## Decomposition of 2-(4-Azidophenyl)benzothiazoles in Trifluoromethanesulfonic Acid: Formation of 2,2'-Diaminobiphenyls

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The  $\pi$ -carbocation reactive species generated by decomposition of 2-(4-azidophenyl)benzothiazoles in trifluoromethanesulfonic acid undergo intermolecular C–C or N–N coupling to afford benzothiazole-substituted 2,2'-diaminobiphenyls.

Mesomeric arylnitrenium ions ( $\pi$ -carbocations) generated from aryl azides in strong acids participate in a range of intraand inter-molecular reactions;<sup>1,2</sup> the synthetic utility of the former reactions has been explored extensively by Abramovitch.<sup>3</sup> When trifluoromethanesulfonic acid (TFSA) is employed as the acid in a trifluoroacctic acid-anhydride mixture at 0 °C, the  $\pi$ -carbocation reactive species can be trapped in an intermolecular process by the triflate ( $-OSO_2CF_3$ ) counter-anion, with the triflate residue usually substituting *para* to the (incipient) amine group, often in very high yield;<sup>4</sup> alternatively, diphenylamine or biphenyl derivatives can be formed in decompositions in aromatic hydrocarbon substrates.<sup>5</sup>

We were interested to examine the decompositions of the 2-(4-azidophenyl)benzothiazoles **3** and **4**, prepared from the amines **1** and **2**, to determine if the hetero-atoms of the thiazole ring participated in the capture of the  $\pi$ -carbocation. They did not, but novel 2,2'-diaminobiphenyls of a type hitherto unreported in azide decomposition were isolated. Thus, when azide **3** was decomposed in TFSA<sup>†</sup> a mixture of the triflates 5 (12%) and 7 (23%) and the symmetrical



biphenyl 9 (7%) was separated by flash chromatography. Similarly azide 4 afforded a comparable mixture of triflates 6 and 8 and the symmetrical biphenyl 10 in 14, 18 and 32% yields, respectively.

Formation of the triflates 5 and 6 can be explained simply by invoking nucleophilic attack by triflate at the *ortho* positions of the  $\pi$ -carbocations derived from 3 and 4 [see Scheme 1(*a*)] but accounting for the biphenyl products is more problematical. The simplest explanation for the formation of the triflate-substituted biphenyls 7 and 8 would involve C-C aryl



<sup>+</sup> Experimental procedure: the azide **3** was added in small portions  $(10 \times 0.1 \text{ g})$  to a mixture of trifluoromethanesulfonic acid (4 ml), trifluoroacetic acid (5 ml) and trifluoroacetic anhydride (1 ml) at 0 °C. After evolution of nitrogen ceased, the mixture was stirred at 20 °C for 18 h, basified with aqueous ammonia and the products were extracted into ethyl acetate. The organic layer was washed with water, dried (MgSO<sub>4</sub>) and evaporated to give a gum which was separated on silica (hexane–ethyl acetate, 6:4).

Scheme 1 In structures 3, 5, 7 and 11 B = benzothiazol-2-yl; in structures 4, 6, 8 and 12 B = 6-methylbenzothiazol-2-yl

<sup>&</sup>lt;sup>‡</sup> All compounds were fully characterised by C, H and N elemental analysis, <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy (for fluorinated compounds) and accurate mass measurement (CI or FAB mass spectrometry).



Scheme 2 In structures 3, 9 and 13 B = benzothiazol-2-yl; in structures 4, 10 and 14 B = 6-methylbenzothiazol-2-yl

coupling between the  $\pi$ -carbocations generated from azides 3 and 4 and the arylamine by-products of the reaction 5 and 6, respectively. However, in the strongly acidic conditions the latter amines would be protonated and poor substrates for electrophilic substitution. A realistic alternative would involve coupling between undecomposed azides 3 and 4 with their derived  $\pi$ -carbocations to generate transient 2-amino-2'azidobiphenyls 11 and 12 which are subsequently processed as above by TFSA to yield the observed products 7 and 8 [Scheme 1(b)].

The symmetrical 2,2'-diaminobiphenyls 9 and 10 could be formed by C–C coupling between the  $\pi$ -carbocations derived

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from the starting materials 3 and 4 and 2-(4-aminophenyl)benzothiazoles 1 and 2. However, the latter amines were not detected among the degradation products. Also the azidobiphenyls 11 and 12 are unlikely precursors since direct 'reduction' of aryl azides to amines is not normally encountered in strong acids without the incorporation of a nucleophile in the ring (*cf.* photo- and thermal-decompositions).<sup>2</sup> Instead we propose, tentatively, that an N–N coupling could lead to protonated hydrazo species 13 and 14 which then undergo an *ortho*-benzidine rearrangement to the observed products 9 and 10 (Scheme 2).

Careful analysis of reaction products from the acid decomposition of other *p*-substituted aryl azides might reveal similar products.

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