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THE SYNTHESIS OF ALKENES FROM CARBONYL COMPOUNDS AND CARBANIONS α TO SILICON.

IX: STEREOSELECTIVE SYNTHESIS OF TETRASUBSTITUTED ALKENES[1].

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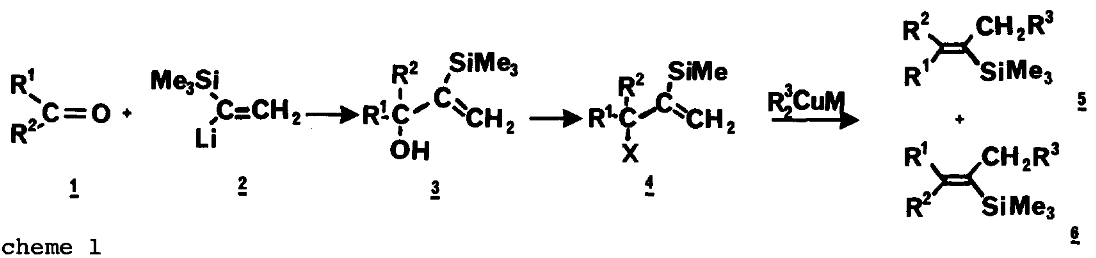
A number of methods have been developed for the stereoselective synthesis of di- and tri-substituted alkenes[3], however, many of them are not applicable to the synthesis of tetra-substituted alkenes. Recently, vinylsilanes are recognized to be versatile synthetic intermediates[4,5], and their use for the stereoselective synthesis of di- and tri-substituted alkenes have been reported by us[6,7] and others[8,9]. Extension of the vinylsilane approach to tetra-substituted alkenes appears to be desirable. Two such approaches, both starting with silylacetylenes, have been reported[10,11], and both suffer some disadvantages. The tetraorganoborate route[10] is applicable only to the synthesis of alkenes with two identical groups at one end of the double bond, whereas the organo-nickel route[11] is limited to alkenes with at least one methyl group on the double bond. We wish to report here our approach to tetra-substituted alkenes starting from carbonyl compounds.

The overall transformation can be illustrated by Scheme 1. Reaction of ketones **1** with α-trimethylsilylvinyl lithium **2** at -78° gave the alcohols **3** in good yields[12]. Conversion of the tertiary alcohols **3** into compounds **4** proved to be difficult. Reaction of **3** with thionyl chloride to give **4** (X = Cl) yielded mainly products of elimination[12]. The trifluoroacetates **4** (X = CF_3CO_2) also eliminated trifluoroacetic acid to give dienes rather readily[12]. The benzoates **4** (X = $C_6H_5CO_2$) could be prepared in moderate yields (~ 50-60%) from **3** but their subsequent reaction with organocopper reagents to give tetra-substituted alkenes **5** and **6** did not proceed with good stereoselectivity (Table 1).

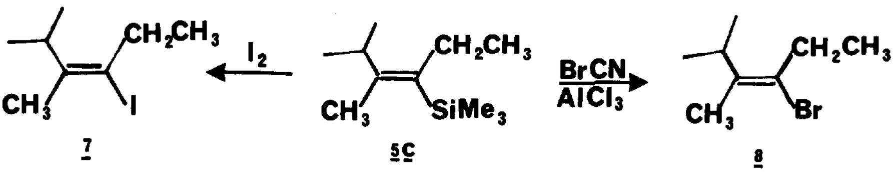


Scheme 1

Attempts to convert the alcohols 3 into the corresponding acetates 4 gave ($X = CH_3CO_2$) low yield with most conventional reaction conditions. A recent procedure, using acetylchloride/silver cyanide[13] eventually turned out to be extremely satisfactory. The acetates 4 ($X = CH_3CO_2$) could be obtained consistently in ~80% yield.

Reaction of 4 ($X = CH_3CO_2$) with organocopper reagents gave mixtures of the tetra-substituted alkenes 5 and 6 in a yield of ~70-80%. The stereoselectivity of the reaction depends on the relative steric size of the two groups R^1 and R^2 (Table 1). With R^1 being methyl, stereoselectivity increases from 2:1 for R^2 = ethyl, to 4:1 for R^2 = i-butyl and to > 11:1 for R^2 = i-propyl. This indicates that the major isomer is the one with the bulky trimethylsilyl group <u>trans</u> to the larger of the two, <u>viz</u> R^2. This assignment of stereochemistry is also consistent with ^{13}C chemical shifts and relative retention times in gas chromatography of the two isomers, criteria which we have developed for the differentiation of geometric isomers of tri-substituted vinylsilanes[14].

Compound 5c has been halodesilylated to give the corresponding iodo- and bromo-compounds (7 and 8) according to scheme 2. The reactions proceeded with high stereospecificity. Even though the stereochemistry of the reactions have not been ascertained with rigor, it is assumed to proceed with retention on the basis of similar experience with the less substituted vinylsilanes[7].



Scheme 2

Acknowledgement

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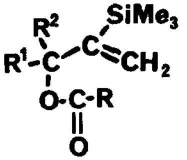
Table 1. Synthesis of tetra-substituted vinylsilanes starting from allylic esters 4 and organocopper reagents.



4

		R^3_2CuM	Products	(% isolated yield)	Stereoselectivity E:Z
4a	R^1=Me,R^2=Et,R=Ph	Me_2CuLi	$\mathrm{(Et,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(70)	50:50
4a	R^1=Me,R^2=Et,R=Ph	Me_2CuMgI	"	(-)	65:35
4b	R^1=Me,R^2=i-Bu,R=Ph	Me_2CuLi	$\mathrm{(iBu,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(70)	50:50
4b	R^1=Me,R^2=i-Bu,R=Ph	Me_2CuMgI	"	(60)	58:42
4c	R^1=Me,R^2=iPr,R=Ph	Me_2CuLi	$\mathrm{(iPr,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(65)	53:47
4d	R^1=Me,R^2=Et,R=Me	Me_2CuMgI	$\mathrm{(Et,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(80)	65:35
4d	R^1=Me,R^2=Et,R=Me	n-$Bu_2CuMgBr$	$\mathrm{(Et,Me)C{=}C}{<}^{\mathrm{n\text{-}C_5H_{11}}}_{\mathrm{SiMe_3}}$	(75)	62:38
4e	R^1=Me,R^2=i-Bu,Re=Me	Me_2CuLi	$\mathrm{(iBu,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(75)	70:30
4e	R^1=Me,R^2=i-Bu,R=Me	Me_2CuMgI	$\mathrm{(iBu,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(70)	80:20
4f	R^1=Me,R^2=i-Pr,R=Me	Me_2CuMgI	$\mathrm{(iPr,Me)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(75)	92:8
4g	R^1=Et,R^2=CH_2Ph,R=Me	Me_2CuMgI	$\mathrm{(PhCH_2,Et)C{=}C}{<}^{\mathrm{Et}}_{\mathrm{SiMe_3}}$	(75)	76:24

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