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ONE-POT SYNTHESIS OF ALLYLSILANES FROM α-CHLOROCARBONYL COMPOUNDS

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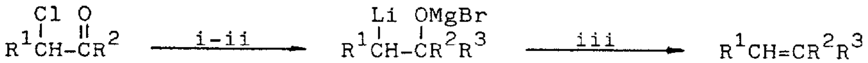
Summary: The successive treatment of different α-chlorocarbonyl compounds with trimethylsilylmethylmagnesium chloride and lithium powder leads to allylsilanes in a regioselective manner.

Much attention has been recently focused on synthesis and applications of allylsilanes as synthetic reagents.[1] Allylsilanes are thermally stable and relatively inert to water and oxygen, they are isolable and storable without special precautions and it is possible to functionalize simple allylsilanes and to transfer functionalized allyl groups onto carbon electrophiles with high regio-, stereo- and chemoselectivity.[2] However, one of the major limitations of allylsilanes chemistry is that there are relatively few versatile methods for their preparations.[1b] Starting from carbonyl compounds, the Wittig reaction can be used to prepare allylsilanes,[3] although it is unsuitable for ketones with α-hydrogen atoms[4] and, in addition, it is very difficult to prepare 2-substituted allylsilanes.[3]

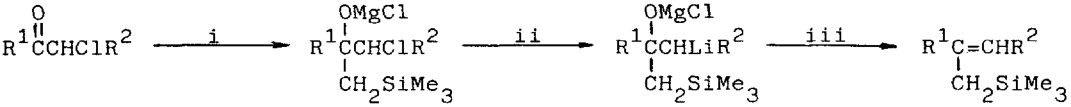
In previous papers[5] we described the addition of Grignard reagents to α-chlorocarbonyl compounds (1) followed by metallation with lithium powder to give β-substituted organolithium compounds (2) which undergo a spontaneous β-elimination affording olefins (3) (Scheme 1).



$$\underset{(1)}{R^1\overset{Cl}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}R^2} \xrightarrow{\text{i-ii}} \underset{(2)}{R^1\overset{Li}{\overset{|}{C}}H-\overset{OMgBr}{\overset{|}{C}}R^2R^3} \xrightarrow{\text{iii}} \underset{(3)}{R^1CH=CR^2R^3}$$

Scheme 1. i) R^3MgBr, -78°C; ii) Li, -78°C; iii) -78 to 25 °C.

We report now a new and general route to allylsilanes from α-chlorocarbonyl compounds, trimethylsilylmethylmagnesium chloride and further lithiation . Thus, the reaction of different α-chlorocarbonyl compounds (1) with trimethylsilylmethylmagnesium chloride at -78°C led to the expected chlorohydrin salt (4); this intermediate was in situ lithiated with lithium powder between -60 and 20°C to yield a β-substituted organolithium intermediate (5) which underwent spontaneous β-elimination yielding, after hydrolysis, the expected allylsilanes (6) (Scheme 2 and Table).[6]



$$R^1\overset{O}{\overset{\|}{C}}CHClR^2 \xrightarrow{i} R^1\underset{CH_2SiMe_3}{\overset{OMgCl}{C}}CHClR^2 \xrightarrow{ii} R^1\underset{CH_2SiMe_3}{\overset{OMgCl}{C}}CHLiR^2 \xrightarrow{iii} R^1\underset{CH_2SiMe_3}{C}{=}CHR^2$$

(**1**) (**4**) (**5**) (**6**)

Scheme 2. i) Me_3SiCH_2MgCl, -78°C; ii) Li, -78°C; iii) -78 to 25°C.

In the case of α-chloroacetophenone (R^1= Ph, R^2= H) the lithiation reaction was carried out at -78°C with stoichiometric lithium 1-dimethylaminonaphthalenide in order to avoid the reduction of the resulting conjugated double bond by the excess of metal.

Table. Preparation of allylsilanes (**6**) from α-chlorocarbonyl compounds (**1**)

Entry	Carbonyl compound (**1**)	Allylsilane (**6**)	Yield[a]
1	$Pr^nCHClCH{=}O$	$Pr^nCH{=}CHCH_2SiMe_3$	65[b]
2	$Pr^iCHClCH{=}O$	$Pr^iCH{=}CHCH_2SiMe_3$	52[b]
3	$(CH_2)_3CHClC{=}O$	$(CH_2)_3CH{=}CCH_2SiMe_3$	60
4	$(CH_2)_4CHClC{=}O$	$(CH_2)_4CH{=}CCH_2SiMe_3$	68
5	$PhCOCH_2Cl$	$CH_2{=}C(Ph)CH_2SiMe_3$	57

[a] Isolated yield based in the carbonyl compound; all allylsilanes (**6**) were fully characterized by spectroscopic methods (I.r., ^{1}H and ^{13}C-N.m.r., and mass spectra); purity (>95%) was checked by g.l.c. [b] E/Z isomeric mixture in ca. 1:1 (g.l.c. and n.m.r.).

Regarding the synthesis of allylsilanes we think that the method described is complementary with the Wittig reaction by the following reasons: (a) allylsilanes can be obtained starting from ketones (see Table, entries 3,4 and 5), (b) it is possible to prepare 2-substituted allylsilanes (see Table, entries 3, 4 and 5) and (c) allylsilanes with the endocyclic olefinic bond were synthesized (see Table, entries 3 and 4).

References and Notes

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6 In a typical procedure: to a solution of trimethylsilylmethylmagnesium chloride (11 mmol) in diethyl ether (11 ml) was added a solution of carbonyl compound (6 mmol) in THF (10 ml) at -78°C. The mixture was stirred for 3 h at the same temperature. The lithium powder (Aldrich,-325 mesh, 15 mmol) was added and the mixture was stirred and allowed to warm to room temperature overnight. The resulting solution was hydrolyzed with saturated aqueous NH_4Cl, and extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and carefully distilled to afford the corresponding allylsilane.

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