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On dulcin detection by halochromism

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Abstract

Dulcin has been detected by reaction with fuming nitric acid followed by interaction with phenol and sulphuric acid. Other tests use electron capturing reagents such as mercuric nitrate or silver nitrate. The test under study is not based in degradations initiated by nitration, nor by oxidations by electron removal, but by molecular fission after prototropy enhanced by heating. p-Phenetidine is obtained and forms the ammonium salt with sulphuric acid. After cooling and water addition, the solution is carefully covered with ammonium or sodium hydroxide. The interphase is coloured blue or violet-blue due to formation of the halochromic salt p-ethoxyphenylammonium phenoxide, from phenol and after ion switching.

Keywords: Halochromic salt; Ion switching; Morpurgo test; p-Phenethol carbamide; Phenol; Sulphuric acid

1 Introduction

Dulcin is an artificial sweetener about 250 times sweeter than sugar, discovered in 1883 by the Polish chemist Jósef Berlinerblau (1859-1935), [1]. Dulcin is p-phenethol-carbamide, Figure 1.

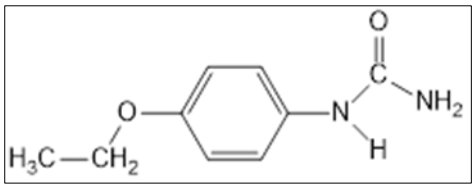

Figure 1 Dulcin structure

Dulcin can be prepared by the addition of potassium cyanate to p-phenetidine hydrochloride in aqueous solution at room temperature. Other way is by refluxing an aqueous solution of p-phenetidine hydrochloride with urea during 6 hours, [2].

p-Phenetidine is prepared by reduction of p-nitrophenethole with iron fillings and hydrochloric acid. p-Nitrophenethole is obtained by reaction of p-nitrophenol sodium salt with ethyl chloride in an autoclave, [3].

There is an interesting study about Dulcin, [4]. This compound on treatment with water is hydrolysed to p-phenetidine which reacts with unchanged Dulcin to give the disubstituted product, di-p-phenethole-carbamide. This substance can be converted into the simple carbamide, Dulcin, by treating with urea at 160° under pressure.

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G. Morpurgo found that Dulcin mixed with phenol and concentrated sulphuric acid and heated, cooled, diluted with water, and covered carefully with ammonia produces a blue or violet-blue colour. Since the reaction route is unknown, this is provided in the present communication.

This paper is a follow up of our studies on reaction mechanism, [5-9).

2 Study Method and Process

This is an Organic Chemistry Theoretical Study. It is based in the chemical deportment of reagent and substrate. All is in accordance with the reaction medium and the catalyst present. The several steps leading to the final product have been entirely commented and the reaction mechanism is given too.

3 Antecedents

G. Morpurgo published his test in Germany [10] and it was registered in two books on colour reactions [11, 12] and in a book on Methods of Organic Analysis [13].

The test is as follows: A little Dulcin is mixed with 2 drops of phenol and 2 drops of concentrated sulphuric acid and heated for about 5 minutes on the water bath; cooled and diluted with a few ml. of water is transferred to a test tube and covered with ammonium hydroxide or sodium hydroxide with the least possible mixing. The contact surface of the liquids is coloured blue or violet-blue.

It is important to know what is happening at molecular level during the assay, and this is explained in the next section.

4 Discussion

The first step is degradation of Dulcin due to heating in acidic medium. There is prototropy to the imidol tautomeride [14] of the external amido group of the carbamide, Figure 2.

A second isomerization takes place, a hydrion shift from the acidic enol-type imidol to the basic aromatic amino group. A dipolar intermediate is formed whose neutralization breaks down the molecule (C—N cleavage), and phenetidine and isocyanic acid are formed. The amine reacts with sulphuric acid giving arylammonium hydrogensulphate.

On diluting with water, isocyanic acid is hydrated to carbamic acid. This decomposes to carbon dioxide and ammonia, via a zwitter ion coming from an acid-base interaction.

Finally, ammonium hydroxide reacts with phenol (phenic acid) giving water and the phenoxide ion. The latter forms a salt with the arylammonium cation, this salt is coloured due to halochromism, [15-17]. The other compound obtained is ammonium hydrogensulphate, instead of arylammonium hydrogensulphate.

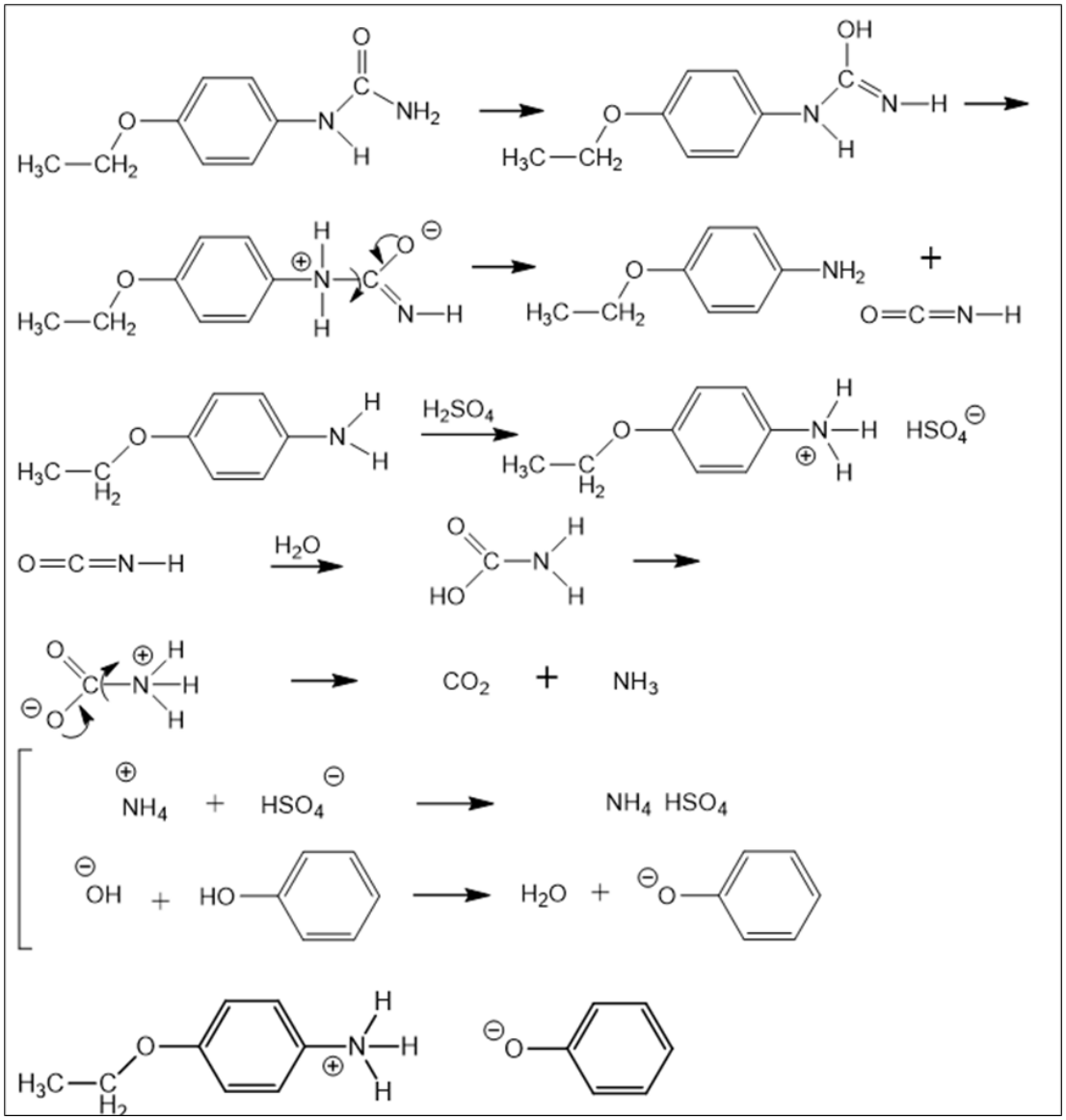

Figure 2 Reaction route of Dulcin detection by halochromism

Note that in this test there is no redox reaction, only acidolysis, hydration, degradation, and ionic interchange leading to p-ethoxyphenylammonium phenoxide, the blue or violet-blue halochromic salt. Halochromism can be formed either in acidic or in basic medium.

5 Conclusion

The reaction route from Dulcin to the halochromic blue-violet salt has been provided. There are no redox reactions since no oxidiser was employed. Only acidolysis, hydration and degradations occur, and there is ionic interchange leading to p-ethoxyphenylammonium phenoxide, the coloured halochromic salt.

Each experimental step has been commented from the theoretical point of view, the electron flow is given when it is pertinent.

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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