

Bruylant's test for 2,2'-bimorphine

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Abstract

The chemistry and the mechanism of the Bruylant's test for 2,2'-dimorphine have been cleared. Molybdic acid is obtained via metathesis from ammonium molybdate and sulphuric acid, The reactive species is protonated molybdic acid which in combination with the electrodot property of a phenol in the bimorphine forms a mixed molybdate. Interaction of the remaining hydroxyl group in the molybdate moiety with a hydron produces a synchronous mechanism involving five electron-shifts. Water and molybdenum dioxide are formed. An electron deficient oxygen originates two double bond shifts and an enedione is afforded as final product. This grouping is present also in indigo blue and besides MoO₂ is violet.

Keywords: 2,2'-Bimorphine; Enedione; Mixed molybdate; Molybdenum oxide; Molybdic acid; Redox reaction

1. Introduction

2,2'-Bimorphine has been known as oxydimorphine, pseudomorphine and dehydromorphine. There is an interesting article on this compound [1], which was discovered by Pelletier [2]. Experimental data on this compound have been given, [3]. The structure of pseudomorphine was published in England, [4]. The determination of morphine has been done by means of potassium ferricyanide [5], via formation of pseudomorphine.

Bruylants [6-8] using the Froehde-Buckingham reagent [9-11], found that oxydimorphine gives blue colour in this test. In the present communication we provide the chemistry and the mechanism of the Bruylants test for 2,2'bimorphine.

This contribution is a follow up of our studies on reaction mechanism, [12-16].

2. Antecedents

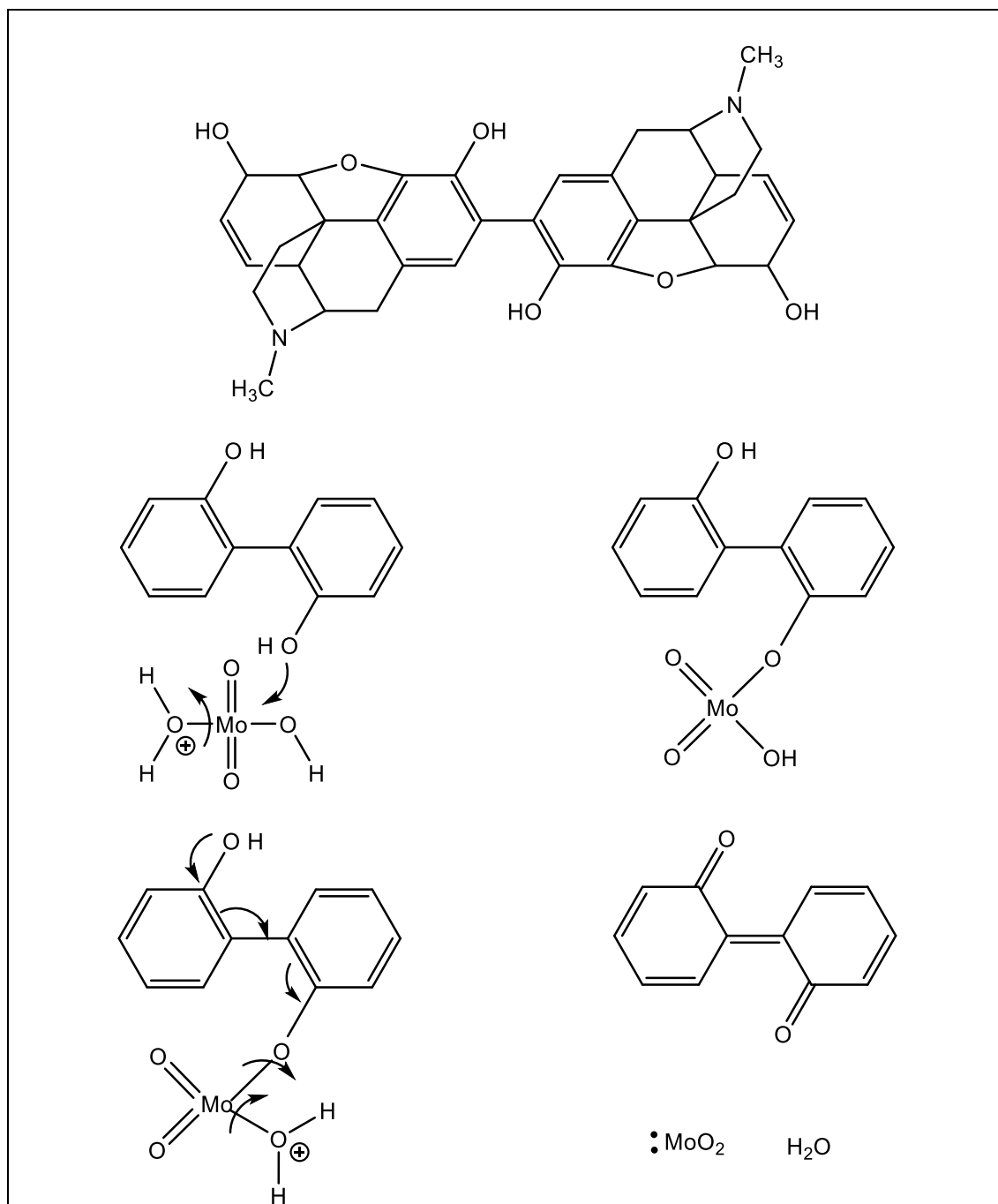
Froehde used ammonium molybdate in sulphuric acid for morphine detection, [17-20]. It was Buckingham who extended the use of this reagent to many other compounds, see above. However, his list was not exhaustive and Bruylants added more results with other opium alkaloids, among them oxydimorphine.

The chemistry and mechanism provided for this test are based on the chemical deportment of both substrate and reagent, taking into account the acidic medium that act as catalyst.

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3. Discussion

The Bruylants test for oxydimorphine employs the Froehde-Buckingham reagent, ammonium molybdate in concentrated sulphuric acid, sulpho-molybdate of ammonia. The first reaction is a metathesis, and molybdic acid is formed. The reactive species is protonated molybdic acid, whose interaction with a phenolic group in 2,2'-bi-



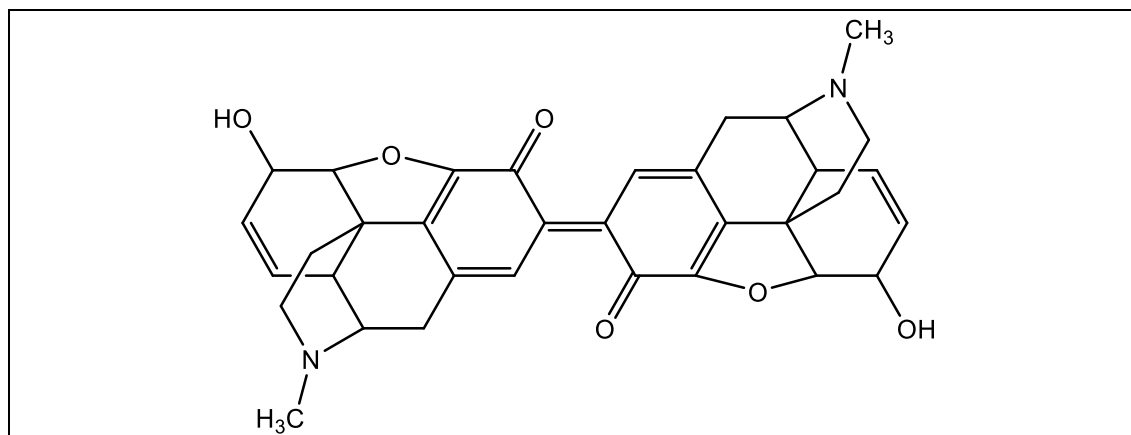


Figure 1 Bruylant's oxidation of 2,2'-bimorphine with molybdic acid in acidic medium

morphine (electrodotic reaction) [21, 22], gives a molybdic ester. A hydrion eliminates water from this intermediate, producing a concerted mechanism involving five electron-shifts. Figure 1. An enedione is formed, the double bond connecting two rings. That is, two α,β -unsaturated ketones with a common double bond. This grouping is found in the indigo blue molecule. It consists of two identical molecules linked by a central carbon-carbon double bond with a planar, highly-conjugated structure (chromophore) responsible for its intense blue colour. The Bruylants test gives blue colour with oxydimorphine (2,2'-bimorphine), in agreement with the above commentary. Lesser intensity can be due to the minute quantity used in the test.

On the other hand, molybdenum dioxide is violet [23] and two products derived from it: dimolybdenum pentoxide (dark violet) and molybdenum blue [20].

Cf. Enedione in a single ring, [24].

4. Conclusion

The chemistry and the mechanism of the Bruylant's test for 2,2'-dimorphine have been cleared. The reactive species is protonated molybdic acid formed in situ which in combination with the electrodotic property of a phenol in the bimorphine forms a mixed molybdate. Interaction of the remaining hydroxyl group in this ester with a hydrion produces a synchronous mechanism involving five electron-shifts. Water and molybdenum dioxide are formed, and after two double bond shifts an enedione is afforded as final product. This grouping is present in indigo blue and besides MoO_2 is violet.

Compliance with ethical standards

Disclosure of conflict of interest

There is no conflict of interest to declare.

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