

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 γ -product with trans geometry at the double bond. Application of this approach to the synthesis of Z-9-tricosene and the Gypsy moth sex pheromone is demonstrated.

α -Trimethylsilylallyl lithium (I, $M = Li^+$) generated readily from the reaction of trimethylallylsilane and n-butyllithium in TMEDA-THF, was reported¹ to react with methyl iodide to give exclusively the γ -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 γ - and α -products II and III (Table I). The presence of two regioisomers were verified by GC, GC-MS, ¹H-nmr and in some cases ²⁹Si-nmr. Furthermore, the ratio of α : γ 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 regioselection² in the reaction of allylic system with electrophiles, the reaction was repeated with addition of various metal salts (MgX_2 , ZnX_2 , CuX), but again without appreciable change in the α / γ ratio.

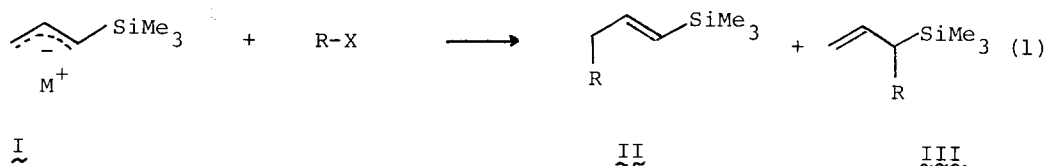


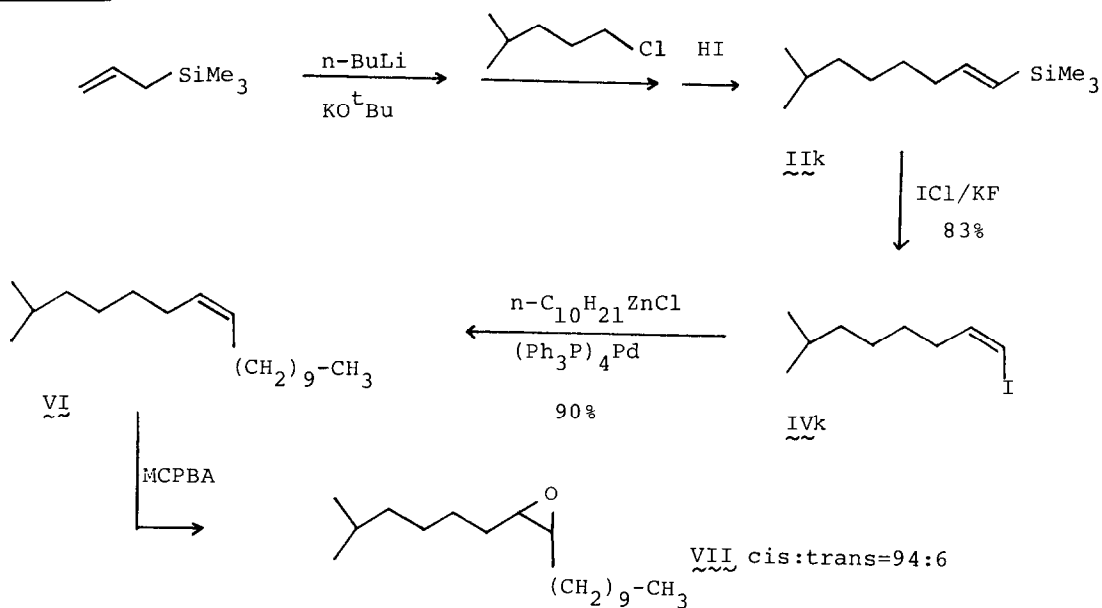
TABLE I: Relative amounts of α - and γ -products in the alkylation of trimethylsilylallyl lithium in TMEDA-THF.

Alkylhalide (R-X)	γ -products (II)	α -products (III)
$CH_3CH_2CH_2I$	65%	33%
$CH_3-(CH_2)_8-CH_2I$	65%	35%
$CH_3-(CH_2)_8-CH_2Br$	57%	42%

[†]the isolated yield of the two products was nearly quantitative.

However, when Schlosser's base³ ($KO^tBu/n-BuLi$ in hexane) was used as the proton-abstracting system to generate I, alkylation with alkyl halides gave predominantly the γ -adduct II

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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- General procedure: A - Alkylation

A suspension of KO^tBu (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°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°C before addition of the alkyl halide (20 mmoles) in 10 ml of ether. The reaction mixture was stirred from -78°C to room temperature for 17 hours then washed with water, dried over MgSO_4 (or K_2CO_3) 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 $\text{Na}_2\text{S}_2\text{O}_3$ (10%), dried over MgSO_4 and evaporated. The residue was purified by distillation.

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