

## Formation of Thiochromans by Cycloaddition Reactions of the Enethione Resulting from Thermal Ring-cleavage Fragmentation of 2-Azidobenzo[*b*]thiophene with Olefins

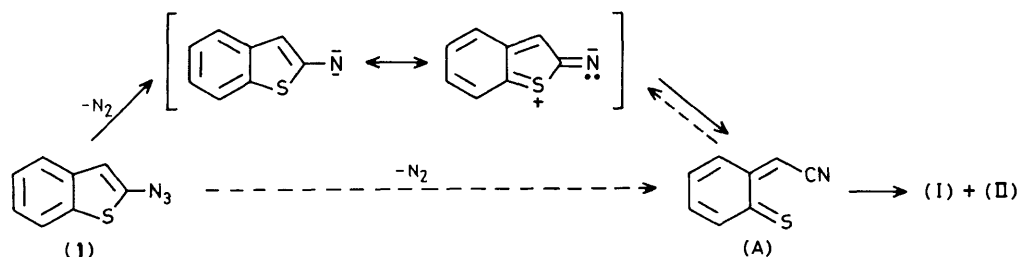
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The enethione arising from thermal ring-cleavage fragmentation of 2-azidobenzo[*b*]thiophene reacts with open chain and cyclic dienophiles to give thiochromans in fairly good yields.

Azidothiophenes have not been investigated systematically but they appear to undergo conventional reactions like those of aryl azides when the azido substituent is linked at a

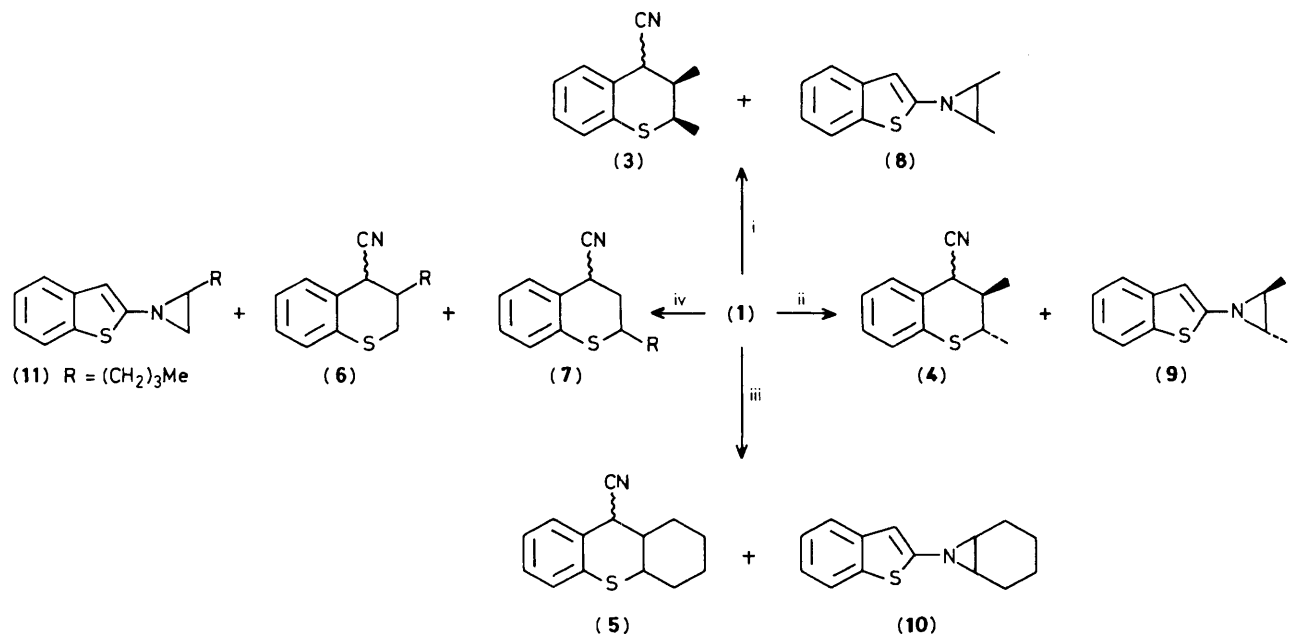
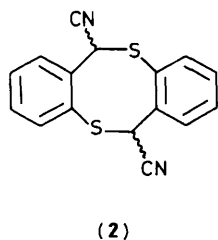
$\beta$ -position.<sup>1</sup> In the course of our study of the chemistry of azidothiophenes we have observed that  $\alpha$ -azidothiophenes are rather unstable compounds which can afford decomposition



Scheme 1

products by extrusion of molecular nitrogen at room temperature.<sup>2</sup> Some evidence was previously provided that the decomposition of these azides may result in ring-cleavage fragmentation in agreement with the general behaviour exhibited by five-membered  $\alpha$ -azido- (or -nitreno-) heteroarenes.<sup>1,3</sup> Now we report that thermal decomposition of 2-azidobenzo[*b*]thiophene (**1**) results in smooth ring-opening fragmentation presumably leading to the enethione *ortho*-quinoidal intermediate (A). Azide (**1**), which can be readily prepared in *ca.* 75% yield by a slight modification of our previously reported procedure,<sup>2a</sup> in benzene or cyclohexane solution exhibited first-order decomposition at 60 °C with a half-life of approx. 150 min leading substantially to two isomeric compounds, (I) and (II), in a 1:2 ratio. The mass spectra of the compounds (I) and (II) exhibited, in addition to the molecular ion at *m/z* 294 (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub><sup>+</sup>) (100 and 70% respectively), predominant fragmentation ions at *m/z* 293(50), 262(50), and 146(40) and at *m/z* 261(70) and 229(100), respectively. C≡N stretching absorption bands at *ca.* 2260 and 2250 cm<sup>-1</sup> were exhibited in the i.r. spectra of (I) and (II). Although at present a definite structure is not assigned to the two isomeric compounds (I) and (II) we suggest that these dimeric compounds result from ring-opening fragmentation of the azide (**1**) and subsequent cyclodimerization of the resulting enethione (A) (Scheme 1). On this basis,<sup>4</sup> we believe that (I) or (II) might be one of the two geometrical isomers of the 6,12-dicyanodibenzo[*b,f*][1,5]dithiocine (**2**) (or a mixture of the two isomers).

In line with the suggested involvement of the enethione (A),



Scheme 2. Reagents: i, *cis*-butene; ii, *trans*-butene; iii, cyclohexene; iv, hex-1-ene.

the decomposition of the azide (**1**), carried out in the presence of olefinic dienophiles, was found to lead to the formation of thiochromans as main products at the expense of (I) and (II). In fact when solutions of (**1**) (0.2 M) in *cis*-butene, *trans*-butene, cyclohexene, or hex-1-ene were allowed to react at 45 °C for *ca.* 50 h [until t.l.c. showed disappearance of (**1**)], column chromatography gave the thiochromans (**3**), (**4**), (**5**), and (**6**) and (**7**), respectively, in 63–72% yields in addition to minor amounts of the appropriate aziridines (**8**)–(**11**) (12–15%) (Scheme 2 and Table 1). Structural assignment of products (**3**)–(**7**)<sup>5</sup> and (**8**)–(**11**) was made on the basis of <sup>1</sup>H n.m.r., i.r., and mass spectral data.

Thus it would appear that the 2-azidobenzo[*b*]thiophene (**1**) can suffer smooth, thermal ring-opening fragmentation to give presumably the heterodiene enethione (A), which can effectively undergo cycloaddition reactions with alkenes affording thiochromans,<sup>4</sup> at the expense of cyclodimerization processes leading to (I) and (II).

As for aziridines (**8**)–(**11**), their formation might be taken as possible evidence that a nitrene intermediate is involved in the decomposition of the azide (**1**), ultimately affording the enethione (A). In fact aziridines can usually be formed by nitrene addition to double bonds.<sup>1,6,7</sup> However, the aziridines (**8**)–(**11**) might alternatively result from thermal fragmentation of initially-formed 1,2,3-triazolines<sup>7,8</sup> although in all cases investigated we could obtain no evidence for the formation of triazolines, which might be expected to survive our mild reaction conditions.<sup>6</sup>

Table 1. Product yields (%) for the decomposition of the azide (**1**) in the presence of alkenes.

Alkene	Thiochroman	Aziridine
<i>cis</i> -Butene	( <b>3</b> ) (68)	( <b>8</b> ) (15)
<i>trans</i> -Butene	( <b>4</b> ) (72)	( <b>9</b> ) (12)
Cyclohexene	( <b>5</b> ) (63)	( <b>10</b> ) (12)
Hex-1-ene	( <b>6</b> ) (68) + ( <b>7</b> ) (4)	( <b>11</b> ) (13)

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### References

- 1 P. A. Smith, in 'Azides and Nitrenes; Aryl and Heteroaryl Azides and Nitrenes,' ed. E. F. V. Scriven, Academic Press, London, 1984, ch. 3, pp. 182—193 and references cited therein.
  - 2 (a) P. Spagnolo and P. Zanirato, *J. Org. Chem.*, 1978, **43**, 3539; (b) S. Gronowitz, P. Spagnolo, and P. Zanirato, *J. Org. Chem.*, 1982, **47**, 3177; (c) P. Spagnolo, G. Zanardi, and P. Zanirato, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2551.
  - 3 B. Iddon, *Heterocycles*, 1983, **20**, 1127.
  - 4 (a) K. Kanakarajan and M. Meier, *J. Org. Chem.*, 1983, **48**, 881; (b) W. J. M. van Tilborg and R. Plomp, *J. Chem. Soc., Chem. Commun.*, 1977, 130.
  - 5 S. W. Schneller, 'Thiochromanones and Related Compounds,' in 'Advances in Heterocyclic Chemistry,' eds A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1975, vol. 18, pp. 59—96.
  - 6 T. Sheradsky, 'Azides as synthetic starting materials,' in 'The Chemistry of the Azido Group,' ed S. Patai, Interscience Publishers, London, 1971, pp. 359—361.
  - 7 W. Lwowski, in 'Azides and Nitrenes; Acyl Azides and Nitrenes,' ed. E. F. V. Scriven, Academic Press, London, 1984, ch. 3, pp. 210—211.
  - 8 P. Scheiner, *Sel. Org. Transform*, 1970, **1**, 327.
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