Thermolysis of Aryl Azides in Phenyl Isocyanate

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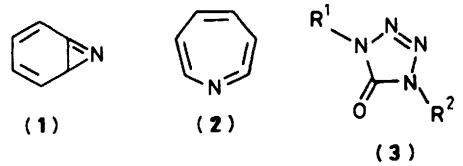
Aryl azides (p-$XC_6H_4N_3$) decompose in boiling phenyl isocyanate to give mainly 1-phenyl-3-phenylcarbamoyl-2-oxo-1,3-dihydrobenzimidazoles and azo-compounds. In some cases, however (X = Ac, CO_2Me, or CN) work-up in methanol solution produces methyl *N*-arylcarbamates (p-$XC_6H_4NHCO_2Me$) indicative of the formation of substituted isocyanates (p-XC_6H_4NCO) during thermolysis. A mechanistic rationale is offered.

The decomposition of aryl azides in nucleophilic solvents, *e.g.* amines is well-documented[1], and generally results in ring-expansion to 3*H*-azepines.

In contrast, we have found that with electrophilic reagents *ortho*-disubstituted benzenes are formed rather than azepines. For example, in hot acetic anhydride or benzoyl chloride, aryl azides decompose to yield *o*-aminophenols (initially as their *N,N,O*-triacetyl derivatives)[2] and *o*-chlorobenzanilides,[3] respectively.

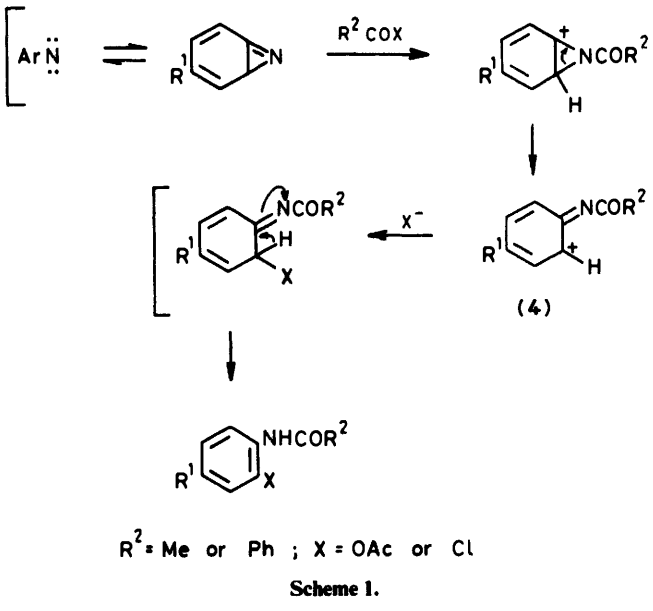
The nature of the intermediate involved in nitrene-mediated ring-expansions and related reactions is currently the subject of debate, the two main contenders being the traditionally accepted benzazirine (**1**),[4] and the more recently proposed and equally viable cumulated azacycloheptatetraene (**2**).[5,6] Low-temperature (< 10 K) i.r. spectroscopic evidence in support of both species is available.[7]



(1) (2) (3)

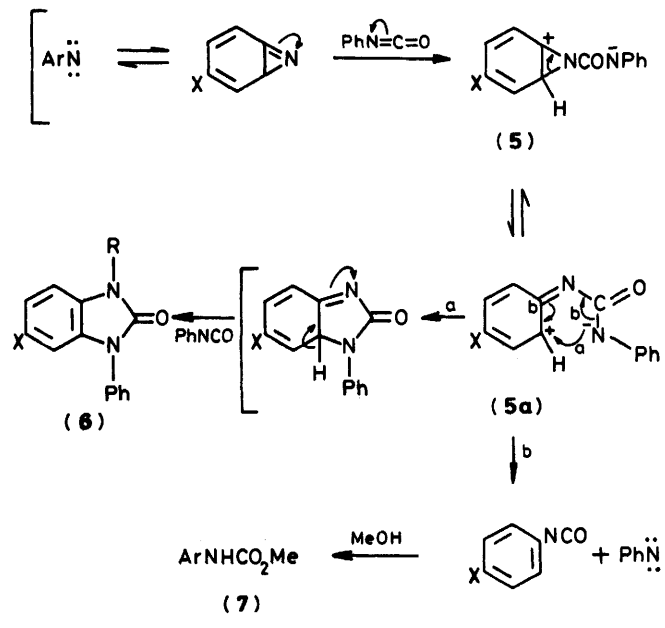
We have proposed a mechanistic rationale (Scheme 1) involving a benzazirine intermediate † to explain the formation of di- and tri-substituted arenes. On this basis we were hopeful that phenyl isocyanate would be sufficiently electrophilic to react with the benzazirine (or azacycloheptatetraene) and so yield, ultimately, 1-phenyl-2-oxo-1,3-dihydrobenzimidazoles (**6**) as outlined in Scheme 2.

Previous work on the decomposition of azides in isocyanates has been reported by L'Abbé,[9] and by Lwowski,[10] and their co-workers. The former found that at moderate temperatures (60 °C) aryl azides fail to react with aryl isocyanates whereas alkyl azides undergo 1,3-dipolar cycloaddition with a variety of isocyanates (aryl, acyl, and sulphonyl) to yield tetrazolin-5-ones (**3**). In contrast, Lwowski found that photolysis or thermolysis of ethyl azidoformate in ethyl isocyanate produces the triazolinedione (**8**; $R^1 = CO_2Et$, $R^2 = Et$). The high thermal stability (undecomposed at 250 °C)[9] precludes the tetrazolinone as a precursor of the triazolinedione. In fact, the dione is thought to be formed by attack of the α-nitrogen of the azide at the isocyanate carbonyl followed by addition of a further molecule of isocyanate and cyclisation with loss of nitrogen as in Scheme 3.



R^2 = Me or Ph ; X = OAc or Cl

Scheme 1.



Scheme 2.

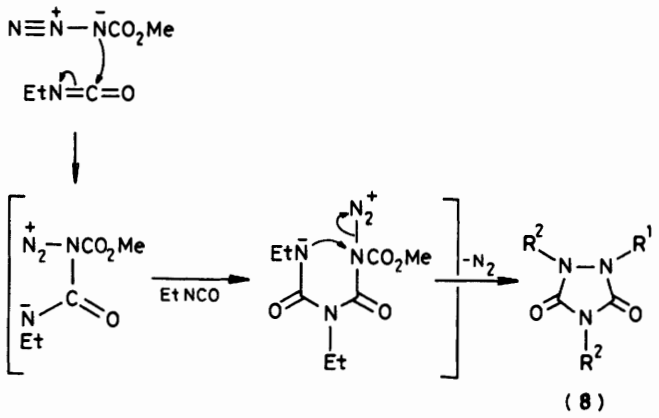
In view of these results we were surprised to find that aryl azides on thermolysis in boiling phenyl isocyanate yield, besides the ubiquitous azo-compounds, crystalline products of mole-

† We acknowledge that an equally tenable reaction scheme can be drawn in which acylation of the azacycloheptatetraene is followed by ring-contraction of the resulting 1-acyl-1*H*-azepine.[8]

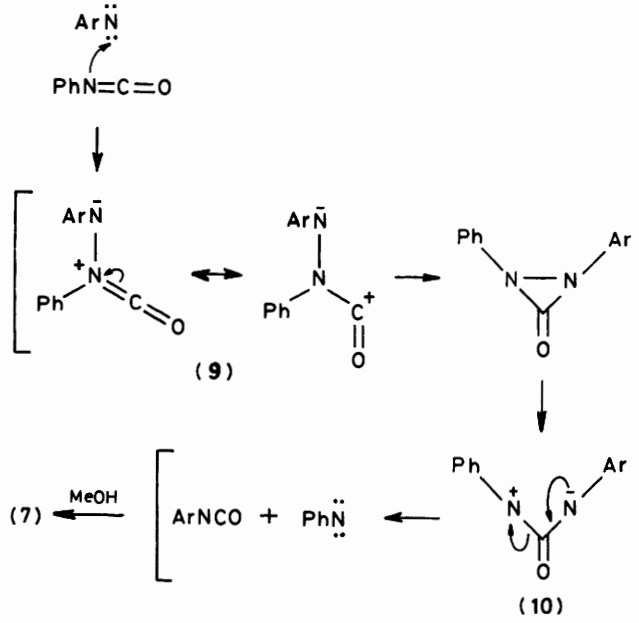
Table. Products from the decomposition of aryl azides in phenyl isocyanate.

	Azide p-$XC_6H_4N_3$ X	2-Oxo-1,3-dihydro-benzimidazole (**6**) % Yield	Azo-compound (p-$XC_6H_4N{=})_2$ % Yield	Other products† (% Yield)
a	H	14 (7.5)	12 (23)	—
b	OMe	27 (6.2)	8 (55)	—
c	Br		14.7	—
d	CN		26 (17.5)	p-$NCC_6H_4NHCO_2Me$ (36)
e	CH_3	5.5	30	—
f	CO_2Me	9.3 (6.4)	22 (15)	p-$MeO_2CC_6H_4NHCO_2Me$ (10)
g	COMe		13	p-$MeOCC_6H_4NHCO_2Me$ (38)
h	CF_3	5	18	—
i	NO_2		—	Polymer

* Lower yields (figures in brackets) of 2-oxo-1,3-dihydrobenzimidazoles and variable yields of azobenzenes are obtained by heating a mixture of the two reactants under reflux rather than by adding the azide dropwise to boiling phenyl isocyanate.
† In all cases intractable tars are also obtained.



Scheme 3.



Scheme 4.

cular composition ArN + 2PhNCO units. However, it soon became apparent that the product from the thermolysis of phenyl azide in phenyl isocyanate was not the triphenyl triazolinedione (**8**; $R^1 = R^2 = Ph$), corresponding to the product obtained by Lwowski, but the known[11] 1-phenyl-3-phenylcarbamoyl-2-oxo-1,3-dihydrobenzimidazole (**6**; R = CONHPh, X = H). Mass, u.v., i.r., and ^1H n.m.r. data were in accord with literature values, and unequivocal proof of structure was obtained by comparison with an authentic sample prepared by heating 1-phenyl-2-oxo-1,3-dihydrobenzimidazole with phenyl isocyanate.

The results for the decomposition of substituted aryl azides in phenyl isocyanate are given in the Table. The structures of the benzimidazolinones were confirmed by elemental analysis and spectral data and in particular by their mass spectra which in every case showed loss of PhNCO $(M - 119)^+$ as the base peak. A plausible explanation for the formation of the 1,3-disubstituted 2-oxobenzimidazoles is *via* carbamoylation of the benzimidazolinone formed initially, as predicted in Scheme 2 (path a).

In previous work on the thermolysis of aryl azides in acylating agents[2,3] significant increases in product yields were noted with electron donating *para*- substituents (*e.g.* R^1 = MeO or Me; Scheme 1). It was argued[3] that such substituents stabilise, by mesomeric interactions, the positively charged intermediate (**4**) and hence promote regioselective ring-opening of the aziridine ring to yield products in which the nitrogen function retains its position relative to the substituent (R^1), *i.e.* no 'nitrogen walk'.[12] In a similar manner we expected the yield of benzimidazolinone (**6**) to be influenced by substituent X. However, no obvious trend in substituent effect is apparent from the results given in the Table. Curiously, however, there is a marked difference in behaviour of some azides bearing electron-withdrawing groups. For example, the isolation of carbamates (**7**) from the thermolyses of p-cyano-, p-acetyl-, and p-methoxycarbonyl-phenyl azides in phenyl isocyanate is intriguing and can only be explained by the generation, during the thermolysis, of the correspondingly substituted aryl isocyanate and its subsequent trapping by methanol during work-up.

A feasible, but as yet speculative mechanism to explain these anomalous products is that the polar intermediate (**5** ⇌ **5a**) is destabilised by the electron-withdrawing group X and so fragments to ArNCO and PhN (as in Scheme 2; path b) rather than ring-closing to the benzimidazolinone. Alternatively, it is

possible that with these more electrophilic nitrenes, attack by the nitrene takes place initially at the isocyanate* to yield the resonance-stabilised ylide-like intermediate (**9**), which by rearrangement to the alternative dipolar structure (**10**) can, by retro-addition, furnish the substituted isocyanate and phenyl nitrene (Scheme 4).

The structures of the carbamates (Table) have been confirmed by unambiguous synthesis and spectroscopic data.

Variations in the reaction conditions have given disappointing results. For example, a decomposition of phenyl or *p*-methoxyphenyl azide in a 10% solution of phenyl isocyanate in xylene produced, in addition to much tar, only the *N,N'*-diarylurea. Presumably, the nitrene, as the triplet species, is abstracting hydrogen from the solvent to give arylamines (a well-known process[1]) which with isocyanate furnishes the urea.

Experimental

I.r. spectra were recorded as Nujol mulls or liquid films on a Perkin-Elmer 297 or 257 grating i.r. spectrophotometer. ^{1}H N.m.r. spectra were measured for $CDCl_3$ solutions ($SiMe_4$ as internal standard) on a Perkin-Elmer R-32 90 MHz spectrometer. Mass spectra were obtained on an A.E.I. MS12 mass spectrometer, and u.v. spectra as methanol solutions on a Unicam SP800A spectrophotometer. All m.p.s are uncorrected. T.l.c. was on Alumina G (type E) whereas column chromatography was carried out on Alumina (type H).

Preparation of Aryl Azides.—The aryl azides were prepared as reported previously[13] from the arylamines, by diazotisation and subsequent azidation with sodium azide in buffered (sodium acetate) solution. They were purified by chromatography on alumina, with light petroleum (b.p. 40—60 °C) as eluant.

Thermolysis of Aryl Azides (p-$XC_6H_4N_3$) *in Phenyl Isocyanate: General Method.*—The aryl azide was added dropwise to a boiling solution of freshly distilled phenyl isocyanate. The mixture was heated under reflux until azide decomposition was complete, as shown either by disappearance of $\nu(N_3)$ at 2 120 cm^{-1} or by t.l.c. The mixture was cooled and the excess of phenyl isocyanate removed either by vacuum distillation (water pump), or better by conversion into methyl *N*-phenylcarbamate by addition of methanol (50 ml). In the latter case, excess of methanol was removed by distillation (rotary evaporator) and the residual semisolid distilled carefully (bulb-to-bulb) to remove the *N*-phenyl carbamate. The final residue was separated by column chromatography.

Products, % yields, and reaction times are given in the Table. Chromatographic separations were achieved on alumina and unless stated otherwise azo-compounds were eluted first, with light petroleum (b.p. 60—80 °C) as eluant, followed successively by the 2-oxobenzimidazoles and the methyl *N*-arylcarbamates (**7**) [light petroleum (b.p. 60—80 °C)–ethyl acetate (1 : 1; v/v) as eluant].

(*a*) Phenyl azide (0.87 g) in phenyl isocyanate (10 ml) gave on chromatographic separation azobenzene (0.16 g), m.p. 68 °C, and 3-phenyl-1-phenylcarbamoyl-2-oxo-1,3-dihydrobenzimidazole (**6a**) (0.33 g), m.p. 172 °C (from light petroleum–ethyl acetate) (lit.,[11] m.p. 168 °C) (Found: C, 73.0; H, 4.6; N, 12.7. Calc. for $C_{20}H_{15}N_3O_2$: C, 72.9; H, 4.6; N, 12.8%), *m/z* 329 (M^+) and 210 $(M - 119)^+$ (100%). ^{1}H N.m.r. and i.r. spectra were in agreement with published values.[11]

(*b*) *p*-Methoxyphenyl azide (2 g) in phenyl isocyanate (20 ml) gave on chromatographic separation 4,4'-dimethoxyazobenzene (0.27 g), m.p. 162 °C (lit.,[14] m.p. 162 °C) and 6-*methoxy*-1-*phenyl*-3-*phenylcarbamoyl*-2-*oxo*-1,3-*dihydrobenzimidazole* (**6b**) (1.3 g), m.p. 181 °C (from light petroleum–ethyl acetate) (Found: C, 70.05; H, 4.7; N, 11.8. $C_{21}H_{17}N_3O_3$ requires C, 70.2; H, 4.8; N, 11.7%); $\nu_{max.}$ (Nujol) 3 200—3 000 (NH), 1 680, and 1 720 cm^{-1} (C=O); $\lambda_{max.}$ (log ε) (MeOH) 230 (4.45) and 245.5 (4.39) nm; δ_H (90 MHz; $CDCl_3$) 3.75 (3 H, s, OMe), 6.55—7.80 (12 H, m, ArH), 8.3 (1 H, d, *J* 7 Hz, 4-H), and 10.9 (1 H, br, NH); *m/z* 359 (M^+) and 240 $(M - 119)^+$ (100%).

(*c*) *p*-Bromophenyl azide (1 g) in phenyl isocyanate (10 ml) on chromatographic separation gave 4,4'-dibromoazobenzene (0.25 g), m.p. 204 °C (lit.,[15] m.p. 205 °C) and tarry material.

(*d*) *p*-Cyanophenyl azide (0.5 g) in phenyl isocyanate (10 ml) on chromatographic separation gave 4,4'-dicyanoazobenzene (0.14 g), m.p. 272 °C (lit.,[16] m.p. 272 °C), and *methyl* N-(*p*-*cyanophenyl*)*carbamate* (**7**; Ar = p-NCC_6H_4) (0.22 g), m.p. 149 °C (Found: C, 61.1; H, 4.5; N, 15.8. $C_9H_8N_2O_2$ requires C, 61.4; H, 4.6; N, 15.9%); $\nu_{max.}$ (Nujol) 3 340 (NH), 2 220 (CN), and 1 700 (CO) cm^{-1}; δ_H 90 MHz ($CDCl_3$) 3.8 (3 H, s, OMe), 7.05 (1 H, br, NH), and 7.5 (4 H, br s, ArH); *m/z* 176 (M^+).

The carbamate was identical with an authentic sample prepared by condensing *p*-cyanoaniline with methyl chloroformate in hot pyridine solution.

(*e*) *p*-Methylphenyl azide (0.9 g) in phenyl isocyanate (10 ml) on chromatographic separation gave 4,4'-dimethylazobenzene (0.45 g), m.p. 145 °C (lit.,[17] m.p. 114 °C) and 6-*methyl*-1-*phenyl*-3-*phenylcarbamoyl*-2-*oxo*-1,3-*dihydrobenzimidazole* (**6e**) (0.12 g), m.p. 163 °C (from light petroleum–ethyl acetate) (Found: C, 73.3; H, 4.9; N, 12.3. $C_{21}H_{17}N_3O_2$ requires C, 73.45; H, 5.1; N, 12.2%); $\nu_{max.}$ (Nujol) 3 000—3 200 (NH), 1 725, and 1 695 (CO) cm^{-1}; $\lambda_{max.}$(MeOH) 214 (4.42) and 245 (4.44) nm; δ_H (90 MHz; $CDCl_3$) 2.5 (3 H, s, Me), 7.1—7.9 (12 H, m, ArH), 8.5 (1 H, d, *J* 7 Hz, 4 H), 10.95 (1 H, br, NH); *m/z* 343 (M^+) and 224 $(M - 119)^+$ (100%).

(*f*) Methyl *p*-azidobenzoate (1 g) in phenyl isocyanate (10 ml) gave, on cooling of the reaction mixture, 4,4'-bismethoxycarbonylazobenzene (0.36 g), m.p. 197 °C (lit.,[18] 198 °C). Chromatographic separation, light petroleum (b.p. 60—80 °C)–ethyl acetate (1 : 2 v/v), gave 6-*methoxycarbonyl*-1-*phenyl*-3-*phenylcarbamoyl*-2-*oxo*-1,3-*dihydrobenzimidazole* (**6f**) (0.22 g), m.p. 199 °C (from light petroleum–ethyl acetate) (Found: C, 68.2; H, 4.45; N, 10.7. $C_{22}H_{17}N_3O_4$ requires C, 68.0; H, 4.4; N, 10.85%); $\nu_{max.}$(Nujol) 3 000—3 200 (NH), 1 705, and 1 725 (CO) cm^{-1}; $\lambda_{max.}$ (log ε) (MeOH), 211.5 and 239 (4.37); δ_H (90 MHz; $CDCl_3$) 3.85 (3 H, s, OMe), 7.05—8.1 (12 H, m, ArH), 8.35 (1 H, d, *J* 7 Hz, 4-H), and 10.95 (1 H, br, NH); *m/z* 387 (M^+) and 268 $(M - 119)^+$ (100%).

Further elution gave *methyl* N-(4-*methoxycarbonylphenyl*)-*carbamate* (**7**; Ar = 4-$MeO_2CC_6H_4$) (0.12 g), m.p. 170 °C (Found: C, 57.5; H, 5.3; N, 6.7. $C_{10}H_{11}NO_4$ requires C, 57.4; H, 5.3; N, 6.7%); $\nu_{max.}$(Nujol) 3 300 (NH), 1 725 and 1 695 (CO) cm^{-1}; δ_H (90 MHz; $CDCl_3$) 3.75 (3 H, s, OMe), 3.85 (3 H, s, OMe), 7.0 (1 H, br, NH), 7.45 (2 H, d, *J* 7 Hz, 3- and 5-H), and 8.0 (2 H, d, *J* 7 Hz, 2- and 6-H).

The product was identical with the *N*-arylcarbamate prepared by heating a mixture of methyl *p*-aminobenzoate (5 g) with methyl chloroformate (2.6 g) in pyridine (20 ml) for 2 h.

(*g*) *p*-Azidoacetophenone (1 g) in phenyl isocyanate (10 ml) on chromatographic separation gave 4,4'-*diacetylazobenzene* (0.22 g) m.p. 218 °C (Found: C, 71.95; H, 5.3; N, 10.5. $C_{16}H_{14}N_2O_2$ requires C, 72.2, H, 5.3; N, 10.9%). Further elution with a (4 : 1) mixture of light petroleum (b.p. 60—80 °C) and ethyl acetate gave methyl *N*-(4-acetylphenyl)carbamate (**7**; Ar = 4-AcC_6H_4), m.p. 164 °C (lit.,[19] m.p. 162 °C); $\nu_{max.}$ 3 310 (NH), 1 730 and 1 690 (C=O) cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.55 (3 H, s, $COCH_3$), 3.8 (3 H, s, CO_2CH_3), 7.35 (1 H, b, NH), 7.55

* It is most unlikely under our reaction conditions, that the α-nitrogen of the azide is the attacking species as suggested by Lwowski[10] in related reactions (Scheme 3).

(2 H, d, *J* 7 Hz, 2- and 5-H), and 8.0 (2 H, d, *J* 7 Hz, 2- and 5-H). The product was identical with the *N*-arylcarbamate prepared by heating *p*-aminoacetophenone with methyl chloroformate in pyridine solution.

(*h*) *p*-(Trifluoromethyl)phenyl azide (1.5 g) in phenyl isocyanate (15 ml) on chromatographic separation gave 4,4′-bis(trifluoromethyl)azobenzene (0.31 g), m.p. 101 °C (lit.,[16] m.p. 102 °C), followed by *1-phenyl-3-phenylcarbamoyl-6-trifluoromethyl-2-oxo-1,3-dihydrobenzimidazole* (**6h**) (0.11 g,), m.p. 196 °C (from light petroleum–ethyl acetate) (Found C, 63.5; H, 3.55; N, 10.6. $C_{21}H_{14}F_3N_3O_2$ requires C, 63.4; H, 3.5; N, 10.5%); $\nu_{max.}$(Nujol) 3 200—3 000 (NH), 1 720 and 1 690 (CO) cm^{-1}; $\lambda_{max.}$(log ε) (MeOH) 212 (4.42), and 247 (4.33) nm; δ_H (90 MHz; $CDCl_3$) 7.3—8.4 (12 H, m, ArH), 8.85 (1 H, m, 4-H), 10.95 (1 H, s, NH); *m/z* 397 (M^+) and 278 $(M-119)^+$ (100%).

(*i*) 4-Nitrophenyl azide (0.5 g) in phenyl isocyanate (10 ml) gave a black polymeric material from which no identifiable products were isolated.

Acknowledgements

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