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Preliminary communication

REGIOSELECTION IN THE REACTION OF α-SILYLOXYALLYL CARBANIONS WITH ELECTROPHILES

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Summary

Regioselection in the reaction of α-silyloxyallyl carbanion with electrophiles has been found to change with the nature of leaving groups in the electrophiles.

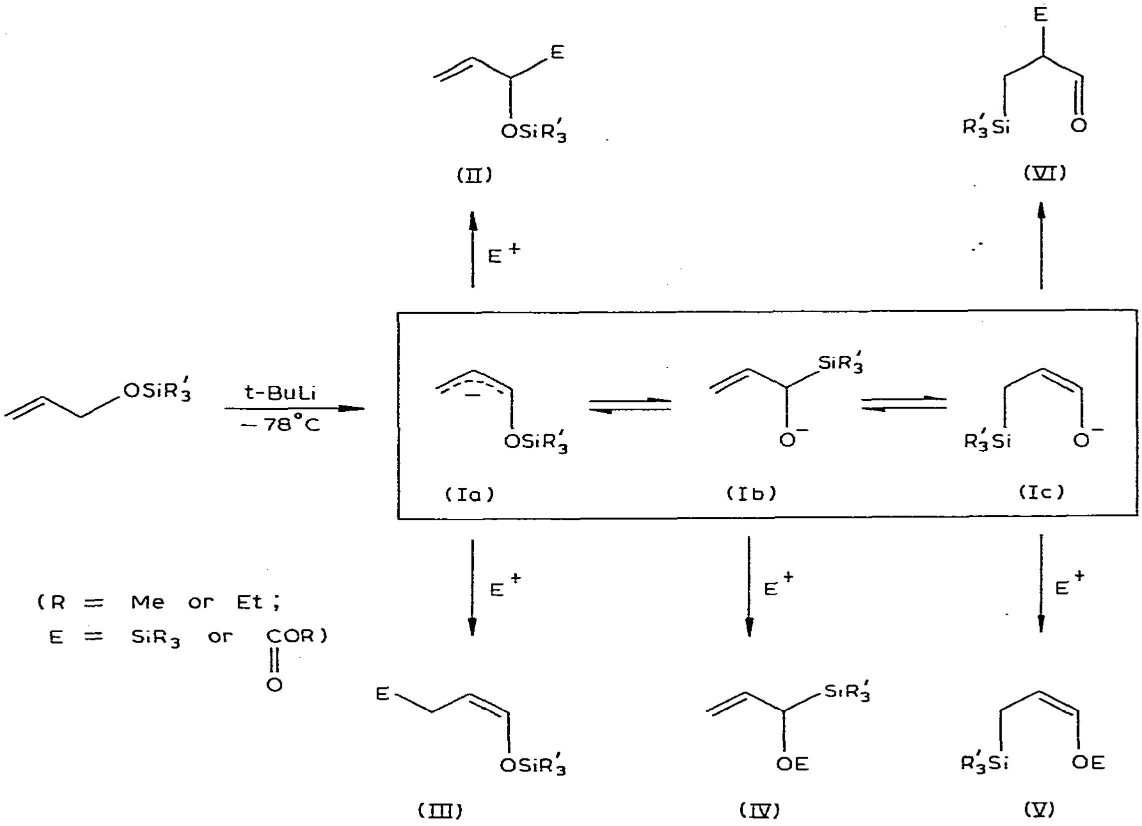
α-Silyloxyallyl carbanions (Ia) have been used as β-acyl carbanion equivalents in a number of synthetic reactions [1—3]. Because of the possibility [4] that Ia can rearrange to the corresponding silyl alkoxides Ib and Ic, the control of regiochemistry in the reaction of I with electrophiles poses a challenging question.

In all, there could be five different products, II—VI, as well as possible geometric isomers of III and V. Reactions of I with alkyl halides [1], proton sources [5], carbonyl compounds and silyl chlorides [3,5] have been reported. We report here the reactions of I with chloroformates, carbonates and silyl halides, with special emphasis on factors which may influence the regioselectivity of the reaction.

1. Reaction with silyl halides

In agreement with previous reports [3,5], we find that I reacts with trialkylchlorosilane in THF at −70°C to give exclusively IV by way of Ib (Table 1, entries 1 and 2). The regioselectivity is thus independent of the nature of the alkyl group on silicon. We find further that under these reaction conditions, the regioselectivity also is independent of the nature of the halide (Table 1, entries 3—6).

However, when the silylation reaction is carried out in a solvent system of THF and HMPA at −78°C, compounds III and IV are formed to varying extent. By reaction of trimethylchlorosilane with α-triethylsilyloxyallyl carbanion (entry 11), it can be demonstrated that III and IV are derived from silylation of Ia and Ib, respectively. The absence of involvement of Ic is not unexpected since it is known that the rearrangement to Ic occurs only at a higher temperature

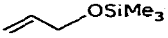
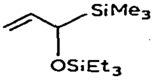
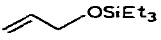
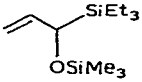
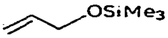
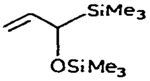
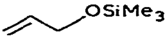
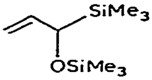
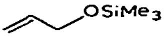
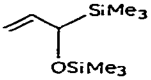
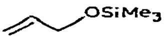
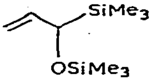
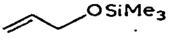
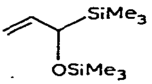
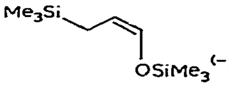
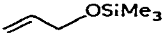
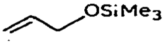
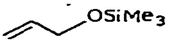
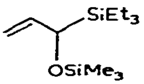
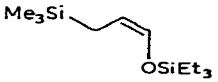
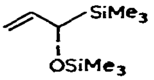


(~ −10°C) [2]. The extent of *C*-silylation (III) vs. *O*-silylation (IV) is, however, dependent on the nature of the halide, with a decreasing ratio of *C*-silylation/*O*-silylation as the halide is changed from fluoride to iodide (entries 7 to 10).

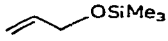
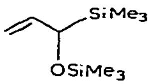
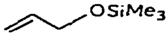
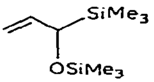
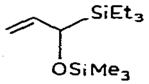
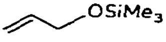
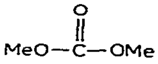
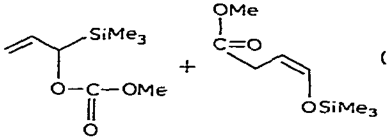
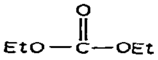
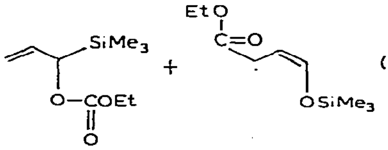
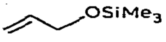
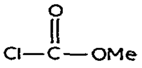
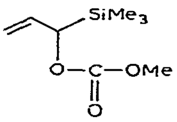
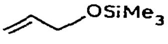
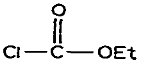
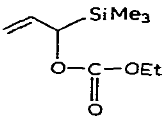
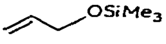
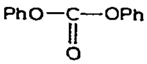
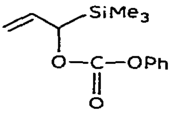
The change in *C*/*O*-silylation with the leaving group of the silyl halides is reminiscent of the change in *C*- vs. *O*-alkylation of enolate anion with alkyl halides [6]. It is tempting to accord the same rationale to both observations. There are, however, subtle differences between the two cases. In the case of alkylation, alkyl halide reacts with different sites of the same enolate anion; whereas in the present case silyl halide reacts with two distinctly different species Ia and Ib which are in rapid equilibrium. Enolate reacts with methyl iodide to give more *C*-alkylation than with methyl bromide, whereas in the present case, more *O*-silylation is obtained with silyl iodide than with silyl bromide. The change in *C*/*O*-silylation, we feel, can be attributed to two co-operative factors. With hexamethylphosphoramide as a co-solvent, the reactivity of carbanion is known to be enhanced. The rate of silylation of carbanion Ia may thus be competitive with that of oxyanion Ib. It is known that the reactivity of silyl halides with oxyanion increases along the order Si—F < Si—Cl < Si—Br < Si—I (which is the same order of decreasing bond energies) [8]. On the other hand, fluorosilanes are more reactive towards organolithium than chlorosilanes, possibly due to steric reasons [9]. The higher ratio of *C*/*O*-silylation for fluorosilane is therefore in agreement with these arguments.

TABLE 1

REACTION OF α-SILYLOXYALLYL CARBANION (I) WITH ELECTROPHILES

Entry	Precursor	Electrophile	Conditions[a]	Products[b]	(isolated yield)
1		Et_3SiCl	THF/−78°C		(75)
2		Me_3SiCl	THF/−78°C		(85)
3		Me_3SiF	THF/−78°C		(50)
4		Me_3SiCl	THF/−78°C		(75)
5		Me_3SiBr	THF/−78°C		(50)
6		Me_3SiI	THF/−78°C		(50)
7		Me_3SiF	THF/HMPA/−78°C	 +  35% 65%	(–)[c,d]
8		Me_3SiCl	THF/HMPA/−78°C	50% 50%	(75)[d]
9		Me_3SiBr	THF/HMPA/−78°C	75% 25%	(70)[d]
10		Me_3SiI	THF/HMPA/−78°C	85% 15%	(50)[d]
11		Me_3SiCl	THF/HMPA/−78°C	 +  50% 50%	(87)[d]
12		$Me_3SiF/ZnCl_2$	THF/HMPA/−78°C		(45)

[a] Experimental conditions: To a solution of 25 mmol of trialkylallyloxysilane (precursor) in 40 ml of tetrahydrofuran at −78° was added slowly 27.6 mmol of t-butyllithium in n-pentane. The reaction mixture was stirred at ~−78° for 1½ h. (For those experiments with HMPA, 0.5 ml HMPA was added after the addition of t-butyllithium). A solution of 25 mmol of the electrophile in 2 ml of tetrahydrofuran was added and the resulting mixture stirred for ½ h. The reaction mixture was poured into water and ether. The organic phase was washed with aqueous sodium bicarbonate and water and dried. The solvent was evaporated to give the

Entry	Precursor	Electrophile	Conditions[a]	Products[b]	(isolated yield)
13		$\mathrm{Me_3SiCl/ZnCl_2}$	THF/HMPA/–78°C		(68)
14		$\mathrm{Me_3SiBr/ZnCl_2}$	THF/HMPA/–78°C		(40)
15		$\mathrm{Me_3SiCl/ZnCl_2}$	THF/HMPA/–78°C		(20)
16		 $\mathrm{MeO{-}\overset{O}{\overset{\|}{C}}{-}OMe}$	THF/–78°C	 33 % 67 %	(42)[d,e]
17		 $\mathrm{EtO{-}\overset{O}{\overset{\|}{C}}{-}OEt}$	THF/–78°C	 45 % 55 %	(43)[d,e]
18		 $\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}OMe}$	THF/–78°C		(68)
19		 $\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}OEt}$	THF/–78°C		(74)
20		 $\mathrm{PhO{-}\underset{O}{\underset{\|}{C}}{-}OPh}$	THF/–78°C		(45)

product which was purified by distillation or thin layer chromatography. [b] Products were characterised by the usual spectroscopic means and their purity were ascertained by GC/MS. The α-trialkylsiloxy trialkylsilanes have been reported previously [3]. We have independently confirmed their structures by chemical conversion of the trialkylsiloxy group into acetoxy group. [c] The isolated yield was not determined. [d] The enol silyl ether was not stable during purification by thin layer chromatography. [e] Crude yield.

We have also found that the addition of zinc chloride leads to exclusive *O*-silylation (entries 12—14). We have further established, in a control experiment, the addition of zinc chloride does not alter the course of reaction, i.e. IV is still derived from Ib (entry 15). Zinc chloride may well have reacted with organolithium to give an organozinc compound [10]. The rate of *C*-silylation is therefore diminished leading to exclusive *O*-silylation.

2. Reaction with chloroformates and carbonates

A change in regioselectivity in the reaction of I with carbonates also has been found to occur with a change of the leaving group. Trimethylsilyloxyallyl carbanion (I) reacts with dimethyl or diethyl carbonate to give a mixture of two products (entries 16, 17). On the other hand, reaction of I with either methyl or ethyl chloroformate gives exclusively the product derived from Ib (entries 18, 19). We again attribute such a change to the better leaving group in the chloroformate case, thus making the chloroformate a stronger electrophile. Diphenyl carbonate also reacts with I to give exclusively the carbonate IV. This is in agreement with the fact that phenoxide is a better leaving group than alkoxide.

Conclusion

In view of the extensive use of *C*-silyl and *O*-silyl compounds in organic synthesis [11], the demonstration that selective silylation can be controlled in rapidly equilibrating species such as I simply by varying the halide in the silylation agents will find considerable application. We are exploring such possibilities.

Acknowledgement

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