CHEMISTRY LETTERS, pp. 331-334, 1981.

DIMETHYLBENZOPYRAZOLOTRIAZOLE *vs* METHYLPYRAZOLOQUINOXALINE FROM 3,5-DIMETHYL-1-(2-NITRENOPHENYL)PYRAZOLE

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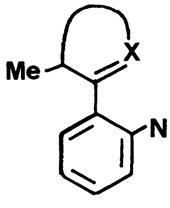
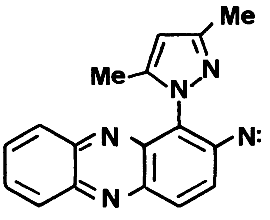
The chemistry of singlet and triplet 3,5-dimethyl-1-(2-nitrenophenyl)pyrazole is examined. Intramolecular electron transfer is found to play a key role in determining the easy reaction to the ylide (VII) from the singlet state and the "lazyness" of the triplet state.

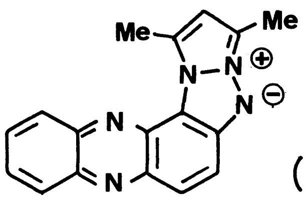
Arylnitrenes have been extensively investigated, also in view of the synthetic possibilities they offer.[1)] A typical application is the preparation of carbazoles via o-nitrenobiphenyls (formula 1). This synthesis has been extended to several derivatives bearing a heterocyclic ring in the place of a phenyl ring. We recently found that 1-(3,5-dimethylpyrazolyl)-2-nitrenophenazine (II) cyclizes to the inner salt (III) both from the singlet and from the triplet state, the only difference being the formation also of some products from intermolecular reactions in the case of the triplet nitrene.[2)]



(I)
X = CH,N

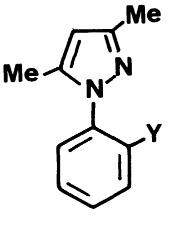


(II)

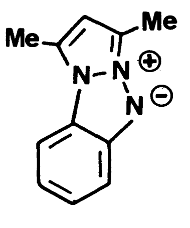


(III)

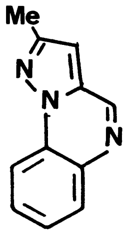
3,5-Dimethyl-1-(2-nitrenophenyl)pyrazole (IV), strictly related to the nitrene (II), had been proposed as a model offering the possibility of intramolecular attack both from the electrophilic singlet state (onto the nitrogen atom) and from the radicalic triplet state (onto the methyl group).[3a)] Since no intramolecular radical attack was observed in the case of nitrene (II) and, on the other hand, the above mentioned study on nitrenes of type (IV) had been mainly based on the effect of substituent groups, the unsubstituted nitrene having been incompletely investigated, we decided to study further the chemistry of nitrene (IV). The appearance of the full report on this type of nitrene,[3b)] which was published when our study had been completed, prompted us to refer here our data which complement those reported in that paper and our conclusions on this subject. The nitrene (IV) was produced in various experimental conditions, either by deoxygenation of the corresponding nitrocompound (V)[4)] or by thermal or photolytic decomposition of the azide (VI).[5)] As it is shown in Table 1, both thermal methods from (V) and (VI) and direct irradiation of (VI) lead in high yield to the product of intramolecular electrophilic attack, 1,3-dimethyl-5H-pyrazolo[1,2-a]benzotriazol-4-ium inner salt (VII). When the triplet nitrene is formed



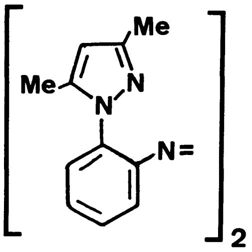
(IV) Y = N:
(V) Y = NO_2
(VI) Y = N_3
(IX) Y = NH_2



(VII)



(VIII)



(X)

through sensitized decomposition of the azide (VI), intramolecular radical attack to yield (VIII) takes indeed place. However, this process is a minor one and is accompanied by intermolecular processes, namely reduction to the amine (IX) in hydrogen donating solvents or formation of the azo derivative (X) in "inert" solvents. Moreover, some (VII) is formed also in these experiments, although direct excitation of the azide in these conditions is excluded by control experiments.

The following rationalizations, which are valid also for the data of ref. 3, can be applied to our data. Intramolecular electrophilic attack to yield (VII) takes place from the singlet nitrene (IV) in the same high yield as from its derivatives bearing an electron-withdrawing substituent in the phenyl ring[3] or from the phenazinyl nitrene (II).[2] Thus, the previously invoked effect of electron-withdrawing substituents[3] appears to have little importance. In our opinion the high yield of the intramolecular electrophilic process is due to the fact that intramolecular electron transfer[6] from the pyrazole ring to the nitrene function occurs as soon as the latter is formed from its precursors, thus directly leading to the inner salt (VII). The intersystem crossing to the triplet state is of minor importance, apparently occurring at a lower rate compared with electron transfer. As for the triplet nitrene, there is no reason to suppose that an analogous intramolecular electron transfer does not take place also in this case. The triplet zwitterion has obviously little tendency to close to the inner salt (VII) but has also a limited radical character, and therefore the otherwise attractive radicalic attack occurs only poorly. Nitrene (IV) in its triplet state is indeed a "lazy" nitrene, as evidenced by the formation of the azocompound (X) in non hydrogen-donating solvents, a process, which is typically "the last resort" of unreactive nitrenes.[3b] In fact, an examination of the literature data shows that intramolecular cyclization onto the methyl group occurs in very poor yield from nitrenes of type (I), unless intramolecular electron transfer is precluded, e.g. by the presence of strong electron donating groups in the phenyl ring. In the case of phenazinyl nitrene (II), the high yield of formation of the ylide (III) also from the triplet state must be due to a higher rate of spin inversion from the zwitterion, probably due to a reduced energetic gap between the singlet and the triplet state.

In conclusion, the possibility of intramolecular electron transfer must be taken into account in order to understand the chemistry of this type of nitrenes and to use them for heterocyclic syntheses.

Table 1. Results from decomposition of compounds (V) and (VI)[a]

Starting material	Solvent	Temperature (°C)	Reaction time (h)	% Conversion	% Yield of Products			
					(VII)	(VIII)	(IX)	(X)
(V)	Cumene/P(OEt)$_3$	150	24	100	57	-	5	-
"	"	"	8	55	68	-	5	-
(VI)	Cyclohexane	180	1	100	57	-	tr	-
"	"	20[b]	0.5	63	53	-	tr	-
"	Acetone	20[c]	1.5	75	10	12	tr	37
"	Cyclohexane/Acetone(7/3,	20[c]	0.5	42	15	tr	6	tr
"	Cyclohexane/Acetophenone 2%)	20[c]	0.5	85	-	6	28	-

a) Control experiments showed that all products are sufficiently stable in the conditions employed to produce them by decomposition of (V) and (VI), so that it can be excluded that the yields obtained are significantly altered by secondary decomposition. The azide (VI) is stable to Pyrex-filtered light, as it practically does not absorb in this region.

b) Irradiation through a quartz jacket by means of a low pressure mercury arc (after flushing the solution with nitrogen).

c) Irradiation through a Pyrex filter by means of a high pressure mercury arc (after flushing the solution with nitrogen).

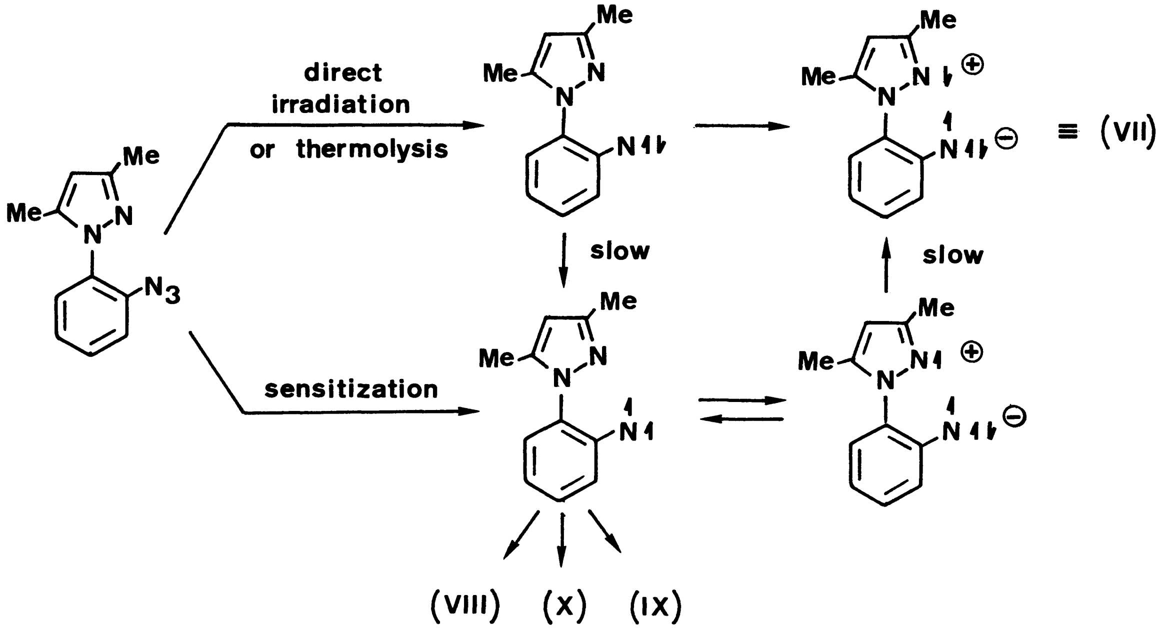


Table 2. Relevant data for the new compounds[a)]

Compound	Mp(°C)	NMR[b)] Me groups	>C-H	aromatics	$-\mathrm{C}^{\nearrow \mathrm{H}}_{\searrow \mathrm{N}-}$	IR[c)]
(VI)	54-5[d)]	2 2.2	5.93	7.05 - 7.4		2140vs, 2110s
(VII)	60-1[e,f)]	2.45 2.58	6.15	6.6 - 7.6		1610s, 1590m
(VIII)	82-3[d)]	2.6	6.7	7.5 - 7.8	9	1660w, 1520w, 1480s
(X)	181-2.5[e)]	2.05 2.37	6.12	7.5 - 7.8		1590w, 1550w, 1490s

a) All compounds gave satisfactory analytical values; b) in δ values, in $CDCl_3$; c) in nujol mull; d) purified by chromatography; e) crystallizes from cyclohexane; f) crystallizes with one molecule of water; the anhydrous material is an oil.

REFERENCES AND NOTES

* To whom inquires should be addressed.

1 B. Iddon, O. Meth-Cohn, E.F.V. Scriven, H. Suschitzky, and P.T. Gallagher, Angew.Chem., 91, 965 (1979); i.e.e. 18, 800 (1979) and therein cited references.

2 A. Albini, G.F. Bettinetti, and G. Minoli, J.C.S. Perkin I, in press.

3 a) I.M. McRobbie, O. Meth-Cohn, and H. Suschitzky, Tetrahedron Lett., 925 (1976); b) J.M.Linley, I.M. McRobbie, O. Meth-Cohn, and H. Suschitzky, J.C.S. Perkin I, 982 (1980).

4 The deoxygenation of the nitrocompound (V) was previously reported to give 6% of product (VII), 5% of the amine (IX) and trace of product (VIII).[3a,b)] This is likely due to the excessive reaction time (72 h).

5 The azide (VI) was prepared in 75% yield by adding 1 g NaN_3 and stirring for 30 min at 15°C the diazotized solution previously obtained by adding 690 mg $NaNO_2$ to a solution of 0.935 g of the amine (IX) in a mixture of acetic acid (10 cc), water (10 cc), and 40% fluoboric acid (10 cc) at -5°C.

6 Intermolecular electron transfer has been many times invoked to explain nitrene stabilization.[1,7)] However, intramolecular electron transfer will also take place when the situation is favorable, as in the present case.

7 G.F. Bettinetti, E. Fasani, G. Minoli, and S. Pietra, Gazz.Chim.Ital., 110, 135 (1980).

(Received November 8, 1980)