The Aromatic Nitrene–Carbene Interconversion

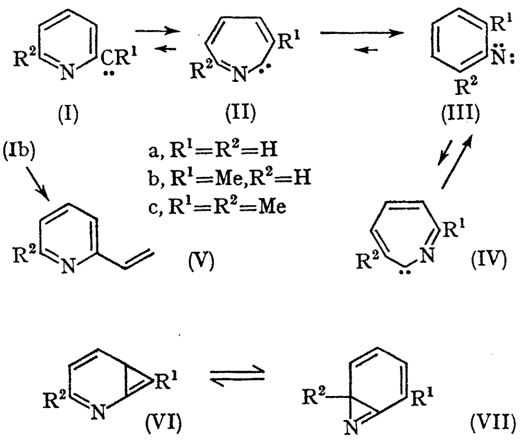
By CURT WENTRUP

(*Institut de Chimie Organique, Université de Lausanne,* 1005 *Lausanne, Switzerland*)

Summary Gas-phase pyrolysis of 2,6-dimethylphenyl azide (IIIc) gives 2-vinyl-6-methylpyridine (Vc) in agreement with nitrene–carbene interconversion *via* 2-azatropylidene (II) or valence isomers thereof.

IN previous work[1] we described the isomerisation in high yield of 2-pyridylcarbenes (I) to phenylnitrenes (III) with a substituent pattern indicative of an intermediate with the skeletal geometry of 2-azatropylidene (II).†

The reverse reaction, (III) → (I), explains the formation, in low yield, of pyridines by pyrolysis of phenyl azides[2,3] and by the photochemical triethyl phosphite deoxygenation of aromatic nitro-compounds reported by Sundberg and his co-workers.[4] However, Sundberg's pyridines were formed only when an *ortho*-methyl group was present in the nitrene (IIIb). According to the mechanism above, this should lead to a pyridylmethylcarbene (Ib), which is known[1] to isomerise to 2-vinylpyridine (V). No vinylpyridines were reported in the work of Sundberg *et al.*,[4] but only the coupling product of the carbene (Ib) and the nitrene (or nitroso-compound when the starting material was a nitrosobenzene[4a]). This could conceivably be due to solvent-participation: triethyl phosphite is a good nucleophile, and in fact Sundberg's group [4c] was able to isolate both *N*-arylphosphorimidates [ArN : P(OEt)$_3$] and a phosphorylated azepine corresponding to trapping of the ring-expanded intermediate (IIb) by solvent. Cadogan and his co-workers[5] have similarly isolated azepines corresponding to the isomeric intermediate (IVb) in thermal deoxygenation. If, therefore, both the nitrene (III) and the resulting carbene (I) are stabilised by complexing with the solvent, this



SCHEME

---

† Only the gross arrangement of atoms in the intermediate(s), not the exact nature of the bonding is known.[1] The bicyclic valence isomers (VI) and (VII) of (II) suffice to explain the reaction, as has been suggested by Cadogan[5] concerning the mechanism of formation of pyridines in the reaction of nitroso-compounds with phosphites (*vide infra*), and all the intermediates (VI, VII, II, IV, *etc.*) may be in equilibrium.[1] Since there is no evidence for the actual involvement of any one of the possible isomers, we choose to represent them by the simplest and least space-consuming, (II) and (IV).

provides the explanation why the carbene (Ib) does not rearrange to (V). No such solvent-effect is possible in the gas phase.

The gas-phase pyrolysis of 2,6-dimethylphenyl azide (IIIc precursor) is now reported to yield 2-vinyl-6-methylpyridine (Vc).‡ The yield increases with temperature and with decreasing pressure; 8% was formed at 900°/0·02 mm.§ This yield is several times higher than the yields of pyridines obtained when no *ortho*-methyl groups are present in the starting azide[2] (1—2%). In the latter case, there is evidence that the pyridines formed[2] arise also according to the above scheme: ^{15}N-labelling showed that the nitrene-N was retained in the pyridines, and labelling of the *ortho*-positions in (IIIa) with deuterium demonstrated *intermolecular scrambling of* ortho-*hydrogens* in the formation of pyridines.[3] This can be explained if the pyridylcarbenes (I) dimerise to 1,2-di-(2-pyridyl)ethylenes (py·CH=CH·py) which are unstable under the reaction conditions, cleaving to pyridine and ethynylpyridine. Full details of this work will be reported elsewhere.

(*Received, September 18th,* 1969; *Com.* 1409.)

---

‡ Identified by i.r., u.v., and mass spectral comparison with an authentic sample. The loss of C_2H_2 on mass spectrometry is characteristic of 2-vinylpyridines.[3]

§ 2,6-Xylidine (30%), benzonitrile (18%), indole (15%), and a methylindole were also formed.

[1] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1968, 6149.
[2] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1968, 5569.
[3] C. Wentrup, Ph.D. Thesis, Australian National University, 1969.
[4] (a) R. J. Sundberg, *J. Amer. Chem. Soc.*, 1966, **88**, 3781; (b) R. J. Sundberg, W. G. Adams, R. H. Smith, and D. E. Blackburn, *Tetrahedron Letters*, 1968, 777; (*c*) R. J. Sundberg, B. P. Das, and R. H. Smith, *J. Amer. Chem. Soc.*, 1969, **91**, 658.
[5] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.