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COMPETITIVE CYCLISATION OF SINGLET AND TRIPLET NITRENES. PART III. THE EFFECT OF TEMPERATURE ON THE REACTIVITY OF THERMALLY AND PHOTOCHEMICALLY DERIVED ARYLNITRENES

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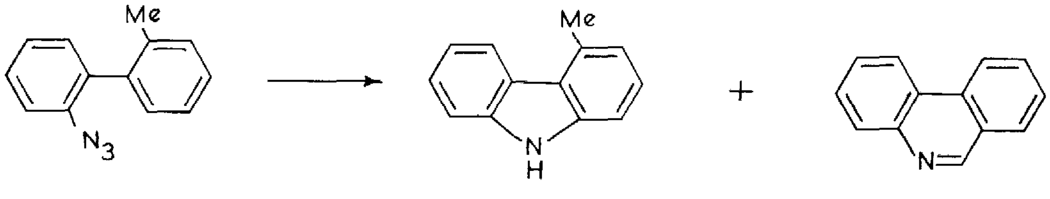
Arylnitrenes are relatively low in the reactivity scale of the nitrene family. High yield reactions of the singlet state are best viewed as concerted cyclisations (e.g. azepine and carbazole formation from phenyl azide and 2-azidobiphenyl respectively) while formation of azoarenes and arylamines are characteristic triplet processes. Yields of all types of products are generally lower from photolytically rather than thermally derived nitrenes. We attribute this largely to the lower energy possessed by the photo-generated nitrenes. Thermal excitation during photolysis of an azide, under both singlet and triplet (sensitised) nitrene-forming conditions, often dramatically enhances product yields. Furthermore, use of the highest reaction temperature, commensurate with reactant and product stability, is vital for optimum yields in both photo and thermally induced nitrene reactions. Thus, Odum[1] observed that photolysis of 1-(2-azidophenyl)-propane in iso-octane gave only traces of 2-methylindoline at ambient temperature but yielded 49% at 99°.

To explore this temperature effect we have examined the competitive formation of 4-methylcarbazole (2) (singlet derived[2]) and phenanthridine (3) (triplet derived[3]) from 2-azido-2'-methylbiphenyl (1). Coffin and Robbins[4] reported that thermolysis of this azide gave 4-methylcarbazole in 91% yield. We find (Table) that even in boiling bromobenzene (heavy atom effect)



(1) (2) (3)

the singlet product is favoured (98%) though a little phenanthridine (1.5%) is also formed (expt.2). At 370° in paraffin, only carbazole (100%) is produced (expt.3). Photolysis of the same azide under nitrogen and at ambient temperature is less effective. In methylene chloride, known to enhance singlet processes[5], only 62% carbazole (2) is isolated while addition of pyrene (a triplet quencher and singlet promoter[6]) raises this to 77% (expts. 4&5). However, photolysis of the azide at 107° in chlorobenzene (at which temperature thermal decomposition is negligible) gives the carbazole in 90% yield (expt.6) together with small amounts of triplet-derived products.

TABLE

Decomposition of 2-Azido-2'-methylbiphenyl (1)

Expt	Method	Solvent (1% solution)	Temp (°C)	Products (%)			
				Carbazole (2)	Phenanthridine	Amine	Azo
1	Δ	Ph_2O[4]		91	-	-	-
2	Δ	PhBr	156	98	1.5	0	0
3	Δ	Paraffin	370	100	0	0	0
4	hν	CH_2Cl_2	15	62	0	0	8
5	hν	CH_2Cl_2/pyrene	15	77	0	0	0
6	hν	PhCl	107	90	4.5	2	3.5
7	hν	PhAc[a]	15	44	0	2.5	2
8	hν	PhAc	15	17	9	12	55
9	hν	PhAc	96	15	28	30	15
10	hν	PhAc	107	18	35.5	39	4.5
11	hν	10% PhAc/PhCl	107	16	36	12	6
12	hν	10% PhAc/PhCl[b]	99	9	40	25	12.5
13	hν	PhAc[c]	107	14	13	27.5	30

[a] With PhAc filter - 32% azide recovered.

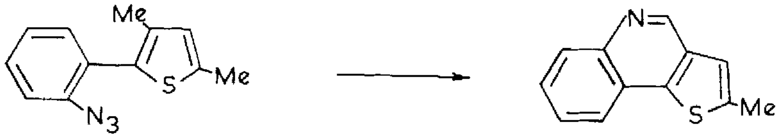
[b] 0.1% Solution used.

[c] 2-Azido-2'-trideuteriomethylbiphenyl was photolysed.

Swenton[6] has shown that photolysis of 2-azidobiphenyl in acetophenone solution yields mainly 2-azobiphenyl. We concur with this observation (after 8 h at 15°; azide (36.5%), azobiphenyl (37.5%), amine (6%), carbazole (16%) formed) and note very little change of products when the same solution is photolysed at 107° (azide (7.5%), azobiphenyl (45.5%), amine (6.5%), carbazole (11.5%)). In all our work involving triplet sensitised reactions we observed formation of the singlet product (17 ± 4%), in this case carbazole[7]. That this is derived by competitive direct photolysis of the azide, using higher wavelength light than that absorbed by the sensitiser is indicated by use of acetophenone filtered light, when virtually only the singlet product, carbazole (2, 42%) is produced together with unchanged azide (expt.7).

Photolysis of 2 azido-2'-methylbiphenyl (1) in acetophenone solution is on the contrary very temperature dependent. At 15° azo-compound formation dominates (55%, expt.8), but at higher temperatures (expts. 9&10) phenanthridine and amine formation are preferred (triplet intra- and intermolecular H-abstraction). We view this as indicative of an energetic hierarchy in triplet pathways with azo-formation at the bottom. The undesirable formation of amine may be diminished by use of 10% acetophenone in chlorobenzene as the photolysis solvent (expt.11) (since fewer aliphatic hydrogens are available for abstraction) while optimum yields of phenanthridine are obtained when a tenfold dilution (0.1%) is photolysed. Much of the amine derives from dehydrogenation of the intermediate dihydrophenanthridine by the nitrene, as borne out by the amine/phenanthridine ratios. In line with the above ideas photolysis of 2-azido-2'-trideuteriomethylbiphenyl under the usual conditions (expt.13) gives considerably more azo-compound (30%) at the expense of phenanthridine (13%), because the greater difficulty of abstracting a deuteron rather than a proton.

We are currently exploring the synthetic potential of this 'hot triplet' method in other systems. For example the thiophen analogue (4) of the above biphenyl, which does not have an obvious site for singlet nitrene attack, gives only the corresponding amine and azo-compound when photolysed in cold acetophenone[7]. However at 107° the phenanthridine analogue (5) is produced in 30% yield.



(4)

(5)

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