

COMPETITIVE CYCLISATION OF SINGLET AND TRIPLET NITRENES. PART II
CYCLISATION OF 2-NITRENOPHENYL- THIOPHENS, -BENZOTHAZOLES AND -BENZIMIDAZOLES.

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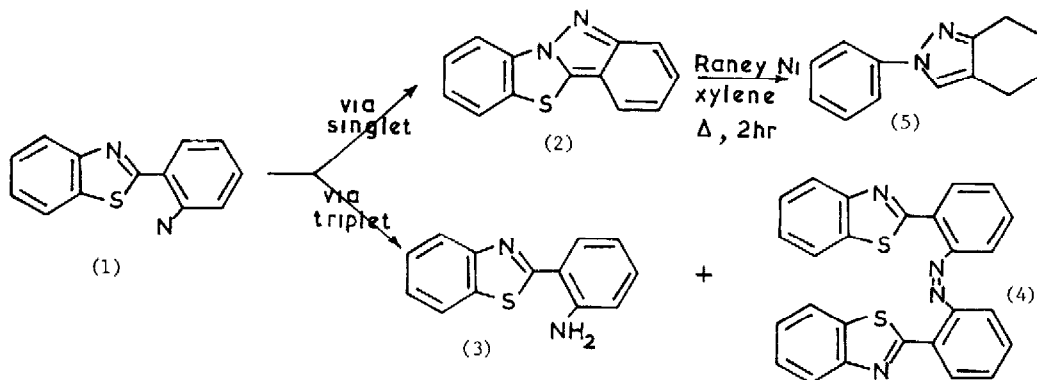
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The competition between singlet and triplet pathways in nitrene cyclisations has been demonstrated in a preceding paper¹. We now wish to report further examples and also to comment on alternative singlet sites of reaction. The electrophilic character of a singlet nitrene is well demonstrated by its proneness to attack by for example nitrogen nucleophiles¹. Surprisingly, only one report has yet appeared of the interaction of sulphur nucleophiles with an arylazide, i.e. the cyclisation of 2-azidothiobenzophenone by a concerted non-nitrene mechanism². We have examined two systems (1 and 6) where such interaction is possible. The singlet nitrene clearly has strong preference for nitrogen nucleophiles since no product in either case derived from attack at sulphur. The structure of the major product (2) from the thermal reactions followed also from desulphurisation with Raney nickel. This gave unexpectedly the tetrahydro-2-phenylindazole, incidentally lending some support to the o-quinonoid nature of (2). The formation of this product (2), even in the triplet-sensitised photolysis in acetophenone solution (in which the pyrazoles¹ gave solely triplet-derived products) suggests that the longer wavelength light excites the conjugated azide directly leading to some singlet nitrene (1). This minor process is in competition with the excitation to the triplet azide (and hence triplet nitrene (1)) via photosensitisation by the triplet acetophenone.

In the case of the thiophen (6) no trace of (10) or any other singlet derived product could be detected even under conditions that strongly favoured the singlet pathway (Scheme 2).

The benzimidazoles (11), analogues of the benzothiazoles (1), have the potential for both singlet (attack at -N=) and triplet (attack at -CHR₂) intramolecular pathways (Scheme 3). As with the benzothiazoles, the singlet reaction is highly efficient and photolysis in acetophenone of the azide (11, R=H) again showed 'leakage' yielding some singlet product by direct irradiation. Only with the isopropyl derivative (11, R=Me) was CH-insertion observed and then only under total 'triplet-control' by use of photosensitisation in acetophenone.

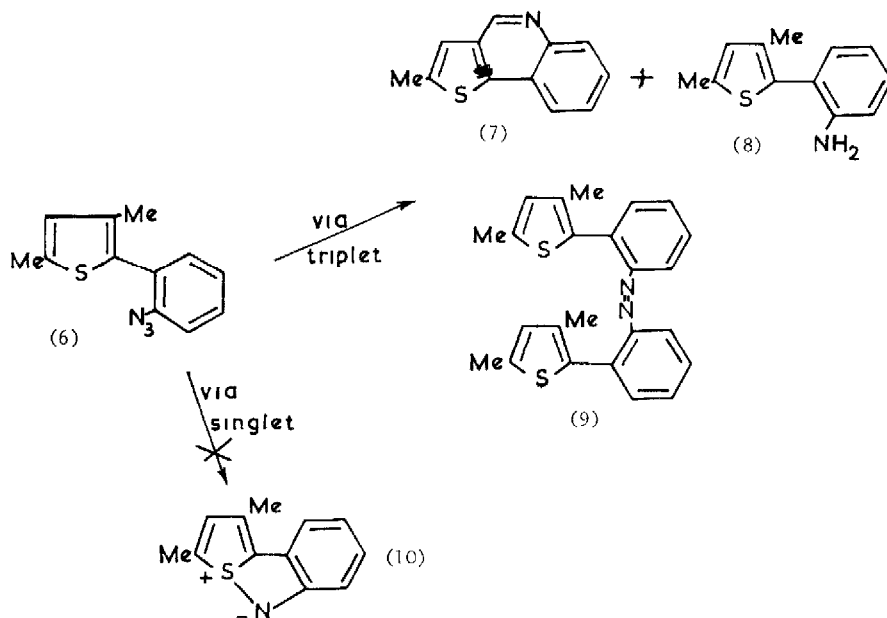
Scheme 1



Conditions (nitrene source/reagent/solvent)	Products (%)			
	(2)	(3)	(4)	S/T
$-\text{NO}_2/\text{TEP}/\text{cumene}$	54	4	0	13.5
$\text{N}_3/\Delta/\text{cumene}^{\text{a}}$	79	1	0	79.0
$\text{N}_3/h\nu/\text{CH}_2\text{Cl}_2$	53	7	8	3.5
$\text{N}_3/h\nu/\text{PhCOCH}_3^{\text{c}}$	19	4	34	0.5

^a Some bicumyl also isolated, ^b singlet stabiliser, ^c triplet sensitiser

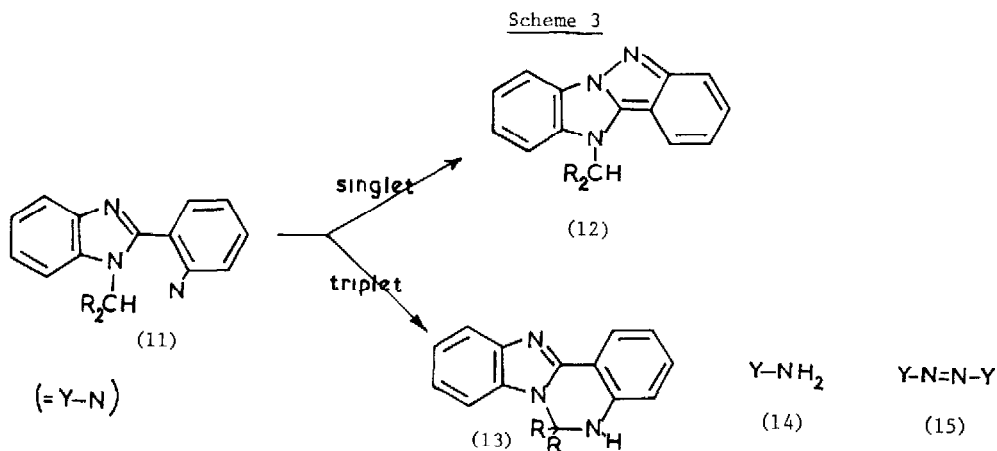
Scheme 2



Scheme 2 continued

Conditions (reagent / solvent)	Products (%)		
	(7)	(8)	(9)
Δ /decalin	35	40	0
$h\nu$ /CH ₂ Cl ₂ ^a	0	trace	62
$h\nu$ /CH ₂ Cl ₂ ^c + pyrene ^b	0	0	17
$h\nu$ /acetophenone	0	46	46

^a Singlet stabiliser, ^b triplet quencher.



R	Source	Conditions		Products (%)			
		Reagent	Solvent	(12)	(13)	(14)	(15)
H	NO ₂	TEP	Cumene	83	0	trace	0
H	N ₃	Δ	Cumene	96	0	4	0
H	N ₃	$h\nu$	PhCOMe ^a	15	0	26	8
Me	N ₃	Δ	C ₆ H ₅ Br ^b	66	0	14	14
Me	N ₃	$h\nu$	PhCOMe ^a	0	59	15	0

^a Triplet sensitiser, ^b triplet promotor - heavy atom effect

The powerful 'substituent control' of the nitrene reaction (see ref 1) is further demonstrated by the thermolysis outlined in Scheme 4. The p-dimethylamino-group totally deactivates the singlet state and hence no attack at N is observed while triplet CH-insertion occurs even into a methyl group. Thus, the ease of triplet insertion into CH bonds follows the expected order ($\text{CH} > \text{CH}_3$) and it seems that all the insertions in this paper are of higher energy than those we have observed before¹. Indeed, the triplet nitrene generated by photosensitisation in acetophenone is seen throughout our studies to be a low energy species. This 'lazy triplet' is only sufficiently energetic to insert into 'active' methyl groups or favourable tertiary centres but otherwise gives rise to azo-compound formation. Thermally produced triplet nitrenes, being vibrationally more excited, have greater potential for attack of unactivated CH bonds. These characteristics are under active investigation.

References

1. I.M. McRobbie, O. Meth-Cohn and H. Suschitzky, preceding paper, Part I
2. J. Ashby and H. Suschitzky, Tetrahedron Letters, 1971, 1315.

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