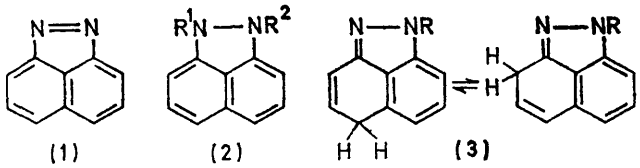
Reactive Intermediates. Part XVII.[1] Conversion of *peri*-Substituted Azidonaphthalenes into Naphthoxazoles, 1,2-Dihydrobenz[*cd*]indazoles and Perimidines [2]

By S. Bradbury, C. W. Rees,*† and R. C. Storr,† Chemistry Department, The University, Leicester LE1 7RH

Pyrolysis of 1-acylamino-8-azidonaphthalenes gives 2-substituted 9-aminonaphth[1,2-*d*]oxazoles by an intramolecular acid-catalysed decomposition of the azide system with concomitant nucleophilic attack by the amide oxygen atom at the naphthalene 2-position. Similar treatment of compounds in which the amide hydrogen atom has been replaced by a methyl or an acetyl group leads to formation of 1,2-dihydrobenz[*cd*]indazole derivatives. Mechanisms for the formation of these indazoles, and of perimidines also formed in the decompositions, are discussed.

We have previously described some of our attempts to obtain benz[*cd*]indazole (1);[1] much of our effort was concerned with the initial preparation of 1,2-dihydrobenz[*cd*]indazole derivatives (2). In this connection we have now studied the thermal decomposition of 1-amino-8-azidonaphthalene and some of its acyl and aroyl derivatives in the hope that generation of an electron-deficient nitrene grouping *peri* to a nucleophilic nitrogen atom would lead to the desired system. Intermolecular versions of this reaction, though rare, are known,[3] and the stereochemistry would be favourable for the intramolecular reaction in the present case.

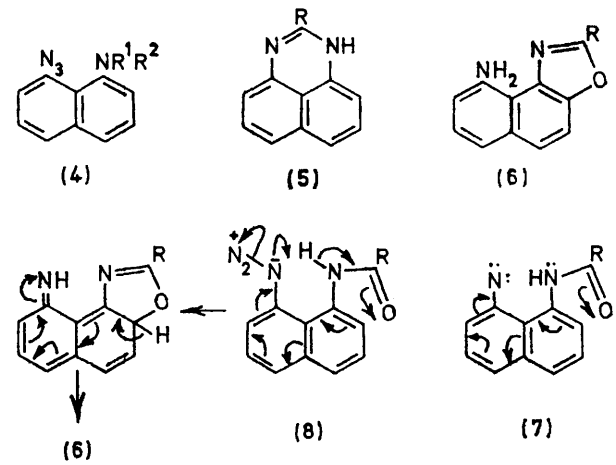
1-Amino-8-azidonaphthalene was readily available as a by-product of the amination of naphtho[1,8-*de*]triazine,[4] and the acyl derivatives were prepared directly from this. A route to the acylamino-azides from monoacyl derivatives of 1,8-diaminonaphthalene was not applicable since such *peri*-substituted naphthalenes spontaneously ring close to give perimidines.[5] This complication also ruled out alternative routes to 1-amino-8-azidonaphthalene from 1-amino-8-nitronaphthalene—*cf.* Hall's method for preparing *ortho*-amino-aromatic azides.[6]



(1) (2) (3)

Pyrolysis of 1-amino-8-azidonaphthalene in refluxing 1,2,4-trichlorobenzene gave 1,8-diaminonaphthalene as the only isolable product. Photolysis of the azide in benzene also gave this, together with 8,8'-diamino-1,1'-azonaphthalene. Neither dihydrobenz[*cd*]indazole (2; $R^1 = R^2 = H$), nor, more significantly, its stable tautomers (3; R = H) [1] were found. Diaminonaphthalene presumably arose by abstraction of hydrogen from the solvent by the nitrene, a reaction always observed in azide pyrolysis. However, when the pyrolysis was carried out by sublimation of the amino-azide at 120° through a hot tube at 300° and 0·04 mm. pressure the dihydrobenzindazoles were obtained in high yield (80%). The conditions were critical: the yield decreased on raising or lowering the temperatures of the furnace and the sublimator. Since the dihydrobenzindazoles would have survived the solution pyrolysis conditions, this is a striking example of the advantages of high temperature gas-phase decomposition over lower temperature decomposition in a solvent, for effecting intramolecular reactions. The nitrene formed from the azide could give the indazoles by intramolecular hydrogen abstraction and ring closure, though at this temperature the nitrene probably inserts directly into the adjacent N–H bond.

Solution pyrolysis and photolysis of 1-acetamido-8-azidonaphthalene (4; $R^1 = H$, $R^2 = Ac$) also gave no trace of a dihydrobenzindazole derivative [(2; $R^1 = H$, $R^2 = Ac$) or (3; R = Ac)]. 2-Methylperimidine (5; R = Me) was formed (37%) together with, unexpectedly, 9-amino-2-methylnaphth[1,2-*d*]oxazole (6; R = Me) (13·5%). The identification of the latter was supported by i.r., n.m.r., and mass spectral data and confirmed by deamination to 2-methylnaphth[1,2-*d*]-



(4) (5) (6) (6) (8) (7)

† *Present address:* The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX.

[1] Part XVI, S. Bradbury, C. W. Rees, and R. C. Storr, preceding paper.

[2] Preliminary communication, S. Bradbury, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1969, 1428.

[3] K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Letters*, 1964, 1733; R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5680.

[4] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 756.

[5] V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.

[6] J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, **89**, 5856.

oxazole, which was compared with an authentic specimen.[7]

This formation of perimidines and amino-oxazoles appears to be a general reaction of 1-amino-8-azidonaphthalene derivatives, and proceeds more smoothly with the aroyl derivatives. The benzamide gave 9-amino-2-phenylnaphth[1,2-*d*]oxazole (30%) and 2-phenylperimidine (10%), the identification of the former again being confirmed by deamination and comparison of the product with authentic 2-phenylnaphthoxazole;[8] the latter was identified by comparison with authentic material.[9] The *p*-methoxybenzoyl derivative gave the corresponding oxazole and perimidine in similar yields; the *p*-nitrobenzoyl derivative gave analogous products in lower yields. Vapour-phase pyrolysis of the benzamide (400°; 0·4 mm.) gave the appropriate oxazole and perimidine in yields similar to those from the reactions in solution.

Several mechanisms can be written for the oxazole formation. One involves formation of the nitrene (7) from the azide and nucleophilic attack at C-2 by the amide oxygen atom under the electron-withdrawing influence of this electrophilic centre at C-8. A second involves the sterically favourable, intramolecular acid-catalysed decomposition of the azide, as shown in formula (8), and nucleophilic attack by the amide anion. This mechanism is analogous to that for the formation of substituted anilines by decomposition of phenyl azides in aqueous acid.[10]

We favour the latter mechanism for the following reasons. If the former mechanism operates, any *meta*-amido-aryl azide should decompose similarly into an amino-oxazole. However no such products could be found from the pyrolysis of *m*-azido-acetanilide and -benzanilide, 1-acetamido-3-azidonaphthalene, and (perhaps most significantly) 6-azido-1-benzamidonaphthalene. This last compound is at least as likely as 1-azido-8-benzamidonaphthalene to decompose by the first mechanism [*via* (7)] and lacks only the *peri*-interaction required by the second [*via* (8)]. Also significant was that the *peri*-substituted azides were less thermally stable than all the others. The former decomposed smoothly at about 140°; the latter required temperatures above 180°.

A further possible mechanism, involving rearrangement of an initially formed 1-acyl-1,2-dihydrobenzindazole (2; $R^1 = H$, $R^2 =$ acyl) [formed either by direct nitrene insertion into the N–H bond or by a mechanism similar to that discussed later for the formation of the acyl(methyl)indazole (4; $R^1 = Me$, $R^2 =$ Ac)], is considered unlikely since such an intermediate should rearrange to, or be in equilibrium with, its tautomer (3; R = acyl). The indazole (3; R = Bz), obtained independently,[1] was shown to be stable and not to rearrange to an amino-oxazole under the pyrolysis conditions.

The intramolecular acid catalysis mechanism (8) is perhaps supported by the observation of its intermolecular counterpart in the formation of 5-amino-2-phenylbenzoxazole (9) (48%) on treatment of *m*-azidobenzanilide with cold concentrated sulphuric acid. Formation of the 5-amino- rather than the 7-amino-isomer presumably reflects the greater stabilisation of the *para*- than the *ortho*-quinonoid transition state. However, oxazoles could not be isolated from *m*-azidoacetanilide, 1-acetamido-3-azidonaphthalene, or 6-azido-1-benzamidonaphthalene in cold concentrated sulphuric acid, and 1-azido-8-benzamidonaphthalene gave only a trace of the amino-oxazole (6; R = Ph) under these conditions.

The proposed mechanism (8) for oxazole formation is unusual in that it involves nucleophilic aromatic substitution by an amide oxygen atom, activated through both rings of the naphthalene system by a decomposing azide group. Possibly the whole process is facilitated by being concerted as shown in (8), the proton transfer activating both electrophilic and nucleophilic centres.

Steric destabilisation of the azido-group by the bulky *peri*-substituent is an explanation alternative to that involving intramolecular catalysis for the decomposition temperatures of 1-acylamino-8-azidonaphthalenes being lower than those of other aryl azides. To check this, pyrolysis of the more hindered *N*-methyl amide (4; $R^1 = Me$, $R^2 = Ac$) was investigated. Significantly, this only decomposed at the normal (higher) pyrolysis temperature (180°). The only isolable product from this reaction was, surprisingly, 1-acetyl-1,2-dihydro-2-methylbenz[*cd*]indazole (2; $R^1 = Me$, $R^2 = Ac$). The *N*-methyl benzamide (4; $R^1 = Me$, $R^2 = Bz$) gave an analogous product in lower yield. No *N*-methylperimidine was found in either case. The diacetyl derivative (4; $R^1 = R^2 = Ac$) gave 1,2-diacetyl-1,2-dihydrobenz[*cd*]indazole, but again no *N*-acetylperimidine was formed. In contrast the phthalimido-azide (10) gave no 1,2-dihydrobenz[*cd*]-indazole derivative * but was converted into the perimidine (11) [9] relatively cleanly. We tentatively rationalise the formation of these 1,2-dihydrobenzindazoles by the mechanism shown (Scheme). In the absence of the more efficient intramolecular catalysis of the azide decomposition by the amide proton, catalysis by electrophilic attack of the amide carbonyl group leads to the six-membered cyclic intermediate (12) which collapses to indazole.

Perimidine formation in the thermolyses of these azides was initially assumed to be the result of spontaneous cyclodehydration of 1-amido-8-aminonaphthalenes, these amines arising by hydrogen abstraction by the initially formed nitrenes. However, although this route probably contributes to perimidine formation in solution, an alternative route is also involved, since

* See ref. 1 for an alternative route to this derivative from the indazole (3) and phthaloyl chloride.

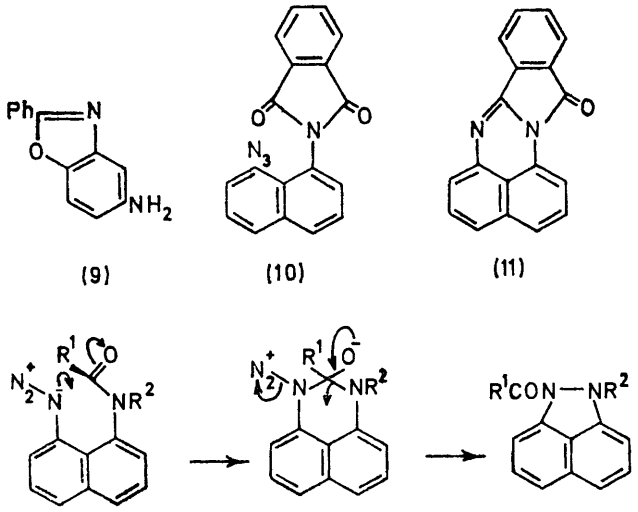
[7] N. I. Fisher and F. M. Hamer, *J. Chem. Soc.*, 1934, 962.

[8] W. Bottcher, *Ber.*, 1883, **16**, 1933.

[9] F. Sachs, *Annalen*, 1909, **365**, 53.

[10] P. A. S. Smith, ' Open Chain Nitrogen Compounds,' vol. II, Benjamin, New York, 1966, ch. 10, p. 225.

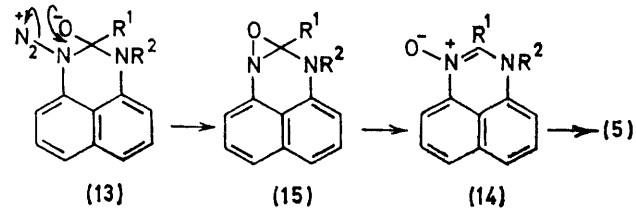
perimidine was also formed in the vapour-phase pyrolyses. Further, pyrolysis of the phthalimido-azide (10) gave 30% of the perimidine (11) in refluxing trichlorobenzene, 60% in tetralin (a better source of hydrogen atoms), and a *quantitative* yield of perimidine when decomposed at the same temperature on dry sand. Quantitative hydrogen abstraction is inconceivable



SCHEME

under these conditions. Mass spectral examination of the gas evolved in this case indicated the presence of nitrogen rather than nitrous oxide. Possibly the perimidines arise from the same type of intermediate suggested for indazole formation (12), by an alternative mode of breakdown (13) through a perimidine *N*-oxide (14) which would be expected to be deoxygenated under the conditions. Alternatively the oxaziridine (15) could arise directly by addition of the corresponding nitrene system to the carbonyl group. Recently, analogous reactions of nitrenes or nitrene precursors with suitably orientated carbonyl groups leading to products formed by stoicheiometric loss of an oxygen atom, have been observed in the reactions of nitro-compounds with triethyl phosphite.[11] Attempts to isolate the postulated perimidine *N*-oxide (14) from compound (10), both from the pyrolysis and by independent preparation from the perimidine (11) by treatment with peroxy-acids, have failed. Photolysis of the azide (10) did however give a product having mass and i.r. spectra consistent with the perimidine *N*-oxide structure, which on heating was converted into the perimidine (11). Attempts to purify this compound and to obtain a satisfactory analysis failed. Lack of formation of perimidines from the azido-amides (4; R^1 = Me, R^2 = Ac) and (4; $R^1 = R^2$ = Ac) and this apparent fine balance between perimidine and indazole formation remains puzzling.

Similar yields and patterns of perimidine and indazole formation were observed for triethyl phosphite deoxygenation of the corresponding nitro-compounds (4; NO_2 for N_3). However, no amino-oxazoles were formed from 1-acyl- or aroyl-amino-8-nitronaphthalenes.



EXPERIMENTAL

Petroleum refers to light petroleum (b.p. 40—60°).

Pyrolysis of 1-*Amino*-8-*azidonaphthalene* (4; $R^1 = R^2$ = H).—1-Amino-8-azidonaphthalene (500 mg.) in dry 1,2,4-trichlorobenzene was added to refluxing 1,2,4-trichlorobenzene. After 5 min. the mixture was cooled; a dark polymeric solid (230 mg.) separated and was filtered off. The filtrate was extracted with dilute hydrochloric acid and the acid layer was basified and re-extracted with ether to give 1,8-diaminonaphthalene (150 mg., 35%) as an oil. Distillation, followed by crystallisation from petroleum, gave needles, m.p. and mixed m.p. 62—63°. No other tractable products were isolated from the trichlorobenzene layer after evaporation under reduced pressure.

Photolysis of 1-*Amino*-8-*azidonaphthalene* (4; $R^1 = R^2$ = H).—1-Amino-8-azidonaphthalene (290 mg.) in dry benzene was exposed in glass apparatus to a 100 W Hanovia medium-pressure mercury lamp for 20 hr.; the heat of the lamp caused the solution to reflux. Polymeric material was filtered off and the filtrate was evaporated onto basic alumina for chromatography. Elution with ether gave 8,8′-diamino-1,1′-azonaphthalene (50 mg., 20%), orange needles from benzene–petroleum, m.p. 275—276° (decomp.), $\nu_{max.}$ 3425 and 3283 cm.$^{-1}$ (NH_2), *m/e* 312, 168, and 115 (identical with a sample obtained by manganese dioxide oxidation of 1,8-diaminonaphthalene), and 1,8-diaminonaphthalene (80 mg., 32%), m.p. and mixed m.p. 62—63°, after distillation and recrystallisation from petroleum.

1-*Amido*-8-*azidonaphthalenes*.—All 1-amido-8-azidonaphthalenes were prepared in high yield by treatment of 1-amino-8-azidonaphthalene [4] in pyridine with a small excess of the appropriate acid chloride or anhydride. The crude amides were recrystallised from ethanol to give: 1-acetamido-8-azidonaphthalene [4] as needles, m.p. 147—148°; 1-*azido*-8-*benzamidonaphthalene* as crystals, m.p. 123—124° (Found: N, 19·4. $C_{17}H_{12}N_4O$ requires N, 19·5%), $\nu_{max.}$ 3355 (NH), 2140 (N_3), and 1668 cm.$^{-1}$ (C=O); 1-*azido*-8-p-*nitrobenzamidonaphthalene* as yellow crystals, m.p. 160—161° (Found: N, 21·0. $C_{17}H_{11}N_5O_3$ requires N, 21·0%), $\nu_{max.}$ 3345, 2140, and 1678 cm.$^{-1}$; 1-*azido*-8-p-*methoxybenzamidonaphthalene* as crystals, m.p. 133·5—144·5° (Found: N, 18·1. $C_{18}H_{14}N_4O_2$ requires N, 17·6%), $\nu_{max.}$ 3340, 2135, and 1680 cm.$^{-1}$; 1-*azido*-8-*propionamidonaphthalene* as crystals, m.p. 115—116° (Found: N, 23·15. $C_{13}H_{12}N_4O$ requires N, 23·3%), $\nu_{max.}$ 3320, 2120, and 1643 cm.$^{-1}$.

1-*Azido*-8-*diacetylaminonaphthalene* (4; $R^1 = R^2$ = Ac).—1-Amino-8-azidonaphthalene was heated to reflux in acetic anhydride for 1 hr.; the resulting mixture was cooled and poured into water. The aqueous suspension was extracted with ether, and after being washed with dilute sodium carbonate solution and water the extracts were dried and evaporated to give the *diacetyl derivative* (27%), m.p. 114—115° (from ether) (Found: C, 62·75; H, 4·6;

N, 20·3. $C_{14}H_{12}N_4O_2$ requires C, 62·7; H, 4·5; N, 20·85%), $\nu_{max.}$ 2120, 1720, and 1700 cm.$^{-1}$, τ 2·05—2·90 (6H, m, aromatic H), 7·7 (6H, s, Ac).

1-*Azido*-8-N-*methylacetamidonaphthalene* (4; R^1 = Me, R^2 = Ac).—Sodium hydride (46 mg.) was added to 1-acetamido-8-azidonaphthalene (200 mg.) in dry dimethylformamide. Dimethyl sulphate (124 mg.) was added and the mixture was left for 30 min. and then poured into water. Extraction with ether gave the N-*methylacetamide* (36%), m.p. 97—98° (from ether) (Found: C, 65·0; H, 5·2; N, 23·1. $C_{13}H_{12}N_4O$ requires C, 65·0; H, 5·0; N, 23·3%), $\nu_{max.}$ 2120 and 1647 cm.$^{-1}$.

m-*Azidobenzanilide and* m-*Azidoacetanilide*.—*m*-Azidoaniline was obtained from *m*-nitroaniline by the method of Smith *et al.*[12] The crude oily product was treated with benzoyl chloride in pyridine to give m-*azidobenzanilide*, needles, m.p. 128—129° (from ethanol) (Found: N, 23·2. $C_{13}H_{10}N_4O$ requires N, 23·5%), $\nu_{max.}$ 3264, 2112, and 1663 cm.$^{-1}$; and with acetic anhydride in pyridine to give m-*azidoacetanilide*, needles, m.p. 123—124° (from ethanol) (Found: N, 32·0. $C_8H_8N_4O$ requires N, 31·8%), $\nu_{max.}$ 3260, 2125, and 1663 cm.$^{-1}$.

1-*Acetamido*-3-*azidonaphthalene*.—Sodium nitrite (1 g.) was added to a stirred suspension of 1-acetamido-3-aminonaphthalene [13] (3 g.) in 2N-hydrochloric acid (30 ml.) at 0°. Sodium azide (2 g.) was added to the filtered solution and the resulting precipitate was collected and recrystallised from ether–petroleum to give the *azide* (0·8 g., 24%), m.p. 199—200° (decomp.) (Found: C, 63·4; H, 5·2. $C_{12}H_{10}N_4O$ requires C, 63·7; H, 4·5%), $\nu_{max.}$ 3272, 2122, and 1663 cm.$^{-1}$.

6-*Azido*-1-*benzamidonaphthalene*.— 1-Amino-6-nitronaphthalene [14] was converted into 1-benzamido-6-nitronaphthalene by treatment with benzoyl chloride in pyridine. The nitro-amide was dissolved in ethanol and hydrogenated over palladium–charcoal. After removal of ethanol the resulting amine (0·8 g.) was suspended in 2N-hydrochloric acid (15 ml.) and diazotised at 0° with sodium nitrite (0·5 g.). Addition of sodium azide (1 g.) to the filtered diazonium solution gave a precipitate of the *azide* (0·25 g., 15·5%), needles from ethanol, m.p. 177—178° (decomp.) (Found: N, 19·2. $C_{17}H_{12}N_4O$ requires N, 19·5%), $\nu_{max.}$ 3218, 2115, and 1635 cm.$^{-1}$.

Pyrolysis of Azides in Solution.—Pyrolyses were carried out by dropwise addition of suspensions of the azides in small volumes of 1,2,4-trichlorobenzene to refluxing 1,2,4-trichlorobenzene. After 5 min. the mixtures were cooled and trichlorobenzene was removed by distillation under reduced pressure. The residues were thoroughly extracted with hot chloroform and the extracts were evaporated on to silica gel for chromatography. 2-Alkyl- or aryl-9-aminonaphth[1,2-*d*]oxazoles were eluted with 10% ether–petroleum and were further purified by sublimation or by distillation through a short horizontal tube. 2-Alkyl- or arylperimidines were eluted with ether and directly compared with authentic samples prepared by treatment of 1,8-diaminonaphthalene with the appropriate acid chloride.

1-Azido-8-benzamidonaphthalene gave 9-*amino*-2-*phenylnaphth*[1,2-d]*oxazole* (6; R = Ph) (29%), crystals, m.p. 126—127° (Found: C, 78·4; H, 4·9; N, 10·9. $C_{17}H_{12}N_2O$ requires C, 78·5; H, 4·7; N, 10·8%), $\nu_{max.}$ 3440 and 3350 (NH_2) cm.$^{-1}$, and 2-phenylperimidine (5; R = Ph) [9] (10·3%).

1-Azido-8-*p*-nitrobenzamidonaphthalene gave 9-*amino*-2-p-*nitrophenylnaphth*[1,2-d]*oxazole* (6; R = *p*-$O_2N{\cdot}C_6H_4$) (12%), yellow crystals, m.p. 217—218° (Found: C, 66·7; H, 3·8; N, 14·1. $C_{17}H_{11}N_3O_3$ requires C, 66·9; H, 3·6; N, 13·8%), $\nu_{max.}$ 3480 and 3370 cm.$^{-1}$, and 2-*p*-nitrophenylperimidine (5; R = *p*-$O_2N{\cdot}C_6H_4$) [15] (3·5%).

1-Azido-8-*p*-methoxybenzamidonaphthalene gave 9-*amino*-2-p-*methoxyphenylnaphth*[1,2-d]*oxazole* (6; R = *p*-MeO·C_6H_4) (27·5%), crystals, m.p. 161—162° (Found: C, 74·8; H, 5·0; N, 9·9. $C_{18}H_{14}N_2O_2$ requires C, 74·5; H, 4·9; N, 9·7%), $\nu_{max.}$ 3470 and 3358 cm.$^{-1}$, and 2-*p*-methoxyphenylperimidine (5; R = *p*-MeO·C_6H_4) [15] (10·5%).

1-Acetamido-8-azidonaphthalene gave 9-*amino*-2-*methylnaphth*[1,2-d]*oxazole* (6; R = Me) (13·5%), m.p. 78° (Found: C, 73·6; H, 5·2. $C_{12}H_{10}N_2O$ requires C, 72·7; H, 5·1%), $\nu_{max.}$ 3430 and 3325 cm.$^{-1}$, τ 2·4—2·9 (4H, complex m, aromatic), 3·37 (1H, q, aromatic H *ortho* to NH_2), 4·43br (2H, s, NH_2), and 7·42 (3H, s, Me), *m/e* 198, 183, 169, 129, and 102, and 2-methylperimidine (5; R = Me) (37%; very impure). A purified sample of the latter was identical with an authentic specimen.[9] Photolysis of 1-acetamido-8-azidonaphthalene in benzene in quartz apparatus with a 450 W Hanovia medium-pressure mercury lamp gave the same products in similar yields (9 and 39%, respectively).

1-Azido-8-propionamidonaphthalene gave 9-amino-2-ethylnaphth[1,2-*d*]oxazole (6; R = Et) (7%), as an oil, $\nu_{max.}$ 3470 and 3365 cm.$^{-1}$ (satisfactory analysis was not obtained), and 2-ethylperimidine (5; R = Et) [9] (18%).

Pyrolyses of *m*-azidoacetanilide, *m*-azidobenzanilide, 6-azido-1-benzamidonaphthalene, and 1-acetamido-3-azidonaphthalene gave substantial amounts of unchanged azide. Prolonged heating gave no trace of amino-oxazoles, giving instead some amido-amines (t.l.c.) together with much polymeric material.

1-Azido-8-diacetylaminonaphthalene (4; R^1 = R^2 = Ac) gave (elution with 30% ether–petroleum) 1,2-*diacetyl*-1,2-*dihydrobenz*[cd]*indazole* (2; R^1 = R^2 = Ac) (7%), needles, m.p. 110—111° after sublimation (Found: C, 69·6; H, 5·15; N, 12·2. $C_{14}H_{12}N_2O_2$ requires C, 70·0; H, 5·1; N, 11·7%), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O), τ 2·3—2·8 (6H, m, aromatic) and 7·6 (6H, s, Me), *m/e* 240, 225, 198, and 197.

1-Azido-8-*N*-methylacetamidonaphthalene (4; R^1 = Me, R^2 = Ac) gave (elution with 30% ether–petroleum) 1-*acetyl*-1,2-*dihydro*-2-*methylbenz*[cd]*indazole* (2; R^1 = Me, R^2 = Ac) (17·5%), prisms, m.p. 84—85° after sublimation, (Found: C, 73·8; H, 6·0; N, 13·45. $C_{13}H_{12}N_2O$ requires C, 73·55; H, 5·7; N, 13·2%), $\nu_{max.}$ 1660 cm.$^{-1}$ (C=O), τ 2·4—3·5 (6H, m, aromatic), 6·8 (3H, s, NMe), and 7·6 (3H, s, Ac), *m/e* 212, 170, 169, 155, 140, 127, and 126.

1-Azido-8-phthalimidonaphthalene (10) gave 12*H*-isoindolo[2,1-*a*]perimidin-12-one (11) [9] (32%), orange crystals, m.p. and mixed m.p. 229—230°. Similar pyrolysis in triglyme gave the perimidine (11) (60%).

Vapour-phase Pyrolyses.—These were carried out by vacuum sublimation (0·02—0·04 Torr) of the azides through a 10 in. Pyrex tube maintained at 400°. Products condensed on the cold part of the sublimation tube and on a cold trap.

[11] T. Kametani, T. Yamanaka, and K. Ogasawara, *J. Chem. Soc.* (*C*), 1969, 1616, and previous papers.
[12] P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Amer. Chem. Soc.*, 1962, **84**, 485.
[13] F. F. Blicke and J. E. Gearien, *J. Amer. Chem. Soc.*, 1954, **76**, 2429.
[14] H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, 1943, 318.
[15] F. Sachs and M. Steiner, *Ber.*, 1909, **42**, 3674.

1-Azido-8-benzamidonaphthalene (4; R^1 = H, R^2 = Bz) gave 9-amino-2-phenylnaphth[1,2-*d*]oxazole (6; R = Ph) (28%) and 2-phenylperimidine (5; R = Ph) (13%).

1-Azido-8-phthalimidonaphthalene (10) gave the perimidine (11) [9] in variable yield (*ca.* 20%) together with several other unidentified minor products.

1-Amino-8-azidonaphthalene (4; R^1 = R^2 = H) gave a mixture of dihydrobenz[*cd*]indazoles (3; R = H) (18%), identical with that obtained by hydrolysis of dimethyl 1,2-dihydrobenz[*cd*]indazole-1,2-dicarboxylate.[1] When an apparatus in which the pyrolysate was condensed directly on to a water-cooled cold finger was used, the yield of mixed dihydrobenzindazoles rose to an optimum 80% with the tube at 300°/0·04 Torr.

Pyrolysis of 1-*Azido*-8-*phthalimidonaphthalene* (10) *on Silica.*—1-Azido-8-phthalimidonaphthalene was adsorbed on to dry, pure precipitated silica and heated at 215° with constant agitation for 10 min. Continuous extraction of the cooled silica with ether gave the perimidine (11) (99%).

Deoxygenations of Nitro-compounds with Triethyl Phosphite.—The nitro-compounds were heated under reflux in triethyl phosphite in an atmosphere of nitrogen. Triethyl phosphite was then distilled off under reduced pressure and the residue was chromatographed on silica gel.

1-Benzamido-8-nitronaphthalene, after 18 hr., gave 9-amino-2-phenylnaphth[1,2-*d*]oxazole (1%) and 2-phenylperimidine (5%). In control experiments 9-amino-2-phenylnaphth[1,2-*d*]oxazole and 2-phenylperimidine were recovered after refluxing for 18 hr. in triethyl phosphite in yields of 48 and 44%, respectively.

1-*N*-Methylacetamido-8-nitronaphthalene gave, after 3 hr., 1-acetyl-1,2-dihydro-2-methylbenz[*cd*]indazole (15%).

8-Nitro-1-phthalimidonaphthalene, after 3 hr., gave a precipitate of the perimidine (11) (90%). The residue after evaporation of triethyl phosphite gave more perimidine (98% in all).

Photolysis of 1-*Azido*-8-*phthalimidonaphthalene* (10).—The azide (0·5 mmole) in benzene (100 ml.) was irradiated at 16° for 20 hr. with a Hanovia 100 W medium-pressure lamp surrounded by a Pyrex jacket. The resulting solution was concentrated and poured into petroleum to give a precipitate probably containing 12*H*-isoindolo[2,1-*a*]perimidin-12-one 7-oxide (14), which decomposed on heating to give the perimidine (11) and other, unidentified products. A satisfactory analysis was not obtained for this *N*-oxide; $\nu_{max.}$ 1720, 1580, 1375, 1262, 1105, 760, and 715 cm.$^{-1}$, *m/e* 286 and 270 ($C_{18}H_{10}N_2O_4$ requires *M*, 286).

Deamination of 9-*Amino*-2-*phenylnaphth*[1,2-d]*oxazole* (6; R = Ph).—Sodium nitrite (50 mg.) was added to an ice-cold suspension of 9-amino-2-phenylnaphth[1,2-*d*]oxazole in 5N-hydrochloric acid. After 15 min., the filtered solution was poured into aqueous sodium fluoroborate (350 mg. in 5 ml.), and the resulting diazonium fluoroborate was filtered off and dissolved in dimethylformamide (3 ml.). This solution was added to a solution of sodium borohydride (1 g.) in dimethylformamide (5 ml.) at 0°, and after 5 min. the mixture was poured into ice and dilute hydrochloric acid. The precipitate was collected, washed with a little water, dried, and sublimed to give 2-phenylnaphth[1,2-*d*]-oxazole (37%), crystals, m.p. and mixed m.p. 130—131° (lit.,[8] m.p. 131°), identical with an authentic specimen.[8]

Similar deamination of 9-amino-2-methylnaphth[1,2-*d*] oxazole gave 2-methylnaphth[1,2-*d*]oxazole (20%), identical with an authentic specimen.[7]

Treatment of m-*Azidobenzanilide with Acid.*—*m*-Azidobenzanilide (200 mg.) in chloroform (5 ml.) was added to conc. sulphuric acid (5 ml.) and the mixture was stirred until gas evolution ceased (*ca.* 10 min.). It was then poured into an excess of ice–water, neutralised with 2N-ammonium hydroxide, and extracted with chloroform. The extracts were dried and evaporated on to silica gel for chromatography. Elution with 2% ether–petroleum gave 5-amino-2-phenylbenzoxazole (85 mg., 49%), identical with an authentic specimen.[16]

Similar treatment of 1-azido-8-benzamidonaphthalene gave only a trace of 9-amino-2-phenylnaphthoxazole (t.l.c.); *m*-azidoacetanilide and 1-acetamido-3-azido- and 6-azido-1-benzamido-naphthalenes gave no trace of amino-oxazoles.

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[16] O. Kym, *Ber.*, 1899, **32**, 1427.