Control of Reactivity in the Solid State Through Principles of Supramolecular Chemistry

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The crystalline solid state provides an environment that supports highly stereoselective reactions, wherein the stereochemistry of the product is largely controlled by the arrangement of molecules in the reactant crystal. However, the solid state has remained unexploited as a medium for synthetic chemistry, due to the difficulties related to achieving the crystal packing suitable for a reaction.

Our research group has approached the issue of controlling solid-state reactivity using principles of supramolecular chemistry, specifically template-controlled reactivity. Template-controlled solid-state synthesis uses linear templates, in the form of resorcinol, to direct solid-state [2+2] photodimerizations. The templates preorganize reactants within finite hydrogen-bonded molecular assemblies. Exposure of the assemblies in the solid state to ultraviolet radiation results in the stereospecific formation of a cyclobutane product.

The supramolecular nature of the liason between the reactant and the template provides the method with modularity that led us to explore the possibility to use the approach as a general way to conduct solid-state reactions. Specifically, we have addressed the construction of molecules with different sizes and shapes. In this contribution we report the construction of biologically relevant [3]- and [5]-ladderane frameworks, as well as the *ortho*-, *meta*- and *para*-[2.2]-cyclophane in quantitative yields and gram amounts.

Keywords: solid-state reactivity, supramolecular assemblies, photochemistry