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THE C_6H_5N ENERGY SURFACE II: ISOMERISATION OF 2-, 3- AND 4-PYRIDYLCARBENES TO PHENYLNITRENE

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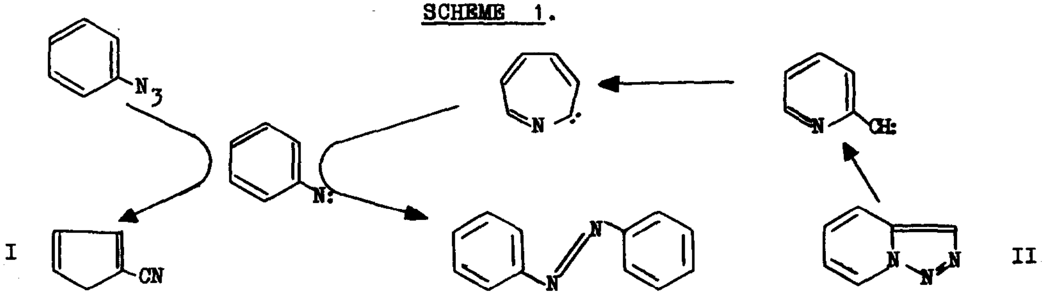
We have previously reported[1] the ring contraction of phenylnitrene to 1-cyanocyclopentadiene (CCPD; I), and the interconversion of 2-pyridylcarbene with phenylnitrene[2]. The reaction sequences (Scheme 1) raised the interesting point that the fate of the phenylnitrene produced (ring contraction vs dimerisation) appeared to be dependent upon the nature of its generator. Our previous work had indicated that CCPD arose from the singlet state, whereas azobenzene was the result of intersystem crossing to the triplet ground state[3]

SCHEME 1.

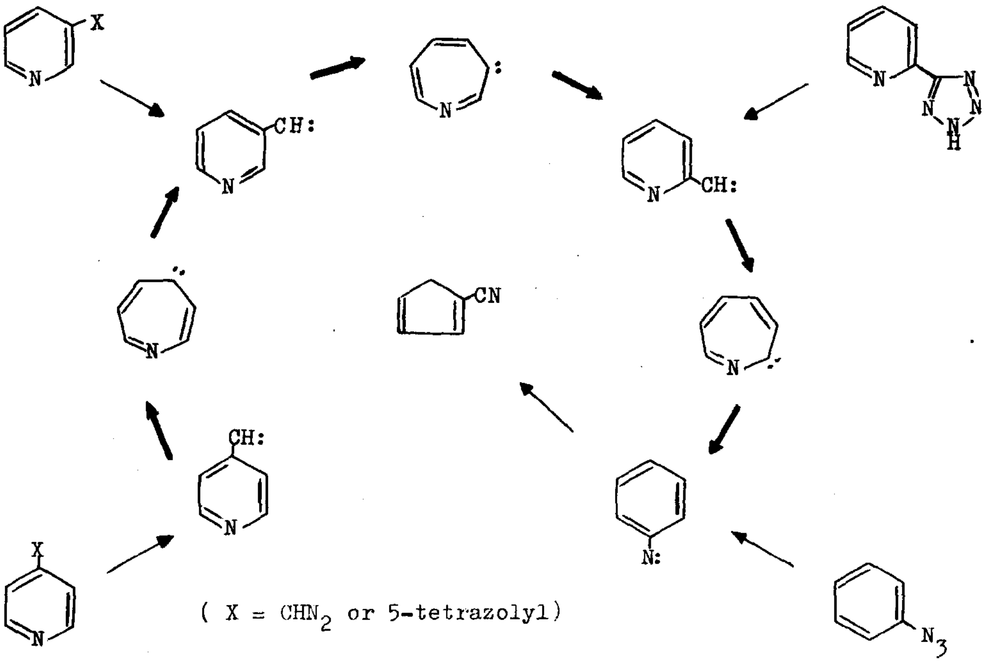


The present work extends the generality of the pyridylcarbene /phenylnitrene conversion, and examines the anomalous situation of v-triazolo[1,5-a] pyridine (II) as a phenylnitrene generator in the gas phase. As a preliminary move, gas-phase pyrolysis of II was re-examined over a wide range of conditions (450°- 850°/0.02- 0.05mm); the earlier results[2] were essentially confirmed, azobenzene being obtained rather than CCPD. All subsequent work was carried out in the same apparatus under a similar range of conditions.

Other generators of 2-pyridylcarbene were now required for comparison with II, and we employed the tosylhydrazones of pyridine-3-and 4-aldehydes (the 2-isomer is a precursor for II, and thus inappropriate) and the 5-pyridyltetrazoles.

The sodium salts of the pyridine aldehyde tosylhydrazones[4] were heated at 90°, the vapours being led directly into the furnace; the pyridyltetrazoles[5] were sublimed in the conventional manner. It is clear from Scheme 2* that any source of 4- or 3-pyridylcarbene should be capable of acting as a source of 2-pyridylcarbene (and hence phenylnitrene), and this proved to be the case. In the five compounds studied the major products were CCPD (I, 20-60%), aniline (2-10%), benzene (1-10%) and benzonitrile (0.5-5%). Traces of pyridines and picolines were also formed, but azobenzene was significantly absent throughout the temperature range.

SCHEME 2*.



(X = CHN_2 or 5-tetrazolyl)

The general conclusion is quite clear — of all the generators of phenylnitrene, v-triazolo[1,5-a]pyridine (II) is the only one which produces the triplet species, capable of dimerisation to azobenzene, as the major product. The "normal" course of events seems to be the formation of the singlet nitrene

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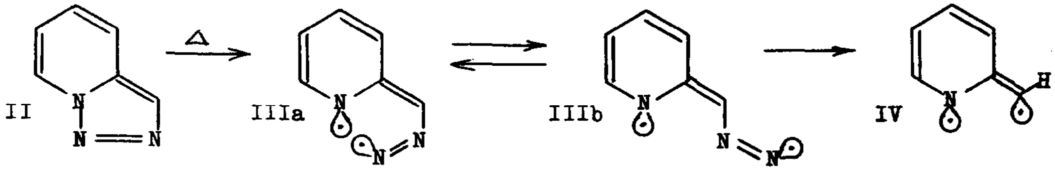
* In the interests of clarity we have omitted the series of bicyclo[4.1.0] heptatrienoid derivatives which are presumed to intervene between the exocyclic and endocyclic carbenes. At this stage we make no assumptions about the exact mechanistic details (e.g. H-shifts) or reversibility of the cycle. The formation of aniline (not shown) also serves to implicate phenylnitrene.

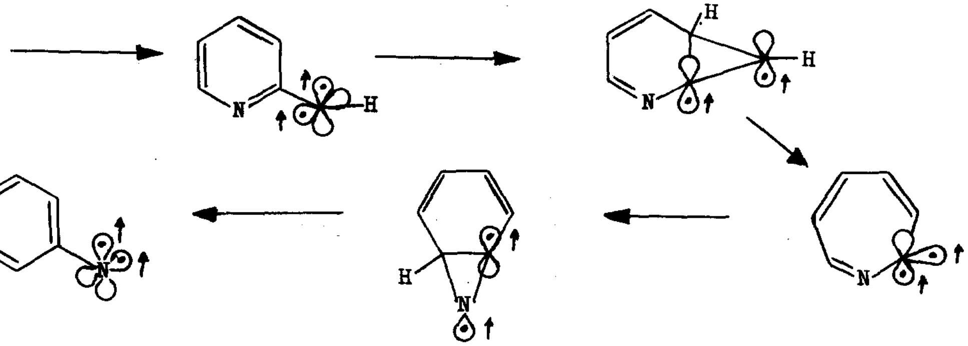
which then undergoes ring contraction, with a small fraction cooling to the triplet state and yielding aniline. The similarity between the products in this work and those derived directly from phenyl azide pyrolysis[6] was striking. As an additional check on the validity of the tetrazoles as carbene generators, we subjected 5-phenyltetrazole to gas-phase pyrolysis. The same H-shift / N_2-elimination was encountered, yielding fulvenallene — the ring-contraction product of phenylcarbene[7].

In seeking to explain the unique position of II as a generator of triplet phenylnitrene, we are led to consider an argument based on the spin state of the intermediate, i.e. that v-triazolo [1,5-a] pyridine gives direct access to triplet 2-pyridylcarbene, and thence by isomerisation to the triplet nitrene. The energy difference between the precursor II and 2-pyridyldiazomethane will not be very great, and it is instructive to consider the consequences of stepwise loss of nitrogen from II in some detail. Cleavage of the 1,5-bond is assumed to occur with spin conservation to give the singlet biradical IIIa. However, rotation about the C_4-N bond will produce other rotamers (e.g. IIIb)where the separation of the radical lobes may be sufficiently large to render the distinction between singlet and triplet states meaningless, i.e. IIIb is more properly considered as a double doublet. Loss of N_2 from IIIb will therefore give mainly ground state IV, whether this be singlet or (more likely) triplet. Alternatively, loss of N_2 from IIIa may be expected to yield a large amount of triplet IV, for the rotational interconversion IIIa $\rightleftarrows$ IIIb provides the means of populating the triplet state of IIIa. Once formed by the electronic reorganisation of IV, conversion of the triplet 2-pyridylcarbene to phenylnitrene with conservation of spin can be represented by the normal ring expansion / contraction cycle implicit in Scheme 2.



We do not in any way imply that, because the 2-pyridylcarbene was formed in the triplet state, it was formed with a low energy content. The evidence that it enters the triplet manifold at a substantial vibronic level is inferred from temperature studies with the related precursors. Even at temperatures as low as 350° both the 3- and 4-pyridyldiazomethanes afford CCPD in good yield, but give rise to no azobenzene. On the other hand, v-triazolo [1,5-a] pyridine gives rise to azobenzene (with only traces of CCPD) even at 800°, where the generated species must be expected to be carrying some excess vibrational energy. It is difficult to rationalise this behaviour on the basis of an intersystem crossing to the triplet from an initially formed singlet nitrene.

IV



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