# Photolysis and Thermolysis of Phenyl Azide in Acetic Acid

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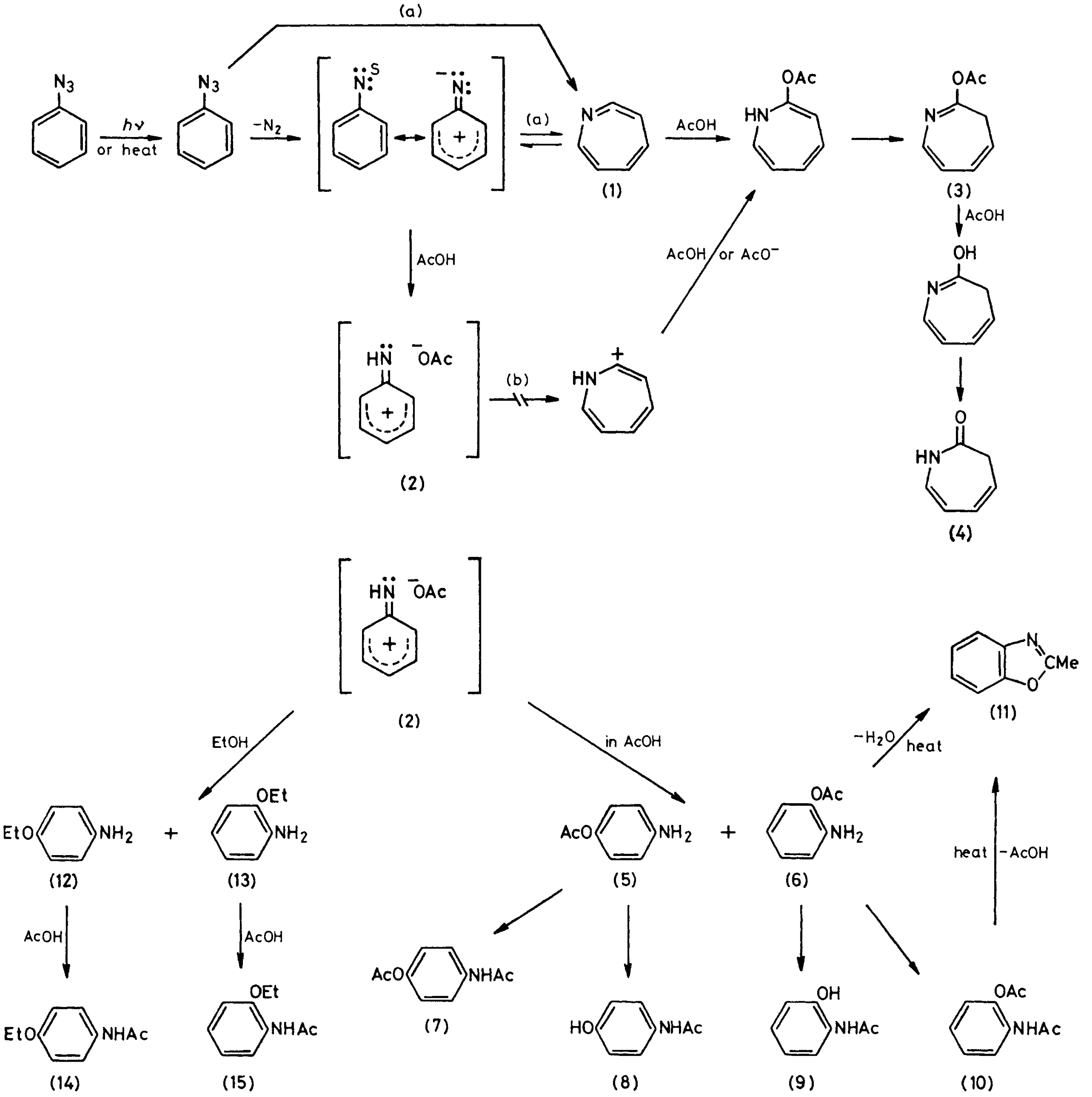
*Summary* The photolysis and thermolysis of phenyl azide in acetic acid gave 2,3-dihydro-1*H*-azepin-2-one *via* 1-azacyclohepta-1,2,4,6-tetraene, and ring-disubstituted products *via* a resonance-stabilized ion formed by attack of singlet phenylnitrene on acetic acid.

Aryl azides undergo ring-expansion to azepines on decomposition in nucleophilic solvents such as amines[1] and methanol[2] or in the presence of a nucleophile ($MeO^-$),[3] and it was thought that the reaction proceeded through the addition of nucleophiles to an intermediate benzazirine. However, Chapman *et al.*[4] have recently reported spectroscopic observation of, not the azirine, but 1-azacyclohepta-1,2,4,6-tetraene (**1**) which reacts with nucleophiles. The structure (**1**) has an eight-electron $\pi$-system and adjacent filled and vacant in-plane orbitals,[4] and thus could be expected to react with electrophiles as well as nucleophiles. We describe the first example of phenyl azide undergoing ring-expansion in the presence of electrophiles, acetic acid, and phenol, and also the transformation of singlet phenylnitrene into a resonance-stabilized ion (**2**) in acetic acid.

A solution of phenyl azide (0·91 M) in acetic acid was irradiated at 25 °C with a high-pressure mercury lamp after purging with dry nitrogen. In a separate experiment, the solution was heated in a sealed tube at 138 °C for 6 h. By chromatographic separation, 2,3-dihydro-1*H*-azepin-2-one (**4**), the ring-disubstituted products (**7**)—(**11**), acetanilide, and azobenzene were obtained, and the structures were confirmed by comparison of the i.r. and n.m.r. spectra with those of authentic samples. The yields, determined by g.l.c., are summarized in the Table.

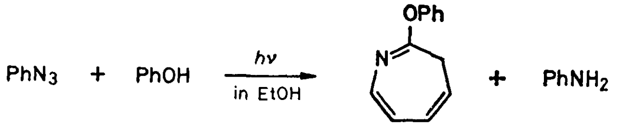


Scheme

Table. Photolysis and thermolysis of phenyl azide in acetic acid and the effect of added ethanol.

| | [EtOH] (% v/v) | 0[a] | 10[a] | 40[a] | 80[a] | 0[b] | 10[b] |
|---|---|---|---|---|---|---|---|
| | % of azide decomposed | 41·2 | 36·9 | 58·9 | 26·6 | 54·8 | 52·9 |
| % Yield | (**4**) | 39·2 | 34·8 | 21·0 | 2·2 | 6·5 | 5·1 |
| | (**7**) | 12·2 | 6·4 | 0·99 | 0·14 | 8·8 | 2·0 |
| | (**8**) | 2·3 | 3·9 | 0·95 | *ca.* 0 | 13·5 | 19·2 |
| | (**9**) | 7·9 | 10·7 | 13·1 | 2·7 | 2·7 | 19·6 |
| | (**10**) | 6·5 | 2·5 | 0·87 | 0·09 | trace | trace |
| | (**11**) | 4·2 | 3·8 | 0·97 | *ca.* 0 | 41·7 | 22·8 |
| | PhNHAc | 8·7 | 7·3 | 5·6 | 2·2 | 16·8 | 18·5 |
| | PhN=NPh | 0·31 | 0·54 | 0·09 | 0·87 | 0·34 | 0·38 |
| | (**14**) | | 2·1 | 2·2 | 0·47 | | 0·90 |
| | (**15**) | | 0·71 | 0·93 | 0·21 | | *ca.* 0 |
| | *o/p* ratio (**15**)/(**14**) | | 0·34 | 0·42 | 0·45 | | |
| | *o/p* ratio for (**7**)—(**11**) | 1·3 | 1·7 | 7·7 | 19·9 | | |

[a] Photolysis. [b] Thermolysis.



(**16**)

The addition of ethanol to the system caused decreases in the yield of (**4**) and in the total yield of (**7**)—(**11**), and the ethyl ethers (**14**) and (**15**) were obtained (Table). Photolysis of phenyl azide (0·91 M) in ethanol, however, did not afford the ring-disubstituted products (**12**) and (**13**), which are precursors of (**14**) and (**15**) in the above reaction. Treatment of (**7**)—(**11**) and acetanilide in AcOH–EtOH did not give (**14**) and (**15**) under the photochemical and thermal conditions. Thus, the formation of the products obtained can be explained by a pathway in which a resonance-stabilized ion (**2**) reacts at the activated *ortho*- and *para*-positions leading to aromatic nucleophilic substitution (Scheme). From the following results, it is evident that (**2**) has an acetate anion adjacent to the nitrogen atom or the *ortho*-rather than the *para*-position. (i) The *o/p* ratio for (**7**)—(**11**) was $>$ 1, but for (**15**)/(**14**) was $<$ 0·5. (ii) The yield of (**14**) and (**15**) was small in spite of the greater nucleophilicity of ethanol over acetic acid, and the total yield of *para*-products (**7**) and (**8**) was decreased by the addition of ethanol more markedly than that of the *ortho*-products (**9**)—(**11**). Product (**11**) was formed almost quantitatively from (**10**) or from (**6**) under thermal conditions, and the reaction of (**7**) or (**10**) in AcOH–EtOH gave (**8**) (47%) or (**9**) (45%), and (**11**) (39%) under the above conditions. The formation of (**8**) and (**9**) is difficult to explain but appears to result from the reaction of (**5**) or (**6**) with acetic acid, ethanol, or water in the system.

There are two possible mechanisms for the formation of (**4**) (Scheme): the reaction of acetic acid with 1-azacyclohepta-1,2,4,6-tetraene (**1**) formed by ring-expansion [pathway (a)] or a mechanism involving rearrangement of (**2**) [pathway (b)]. The fact that the photolysis of phenyl azide (0·91 M) in ethanol in the presence of phenol (0·94 M) produces 2-phenoxy-3*H*-azepine (**16**) (8%) and aniline (2·5%) but no aromatic substituted compounds (**12**) and (**13**) rules out the aromatic nucleophilic substitution [pathway (b)] as the intermediates are different. Therefore the formation of (**1**) by pathway (a), followed by acetolysis of 2-acetoxy-3*H*-azepine (**3**), is no longer in doubt. No azepines were detected in the photolysis of phenyl azide in ethanol, and the yield of (**4**) decreased linearly with increase in the concentration of ethanol. This perhaps supports the idea that ethanol causes (**1**) to decay to phenylnitrene.

The intermediates (**1**) and (**2**) may be formed *via* the singlet state of the nitrene or excited azide from the following results. The yield of (**4**) and the total yield of (**7**)—(**11**) are independent of the presence of piperylene (0·01 M) in the photolysis, and are somewhat decreased on addition to the system of a heavy atom solvent, bromobenzene (20% v/v), compared with addition of the same amount of benzene.

The rate of thermolysis in acetic acid was not accelerated in comparison with that in 1,4-dioxan, and the activation parameters in both solvents did not differ much. This shows that the decomposition in acetic acid does not proceed *via* an azide conjugate acid, but *via* a singlet nitrene which appears to abstract a proton from acetic acid to give (**2**) (a large contribution to the structure of phenylnitrene by the dipolar resonance form would diminish the electron deficiency at nitrogen)[5] (Scheme). The differences between the product ratios on photolysis and thermolysis presumably depend upon both the ease of formation of (**1**) or (**2**) and the stability of some of the precursors.

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