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Preliminary communication

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

IV*. STEREOSELECTIVE CONVERSION OF RCHO INTO *E*-RCH=CHCH$_2$Cl

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Summary

The stereochemistry of the allylic rearrangement of (α-trimethylsilylvinyl)carbinyl chloride was investigated. From these results, a method for the stereoselective conversion of RCHO into *E*-RCH=CHCH$_2$Cl was proposed.

The condensation of carbonyl compounds with α-silyl carbanions to give alkenes [1-4] has now been established as a useful synthetic reaction. Applications of this reaction include the synthesis of a terpene [5], an insect pheromone [1], α,β-unsaturated esters [6], α,β-unsaturated nitriles [7], allenes [4] and various hetero-substituted alkenes [8]. When the alkenes to be synthesized can display geometric isomerism however, the potential synthetic value of the reaction suffers somewhat because of a lack of stereoselectivity [9]**. The alkenes obtained by this reaction have been found to be usually a mixture of *E* and *Z* isomers in nearly equal proportions [1,6,7].

We wish to report a sequence of reactions which permits the conversion of aldehydes (RCHO) stereoselectively into the corresponding *E* isomers of RCH=CHCH$_2$Cl. The presence of a reactive chloride in the resulting alkene is often desirable since it allows further elaboration into other functionalities.

The known (1-bromovinyl)trimethylsilane [11] was converted into the lithium reagent II by metal—halogen exchange with one equivalent of t-butyllithium at −78°C [12-14]. Treatment of the α-silyl carbanion II with an equivalent of aldehyde at −78°C afforded the alcohols III in good yields [13-15] (>75%).

To a solution of 5 mmole of the alcohol III in 4 ml of anhydrous ether was added dropwise a solution of thionyl chloride (20% excess) in 2 ml of ether at room temperature. After 1/2 hour, the reaction mixture was worked-

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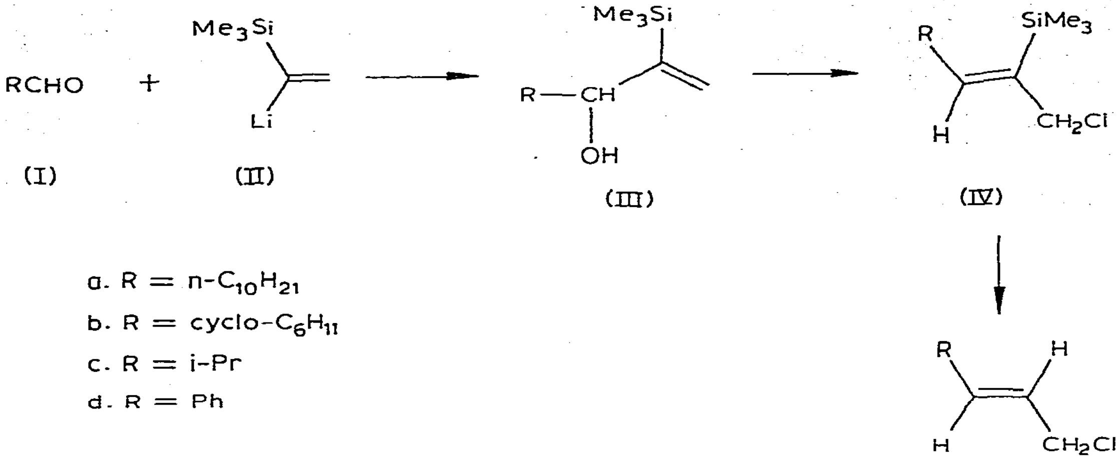
[*] For part III see ref. 1.

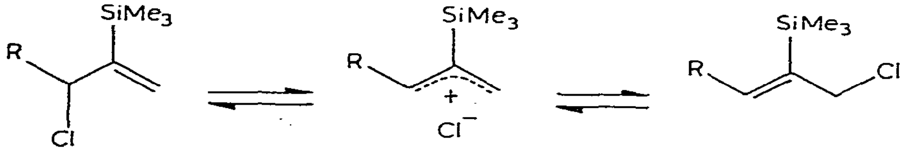
[**] The lack of stereoselectivity may be desirable in certain limited cases. See for example ref. 10.

SCHEME 1


(I) (II) (III) (IV) (V)

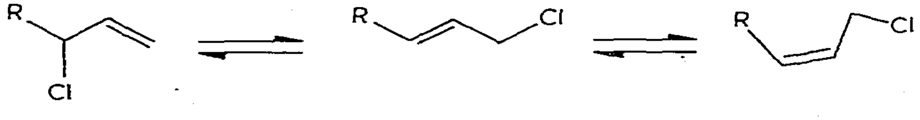
a. R = n-$C_{10}H_{21}$
b. R = cyclo-C_6H_{11}
c. R = i-Pr
d. R = Ph

up to give the chloride IV. Chloride IV was likely derived from the allylic rearrangement of VI by an ionic mechanism.


(VI) (IV)

Support for this mechanism was gained by effecting the conversion (III→IV) with thionyl chloride in carbon tetrachloride. In these cases, a mixture of VI and IV was obtained. Equilibration of VI⇌IV can also be achieved by heating.

The conversion of III to IV is highly stereoselective in all cases giving the *Z* isomer (the *E* isomer is sometimes present, however always in less than 10% as determined by PMR spectroscopy). This result is somewhat different from the rearrangement of allylic chlorides in a protiated system such as VII where a mixture of three compounds was obtained, albeit often with the *E* isomer (VIIb), as the major component [16,17]. It thus appears that the silyl group has considerable influence on the stereochemistry of such reactions.


(VIIa) (VIIb) (VIIc)

The assignment of *Z* stereochemistry to compound IV rests on the following transformation. Dry gaseous HCl was bubbled in excess into a

TABLE 1

BOILING POINTS, YIELDS AND ISOMERIC RATIOS FOR COMPOUNDS ACCORDING TO SCHEME 1

	B.p. (°C/mmHg)	Yield (%)	E/Z
IIIa	118-119/0.03	75 [a]	
IIIb	64-66/0.025	75 [a]	
IIIc	82-84/16	76 [a]	
IIId	82-84/0.9	80 [a]	
IVa	99-100/0.05	79 [a]	
IVb	66-67/0.35	75 [a]	
IVc	73-75/12	88 [a]	
IVd	89-90/1.5	79 [a]	
Va	76-77/0.06	74(66)[d]	85/15
Vb	53/1.3	65(62)[d]	85/15
Vc	58-60/89	75(45)[e]	90/10
Vd	-[b]	>90 [f]	100%E[c]

[a] Isolated yield after distillation. [b] Compound compared with authentic sample. [c] Any *Z* isomer, if formed, may have isomerized to the *E* isomer under the reaction conditions. [d] Yield determined by VPC with isolated yield in parentheses. [e] Lower isolated yield was due to loss in distillation because of the relatively low boiling point of the compound. [f] NMR showed that Vd was the only compound in the product.

solution of IV (1 g) in 10 ml of chloroform for ca. 5 minutes. The mixture was stirred for 2-5 days. After work-up, the product V was obtained in good yield. The stereochemistry of the major isomer of each V was assigned to be *E*- on the basis of its 220 MHz PMR spectrum. The olefinic protons displayed a coupling constant of 15-19 Hz, characteristic of *trans* coupling. The assignment is also supported by their infrared spectra where the prominent band at ca. 960 cm^{-1} is observed. The presence of the minor *Z*-isomer was also evident from the 220 MHz PMR spectra and the relative ratio of the *E*/*Z* isomers could be deduced (Table 1). The replacement of the trimethylsilyl group in vinylsilanes by a proton under electrophilic conditions has been firmly established to proceed with retention of stereochemistry [18-20]. The sequence of reactions outlined in Scheme 1 therefore constitutes a viable method of transforming stereoselectively RCHO into *E*-$RCH{=}CHCH_2Cl$. Further experiments are in progress which will permit the stereoselective conversion of RCHO into *Z*-$RCH{=}CHCH_2Cl$.

Acknowledgement

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