Accelerating Hydrazone Exchange by UV Irradiation

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Hydrazone exchange, a popular tool in systems chemistry, especially in ABSTRACT dynamic combinatorial chemistry, suffers from relatively slow rates of equilibration, particularly when working with macrocyclic systems. This problem has been addressed by several different approaches, in general involving nucleophilic catalysis. In this report we present the application of UV irradiation to accelerate hydrazone exchange, using (E) - to (Z)-isomerization as the means of activating library members. A photostationary state was reached within one day, which, in the present system, resembled the state that took two weeks to reach in the absence of irradiation. This approach overcomes the use of excessive amounts of catalysts, working in forcing conditions, or the design of the systems being restricted to quickly exchanging species. It also broadens the connection between dynamic combinatorial chemistry and photochemistry, as photo-equilibration gives rise to photodynamic combinatorial libraries, an emerging phenomenon at the interface of these two chemistries.

Keywords: systems chemistry; dynamic combinatorial chemistry; hydrazone exchange; reversible covalent chemistry; photoswitching.

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