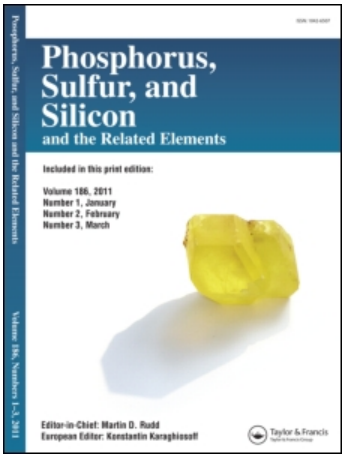

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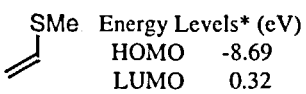
Carbon-Carbon Bond Formation Using Alkenylsulfides

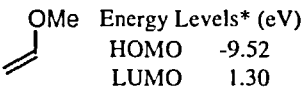
KEIJI TANINO and ISAO KUWAJIMA*
Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Highly stereoselective C-C bond forming reactions were developed on the basis of nucleophilic addition of alkenylsulfides to aldehydes, imines, and α,β-unsaturated carbonyl compounds.

KEY WORDS: ene reaction, diastereoselection, Lewis acid

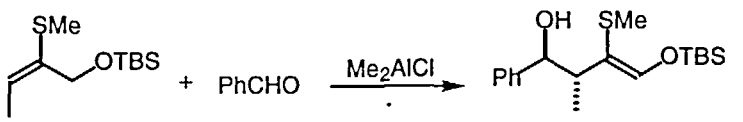
Although nucleophilic addition of enol ethers to electrophiles has been found widespread use in organic synthesis, much less attention has been given to alkenylsulfides as a nucleophile. The HOMO energy level of an alkenylsulfide is even higher than that of an enol ether. On the other hand, alkenylsulfides also show electrophilic character which is attributable to low LUMO energy level.



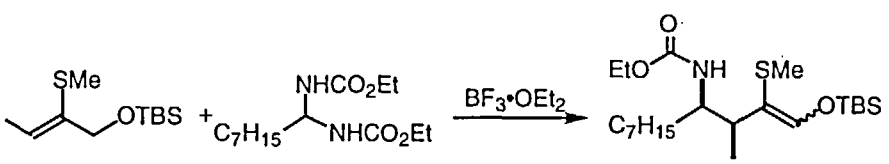


*calculated by PM3.

On the basis of these characteristic features of alkenylsulfides, we designed 2-(alkylthio)allyl silyl ethers to develop a carbonyl ene reaction which is applicable to a wide range of aldehydes. Under the influence of Me_2AlCl, the reactions of 2-(methylthio)crotyl silyl ether with aldehydes afforded corresponding adducts with high diastereoselectivity.[1] A highly stereoselective ene.reaction of aldimines was also achieved by using geminal biscarbamates as enophiles.[2]

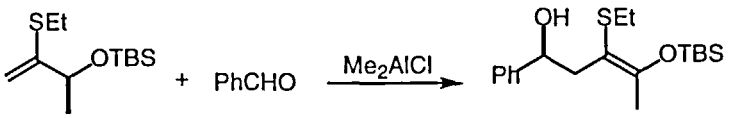


81% (*anti* : *syn* = >99 : <1)



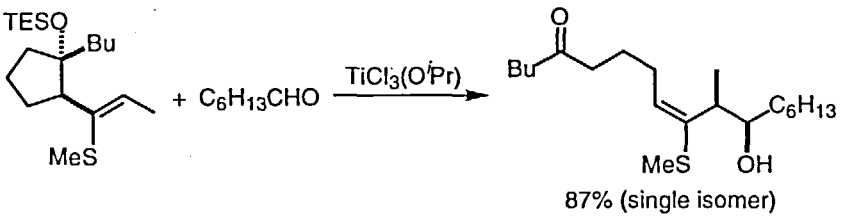
84% (*syn* : *anti* = 96 : 4)

On the other hand, optically active products were obtained through chirality transfer by the reaction of an optically pure ene substrate.[3]

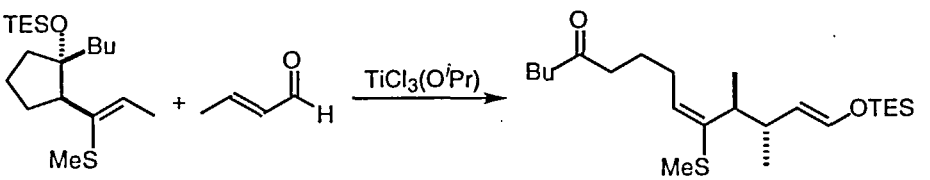


96% (96% ee)

A novel method involving intermolecular C-C bond formation and C-C bond cleavage was also developed utilizing the propensity of alkenylsulfides to undergo double-bond shifts.[4] The diastereoselectivity of the reaction with an aldehyde could be explained by assuming the cyclic transition state which imposes coordination of both carbonyl oxygen and sulfur to the titanium atom.



87% (single isomer)



88% (single isomer)

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