Solid State Photoreactivity of Cinnamic Acid and Crotonic Acid Compared

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Solid state reactions are highly advantageous from various perspectives. Some of the remarkable characteristics of solid state reactions are (1) predictability, (2) stereospecificity, (3) no dependence on solvents or precious catalysts, (4) quantitative yields, and consequently (5) fewer or no side products [1-3]. Moreover, unique products can form in a crystalline solid, which either do not appear or do not survive due to their instability in a solution.

In this study, the solid state reactivity of cinnamic and crotonic acids (Figure 1) were compared using a photoreactor setup with two wavelengths of 254 and ~350 nm, 1H NMR, PXRD, and other techniques. It turned out both acids react in their crystalline state to produce a number of photoproducts. Despite similarity of the reactant molecules, the reaction pathways and the sets of products are very different.

The photoreactivity of cinnamic acid is complicated by its polymorphism. While the stable α-polymorph transforms into a single product upon UV irradiation, the metastable β-form yields multiple products. The irradiation of crotonic acid yields even a more complex mixture, with the samples undergoing amorphization and partial melting. Depending on the radiation wavelength and other conditions, crotonic acid yields four to five different products. While using a 254 nm wavelength results in a more complex mixture and partial melting of the samples, with the choice of 350 nm wavelength the number of products becomes restricted and the crystalline samples turn into an amorphous phase but still remain solid. To supress side reactions, we attempted to obtain and test cocrystals of the two acids with a peptide. A cocrystalline form of crotonic acid was successfully prepared. Presumably, the reactant molecules of the acid are incorporated in the interlayer space of the peptide H-bonded framework [4-5]. Our tests show that in cocrystals we can reduce the number of products to a single one. The type of product in the cocrystal system is very dependent on the wavelength used.

References

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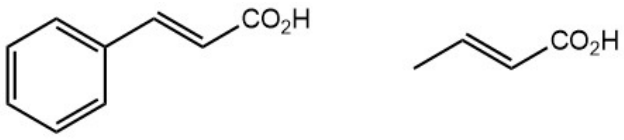

Figure 1. Cinnamic acid (left) versus crotonic acid (right)

Figure 1