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The manuscript of the thesis of Katarzyna Justyna is a 130-page document constituted by a general introduction followed by three chapters. The short introduction discusses the importance of azaheterocycles in various fields of chemistry and biochemistry and reminds some works on these compounds whose thermolysis of bis-tert-butylated diazadienes, reaction likely causing the overall project.

The first chapter is mainly devoted to remind studies by flash vacuum thermolysis (FVT) that most often lead to the synthesis of azacycles or imines. A brief history and the basic principle of the FVT are first recalled. Then, examples of flash pyrolysis reactions of various compounds leading to heterocompounds with oxygen, nitrogen or sulfur atoms are described. The FVT of a small series of compounds having a sp^3 nitrogen substituted by a t-butyl group is described as well as other thermolyses leading to the formation of azacycles. Mechanisms from the literature articles are proposed to explain the formation of the systems. It is interesting to note that this chapter sheds light on the process that will be the one of the following chapter attempting to explain the formation of compounds. A second part is devoted to imines and some approaches are recalled. We may regret the absence of a subsection to remind syntheses starting from various tert-butyl derivatives in the aim to inform the reader on the diversity (or not) of applications of these compounds in thermolysis.

The second chapter reviews all the experimental work of this thesis. It begins with the synthesis of precursors, the tert-butylimines. The conventional synthesis of the condensation of an aldehyde with the tert-butylamine is used, but some difficulties were observed at the level of the synthesis of aldehyde precursors. Then, systematic studies on the FVT of these t-butylimines are described. The second part of the chapter is devoted to the thermolysis of N-tert-butyl(E)-crotonaldimine and 1,4-di-tert-butyl-1,4-diaza-1,3-diene. Various compounds are obtained according to the substitutions at the two nitrogens and the thermolysis temperature. The unstable imine formed was characterized by ^1H NMR spectroscopy and photoelectron spectroscopy from the mixture. A reaction pathway to explain the formation of products is proposed.

The thermolysis of N-(benzylidene)-N-tert-butylamine shows a surprising displacement of a nitrogen atom from position 2 to position 3 for the two main products of thermolysis. This very interesting result has led to a complex theoretical study to propose a reaction pathway involving the formation of an aziridinyll cycle. Thermolysis of N-(tert-butyl)-N-(pyridin-2-ylmethylidene)amine (compound wherein the benzene ring was replaced by a pyridine ring) leads to the formation of compounds in which the one with a displacement of the nitrogen atom has also lost a methyl group.


The fourth part of this chapter examines the thermolysis of N-(tert-butyl)-N-(pyridin-3 and -4-ylmethylidene)amines. The thermolysis of an isomer of the compound previously studied but with a displacement of the substituent in position 4 or 3 also leads, for the first one, to three compounds wherein the ring formed does not contain two nitrogen atoms as before. A similar

approach to that carried out earlier led to the proposal of reaction mechanisms whose plausibility is derived from theoretical calculations. For the second compound, ten products were identified. A long mechanistic study was then performed -that is quite unusual for an approach leading to so many products-. The study continues with di-, tri- and tert-azabicyclic compounds. Some thermolyses give a major product in a yield ranging between 50 and 95% and therefore these approaches have a clear synthetic interest particularly when conventional approaches described in the scientific literature are less effective. It should be noted the synthesis of new compounds.

Chapter 4 is the experimental part. The synthesis and characterizations of compounds are well described.

There is no general conclusion of the thesis nor comprehensive analysis of the results. It would be interesting to try to streamline the pyrolysis of t-butylimines to explain why the t-butyl group is not playing its quite usual masked hydrogen role with imines. To the extent that the t-butyl group loses one or two methyl group(s) during thermolyses, a comprehensive study on pyrolysis of at least one imine with methyl, ethyl, isopropyl or propyl could have provided extensive information on the potentiality of this approach in the synthesis of heterocompounds and on the mechanisms. It is usual in organic chemistry to have doubts about any proposed mechanism because of the capacity of researchers to imagine non-traditional reaction pathways.

This manuscript shows a consistent work on the thermolysis of t-butylimines. A mechanistic study based on experimental and theoretical aspects and supported by analysis by NMR and photoelectron spectroscopies of the products is reported. Three publications in international journals and several communications have followed this work. I would unambiguously recommend the defense of the thesis. The awarding of a prize may be discussed after the defense.

A handwritten signature in dark ink, appearing to read 'Guillemin', with a long horizontal stroke extending to the left and a shorter one to the right.

Dr. Jean-Claude Guillemin