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The mechanism of Mack test for strychnine identification with manganese dioxide

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Abstract

Mack test for strychnine identification uses manganese peroxide (manganese dioxide) and concentrated sulphuric acid, giving a series of colours. The oxidation route is lengthy and intricate. The occurring reactions are: electrophilic attack to C=C double bond, reagent elimination as hypomanganous acid, isomerization to conjugated iminium ion, hydration, carbinolamine oxidation, 1-4-addition of manganous acid, epoxide formation, oxirane opening to alcohol and manganese ester, hydrion promoted synchronous mechanism with simultaneous formation of lactam, ketone, and aldehyde. And finally, oxidation of the latter to carboxylic acid. This sequence is in accordance with elemental analysis of the initial and end products.

Keywords: Carbinolamine; Electrophilic reaction; Epoxide; Hypomanganous acid; Iminium ion; Manganous acid

1 Introduction

Due to the extreme toxicity of strychnine, the colour reactions for its identification are very important since they are used in Toxicology. The pioneering test for strychnine due to Eugene Marchand, published in France in 1843, [1], opened a vast field for research since the test is based in the oxidation of strychnine by means of lead peroxide (lead dioxide) in concentrated sulphuric acid. This finding motivated other researchers try with other oxidizing compounds. The first author was E. Mack, who in 1846 published in London [2], the use of black oxide of manganese (manganese dioxide) for strychnine identification, giving a series of colours as in the Marchand test.

In this communication we provide the mechanism of Mack test for strychnine. This is a follow up of our studies on reaction mechanism, [3-7].

2 Antecedents

As said before, various authors tried different oxidizers in order to detect strychnine. Davy (1853) used potassium ferricyanide, [8]; Lindo (1856) employed potassium chlorate, [9]; Sonnenschein (1870) chose Ce_3O_4, that is, the salt $2CeO.CeO_2$, [10]; and Mandelin (1883), used ammonium meta-vanadate, [11].

Some remarks on the reagent. Manganese dioxide, manganic oxide. Physical state, solid; Appearance, powder; Colour, black; Chemical structure, O=Mn=O, linear; [12]. Occurring naturally in the mineral pyrolusite.

Manganous acid, H_2MnO_3 ($MnO_2.H_2O$) is a reaction intermediate. MnO_2 can be reduced to manganese (II) oxide (manganous oxide, manganese monoxide) or to the hydrated compound. This amphoteric derivative can be considered as manganese di-hydroxide, $Mn(OH)_2$ or as H_2MnO_2, hypomanganous acid, [13, 14].

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3 Discussion

Protonated MnO_2 reacts with the double bind in the cyclic ether, leaving a carbonium ion which is neutralized by proton elimination from the vicinal methylene group, Figures 1 and 2.

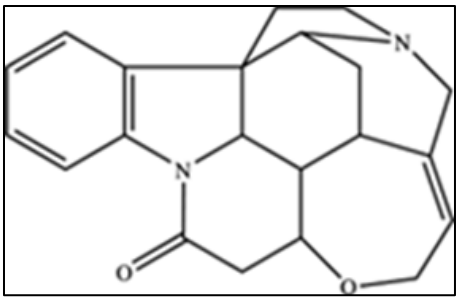
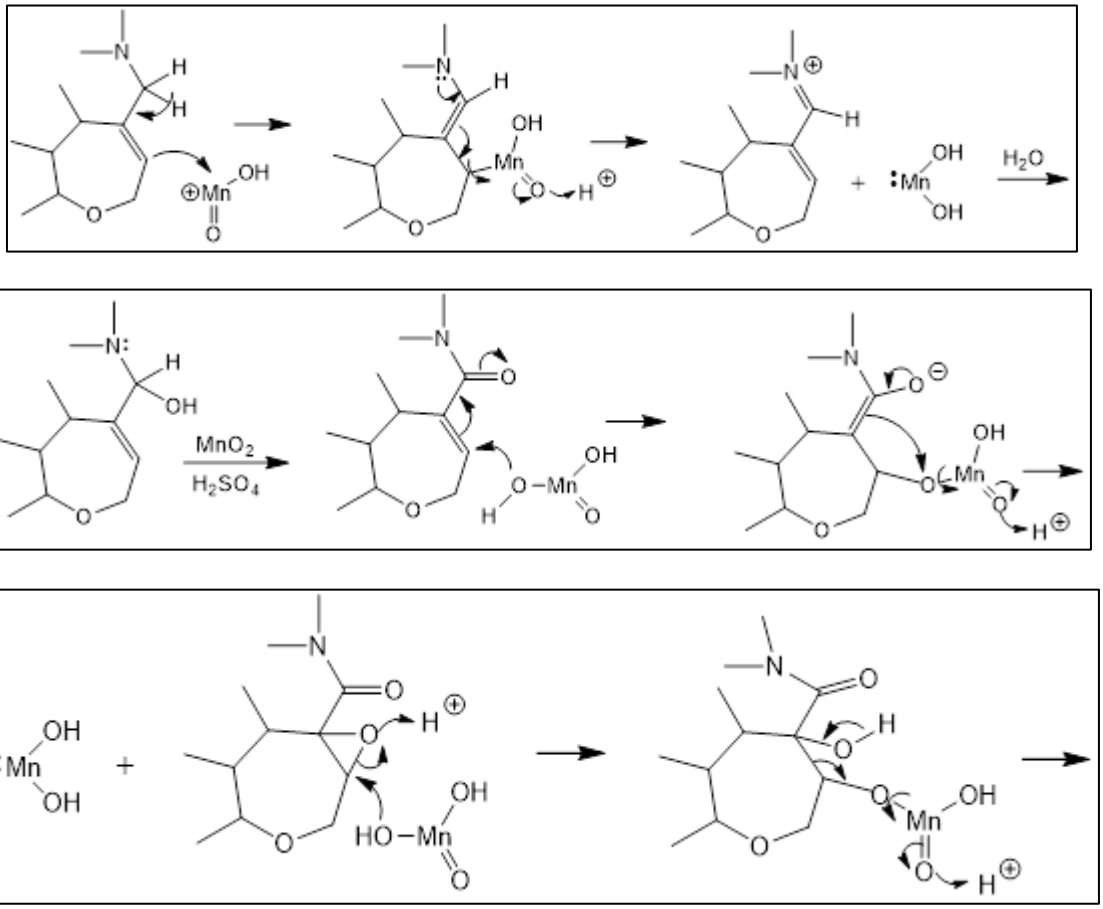


Figure 1 Strychnine chemical structure

Hydrion interaction with the manganese double bond eliminates hypomanganous acid, H_2MnO_2, with simultaneous participation of the enamine. Dehydration of the amphoteric hypomanganous acid, $Mn(OH)_2$, favours hydration of the iminium group to a carbinolamine which is oxidised to carbonyl, yielding a lactam. Addition of H_2MnO_3 ($MnO_2.H_2O$, manganous acid) to the conjugated system and protonation of the manganite eliminates manganese di-hydroxide, and an epoxide is formed. Acidolysis of the oxirane with participation of manganous acid affords an intermediate whose interaction with acid produces five electron-shift. There is opening of the seven-member ring, and a lactam, a ketone and an aldehyde are formed- The last is oxidised to carboxylic acid. This sequence is in accordance with the elemental analysis of the initial and end products, [15].



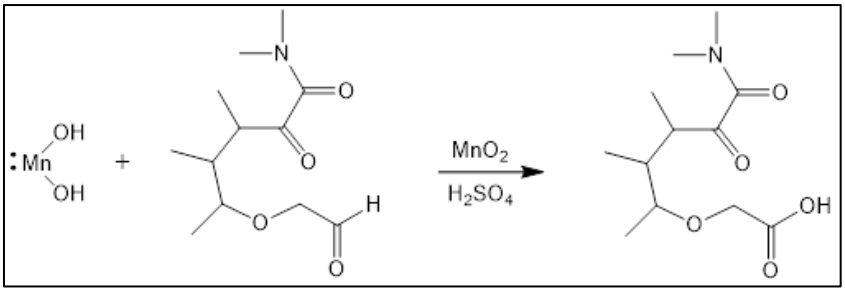


Figure 2 Flow Chart. Sequence of strychnine reaction with MnO_2/H_2SO_4

4 Conclusion

The mechanism of the Mack test for strychnine identification has been provided. The reaction sequence comprises ten principal steps, not counting the mechanism of alcohol or aldehyde oxidations. The entire process has been fully commented in the Discussion.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There is no conflict of interest to declare

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