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THERMOLYSIS OF ARYL AZIDES IN ANILINES

E. F. V. Scriven and H. Suschitzky

Department of Chemistry and Applied Chemistry, University of Salford,
Salford M5 4WT, England

and G. V. Garner

Department of Chemistry, Manchester Polytechnic,
John Dalton Faculty of Technology, Manchester, M1 5GD, England.

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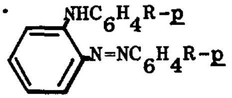
The ring expansion of aryl azides to azepines when heated with nucleophiles, e.g., aniline, is well known[1]. By contrast, insertion of arylnitrenes into N-H bonds is an unexplored reaction since only isolated examples have been reported[2]. A systematic study of the decomposition of certain substituted aryl azides in various anilines has revealed that N-H insertion, to give mixed azo-compounds, can in fact predominate over 2-anilino-3H-azepine formation provided certain structural requirements are fulfilled.*



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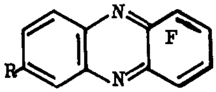

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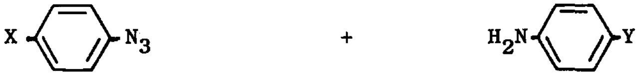
a) R = OMe
b) R = Me

The Table lists the products obtained when a series of aryl azides, with different para-substituents were decomposed in substituted anilines. It appears that mixed azo-compound formation depends on "pairing up" an azide with an aniline with the right para-substituent as illustrated in the Scheme.

Scheme



A) X-electron-donating Y-electron-withdrawing (or H).

B) X-strongly electron-withdrawing Y-electron-donating (or H).

The reaction seems to be most favoured when the elctronic effects of X and Y act in opposition to each other with reference to the ring. The nature of the substituent on the azide is more important than that on the amine since aniline yields mixed azo-compounds with aryl azides carrying electron-donating or withdrawing groups. For successful insertion the azide must be para-substituted. Thus, no unsymmetrical azo-compounds are formed in the thermolyses of o- or m-tolyl- or phenylazide in pentafluoroaniline or from m-nitrophenylazide in p-toluidine. Therefore, in absence of these structural features the thermolysis of aryl azides in anilines merely gives the respective anilines, symmetrical azo-compounds and tars but surprisingly no 2-anilino-3H-azepines were isolated. The ubiquitous formation of sym. azo-compounds in aryl azide pyrolysis does, therefore, most probably not arise from an aryl nitrene-aniline interaction.

The first step in these insertion reactions is at present not clear, but preliminary kinetic studies indicate nitrene involvement. Some support for a hydrazo-intermediate that dehydrogenates to the observed mixed azo-compounds comes from Huisgen's work[2a]. There it was shown that the mixed azo-compound formed from 4,6-dimethylpyrimidyl azide in hot aniline arises from the corresponding hydrazo-compound. The formation of the azo-compounds 1a and 1b and the phenazines 2a and 2b in our reactions could possibly also involve the appropriate hydrazo-compound. We found that pentafluoro-p'-methoxyazobenzene when heated with p-anisidine under the reaction conditions gave 1a, excluding possible substitution in the azo-compound by p-anisylnitrene[3]. Further support for a concomitant nucleophilic attack on the azo-compounds formed in these reaction comes from the isolation of the respective anilinium fluorides. It is tempting to assume that the presence of the phenazines 2a and 2b is due to intermediate dialkylhydrazine formation followed by an o-semidine rearrangement, possibly catalysed by hydrogen fluoride. This is followed by cyclisation of the o-semidine with fluorine replacement and oxidation to the phenazine

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Products of the Thermolysis of Arylazides in Anilines at 155° for 8 Hours

Phenylazide (1 c mole)	Aniline (3 c mole)	Product (Yield %)
p-Methoxy-	pentafluoro-	mixed azo-compound (5.5)[a] 1a(16), 2a(5.7)
	p-chloro-	mixed azo-compound (3.5)
	aniline	mixed azo-compound (4.7)
	p-methyl- *p*-methoxy-	symmetrical azo-compound, anilines and tars
p-Methyl-	pentafluoro-	1b (15.4) 2b(1.1)
	p-chloro-	symmetrical azo-compound, aniline and tars
	aniline	mixed azo-compound (7.7) 2-(4'-toluidino-)-3H-azepine(4.6)
	p-methoxy-	symmetrical azo-compound, aniline and tars
p-Chloro-	pentafluoro- aniline *p*-methyl- *p*-methoxy	symmetrical azo-compound,aniline and tars
p-Nitro-[b]	pentafluoro-	symmetrical azo-compound, aniline and tars
	aniline	mixed azo-compound, (8.3)
	p-methyl-	mixed azo-compound, (16.3)
	p-methoxy-	mixed azo-compound, (10)

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[a] symmetrical azo-compounds, anilines and tars were found in all decompositions.

[b] Carried out at 135° for 48 hours.

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2b. R. A. Odum and A. M. Aaronson, J.Amer.Chem.Soc., 1969, 91, 5681.

2c. P. A. S. Smith and H. Dounchis, ref. 1, p.110.

3. J. Ashby, E. F. V. Scriven and H. Suschitzky, J.C.S. Chem. Comm., 1972, 366.

*The formation of azo-compounds of the type $Ar_FN = NC_6F_5$ ($Ar_F = C_6F_5$, p-$CF_3C_6F_4$, tetrafluoro-4-pyridyl) *via* thermal reaction of aryl azides with pentafluoroaniline has been observed independently by R. E. Banks and A. Prakash, (see the accompanying letter).