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# THE $C_6H_5N$ ENERGY SURFACE: I : RING CONTRACTION IN PHENYL NITRENE - A $^{14}C$- STUDY

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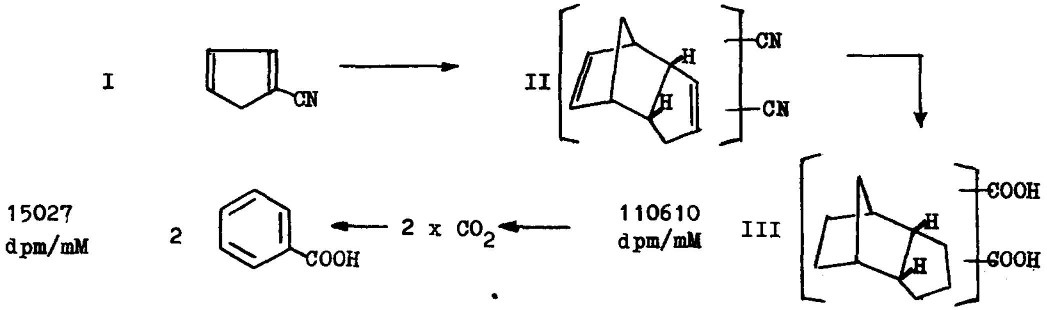
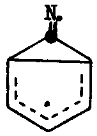
Gas-phase thermolysis of phenyl azide is a complex, low-yield reaction in which ring contraction[1-4] to cyanocyclopentadiene I as well as a ring-expansion/contraction cycle leading to pyridines is apparently involved.[3,5] Despite its complexity, it remains central to the theme of reaction mechanism in the aryl nitrene/carbene rearrangements. We report here findings which cast some light on the details of the ring contraction mechanism. The reaction scheme, summarised below, was used to determine that part of the labelled atom (1-$^{14}C$) from phenyl azide which appeared in the CN-group of the product I.



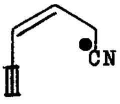
The azide was pyrolysed at 600°/0.05 mm (initial pressure) under conditions of rapid sample introduction.[1,2] The volatile products were allowed to dimerise (24 h under $N_2$) to II, then scavenged with pure II, allowing 0.5 h at 110° for equilibration of the cold and labelled materials. The dimers II, purified by chromatography, were then converted to III and the radiochemical purity checked by purification through the sodium salts; the specific activity (110610 dpm/mM) was unaltered by this process. Electrolytic decarboxylation under $N_2$ and trapping with phenylmagnesium bromide led to benzoic acid (15027 dpm/mM); the electrolysis conditions precluded radiochemical assay on the electrolysate.

Comparison of the specific activities indicated that 27 ± 2% of $C_1$ in the phenyl azide had appeared in the CN-group of I. While this result alone does not resolve the mechanism of the ring contraction, it does permit us to reject a number of proposals. It is evident that some degree of randomisation of $C_1$ has occurred prior to ring contraction; direct 2,6-bonding to the prefulvene intermediate IV, as proposed by ourselves and by Hedaya and co-workers[4], is thus ruled out, since it requires that <u>all</u> of $C_1$ should appear in the CN-group.

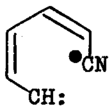
IV



Va



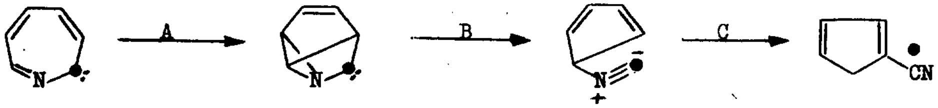
Vb

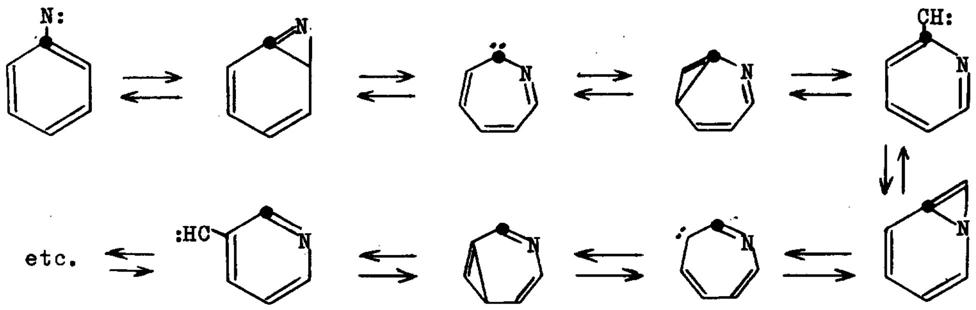


For the same reason, any device involving 1,6-bond cleavage/recyclisation (e.g. the acetylenic nitrile Va or the cyanocarbene Vb) can be eliminated. We can envisage two routes by which the requisite degree of randomisation may be achieved — ring expansion to azacycloheptatrienylidenes or a cycloperambulatory motion of the nitrene N.

Ring expansion of phenylnitrene to 2-azacycloheptatrienylidene (VI) is likely as there is ample precedent for this type of process in the gas phase reactions of 2-pyridylnitrene[6a] and arylcarbenes[6b]. Direct collapse of VI to I may best be envisaged as a ($\pi 4_a + \pi 2_a$) cyclization A, followed by a ($\pi 2_s + \sigma 4_s$) fragmentation B and sigmatropic shifts C. This would normally result in the labelled $C_1$ (designated as ●) appearing in the CN-group of I. Complete scrambling of the $C_1$ atom may be achieved through a series of ring expansion/contraction cycles (D) coupled with H-shifts (e.g. E); in this way the $^{14}$C-atom and the carbene site are distributed independently over the ring. Such a process would lead to 16.7% $^{14}$CN in I. Alternatively, complete scrambling may be rationalised in terms of a cycloperambulatory mechanism (F) <u>via</u> H-shifts in the bicyclic intermediates VII; the experimental result is identical, and it is worth noting that a distinction between the alternative routes (D/E and F) cannot be made using any kind of labelling technique. In terms of either of these mechanisms our result represents 87% scrambling.

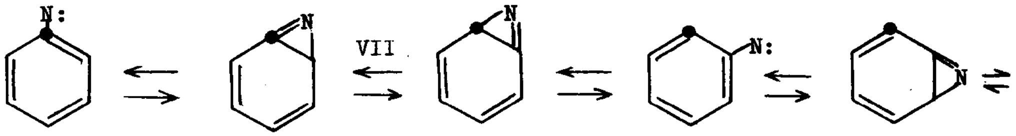
VI





Expansion/Contraction Cycle D

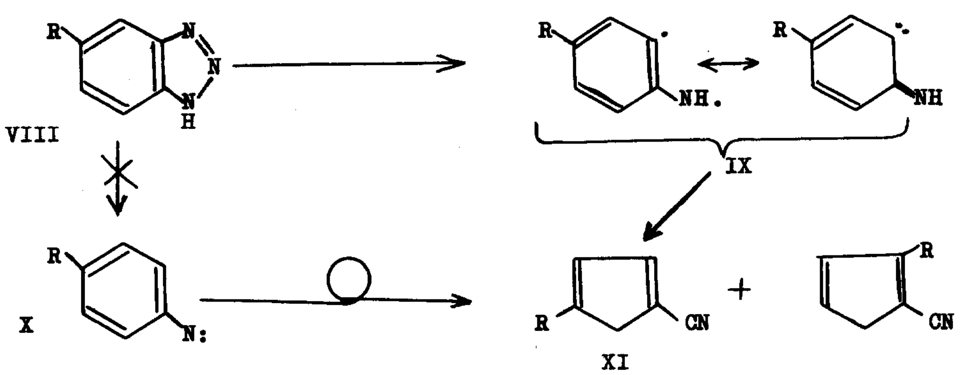
H-Shift Cycle E



Cycloperambulatory Nitrene/ H-Shift

The significant point emerging from this work is the necessity to invoke H-shifts as part of the mechanism, in contrast with the work of Hedaya and Kent[7] with $^{13}$C-labelled p-tolylcarbene, where a mechanism analogous to the process D was indicated. These authors, however, were dealing with a process different to that of ring contraction and probably of lower energy than the decomposition of phenyl azide. In the completely analogous case of ring contraction of phenylcarbene to fulvenallene[9] we have, indeed, shown[8] the occurrence of H-shifts prior to ring contraction.

The existence of a randomisation process which proceeds faster than ring contraction lends support to the theory[5,10] that ring contraction of 1(H)-triazoloarenes (VIII) gives only one nitrile (XI) (under conditions where the product is stable to sigmatropic CN-shift) because it proceeds <u>via</u> the biradical (or iminocarbene) IX rather than through the nitrene X.



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10. We stress, however, that formation of I from phenyl azide is observed under conditions approaching that of a "controlled explosion"[1,2]. Our ignorance of the exact temperature and pressure dictates that we make our extrapolation to the case of triazoloarene pyrolysis with some reservations.