

ROSKAMP-FENG REACTION



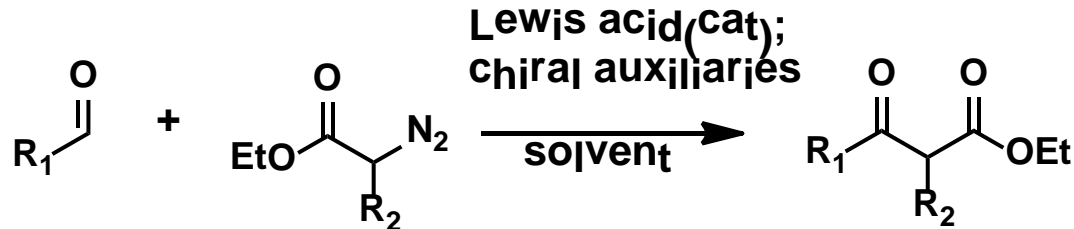
Background

Initially our aim was to generate an alkylidene-type reagent by reacting ethyl diazoacetate with a low-valent main group metal. This reagent could then convert an aldehyde into an alkene via a pseudo-Wittig type reaction. When we attempted this reaction to our surprise no olefinic products were observed; however, the reaction did produce a single product, a β-keto ester.

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Feng groups describe the first catalytic asymmetric Roskamp reaction using chiral N,N'-dioxide-scandium(III) complexes.

J.AM.CHEM.SOC.2010, 132, 8532-8533



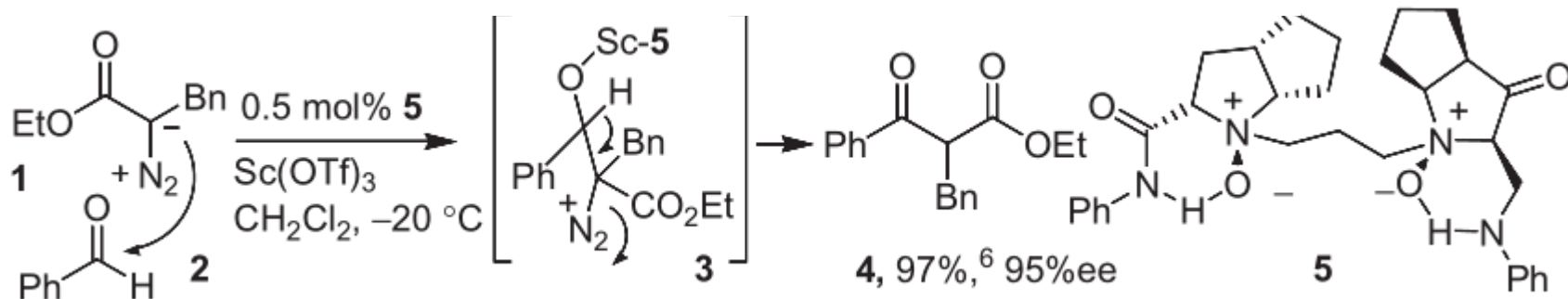
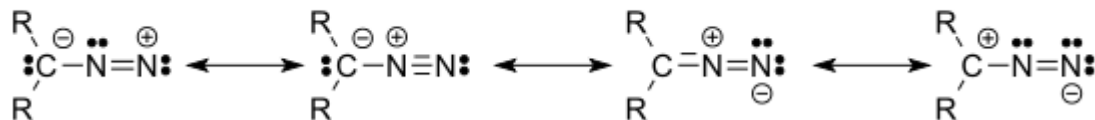
R_1 =alkyl, aryl; R_2 =alkyl, aryl or H; Lewis acid= BF_3 , ZnCl_2 , ZnBr_2 , AlCl_3 , SnCl_2 , GeCl_2 , SnCl_4 ;
 Solvent= THF , Et_2O , DME , CH_3CN , CH_2Cl_2 , PhCH_3

• Feature

- 1) The yields and relative rates of reaction were lower with aromatic substances. This suggested that a differentiation of two types of aldehydes might be possible.
- 2) Phenylacetaldehyde does not readily enolize under mild conditions.
- 3) The tertiary aldehydes react much slower.
- 4) When R_2 was not H, asymmetric reaction of β -keto ester with aldehydes use chiral auxiliaries.
- 5) Diazo sulfones, diazo phosphine oxide, and diazo phosphonates add to aldehydes in the presence of catalysts to yield β -keto sulfones, β -keto phosphine oxide, β -keto phosphonates, respectively.

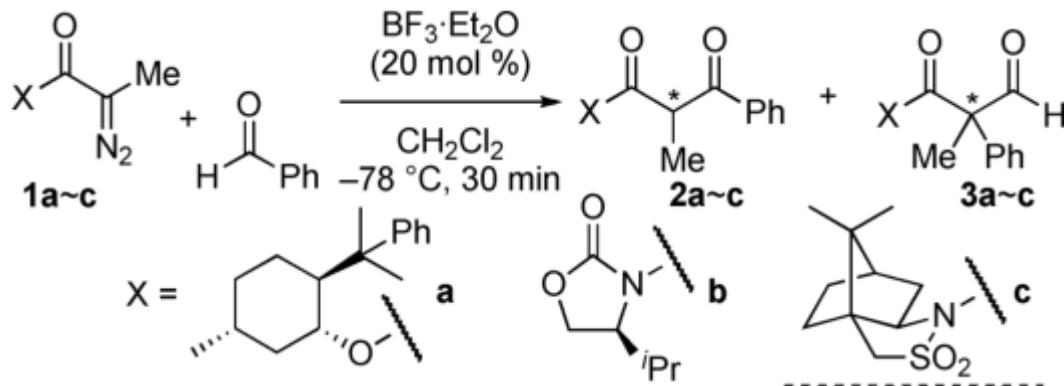
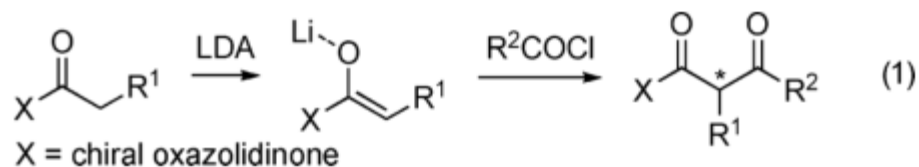
Mechanism

重氮化合物有如下共振式：

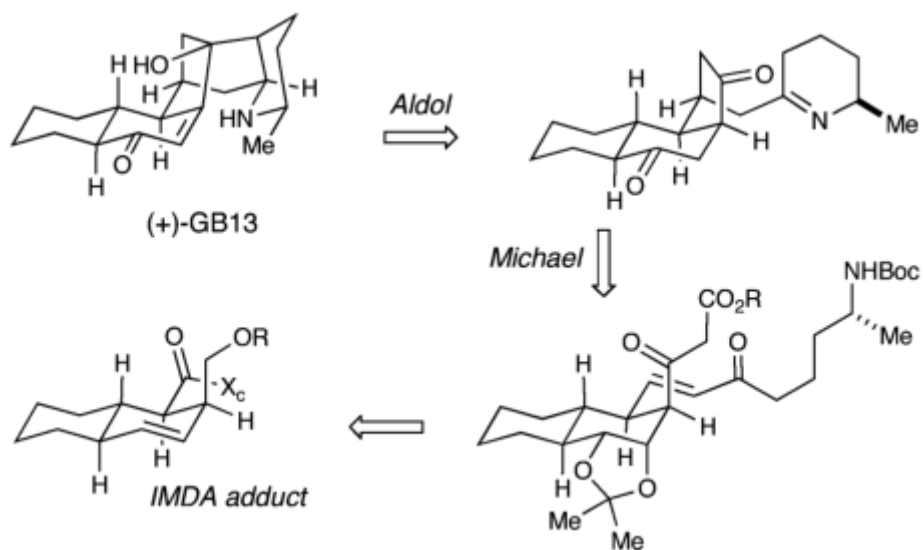
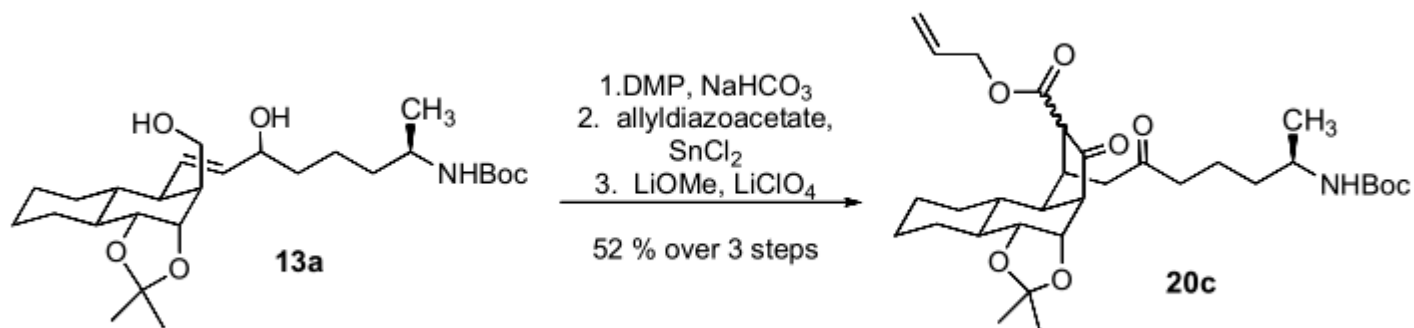


Chiral Lewis acid catalyst

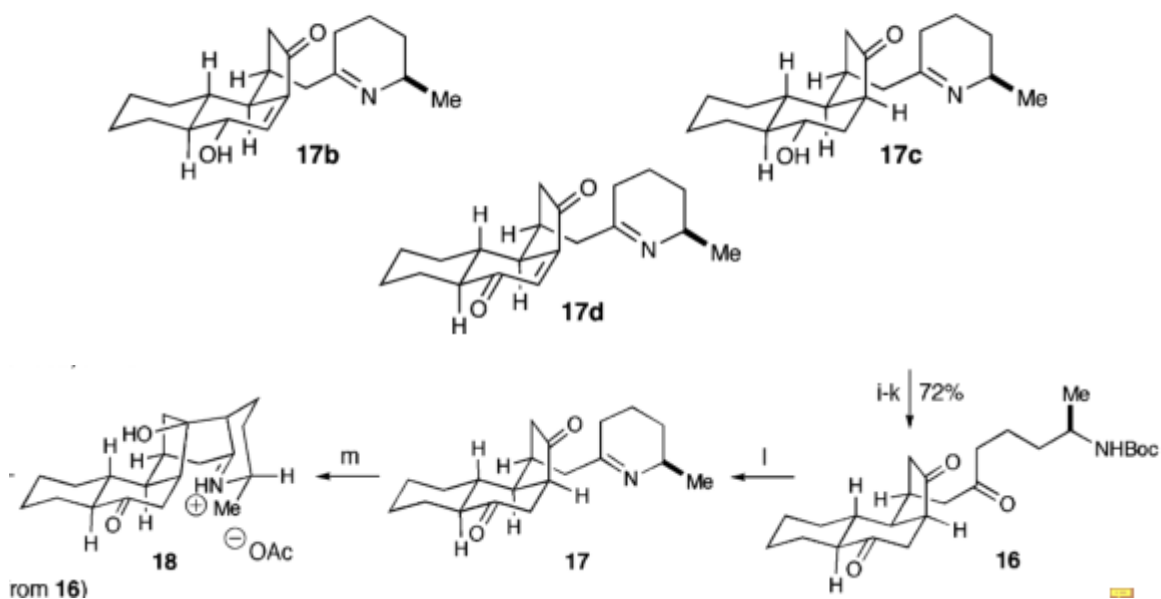
Claisen condensation



- Application



We next turned our attention to the intramolecular enamine aldol addition. To our gratification, after deprotection of the amine under acidic conditions, dehydration to the cyclic imine, and treatment with excess acetic acid in THF, the desired addition took place to give the aldol adduct isolated as its iminium ion **18**. Interestingly, the related structures depicted below failed to undergo the desired aldol addition. Alcohols **17b** and **17c** were inert to a variety of reaction conditions, highlighting the influence of the conformation of the decalin on cyclopentanone reactivity. Enedione **17d** appeared to undergo conjugate addition in preference to the desired 1,2-addition.



- *THANKS FOR YOUR ATTENTION!*