

COMPETITIVE CYCLISATIONS OF SINGLET AND TRIPLET NITRENES. PART I.

CYCLISATION OF 1-(2-NITRENOPHENYL)PYRAZOLES

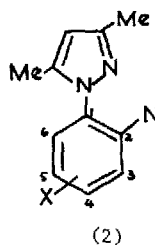
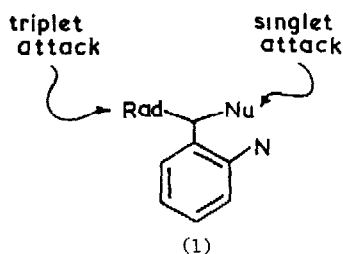
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Arylnitrenes are known to prefer a triplet ground-state but (apart from the photosensitized decomposition of azides) are first formed in the higher energy singlet state which by inter-system crossing, yields the ground-state intermediate¹. The electrophilic nature of the singlet and radical character of the triplet nitrene are well known¹. We have embarked on a study of reactions in which the nitrene has a choice of intramolecular reaction sites which preferentially engage with one or the other nitrene species (1). In order to establish this principle, we have



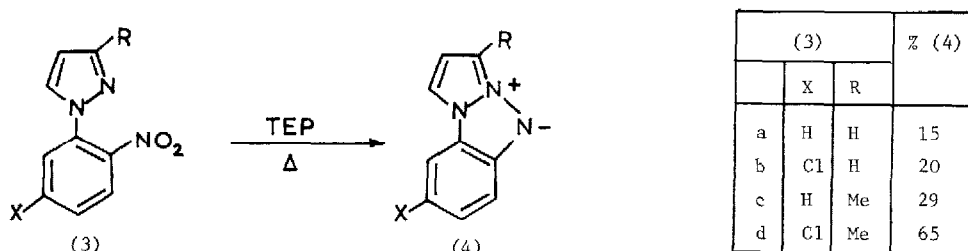
made a series of *o*-nitreno-phenylpyrazoles (2). The nitrene was generated by the thermal or photolytic decomposition of the corresponding azide in various solvents or by the deoxygenation of the appropriate nitro-compounds with triethyl phosphite (TEP)*

Lynch and Hung have previously studied the deoxygenation of 1-(*o*-nitrophenyl)pyrazole (3a) which gave low yields of the ylid (4a)². We have optimised the reaction conditions by use of molar amounts of the reactants in dilute cumene solution under a nitrogen atmosphere, and observe that increasing the nucleophilicity of the pyrazole nitrogen (3-Me-substituent; 3c or d) and/or increasing the electrophilicity of the nitrene (eg X=Cl; 3b or d), enhances the yield of

* It is recognised that the deoxygenation work could be equally explicable on the basis of intermediates such as $\text{Ar-N-O-P}(\text{OEt})_3$, however, the close similarity of the products from the two routes makes a nitrene intermediate feasible³.

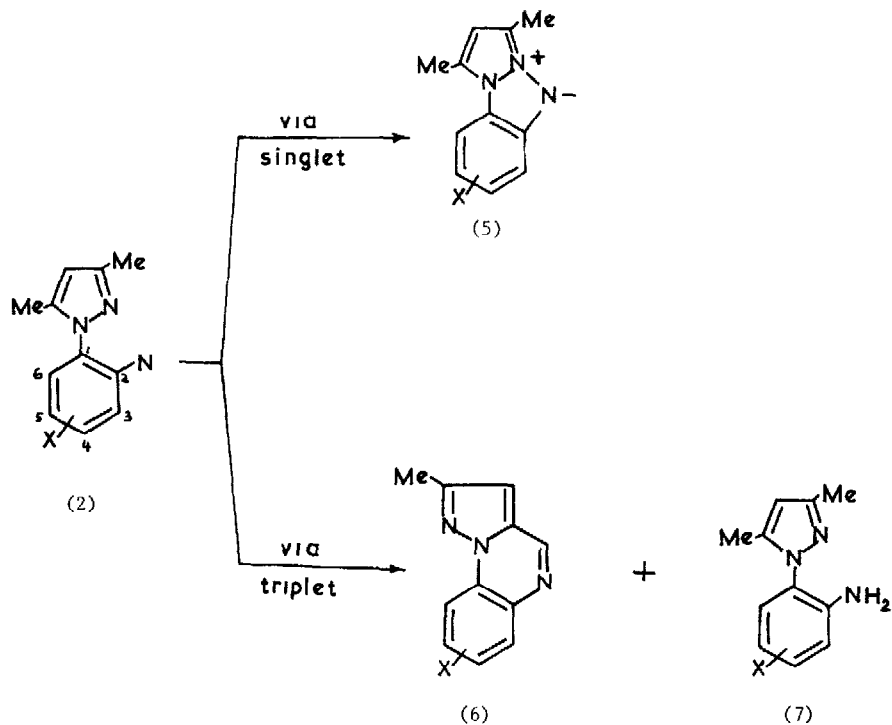
the ylid (4), supporting the singlet origin of this product (Scheme 1)

SCHEME 1



The corresponding azide (3a, N_3 instead of NO_2) gives a similar yield of the ylid (4) by thermolysis, together with the related amine (19%) and a trace of bicumyl. However, the photolysis of the azide in acetophenone solution (giving the triplet nitrene), gave as expected no ylid (4a) but the corresponding aniline and azo-compound. The related reactions of a series of 3,5-dimethylpyrazole derivatives gives products summarised in Scheme 2, and Table 1

SCHEME 2



These results show some significant features

(a) In many cases the singlet cyclisation product (5) or triplet product (6) may be selectively produced by choice of suitable conditions

(b) Electron-withdrawing groups, particularly para to the nitrene increase the electrophilic character (and hence reactivity) of the singlet nitrene and thus give higher yields of the ylid (5) (eg Expts 2,3,6-9) Electron-releasing substituents decrease the electrophilicity and enhance the yield of triplet products (eg Expts 4,5)

(c) Solvents that promote the formation of triplet nitrenes (C_6H_5Br - heavy atom effect, $PhCOCH_3/h\nu$ - triplet sensitizer) favour triplet-derived products (Expts 15,17)

(d) Photolysis of the azide in acetophenone solution eliminates all singlet nitrene products (Expts 16,18,20)

The ylid products could in principle be derived by concerted cyclisation with nitrogen expulsion. However, this is unlikely since (a) the azides have normal decomposition temperatures ($>140^\circ$), (b) the kinetic plots of the log of azide concentration vs time for the thermal decomposition of 1-(2-azido-5-chlorophenyl)-3,5-dimethylpyrazole at 150° in both cumene and diglyme (Expts 10,11) (k (cumene) = $4.12 \times 10^{-4} \text{ sec}^{-1}$, k (diglyme) = $4.48 \times 10^{-4} \text{ sec}^{-1}$), gave almost identical first-order plots suggesting that the different products in the two reactions derived from the same intermediate. Also the ylid is not converted thermally or photolytically or by action of TEP into the other reaction products (6 and 7)

Products from 1-(2-nitrenophenyl)-3,5-dimethylpyrazoles (2)

(a) By $-NO_2/TEP/\Delta$ in cumene at $\sim 150^\circ$

Expt No	X	Product (%) [*]			S/T [†]
		5	6	7	
1	H	6	t	5	1/2
2	5-Cl	62	16	11	2/3
3	5-Br	70	6	2	8/75
4	5-NMe ₂	0	47	19	low
5	5-OMe	0	23	32	low
6	4-Cl	57	0	t	high
7	4CF ₃	63	0	t	high
8	4-NO ₂	26	0	t	high
9	4-NMe ₂	63	0	t	high

*t = trace

†S/T = ratio of singlet to triplet derived products.

(b) By $-N_3/\Delta$ at $150-160^\circ$

Expt No	X	Solvent	Product (%) [*]			S/T [†]
			5	6	7	
10	5-Cl	cumene	39	5	2	5.6
11	5-Cl	diglyme	t	9	84	low
12	5-Cl	PhBr	8	6	21	0.3
13	4-CF ₃	decalin	67	0	0	high
14	5-NMe ₂	cumene	0	44	41	low

(c) By $-N_3/h\nu$ at $\sim 20^\circ$

Expt No	X	Solvent	Product (%) [*]			S/T [†]
			5	6	7	
15	5-Cl	CH ₂ Cl ₂	28	6	t	4.6
16	5-Cl	PhAc	t	48	43	low
17	4-CF ₃	CH ₂ Cl ₂	33	0	13	2.5
18	4-CF ₃	PhAc	0	41	22	low
19	5-NMe ₂	CH ₂ Cl ₂	0	12	19	low
20	5-NMe ₂	PhAc	0	50	38	low

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