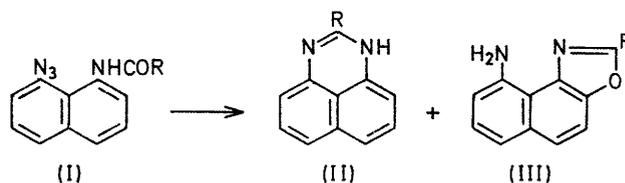


## Pyrolysis of 1-Amino-8-azidonaphthalene Derivatives. New Routes to Oxazoles, Perimidines, and Benz[*cd*]indazoles

By S. BRADBURY, C. W. REES,\*† and R. C. STORR†

(Chemistry Department, The University, Leicester LE1 7RH)

**Summary** Brief heating of monoacyl and aroyl derivatives of 1-amino-8-azidonaphthalene gives 9-amino-2-substituted naphth[1,2-*d*]oxazoles and 2-substituted perimidines, whilst the *N*-acetyl-*N*-methyl and *N,N*-diacetyl derivatives give 1,2-disubstituted 1,2-dihydrobenz[*cd*]indazoles: mechanisms are suggested for these novel transformations.



R = Me, Et, Ph, C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>-*p*, C<sub>6</sub>H<sub>4</sub>-OMe-*p*

We have studied the thermolysis of various derivatives of 1-amino-8-azidonaphthalene in the hope that generation of

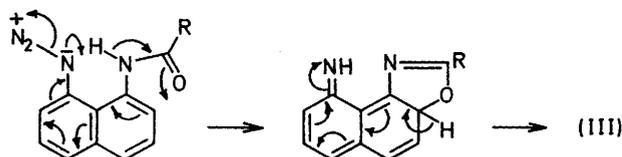
an electron-deficient nitrogen *peri* to nucleophilic nitrogen

† Present address: Department of Chemistry, University of Liverpool, Liverpool L69 3BX.

would give 1,2-dihydrobenz[*cd*]indazole derivatives, such as (VI).

When heated<sup>†</sup> in 1,2,4-trichlorobenzene, 1-amino-8-azidonaphthalene gave 1,8-diaminonaphthalene rather than 1,2-dihydrobenz[*cd*]indazole or its more stable tautomers.<sup>1</sup> Similar decomposition of the monoacyl and aroyl derivatives (I) again gave no indazoles but 2-substituted perimidines (II) (10–40%) and, unexpectedly, 9-amino-2-substituted naphth[1,2-*d*]oxazoles§ (III) (10–30%).

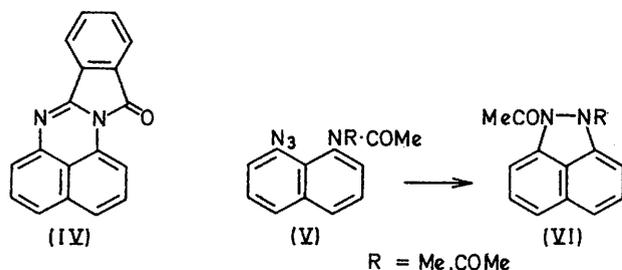
The oxazoles are thought to arise by a sterically favoured, intramolecularly acid-catalysed decomposition of the azide with concerted nucleophilic attack by the amide oxygen on the aromatic ring (Scheme 1). Support for the intra-



SCHEME 1

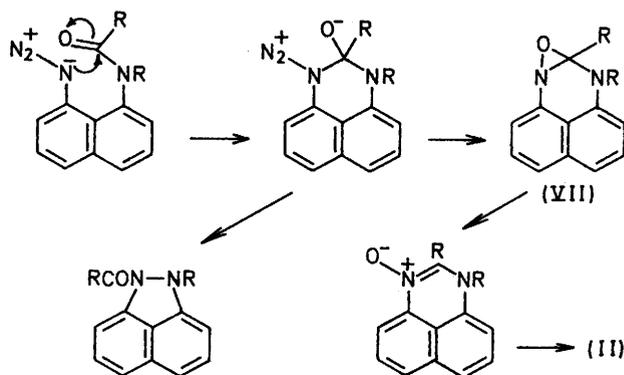
molecular catalysis shown comes from the lower temperatures required for decomposition of these azides than for other 8-substituted 1-azidonaphthalenes, and from the failure to observe any oxazole formation in the decomposition of 6-azido-1-benzamidonaphthalene and other "meta"-amidoazides where this *peri*-interaction is not possible.

Since amines are usually formed when aryl azides are heated in solution, possibly as a result of hydrogen abstraction by nitrene intermediates, the perimidines (II) could



R = Me, COMe

arise by cyclodehydration of 8-amido-1-aminonaphthalenes. However, this is not the main route to perimidines, since when the pyrolyses were repeated on dry sand their yields increased markedly. Thus perimidine (IV) was formed quantitatively from 1-azido-8-phthalimidonaphthalene under such conditions. We suggest that the azide group (or, less likely, the nitrene derived from it) reacts with the carbonyl group to form an oxaziridine (VII) which decomposes to the perimidine *via* the *N*-oxide (Scheme 2).¶



SCHEME 2

Thus, formation of oxazoles and perimidines is initiated by competitive attack by the nucleophilic azide nitrogen on amide hydrogen (Scheme 1) or carbon (Scheme 2) respectively.

None of the above azides gave products with an N–N bond; however, the *N*-acetyl-*N*-methyl (V; R = Me) and *N,N*-diacetyl (V; R = Ac) derivatives gave dihydrobenzindazoles (VI) on heating, possibly by alternative rearrangement of the tetrahedral intermediate of Scheme 2. These *N* to *N* acyl migrations represent a new route to the elusive benz[*cd*]indazole system. Alder, Niazi, and Whiting have made the *N*-oxides of benz[*cd*]indazole somewhat similarly by pyrolysis of 1-azido-8-nitronaphthalene and oxidation of 1,8-diaminonaphthalene.<sup>2</sup>

We thank Imperial Chemical Industries, Limited, Dyestuffs Division, for secondment of S.B.

(Received, September 24th, 1969; Com. 1446.)

<sup>†</sup> A slurry of the azide in trichlorobenzene was added rapidly to boiling trichlorobenzene and heated for 5 min.

<sup>§</sup> The structures of all new compounds were fully supported by analytical, spectroscopic, and mass spectral data.

<sup>¶</sup> The interaction of nitrenes (or other intermediates), generated by triethyl phosphite deoxygenation of nitro-groups, with favourably orientated carbonyl groups has recently been reported, and oxaziridines suggested as intermediates (T. Kametani, T. Yamanaka, and K. Ogasawara, *J. Chem. Soc. (C)*, 1969, 138, 385, and 1616). Significantly, deoxygenation of the corresponding nitro-compounds in our series (nitro in place of azide) led to indazoles and perimidines in a similar pattern of yields to the azide decompositions, but gave only traces of oxazoles.

<sup>1</sup> S. Bradbury, C. W. Rees, and R. C. Storr, following communication.

<sup>2</sup> R. W. Alder, G. A. Niazi, and M. C. Whiting, Lecture at the Autumn meeting of the Chemical Society, Durham, 1967.