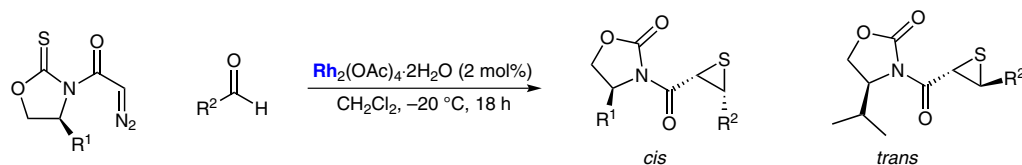


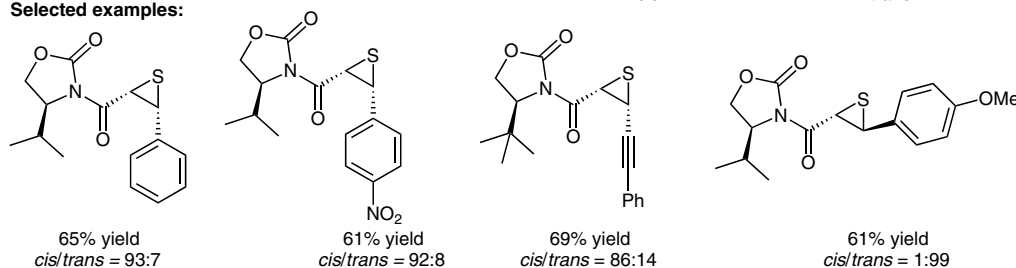
I. CANO, E. GÓMEZ-BENGOA, A. LANDA, M. MAESTRO, A. MIELGO, I. OLAIZOLA, M. OIARBIDE, C. PALOMO* (UNIVERSIDAD DEL PAÍS VASCO, SAN SEBASTIÁN AND UNIVERSIDADE DA CORUÑA, SPAIN)

N-(Diazoacetyl)oxazolidin-2-thiones as Sulfur-Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes
Angew. Chem. Int. Ed. **2012**, *51*, 10856–10860.

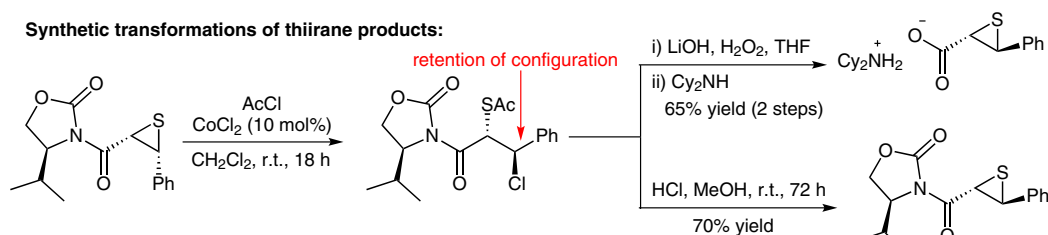
Asymmetric Synthesis of α,β -Thioepoxy Carbonyls by Rhodium Catalysis



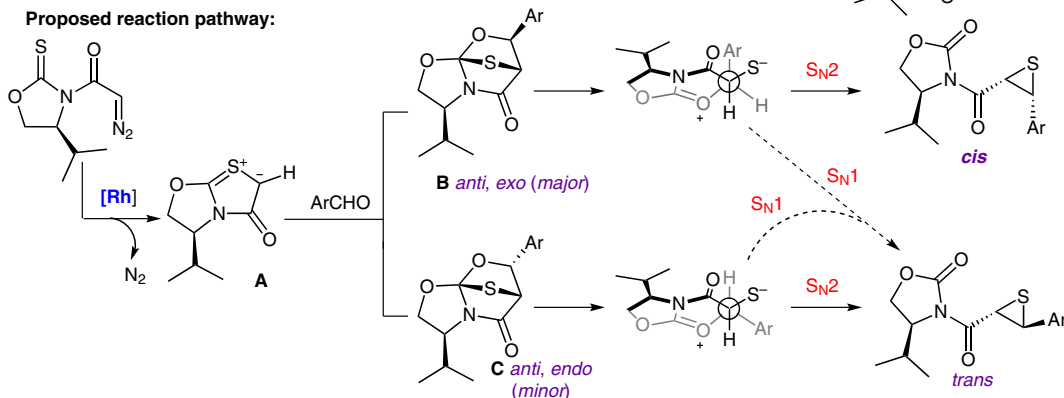
Selected examples:



Synthetic transformations of thirane products:



Proposed reaction pathway:



Significance: Stereoselective formation of C–S bonds is a difficult yet important challenge. This report describes the use of diazo thianes as intramolecular sulfur-donor reagents. Under rhodium catalysis, reaction with aldehydes forms thiiranes with high selectivity.

SYNFACTS Contributors: Hisashi Yamamoto, Patrick Brady
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DOI: 10.1055/s-0032-1317773; **Reg-No.:** H15312SF

Comment: Computational studies indicate formation of thiocarbonyl ylide intermediate **A**. Reaction with an aldehyde yields a tricyclic adduct, with preferential formation of *anti,exo*-product **B** by 0.8–1.2 kcal/mol, which collapses to the *cis* product by an S_N2 reaction. However, when the aryl substituent is anisyl, the *trans* product forms by an S_N1 mechanism.