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Thermal Reaction of Phenylnitrene with Sulphides

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Thermolysis of phenyl azide in the presence of sulphides bearing α -hydrogen atoms leads to the formation of significant amounts of 2-substituted anilines, presumably by Sommelet–Hauser type rearrangements of the intermediate *N*-phenylsulphimides.

Reactions of several sulphonyl-, carbonyl-, and acylaminonitrenes with sulphides leading to sulphimides by singlet attack on the sulphur atom have been observed in a number of instances; in other cases products arising from rearrangement of unstable sulphimides have been isolated.¹ Despite much effort, attempts to observe attack at sulphur by an aryl-nitrene



have been so far unsuccessful.² This could be owing to the fact that in the cases examined cleavage of the S-N bond, giving back the arylnitrene and the sulphide, would be the most feasible decomposition pathway opened to the possibly formed N-arylsulphimides which are incapable of surviving the reaction conditions.²^e We reasoned that arylnitrene attack at the sulphur atom might be shown by reactions with suitable sulphides bearing α -hydrogen atoms. These would be expected to produce N-arylsulphimides which would undergo the well-documented Sommelet-Hauser type rearrangement leading to 2-substituted anilines.^{1a} In fact thermal decomposition of phenyl azide into thioanisole (0.2 M) at 152 °C for ca. 20 h (until the disappearance of the azido i.r. band at 2120 cm⁻¹) led, after column chromatography, to the isolation of 2-[(phenylthio)methyl]aniline (1a)³ (30%), diphenyl disulphide (6%), aniline (12%), and trace amounts of azobenzene.

Formation of the aniline derivative (1a) can be most easily rationalized by assuming an initial attack of the singlet phenylnitrene[†] on the sulphur atom of thioanisole followed by a Sommelet-Hauser type rearrangement of the resulting sulphimide (2a) (Scheme 1). Intermediacy of phenylnitrene appears to be supported by kinetic studies which showed that the first-order decomposition rate of phenyl azide in bromobenzene at 152 °C is not affected by the presence of thioanisole or its concentration.



The diphenyl disulphide probably arises from some decomposition of the aniline derivative (1a) occurring under the reaction conditions, as shown by control experiments. Similar results were obtained from the thermolysis of phenyl azide in dimethyl sulphide and tetrahydrothiophen at 155 °C in a sealed tube, which led to the separation of 2-[(methylthio)methyl]aniline (1b)⁴ and 2-*o*-aminophenyltetrahydrothiophen (1c)⁴ in 35% and 30% yields respectively.

Moreover thermal decomposition of phenyl azide in refluxing bromobenzene (0.2 M) in the presence of equimolar amounts of 6H-dibenzo[b,d]thiopyran⁵ gave (i) 6-(2-aminophenyl)-6*H*-dibenzo[b,d]thiopyran (1d) (13%, m.p. 55-57 °C), \ddagger (ii) 6-phenylimino-6*H*-dibenzo[*b*,*d*]thiopyran (3) (7%, m.p. 79-81 °C),‡ (iii) 6,6'-bi-6H-dibenzo[b,d]thiopyran (4) (15%, m.p. 175-177 °C),‡ and (iv) aniline (24%). Formation of compound (1d) can be readily rationalized by a mechanism analogous to that suggested for the anilines (1a-c), whereas compounds (3) and (4) (in addition to aniline) may be ascribed to the hydrogen abstraction from 6H-dibenzo[b,d]thiopyran by triplet nitrenes, leading to 6Hdibenzo [b,d] thiopyran-6-yl and anilino-radicals. Dimerization of the former radicals would produce (4), whereas (3) might be due to further reaction of 6-anilino-6H-dibenzo [b,d] thiopyran (5) arising from coupling of the two types of radicals. Finally from thermolysis of phenyl azide in refluxing bromobenzene (0.2 M) containing a four-fold excess of *m*-dithiane we could only isolate 2-o-aminophenyl-1,3-dithiane (1e)³ (7%), formanilide (5%), presumably resulting from hydrolysis of the dithioacetal (6) during work-up, and aniline (10%). Such reaction led to a complex reaction mixture and was accompanied by much tarring; a serious limitation was observed in the noticeable decomposition of products under the reaction conditions.

Our findings would suggest that phenylnitrene is generally capable of reacting with the sulphur atoms of sulphides presumably by singlet attack; moreover these findings appear

[†] Singlet phenylnitrene attack is invoked only on the basis of the general acceptance that the singlet states of nitrenes and carbenes are those which react with sulphides by attack on sulphur (see ref. 1a,b).

[‡] Satisfactory analyses and spectral data were obtained for all new compounds.

to indicate that the reactivity of singlet phenylnitrene towards the sulphur atom must be fairly high as shown by the formation of the anilines (1a-c) in observable yields in addition to the fact that the aniline (1d) is still produced in significant amounts even under conditions which could be expected to discourage singlet attack at sulphur, such as a low sulphide concentration and use of bromobenzene as solvent known to promote singlet \rightarrow triplet intersystem crossing.⁶

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