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DECOMPOSITION OF ARYLAZIDES IN PIPERIDINE: THE EFFECT OF TETRAMETHYLETHYLENEDIAMINE ON THE NATURE OF THE PRODUCTS

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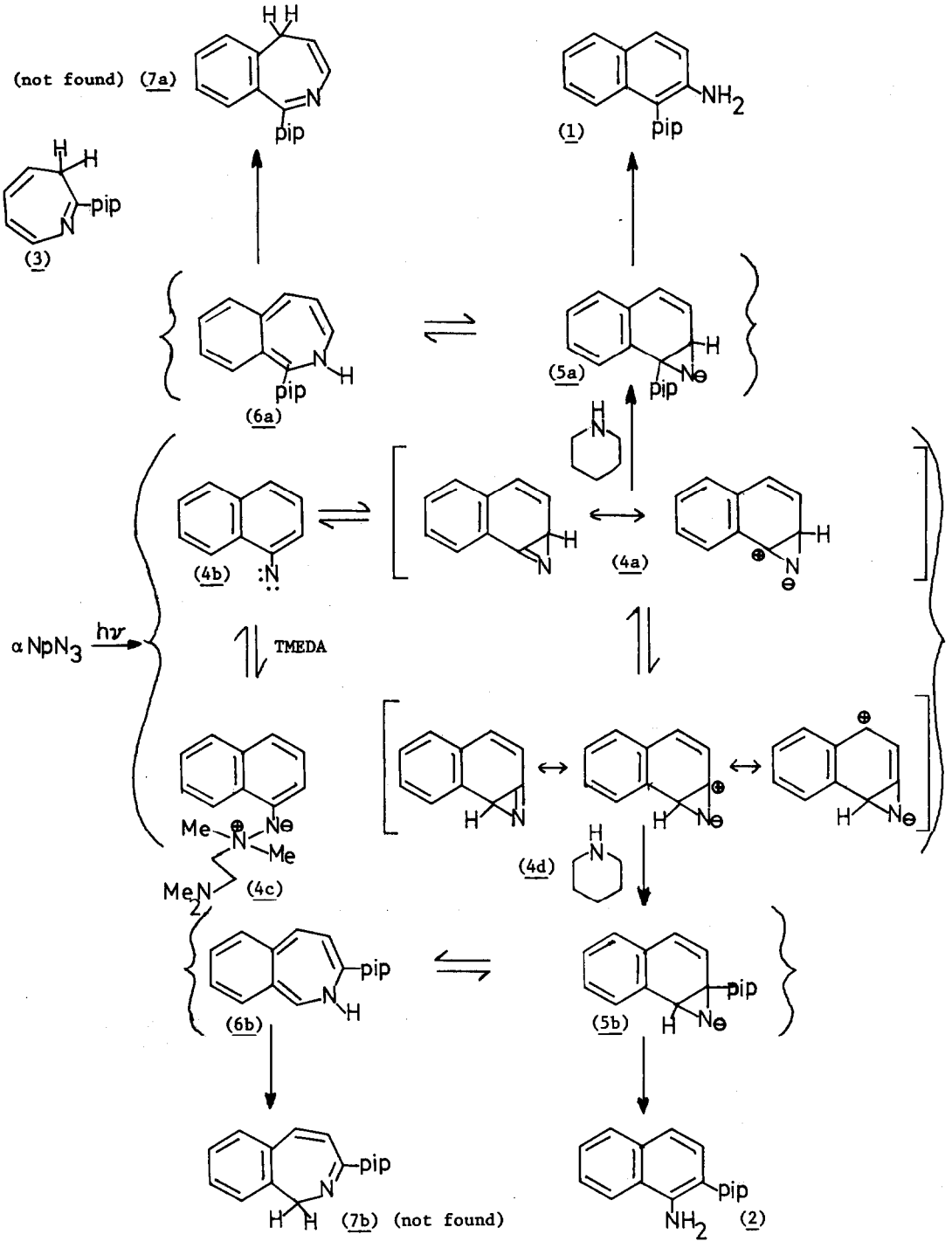
Continuing our comparative investigation of mono- and bicyclic aromatic azides[1], we have studied the effect of TMEDA (tetramethylethylenediamine) on the photolysis products of phenyl and naphthylazides in piperidine. Irradiation of α-naphthylazide in piperidine merely gives a small yield of α-naphthylamine and α-azonaphthalene attributable to typical triplet nitrene reactions[2] but the use of TMEDA as a co-solvent changes the nature of the products dramatically. The isomeric o-diamines 1 and 2 (singlet-derived products)[1a] now predominate, and again a small amount of α-naphthylamine is formed. This result is noteworthy as it is to our knowledge the first example of two isomeric diamines being formed in arylazide decompositions. The effect of TMEDA on the photolysis products derived from phenyl azide and β-naphthylazide in piperidine is not as great, although an increase in singlet-derived azepine 3 and diamine 2, respectively, is observed.

Table

Photolysis of Azides in Piperidine

Azide R-	Product, Yield (%)				
	Singlet-Derived			Triplet-Derived	
	1	2	3	RNH_2	RN:NR
α-Naphthyl-	-	-	-	11	8
α-Naphthyl- + TMEDA	50	25	-	8	-
β-Naphthyl-	-	75	-	t	-
β-Naphthyl- + TMEDA	-	80	-	-	-
Phenyl-	-	-	35	-	-
Phenyl- + TMEDA	-	-	58	8	-

Scheme



pip = N-piperidyl

Identification of the diamines (1 and 2) was by reference to authentic material[3] and in addition by NOE measurements which established the position of the amino-groups unequivocally[2].

A feasible mechanism for the formation of the isomeric diamines 1 and 2 in α-naphthylazide photolysis in piperidine-TMEDA is illustrated in the Scheme; decomposition of arylazides is considered to generate a singlet nitrene-azirine equilibrium[4] (4b ⇌ 4a), before the singlet nitrene collapses to the triplet ground state. Nucleophilic attack on such azirines is thought to be the first step in the formation of azepines from phenyl azide[5], and benzazepines[6] and o-diamines[1a] from β-naphthylazide. We propose that TMEDA coordinates with the singlet nitrene to give an equilibrium concentration of the ylid (4c) which effectively suppresses intersystem crossing to the ground state triplet nitrene. This has the effect of promoting the benzazirines 4a and 4d in a similar manner to the stabilisation of aliphatic azirines by DABCO[7]. Ylids similar to 4c have been postulated[8] and actually isolated[9] in some other intermolecular nitrene reactions. At present we cannot discount the possibility that TMEDA stabilises the singlet nitrene by chelation as has been suggested for the stabilisation of ethoxycarbonylnitrene by dioxan[10].

Formation of two isomeric o-piperidinonaphthylamines can be explained by some of the benzazirine 4a rearranging to the more stable 4d before nucleophilic attack by piperidine takes place. Two aziridines 5a and 5b result which can undergo C-N bond-fission and rearomatisation to give the observed products 1 and 2. The possibility that these two aziridines may expand to the isomeric 1-H-azepines 6a and 6b, by C_1-C_2 bond-fission was considered. 1-H-Azepines have rarely[5] been isolated but have been postulated as unstable intermediates in the formation of mono-[5] and bicyclic[11] azepines. Therefore, if formed, 6a and 6b might be expected to rearrange to the azepines 7a and 7b, respectively, which contain the stabilising features of an annelated aromatic ring and an amidine structure. Careful chromatography of the photolysis mixtures failed to reveal these compounds. Possibly these 1-H-azepines did form but rearranged to the thermodynamically more stable diamines as has been observed for some other systems[12]. Conversely, a careful hplc analysis of the product of photolysis of phenyl azide in morpholine failed to detect even 1 ppm of o-morpholinoaniline[13].

We are continuing to study the effect of TMEDA on arylazide reactions and the factors that determine whether azepines or o-substituted amines are formed in these decompositions.

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References

1a. S.E. Hilton, E.F.V. Scriven and H. Suschitzky, J.C.S. Chem. Comm., 1974, 853.

1b. S.E. Carroll, B. Nay, E.F.V. Scriven and H. Suschitzky, Synthesis, 1975, 710.

2. R.A. Abramovitch in "Organic Reactive Intermediates", Ed. S.P. McManus, Academic N.Y., N.Y., 1973, p. 127.

3. H. Suschitzky and M.E. Sutton, J. Chem. Soc. (C), 1968, 3058.

4. R.A. Abramovitch and B.A. Davis, Chem. Rev., 1964, 64, 149.

5. R.J. Sundberg, S.R. Suter and M. Brenner, J. Amer. Chem. Soc., 1972, 94, 513.

6. J. Rigaudy, C. Igier, and J. Barcelo, Tetrahedron Letters, 1975, 3845.

7. M. Komatsu, S. Ichijima, Y. Ohshiro, and T. Agawa, J. Org. Chem., 1973, 38, 4341.

8. R.A. Abramovitch, S.R. Challand and E.F.V. Scriven, J. Org. Chem., 1972, 37, 2705.

9. R.A. Abramovitch and T. Takaya, J. Org. Chem., 1972, 37, 2022.

10. H. Takeuchi, K. Kinoshita, S.M. Abdul-Hai, M.Mitani, T. Tsuchida and K. Koyama, J. Chem. Soc. Perkin II, 1976, 1201.

11. B. Iddon, M. Pickering and H. Suschitzky, J.C.S. Chem. Comm., 1974, 759.

12. R.A. Abramovitch, S.R. Challand, and E.F.V. Scriven, J. Amer. Chem. Soc., 1972, 94, 1374.

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