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THE MECHANISM OF THE PELLIZZARI TRANSFORMATION OF α-CYANOPHENYLHYDRAZINE

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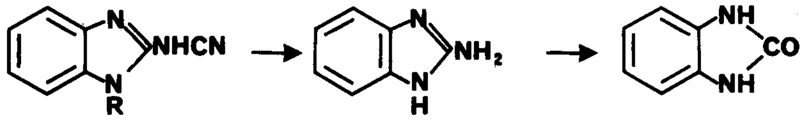
Despite the mechanistic attention paid to other transformations of hydrazine derivatives that of α-cyanophenylhydrazine into 1-cyano-2-cyanaminobenzimidazole by ethanolic cyanogen bromide, has received no attention since its original description[3]. A suspicion, subsequently justified, that it was related to a class of molecular rearrangements being studied in this laboratory[2] led to the present investigation.

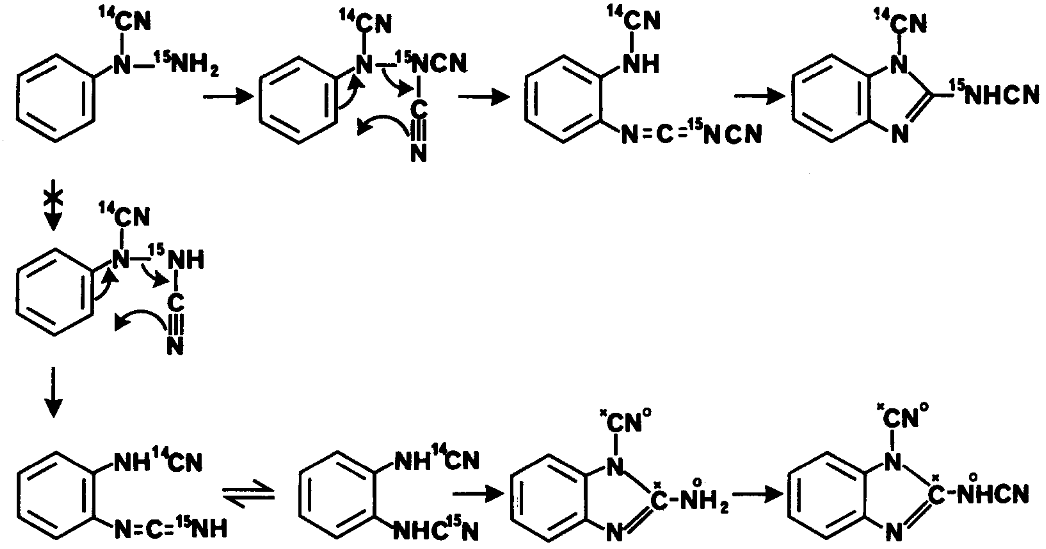
As preliminary attempts to identify possible intermediates were unsuccessful, isotopic labelling experiments have been employed to establish the mechanistic pathway. Application of established selective hydrolysis reactions permit the stepwise removal of the N-cyano groups of (I) and the resulting 2-aminobenzimidazole (III) can be converted into benzimidazolidinone (IV) by treatment with nitrous acid. Treatment of α-^{14}C-cyano)phenylhydrazine (6.88×10^7 d.min^{-1} mole^{-1}) with cyanogen bromide gave (I) (6.93×10^7 d.min.$^{-1}$ mole^{-1}) which gave inactive (II) on hydrolysis. Conversely, ^{14}C-cyanogen bromide converted α-cyanophenylhydrazine into (I) (14.61×10^7 d.min.$^{-1}$ mole^{-1}), which was successively hydrolysed to (II) (13.62×10^7 d.min.$^{-1}$ mole^{-1}) and (III) (6.58×10^7 d.min.$^{-1}$ mole^{-1}). Subsequently α-cyanophenylhydrazine with the β-nitrogen atom enriched with ^{15}N was prepared and converted into (I). The initial ^{15}N enrichment of 2.16% was retained through the degradation sequence as far as (III) but was completely lost on conversion to (IV). These experiments show that the α-cyano group of the starting material furnishes the 1-cyano substituent of (I), and that the β-nitrogen atom of α-cyanophenylhydrazine supplies the exocyclic amino nitrogen.

The fairly high yields of (I) obtained in this reaction and the apparent absence of p-phenylenediamine derivatives from the reaction mixture suggest an intramolecular mechanistic pathway analogous to that established[2,3] for the thermal rearrangement of N-aryl-N'-cyanohydrazine derivatives. Two variants may be considered depending on whether the αβ-dicyano- or α,β,β-tricyanophenylhydrazine undergoes the key [3.3]-sigmatropic rearrangement. As Scheme 1 demonstrates these two pathways predict differing locations of labelled carbon



I R = CN
II R = H
III
IV

Scheme



and nitrogen atoms in the product. Only the sequence proceeding *via* the αββ-tricyanophenylhydrazine is in accord with the foregoing labelling experiments.

The synthetic scope of this reaction and the generation of polycyanohydrazines are being studied.

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