

An Autogenic Electromeric Effect as Inductor of an Abnormal Polarization in Pyridine N-Oxide

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Abstract Nitration of pyridine N-oxide gives 4-nitropyridine N-oxide. This is an abnormal nitrene reactivity involving an electronic back-donation. However, the textbooks treat this result in a very brief way, without any insight. Which are the experimental antecedents of this reaction? What theory was proposed to explain them? What reactivity is overturned by these proposals? How theory and practice can come to agree on this subject? All these questions will be treated and answered in this communication.

Keywords: nitrene reactivity, electron back-donation, 1,3-Cycloaddition, 1,3-Dipolar structures, Pyridine N-oxide

Cite This Article: Francisco Sánchez-Viesca, and Reina Gómez, "An Autogenic Electromeric Effect as Inductor of an Abnormal Polarization in Pyridine N-Oxide." *World Journal of Chemical Education*, vol. 5, no. 1 (2017): 9-11. doi: 10.12691/wjce-5-1-2.

1. Introduction

We present to the teaching community our theoretical findings correcting and up-dating the three excited states proposed by Linton in order to explain the unexpected dipole moment found in pyridine N-oxide [1]. Since the nitration experiments and the ^{13}C -NMR studies only support one of the three proposed high energy structures, we discarded the other two. The mechanism involved in the formation of the remaining electromer, an ylide, is problematic and it is discussed. New concepts such as autogenic electromeric effect are invoked in order to explain a back-donation effect. Part of this study is in a preliminary communication [2]. The second part here presented deals with the abnormal chemical department exhibited by the nitrene group present in pyridine N-oxide.

This will change the simplistic point of view about this subject found in the Organic Chemistry text books.

2. Discussion

Linton studied the dipole moments of several amine oxides [1] and found that the dipole moment of pyridine N-oxide is appreciably smaller than the expected theoretical value.

Thus, in addition to the ordinary resonance structures derived from the ground state, Figure 1, he proposed the existence of three "excited structures" as contributors.

The high energy structures have an electric negative charge on the ring, instead on the oxygen atom, in order to explain the observed small dipole moment in pyridine N-oxide, Figure 2.

There is no doubt about the low dipole value since the microwave spectrum of pyridine N-oxide gave a value

even a little smaller [3]. However, only one of the three excited structures has been confirmed, as it will be seen.

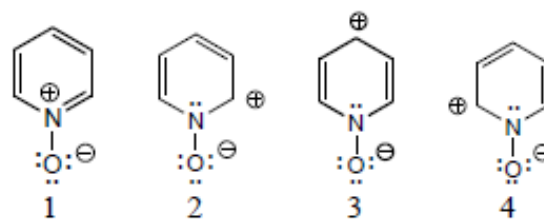


Figure 1. Normal electromers in pyridine N-oxide

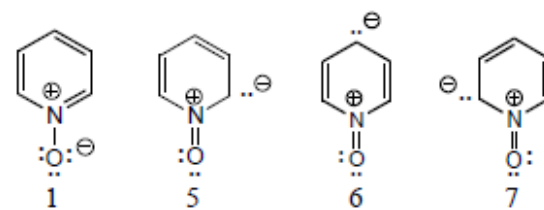


Figure 2. Ground state and „excited“ (high energy) electromers proposed by Linton in the pyridine N-oxide molecule

Nitration experiments with pyridine N-oxide [4,5,6,7,8] showed that the reaction product is 4-nitropyridine N-oxide, i.e., there is regioselectivity. It is important to note that reaction at C-2 and at C-6 would yield 2-nitropyridine N-oxide, and in a double quantity than that obtained of 4-nitropyridine N-oxide, which is not the case at all. From these experimental results, we discard the excited structures with negative charge at C-2 and at C-6.

Moreover, ^{13}C -NMR spectroscopy [9] only indicates higher electronic density at C-4 in pyridine N-oxide. This is in agreement with the results of reactions performed much earlier. However, the only acceptable of Linton's structures presents several problems.

The comparison of the reactivity of pyridine has been made [10]. The N-oxide nitration (at C-4) can be effected

much more readily than with pyridine, although the reaction is still more difficult than the nitration of benzene [11,12,13]. This comparison is interesting because it lets us see that even a structure with a carbanion at C-4, and reacting with a nitronium ion, presents a lower reactivity than benzene. So, we deduce that there must be a low population of molecules having that structure.

Moreover, Linton did not give an explanation as how the high-energy excited-structures can result. The formation of any of them implies an electronic shift contrary to the mesomeric effect of the iminium ion present in the ground state of pyridine N-oxide. In order to form the proposed ylides, the electron-donor effect of the oxygen atom must surpass the opposite mesomeric effect. Thus, a promoter is required. We propose the existence of polarization by intermolecular induction, i.e., participation of an external ion (electromeric effect). In the absence of other reactant, since the dipole moment of pyridine N-oxide was determined in benzene, a non-polar molecule, we deduce the participation of the resonance structure with a positive charge at C-4. This electromer [14,15], with a 1,5-dipole is the most unstable of the ordinary resonance structures, and therefore most reactive, can attract electrons from a molecule in the ground state, as is shown in Figure 3.

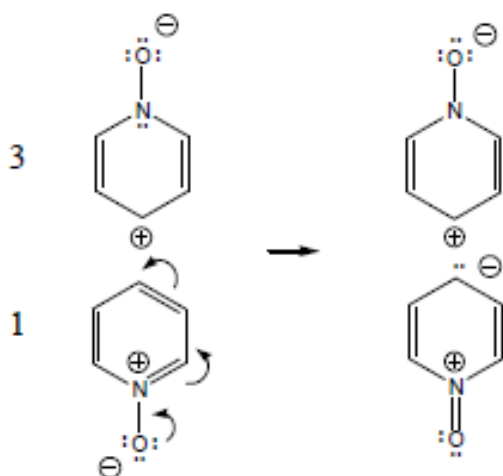


Figure 3. Electronic shift by intermolecular induction (autogenic electromeric effect) in pyridine N-oxide

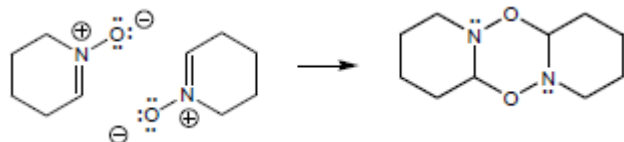
This intermolecular induction can be considered an especial case of the electromeric effect since the external ion does not come from an added reagent.

Thus, this novel interaction was termed Autogenic Electromeric Effect.

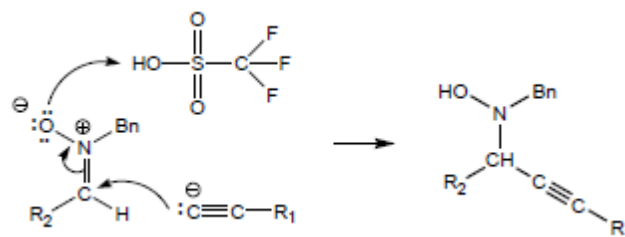
The formation of an ylide in pyridine N-oxide, involving electron back-donation, is an abnormal chemical deportment. The ordinary nitronium reactivity takes place through a 1,3-dipole, without formation of any carbanion nor 1,5-dipole.

We can observe the normal nitronium reactivity in the following examples:

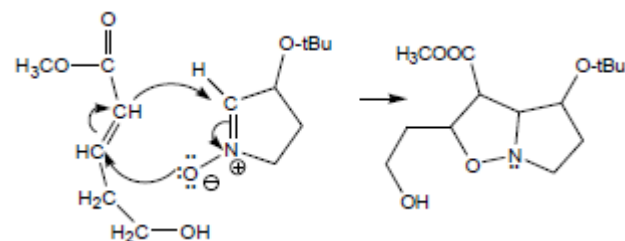
a) Dimerization, [16]



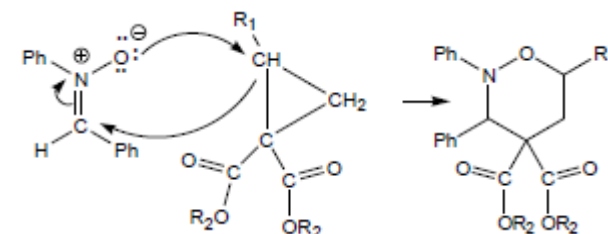
b) Catalyzed Addition, [17]



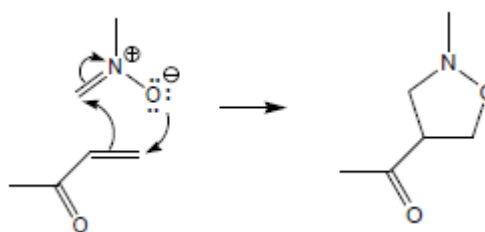
c) Reaction with a cyclic nitronium [18]



d) Homo [3+2] dipolar cycloaddition [19]



e) Cycloaddition [20]



In the above examples there is no formation of any ylide in the nitronium molecule, as it occurs in pyridine N-oxide.

3. Conclusions

1. In order to explain the low dipole moment present in pyridine N-oxide Linton proposed the contribution of three "excited structures", in addition to the canonical electromers.

2. However, only one of the proposed high energy ylides was confirmed experimentally by nitration experiments and ¹³C NMR spectroscopy.

3. The formation of the remaining acceptable structure requires a theoretical explanation since it implies an electron shift contrary to the ordinary mesomeric effect of the nitronium iminium-ion, i.e., implies electron back-donation.

4. We have proposed the existence of polarization by intermolecular induction (electromeric effect). In the absence of an external positive ion, as in dipole moment

determination in benzene solution, we propose the existence of an autogenic electromeric effect.

5. Due to the above factors, nitration of pyridine N-oxide can be considered an abnormal chemical department. This was confirmed by comparison with other reactions involving nitrones and very different reagents, there is no electron back-donation in any other case.

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