

THERMOLYSIS OF ARYL AZIDES IN BENZOYL CHLORIDE

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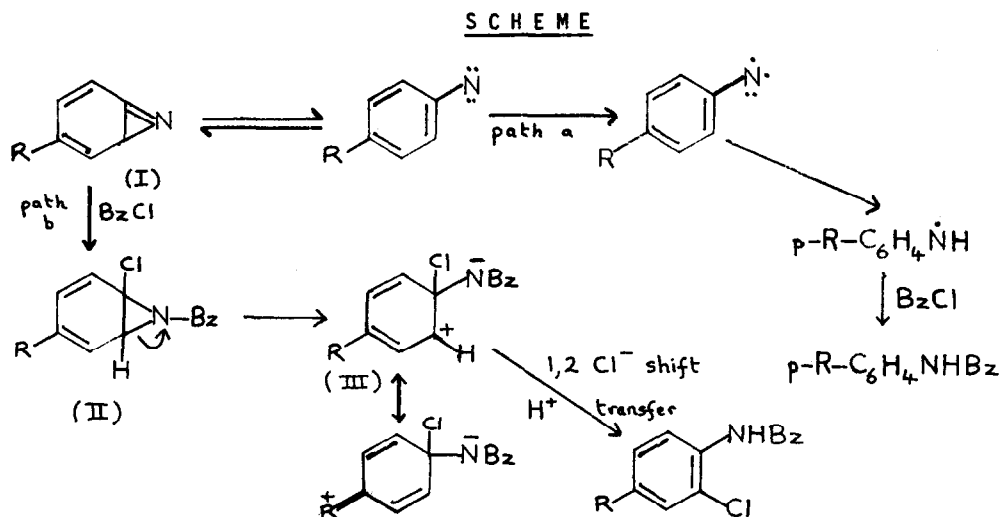
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In continuation of our studies¹ on the decomposition of aryl azides in various solvents, we thermolysed various aryl azides in boiling benzoyl chloride with results given in the Table.

As expected, *o*-nitrophenyl azide and *o*-azidobiphenyl yielded benzofuroxan and carbazole respectively, while *p*-nitrophenyl azide gave only tars. In the other examples, the formation of azo-compounds and substituted benzanilides is probably due, particularly in the latter case, to triplet nitrene² participation (see Scheme; path a)³. However, the reasons for *o*-chlorobenzanilide⁴ formation in the case of phenyl, *p*-methylphenyl, and *p*-methoxyphenyl azide are less obvious. If, as anticipated, the nitrene was first inserted into the carbon-halogen bond of the acyl halide, then the resulting *N*-chlorobenzanilide (ArN(Cl)COPh) would have to undergo an ortho Orton-type rearrangement. However, Orton has reported⁵ that *N*-chlorobenzanilide on thermolysis in an inert solvent yields only *p*-chlorobenzanilide. We have confirmed this result and also shown that the *N*-chlorobenzanilide behaves similarly in boiling benzoyl chloride. The possibility of a radical or electrophilic chlorination yielding *o*-chloro-anilides is unlikely because of the high ortho selectivity of the halogenation process. For instance, *o*-methoxyphenyl azide in boiling benzoyl chloride gave 2-chloro-6-methoxybenzanilide and much tar from which no products could be isolated. Photolysis of the azides in benzoyl chloride gave the same products in much reduced yield. For example, 4,4'-dimethoxyazobenzene (2%) and 2-chloro-4-methoxybenzanilide (20%) were obtained by irradiation of *p*-methoxyphenyl azide for 24 h. (medium pressure 100 W. lamp).

We propose a mechanism as outlined in the reaction scheme (path b) which explains our results and rationalises the fact that the yield of *o*-chloro-anilide diminishes with a decrease in the electron donation of the para substituent (i.e., MeO > Me > H > Cl).



There is evidence⁶ that the initially formed singlet nitrene is in equilibrium with the aziridine (I), and as such can react with benzoyl chloride to give the adduct (II). When substituent R is electron donating, (i.e., Me, MeO, and to a lesser extent, H), the aziridine intermediate (II) opens, not by an electrocyclic process as in the case of azepine formation⁷, but by heterolysis of the C-N bond to give the resonance stabilised dipolar species (III). A 1,2-chloride ion shift⁸ and proton transfer then yields the *o*-chlorobenzanilide. Similar reactions have been invoked to explain the intermolecular substitution reactions of aryl-, sulphonyl-, ethoxycarbonyl-, and cyanonitrenes with aromatic substrates⁹. That *o*-chlorobenzanilide is a reaction of singlet nitrene was demonstrated by carrying out the decomposition of phenyl azide in boiling benzoyl chloride under oxygen, a well-known triplet quencher. *o*-Chlorobenzanilide was obtained in undiminished yield, whereas triplet based products, such as benzanilide, were isolated in much reduced amounts (20%), and azobenzene could not be detected.

The above considerations may throw new light on the formation of *o*-aminophenols, in the decomposition of aryl azides in acetic anhydride^{1a}. Although *N,O*-diacylhydroxylamines, which we postulated as first step in this decomposition, undergo thermal rearrangement to *o*-aminophenols¹⁰, we now favour a pathway analogous to the one proposed above (i.e., addition of acetic anhydride to the aziridine¹¹ followed by ring opening to give the rearranged product).

T A B L E

Decomposition of Aryl Azides in Boiling Benzoyl Chloride^a

<u>Azide</u>	<u>Products</u>	<u>Yield (%)</u>
PhN_3^{b}	azobenzene	2
	benzanilide	50
	2-chlorobenzanilide	11
$\text{p-MeC}_6\text{H}_4\text{N}_3$	4,4'-dimethylazobenzene	2
	4-methylbenzanilide	34
	2-chloro-4-methylbenzanilide	19
$\text{p-MeOC}_6\text{H}_4\text{N}_3$	4,4'-dimethoxyazobenzene	6
	2-chloro-4-methoxybenzanilide	67
$\text{p-Cl.C}_6\text{H}_4\text{N}_3$	4,4'-dichloroazobenzene	9
	4-chlorobenzanilide	24
$\text{p-NO}_2\text{C}_6\text{H}_4\text{N}_3$	tars	-
$\text{o-MeOC}_6\text{H}_4\text{N}_3$	2-chloro-6-methoxybenzanilide	55
$\text{o-NO}_2\text{C}_6\text{H}_4\text{N}_3$	benzofuroxan	83
$\text{o-N}_3\text{.C}_6\text{H}_4\text{.C}_6\text{H}_5$	carbazole	75
	<u>N</u> -benzoylcarbazole	10

^aDecompositions were carried out in freshly distilled deoxygenated benzoyl chloride under dry nitrogen.

^bA low yield (ca. 2%) of 6-chloro-2-phenylbenzoxazole was also isolated. The origin of this interesting by-product is being investigated.

REFERENCES

1. R. K. Smalley and H. Suschitzky, J. Chem. Soc.; a) 1963, 5571; b) 1964, 5922.
2. P. A. S. Smith in "Nitrenes", ed. W. Lwowski, Interscience Publishers, 1970, p.99.
3. Kinetic data indicate that nitrene formation occurs without solvent participation.
4. The identity of all reaction products was established by unambiguous synthesis and the usual spectral data.
5. F. D. Chattaway and K. J. P. Orton, J. Chem. Soc., 1899, 75, 1046.
6. F. R. Atherton and R. W. Lambert, J. Chem. Soc. Perkin I, 1973, 1079, and references cited therein.
7. R. Huisgen and M. Appl, Chem. Ber., 1958, 91, 1 and 12.
8. Chloride ion migration may be synchronous with aziridine ring opening.
9. R. A. Abramovitch, S. R. Challand and E. F. V. Scriven; J. Org. Chem., 1972, 37, 2705. and references cited therein.
10. L. Horner and H. Steppan, Annalen, 1957, 606, 24.
11. The addition of acetic anhydride and benzoyl chloride to 1H-azirines is well documented; see F. W. Fowler, Advances in Heterocyclic Chemistry, 1971, 13, 67.