1142. *Decomposition of Halogen-substituted Phenyl Azides.*

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Thermal decomposition of the three monosubstituted fluoro-, chloro-, and bromo-phenyl azides in various solvents is accompanied by a sublimate of the corresponding anilinium halide ($X{\cdot}C_6H_4{\cdot}NH_3^+X^-$). The probable cause of the formation of this salt is discussed.

Several recent studies of azide decompositions have been undertaken in order to gain information about the electronic nature of the azene intermediate.[1–5] Some evidence has been presented that this free-radical intermediate is an electrophilic species ($R{-}\dot{\underset{\cdot\cdot}{N}}{:}$). We thought that decomposition of *p*-fluorophenyl azide might confirm the electrophilic character of the imino-radical by rendering the fluorine atom labile towards nucleophilic attack. This situation would be analogous to the effect of an aromatic diazonium group ($Ar{\cdot}N_2^+$) on a *para*- or *ortho*-substituted fluorine.[6] Indeed, we found that decomposition of *o*- or *p*-fluorophenyl azide (I; X = 2- or 4-F) in boiling chlorobenzene to which a few drops of aniline had been added produced a sublimate consisting mainly of aniline hydrofluoride, a little fluoroaniline hydrofluoride, and ammonium fluoride. Similarly, the chloro- and bromo-analogues (I; X = 2- or 4-Cl or -Br) gave rise to a sublimate of a corresponding composition in this and other solvents (xylene, toluene). Even in absence of aniline a sublimate formed, though at a slower rate and in smaller quantity, which proved to be predominantly the corresponding halogenoanilinium halide ($X{\cdot}C_6H_4{\cdot}NH_3^+X^-$) together with a little ammonium halide.

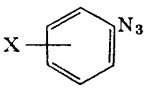
Evolution of hydrogen halide during decomposition of aryl azides has, to our knowledge, not been noticed so far, although the thermolysis[1,7] and photolysis[8] of various halogenophenyl azides in solvents have been studied. That the halogen mobility was not due to the presence of the azide group was shown by the fact that heating of the reaction mixture below the decomposition point of the azide produced no HX evolution. Moreover, the azide group is known to activate the benzene ring to electrophilic substitution such as nitration[9] and bromination[10] and is, therefore, unlikely to cause nucleophilic lability. Unexpectedly, the *meta*-substituted phenyl azides (I; X = 3-F, -Cl, or -Br) also produced a sublimate of anilinium halide when decomposed in a solvent. This fact makes it unlikely that it is "aromatic" halogen which is being displaced, as for instance in the nitrene intermediate (II), because no atoms or groups are known that make nucleophilic aromatic substitution practicable in the *meta*-position. A non-specific abstraction of halogen by the free-radical intermediate (II) was also ruled out since phenyl azide in boiling chlorobenzene did not produce hydrogen chloride, even in presence of aniline. Product analysis threw no light on the problem since the reaction mixtures contained only halogenated anilines and azobenzenes besides intractable tars. Among the many observed products[11] resulting from aryl azide decompositions, phenazine[4] (III) and azepine[7] (IV)* seemed to be of topical interest. Various dihalogenophenazines (III) could arise from the dimerisation of the intermediate (II; X = hal). However, halogen

* This structure appears to be preferred.[12]

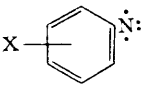
1 P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, 1962, **84**, 480.
2 G. Smolinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 2489.
3 G. Smolinsky, *J. Org. Chem.*, 1961, **26**, 4108.
4 P. Walker and W. A. Waters, *J.*, 1962, 1632.
5 G. Smolinsky and B. I. Feuer, *J. Amer. Chem. Soc.*, 1964, **86**, 3085.
6 P. Miles and H. Suschitzky, *Tetrahedron*, 1962, **18**, 1369; 1963, **19**, 385.
7 R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, 1958, **91**, 1; R. Huisgen and M. Appl, *ibid.*, 1958, **91**, 12.
8 L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, 1963, **96**, 399.
9 P. Drost, *Annalen*, 1899, **307**, 49; M. D. Forster and H. E. Fierz, *J.*, 1907, **91**, 1942.
10 P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Amer. Chem. Soc.*, 1962, **84**, 485.
11 R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; L. Horner and A. Christmann, *Angew. Chem.*, 1962, **75**, 707.
12 K. Hafner, *Angew. Chem., Internat. Edn.*, 1964, **3**, 165, (reference to unpublished work).

in the 2-position only [cf. (III)] would be readily replaceable by the aniline formed during the reaction, as 1-halogenophenazines are reported to be resistant to nucleophilic attack.[13] This we confirmed by showing that, even on prolonged reflux in a solution of chlorobenzene and aniline, 1-chlorophenazine did not lose its halogen. Since the *ortho*-substituted azides (I) would give the phenazines (III; both X's in position 1) the presence of the heterocycle cannot fully account for the release of hydrogen halide from the three halogenated phenyl azides.

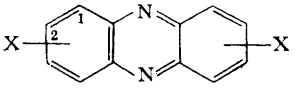
Azepine formation[7,12] (IV) in presence of bases such as aniline is a well-established outcome of aryl azide pyrolysis. Since the requisite aniline is invariably formed in azide decompositions, it is feasible that azepine is an unavoidable product, although it has only been detected when a large excess of base is present and the temperature is carefully controlled.[7] A small quantity of azepine could in fact be isolated when phenyl azide was decomposed in hot chlorobenzene. Ring enlargement of a decomposing *o*-, *m*-, or *p*-halogenated phenyl azide (I) to azepine could thus yield, by mediation of the postulated[7] intermediate (V), the 6-, the 3- and the 5-, and the 4-halogen-substituted heterocycle, respectively (IV; X = hal). Whilst the "allylic" halogen (IV; X in the 3-position) would undoubtedly be mobile, we were anxious to ascertain the anionic lability of the "olefinic" halogen. For this purpose we attempted the preparation of the 4-chloroazepine (IV; X = 4-Cl) by thermolysis of 4-chlorophenyl azide (I; X = Cl), but could only confirm its failure:[7] *p*-chloroaniline, ammonium chloride, and 4,4'-dichloroazobenzene were the only products. We succeeded, however, by a photochemical synthesis which had been successful in the preparation of ethyl 4-chloroazepine-1-carboxylate.[14] From a cold phenyl azide solution in aniline a low yield (10%) of the 2-anilinoazepine (IV; X = H) was obtained on irradiation. This low yield may be due to the fact that azepine when exposed to ultraviolet light quickly deposited polymeric material and gave a little of the isomeric 2-aminodiphenylamine (VI). Similarly, a mixture of *p*-chlorophenyl azide and aniline produced a small amount of the 2-anilino-4-chloroazepine (IV; X = Cl) when irradiated, besides some polymeric material. On treating the chloroazepine with boiling aniline a sublimate of anilinium chloride appeared quickly in the condenser and an intractable mixture remained. It is pertinent that nucleophilic reactivity of vinylic as well as allylic halogen in another ring-system, namely in a bromo- and also in 1,6-dichloro-cyclo-octa-1,5-diene,[15] has been demonstrated.



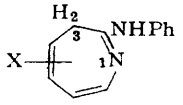
(I)



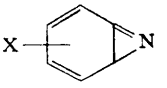
(II)



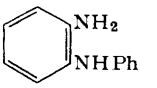
(III)



(IV)



(V)



(VI)

On the basis of the foregoing evidence we believe that formation of anilinium halide accompanying the thermolysis of halogenated phenyl azide is due to the interaction of the corresponding halogenoaniline with the halogenoazepine, both of which are unavoidably produced during decomposition. The causative role of aniline is strikingly demonstrated by the following observation on *p*-chlorophenyl azide: without aniline the chlorine liberated

[13] F. Wrede and O. Mühlroth, *Ber.*, 1930, **63**, 1931; V. P. Chernetskii, L. M. Yagupolskii, and S. B. Serebryanyi, *Zhur. obshchei Khim.*, 1955, **25**, 2161.

[14] K. Hafner, D. Zinser, and K. L. Moritz, *Tetrahedron Letters*, 1964, 1733.

[15] R. E. Foster and R. S. Schreiber, *J. Amer. Chem. Soc.*, 1948, **70**, 2303; A. C. Cope and W. J. Bailey, *ibid.*, 1948, **70**, 2305.

corresponds to about 7%, and in presence of excess of the base to about 70% of azide used. Owing to the intractable nature of the products, it cannot be decided whether halogen removal is the result of a substitution or elimination reaction. The latter process, which is more favoured for vinylic halogen compounds, should lead to an intermediate azepyne. Because of the sterical demand of a triple bond, such a ring structure will presumably break up and polymerise or undergo addition reactions which could well explain the intractable nature of the products.

The ammonium halide which was found in most sublimates derives undoubtedly from the interaction of an aniline on the anilinium halide under reflux conditions. This was borne out by test experiments.

We have reported[16] that *p*- and *m*-nitrophenyl azides decompose with evolution of brown fumes. An explanation of this phenomenon analogous to that given above for the halogenated azides seems plausible. Previous[7] as well as our own attempts to prepare a nitroazepine (IV; X = NO_2), have failed so far.

Experimental

Preparation of Halogenated Phenyl Azides.—Azides were prepared as previously described[17] and purified by distillation *in vacuo*. p-*Fluorophenyl azide* had b. p. 23°/1 mm. (Found: N, 31·0. $C_6H_4FN_3$ requires N, 30·65%), the meta-*isomer*, b. p. 32°/2·5 mm. (Found: N, 30·3%), and the ortho-*isomer*, b. p. 38°/3·5 mm. (Found: N, 30·2%).

Decomposition of Aryl Azides.—(*a*) Each of the three monofluoro-, monochloro-, and monobromo-phenyl azides (1 g.) was refluxed in chlorobenzene (20 ml.) containing a few drops of aniline for 5—10 hr. Within a few hours a white sublimate of anilinium and halogenoanilinium halide (0·1—0·3 g.) and a little ammonium halide collected in the condenser. The second compound was also produced when no aniline was added. Other solvents (toluene, xylene, or decalin) gave similar results.

(*b*) *p*-Chlorophenyl azide (10 g.) was decomposed in boiling chlorobenzene (50 ml.) and the liberated hydrogen chloride trapped by absorption in aqueous sodium hydroxide. Hydrogen chloride was estimated ($AgNO_3$ and dichlorofluorescein as indicator) to account for 7·8% (duplicate experiments) of the phenyl azide. In a similar experiment in which the solvent was aniline the amount of hydrogen chloride was *ca.* 70%.

(*c*) Phenyl azide (1 g.) in boiling chloro- or bromo-benzene (20 ml.), with or without addition of aniline, gave no sublimate.

Preparation of Azepines.—(*a*) 2-Anilino-3*H*-azepine (IV; X = H) was prepared according to Huisgen's method.[7]

(*b*) A well-stirred solution of phenyl azide (10 g.) in aniline (600 ml.) was irradiated for 36 hr. in a Hanovia photochemical reactor (medium-pressure mercury lamp) with cold water circulating through the inner jacket, while a stream of nitrogen was passed through the mixture. The solvent was evaporated to 20 ml. and the residue dissolved in benzene (500 ml.) and chromatographed over alumina. The first fractions consisted mainly of aniline, whilst later fractions deposited crude azepine after removal of the solvent. Recrystallisation (methanol) gave the pure compound (IV; X = H) (10%), m. p. 150—151°, undepressed on admixture with a sample from (*a*).

(*c*) A cooled and stirred solution of *p*-chlorophenyl azide (5 g.) in aniline (250 ml.) was irradiated as in (*b*) for 10 hr. A polymeric, chlorine-free residue (Found: C, 63·9; H, 5·3; N, 11·1%) was filtered off. The filtrate, when treated and chromatographed as in (*b*) gave 4,4′-dichloroazobenzene (0·15 g.), m. p. 188°. Subsequent fractions yielded a semi-solid which was best purified by thin-layer chromatography on alumina with benzene, yielding 2-*anilino*-4-*chloroazepine* (IV; X = 4-Cl) (4%), m. p. 165—166° (Found: C, 65·8; H, 5·4; N, 13·0. $C_{12}H_{11}ClN_2$ requires: C, 65·9; H, 5·0; N, 12·8%).

(*d*) Phenyl azide (5 g.) was refluxed in chlorobenzene (30 ml.) for 4 hr. The solvent was removed and the residue chromatographed in benzene on a silica column and all bands removed by elution with ethanol. The top half of the column was extracted with hot acetone which was driven off. The residue yielded, on sublimation, a white solid which was identical with 2-anilinoazepine from (*a*) (mixed m. p. and infrared spectrum).

[16] R. K. Smalley and H. Suschitzky, *J.*, 1963, 5571.
[17] O. Meth-Cohn, R. K. Smalley, and H. Suschitzky, *J.*, 1963, 1666.

Reactions of Azepines.—(*a*) A solution of 2-anilino-4-chloroazepine (0·22 g.) in chlorobenzene (5 ml.) containing a few drops of aniline was refluxed for 2 hr. A sublimate of aniline hydrochloride (0·07 g.) collected in the condenser. Removal of the solvent left an intractable tar.

(*b*) Irradiation of a benzene solution of 2-anilinoazepine for 12 hr. produced a polymeric deposit (m. p. > 300) (Found: C, 61·1; H, 5·2; N, 10·0%). A concentrated solution of the solvent, when analysed by thin-layer chromatography on alumina, showed the presence of a small amount of 2-aminodiphenylamine, m. p. and mixed m. p. 79°.

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