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ORIGINAL PAPER

Mechanism of α-acetyl-γ-butyrolactone synthesis

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The mechanism of α-acetyl-γ-butyrolactone (ABL) synthesis from γ-butyrolactone (GBL) and ethyl acetate (EtOAc) was explored by detecting the material changes involved and the enthalpies of formation of the synthons, products, and possible intermediates were calculated using the density functional theory. GBL forms a carbanion of γ-butyrolactone by losing an α-H under strongly alkaline conditions. ABL is then obtained via two reaction mechanisms. One of the reaction mechanisms involves direct reaction of the carbanion of GBL with EtOAc to produce ABL. The other involves the formation of a carbanion of α-(2-hydroxy-tetrahydrofuran-2-yl)-γ-butyrolactone through the reaction of two molecules of GBL, and the subsequent combination of this anion with EtOAc to produce ABL. ABL is thus formed through the above two kinds of competitive ester condensation reactions. It is unnecessary to take into account synthons' local thickness, and their self-condensation under these conditions. Both reactions of the carbanion of GBL with EtOAc and GBL are exothermic, so the control of their reaction rate is the key to their security. Considering the reasons above, this work applied synthon as the solvent, and avoided environmental pollution by alkylbenzene; also, accidents such as red material and fire were avoided by specific surface area of sodium metal control. Effective isolation of the organic and aqueous phases was performed using the salting out method. Thus, an environmentally friendly, safe, simple, and efficient new method for the synthesis of ABL with the yield higher than 90 % has been established.

Keywords: mechanism, enthalpy of formation, α-acetyl-γ-butyrolactone, synthesis

Introduction

As a five-membered oxygen-containing heterocyclic derivative, α-acetyl-γ-butyrolactone (ABL) is an important synthon in organic chemistry. As an intermediate product, ABL has been used in the synthesis of vitamin B1 and chlorophyll, to delay heartache and as an anti-angina agent. So far, there are only two published methods for ABL synthesis. The first one uses ethylene oxide and ethyl acetoacetate as synthons (Elsasser & Korte, 1993). Ethylene oxide is an inflammable and explosive chemical that has the disadvantages of very dangerous storage and reaction. The reaction proceeds slowly, giving low yields, and the product is difficult to purify. The other method uses γ-butyrolactone (GBL) and acetyl chloride or ethyl acetate (EtOAc) as synthons and alkylbenzene as the solvent (Jedliński et al., 1987; Koehler & Uhlenbrock, 1998; Lipkin et al., 1988; Qian, 2008). However, this method also has many disadvantages; such as serious safety issues, high costs, and environmental pollution, etc. On the other hand, the use of synthon as the solvent (Zhang et al., 2010a) is safe, proceeds under mild reaction conditions, and causes minimum environmental pollution and low energy consumption.

In the present work, the method of ABL synthesis using GBL, AcOEt, and metallic sodium as synthons was systematically studied. First of all, changes in the composition of the material in the reaction process were tracked and detected by GC. The variation correlation diagram of the content of the intermediates, products, and by-products with the reaction time was obtained. The values of the enthalpy of formation of the synthons, products, and possible intermediates, as

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