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DECOMPOSITION OF AROMATIC AZIDES IN ETHANETHIOL

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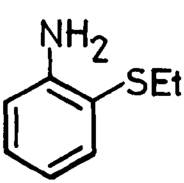
Photolytic decomposition of phenyl azide in ethanethiol gives o-thioethoxyaniline (1) in 39% yield. This is an unexpected result as phenyl azide usually undergoes ring expansion to 2-substituted 3H-azepines when decomposed in nucleophilic solvents, such as primary[1], secondary[1], and tertiary[2] aliphatic amines, methanol[3], and hydrogen sulphide-diethyl ether[4]. Photolysis of 8-azidoquinoline and β-azidonaphthalene in ethanethiol gives 8-thioethoxy-7-aminoquinoline (2) (48%) and 2-thioethoxy-1-naphthylamine (3) (40%), which is comparable to their conversion into o-diamines on photolysis in secondary amines[5]. The decomposition of these two bicyclic azides involves a 1,2-nitrogen walk by the azide α-nitrogen (Scheme) which is not obvious for phenyl azide. Therefore, p-tolylazide was decomposed under similar conditions to give 2-thioethoxy-5-methylaniline (4) (15%), the product of a 1,2-nitrogen walk. This observation also rules out the possibility of direct radical attack by EtS·, a process that is believed to be involved in the formation of o-aminodiphenyl sulphide from photolysis of phenyl azide in benzenethiol[6].



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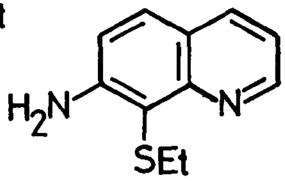

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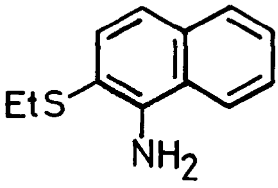

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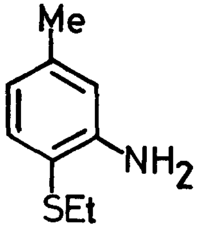

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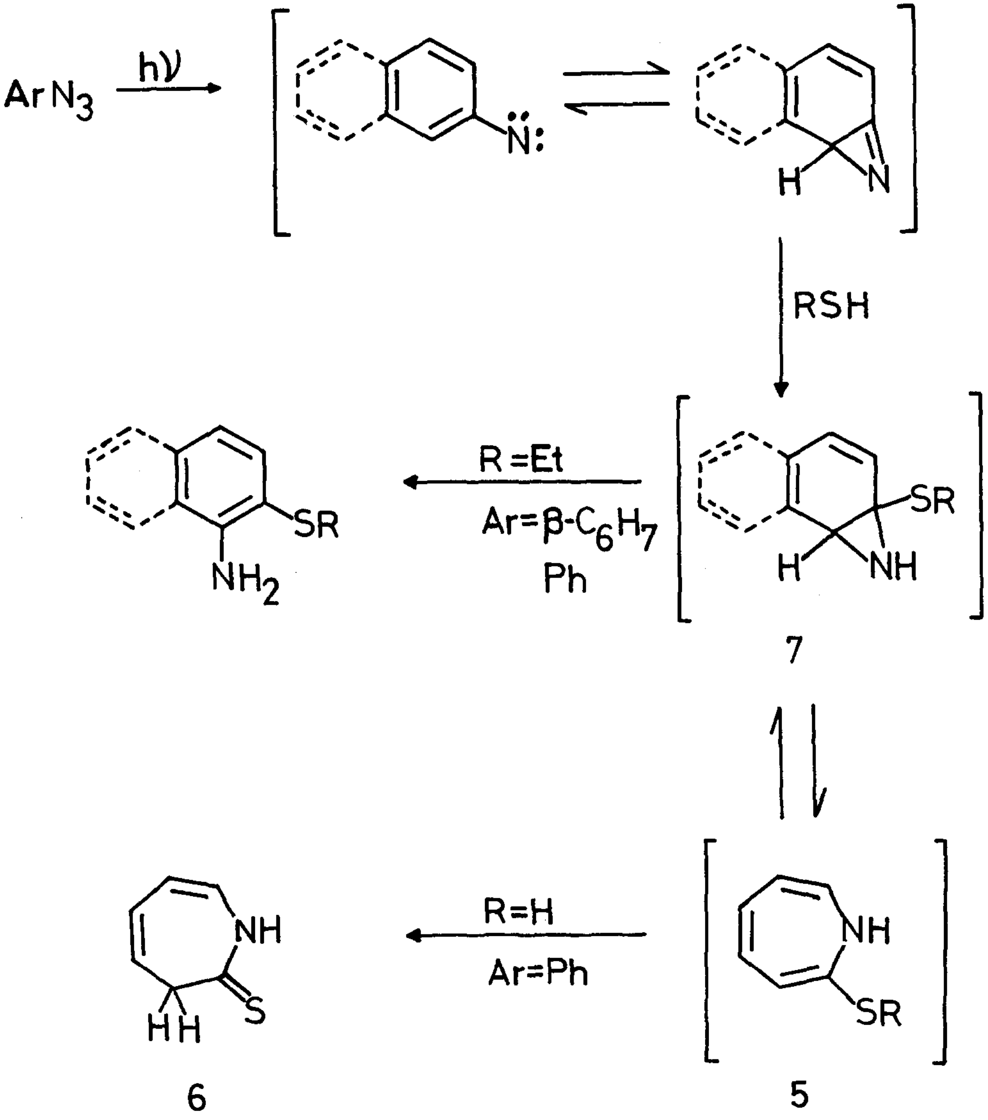
The structures of new compounds (2), (3), and (4) are supported by ^{1}H n.m.r., i.r., and high resolution m.s. The orientation of substituents in (4) was ascertained by irradiating the amino group, which gave a NOE enhancement (∿20%) in the intensity of the 6-proton signal at τ2.80. Similarly, NOE enhancements were observed in the α-proton signals of (3) and in the 6-proton signal of (2).



A general mechanism is proposed for the reaction of mono- and bicyclic aryl azides with ethanethiol and hydrogen sulphide (Scheme), which is closely analogous to that for reaction of azides with amines[7]. The behaviour of phenyl azide in ring expanding to an azepinthione on photolysis in hydrogen sulphide-diethyl ether, may be attributable to the ease of tautomerism of (5) to (6) when R=H. This tautomerism is not possible when R=Et and rearomatisation to (1) takes place, even though it is reasonable to assume that the equilibrium (7) $\rightleftarrows$ (5) still favours (5)[8]. This is the only example we know of phenyl azide reacting with a nucleophile to give an *o*-disubstituted benzene and not ring expanding to an azepine. It contrasts with the behaviour of phenyl azide and amines; for example, not even 1 ppm of *o*-morpholinoaniline could be found amongst the products of photolysis of phenyl azide in morpholine[9]. Two other monocyclic azides (6-azido-1,3-dimethyluracil[10] and 2-phenyl-5-azido-6-chloropyridazin-3-one[11]) do give *o*-diamines on photolysis in aliphatic amines but they have certain structural features that would appear to prevent ring expansion.

This work indicates that decomposition of aryl azides in thiols might provide a useful synthetic approach to *o*-thioalkoxy aromatic amines. The above reaction of benzazirines is also interesting because it is analogous to the reaction of arene oxides with thiols such as glutathione[12].

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