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A "TUNABLE" STEREOSELECTIVE ALKENE SYNTHESIS BY IODODESILYLATION OF VINYLSILANES

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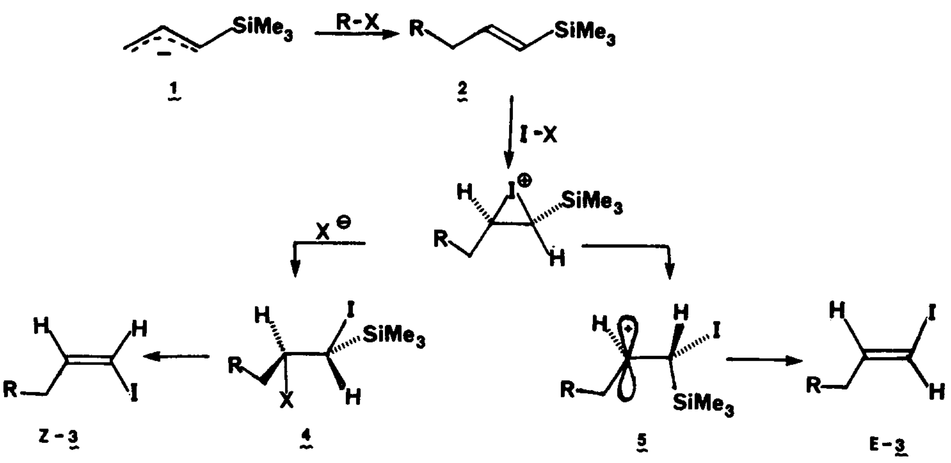
Abstract: The stereoselectivity of iododesilylation of terminal E-vinylsilanes varies with changing amount of Lewis acid. The use of this "tunable" stereoselective reaction was demonstrated by the syntheses of two insect sex pheromones with defined E/Z isomeric ratios.

The sex pheromones of a number of insects are often specific blends of E and Z geometrical isomers of alkenes. Particularly interesting are the sex pheromone systems of closely related tortricid moth species where slight changes in the stereoisomeric ratio of the same two components of 11-tetradecenyl acetate can effect specificity among sympatric species[1]. The most common approach to the synthesis of alkenes with specific E:Z ratio is by stereospecific semihydrogenation of the precursor alkynes to give separately the E- and the Z-alkenes[2] followed by blending of the two geometrically "pure" isomers in the required ratio. Conceptually, such an approach is inherently inelegant. We wish to describe here a "tunable" stereoselective alkene synthesis where the ratio of stereoisomers can be controlled at will in one critical step.

Recently, we reported that trialkylsilylallyl anion (1) reacts with alkyl halides to give regio- and stereoselectively the E-vinylsilanes 2.[3] Iododesilylation of 2 with iodine monochloride followed by KF treatment gave the Z-vinyliodide 3 with inversion of stereochemistry.[3] Coupling of Z-3 with organometallic reagents provided a convenient method for the synthesis of Z-alkenes and this route has been used for the synthesis of a number of insect sex pheromones[4] [5]. In trying to extend this approach to the synthesis of E-alkenes, iododesilylation of 2 with iodine was attempted. In the literature, this reaction was implied to proceed with retention of stereochemistry.[4] [5] It was with some surprise that we found that the reaction gave Z-vinyliodide mainly as well. In order to explain the discrepancy, we rationalize that for terminal E-vinylsilanes, addition of iodine to give the di-iodo intermediate 4 is favoured over the ionic intermediate 5, leading to overall inversion. One



way to overcome the addition pathway is to use Lewis acid to diminish the reactivity of X^-. Indeed, when one or more moles of Lewis acid ($AlCl_3$, $SnCl_4$ or $SbCl_5$) was added together with iodine, mainly E-vinyliodide 3 was obtained[7]. It seemed to us that by varying the amount of Lewis acid added, the ratio of E to Z-vinyliodide in the iododesilylation reaction can be varied. This was found to be the case (Figure 1). Depending on the Lewis acid used,

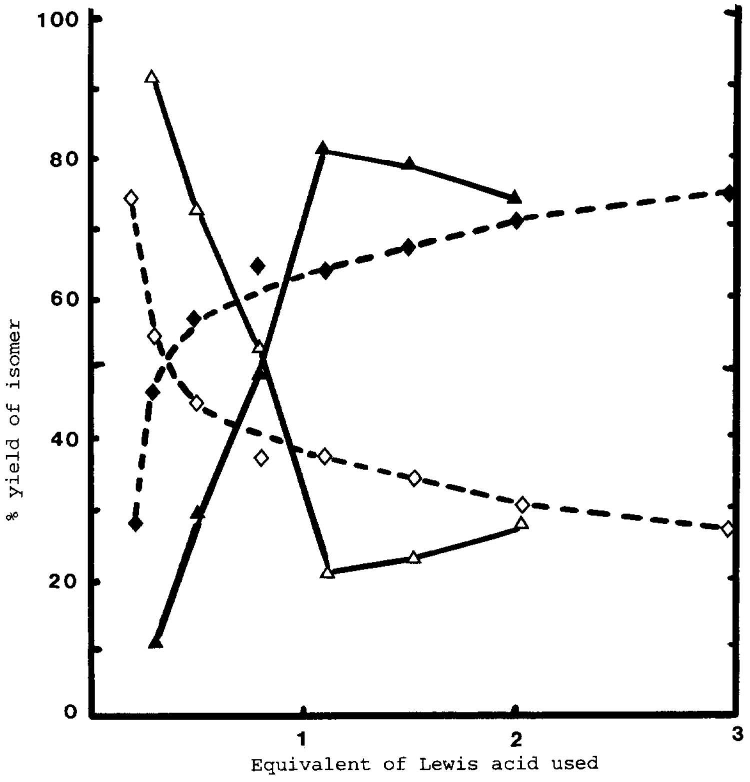
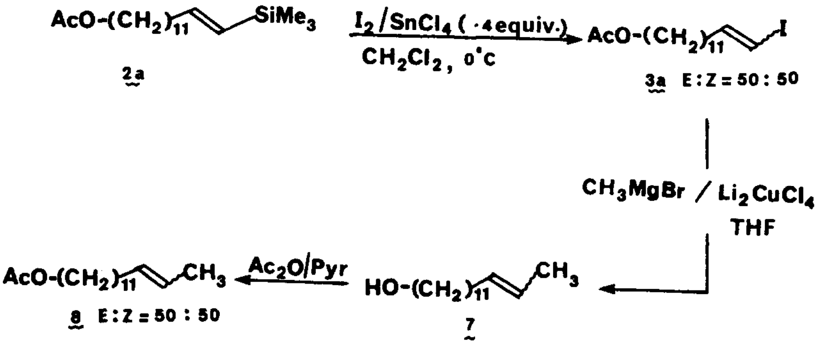


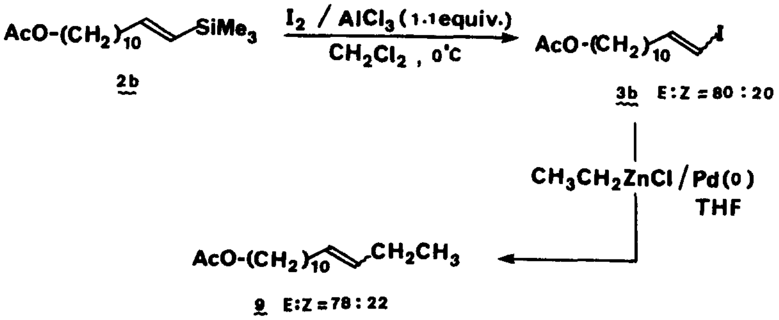
Figure 1. Variation in the E/Z isomeric ratio of 3b in the iododesilylation of 2b according to the amount of Lewis acid used.
——— $AlCl_3$, △ Z, ▲ E; - - - - - $SnCl_4$, ◇ Z, ◆ E.

ratio of E/Z can vary between 20:80 to 95:5, with $SnCl_4$ being the Lewis acid of choice in giving the cleanest products in good yields. We use the term "tunable" to describe the nature of the stereoselectivity of the reaction, i.e. the E/Z ratio can be reversed by using different amounts of Lewis acid for the iododesilylation.



Scheme 1

The use of this "tunable" stereoselective alkene synthesis was demonstrated by the syntheses of the sex pheromones of Asian corn borer[6], 8 (E:Z = 50:50) (scheme 1) and of oak leaf roller moth[1], 9 (E:Z = 78:22) (scheme 2).



Scheme 2

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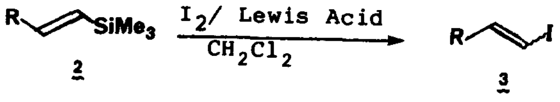
7. The vinylsilanes were prepared following the procedure described in reference 3. The mixture of γ and α addition products was treated successively with catalytic amount of HI/C_6H_6 and HCl in methanol. The hydroxyvinylsilanes were purified by HPLC and acetylated in usual manner (Ac_2O/Pyr). The Lewis acid mediated iododesilylation of the vinylsilanes was carried out according to the following general procedures: A solution of iodide (1 equivalent, freshly sublimed) and Lewis acid (0.1 to 3.0 equivalent) in methylene chloride (2 ml/mmole) was prepared and cooled to 0°. To this mixture, a solution of vinylsilane (1 equivalent) in CH_2Cl_2 (2 ml/mmole) was added dropwise. The reaction mixture was stirred for 1 h. and quenched with aqueous sodium thiosulfate. The organic solution was dried (Na_2SO_4), filtered and evaporated to give vinyliodide 3 in 60-95% yield (Table 1). Compound 3 was purified by Flash Chromatography (hexane-Ethyl acetate 10:0.2) and used for subsequent alkylation. The ratio of stereoisomers of 3 was determined by capillary gas chromatography.

TABLE 1:
Stereoselectivity in the Iododesilylation of 2 in the Presence of Lewis Acid



Entry[7]	2(R-)	Lewis Acid	Reaction Condition	% yield of 3	E/Z ratio
1	$CH_3-(CH_2)_{12}-$	$SnCl_4$	2.0 equiv. -78°C	95	18:1
2	$CH_3-(CH_2)_{12}-$	$SnCl_4$	1.1 equiv. -78°C	95	14:1
3	$CH_3-(CH_2)_{12}-$	$AlCl_3$	1.1 equiv. - 0°C	82	4:1
4	$AcO-(CH_2)_{10}-$	$AlCl_3$	1.1 equiv. 0°C	82	4:1
5	$AcO-(CH_2)_{11}-$	$SnCl_4$	2.0 equiv. -78°C	92	13:1
6	$AcO-(CH_2)_{11}-$	$SnCl_4$	1.1 equiv. -78°C	90	8:1
7	$AcO-(CH_2)_{11}-$	$SbCl_5$	1.1 equiv. -78°C	[a] 82	7:1
8	$AcO-(CH_2)_{11}-$	$SbCl_5$	2.0 equiv. -78°C	[a] 60	3:1

a) Vinyl chloride side products were obtained in 10% and 26% yields in entries 7 and 8 respectively.

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