# REGIOSELECTION IN THE ALKYLATION OF TRIMETHYLSILYLALLYL ANION - STEREOSELECTIVE SYNTHESIS OF DISUBSTITUTED ALKENES

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Abstract: The regioselection in the alkylation of trimethylsilylallyl anion can be controlled by the use of Schlosser's base to give predominately  $\gamma$ -product with transgeometry at the double bond. Application of this approach to the synthesis of Z-9-tricosene and the Gypsy moth sex pheromone is demonstrated.

 $\alpha$ -Trimethylsilylallyl lithium (I,M = Li<sup>+</sup>) generated readily from the reaction of trimethylallylsilane and n-butyllithium in TMEDA-THF, was reported to react with methyl iodide to give exclusively the  $\gamma$ -product II (R = Me) (Equation 1) with trans geometry at the double bond. In our hands however, alkylation of I with a number of alkyl halides was found to give a mixture of  $\gamma$ - and  $\alpha$ -products II and III (Table I). The presence of two regioisomers were verified by GC, GC-MS,  $^{1}$ H-nmr and in some cases  $^{29}$ Si-nmr. Furthermore, the ratio of  $\alpha$ : $\gamma$  products does not seem to vary significantly with the change of the substitution on silicon (Me or Ph), the solvent system used (HMPA-THF) or by the addition of DABCO or 12-crown-4. Since the nature of the counter ion is known to affect the regionselection in the reaction of allylic system with electrophiles, the reaction was repeated with addition of various metal salts (MgX<sub>2</sub>, ZnX<sub>2</sub>, CuX), but again without appreciable change in the  $\alpha/\gamma$  ratio.

TABLE I: Relative amounts of  $\alpha$ - and  $\gamma$ -products in the alkylation of trimethylsilylallyl lithium in TMEDA-THF.

Alkylhalide (R-X)	$\gamma$ -products ( $\widetilde{II}$ )	$\alpha$ -products ( $\underbrace{\text{III}}_{}$ )	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	65%	33%	
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub> -CH <sub>2</sub> I	65%	35%	
Ch <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub> -CH <sub>2</sub> Br	57%	42%	

<sup>&</sup>lt;sup>†</sup>the isolated yield of the two products was nearly quantitative.

However, when Schlosser's base  $^3$  (KO $^t$ Bu/n-BuLi in hexane) was used as the proton-abstracting system to generate I, alkylation with alkyl halides gave predominantly the  $\gamma$ -adduct II

(Table II)  $^4$ . Furthermore, we found that the minor  $\alpha$ -adduct (III) can be readily removed by treating the crude mixture with a catalytic amount of hydroiodic acid (57%) in benzene at room temperature. We have thus been able to obtain the pure  $\gamma$ -adduct II consistently in about  $\sim\!80\%$  yield by simple distillation.

Table II: Yield of Product II in the alkylation of I when KO<sup>t</sup>Bu/n-BuLi was used.\*

	Alkyl halides	γ-products (II)	α-products (III)	b.p torr**
a.	CH3-(CH2)7-CH2I	86%	14%	120°C - 24
b.	CH3-(CH2)10-CH2Br	85%	15%	180°C - 4
с.	CH3-(CH2)6-CH2CT	80%	16%	146°C - 50
d.	CH3-(CH2)5-CH2Br	80%	18%	86°C - 24
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	83%	17%	
	CH3CH2CH2I	81%	17%	
	CH3-(CH2)3CH2C1	80%	18%	85°C - 42
	CH3CH2CH2CH2I	81%	19%	78°-80°C-60
	CH2=CH-CH2Br	76%	-	
	CH3CH=CH-CH2C1	67%	-	~~~
	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C1	78%	20%	98°C - 760
	THPO-(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> Br	90%	10%	

<sup>\*</sup> For experimental procedures, see footnote 4.

Since vinylsilanes can react with electrophiles with high stereospecificity  $^{5,6}$ , the present stereoselective synthesis of E-vinylsilane II offers a facile method for the stereoselective synthesis of disubstituted alkenes. Thus vinylsilane IIb reacted with I $_2$  to give the E-vinyliodide IVb, and with ICl KF to give Z-vinyliodide IVb. By the same way, the vinylsilane IIk was converted into Z-vinylhalide IVk. The vinyl halides coupled with organizinc and catalytic amount of  $(Ph_3P)_4Pd$  to give disubstituted alkenes stereospecifically. We have demonstrated the usefulness of this approach by the synthesis of Z-9-tricocene(V) and the gypsy moth sex pheromone (VII) according to Scheme I and Scheme II.

#### Scheme I:

<sup>\*\*</sup> The boiling points of pure  $\gamma$ -product II and are uncorrected.

<sup>†</sup>e,f,i the trans-vinyl silanes were purified by simple evaporation of solvent.

<sup>††1,</sup> the reaction time was 36 hours.

## Scheme II:

Since functionalized alkyl halides also react with I with the same regio and stereoselectivity (eg. III), the present method offers a general approach to the synthesis of a number of other insect pheromones with either Z or E double bond geometry.

#### References and notes:

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### 4. General procedure: A - Alkylation

A suspension of K0<sup>t</sup>Bu (3.37g, 30 mmoles) in dry hexane (15 ml) was cooled in ice bath, and n-BuLi (18.8 ml, 1.6M) was added dropwise. The ice bath was removed and the mixture was stirred for 30 min then cooled, down to  $-78^{\circ}$ C. Freshly distilled anhydrous ether (25 ml) was added followed with allyltrimethylsilane (3.43g, ~4.8 ml). The solution was allowed to warm to r.t. for 3 hr 30 min and cooled back to  $-78^{\circ}$ C before addition of the alkyl halide (20 mmoles) in 10 ml of ether. The reaction mixture was stirred from  $-78^{\circ}$ C to room temperature for 17 hours then washed with water, dried over MgSO<sub>4</sub>(or K<sub>2</sub>CO<sub>3</sub>) and evaporated. The residue was dissolved in pentane and filtered through a layer of silica gel, a colourless liquid was obtained after concentration.

# B - Selective desilylation

The mixture of II and III obtained from A was diluted with 100 ml of benzene and 0.10 ml of HI (57%) was added. The solution was stirred for 4-6 hrs. and the reaction was followed by GC. The reaction mixture was washed with  ${\rm Na_2S_2O_3}$  (10%), dried over MgSO<sub>4</sub> and evaporated. The residue was purified by distillation.

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