Tetrahedron Letters No.36, pp. 3151-3154, 1970. Pergamon Press. Printed in Great Britain.

THE ORIGIN OF THE C≡N GROUP OF BENZONITRILE FORMED ON PYROLYSIS OF OXINDOLE AT 850°

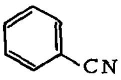
R. F. C. Brown and M. Butcher

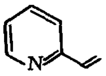
Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

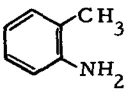
(Received in UK 23 June 1970; accepted for publication 2 July 1970)

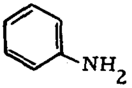
The five-membered lactam system of oxindole is substantially decarbonylated on flash pyrolysis in a vacuum flow system, and a complex mixture of products is formed. The evidence presented below suggests the occurrence of unexpected sequences of contraction and expansion of the benzene ring in this process.

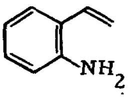
Pyrolysis of oxindole (2.0 g) over a silica packing at 850°/0.1 mm[1] gave a black tar which collected immediately outside the hot silica tube, together with a more volatile liquid fraction (0.66 g) which contained benzonitrile (26% yield) and other products[2] shown below :







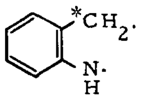


Our interest in the mechanism of formation of benzonitrile was aroused by the further observation that similar pyrolysis of 5-methyloxindole gave a mixture of all three tolunitriles, although the individual tolunitriles did not isomerise under the same conditions.

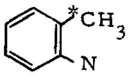
Pyrolysis of 3-[^{14}C]-oxindole (V) gave radioactive benzonitrile, which was diluted with unlabelled benzonitrile and hydrolysed to benzoic acid. Schmidt degradation of the purified benzoic acid (3.98×10^4 c.p.m./mM; 100%) gave aniline, isolated as acetanilide (3.82×10^4 c.p.m./mM; 96.1%), and carbon dioxide which was counted as barium carbonate (uncorrected scintillation count[3] 8×10^2 c.p.m./mM; 2.0%). Thus the nitrile group of benzonitrile formed in this pyrolysis is derived almost exclusively from the benzene ring of oxindole, and C-3 of oxindole is incorporated into the ring of benzonitrile.

Pyrolysis of 3-[^{13}C]-oxindole (59% enriched; 32 mg) gave labelled benzonitrile which, likewise, was not significantly labelled in the nitrile group; the infrared spectrum showed an intense sharp band at 2230 cm^{-1} (^{12}C≡N) accompanied by a barely detectable band at 2180 cm^{-1} (^{13}C≡N), just as in unlabelled benzonitrile with ^{13}C in natural abundance[4]. Comparison of the ^{13}C-satellite band pattern (J_{C-H} ca 165 Hz) in the 100 MHz p.m.r. spectrum of this sample with the reported analysis[5] of the p.m.r. spectrum of benzonitrile, and with the ^{13}C-satellite pattern of unlabelled benzonitrile (neat liquid), indicated that ^{13}C was certainly present in the ortho and meta positions, and was probably randomly distributed over the ring positions.

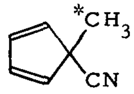
Any pathway proposed for the pyrolytic formation of benzonitrile must account for the results of these experiments using methyl and isotopic labels. Amongst a number of possible intermediates related to the probable initial species (I) we have given particular attention to o-tolylnitrene (II) and the nitriles (e.g. III) derivable from it by ring contraction[6,7], and also to tropyl systems (e.g. IV) which might be formed by ring expansion. The relevance of such intermediates is shown by the results of experiments with o-tolyl and tropyl azides (Table 1).



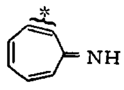
I



II



III



IV

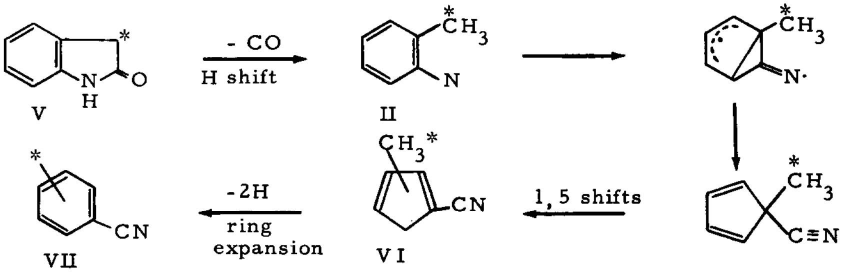
Table 1. Percentage yields of liquid products of pyrolysis at 850°.

	Oxindole	o-Tolyl Azide	Tropyl Azide
Benzene	8	3	62
Toluene	-	1.5	-
Benzonitrile	26	8	8
2-Vinylpyridine	3	0.7	3
o-Toluidine	4	10	-
Aniline	4	4	-
o-Aminostyrene	0.8	2.5	-
Indole	-	0.7	-

(A dash, -, indicates a low yield (< 0.2%) rather than total absence of a product).

Even allowing for the difficulty of performing truly comparable experiments, it is clear that o-tolylnitrene is a likely intermediate, and that tropyl systems may also be involved, although neither type of intermediate adequately accounts for the distribution of products from oxindole.

The labelling results for benzonitrile, however, are well accommodated by the sequence arylnitrene →cyanocyclopentadiene[6,7], which in the m- and p-tolyl series leads further to benzonitrile[6b] above 600°. o-Tolyl nitrene formed from o-tolylazide at 450° dimerises to o-azotoluene[6b], but the products shown above suggest that formation of benzonitrile via cyanomethylcyclopentadienes must be important at 850°. A possible pathway of formation of labelled benzonitrile (VII) from labelled oxindole (V) is shown below; however, a similar pattern of labelling could result from the intermediacy of tropone imine (IV).



The mass spectrum of oxindole[8,9,10] is dominated, after initial loss of CO, by two processes each involving loss of HCN : (i) m/e 105 →78, and (ii) 104 →77. It has been proposed that the loss of HCN from the ion of m/e 104 involves loss of C-3 of oxindole[10], but in view of our pyrolytic results and the parallelism of many mass spectral and pyrolytic fragmentations[11,12] we considered loss of a carbon atom of the benzene ring to be more likely.

The 70eV mass spectrum of the sample of 3-[^{14}C]oxindole was examined using high resolution measurements in the regions m/e 104 - 106 and 76 - 79; abundance ratios in the latter region were estimated by a procedure following that of Robertson and Djerassi[13]. As expected, the loss of unlabelled HCN (and hence of a benzene ring carbon) was the major process (ca. 70% for (i) and 75% for (ii)), and the loss of H^{13}CN was a minor process (ca. 30% and 25% respectively). It is our view that this similarity between the pyrolytic and mass spectral results is not fortuitous, and that if discrete structures are to be written for the ions of m/e 104 and 105, then structures related to (IV) and (VI) must be considered.

We thank Dr. S. Middleton (Monash) and Dr. A. V. Robertson (Sydney) for mass spectral measurements, and for valuable discussion. This work was supported by a grant from the Australian Research Grants Committee.

Notes and References

1 The apparatus used has been described by R. F. C. Brown and M. Butcher, Aust. J. Chem., 22, 1457 (1969).

2\. Products were isolated by preparative gas chromatography (12' x $\frac{1}{4}$" column of 20% fluorosilicone QF-1 on silanised Chromosorb W) and identified by i.r., n.m.r., u.v. and mass spectrometry.

3\. Organic compounds were counted in a toluene scintillator solution. Barium carbonate was suspended in the scintillator containing 4% Cab-o-sil; the count has not been corrected for reduced counting efficiency.

4. B. Bak, J. T. Bielsen, and L. Lipschitz, Acta Chem. Scand., 15, 949 (1961).
5. K. Hayamizu and O. Yamamoto, J. Mol. Spectrosc., 25, 422 (1968).
6. (a) W. D. Crow and C. Wentrup, Tetrahedron Lett., 4379 (1967).
   (b) W. D. Crow and C. Wentrup, Tetrahedron Lett., 5569 (1968).
7. E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, Tetrahedron Lett., 3415 (1968).
8. J. C. Powers, J. Org. Chem., 33, 2044 (1968).
9. T. Hino, M. Nakagawa, K. Tsuneoka, S. Misawa, and S. Akaboshi, Chem. Pharm. Bull. (Tokyo), 17, 1651 (1969).
10. J. A. Ballantyne, R. G. Fenwick, and M. Alam, Organic Mass Spectrometry, 1, 467 (1968).
11. E. K. Fields and S. Meyerson, Acc. Current Res., 2, 273 (1969).
12. R. F. C. Brown and R. K. Solly, Aust. J. Chem., 19, 1045 (1966).
13. A. V. Robertson and C. Djerassi, J. Amer. Chem. Soc., 90, 6992 (1968).