Gas-phase Photochemistry of Picolines and Lutidines

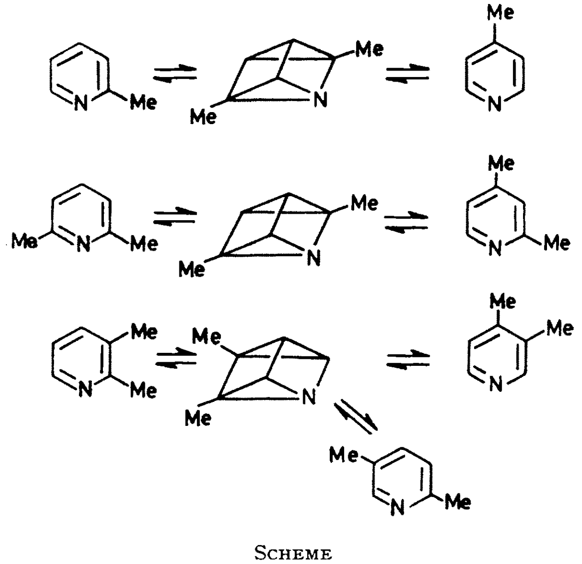
By S. CAPLAIN and A. LABLACHE-COMBIER*

(*Laboratoire de Chimie Organique Physique, Faculté des Sciences de Lille, B.P.* 36, 59-*Lille-Gare, France*)

Summary The photorearrangements of picolines and lutidines have been studied: these can proceed either by a methylation–demethylation process or by formation of azaprismanes.

THE photoisomerizations of benzene[1] and pyrazine[2] have been widely studied. Both proceed by a rearrangement of the atoms of the aromatic ring. Very few studies have been done on the photoisomerization of pyridine. Pascual and Tuazon[3] have shown that in the gas phase there is an interconversion between 2- and 4-picoline. We repeated their work, extended it to the 3-picoline and the lutidines. The Table summarizes our results.

For their experiments with 2-picoline, Pascual and Tuazon used a 2-picoline containing small amounts of pyridine and 2,4-lutidine. We used 2-picoline[4] shown to be pure by g.l.c.



SCHEME

Irradiations were performed with a Rayonnet R.S. reactor at 2537 Å in a quartz vessel for 1 h, at a pressure of 10 mm Hg of starting material vapour. The experiments with the picolines were performed with deoxygenated (by three freeze–thaw cycles) material for 24 h, the reactor being cleaned after 12 h. A large quantity of polymer is formed in all the experiments. If the photoreactions are done in the presence of mercury vapour no change in the experimental results occurs.

The products formed were characterised by g.l.c., on a Perkin–Elmer F 20 chromatograph with a Carbowax 20M + 1%-KOH capillary column. The picolines formed in the photorearrangement of other picolines[5] were characterised by n.m.r.

TABLE

Starting material[a]	Products[b]
2-Picoline	4-Picoline (5) + 2,4-lutidine (2·5) + pyridine (1)
4-Picoline	2-Picoline (5) + pyridine (1)
3-Picoline	Pyridine[c]
2,4-Lutidine	2,6-Lutidine
2,6-Lutidine	2,4-Lutidine
2,5-Lutidine	2,3-Lutidine (1) + 3,4-lutidine (1)
3,4-Lutidine	2,5-Lutidine (1) + 2,3-lutidine (1)
2,3-Lutidine	2,5-Lutidine (1) + 3,4-lutidine (1)
3,5-Lutidine	No isomerization products

[a] About 1—2% of the starting material is isomerized.

[b] The figures in brackets are the relative ratio of the compounds formed.

[c] 0·3% of the 3-picoline is converted into pyridine.

The results in the Table suggest that in these reactions there is an interconversion between carbons at positions 2 or 6 and 4 and between carbons at positions 3 and 5 or 2 and 6 (even a pyridine with 5 different substituents should give the same product by interconversion of C-3 and -5 or -2 and -6). The formation of 2,4-lutidine from 2-picoline and of pyridine from the three picolines suggests that the photoisomerization may proceed by a methylation–demethylation process. This hypothesis cannot be excluded *a priori*, but one would expect the formation of lutidines from 3- and 4-picolines if it were correct.

If pyridine behaves as benzene and pyrazine, two intermediates can be postulated: (i) an azabenzvalene—this can be excluded as it would lead to a 1,2-isomerization; (ii) an azaprismane—the isolation of a Dewar pyridine[6] by Wilzbach and Rausch agrees with this intermediate. The Scheme shows the azaprismanes which may be the intermediates of the photoisomerization of the lutidines.

(*Received, June 8th*, 1970; *Com.* 887.)

---

[1] K. E. Wilzbach, A. L. Karkness, and L. Kaplan, *J. Amer. Chem. Soc.*, 1968, **90**, 1116, and references cited therein.
[2] F. Lahmani and N. Ivanoff, *Tetrahedron Letters*, 1967, 3913.
[3] O. S. Pascual and L. O. Tuazon, *Philippines Nuclear J.*, 1966, **1**, 51; *Chem. Abs.*, 1967, 115127.
[4] A. I. Vogel, "Practical Organic Chemistry," Longmans, London, 3rd. edn., 1967, p. 177.
[5] A. Bovey in "N.M.R. Data for Organic Chemistry," Interscience, New York, 1967, p. 124.
[6] K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178.