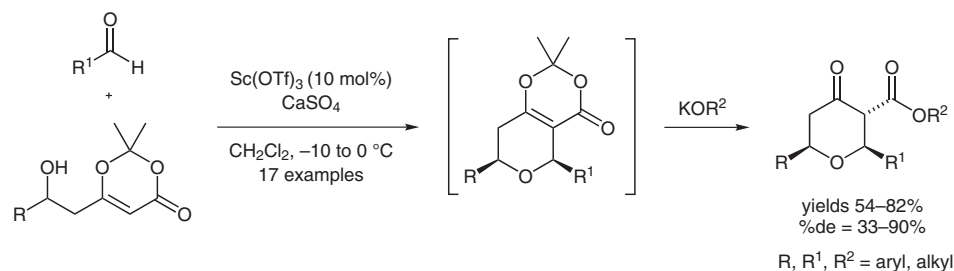


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Stereoselective Synthesis of Tetrahydropyran-4-ones from Dioxinones Catalyzed by Scandium(III) Triflate
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Scandium(III) Triflate-Catalyzed Stereoselective Synthesis of Tetrahydropyran-4-ones



Significance: Tetrahydropyran-4-ones were synthesized with high diastereoselectivity using a scandium(III) triflate-catalyzed cyclization between an aldehyde and β -hydroxydioxinones. Either the dioxinone intermediate could be isolated or direct addition of an alkoxide would generate the 2,6-disubstituted tetrahydropyran-4-one. Aromatic and aliphatic substituents including α -branched aldehydes were tolerated. A variety of substituents on the dioxinone were also explored.

Comment: Tetrahydropyrans and tetrahydropyran-4-ones are found in many biologically active compounds. Although there are several existing methods to create these structures, the novel approach developed here exploits the previously unexplored nucleophilic character of dioxinones. The mechanism is proposed to occur via formation of an oxocarbenium ion and intermolecular cyclization via a chair transition state. The dioxinone functionality in the products allow further synthetic manipulation; for example the addition of an alkoxide would form 2,6-disubstituted tetrahydropyran-4-one. Alternatively, acylketenes can be formed from the dioxinone intermediate and trapped with amine nucleophiles to yield β -keto amides.