Tetrahedron Letters No.53, pp. 5569-5572, 1968. Pergamon Press. Printed in Great Britain.

REACTIONS OF EXCITED MOLECULES: VI
REACTIONS INVOLVED IN PYROLYSIS OF AROMATIC AZIDES.

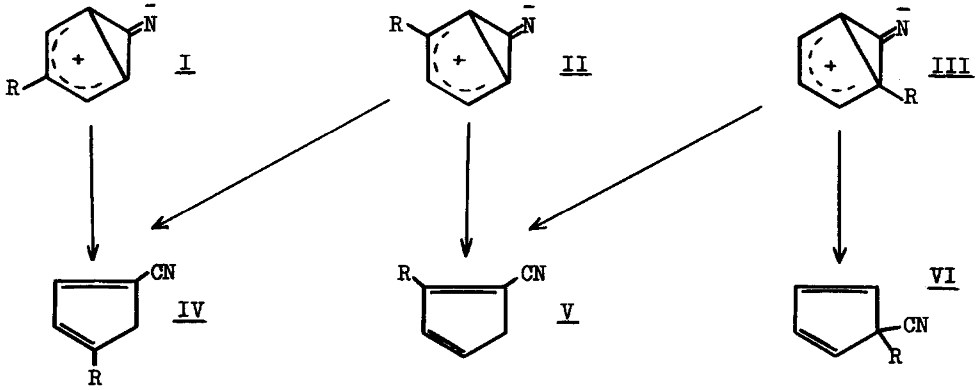
W.D. Crow and C. Wentrup
Chemistry Department, Australian National University,
Canberra, A.C.T. 2600, Australia.

(Received in UK 21 June 1968; accepted for publication 2 October 1968)

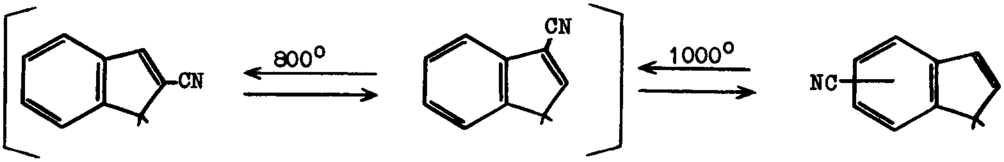
Vapour-phase pyrolysis of phenyl azide (1,2) results in the generation of a complex mixture of compounds, including the nitrene ring contraction product 1-cyanocyclopentadiene. In the course of mechanistic studies of this ring contraction we have extended the pyrolysis reaction to a variety of azides, and compared the results with those obtained from similar pyrolysis of benzotriazoles (3), which also undergo ring contraction. Elucidation of the mechanism(s) is complicated by the presence of unexpected group migrations, fragmentations and ring expansions, reported in this paper; full analysis of the mechanisms will require extensive $^{14}C/^{15}N$ labelling experiments.

Thermal Migration of Substituents. Pyrolysis of phenyl azides bearing a substituent marker (R) might be expected to give a discrete mixture of products, depending upon the nature of the transition state — Chart I describes the situation for one of the more likely possibilities (4), in which the only source of the CN-group carbon is assumed to be C_1 of the parent azide.

CHART I



Pyrolysis of substituted phenyl azides R = Me (m-, p-)(5) and R = F (o-,m-, p-) at 450°/1.0 mm. did not, in fact, proceed in accord with this scheme, the same mixture of IV and V (2 :1) being obtained in each case. Such results would normally be accepted as ruling out the mechanism proposed, but the constancy of the isomer ratio prompted us to investigate the reaction more closely. The products IV and V were separated by GLC and separately subjected to pyrolysis at 650°/0.001 mm., when it was found that each isomerised to the appropriate IV/V mixture. Since this was independent of the nature of R, it was assumed that the reaction was due to sigmatropic shifts of the cyano-group. A similar examination of the cyanoindenes showed that the 2- and 3-isomers equilibrated on pyrolysis at 800°/0.02 mm., and, further, that the CN-group could be induced to migrate into the benzenoid ring at 1000° to give 4(7)- and 5(6)-cyanoindenes.

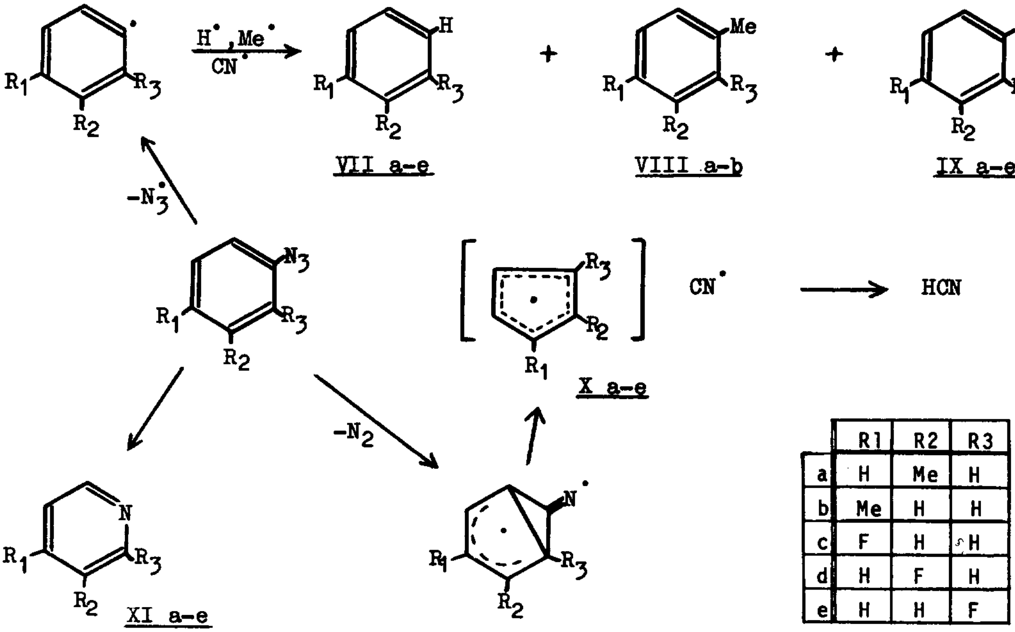


Thermal migration of the methyl-group in cyclopentadienes has recently been reported by other workers (6,7), and is consistent with our finding that 3,4- and 2,4-dimethyl-1-cyanocyclopentadienes equilibrate on pyrolysis at 500-800°.

By contrast with these results, pyrolysis of the benzotriazoles followed a quite predictable (8) course at 500°/0.01 mm, and mixtures of nitriles were not obtained until the furnace temperature was raised to 600°. The failure to obtain discrete products from pyrolysis of substituted azides could be due to the operation of a different mechanism in this case, or, alternatively, to a false concept of the actual reaction temperature. With high throughput rates, azide decomposition becomes quite violent once the furnace temperature exceeds 325°, and would be expected to generate a zone of adiabatic compression rather like a shock wave. Under these conditions the reaction zone could be at much higher temperatures than indicated by the furnace settings (9). The higher pressure (1.0 mm.) recorded during "fast" azide pyrolysis, and the carbonisation encountered, are in accord with this theory. The conclusion reached is that the position of a substituent marker in high energy reactions cannot always be relied upon to produce unequivocal evidence of the mechanism involved.

Formation of Benzene, Benzonitrile and Pyridine. The formation of substituted benzenes in azide pyrolysis is summarised in Chart II, and seems to reflect the presence of competing intermolecular processes which involve prior fragmentation of intermediates. Formation of phenyl radicals (the source of VIIa-e, VIIIa-b and IXa-e) has been ascribed (2) to a secondary reaction of vibronically excited azobenzene. The observation (10) that more than one mole of N_2 can arise from aromatic azides, even in solution, suggests that azide radical loss may also be involved, and this has recently been shown to occur in photolysis of trityl azide (11). Although we have no accurate quantitative data, azide pyrolysis does produce substantial amounts of HCN, and this is undoubtedly one of the sources of the benzonitriles IXa-e. The formation of HCN from Xa-e is in line with the demonstrated lability of the CN-group, and with our earlier postulate that a vibronically excited singlet nitrene is involved. Higher vibrational levels of the nitrene may be expected to fragment directly, or lead to hot ring-contraction products which will subsequently fragment. The stability of IV-V (R = H) to pyrolysis (99% recovery at 800°) suggests that the bulk of the HCN arises directly from the nitrene. Products arising from X a-e are not isolated (presumably fragmenting further) unless stabilised by one or two benzene rings, when indenes and fluorenes are isolated in low yield. In general, the yields of cyanocyclopentadienes and benzonitriles are roughly parallel, in the range 0-10%.

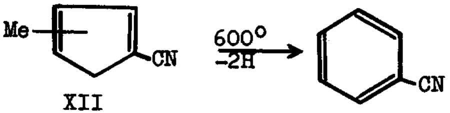
CHART II



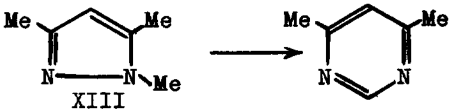
	R1	R2	R3
a	H	Me	H
b	Me	H	H
c	F	H	H
d	H	F	H
e	H	H	F

In addition to the benzenoid products of azide pyrolysis, a small and variable yield of pyridines (XIa-e) is obtained. The substitution pattern seen in these compounds is that obtained by formal exchange of nitrene N (or one of the azide N-atoms) for C_1 of the aromatic ring, with subsequent C-loss. Provided that this is a genuine unimolecular reaction of the aromatic nitrene, the nature of the leaving group presents a problem, although photochemical loss of O from pyridine-N-oxide has been recorded (12), as has that of N from the ion $CH_2N_2^+$ observed in the mass spectrum of s-triazole (13). Some degree of prior H-capture would seem more acceptable.

Ring Expansion Reactions. The study of tolyl azides is complicated by a ring expansion of the intermediates to benzonitrile, with loss of 2H. With the pure cyanocyclopentadienes XII the reaction is not observed at temperatures below 600°, but is nevertheless found in azide pyrolysis even at 300°, further evidence that the furnace temperature may not accurately reflect that of the reaction zone. The yield of benzonitrile is enhanced at the expense of XII. The dimethylcyanocyclopentadienes similarly give rise to the tolunitriles. A similar reaction in the heterocyclic field, not related to nitrene generation, is seen in the conversion (8-10%) of XIII to 4,6-dimethylpyrimidine, which occurs at 900°/0.15 mm. Such reactions are thermal analogues to the ring expansion of the benzyl ion and the M-1 ions derived from N-methylindole and N-methylpyrrole (14) on electron impact, and stress the similarities observed in high energy reactions. Both XII and XIII show prominent M-1 ions in their mass spectra, and it seems likely that subsequent reactions are due to rearranged ions.



XII



XIII

NOTES AND REFERENCES

1. W.D. Crow and C. Wentrup, Tetrahedron Letters, **1967**, 4379
2. E. Hedaya, M.E. Kent, D.W. McNeil, F.P. Lossing and T. McAllister, Tetrahedron Letters, **1968**, 3415
3. W.D. Crow and C. Wentrup, Chem. Comm., **1968**, in press
4. The transition state I-III is analogous to that proposed by Bryce-Smith and Longuet -Higgins (Chem.Comm., **1966**, 593) for conversion of the benzene singlet to fulvene. Our initial postulate of a singlet nitrene (1) is supported by the photolytic ring expansion reported by Splitter and Calvin (Tetrahedron Letters, **1968**, 2211)
5. o-Tolyl azide yields only o-toluidine and 2,2'-dimethylazobenzene. This is tentatively put down to stabilisation of the nitrene by H-bridging, with consequent decay to the triplet state. A similar effect is seen in 2,4,6-trichlorophenyl azide, which yields the corresponding azobenzene at 450° in 68% yield, presumably due to the operation of the heavy atom effect in promoting singlet-triplet transition.
6. J.W. de Haan and H. Kloosterziel, Rec. Trav. Chim., **87**, 298 (1968)
7. V.A. Mironov *et al*., Tetrahedron Letters, **1968**, 3997
8. W.D. Crow and C. Wentrup, Chem. Comm., **1968**, in press
9. An analogous situation may be seen in gas phase photolysis, where the initial excited state may convert to a high vibronic level of the ground state. In the absence of efficient collisional deactivation by a solvent, the temperature of the photolysis cell bears no relation to the energy of the reacting species. (cf. Ward, J. Amer. Chem. Soc., **89**, 2367 (1967); Crow and Wentrup, Tetrahedron Letters, **1968**, 3111)
10. P.A.S. Smith and J.H. Hall, J. Amer. Chem. Soc., **84**, 480 (1962)
11. F.D. Lewis and W.H. Saunders, Jr., J.Amer.Chem.Soc., **90**, 3828 (1968)
12. J. Streith, B. Danner and C. Sigwalt, Chem. Comm., **1967**, 979
    N. Hata and I. Tanaka, J.Chem.Phys., **36**, 2072, (1962)
13. P.R. Riggs, N.L. Parker and T.W. Shannon, Chem. Comm., **1968**, 727
14. M. Marx and C. Djerassi, J.Amer.Chem.Soc., **90**, 678 (1968).