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Cationic Au(I)- and Pt(II)-Catalyzed Silylation of Alcohols Using Allylsilanes

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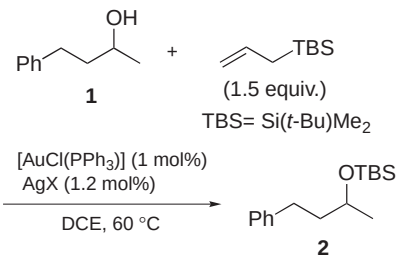
The silylation of alcohols using allylsilanes was catalyzed by cationic Au(I) and Pt(II) species, which were prepared in situ from the metal chlorides ([AuCl(PPh_3)], $PtCl_2$) and a silver salt. TBS-, TES-, and TIPS-protections of various alcohols and carboxylic acids could be possible.

The trialkylsilyl group is one of the most useful protective groups in organic synthesis because its reactivity and stability can be controlled by the choice of substituents on the silicon.[1] The reaction of alcohol with silyl chloride or its synthetic analogue in the presence of a stoichiometric amount of base is the most conventional protocol for the synthesis of silyl ethers. Transition metal-catalyzed dehydrogenative silylation of alcohol using hydrosilanes is another protocol;[2] however, the reductive conditions and relatively low activity of the catalysts limit the variety of alcohols in some reactions.[3] Recently, very practical dehydrogenative silylation was achieved with Cu(I) and Au(I) catalysts.[4] On the other hand, allylsilane also has been recognized as a silylating reagent of alcohols in the presence of protic acid catalysts, obtaining silyl ethers along with the generation of propene.[5] In 2000, the Lewis-acid catalyst $Sc(OTf)_3$ was found be a good catalyst for silylation with metallylsilanes.[6] We here disclose cationic Au(I) and Pt(II) as new active catalysts for silylation with various allylsilanes.

Table 1. Screening of Reaction Conditions Using Au(I)-Catalyzed Reactions

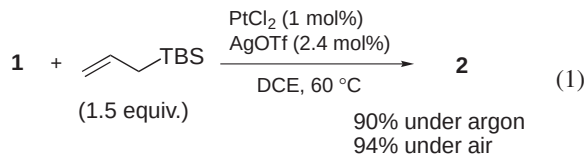


Entry	X	Time/h	Yield/%
1	OTf	3	77
2	SbF_6	3	<5
3	BF_4	3	trace
4[a)]	OTf	1	93
5[a),b)]	OTf	1	95

a) At 80 °C. b) Under an atmosphere of air.

We chose 4-phenylbutan-2-ol (**1**) and allyl(*tert*-butyl)dimethylsilane as a model alcohol and allylsilane, respectively, and examined Au(I)-catalyzed silylation in dichloroethane (DCE) (Table 1). [AuCl(PPh_3)] itself did not catalyze the reaction but the addition of AgOTf produced an active catalyst: The secondary alcohol was consumed at 60 °C within 3 h in the presence of 1 mol % catalyst and the TBS-protected alcohol **2** was obtained in good yield (Entry 1). The choice of counter anions was very important (Entries 1–3) and the higher reaction temperature realized shorter reaction time and higher yield (Entry 4).[7] It is noteworthy that the silylation efficiently proceeded even under an atmosphere of air (Entry 5).[8]

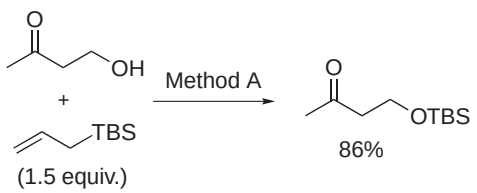
Cationic Pt(II), which was prepared from $PtCl_2$ and AgOTf, was also a good catalyst for silylation; it also worked efficiently under an atmosphere of air (Eq. 1).



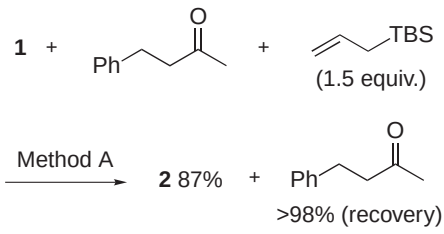
(1)

Using cationic Au(I) and Pt(II) catalysts, the silylation of various alcohols was examined (Table 2). The TBS-protection of primary alcohols readily proceeded to give the corresponding silyl ethers under an atmosphere of argon and air (Entries 1–3).[9] It required a longer reaction time and excess amounts of allylsilane for the Au(I) catalyst; however, phenol was also silylated in high yield (Entry 5). Silyl esterification of carboxylic acids was also possible (Entries 6 and 7). We chose the Au(I) catalyst and further examined other silylations: allyl(triethyl)silane and allyl(triisopropyl)silane were also good silylating reagents, and the TES- and TIPS-protected compounds were obtained using the corresponding allylsilanes in good to excellent yield (Entries 8–12). In particular, TES-protection smoothly proceeded even at room temperature; however, it required excess amounts of allylsilane (Entries 8 and 9).

Selective silyl-protection of a β-hydroxy ketone was possible and no allylated product to the ketone moiety was detected (Eq. 2). When the mixture of the secondary alcohol **1** and a ketone was subjected to the reaction conditions, silylation of the alcohol **1** selectively proceeded and the ketone was recovered (Eq. 3).



(2)



(3)

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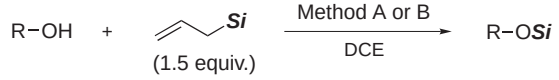
Table 2. Cationic Au(I)- and Pt(II)-Catalyzed Silylation of Various Alcohols and Allylsilanes



Method A: [AuCl(PPh$_3$)] (1 mol%), AgOTf (1.2 mol%), 80 °C
Method B: PtCl$_2$ (1 mol%), AgOTf (2.4 mol%), 60 °C

Entry	R–OH	*Si*[a]	Method A[b]		Method B	
			Time/h	Yield/%	Time/h	Yield/%
1	$Ph(CH_2)_3OH$	TBS	0.5	94	1	91
2[c]	$Ph(CH_2)_3OH$	TBS	1	96	1	98
3	$CH_3(CH_2)_6OH$	TBS	1	96	2	94
4	$CH_3(CH_2)_5CH(CH_3)OH$	TBS	1	90	2	97
5	PhOH	TBS	12 (12)	65 (90)	9	88
6	$Ph(CH_2)_3CO_2H$	TBS	2	71	5	94
7	$PhCO_2H$	TBS	1	85	2	81
8[d]	$Ph(CH_2)_3OH$	TES	3 (16)	84 (98)	—	—
9[d]	PhOH	TES	2 (1)	68 (84)	—	—
10	$Ph(CH_2)_3OH$	TIPS	2	97	—	—
11	$Ph(CH_2)_2CH(CH_3)OH$	TIPS	10	91	—	—
12	$Ph(CH_2)_3CO_2H$	TIPS	4	90	—	—

a) TES: triethylsilyl, TIPS: triisopropylsilyl. b) The results in parentheses are the case that allylsilane (3.0 equiv) was used. c) Under an atmosphere of air. d) At room temperature.

In summary, we have disclosed cationic Au(I)- and Pt(II)-catalyzed silylation of alcohols using allylsilanes. Recently, many groups, including us,[10] have reported a variety of cationic Au(I)- and Pt(II)-catalyzed reactions. The present reaction is a new entry, where their high Lewis acidity was utilized.

Experimental

Typical Experimental Procedure for Silylation of Alcohols Using Cationic Au(I) Catalyst. [AuCl(PPh$_3$)] (1.2 mg) was placed in a flask and a 1,2-dichloroethane solution (1.2 mL) of an alcohol (0.25 mmol) and allylsilane[11] (0.345 mmol) was added. To the resulting mixture was added AgOTf (0.8 mg), and the mixture was stirred at 80 °C for the hours cited in Table 2. The obtained mixture was purified by column chromatography to give a pure silyl ether.

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3 For an example, see: M. P. Doyle, K. G. High, V. Bagheri, R. J. Pieters, P. J. Lewis, M. M. Pearson, *J. Org. Chem.* **1990**, *55*, 6082.

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7 In the presence of AgOTf (1 mol %) without [AuCl(PPh$_3$)], the silylated product **2** could not be detected at 80 °C for 1 h.

8 The external addition of water (10 equiv) deactivated the catalyst and the yield of the silylated product **2** decreased to 54% along with the recovery of the alcohol **1**.

9 In the case of 2-methyl-4-phenylbutan-2-ol, a tertiary alcohol, dehydration dominantly proceeded and TBS-protected alcohol could not be detected under the same reaction conditions.

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