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A Stereoselective Approach to S-Vinyl Thioesters from Alkynes, Elemental Sulfur and Acyl Chlorides

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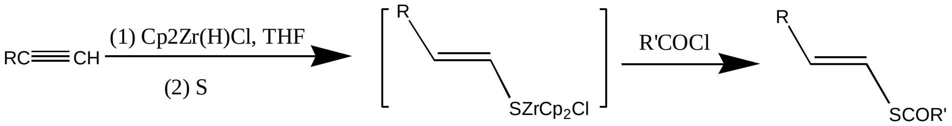
Abstract: A facile, stereoselective synthesis of S-vinyl thioesters from easily available starting compounds and reagents is showed.

Keywords: S-vinyl thioesters, hydrozirconation.

Thioesters are activated derivatives of carboxylic acids and exhibit acylating properties similar to carboxylic acid anhydrides[1]. S-vinyl thioesters are useful precursor for various sulfur-containing compounds[2], however, their synthetic methods are limited and most of the methods need somewhat tedious procedures. Reactions of α-carbanions of ethanethioate with carbonyl compounds such as Wittig reaction, Wittig-Horner reaction and Peterson reaction give S-vinyl thioesters [3]. Cu (I) –promoted coupling reaction of vinyl bromides and PhC(O)SNa is stereoselective approach if only vinyl bromides with certain stereochemistry are available[4]. Treatment of vinyl alane[5] or vinylmagnesium bromide[6] with sulfur followed by acid derivatives also give S-vinyl thioesters. Recently synthesis of S-vinyl thioesters by Meyer-Schuster rearrangement of sulfur-substituted propargyl alcohols was reported[7]. Herein we report a facile, stereoselective synthesis of S-vinyl thioesters from easily available starting compounds and reagents.



1 **2** **3a-3f**

3a: R=Ph, R'=Me
3b: R=Ph, R'=Ph
3c: R=Ph, R'=Et
3d: R=Ph, R'=n-C_5H_{11}
3e: R=$MeOCH_2$, R'=Ph
3f: R=n-C_4H_9, R'=Ph

The insertion of elemental sulfur into Csp^2-Zr bond of alkenylchlorozirconocenes, derived from hydrozirconation of alkynes, undergoes smoothly in THF at about 0°C and usually completes in 30 minutes, giving a yellow solution. The produced vinylthio zirconocenes **2** were trapped with acyl chlorides, giving S-vinyl thioesters **3** in moderate yields. The results are summarized in **Table 1**.

The stereochemistry of compounds **3** can be easily determined, since in their ^{1}H-NMR spectra the vinyl protons show coupling constants of 14-16Hz, typical for *trans* positioned protons[8]. The IR spectra show strong absorption at about 1700 cm^{-1}, which is characteristic of carbonyl group.

Table 1. Synthesis of S-vinyl thioesters and some of their spectra data.

Products	$J_{vinyl\ protods}$ (Hz)	$\nu_{C=O}$ (cm^{-1})	Isolated yields (%)
3a	16.0	1710	48
3b	16.0	1690	57
3c	16.0	1710	46
3d	16.2	1720	54
3e	16.0	1690	59
3f	16.0	1680	51

According to our knowledge, the insertion of elemental sulfur into Csp^2-Zr bond of alkenylchlorozirconocenes, derived from hydrozirconation of alkynes, has not yet been reported. The present method has provided a stereoselective synthesis of S-vinyl thioesters from easily available starting compounds and reagents.

Acknowledgments

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