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(RESEARCH ARTICLE)

Mechanism of the interaction of uric acid with bromine in acetic acid

F. Sánchez-Viesca *, Reina Gómez and Luz Clarita

Department of Organic Chemistry, Faculty of Chemistry, National Autonomous University of Mexico, Mexico City (CDMX), Mexico.

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Abstract

The mechanism of the interaction of uric acid with bromine in acetic acid is provided.

Electron return from the lower lactim in the uracil ring permits reaction with a bromine molecule. Protonation of the carbonyl at C-6 and reaction with water gives rise to hydrolysis of the N-bromoimide. There are ring opening and formation of nitrene and carboxylic acid. A five-member ring is formed by intervention of the carbon-carbon double bond. The dipolar intermediate is neutralised by water. A symmetrical carboxy-hydroxy-acetilenediurea is formed. Acidolysis of a semi-hemiaminal produces ring opening and carbonyl formation in the other ring, at β-position to the acid, enhancing decarboxylation. This way allantoin has been formed.

Keywords: Acetilenediurea; N-bromoimide; Decarboxylation; Lactim; Nitrene; Semi-hemiaminal; Uracil; Uric acid

1. Introduction

It has been informed that uric acid is oxidised to allantoin and allanturic acid by bromine and glacial acetic acid, [1].

Since this procedure is not registered in the list of preparations of allantoin [2], it was considered of interest study the reaction route of this process, giving the mechanism of each step and commenting it. The electron flow is also provided.

This communication is a follow up of our studies on reaction mechanism, [3-7].

2. Antecedents

Uric acid is an analyte; it is a common practice analyse its concentration in blood plasma and urine tests since hyperuricemia produces gout and kidney stones.

Many colour tests for uric acid are recorded in analytical books, [8-10]. This is an indication of the clinical importance of this heterocyclic compound which contains the classical four atoms of Organic Chemistry: CHON. Its structure is 2,6.8-trioxopurine.

The colour tests are very important for preliminary identification, and two or three positive tests are sufficient for secure identification.

Apart from the analytical importance of these tests, there is a theoretical interest in knowing what is going on in the test tube, or in the porcelain dish, at molecular level. This interest is also common in a synthesis in which the reactants and

* Corresponding author: F. Sánchez-Viesca

the final product are known but not the reaction sequence and the mechanism of the whole process. This is the case of allantoin formation from uric acid, bromine and acetic acid. This is discussed in the next section.

3. Discussion

The six-member ring in uric acid presents an imido group which has an acidic hydrogen that can be extracted in alkaline medium forming a negatively charged nitrogen at position one. However, in acidic medium, the process is not direct and other groups in this poly-functional ring must be taken into account. Figure 1.

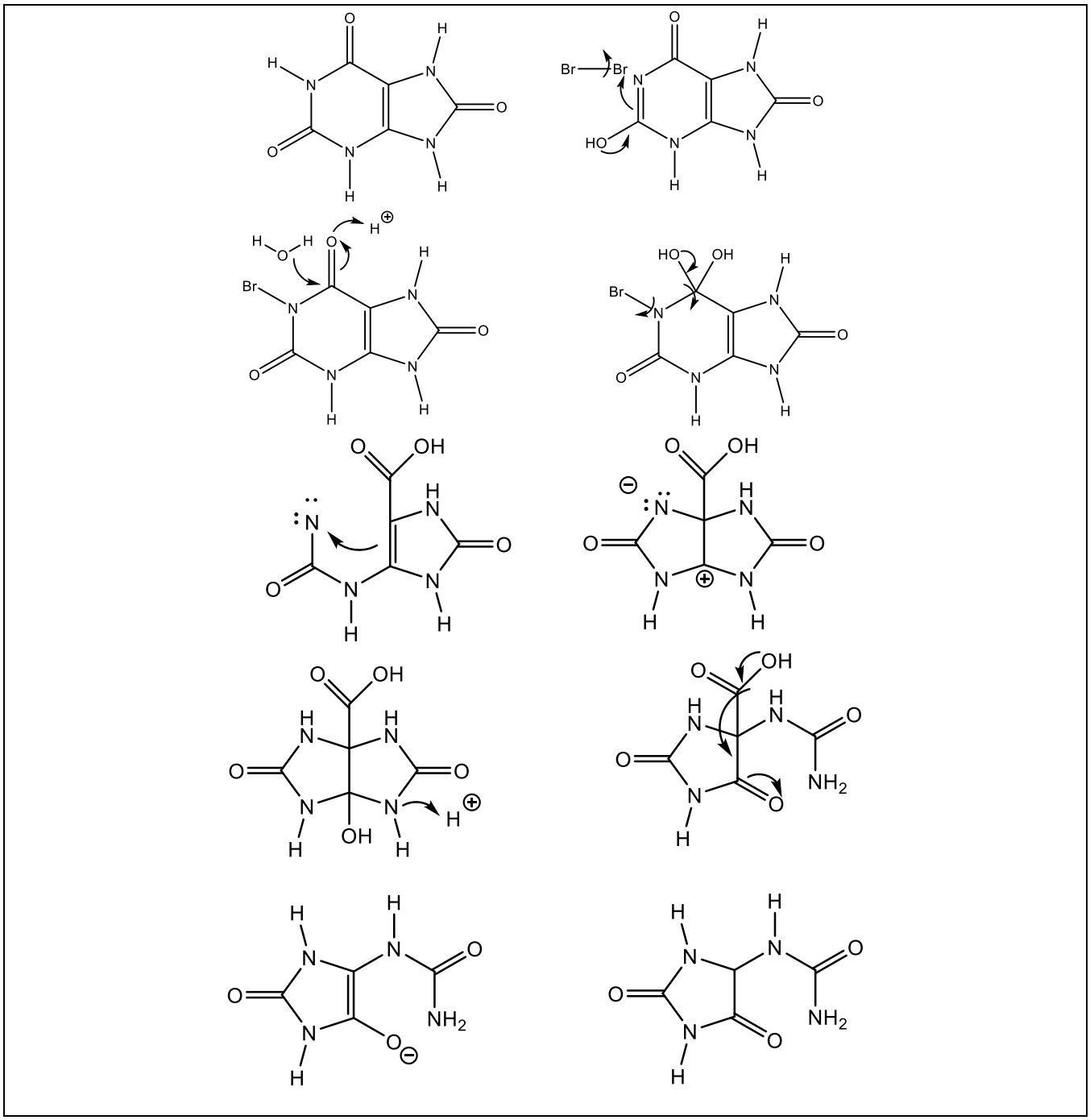

Figure 1 Reaction of uric acid with bromine in acetic acid

Uric acid is a weak dibasic acid, the lactimic hydrogens at 2 and 8 positions are ionisable, [11]. The imidate with cross conjugation has been proposed as the structure of uric acid monosodium salt, [12]. Electron return from the 2-imidol

[13] to the lactam form produces a negatively charged nitrogen atom capable to react with a bromine molecule, taking a bromonium ion and releasing a bromide ion.

This N-bromo imide reacts as a weak amide having a d**+** at nitrogen due to the d**-** in the bromine atom. This situation favours hydrolysis, but apparently there is no water. The uric acid was dissolved in alcohol, but pure alcohol was 80-90% in the 19th century.

So, protonation of the carbonyl at C-6 and reaction with water gives a gem-diol capable of ring opening with concomitant bromide elimination (oxidation step). A carboxyl and a nitrene [14] are formed. The last attracts electrons from the double bond, and the resulting zwitter ion is neutralised by water. This intermediate is a carboxy, hydroxy derivative of acetilene-diurea, glycoluril, [15]. There is ring opening (acidolysis) of one semi-hemiaminal in this symmetric compound, and a carbonyl and a ureido chain are formed.

Finally, the carbonyl at β-position to the carboxylic acid favours decarboxylation to 5-ureido-2,4-dioxoimidazolidine. 5-ureido-hydantoin (allantoin).

This sequence of reactions from uric acid is in accordance with the observation that alloxan is formed in strong oxidation conditions, whereas in weak acid conditions, or in neutral, or alkaline medium, allantoin is formed, [16, 17].

Allantoin is prone to hydrolysis leading to allantoic acid, [18]. By changing the depth of allantoin hydrolysis it was found that 5-aminohydantoin and fulminic or carbamic acid are the products of this reaction, [19].

Allantoin presents reversible isomerization, keto-enol tautomerism, [20]. It is interesting to note that in this case a lactamic oxygen is involved, but the ureido group remains intact.

There is an interesting review on allantoin synthesis and chemical properties, [21].

4. Conclusion

The chemical deportment of the uracil ring was revised. This poly-functional part of uric acid presents an imide, an ureido and a lactam, with a nitrogen that is common to the three groups. Besides, this ring has the capacity to form lactim forms. Electron reversal in a lactim at the bottom of the ring reacts with a bromine molecule. Hydrolysis of the bromo-imide brings ring opening and formation of a nitrene and a carboxylic acid. There are ring contraction and neutralization of the dipolar intermediate. Finally, occurs rupture of the imidazolone ring and decarboxylation, yielding allantoin.

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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