**NMR Detection of the Enamine Intermediate in Proline-Catalyzed Aldol Reactions**

**Significance:** An enamine intermediate in proline-catalyzed aldol reactions was identified in situ by NMR studies on self-aldolization of aldehydes in DMSO. Only E-configured s-trans-enamines were detected in accordance with the generally accepted mechanism of enamine catalysis. The enamines were found to form directly from oxazolidinones (e.g., 3), and not via central iminium or iminium-like intermediates (e.g., 2) as evidenced by NMR exchange spectroscopy (EXSY). These results indicate a possible role of oxazolidinones in the catalytic cycle, beyond their involvement in ‘parasitic equilibria’.

**Comment:** In enamine catalysis iminium species (e.g., 2) are generally proposed as intermediates in the interconversion between aldehydes, enamines, and oxazolidinones. In the current paper, the iminium intermediate 2 was not detected by NMR spectroscopy, probably due to its low concentration. However, the absence of EXSY cross-peak (for the proton circled red in the Scheme) between aldehyde 5 and enamine 4 suggested that enamine 4 might not be formed via the iminium intermediate 2, but directly from oxazolidinones 3a. A concerted E2 mechanism was recently proposed by Seebach (Helv. Chim. Acta 2007, 90, 425). As the unobserved 4/5 EXSY cross-peak might simply be below detection limit, more conclusive evidence was offered by the observation that the relative rate $k_{al}/k_{en}$ (calculated from the volumes of EXSY cross-peaks of 5 and 4 with 3a or 3b) was highly dependant on the oxazolidinone from which the aldehyde and enamine originate. This excludes a common intermediate (e.g., 2) and supports the consecutive mechanism.