

Thermal Rearrangements of Azathiabenzenes; [1,4] Shifts in Cyclic Sulphur–Nitrogen Ylides

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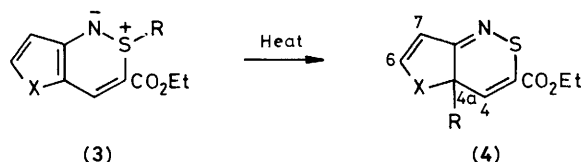
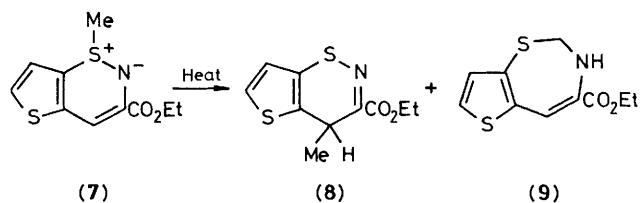
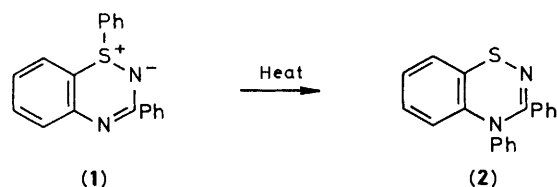
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The azathiabenzene derivatives (**3**), (**7**), and (**11**) rearrange on heating by a [1,4] shift of the sulphur substituent to carbon rather than a [1,2] shift to nitrogen, even though for ylides (**3**) this rearrangement involves loss of thiophen and furan aromaticity.

The high reactivity of conjugated six-membered rings containing a sulphur(IV) atom is associated with the fact that these systems are ylidic rather than aromatic in character. Thus, thiabenzenes readily rearrange by migration of the sulphur substituent to carbon *via* both [1, 2] and [1, 4] shifts, typical of acyclic sulphonium ylides, although the [1, 4] shift often predominates.¹ The possibility for both [1, 2] and [1, 4] shifts also exists in the aza-analogues, the 1 λ^4 ,2,4-benzothiadiazines (**1**), although it has been shown that these rearrange exclusively by the [1, 4] pathway to give the benzothiadiazines (**2**).² We have recently reported the preparation of the azathiabenzene derivatives (**3a**) and (**3b**),³ and we now

report that these and the related ylides (**3c**), (**7**), and (**11**) rearrange thermally by a [1, 4] shift to carbon.

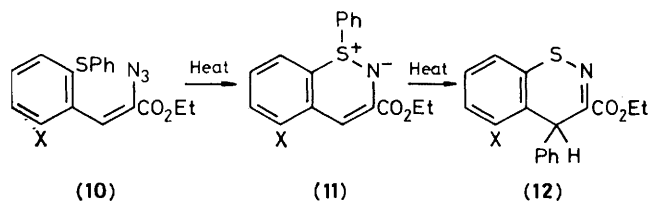
The thieno[3,2-*c*] [1 λ^4 ,2]thiazine (**3a**) is thermally stable up to about 120 °C, but on heating in bromobenzene (156 °C) for 1.5 h it was completely consumed, the major product (40%) being an isomer of the starting ylide. This rearrangement product, m.p. 71–72 °C, was assigned the non-aromatic 4a*H*-thienothiazine structure (**4a**) on the basis of its spectral properties which established that the methyl group had migrated to carbon rather than nitrogen. Thus, its ¹H n.m.r. spectrum has resonances at δ (CDCl₃) 1.19 (3H, s, 4a-CH₃), 6.30 (1H, d, *J* 6 Hz, H-7), 7.02 (1H, s, H-4), and 7.27 (1H,



a; X = S, R = Me; b; X = S, R = Ph; c; X = O, R = Ph



a; R = Ph
b; R = Me



a; X = Cl; b; X = SPh

d, J 6 Hz, H-6) in addition to the ethyl ester signals. The non-aromatic nature of the thiophen ring was further established by its ^{13}C n.m.r. spectrum which showed a quaternary carbon signal at δ 53.1 for C-4a, and the structure was finally confirmed by X -ray crystallography. \dagger

The corresponding S -phenylsulphimide (3b) rearranged similarly on heating in xylene (138 °C) to give the non-aromatic thiophen (4b) as a yellow oil in much higher yield (95%). The analogous furothiazine (3c), m.p. 112–113 °C, prepared from 3-azidofuran-2-carbaldehyde⁴ in the standard way,³ also rearranged on heating in xylene to give the expected furothiazine (4c) as an oil (95%).

Thus, the azathiabenzenes (3a–c) undergo a thermal rearrangement which involves the [1, 4] migration of the sulphur substituent to carbon and the consequent disruption of the thiophen and furan aromaticity; the alternative [1, 2] shift to nitrogen was not observed. In order to test further the generality of this [1, 4] rearrangement, the benzo-fused azathiabenzenes (5a), m.p. 110–112 °C, and (5b), oil, were prepared from 2-azidobenzaldehyde.⁵ These benzo-fused sulphimides are much more thermally stable than their heterocyclic counterparts, and require prolonged refluxing in 1,2-dichlorobenzene (180 °C) to effect decomposition. However, under these conditions the materials were completely degraded and no products were isolated. Clearly, the [1, 4] shift with its consequent disruption of the benzenoid aromaticity is now much less favoured, although it is perhaps surprising that no products resulting from the alternative [1,2] shift to nitrogen were detected. This [1,2] shift is apparently a highly disfavoured process, and indeed it is rarely observed in sulphimides generally.

The thermal [1,4] migration of the sulphur substituent occurs more readily in isomeric azathiabenzenes when the fused aromatic ring is not directly involved. The sulphimide (7), m.p. 58–62 °C, was prepared by thermolysis of the azide (6), m.p. 61–64 °C, in benzene. The thienothiopyran (7) is less thermally stable than the isomeric ylide (3a) and rapidly decomposes in boiling toluene to give a complex

mixture of products. Two compounds were identified as the [1,4] shift-product (8), and the ring-expansion product (9). Similar ring-expansion products have been reported in the thermolysis of other cyclic sulphimides,⁶ and are best rationalised by a Stevens-type rearrangement in the tautomeric sulphonium ylide, a reaction which is well known in acyclic sulphimides.⁷

The corresponding [1,4] rearrangement of the benzo-fused S -phenylsulphimides (11) was so fast that the sulphimides themselves could not be isolated. The azide (10a) was prepared by condensation of 2-chloro-6-phenylthiobenzaldehyde, m.p. 59–60 °C, with ethyl azidoacetate in the usual way.⁸ Under the conditions required to decompose the azide the sulphimide (11a) was not isolated, and the product (60%) was the benzothiazine (12a), m.p. 100–102 °C. Thermolysis of the azide (10b) gave the corresponding [1,4] shift product (12b) albeit in low yield.

Thus, there is a thermal rearrangement pathway common to these cyclic sulphur–nitrogen ylides which involves a [1,4] shift of the sulphur substituent to carbon; although a [1,4] shift to nitrogen, (1) \rightarrow (2), has also been observed, [1,2] shifts to nitrogen are clearly very unfavourable. Experiments are underway⁹ to establish whether this new rearrangement involves suprafacial geometry of the 6π -electron system and retention of configuration in the migrating group; such thermally allowed, [1,4] sigmatropic rearrangements are rare.¹⁰

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