Tetrahedron Letters No.59, pp. 6149-6152, 1968. Pergamon Press. Printed in Great Britain.

REACTIONS OF EXCITED MOLECULES: VII

Thermal Interconversion of 2-Pyridylcarbene and Phenyl Nitrene

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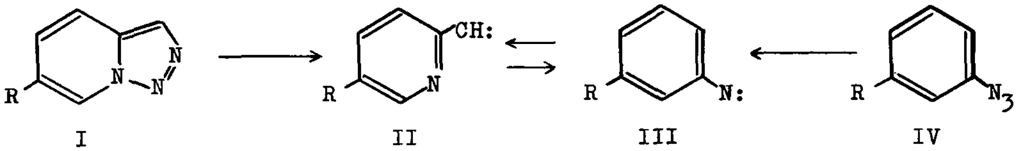
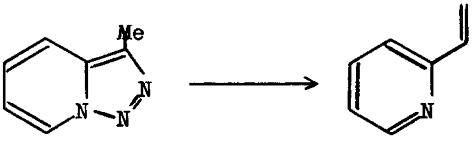
(Received in UK 28 October 1968; accepted for publication 11 November 1968)

We have earlier reported isomerisation of phenyl nitrenes to 1-cyanocyclopentadienes (1), and formation of pyridines (2) from the same source, during gas phase pyrolysis of phenyl azides. We now report the thermal interconversion of 2-pyridylcarbene and phenyl nitrene, a further isomerisation on the C_6H_5N energy surface. The ethynylpyrroles, another stable molecule likely to be encountered as a component of the surface, have not so far been detected.

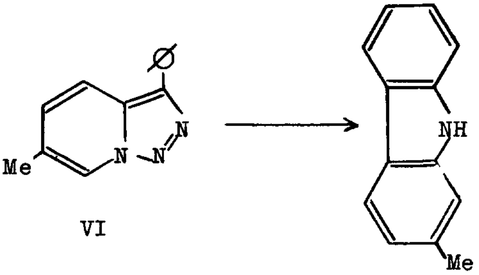
Formation of pyridines in pyrolysis of phenyl azides must involve some form of N-insertion / C-extrusion cycle, with (in this case) loss of the extruded C-atom. The possibility of an equilibrium between II and III prompted us to approach the system from the 2-pyridylcarbene side; pyrolysis of triazolopyridines (3) was accordingly extended to the 2-pyridylcarbene generator v-triazolo[1,5-a]pyridine (I, R = H). At 500°/0.04mm. this afforded aniline (4%) and azobenzene (77%), products characteristic of phenyl nitrene as formed in the mild pyrolysis of phenyl azide (1). Similarly, I (R = Me) (4) gave 3,3'-dimethylazobenzene and m-toluidine under the same conditions. At 800°/0.10 mm. the reaction products were very similar to those from violent pyrolysis of m-tolyl azide; the GLC traces of the two pyrolysates showed striking similarity (5). Table I lists the main identified products from the reactions.



The pyrolysis products from I (R = Me) are indicative of a mechanism in which carbene insertion into the 2,3-bond of the pyridine ring is followed by the extrusion of the pyridine-N onto C_2, although other possibilities exist. Confirmatory evidence was sought by marking the triazole ring itself, in an attempt to fix the location of C_1 in the products. The triazolopyridine V did not isomerise, the initial carbene stabilising preferentially by insertion into the C-H bond to give only 2-vinylpyridine (quantitative at 5-800°/0.1-0.2 mm.). The corresponding phenyl derivative, however, isomerised smoothly at 500°/0.02 mm., and gave carbazole in high yield. When the pyridine ring was simultaneously tagged with a methyl group, as in VI, 2-methylcarbazole was formed in 94% yield.



V



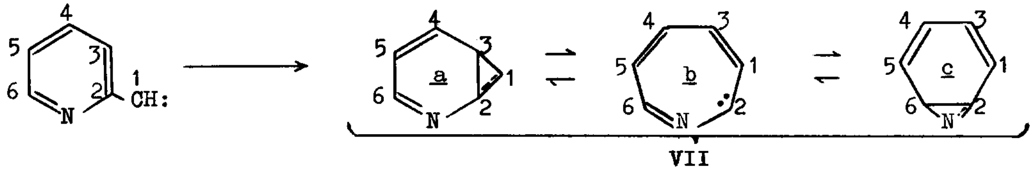
VI

TABLE I

Pyrolysis of I and IV (R = Me). (%Yield)*

	I	IV
Toluene	10.2	3.7
m-Xylene	0.34	0.18
Pyridine	0.11	----
α-Picoline	0.38	0.26
β-Picoline	15.3	2.1
γ-Picoline	---	---
2,5-Lutidine	4.1	0.05
2,3-Lutidine	---	0.05
4-Vinylpyridine	trace	trace
3-Vinylpyridine	trace	0.09
1-Cyano-2-methyl-cyclopentadiene	trace	0.2
1-Cyano-4-methyl-cyclopentadiene	trace	0.4
Benzonitrile	0.60	0.95
m-Tolunitrile	1.1	0.58
m-Toluidine	4.3	2.28
2-Cyano-5-methyl pyridine	2.0	trace (VPC only)

These results are consistent with the existence of an intermediate (or transition state) in which the atoms are disposed as in VII. The nature and extent of the bonding in VII is difficult to assess under the high energy conditions of the reaction. Examination of Table I reveals some evidence for a more concerted mode of reaction, in which ring expansion, ring contraction, and elimination of a leaving group occur simultaneously. We have previously (2) suggested the loss of $N_3^{\cdot}$ from phenyl azides as a source of the phenyl radicals which give rise to benzenes and benzonitriles observed in azide pyrolysis.



VII

The formal analogy to this in the triazolopyridines would be loss of $CHN_2^{\cdot}$ to form the 2-pyridyl radical; it is tempting to assume that concerted loss of either fragment ($N_3^{\cdot}$ or $CHN_2^{\cdot}$) may occur in both types of compound. Thus the formation of toluene (10%. $-N_3^{\cdot}$) and β-picoline (15%. $-CHN_2^{\cdot}$) from I (R = Me) would correspond to the formation of the same products (4%. $-N_3^{\cdot}$ and 2%. $-CHN_2^{\cdot}$ respectively) from IV (R = Me). Similarly, production of 2-cyano-5-methyl-

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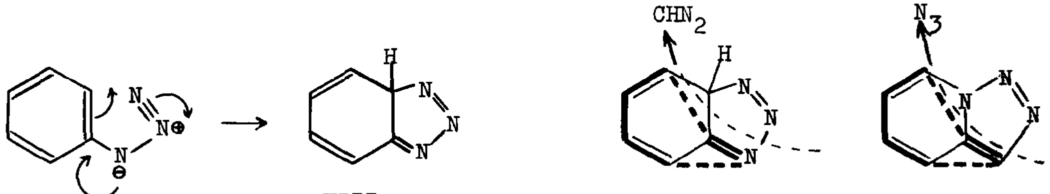
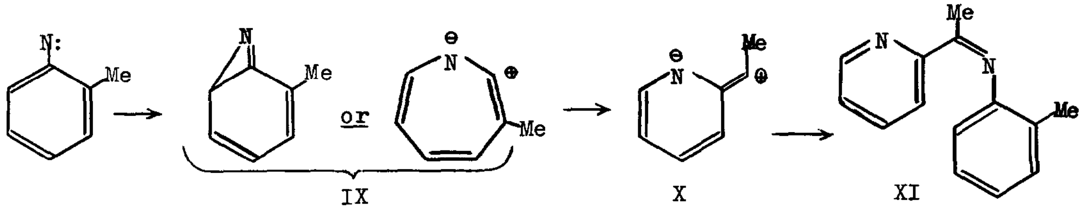
*GLC on a 12' x 1/6" column (20% Carbowax 20M on Embacel). Temperature 90°, programmed at 2°/min. Carrier gas, helium at a flow rate of 60 ml./min.

pyridine from I (R = Me) (2%. -CHN$_2^\bullet$ + CN$^\bullet$) would correspond to formation of m-tolunitrile (0.6%. -N$_3^\bullet$ + CN$^\bullet$) from IV (R = Me). Although this is far from compelling evidence for a concerted reaction mechanism, it is of interest to note that phenyl azide is converted to benzotriazole on irradiation (6), presumably *via* the intermediate VIII, which possesses a structure permitting ready loss of CHN$_2$ with formation of the 2-pyridyl radical. This, coupled with the fact that benzotriazole does not itself form pyridine on pyrolysis (3), suggests the possibilities for concerted modes of fragmentation as shown by the dotted lines in the formulae below.

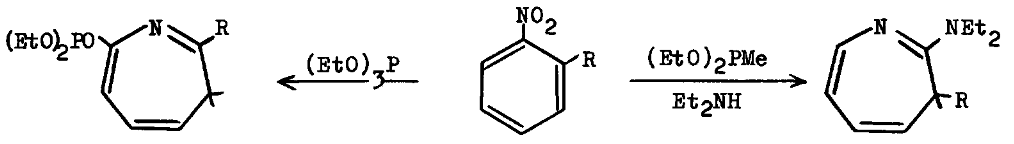


VIII

A similar type of N-insertion/C-extrusion reaction has been reported by Sundberg and co-workers (7), in the deoxygenation of *o*-nitrotoluenes by triethyl phosphite, and the reaction sequence IX-XI, involving nitrene insertion, has been proposed. The reaction product XI presumably results from coupling of two fragments, one derived from the parent nitrene and the other from the isomerisation product X, which corresponds to the carbene from V. Setting aside the mechanistic complications which may arise from triethyl phosphite participation, it seems that the overall reaction is similar to that described here. The major difference appears to lie in stabilisation of the electron-deficient intermediates by nucleophile participation, e.g. the isolation of triethyl N-arylphosphorimidates (ArN:P(OEt)$_3$) is strongly suggestive of nitrene-trapping by (EtO)$_3$P; the final product could arise by the attack of X (or the related carbene) on this compound. Our results indicate that, in the absence of stabilising nucleophiles, the nitrene is the preferred structure, and that the carbene related to X would normally transform to 2-vinylpyridine. The fact that both these findings are at variance with the isolation of XI may indicate that participation by tervalent phosphorus is involved in the intermediate IX. A similar conclusion was reached by Cadogan and co-workers (8), who isolated the 3-H-azepinyl-7-phosphonate XII from triethyl phosphite reduction of *o*-nitroethylbenzene. The effect of foreign nucleophiles in stabilising ring expansion of nitrenes is well documented, including the isolation of XIII



IX X XI



XII (R = Et) XIII (R = H, ϕ)

from tervalent phosphorus reduction of nitrocompounds in the presence of Et$_2$NH (9), and the isolation of azepines from pyrolysis (10) or photolysis (11,12) of phenyl azides in amines, and from photolysis of anthranils in methanol (13).

In the present work, the intermediate VII is at no stage trapped by nucleophiles, and must transform intramolecularly to escape from its energetic dilemma. Since dimerisation is the final escape route sought by the nitrene, rather than the ring contraction characteristic of the hot singlet (1), it is tempting to assume that decay to the triplet state has occurred. Regardless of the accuracy of this assumption, it does seem clear that the ring contraction of phenyl nitrenes to cyanocyclopentadienes does not occur through the intermediacy of a ring-expanded form such as VIIb, since in this case the v-triazolopyridines I should give rise to much greater yields of these products than they do.

(Compounds in Table I were identified initially by retention time, then by comparison of UV, IR, NMR and mass spectra with authentic data).

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4. Prepared from 5-methylpyridine-2-aldehyde by the method of J.H.Boyer, R. Borgers and L. T. Wolford (J. Amer. Chem. Soc., 79, 678 (1957)). Yield of hydrazone 98% (oil), of triazolopyridine 65% (m.p. 93-95°).
5. The mass spectra of phenyl azide and v-triazolo[1,5-a]pyridine are identical, even down to the metastables shown, suggesting a common structure (or set of structures) for the ion $C_6H_5N^{+\cdot}$. The similarity of thermal fragmentation patterns is not surprising in view of this.
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