Thermal Reactions of Aryl Azides with 1,2,3-Benzothiadiazole

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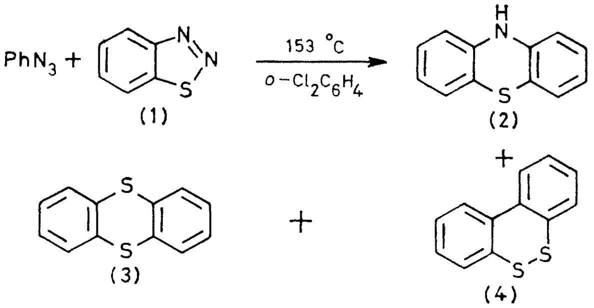
Summary Thermolysis of phenyl azide in the presence of 1,2,3-benzothiadiazole (**1**) affords phenothiazine (**2**), thianthrene (**3**), and dibenzo[*c*,*e*]-*o*-dithiin (**4**) together with aniline and traces of azobenzene, while *p*-nitrophenyl azide gives no phenothiazine derivative and decreased yields of (**3**) and (**4**), whereas increased yields of (**3**) and

(**4**) are observed with *p*-methoxyphenyl azide, together with small amounts of the phenothiazine derivative, evidence in favour of an initial attack on the sulphur of (**1**) by triplet arylnitrenes is presented.

NITRENE attack on sulphur atoms has been observed in a number of instances, with *e.g.* carbonyl-,[1,2] sulphonyl-,[1,3] acylamino-,[4,5] and 2,4-dinitrobenzenesulphenyl-[6] nitrenes, however, no evidence for an arylnitrene attack at sulphur has been found. 2-(*o*-Nitrophenyl)-thiophens and -benzothiadiazoles form no products by intramolecular N–S cyclization[7] and 2-azidothiobenzophenone appears to lose N_2 by a concerted mechanism.[8]

To obtain further information on the reactivity of arylnitrenes towards a sulphur atom we have studied the thermal reaction of aryl azides with 1,2,3-benzothiadiazole (**1**). Thermolysis[†] of phenyl azide in *o*-dichlorobenzene (0·2 and 0·4 M) containing 2 or 5 mol. equiv. of benzothiadiazole (**1**) at 153 °C for *ca.* 7 h (until the disappearance of the azido i.r. band at 2120 cm^{-1}) led, after column chromatography, to phenothiazine (**2**), thianthrene (**3**), and dibenzo[*c,e*]-*o*-dithiin (**4**), as well as aniline and trace amounts of azobenzene (Scheme 1). Yields of products, determined by g.l.c. analysis, are summarized in the Table.



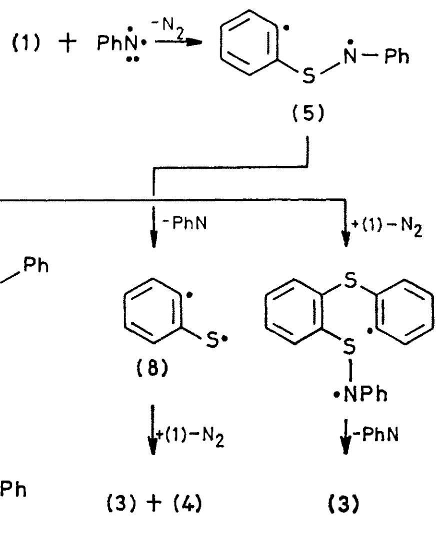
SCHEME 1

TABLE. Yields of products from the thermolysis of phenyl azide in *o*-dichlorobenzene at 153 °C in the presence of benzothiadiazole (**1**)

$[PhN_3]$/M	(**1**)/PhN_3 (molar ratio)	% Yield[a] (**2**)	(**3**)	(**4**)
0·2	2	3·7	3·2	0·7
	5	9·5	15	2
0·4	2	4·5	9	2
	5	11	35	5

[a] Yields are based on starting phenyl azide.

Reaction of *p*-nitrophenyl azide with (**1**) gave no phenothiazine derivative and a remarkable decrease in yields of (**3**) and (**4**), whereas yields of (**3**) and (**4**) were found to be considerably increased with *p*-methoxyphenyl azide, in the latter case only small amounts of phenothiazine derivative could be observed, owing to its instability under the reaction conditions. Reaction products (**2**)—(**4**) could be rationalized by invoking an initial attack by a triplet nitrene on the sulphur of (**1**) and formation, after nitrogen loss, of a diradical intermediate (**5**) by a mechanism analogous to that by which (**1**) spin-traps radicals (Scheme 2).[9]



SCHEME 2

Attack at the sulphur of (**1**) by a singlet nitrene does not appear to be likely, if a singlet nitrene were the attacking species yields of the reaction products would be expected to increase with the strongly electrophilic *p*-nitrophenylnitrene and decrease with the more weakly electrophilic *p*-methoxyphenylnitrene.

Diradical (**5**) has available three reaction pathways (i) 1,4-cyclization to the benzothiazete (**6**) leading to (**2**) by valence isomerization to (**7**) followed by electrocyclic closure and aromatization,[‡] (ii) cleavage of the S–N bond affording the diradical (**8**) from which (**3**) and (**4**) are the expected products,[10] (iii) radical attack on the sulphur atom of (**1**) giving (**3**) by a mechanism analogous to that observed with *ortho*-thio-substituted aryl-radicals (Scheme 2).[9] Intermediacy of the diradical (**5**) appears to be supported by results of the thermolysis of phenyl azide in tetralin with 5 equiv. of (**1**). In this case only traces of phenothiazine (**2**) were obtained, benzenethiol and diphenyl disulphide were the major products together with minor

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[†] The first-order decomposition rate of phenyl azide in *o*-dichlorobenzene is not affected by the presence of benzothiadiazole (**1**), moreover (**1**) is stable under the reaction conditions.

[‡] Thermal conversion of 2-phenyl-2*H*-benzothiazete 1,1-dioxide into phenothiazine 5,5-dioxide has been reported, most probably occurring *via* a route analogous to that suggested in the formation of phenothiazine (**2**) (M. S. Ao and E. M. Burgess, *J. Am. Chem. Soc.*, 1971, **93**, 5298).

amounts of (**3**) and (**4**). In tetralin, hydrogen abstraction from the solvent appears to be the most favoured reaction pathway of (**5**), giving rise to some species (possibly sulphenanilide§ or its radical precursor) from which thiyl-radicals and ultimately benzenethiol and diphenyl disulphide would be produced by cleavage of the S–N bond. In this case formation of (**3**) and (**4**) is most probably due to the reaction of thiyl radicals with (**1**).[9b]

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§ Sulphenanilide could not be detected in our reactions. However, control experiments showed that it would not survive the experimental conditions, readily affording benzenethiol, diphenyl disulphide, and aniline.

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