3-Thiabicyclo[3,2,0]hepta-1,4-diene

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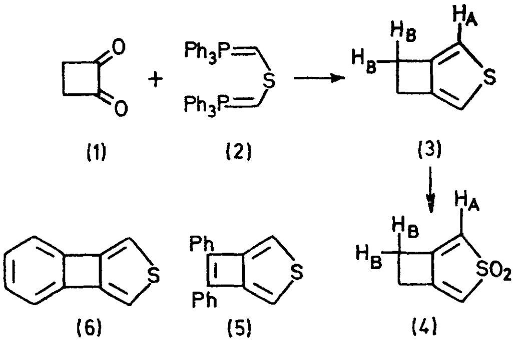
Summary 3-Thiabicyclo[3,2,0]hepta-1,4-diene (**3**) has been synthesised by a Wittig reaction between cyclobutane-1,2-dione (**1**) and the bis-ylide (**2**). Oxidation of (**3**) gave the corresponding sulphone (**4**).

3-THIABICYCLO[3,2,0]HEPTA-1,4-DIENE (4,5-dihydrocyclobuta[*c*]thiophen) (**3**) is a molecule of considerable current interest for which an unusual chemistry has been predicted.[1] Compound (**3**) also provides a model system with which to compare the properties of thienocyclobutadienes [*e.g.* (**5**)] and related systems.[2] Recently four highly halogenated derivatives of (**3**) were reported,[3] but the degree of substitution precluded the observation of much spectroscopic data. We now report the synthesis of the parent system (**3**).

Reaction of cyclobutane-1,2-dione[4] with the bis-ylide (**2**), prepared from thiodimethylenebis(triphenylphosphonium) dichloride,[5] in ether at −65° under nitrogen gave *ca.* 5% of (**3**) as a colourless liquid,†‡ τ ($CDCl_3$) 3·24 (s, H_A) and 6·98 (s, H_B) (ratio 1 : 2), λ_{max} (EtOH) 244 nm (ϵ 7800). Oxidation of (**3**) with H_2O_2 in acetic acid gave 65% of the sulphone (**4**), m.p. 127·5—128·5°,‡ τ ($CDCl_3$) 3·98 (s, H_A) and 6·67 (s, H_B) (ratio 1 : 2), λ_{max} 225 (ϵ 3300) and 292 nm (1300), the electronic spectrum being characteristic of a thiophen dioxide. 3-Thiabicyclo[3,2,0]hepta-1,4-diene readily adds bromine to give a tetrabromide, and this and other aspects of its chemistry are under investigation.

The chemical shift (τ 3·24) of H_A in (**3**) is that expected for a proton on a 3,4-dialkyl-substituted thiophen,[5] and differs significantly from the chemical shifts of the corresponding protons in 6,7-diphenyl-3-thiabicyclo[3,2,0]heptatriene (**5**) (τ 3·84) and 2-thianorbiphenylene (**6**) (τ 3·51).[2] On oxidation of (**3**) to the sulphone (**4**), the H_A signal experiences an upfield shift (0·74 p.p.m.) similar to that observed on oxidation of 3,4-dimethylthiophen to its sulphone (0·54 p.p.m.),[7] but in marked contrast to the shift observed (0·09 p.p.m.) when (**6**) is oxidised to its corresponding sulphone.[2] These differences can be explained if it is assumed that compounds (**5**) and (**6**) have paramagnetic contributions to the ring current arising from the four-membered ring, as previously suggested,[2] whereas (**3**) does not.



(1) (2) (3)

(6) (5) (4)

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† Compound (**3**) was isolated by a combination of column chromatography (Al_2O_3), distillation, and g.l.c.

‡ Satisfactory high resolution mass spectra and microanalytical results were obtained.

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[6] See L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, Oxford, 1969 p. 214.

[7] S. B. Neoh, unpublished results.