Tetrahedron Letters No.44, pp. 4379-4384, 1967. Pergamon Press Ltd. Printed in Great Britain.

REACTIONS OF EXCITED MOLECULES. II. THERMAL AND ELECTRON IMPACT GENERATION OF PHENYLNITRENES - A FACILE RING CONTRACTION

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(Received in UK 6 August 1967)

During an investigation (1,2) of high energy rearrangements in the gas phase we have become interested in the more specific topic of rearrangements which occur within aromatic rings. Photochemical scrambling has been observed in the benzene ring (3,4) and also in a variety of heterocyclic molecules (5,6,7); in the case of benzenes, valence tautomers have been isolated (8,9). Products of this nature evidently arise from the electronically excited states (or, to be more precise, from vibrational sublevels of such states) by consolidation of new electron density patterns. The question as to whether such excited states contribute to the rearrangements observed in pyrolysis and mass spectrometry is not so readily answered, although from first principles it might be assumed that electron impact* would surely give rise to excited states - an electron is, after all, promoted right out of the molecule.

In comparing the reactions of phenylhydrazones of aryl ketones (ϕCR:N$\cdot$NHϕ) on pyrolysis (1) and on electron impact (10,11) certain parallels were observed; the cleavage of the N-N bond was common to both, as might be expected from the weakness of such bonds. Our attention was drawn to the ion m/e 92 (HNϕ^+) and its subsequent loss of 27 mass units (HCN) to m/e 65 ($C_5H_5^+$), a process readily formulated as I→II→III. The ion bears a formal resemblance

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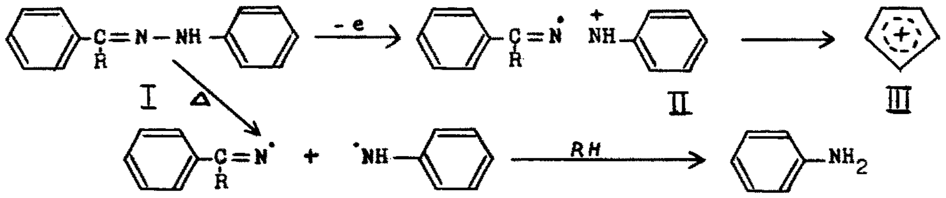
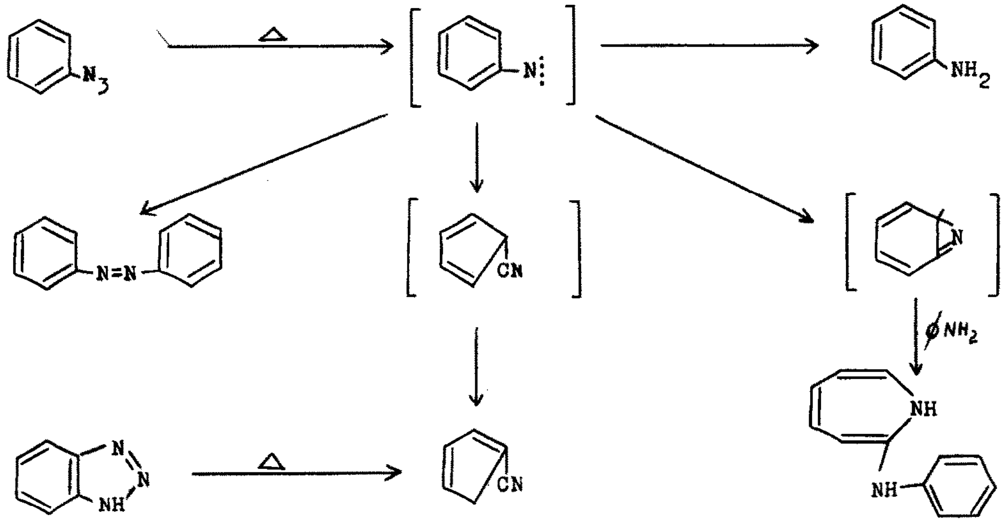
*Interpretation is possibly influenced by the choice of words. A 10 eV electron is involved in "impact", whereas a photon of λ = 124 mμ ($h\nu$ = 10 eV) is "absorbed". The existence of M^- as a species in the mass spectrometer suggests that a more thoughtful approach might be profitable.



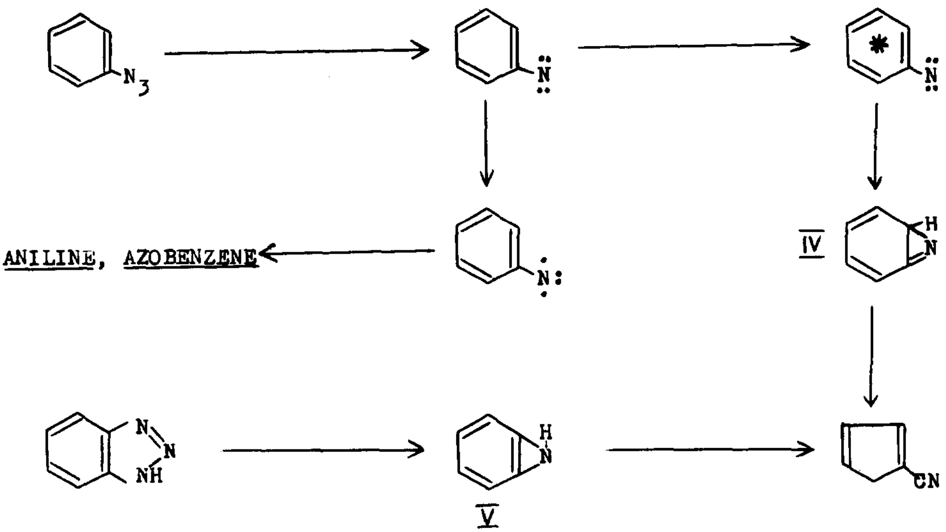
to phenylnitrene (there is also a peak at m/e 91 corresponding to $C_6H_5N^+$), and prompted an enquiry into the behaviour of the isolated phenylnitrene molecule in the gas phase. As formed from decomposition of phenyl azide, phenylnitrene normally reacts by hydrogen abstraction (12) to form aniline, by insertion (13,14) into C-H bonds, or by dimerisation to form azobenzene (12,14). In the presence of aniline it has been shown to undergo ring expansion (15) to 2-anilino-7H-azepine, a consequence of intramolecular attack by nitrene N, followed by nucleophilic displacement by the aniline.

Pyrolysis of phenyl azide at temperature in the range 600-970°K led either to the production of azobenzene and aniline, as previously reported, or to the formation of a liquid nitrile, depending upon the experimental conditions. The nitrile was identified by UV, IR, NMR and mass spectral comparison with a sample of 1-cyano-1,3-cyclopentadiene prepared by a modification of the described method (16). Both samples dimerised on



standing. Attempts to generate the same fragment from phenyl isocyanate, which in the mass spectrometer is known (17) to lose 28 mass units, followed by 27 mass units, were unsuccessful. Even on pyrolysis at much higher temperatures, this compound was recovered largely unchanged. On the other hand, considerable success was achieved in the pyrolytic elimination of N_2 from benzotriazole, which yielded the same nitrile as was obtained from phenyl azide; no azobenzene was obtained, however. Full details of this work will be presented in later publications.

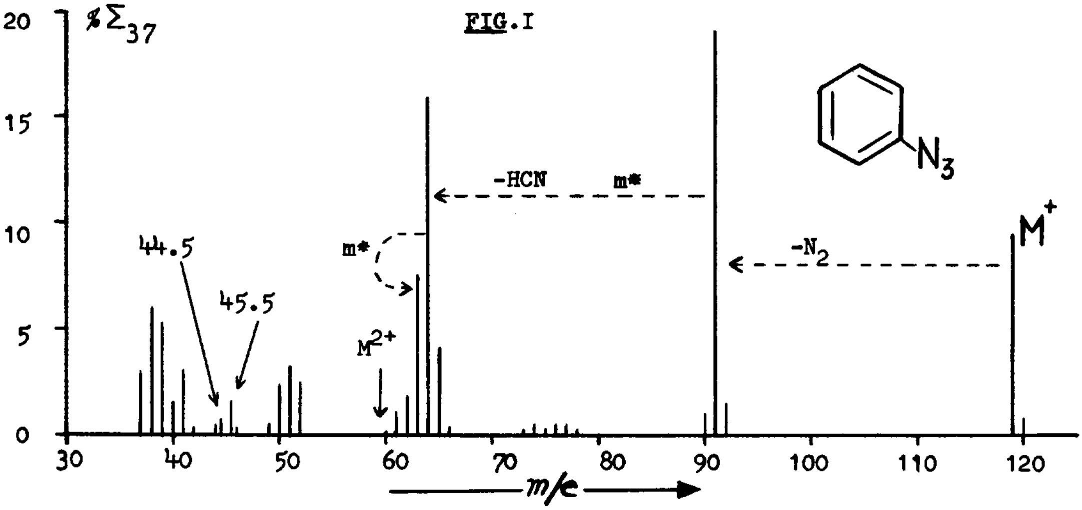
The nature of the reaction products is dependent upon the exact experimental conditions, in particular upon the rate at which phenyl azide vapour is introduced into the heated zone of the pyrolysis furnace. With high rates of sample introduction, cyanocyclopentadiene is formed, whereas slow rates lead to the production of azobenzene and aniline. (The interrelationship of pressure, distillation time and residence time make it rather more difficult to establish the significance of residence time to the choice of reaction pathway, and experiments are now in progress to establish this.) While it is clear that the reaction mechanism and conditions require more study, the results are sufficiently unusual to warrant some comment. The higher pressure in the furnace on rapid sample introduction should lead to increased dimerisation and H-abstraction, provided that the same species are involved. Since the exact opposite is observed, one conclusion might be that a different species was involved. Under conditions of higher pressure, diffusion away from the hot surfaces will be more difficult, involving increased collision with other molecules. The phenylnitrene generated near the hot surfaces will initially be in the singlet state, but, if not able to diffuse away fairly rapidly, might be expected to absorb sufficient energy to raise it to a vibrationally excited singlet state, i.e., a "hot" singlet. It is this species, we suggest, that undergoes intramolecular insertion in an aromatic double bond, leading to cyanocyclopentadiene in the present case, or to 2-anilino-7H-azepine in the presence of aniline. Under conditions of lower pressure the singlet nitrene would escape



from the hot zones with the absorption of less energy, with the result that decay to the triplet state could effectively compete with the insertion reaction of the hot singlet. The implication that H-capture and coupling are essentially reactions of triplet nitrene, whereas insertion in a double bond is due to singlet nitrene, is perhaps an over-simplification, but it is consistent with the experimental findings and conclusions of other workers (18). It is of some interest to note that the insertion product from the hot singlet (IV) (by insertion into the π-band) differs in structure from that (V) postulated as arising from benzotriazole (which corresponds to insertion in a C-H bond, although presumably not formed in that way). As to whether the distinction between IV and V has any reality under the experimental conditions is a matter which, although open to argument, is difficult to resolve experimentally.

The mass spectrum of phenyl azide (FIG. 1) shows the expected loss of nitrogen, followed by the loss of HCN to give the ion $C_5H_4^+$; the same course is followed by the isomeric benzotriazole. Thus the series of ions $C_6H_7N^{+\cdot}$ (aniline), $C_6H_6N^+$ (phenylimine) and $C_6H_5N^{+\cdot}$ (phenylnitrene or 1-cyano-1,3-cyclopentadiene) shows consistent behaviour, based on the

FIG.I



intramolecular attack by the nitrogen atom. The decision as to the structure of any of these ions is probably one of rate processes, i.e., the structure is changing from the moment of origin. Thus fragment ions arising at different times in the history of M^+ may well arise from different structures.

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