Tetrahedron Letters No.27, pp. 3115-3118, 1968. Pergamon Press. Printed in Great Britain.

REACTIONS OF EXCITED MOLECULES V.
THERMAL DECOMPOSITION OF PYRAZINE

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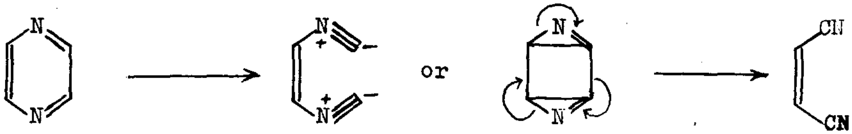
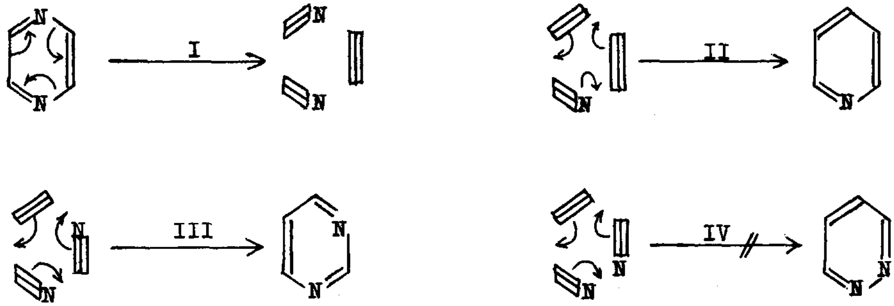
(Received in UK 25 March 1968; accepted for publication 5 April 1968)

In a previous publication (1) it was reported that pyrolysis of pyrazine-2,3-dicarboxylic anhydride led to the production of cis- and trans-dicyanoethylene, presumably through the intermediacy of 2,3-dehydropyrazine.



The required reorganisation of the N-C-C-N system to N-C-C-C-C-N could occur by either of two mechanisms, and in this connection it was of some interest to examine the thermal stability of pyrazine itself. Pyrazine may be considered as a substituted benzene in which the π-cloud has been distorted by N-substitution of the 1- and 4-atoms, and as such might be expected to undergo some thermal isomerisation, as do the xylenes (2). The stability of the products to be expected from a reverse cycloaddition reaction, however, leads to the expectation that fragmentation of vibrationally excited molecules might prove to be a major competing process. Lahmani et al.(3) have recorded a low yield of pyrimidine on photolysis of pyrazine at 2537 A, and have subsequently extended this work to the dimethylpyrazines (4), explaining the formation of the products through a diazabenzvalene intermediate.

Vapour-phase pyrolysis of pyrazine was carried out at 1270°K/2m.m. in a packed silica tube, as described previously (5). The reaction proceeded smoothly, yielding acetylene and hydrogen cyanide (36%), pyrimidine (3%), pyridine (0.7%) and 45% recovery of unreacted pyrazine. No other solid or liquid products were formed, so that the residual 15% represents gas loss to the pumping system. When lower pressure was employed, acetylene and hydrogen cyanide were still produced, but no pyrimidine or pyridine was detected - a result completely analogous to that observed with the xylenes (2), and susceptible of similar explanation. The production of pyrimidine and the absence of pyrazine seem to support the concept of ring-isomerisation, but the validity of this viewpoint is weakened by the presence of pyridine, which must arise by a cycloaddition process (I,II) between acetylene and hydrogen cyanide. The formation of pyrimidine can be ascribed to the process III; absence of pyrazine is consistent with the theory, since the N-to-N orientation (IV) would be unfavourable. Since the HCN:C_2H_2 ratio on breakdown is 2:1, the pyrimidine:pyridine ratio of 4:1 would not be surprising, and probably reflects greater thermal stability of pyridine. The absence of benzene is to be expected on similar arguments. Although HCN polymerisation was not observed in our experiments, photolysis has been reported (3) to yield a brown polymer among the products. It seems possible, then, that excitation of pyrazine to high vibrational levels may result only in fragmentation-recombination, although the possibility of ring-isomerisation cannot be ignored.



In considering the general problem of ring-isomerisation, in particular the intervention of intermediates of the benzvalene - Dewar benzene, it is interesting to speculate on the possible role played by vibrationally excited molecules in which suitable distortion has occurred. Since electronic excitation occurs too rapidly for appreciable molecular distortion to occur, according to the Franck-Condon principle, the distances involved in 1,3- or 1,4-overlap are appreciable; it seems logical to assume that conversion to vibrational energy, with consequent distortion of molecular geometry, could in many cases precede bond formation. The process could be envisaged as shown in Chart I. The production of VI by thermal excitation or by internal conversion from the electronically excited state V could lead, by twisting of the 1,2-bond, to the distorted species VII. If any reaction (other than fragmentation or reversion to starting material) is to result from this, it is necessary to invoke some reason for prolonging the lifetime of such a species. From the electronic point of view, VII bears a marked resemblance to the spirene VIII, lacking only the sterically stabilising influence of the spiro-atom. Fragmentation of VII would be a likely process, but if the principle of spiroconjugation (6,7) permits the required overlap, electronic reorganisation to a distorted form of IX could compete successfully.

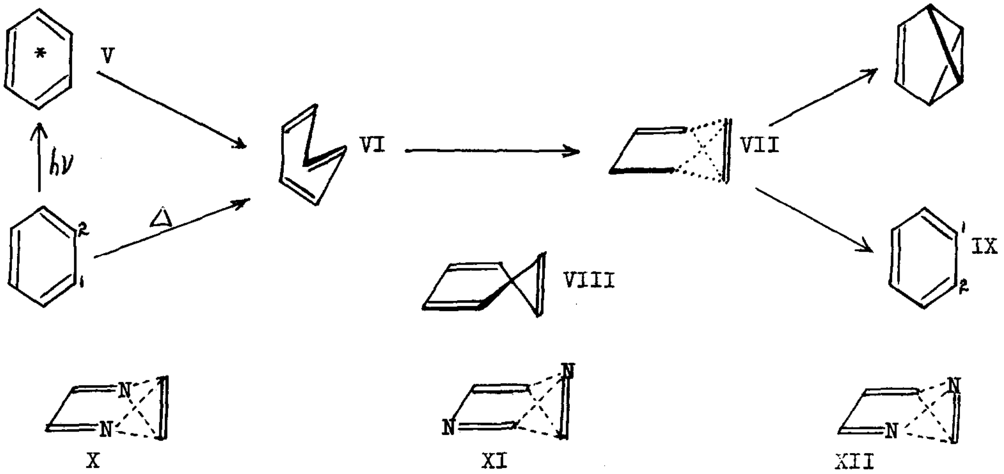


CHART I

The characteristics of the 2,1-spiropolyenes such as VIII, classified as Class III (6) include a "spiro" bond order of 0.204, with charge transfer from diene to monoene. Both should react against fragmentation, and lead to a greater probability of intramolecular formation of valence isomers. The energy of a system such as VII, plotted against the interplanar angle ϕ,might be represented as shown in Fig.I (solid line). In the presence of bulky groups, which preferentially destabilise the planar state, the depth of the energy trough (dotted line, Fig.I) may permit the isolation of compounds such

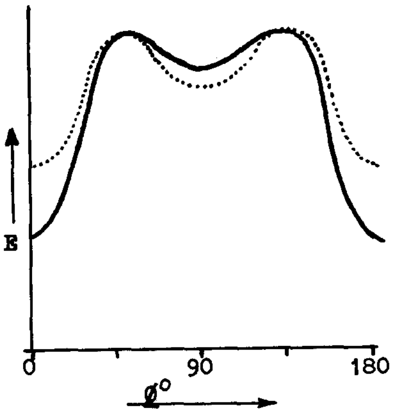


Fig. I

Dewar benzene, benzvalene etc.,as is observed in the case of the 3°-butylated benzenes (8,9). The isolation of fulvene (10) from benzene photolysis suggests the stabilising influence of steric crowding in benzvalene.

Fragmentation would always be a competing pathway, and it is instructive to consider the two possible intermediates for the isomerisation of pyrazine, X and XI. Operation of the postulated mechanism through X would not normally be detected, due to the symmetry factor, but the presence of two N-atoms in the diene system, with a consequent loss of electron-donating power, would be expected to favour fragmentation. The alternative species XI, which could lead to pyrimidine, would be energetically more attractive (diene less electron-attracting,monoene more so). One might also predict the failure of pyrimidine, once formed, to isomerise to pyridazine, due to N - N repulsion in the intermediate species XII.

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