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Preliminary communication

Reactivity of hypervalent species of silicon: cleavage of the allyl–silicon bond

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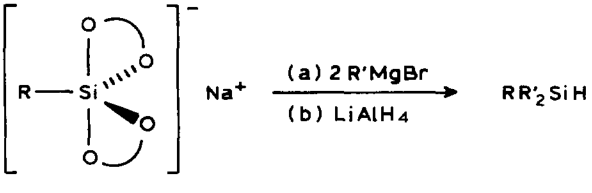
Abstract

The reactivities of the silicon–allyl bonds in two kinds of pentacoordinated silicon species $CH_2{=}CHCH_2Si(o\text{-}O_2C_6H_4)_2{}^-NMe_4{}^+$ (1) and $CH_2{=}CHCH_2\text{-}Si(OCH_2CH_2)_3N$ (2) has been compared. In the allyl transfer to carbonyl compounds under nucleophilic conditions (NaOMe, KF or Bu_4NF) and electrophilic conditions ($TiCl_4$, $AlCl_3$, BF_3) these two species show quite different behaviour. Complex **1** is activated by nucleophiles, while for **2** transfer occurs under electrophilic conditions. These results indicate that the reactivity of these species is a function of their overall charge and geometry.

We are interested in the reactivity of hypervalent species of silicon. We have shown previously [1] that anionic penta-(and even hexa-) coordinate siliconates of catechol, even though they are negatively charged react readily with nucleophiles such as hydrides and Grignard and organolithium reagents (e.g. eq. 1).



(1)

(R = Me , R' = PhCH$_2$; 86%)

We consider here the reactivity of silicon–allyl bonds in pentacoordinate silicon species. Allylsilanes have been extensively studied [2,3] and used in organic syntheses and it is well known that allyl transfer to a carbonyl compound takes place when allylsilanes are activated either by a Lewis acid ($TiCl_4$ [4], $AlCl_3$ [5]) or by fluoride ion ($n\text{-}Bu_4NF$ [6]). We have compared the reactivity of two kinds of pentacoor-

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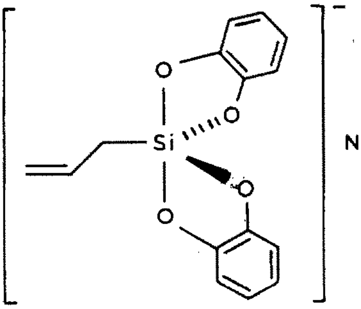
Table 1

Reactions of $CH_2{=}CHCH_2Si(o\text{-}O_2C_6H_4)_2^-$ NMe_4^+ with carbonyl compounds under nucleophilic conditions in DMSO

Carbonyl compound	Catalyst	Reaction conditions	Products (% yield) [a]
		Time (h)/temp. (C°)	
PhCHO	KF (1 equiv.)	3/75	$PhCH(OH)CH_2CH{=}CH_2$ (71)
	NaOMe (1 equiv.)	0.25/20	$PhCH(OH)CH_2CH{=}CH_2$ (49)
$PhCH_2CH_2CHO$	KF (1 equiv.)	3/60	$Ph(CH_2)_2CH(OH)CH_2CH{=}CH_2$ (52)
	Bu_4NF [b] (0.2 equiv.)	8/40	$Ph(CH_2)_2CH(OH)CH_2CH{=}CH_2$ (68)
$CH_3(CH_2)_2CHO$	KF (1 equiv.)	1/60	$CH_3(CH_2)_2CH(OH)CH_2CH{=}CH_2$ (42)
$CH_3(CH_2)_5CHO$	NaOMe (1 equiv.)	2/20	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH_2$ (84)
$PhCOCH_3$	NaOMe (1 equiv.)	23/85	$PhC(OH)(CH_3)CH_2CH{=}CH_2$ (47)
$(\overline{CH_2)_5C}{=}O$	KOMe (1,5 equiv.)	10/85	$\overline{CH_2(CH_2)_4C}(OH)CH_2CH{=}CH_2$ (48)
$CH_2{=}CHCO_2Et$	KF (1 equiv.)	10/70	$CH_2{=}CH(CH_2)_3CO_2Et$ (39)
PhCHO $PhCOCH_3$	KF (1 equiv.)	7/60	$PhCH(OH)CH_2CH{=}CH_2$ (83) [c] + $PhC(OH)(CH_3)CH_2CH{=}CH_2$ (7) [c]
$CH_3(CH_2)_5CHO$ $(\overline{CH_2)_5C}{=}O$	KF (1 equiv.)	10/50	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH_2$ (97) [c] $+\overline{CH_2(CH_2)_4C}(OH)CH_2CH{=}CH_2$ (3) [c]

[a] Yields are not optimised. [b] In CH_2Cl_2 as a solvent. [c] Yields were determined by VPC.

dinated silicon species, the anionic allylsiliconate **1** [7 *] and the 1-allylsilatrane **2** [8*].



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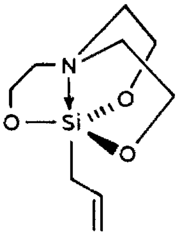

(2)

X-Ray crystallographic data are not available for either compound, but from the structures of analogous species it can be inferred that the allyl group is in an apical position in **2** [9] and in an equatorial position in **1** [10,11,12]. Indeed, most of these anionic pentacoordinate siliconates have structures intermediate between a rectangular square pyramid and a trigonal bipyramid.

The results of reactions of **1** with aldehydes, ketones, and ethyl acrylate under nucleophilic activation are summarized in Table 1. In the case of aldehydes, the reaction occurs easily in the presence of NaOMe, KF or Bu_4NF. Allyl transfer to ketones is more difficult; the reaction is very slow in the presence of KF, and

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* This and other references marked with asterisks indicate notes occurring in the list of references.

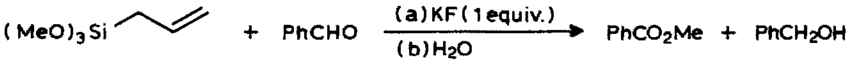
Table 2

Reactions of 1-allylsilatrane with carbonyl compounds

Carbonyl compound	Catalyst	Reaction conditions		Products (% yield)
		Solvent	Time (h)/ temp (C °)	
$\mathrm{Ph(CH_2)_2CHO}$	KF (1 equiv.)	DMSO	20/75	$\mathrm{Ph(CH_2)_2CH{=}\underset{CH_2Ph}{\underset{\vert}{C}}CHO}$ (95)
$\mathrm{Ph(CH_2)_2CHO}$	NaOMe (1 equiv.)	DMSO	0.33/25	$\mathrm{Ph(CH_2)_2CH{=}\underset{CH_2Ph}{\underset{\vert}{C}}CHO}$ (90)
$\mathrm{Ph(CH_2)_2CHO}$	$\mathrm{TiCl_4}$ (0.5 equiv.)	$\mathrm{CH_2Cl_2}$	0.16/25	$\mathrm{Ph(CH_2)_2CH(OH)CH_2CH{=}CH_2}$ (96)
$\mathrm{Ph(CH_2)_2CHO}$	$\mathrm{AlCl_3}$ (1 equiv.)	$\mathrm{CH_2Cl_2}$	1/25	$\mathrm{Ph(CH_2)_2CH(OH)CH_2CH{=}CH_2}$ (84)
$\mathrm{Ph(CH_2)_2CHO}$	$\mathrm{BF_3}$ (0.5 equiv.)	$\mathrm{CH_2Cl_2}$	0.16/25	$\mathrm{Ph(CH_2)_2CH(OH)CH_2CH{=}CH_2}$ (52)
$\mathrm{CH_3(CH_2)_6CHO}$	$\mathrm{TiCl_4}$ (0.5 equiv.)	$\mathrm{CH_2Cl_2}$	0.16/25	$\mathrm{CH_3(CH_2)_6CH(OH)CH_2CH{=}CH_2}$ (96)
$\mathrm{CH_2{=}CHCO_2Et}$	$\mathrm{TiCl_4}$ (1 equiv.)	$\mathrm{CH_2Cl_2}$	10/60	$\mathrm{CH_2{=}CH(CH_2)_3CO_2Et}$ (23)
$\mathrm{(\overline{CH_2)_5C}{=}O}$	$\mathrm{TiCl_4}$ (1 equiv.)	$\mathrm{CH_2Cl_2}$	20/70	$\mathrm{\overline{CH_2CH_2CH_2CH_2{=}CHC}CH_2CH{=}CH_2}$ (82) $\mathrm{\overline{CH_2(CH_2)_4C}C(OH)CH_2CH{=}CH_2}$ (14)

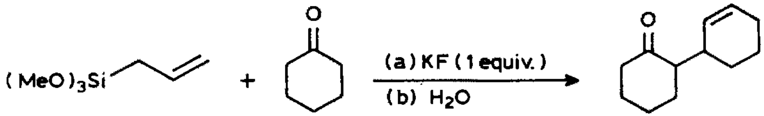
NaOMe or KOMe is required for efficient transfer, and so it is possible to transfer the allyl group selectively to an aldehyde even in presence of a ketone (Table 1).

It is noteworthy to point out that under the same conditions KF promotes cleavage of the Si–O bond rather than the Si–C bond in the tetracoordinate silicon compound **3** (eq. 2 and 3). In these reactions the allyl transfer is not observed; instead crotonisation or the Cannizzaro reaction takes place, as a result of the generation of $\mathrm{MeO^-}$ [13].



(**3**)

(2)



(**3**)

(3)

Allyl transfer does not take place with **1** under electrophilic conditions. Thus $\mathrm{TiCl_4}$ reacts with **1** by cleavage of the Si–O bond and exchange of the ligands [14].

The reactivity of the allyl–silicon bond is quite different in the 1-allylsilatrane **2**, as shown by the results outlined in Table 2. Allyl transfer to carbonyl compounds does not occur under nucleophilic activation, the only reaction observed being crotonisation. In contrast the reaction with aldehydes proceeds smoothly in the presence of $\mathrm{TiCl_4}$, and the γ,δ unsaturated alcohol is obtained after hydrolysis, generally in good yield. The reaction is also catalysed by other Lewis acids, such as $\mathrm{AlCl_3}$ or $\mathrm{BF_3{-}OEt_2}$, but the yield is usually lower. Allyl transfer occurs with ketones, but a mixture of the homoallyl alcohol and the corresponding dehydrated compound is always obtained regardless of the hydrolysis conditions.

It is evident that the pentacoordinate species **1** and **2** have characteristic reactivities which differ from those of a related tetra-coordinate silicon compound such as **3**. New synthetic methods based on such pentacoordinate species can be expected as is the case with $(RSiF_5)^{2-}$ [15,16]. The fact is that the anionic pentacoordinate silicon complex **1** is activated only by nucleophiles, and the silatrane **2** only by electrophiles. These results indicate that the reactivities of these pentacoordinate species depend on the overall charge and geometry, the allyl group being in an equatorial position in the negatively charged **1** and in apical position in the neutral **2**.

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7 Preparation of **1**: 100 mmol of catechol and 50 mmol of allyltrimethoxysilane are dissolved in 50 ml of methanol in a Schlenk tube; 25.75 ml of a 20 wt% solution of Me_4NOH in methanol are added dropwise at $-20\,^{\circ}C$ and the mixture is stirred for about 15 min at this temperature. The solvent is removed under vacuum and the residue washed once with anhydrous ether to give 17.59 g of a white powder (98% yield). ^1H NMR ($(CD_3)_2SO$): δ(ppm) 1.58 (2H, d), 3.12 (12H, s), 5.50–6.35 (3H, m), 6.43–6.80 (8H, m).

8 Preparation of **2**: 45 mmol of allyltrimethoxysilane and 45 mmol of triethanolamine are mixed without solvent in the presence of a catalytic amount of NaOH, and the mixture is heated at 75 °C for 4 h. The solid is filtered off and recrystallised twice from chloroform pentane (yield 86%) m.p. 122–123 °C, ^1H NMR ($CDCl_3$) δ(ppm): 1.43 (2H, d), 2.8 (6H, t), 3.7 (6H, t), 4.5–6.28 (3H, m). IR (CH_2Cl_2): ν 1620 cm^{-1}.

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