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

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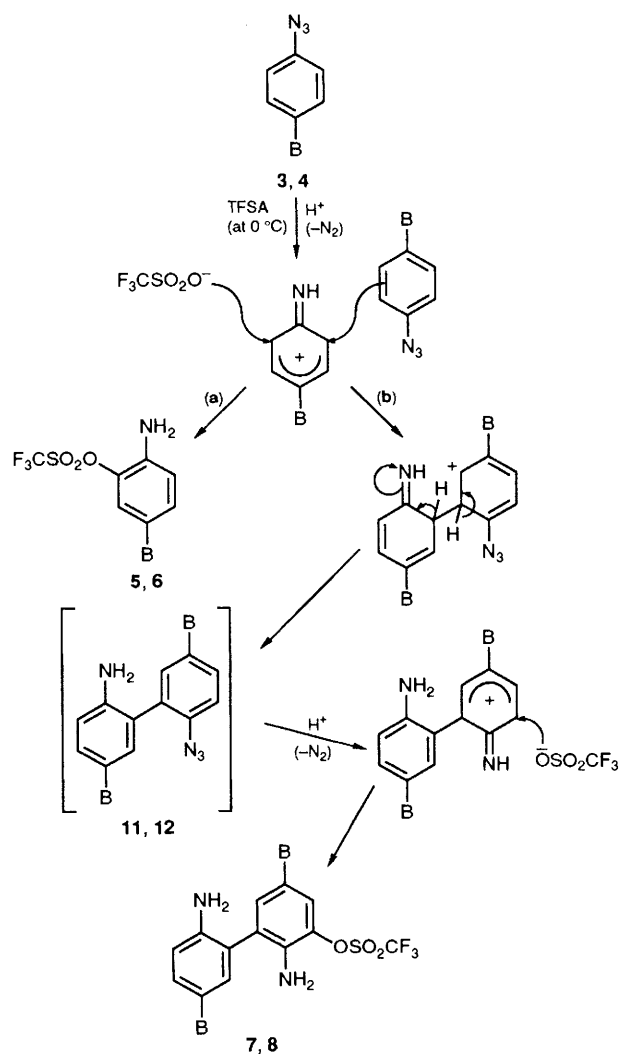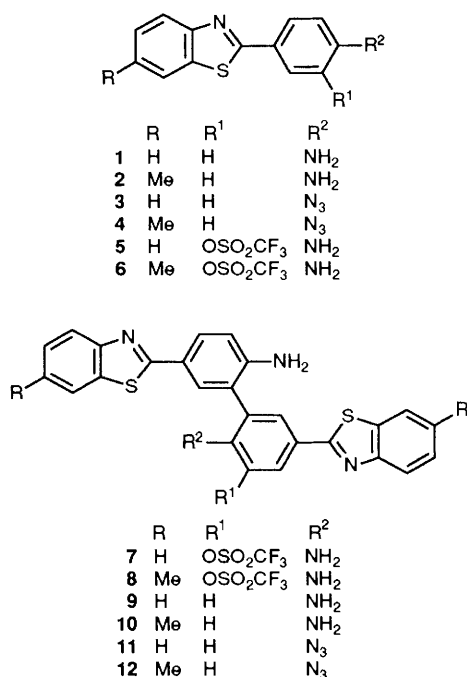[b] Pharmaceutical Sciences Institute, Aston University, Aston Triangle, Birmingham B4 7ET, UK

The π-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 (π-carbocations) generated from aryl azides in strong acids participate in a range of intra- and inter-molecular reactions;[1,2] the synthetic utility of the former reactions has been explored extensively by Abramovitch.[3] When trifluoromethanesulfonic acid (TFSA) is employed as the acid in a trifluoroacetic acid–anhydride mixture at 0 °C, the π-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;[4] alternatively, diphenylamine or biphenyl derivatives can be formed in decompositions in aromatic hydrocarbon substrates.[5]

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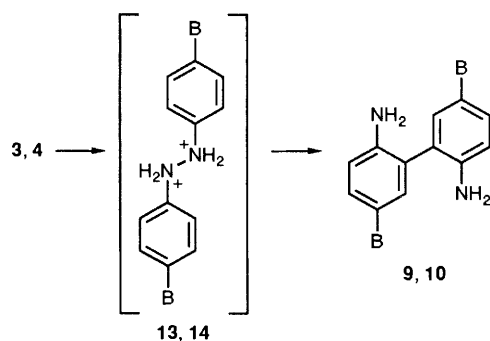
Formation of the triflates 5 and 6 can be explained simply by invoking nucleophilic attack by triflate at the ortho positions of the π-carbocations derived from 3 and 4 [see Scheme 1(a)] but accounting for the biphenyl products is more problematical. The simplest explanation for the formation of the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

R

	R	R¹	R²
1	H	H	NH₂
2	Me	H	NH₂
3	H	H	N₃
4	Me	H	N₃
5	H	OSO₂CF₃	NH₂
6	Me	OSO₂CF₃	NH₂

	R	R¹	R²
7	H	OSO₂CF₃	NH₂
8	Me	OSO₂CF₃	NH₂
9	H	H	NH₂
10	Me	H	NH₂
11	H	H	N₃
12	Me	H	N₃

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

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

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 azido-biphenyls **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).[2] 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.

coupling between the π-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 π-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 π-carbocations derived

References

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