

Photoreactivity and polymorphism of cinnamic acid revisited

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Cinnamic acid is a classical example of molecules that are photoreactive in the solid state. The studies on its photoreactivity contributed to the rise of crystal engineering [1] and solid state organic synthesis [2]. Some of the most attractive features of organic reactions conducted in the solid state include their simplicity, often quantitative yields, stereospecificity, and that they can yield products that are hard or impossible to obtain by other methods. In contrast to the traditional "wet" synthetic methods, the outcome of a solid state reaction is defined by a unique arrangement of reactant molecules in the crystal. Therefore, the same reactant molecule being part of different solids can yield different products. Our recent studies focused on developing strategies for the predictable arrangement of molecules in molecular crystals and their reactivity [3-5]. The purpose of this work was to investigate how relative stability of different forms of a molecular solid can affect the outcome of a solid state reaction.

Cinnamic acid may exist in two photoreactive crystal structure forms (α and β polymorphs) that stereospecifically produce two different four-member ring products, with none of them forming or permitted to form in solution [6]. Our kinetic studies on the two solid state photoreactions also revealed differences other than the main product. From PXRD patterns, NMR spectra, and MS data, the α polymorph produces a single product. At the same time, the β polymorph yielded unreported side products along with the main one. The obtained data imply the presence of the polymorphic β to α transition during the photoreaction experiment. Remarkably, the polymorphic transition could not be induced by heating, in spite of the metastability of the β polymorph up to its melting point. The relationship between the crystal structure, solid state reactivity, and relative thermodynamic and kinetic stability of the two polymorphs have been explained based on our new experimental data.

References

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