

PHOTOISOMERIZATION OF PYRAZINE AND OF ITS METHYL DERIVATIVES

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Wilzbach and Kaplan (1) have shown that different polyalkylbenzenes undergo photoisomerizations which arise from transposition of ring carbon atoms. They explain these reactions by assuming the formation of intermediate structures such as benzvalene, bicyclohexadiene and prismane. In the case of tritertibutylbenzenes (2), they have chemically identified all three structures.

Bryce Smith and Longuet-Higgins (3) proposed for these reactions a mechanism in which two pathways are possible :

- The photoexcitation to the lowest $\pi\pi^*$ singlet state of benzene would lead to the formation of benzvalene.

- The lowest $\pi\pi^*$ triplet state of benzene should be involved in the formation of bicyclohexadiene and prismane.

In the present work, we investigate the photochemical transformation of pyrazine and of its methyl derivatives. The interest of the choice of these compounds is due to the three following reasons :

1) The introduction of nitrogen atoms in the benzene ring labels in a way the position of carbon atoms. The three isomers ortho-, meta- and para-diazines can easily be isolated and identified.

2) Pyrazine as it is shown on the energy levels diagram (4) in Fig. 1 presents $\pi\pi^*$ transitions similar to benzene and, in addition to these, has also $n\pi^*$ transitions. One can see on the diagram that by exciting the molecule into singlet $\pi\pi^*$ at 3130 Å (31948 cm^{-1}) one can obtain triplet $\pi\pi^*$ without exciting the singlet $\pi\pi^*$ (5).

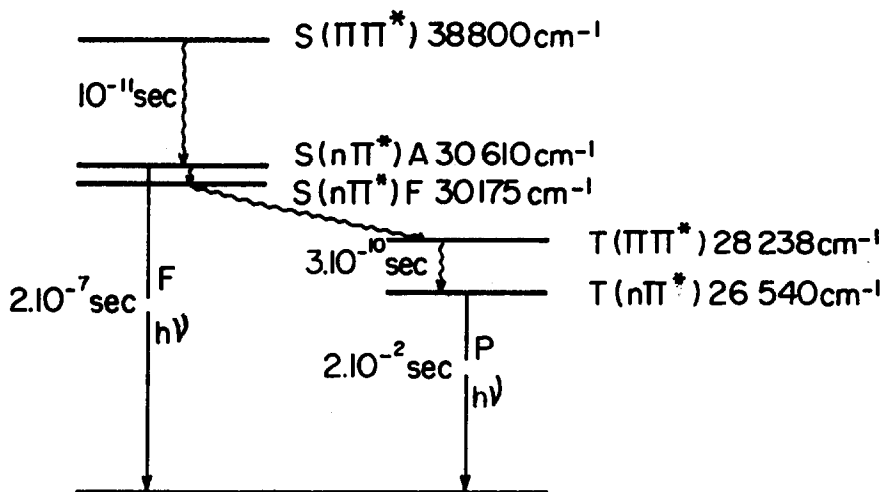


FIG. 1

3) By assuming that the photoisomerization mechanism takes into account either benzvalene or bicyclohexadiene and prismane intermediates, the study of photochemical reaction of disubstituted derivatives of pyrazine such as 2,6- and 2,5-dimethylpyrazines enables us to choose between the two possibilities. In fact, the products will be different whether the intermediates have the structure of benzvalene or those of bicyclohexadiene and prismane. In the first case 2,6-dimethylpyrazine (I) would lead to the formation of 2,4- and 4,5-dimethylpyrimidine (III and IV) while 2,5-dimethylpyrazine (II) should lead to 4,6- and 2,5-dimethylpyrimidine (V and VI). If the reaction occurs by the intermediate of bicyclohexadiene and prismane we should observe the other situation as it is seen from Fig. 2.

I. Experimental conditions.

Irradiations were performed in cylindrical quartz cells with an optical path of 1 and 25 cm. These cells were filled under vacuum at 22°C by the vapour of the product to be studied, under a pressure of 10 mm Hg for pyrazine and 2-methylpyrazine and under a pressure of 3 mm Hg for dimethylpyrazines. Mercury arc lamps (low and medium pressure) were used as light sources. The light intensities were 10^{18} quanta/mn at 2537 Å and 10^{17} quanta/mn at 3130 Å. The total doses were always around 10^{20} quanta. The separation and identification of the products were carried out by vapour phase chromatography and spectrophotometry.

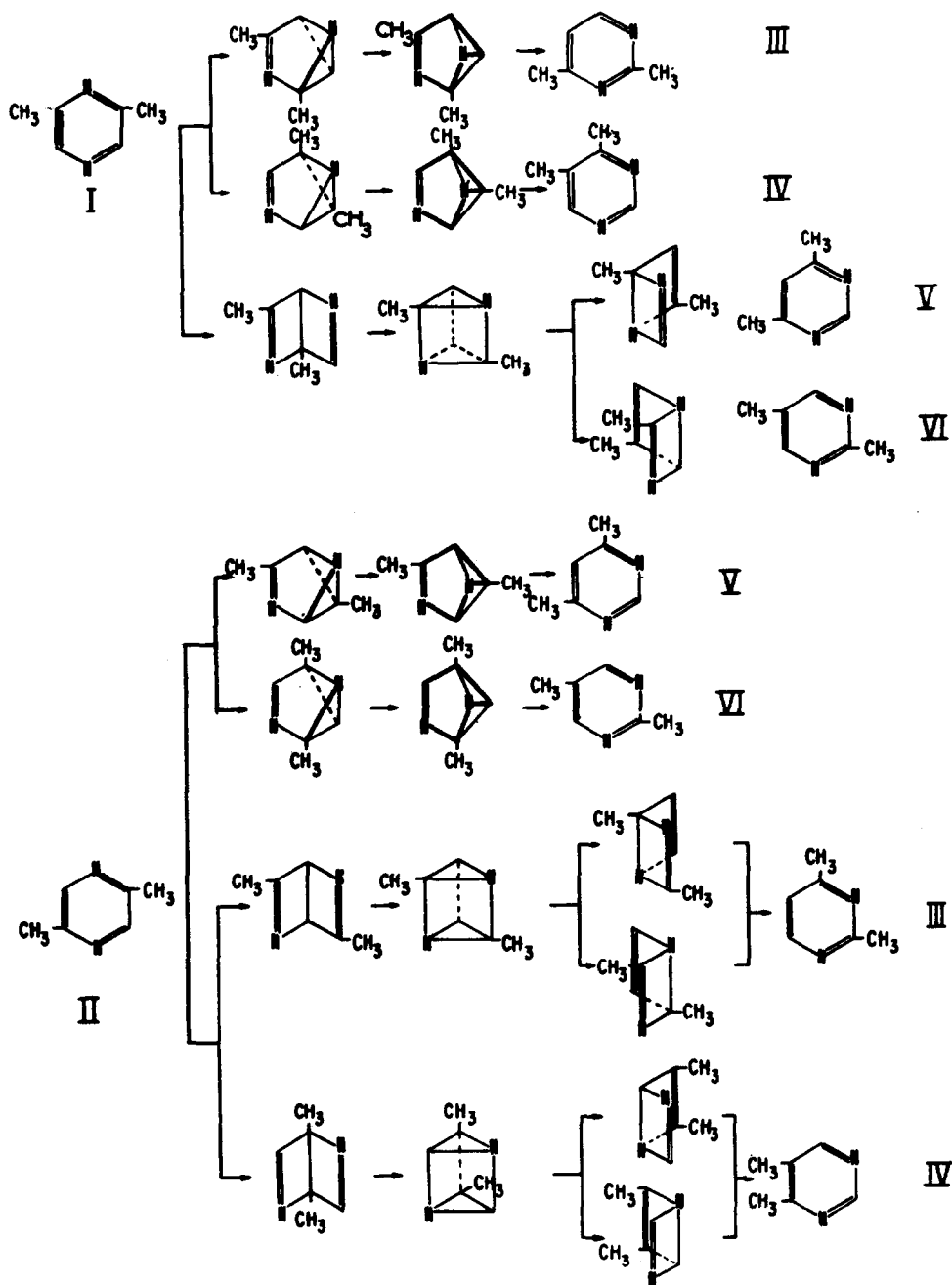


Fig. 2

II. Experimental results.

A - Irradiation of pyrazine and of 2-methylpyrazine at 2537 Å and 3130 Å.

In a previous note (6) we reported the formation of pyrimidine in the photolysis of solutions of pyrazine at 2537 Å. Pyrazine in vapour phase irradiated at the same wavelength also produces pyrimidine with an initial quantum yield : $\Phi(\text{Pyrimidine}) \sim 4 \times 10^{-3}$. But if the irradiation of gaseous pyrazine is performed at 3130 Å we do not find any pyrimidine for a total dose of irradiation equivalent to the dose used for the 2537 Å experiments (which corresponds to a quantum yield of pyrimidine $< 10^{-5}$).

In order to confirm this result, we looked for the isomerization products in the photolysis of 2-methylpyrazine at 2537 Å and at 3130 Å. In the first case, we observe the formation of three main products, two of which have been proved to be 4- and 5-methylpyrimidine[¶]. In the experiments carried out at 3130 Å we could not detect any methylated isomer of pyrimidine even for a total irradiation dose of 7×10^{21} quanta.

B - Irradiation of 2,6- and of 2,5-dimethylpyrazine at 2537 Å in vapour phase.

Photolysis of 2,6-dimethylpyrazine at 2537 Å leads to the formation of 4,5-dimethylpyrimidine with an initial quantum yield : $\Phi(4,5\text{-dimethylpyrimidine}) \sim 3 \times 10^{-3}$. If 2,4-dimethylpyrimidine was also formed, it would be difficult to identify because it may have the same retention time as the starting material.

In the irradiation of 2,5-dimethylpyrazine we observed the formation of 4,6- and 2,5-dimethylpyrimidine^{¶¶}. The initial quantum yield are :

$$\begin{aligned}\Phi(2,5\text{-dimethylpyrimidine}) &\sim 6,8 \times 10^{-3} \\ \Phi(4,6\text{-dimethylpyrimidine}) &\sim 3,2 \times 10^{-3}\end{aligned}$$

[¶] We supposed the third product to be 2-methylpyrimidine but lacking a synthetic sample we could not prove it.

^{¶¶} We also detected 4,5-dimethylpyrimidine with about 100 times lower yield than two other products. We think that it could be produced from 2,6-dimethylpyrazine contained as impurity in the 2,5-dimethylpyrazine which we used for our experiments.

III. Conclusions.

These results lead us to two conclusions :

A) The comparison of the experiments carried out at 2537 Å and at 3130 Å respectively, seems to prove that the excited state involved in the photoisomerisation of pyrazine and of its derivatives is the singlet $\pi\pi^*$. The triplet states $\pi\pi^*$ and $n\pi^*$ which can be obtained from the singlet $\pi\pi^*$ apparently do not play any significant role (see also the results of Leray on benzene ring (7)).

B) Although the corresponding nitrogen derivatives of benzvalene, bicyclohexadiene and of prismane are not known, the results obtained in the photolysis of dimethylpyrazines seem to indicate that a compound of benzvalene type structure is the most probable intermediate in these transformations.

On the whole, our results are in agreement with the mechanism suggested by Bryce-Smith and Longuet-Higgins who postulate that in the case of benzene the lowest singlet state $\pi\pi^*$ is responsible for the formation of benzvalene.

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