Tetrahedron Letters,Vol.29,No.4,pp 489-490,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Journals Ltd.

EXPANSION OF A PYRIDINE RING BY A NITRENE

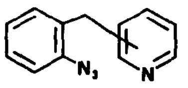
Gurnos Jones* and David C. York

Department of Chemistry, University of Keele

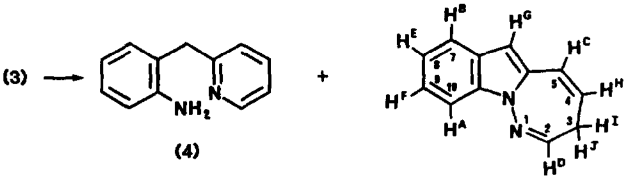
Keele, Staffordshire, ST5 5BG, England.

Summary. Pyrolysis of 2-(*o*-azidobenzyl)pyridine (3) gives 3H-1,2-diazepino[1,7-a]indole (5), in which the intermediate nitrene has expanded the pyridine ring.

We have shown[1-4] that pyrolysis of *o*-azidodiphenylmethane in solution gives azepinoindoles, in which the intramolecular attack of the intermediate nitrene has expanded the adjacent benzene ring. In contrast, pyrolysis of 3- and 4-(*o*-azidobenzyl)pyridines (1) and (2), in solution at 190-200˚C gave largely polymeric material; flash vacuum pyrolysis gave azaacridans and azaacridines, without expansion of the pyridine ring.[5] There are thus no examples of direct ring expansion of a pyridine ring by nitrenes, prior to our presently reported formation of a diazepinoindole from 2-(*o*-azidobenzyl)pyridine.

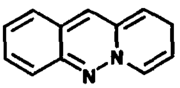


(1) 3-pyridyl
(2) 4-pyridyl
(3) 2-pyridyl

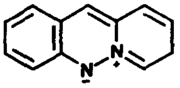


(4)

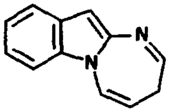
(5)



(6)



(6a)



(5a)

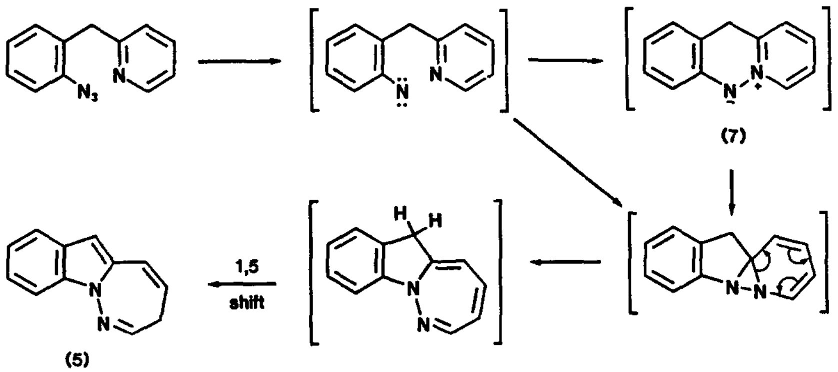
The pyrolysis of compound (3) in trichlorobenzene at 190-120˚C (5 h.) was conducted under an argon atmosphere, as were all working-up procedures. Nevertheless the crude product darkened rapidly, and all fractions from the purification by Chromatotron were reddish to brown. A quantity of amine (4) (25%) was isolated, and a second fraction, pure by ^1H n.m.r., had the molecular formula $C_{12}H_{10}N_2$(M^+ = 182·0844269; required M^+ 182·084394) (41%). Significant peaks in the ^{13}C n.m.r. spectrum were at δ31.9 (CH_2), at δ95.7 (^1J = 173 Hz), matching well with C3 of an indole or C11 of an azepinoindole (δ97 to 98, ^1J = 173 Hz), and at δ140 (^1J = 181 Hz), comparable with the -CH = N of a phenylhydrazone (acetaldehyde phenylhydrazone has δ138 and J = 183 Hz). The ^1H n.m.r. shifts and coupling constants, determined at 400 MHz are listed in Table I; 2D COSY showed the sequences $=CH^D - CH_2^{I,J} - CH^H = CH^C-$ and $-CH^A = CH^F - CH^E = CH^B$. The latter sequence, from the shifts and coupling constants, is in an ortho disubstituted benzene ring. A singlet at δ6.4 corresponds exactly with H11 of an azepinoindole and the sequences shown fit either of the diazepinoindoles (5) or (5a). Two further pieces of evidence confirm structure (5); an NOE difference spectrum shows interaction between H^B, H^G (the indolic proton), and H^C, while $Eu(fod)_3$ caused substantial downfield shifts in H^A and H^D. Two azaacridan structures (6) and (6A) are also possible, but do not fit the spectral evidence and both have allowed [1,5]sigmatropic shifts which would produce more stable structures.

TABLE 1 ^1H N.m.r. shifts of compound (5) in $CDCl_3$

Signal	δ(ppm)	Multiplicity	J values (Hz)	Assignment
H^A	8·2	d of d of d	7·15, 1.5, and 1	H4
H^B	7·29	d of t	9 and 1·5	H1
H^C	6·87	d(br)	9	H10
H^D	6·85	t(br)	4.2	H7
H^E	6·75	d of d of d	9, 6·6, and 1·2	H2
H^F	6·5	d of d of d	7·2, 6·7, and 1·2	H3
H^G	6·4	s(br)		H11
H^H	5·29	d of t of d	9, 6·5, and 0.69	H9
$H^{I,J}$	2·57	d of d of d	6·5, 4·2, and 0.35	H8, H8'

We have already established that ring expansion does not occur with the isomeric 3-substituted pyridine (1) and hence insertion in the 2,3-bond of the pyridine ring in compound (2). Indeed, we would expect attack at the nitrogen atom to give compound (7) which is readily converted into compound (5). If the insertion were into the pyridine 1,2-bond to give compound (8) an electrocyclic disrotatory ring opening, followed by a [1,5]sigmatropic shift would give compound (5). These suggestions are illustrated in the SCHEME.

SCHEME



We thank Drs. O.W. Howarth and A.T. Harrison of the SERC High Resolution N.M.R. Unit at the University of Warwick for the 400 MHz determinations, Dr. J.A. Ballantine of the SERC Mass Spectrometry Service at University College, Swansea for an exact mass measurement, and Mr. J. Clews for skilled technical assistance.

References

1. G.R. Cliff, E.W. Collington and G. Jones, J. Chem. Soc. (c), 1970, 1490.
2. G.R. Cliff and G. Jones, J. Chem. Soc. (c), 1971, 3418.
3. R.N. Carde and G. Jones, J. Chem. Soc. Perkin Trans. I, 1974, 2066.
4. R.N. Carde, P.C. Hayes, G. Jones, and C.J. Cliff, J. Chem. Soc., Perkin Trans. I, 1981, 1132.
5. M.G. Hicks, G. Jones, and D.C. York, J. Chem. Soc., Perkin Trans. I, in press.

(Received in UK 7 December 1987)