

Bridged Ten- π -electron Nine-membered Heterocycles: 9-Phenyl-3,8-methano-1,2-thiazonine and 2,9-Diphenyl-3,8-methano- thionin

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The title compounds, the first examples of bridged ten- π -electron [9]annulenes, were formed by the reaction of benzocyclopropene with a mesoionic oxathiazolone and dithiolone; 9-phenyl-3,8-methano-1,2-thiazonine is unstable, and its formation was deduced from its n.m.r. spectra.

It is well known that bridged [10]annulenes are typically aromatic while monocyclic [10]annulenes are extremely unstable.¹ As heterocyclic counterparts of such systems, monocyclic azonines and an oxonin have been prepared, and were found to possess quite diversified properties which range from aromatic to polyenic depending on the heteroatom or substituent on the ring nitrogen atom.² Methano-bridged aza[10]annulenes are aromatic,³ but attempts to prepare bridged heteronins have not been successful.⁴ We report a simple and potentially general synthetic route for such systems based on the extension of the cycloaddition-extrusion-ring expansion reaction of mesoionic compounds⁵ to benzocyclopropene.

The reaction of benzocyclopropene (1) with the mesoionic 1,3,2-oxathiazolone (2) resulted in a complex mixture consisting mainly of dark polymeric products. Chromatographic separation, however, afforded a low yield of a fraction believed to be composed of crude 9-phenyl-3,8-methano-1,2-thiazonine (3) based on the ^1H [Figure 1(a)] and ^{13}C n.m.r. spectra [δ 48.4 (d,d,t), (J 145.5, 140.6, and 4.9 Hz), 109.6 (s),

122.6(d), 124.4 (d), 127.2 (d), 128.5 (d), 128.9 (d), 129.1 (d), 129.5 (d), 133.2 (s), 151.3 (s), and 168.6 p.p.m. (s)]. One methylene proton signal is split (J 1.2 Hz) by a long-range coupling with the 4- and 7-protons. Structure (3) is fully supported by ^1H - ^1H decoupling and ^1H - ^{13}C selective decoupling experiments, together with a simulated ^1H n.m.r. spectrum. However, the low yield of this substance, coupled with its instability, precluded attempts at isolation or further characterisation.

The reaction between benzocyclopropene and the mesoionic 1,3-dithiolone (4) gave the 1:1 adduct (5) in 41% yield [m.p. 160 °C, decomp.: $\nu(\text{C}=\text{O})$ 1705 cm^{-1}]. The assignment of the stereochemistry and the norcaradiene partial structure of the adduct were deduced from n.m.r. spectra [^{13}C : δ 42.9 (s), 34.1 (s), and 14.3 p.p.m. (d,d), J 163.1 and 168.9 Hz; ^1H : δ 0.56 (d) and 3.58 (d), J 5.3 Hz]. The mass spectrum of the adduct shows only a weak molecular ion peak, and its base peak corresponds to the $[M - \text{SCO}]$ ion, which suggests a ready fragmentation of the adduct to the thionin (6). Pyrolysis of the adduct in boiling xylene gave 2,9-diphenyl-3,8-methanothionin (6) (53%; m.p. 122 °C). This compound gave satisfactory elemental analyses and both its ^1H [Figure 1(b)] and ^{13}C n.m.r. spectra are consistent with the proposed structure, the latter consisting of nine peaks (46.0, 124.8, 125.5, 127.9, 128.5, 128.7, 129.5, 135.0, and 161.0 p.p.m.), reflecting the symmetrical structure of the thionin. The methylene carbon couples differently (J 140.6 and 136.7 Hz) with the two methylene protons and is further split (J 4.9 Hz) by the 4- and 7-protons. A long-range coupling (J 1.2 Hz) is observed

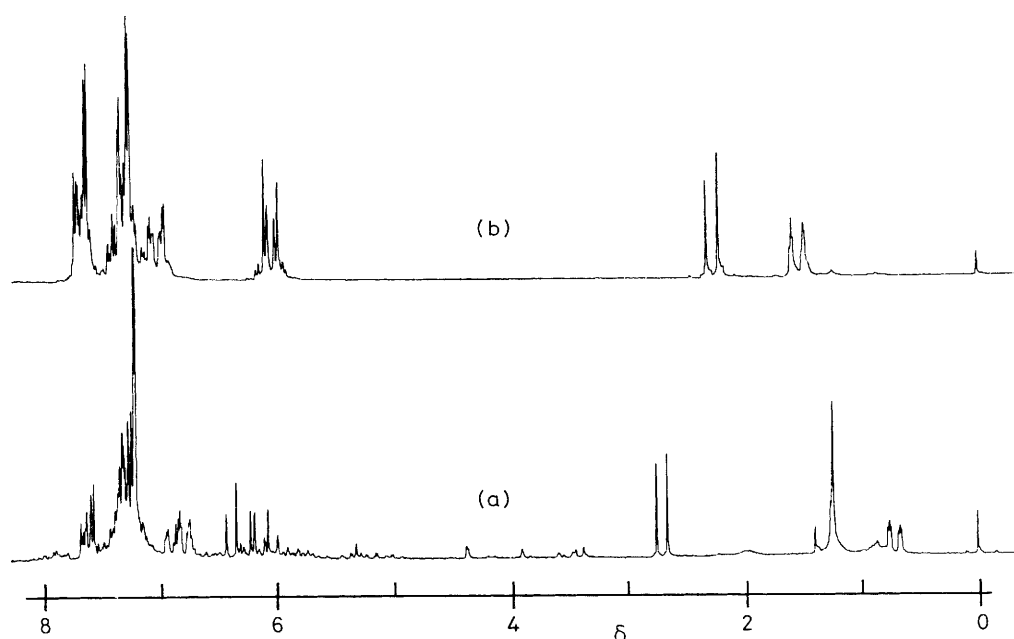
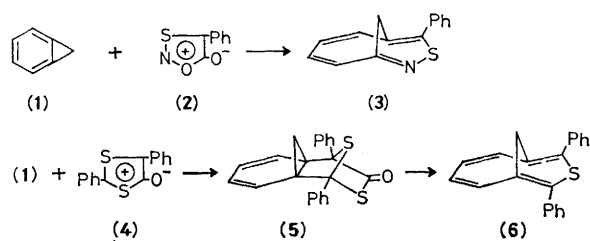


Figure 1. ^1H N.m.r. spectra of (a): 9-phenyl-3,8-methanothiazonine (3); (b): 2,9-diphenyl-3,8-methanothionin (6).

between the 4- and 7-protons (δ 7.09) and the methylene *anti*-proton. The crude thionin (**6**) readily decomposes, especially in solution, but once purified, it is relatively stable, and can be kept without appreciable decomposition.

The relatively low-field n.m.r. signals of the methylene group and the 2- and 9-carbons suggest that they should not be classified as diatropic systems, although they formally satisfy the ten- π -electron requirement for aromaticity.

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