulted in elimination of carbonyl sulphide accompanied by rearrangement to afford (**5**).† Peracid oxidation of the adduct (**2**) gave a quantitative yield of the corresponding sulphoxide (**4**). In accord with our earlier findings,[3] irradiation (high-pressure mercury lamp; Pyrex filter) of a benzene solution of the sulphoxide (**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 sulphoxide (**4**) or the bicycle (**7**). The minor product (6% yield; m.p. 157—158.5 °C) was the desired title compound (**7**).



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

The ^{1}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.‡ 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^{-1}) with that of (**6**) (1595 cm^{-1}). This shows that the carbonyl group of the former is less polarised than that of the latter, and hence, a high degree of delocalisation of the ten π-electrons within the annulenone ring of (**7**) would not be expected.

Received, 17th May 1983; Com. 638

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† All compounds gave satisfactory elemental analyses, and were adequately identified by i.r., ^{1}H and ^{13}C n.m.r., and mass spectral analyses.

‡ N.m.r. data for (**7**): δ_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); δ_C 37.5 (dd, *J* 136 and 138 Hz, CH_2) 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.

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