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INTRAMOLECULAR ADDITION OF ARYL RADICALS TO THE AZIDO GROUP

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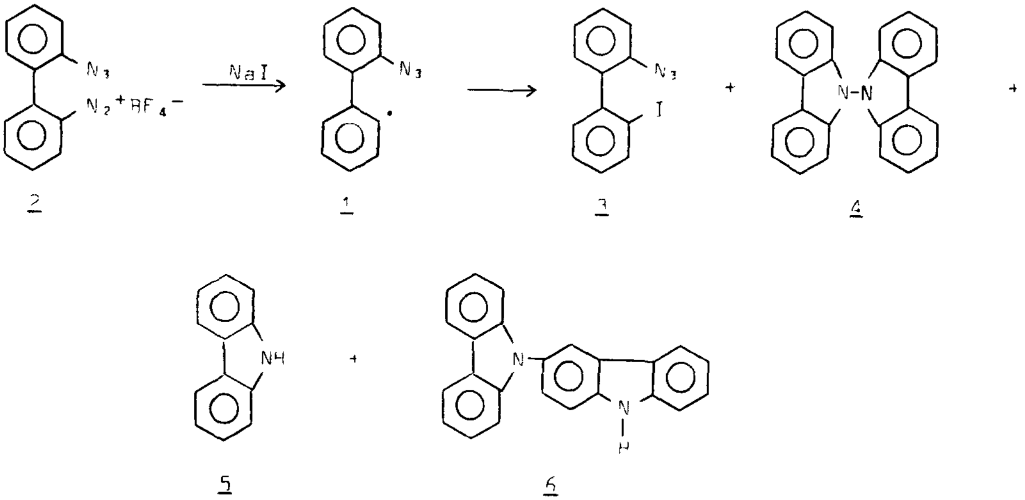
Although decomposition of azides catalysed by acids and nucleophiles have been reported in several cases,[1] there are been very few reports concerning radical induced decomposition of azides.[1] In fact the only examples are confined to decomposition of phenyl azide in thiols, which was found to be accelerated by thiyl radicals,[2] and to decomposition of the same azide in carbon tetrachloride which occurred rapidly at 80° in the presence of benzoyl peroxide.[3] In this case, evidence was presented in favour of a radical mechanism involving addition of trichloromethyl radical on the azido group. More recently it has been shown that t-butoxyl and triorganosilyl radicals add to a number of azides affording iminyl and triazenyl radicals respectively.[4] As for reactions of aryl radicals on the azido group, to our knowledge no examples can be found in the literature. In fact thermolysis of benzoyl peroxide in the presence of phenyl azide at 80° has been shown not to lead to any decomposition of the azide,[3] moreover thermolysis of bis(o-azidobenzoyl)peroxide gave a number of products clearly indicating that reaction with the azido group had not occurred.[3] In this paper we wish to report the first definite evidence of addition of aryl radicals to the azido group.

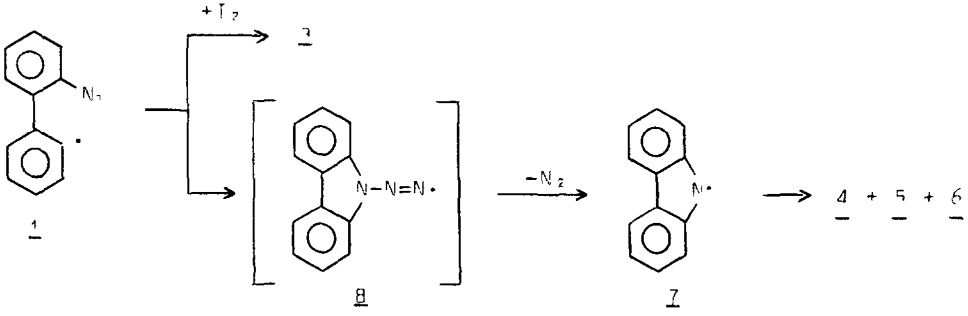
The 2-(2'-azido)biphenylyl radical (1) generated by addition of 1.5 molar equivalent of sodium iodide[5] to an acetone solution of 2-(2'-azido)biphenylyldiazonium tetrafluoroborate (2), which was in turn obtained by diazotization of 2-amino-2'-azidobiphenyl,[6] led, after column chromatography, to the isolation of: (a) 2-iodo-2'-azidobiphenyl[7] (3) (12%), mp 55-56°, m/e 321 (M^+) and 293 (M^+-N_2), ν_{max} 2070 cm^{-1} (N_3); (b) N,N -dicarbazolyl[8] (4) (23%), mp and mixed mp 220-221°; (c) carbazole (5) (23%); (d) 3-(N-carbazolyl)carbazole[8] (6) (17%), mp and mixed mp 208-210° and (e) trace amounts of an unidentified product (Scheme 1).

Scheme 1



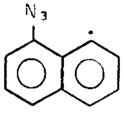
Products 3–6 can be readily accounted for by reaction of radical (1) with iodine leading to (3) and 1,5-intramolecular addition to the 2'-azido group giving carbazolyl radical (7), most presumibly through the intermediacy of 3,3-disubstituted triazenyl radical (8) and following nitrogen loss leading to the expected products 4–6 (Scheme 2).

Scheme 2



Compelling evidence that carbazolyl radical (7) derives by intramolecular addition of aryl radical (1) came from our observation that yields of products 4–6 were considerably lowered when the reaction was carried out in the presence of excess carbon disulphide, which is known to be a very effective aryl radical scavenger;[11] in this case the main reaction product was found to be bis 2-(2'-

azido)biphenylyl disulphide.[12] These findings led us to investigate the behaviour of 8-azido-1-naphtyl radical (9), where intramolecular addition to the peri-azido group appears to be still plausible and would be expected to afford 1,3-disubstituted triazenyl radicals (10) by 1,6-cyclization more likely than 3,3-disubstituted radicals (11) by 1,4-cyclization.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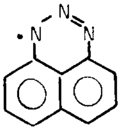
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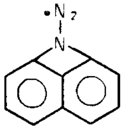
11

However, radical (9) generated by the same procedure from 8-azido-1-naphtyldiazonium tetrafluoroborate (in turn prepared by diazotization of 1-amino-8-azidonaphthalene[9]) did not provide any evidence of addition to the azido group. In fact the only reaction products isolated were found to be 1-azidonaphthalene[10] (28%) and 1-azido-8-iodonaphthalene[7] (60%), mp 70-71°, m/e 295 (M^+) and 267 (M^+-N_2), ν_{max} 2100 cm^{-1} (N_3). Analogous results were obtained from reduction of o-azidobenzendiazonium tetrafluoroborate which gave phenyl azide (12%) and o-iodophenyl azide[13] (77%) as the only identifiable products, thus confirming previous reports that o-azidophenyl radicals (12) are not capable of adding to the azido group.[3] Our results obtained from radical (1) indicate that aryl radicals add to the azido group, at least intramolecularly. The failure of finding intramolecular addition products in the other cases investigated might provide some evidence that the preferred addition of aryl radicals to the azido group is that leading to 3,3-disubstituted rather than to 1,3-disubstituted triazenyl radicals. The former radicals are in fact expected to be formed more readily from radical (1) than from radicals (9) and (12). Evidence in the same line is furnished by previous findings[4] that addition of silyl radicals to the azido group most likely leads to 3,3-disubstituted triazenyl radicals. Further studies are in hand to check this point and to investigate the more general reactivity of carbon radicals towards the azido group.

Acknowledgement

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