Thermal Decomposition of Aromatic Azides. Formation of Phenazines and Related Compounds

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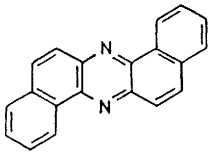
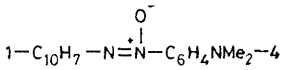
The decomposition of some aromatic azides yielding significant amounts of phenazines, and thereby constituting a potential synthetic procedure, is reported.

THERMAL decomposition of aryl azides has been carried out in various solvents and many products attributed to the solvolytic trapping of especially a singlet arylnitrene have been reported.[1] These products are almost invariably accompanied by azo- and amino-arene formation. Exceptionally a phenazine has been obtained in only one case reported by Waters [2] who isolated 2,7-dimethoxyphenazine (6%) from the thermolysis of 4-methoxyphenyl azide in cumene. The formation of this phenazine was ascribed to the abstraction of one hydrogen by triplet 4-methoxyphenylnitrene and subsequent dimerisation of the so formed anilino-radical.



(1)



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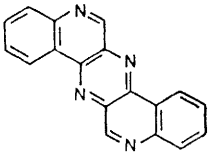

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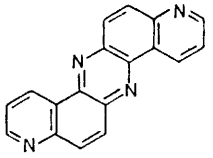

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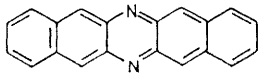

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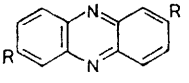
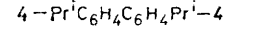


(6) R = OMe

(7) R = NMe_2



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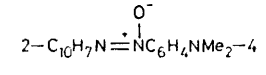

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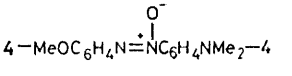

(10)

We have noted in a preliminary report [3] that the thermolysis of 1-azidonaphthalene in cumene yields dibenzo[*a*,*h*]phenazine (1), 1-azonaphthalene, and 1-naphthylamine. The structure of (1) was confirmed by comparison with an authentic sample. The yield of (1) could be increased to 12% by using bromobenzene instead of cumene, a solvent which promotes singlet → triplet intersystem crossing by the heavy atom effect.[4] When these decompositions were carried out in the presence of 4-nitroso-*NN*-dimethylaniline the yields of (1) and other triplet products were almost completely suppressed in favour of the unsymmetric azoxy-compound (2) which was obtained in high yield. A similar effect was observed on the yields of 2,7-dimethoxyphenazine and dimethoxyazobenzene in the decomposition of 4-azidoanisole in cumene and bromobenzene in the presence of 4-nitroso-*NN*-dimethylaniline. This supports the intermediacy of a triplet nitrene in the formation of phenazines and azoarenes. A series of mono- and bi-cyclic aromatic azides was decomposed in bromobenzene to explore the generality and synthetic value of this reaction (Table).

Products of thermolysis of aryl azides in bromobenzene

Azide (RN_3)	Thermolysis temp. (°)	Phenazine (%)	Product (%) RN=NR	RNH_2	Others
1-Naphthyl	155	(1) 12	20	10	
1-Naphthyl [a]	155	(1) 5	11	28	(8) 2
1-Naphthyl [b]	155			Trace	(2) 92
1-Naphthyl [c]	155			Trace	(2) 61
2-Naphthyl	155	(1) 23	21	40	
2-Naphthyl [b]	155			Trace	(9) 93
3-Quinolyl	155	(3) 4	17	59	
3-Quinolyl	140	(3) 9	26	46	
3-Quinolyl	130	(3) 17	31	32	
5-Quinolyl	130	(4) 10	15	39	
6-Quinolyl	130		49	25	
7-Quinolyl	130			71	
8-Quinolyl	130			36	
4-Methoxyphenyl	155	(6) 4	36	3	
4-Methoxyphenyl [b]	155				(10) 69
3-Methoxyphenyl	155		20	12	
2-Methoxyphenyl	155			30	
4-*NN*-Dimethylaminophenyl	155	(7) 2	32	10	
4-*N*-Morpholinophenyl	155		18	7	

[a] Solvent cumene. [b] Bromobenzene + 4-nitroso-*NN*-dimethylaniline. [c] Cumene + 4-nitroso-*NN*-dimethylaniline.

4-Azido-*NN*-dimethylaniline alone of the monocyclic azides employed gave the corresponding phenazine. 2-Azidonaphthalene on thermolysis in bromobenzene gave dibenzo[*a*,*h*]phenazine (23%) in better yield than did the 1-isomer (12%); none of the isomeric dibenzo[*b*,*i*]phenazine was detected.[3] The 3- and the 5-azidoquinolines

underwent decomposition in bromobenzene to yield (3) and (4), respectively, but the 6-, 7-, and 8-isomers gave merely the corresponding amines and in the first case also 6-azoquinoline.

The higher yield of the phenazines (1), (3), and (4) derived from bicyclic aryl azides compared with (6) and (7) derived from monocyclic azides may reflect the fact that bicyclic triplet arylnitrenes have longer lifetimes than their monocyclic counterparts.[5] It is noteworthy that these dimerisations are regiospecific. For example decomposition of 2-azidonaphthalene gives the angular phenazine (1) and not the linear isomer (5).

The thermolysis temperature affects the yields of specific products obtained from 3-azidoquinoline although the overall yield of triplet derived products remains the same. For instance the yield of 3-aminoquinoline rises with an increase in temperature whilst that of 3-azoquinoline and the phenazine (3) fall. This suggests that the triplet quinolylnitrene becomes more reactive but less selective at higher temperature.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument and ^{1}H n.m.r. spectra on a Varian EM 360 or Perkin-Elmer R32 (using tetramethylsilane as internal standard). Low resolution mass spectra were recorded on an AEI MS12 and high resolution spectra on an AEI MS9 instrument.

Light petroleum refers to the fraction of b.p. 60—80°. Yields quoted are based on starting material consumed.

Azides.—These were prepared by the diazotisation of the corresponding amine followed by treatment with sodium azide. All are known compounds, and their physical properties are in agreement with those reported in the literature.

Thermolysis of Azides: General Procedure.—A solution of the azide (0.01 mol) in bromobenzene (or cumene) (10 ml) was heated under nitrogen at 130° (or above) for the time indicated. The solution was evaporated to dryness and chromatographed over alumina (type H). Thermolysis and chromatographic conditions are indicated thus: (solvent, time, temperature, eluant).

Thermolysis of 1-azidonaphthalene. (a) (Bromobenzene, 155°, 12 h, light petroleum–benzene). This gave 1-azonaphthalene (0.28 g, 20%), m.p. 183° (lit.,[6] 205°). Elution with light petroleum–benzene (1 : 1) gave dibenzo[*a*,*h*]phenazine (1) (0.17 g, 12%), m.p. 283° (lit.,[7] 285°).

(b) With 4-nitroso-*NN*-dimethylaniline (0.01 mol) (bromobenzene, 155°, 12 h, light petroleum–benzene). This gave *4′-NN-dimethylaminobenzene*-ONN-*1-azoxynaphthalene* (2) (2.67 g, 92%), m.p. 141°, orange crystals (from ethanol) (Found: C,73.9; H, 5.9; N, 14.4. $C_{18}H_{17}N_3O$ requires C, 74.2; H, 5.85; N, 14.4%); τ ($CDCl_3$) 1.08 (1 H d, *J* 9 Hz, 2-H), 1.4—1.5 (1 H, m), 1.7 (1.7 (2 H, d, *J* 9 Hz, 2′- and 6′-H), 2.05—2.27 (2 H, m, aromatic), 2.34—2.6 (3 H, m, aromatic), 3.35 (2 H, d, *J* 9 Hz, 3′- and 5′-H), 7.03 (6 H, s, NMe_2); *m/e* 291 (M^+).

(c) (Cumene, 155°, 12 h, light petroleum). Bicumenyl (0.85 g), m.p. 113—115° (lit.,[8] 115°) was obtained. Elution with benzene–light petroleum (1 : 4) gave 1-azonaphthalene (0.15 g, 10.6%), m.p. 200—201° (lit.,[6] 205°). Elution with benzene–diethyl ether (1 : 1) gave dibenzo[*a*,*h*]phenazine (1) (accompanied by a purple oil that was not characterised) (0.14 g, 10%), m.p. 286° (lit.,[7] 285°). Elution with diethyl ether gave 1-naphthylamine (0.4 g, 28%), m.p. 203° (lit.,[6] 205°).

(d) With 4-nitroso-*NN*-dimethylaniline (0.01 mol) (cumene, 155°, 12 h, light petroleum–benzene). The product was *4′-NN-dimethylaminobenzene-ONN*-1-azoxynaphthalene (2) (1.77 g, 61%), m.p. 141°, identical with the authentic compound.

Thermolysis of 2-azidonaphthalene (bromobenzene, 155°, 12 h, light petroleum–benzene). 2-Azonaphthalene (0.3 g, 21.3%), m.p. 206° (lit.,[9] 208°) was produced. Elution with benzene–diethyl ether (1 : 1) gave dibenzo[*a*,*h*]phenazine (1) (0.32 g, 22.9%), m.p. 283—284° (lit.,[7] 285°).

(b) With 4-nitroso-*NN*-dimethylaniline (0.01 mol) (bromobenzene, 155°, 12 h, light petroleum–benzene). The product was *4′-NN-dimethylaminobenzene*-ONN-*2-azoxynaphthalene* (9) (2.72 g, 93%), m.p. 169°, yellow crystals (from ethanol) (Found: C, 74.1; H, 5.9; N, 14.5. $C_{18}H_{17}N_3O$ requires C, 74.2; H, 5.85; N, 14.4%); τ ($CDCl_3$) 1.05 (1 H, s), 1.76 (2 H, d, *J* 10 Hz), 2.25—1.95 (4 H, m, aromatic), 2.4—2.6 (2 H, m, aromatic), 3.35 (2 H, d, *J* 10 Hz, 3′- and 5′-H), and 7.0 (6 H, s, NMe_2); *m/e* 291 (M^+).

Thermolysis of 4-azidoanisole (bromobenzene, 155°, 8 h, benzene). 4,4′-Dimethoxyazobenzene (0.43 g, 36%), m.p. 163—165° (lit.,[2] 165—166°) was obtained. Elution with benzene–diethyl ether (1 : 1) gave 2,7-dimethoxyphenazine (6) (0.045 g, 4%), m.p. 252° (lit.,[2] 252°).

Thermolysis of 3-azidoanisole (bromobenzene, 155°, 40 h, benzene). 3,3′-Dimethoxyazobenzene (0.48 g, 20%), m.p. 74—75° (lit.,[10] 75—76°) was obtained.

Thermolysis of 2-azidoanisole (bromobenzene, 155°, 8 h, ethyl acetate). 2-Methoxyaniline (0.37 g, 30%) identical with an authentic sample was separated.

Thermolysis of 4-azido-NN-dimethylaniline (bromobenzene, 155°, 8 h, benzene). This gave 4,4′-bis-*NN*-dimethylaminoazobenzene (0.47 g, 35%), m.p. 166—167° (lit.,[11] 165°). Elution with diethyl ether gave a tarry residue which on t.l.c. on alumina (using chloroform as eluant) gave probably the bis-*NN*-dimethylaminophenazine (7) (0.020 g, <2%), m.p. >350°, $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C=N), *m/e* 266 (Found: M^+, 266.345. Calc. for $C_{16}H_{18}N_4$: *M*, 266.348).

Thermolysis of 4-azidobiphenyl (bromobenzene, 155°, 8 h, benzene–diethyl ether). A trace of 2,7-diphenylphenazine, m.p. 254°, *m/e* 332 (M^+), was isolated.

Thermolysis of 4-morpholinophenyl azide (bromobenzene, 155°, 8 h, diethyl ether–ethyl acetate). *4,4′-Dimorpholinoazobenzene* (0.32 g, 18%), m.p. 125—127° (from benzene) was obtained (Found: C, 68.3; H, 6.6; N, 16.1. $C_{20}H_{24}N_4O_2$ requires C, 68.15; H, 6.85; N, 15.9%); $\nu_{max.}$ (Nujol) 1 650 cm^{-1} (–N=N–); τ ($CDCl_3$) 6.96 (m, NCH_2), 6.20 (m, OCH_2), and 7.09 (s, aromatic); *m/e* 352 (M^+). Elution with ethyl acetate gave 4-*N*-morpholinoaniline (0.12 g, 7%), identical in all respects with an authentic sample.

Thermolysis of 3-azidoquinoline (bromobenzene, 130°, 16 h, benzene). *Pyrazino*[2,3-c:5,6-c′]*diquinoline* (3) (0.24 g, 17%), m.p. >360°, was produced as a yellow powder (washed with ethanol) (Found: C, 76.5; H, 3.8; N, 19.8. $C_{18}H_{10}N_4$ requires C, 76.7; H, 3.6; N, 19.9%); $\lambda_{max.}$ 236 and 297 nm (similar to the values for compounds of this type [13] and different from the linear structure [14]); τ [$(CD_3)_2SO$] 0.26 (2 H, s, H-2) and 0.8—2.1 (8 H, m, aromatic); *m/e* 282 (M^+). Elution with benzene–ethyl acetate (4 : 1) gave 3,3′-azoquinoline (0.45 g, 31%), m.p. 210—212°, red needles (from ethanol) (Found: C, 75.6; H, 4.2; N, 19.5. $C_{18}H_{12}N_4$ requires C, 76.0; H, 4.3; N, 19.7%); τ ($CDCl_3$) 1.1 (2 H, d,

$J_{2,4}$ 2 Hz, H-2), 2.1 (2 H, d, H-4), and 2.5—3.4 (8 H, m, benzenoid aromatic); *m/e* 284 (M^+). Elution with ethyl acetate gave 3-aminoquinoline (0.46 g, 32%), m.p. 94°, identical with an authentic sample. Elution with methanol gave tar (0.3 g).

Thermolysis of 5-*azidoquinoline*(bromobenzene, 130°, 30 h, toluene). Dipyrido[3,2-*a*:3′,2′-*h*]phenazine (4) (0.14 g, 10%), m.p. 366° (lit.,[15] 368°) was separated as yellow crystals (from ethanol) (Found: C, 76.7; H, 3.6; N, 19.8. Calc. for $C_{18}H_{10}N_4$: C, 76.6; H, 3.6; N, 19.9%); $\lambda_{max.}$ 392, 380, 371, 353, 299, and 212 nm; τ ($CDCl_3$) 0.3 (2 H, dd, $J_{2,3}$ 5 Hz, H-2), 0.9 (2 H, dd, $J_{4,2}$ 2 Hz, H-4), 2.2 (2 H, dd, $J_{3,4}$ 6 Hz, H-3), and 1.6 (4 H, t due to two overlapping doublets H-7 and -8); *m/e* 282 (M^+). Elution with ethyl acetate gave 5,5′-azoquinoline (0.23 g, 16%), m.p. 256° (lit.,[16] 257°), red needles from ethanol, followed by 5-aminoquinoline (0.56 g, 39%), m.p. 109°, identical with authentic sample. Elution with methanol gave a black tar (0.41 g).

Thermolysis of 6-*azidoquinoline* (bromobenzene, 130°, 30 h, benzene–ethyl acetate). 6,6′-Azoquinoline (0.7 g, 49%), m.p. 246° (lit.,[17] 248°), red needles from ethanol, was formed. Further elution with ethyl acetate gave 6-aminoquinoline (0.36 g, 25%), m.p. 113°, identical with authentic sample. Elution with methanol gave tar (0.2 g).

Thermolysis of 7-*azidoquinoline* (bromobenzene, 130°, 16 h, ethyl acetate). 7-Aminoquinoline (1.03 g, 71%), m.p. 91—92° (lit.,[18] 91—93°), identical with an authentic sample, was formed. Elution with methanol gave a black tar (0.3 g).

Thermolysis of 8-*azidoquinoline* (bromobenzene, 130°, 12 h, ethyl acetate). 8-Aminoquinoline (0.52 g, 36%), m.p. 64° (lit.,[19] 64—65°) was separated, identical with an authentic sample. Elution with methanol gave a black tar (1.1 g).

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