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CHEMOSELECTIVE REACTION OF ALLYLSILANES WITH α-CHLOROSULFIDES CONTAINING A CARBONYL GROUP

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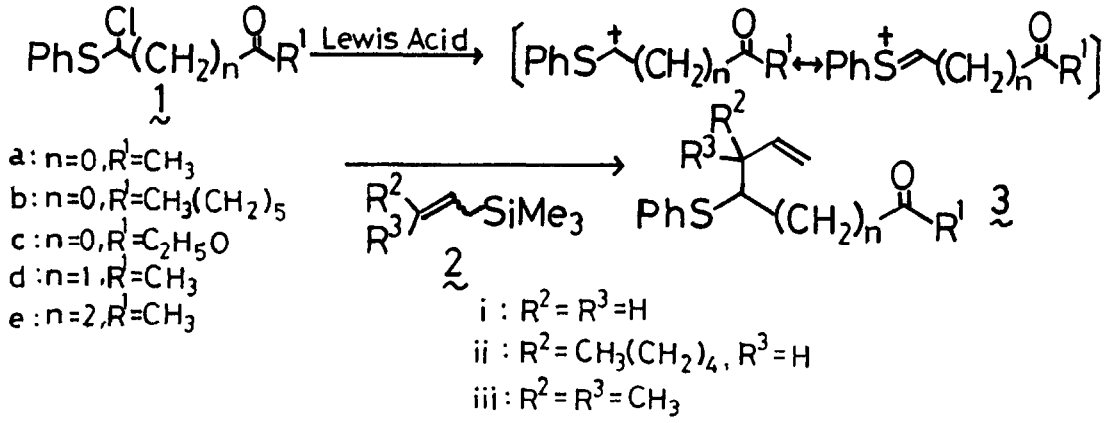
Abstract : Allylsilanes (2) reacted with α-chlorosulfides (1) containing a carbonyl group either at α, β, or γ position to substitute exclusively for the chlorine atom of 1, and the corresponding α-allylsulfides (3) were obtained in high yields.

Recently, allylsilanes or silyl enol ethers have been recognized as useful reagents for organic synthesis, [1] especially for a regiospecific carbon-carbon bond formation. It is well known that allylsilanes or silyl enol ethers react with carbonyl compounds in the presence of Lewis acid to give the corresponding homoallyl alcohols[2] or β-hydroxycarbonyl compounds.[3] On the other hand, to our knowledge, the chemoselective reaction of these reagents with a carbonyl compound which contains another active functionality in a molecule is hitherto unknown except the following two examples.

Chemoselective allylation of bifunctional molecules with allylsilanes catalyzed by Lewis acids was first reported by Ojima and Kumagai on α- and β-keto acetals. In these cases, allylsilanes reacted at the carbonyl group first with 1, 1-dimethoxypropane-2-one but at the acetal group first with 1, 1-dimethoxybutane-3-one.[4] On the other hand, it was reported quite recently that silyl enol ethers reacted at the carbonyl group of α-acyl-α-chlorosulfides, whereas they did at the α-carbon atom of the α-chlorosulfides with an acyl group at β- or γ-position.[5] Therefore, it is still challenging to device a method to introduce allyl or

β-ketoalkyl group into a molecule while retaining its carbonyl group intact. Here we report chemoselective allylation of the α-carbon of α-chlorosulfides (1)[6] to afford α-allylsulfides containing a carbonyl group in a molecule (3).

The α-chlorosulfides (1) were prepared from the corresponding sulfides by treating with N-chlorosuccinimide.[7] 1a, 1b, and 1c are stable and were distilled before use, but 1d and 1e were prepared *in situ* for subsequent reaction due to instability of these compounds. Allylsilanes (2) were added to α-chlorosulfides (1) in the presence of Lewis acids in dichloromethane under argon atmosphere and the results of these reactions are summarized in the Table.



The reaction of 1a with 2i was promoted by several Lewis acids, i.e., $ZnBr_2$, $ZnCl_2$, $TiCl_4$, $SnCl_4$, and $AlCl_3$, to afford 3-phenylthiohex-5-ene-2-one (3a-i) as a sole product. No product due to the attack at the carbonyl group of 1a could be detected. Among these Lewis acids, $SnCl_4$ and $AlCl_3$ were found to be satisfactory for this reaction and the product (3a-i) was obtained in 90 and 91% yield, respectively. Tin tetrachloride was used for subsequent reactions and the products were obtained in high yields (80 - 90%) with α-keto substrates (1a, b, and c). Yields of allylated products were low for β- and γ-acetyl substrates, i.e., 39% for 3d-i and 30% for 3e-i, and it was necessary to employ lower temperature (ca. -50 °C) for the latter case.

Table Chemoselective Allylation of α-Chlorosulfides (1)

α-Chlorosulfide (1)	Allylsilane (2)	Lewis acid	Conditions		Yield of 3 [b] %
1a	2i	$ZnBr_2$	r.t.,	5.5h	75[c]
1a	2i	$ZnCl_2$	r.t.,	24 h	81[c]
1a	2i	$TiCl_4$	r.t.,	10 min	53[c]
1a	2i	$SnCl_4$	r.t.,	40 min	90[c]
1a	2i	$AlCl_3$	r.t.,	30 min	91[c]
1b	2i	$SnCl_4$	r.t.,	20 min	91[d]
1c	2i	$SnCl_4$	0 °C,	20 min	87[d]
1d	2i	$SnCl_4$	r.t.,	20 min	39[d]
1e	2i	$SnCl_4$	-45 -50°C,	4 h	30[d][e]
1a	2ii	$SnCl_4$	r.t.,	20 min	80[d]
1a	2ii	$ZnBr_2$	r.t.,	2.5h	50[d]
1b	2ii	$SnCl_4$	r.t.,	20 min	91[d]
1c	2ii	$SnCl_4$	0 °C,	20 min	78[d]
1a	2iii	$SnCl_4$	-78 °C,	3 h	20[d]
1c	2iii	$SnCl_4$	-78 °C,	3 h	20[d]

a) All reactions were carried out using 1.0 mmol of α-chlorosulfide (1), 1.1 mmol of allylsilane (2), and 1.0 mmol of Lewis acid in 10 ml of CH_2Cl_2 under argon. The reaction mixture was treated with water followed by extraction with CH_2Cl_2. After removal of CH_2Cl_2, the crude product was purified by flash column chromatography on silica gel (Merck Art 9385).

b) Satisfactory IR, NMR, MS and elemental analyses data were obtained for these compounds.

c) Isolated yield using CH_2Cl_2 as eluent.

d) Isolated yield using a mixed solvent (n-hexane : ethyl acetate = 9 : 1) as eluent.

e) When this reaction was carried out at room temperature, the product (3e-i) was obtained in a 14% yield.

Monosubstituted allylsilane (2ii) also reacted with α-keto substrates to afford the expected products (3a-ii, 3b-ii, and 3c-ii) in high yields as shown in the Table. On the other hand, when γ, γ-dimethylallylsilane (2iii) was reacted with 1a or 1c at room temperature or at 0 °C using $SnCl_4$, the reaction mixture was complicated and the expected product was not obtained at all. When the same reaction was carried out at -78 °C, 3a-iii or 3c-iii was obtained in a 20% yield, respectively, accompanied with some by-products.

Chemoselectivity of the present reaction is apparently due to higher reactivity of the α-chlorosulfide moiety compared with that of the acetal moiety, although it is not yet clear why the reactivity of allylsilanes and silyl enol ethers are different for the same substrates (1).

As is apparent from the structure, the present product (3) should be useful as a starting material for several synthetic purposes and such is currently underway.

References and Notes

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