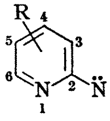
Nitrogen Scrambling in 2-Pyridylnitrene

By W. D. CROW and CURT WENTRUP*†

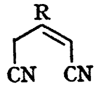
(*Chemistry Department, Australian National University, Canberra, A.C.T. 2600, Australia*)

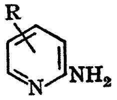
Summary Substituent- and ^{15}N-labelling in 2-pyridylnitrene (V) demonstrates nitrogen scrambling in the gas phase *via* an intermediate which has the geometry of 2,7-diazatropylidene (VI).

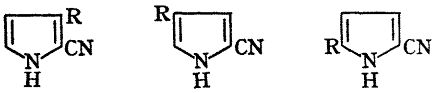
IT was reported previously[1] that 2-pyridylnitrenes (I) and 2- and 4-pyrimidylnitrenes, generated thermally from the corresponding tetrazoloazines, undergo ring contraction to cyanoazoles [*e.g.* (IV)] in the gas phase. Pyrazinylnitrene reacts analogously[2] whereas 3-pyridazinylnitrene loses nitrogen from the ring with formation of a C_4H_3N species, which isomerises to cyanoallene, tetrolonitrile, and prop-2-ynyl cyanide.[2] In the case of 2-pyridylcarbene, isomerisation to phenylnitrene occurs, and it was suggested[3] that this involves a carbene insertion/nitrene extrusion cycle. Assuming a similar mechanism to operate, 2-pyridylnitrene (I) would be degenerate, and thus nitrogen scrambling should be observed.


(I)


(IIa)


(IIb)


(III)

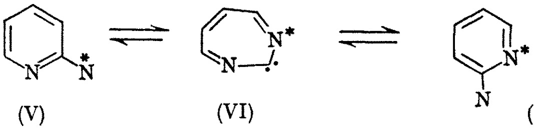

(IV)

R	(IIa)	(IIb)	(III)	(IV)		
3-CH_3	2	0	10[b]			45
4–CH_3	1·6	3	4·4[c]	17	28	
5–CH_3	6	3	4[c]	17	28	
6–CH_3	1·3	0	10[b]			45

[a] By pyrolysis of corresponding tetrazolo[1,5-*a*]pyridines[1] at 380°/0·05 mm.; total yields are given and account for ⩾90% of isolated product. The lost material gave rise to black tar inside the pyrolysis tube. 3-Cyanopyrroles were formed above 500° (ref. 1). Analysis by g.l.c. on 5 ft. × $\frac{1}{8}$ in. column of 5% Carbowax 20M on Aeropak; 60 ml He/min.; programmed at 2°/min. from 125° to 250°.

[b] 1 : 5 Mixture of 3- and 6-methyl-2-aminopyridine. [c] 1 : 1 mixture of 4- and 5-methyl-2-aminopyridine.

In the thermal generation of 2-pyridylnitrenes (I), glutacononitriles (II) and 2-aminopyridines (III) are also formed (1—6% and 1—10%, respectively; see Table). It is now observed that, when a methyl group is present in (I; R = Me), not only are the expected products (II) and (III) formed, but in addition, lower yields of isomeric products where the methyl group appears in another position are formed as well (Table). The products are perfectly stable under the reaction conditions (380°/0·05 mm.), and the peculiar isomer distribution is explicable only in terms of an intermediate which has an arrangement of atoms as in 2,7-diazatropylidene (VI):‡


(V) (VI) (VII)

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† Present address: Institut de Chimie Organique, Université de Lausanne, 1005 Lausanne, Switzerland.

‡ A number of resonance forms and valence isomers, such as 2,7-diazabicyclo[4,1,0]hepta-2,4,7-trienes, can be written. Of these, (VI) is the simplest. The main point is the equivalence of the nitrogen atoms; *cf.* ref. 3.

in which the two nitrogens are equivalent. It is seen that, if the original nitrene (V) carries a methyl group in the 6-position, no glutacononitrile can be formed by simple ring-opening, but by isomerisation *via* (VI), a glutacononitrile derived from (VII) (Me in position 3) can be, and was, formed. If, on the other hand, (V) carries a methyl group in the 3-position, it can, and does, give 2-methylglutacononitrile (IIa), but the new nitrene (VII) cannot give any such product, and indeed, only (IIa) was formed. Irrespective of substitution, both (V) and (VII) can give aminopyridines, as was also observed (Table).

In order to confirm the intermediacy of (VI), [1,3-^{15}N]-tetrazolo[1,5-*a*]pyridine (8·37 atom-% ^{15}N) was prepared from 2-bromopyridine and potassium [1-^{15}N]azide. Pyrolysis will produce the nitrene (V), labelled on the nitrene-N with 4·19% ^{15}N. The isolated 2- and 3-cyanopyrroles[1] and 2-aminopyridine (III; R = H) all showed 4·19 ± 0·02% ^{15}N. Hydrolysis of the cyanopyrroles gave pyrrolecarboxylic acids which still contained 2·15 ± 0·15% ^{15}N, and diazotization and hydrolysis of the aminopyridine gave 2-pyridone with 2·1% ^{15}N. Thus evidently approximately 100% scrambling of the two nitrogens in (V) had taken place, verifying the equilibrium (V) $\rightleftharpoons$ (VI) $\leftrightharpoons$ (VII).

It thus appears that both 2-pyridylnitrene and 2-pyridylcarbene[3] undergo ring-expansion in high yield in the gas phase, whereas phenylnitrene[3] is lower on the energy surface than either pyridylcarbene or azatropylidene. The explanation may be sought in the higher ability of the benzene ring to sustain an electronegative substituent. It may be predicted that phenylcarbene (VIII) should undergo carbon-scrambling *via* tropylidene (IX) only in low yield, whereas tropylidene should rearrange to phenylcarbene at sufficiently high temperature. One indication that this is so has already appeared.[4]

(VIII) (IX)

The isotopic abundances were determined on an A.E.I. MS 902 mass spectrometer and confirmed by high-resolution measurements. We thank Dr J. K. MacLeod for these determinations.

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[1] W. D. Crow and C. Wentrup, *Chem. Comm.*, 1968, 1082.

[2] C. Wentrup, unpublished data.

[3] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1968, 6149; C. Wentrup, preceding communication.

[4] P. Ashkenazi, S. Lupan, A. Schwarz, and M. Cais, *Tetrahedron Letters*, 1969, 817.