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

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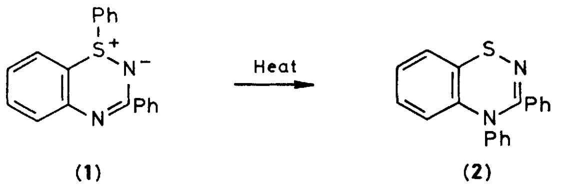
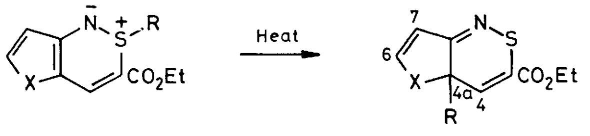
The azathiabenzene derivatives (**3**), (**7**), and (**11**) rearrange on heating by a [1,4] shift of the sulphur substituent to carbon rather than a [1,2] shift to nitrogen, even though for ylides (**3**) this rearrangement involves loss of thiophen and furan aromaticity.

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 1λ^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*] [1λ^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 ^{1}H n.m.r. spectrum has resonances at δ ($CDCl_3$) 1.19 (3H, s, 4a-CH_3), 6.30 (1H, d, *J* 6 Hz, H-7), 7.02 (1H, s, H-4), and 7.27 (1H,

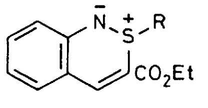


(1) **(2)**



(3) **(4)**

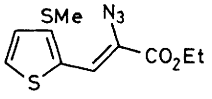
a; X = S, R = Me; b; X = S, R = Ph; c; X = O, R = Ph



(5)

a; R = Ph

b; R = Me



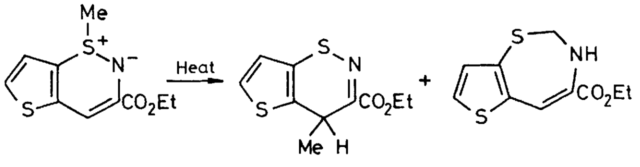
(6)

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.†

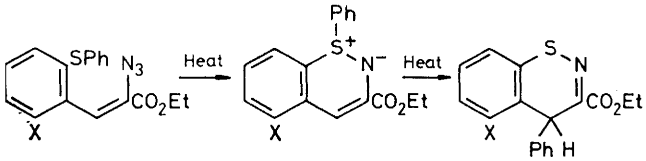
The corresponding *S*-phenylsulphimide (**3b**) rearranged similarly on heating in xylene (138 °C) to give the non-aromatic thiophen (**4b**) as a yellow oil in much higher yield (95%). The analogous furothiazine (**3c**), m.p. 112—113 °C, prepared from 3-azidofuran-2-carbaldehyde[4] in the standard 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 thienothiazine (**7**) is less thermally stable than the isomeric ylide (**3a**) and rapidly decomposes in boiling toluene to give a complex



(7) **(8)** **(9)**



(10) **(11)** **(12)**

a; X = Cl; b; X = SPh

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**) → (**2**), has also been observed, [1,2] shifts to nitrogen are clearly very unfavourable. Experiments are underway[9] 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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