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First anionic silyl migration from sp^2 carbon to carbonyl oxygen. Stereospecific allylation of (*Z*)-β-trimethylsilyl-α,β-unsaturated ketones

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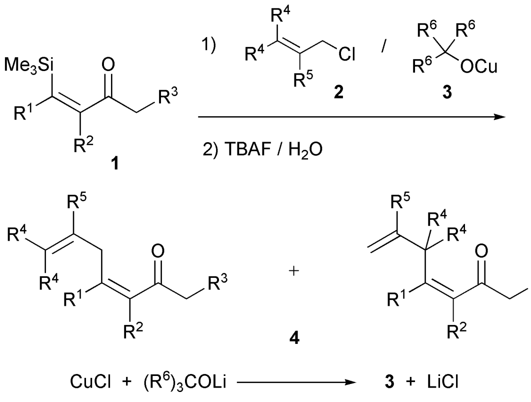
Received (in Cambridge, UK) 25th July 2002, Accepted 20th August 2002
First published as an Advance Article on the web 5th September 2002

1,4-Silyl migration from sp^2 carbon to carbonyl oxygen proceeded by the treatment of (*Z*)-β-trimethylsilyl-α,β-unsaturated ketones with copper(I) *tert*-alkoxide to afford vinylmetal species, which reacted with allylic halides to produce enol trimethylsilyl ethers of β-alk-2-enyl-α,β-unsaturated ketones with complete retention of configuration.

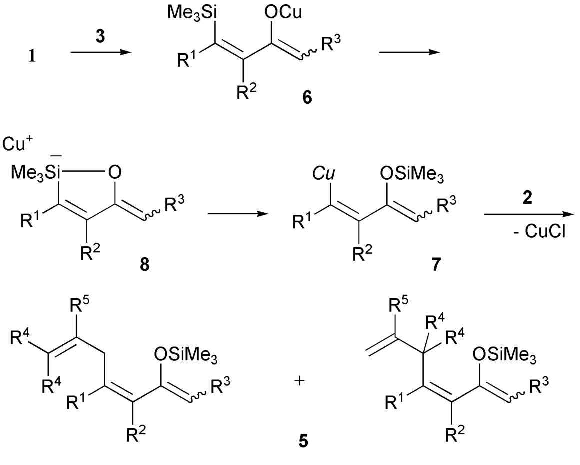
Anionic silyl group shift from carbon to oxygen is known as the Brook rearrangement. A variety of metal alkoxides bearing a trialkylsilyl group have been investigated as substrates for this rearrangement.[1] Silyl migration from carbon to carbonyl oxygen, however, has never been reported except for the thermal rearrangement of α-silyl ketones to enol silyl ethers.[2] Recently we found that the C^{sp^2}-to-O silyl migration proceeded to form vinylcopper species or their equivalents when (*Z*)-γ-trimethylsilyl allylic alcohols were treated with copper(I) *tert*-butoxide.[3] We studied the formation of copper(I) enolates of (*Z*)-β-trimethylsilyl-α,β-unsaturated ketones **1** with interest in whether a similar silyl group shift from sp^2 carbon to carbonyl oxygen proceeds. Here we describe copper(I) *tert*-alkoxide-promoted stereospecific allylation of **1**[4] with allylic halides **2** (Scheme 1).

The treatment of **1a** with copper(I) *tert*-butoxide **3a**, prepared *in situ* by the reaction of copper(I) chloride (1.1 equiv.) with lithium *tert*-butoxide (1.2 equiv.),[5] and methallyl chloride **2a** (1.2 equiv.) gave the allylation product **4a** with complete retention of configuration in 77% yield after tetrabutylammonium fluoride (TBAF)-catalyzed hydrolysis of the initial product (Entry 3, Table 1). No allylation of the intermediary enolate was observed in this reaction. The unsaturated ketone **4a** was produced in comparable yield when the amount of copper(I) chloride was decreased (0.5 equiv.) (Entry 2). When copper(I) iodide was used instead of the chloride, the yield of **4a** decreased (Entry 4). Without aqueous work-up, the enol silyl ether **5a** was isolated as a major product.†

The formation of the enol silyl ether **5** indicates that the reaction proceeds through the formation of the copper(I) enolate **6** and subsequent rearrangement of silicon as we expected (Scheme 2). The resulting vinylcopper species **7** reacts with allylic halide **2** to produce **5**. However an alternative pathway in which the pentavalent silicate **8** serves as nucleophile should not be excluded. Since the preferential allylation of lithium enolate was observed in the reaction of **1a** with **2a** in the absence of copper(I) chloride, the role of the copper(I) counter ion is of crucial importance in any event. The reaction of **1a** with allyl and prenyl chlorides **2b** and **2c** also proceeded under similar reaction conditions. In these reactions, the use of sterically hindered copper alkoxide **3b** improved the yields.



Scheme 1



Scheme 2

In a similar manner, reactions of the acyclic β-trimethylsilyl ketones **1b** and **1c** were performed to produce the enol silyl ethers **5** and/or dienyl ketones **4** depending on the work-up conditions. In the case of **1c**, a small amount (12%) of α-allylation product **9** was obtained. We observed an interesting reversal of regioselectivity in the reactions using prenyl chloride **2c**. When **2c** reacted with the cyclic ketone **1a**, an attack occurred preferencially at the γ-carbon to produce the formal S_N2' product **4c** (Entries 6 and 7). On the other hand, the reaction of **2c** with the acyclic ketone **1b** gave the formal S_N2 products **4f** predominantly (Entry 11). The factors that control the regiochemistry are uncertain at present.

In conclusion, we found the first anionic 1,4-silyl migration from carbon to carbonyl oxygen.[6] This rearrangement provides a convenient way for the preparation of β-vinyl carbanions of α,β-unsaturated ketones or their equivalents. Further study on the Brook-type silyl migration of various copper(I) alkoxides is currently in progress.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) 'Exploitation of Multi-Element Cyclic Molecules' (No. 14044022) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

† A typical experimental procedure: to a DMF (1 ml) solution of copper(I) chloride (15 mg, 0.15 mmol) was added a THF (1 M) solution of lithium *tert*-butoxide (0.36 ml, 0.36 mmol) at 0 °C under argon, and the reaction mixture was stirred for 20 min at room temperature. A DMF (1 ml) solution of **1a** (86 mg, 0.3 mmol) and a DMF (1 ml) solution of **2a** (33 mg, 0.36 mmol) were successively added to the reaction mixture at 0 °C, and the

DOI: 10.1039/b207325k

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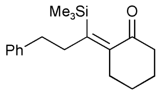
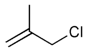
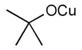
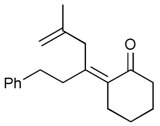
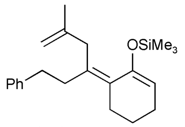
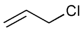
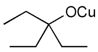
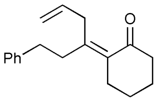
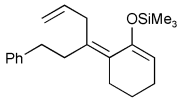
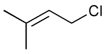
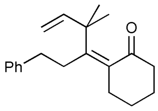
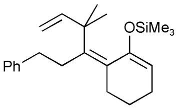
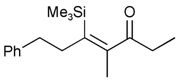
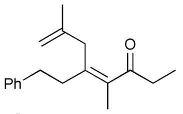
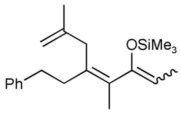
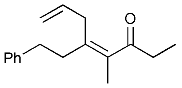
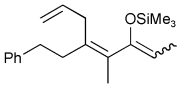
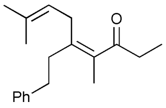
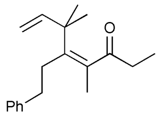
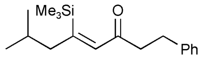
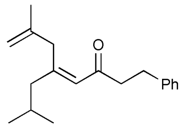
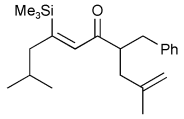
Table 1 Copper(I) *tert*-alkoxide-promoted allylation of (*Z*)-β-trimethylsilyl-α,β-unsaturated ketones **1**[a]

Entry	Ketone **1**	Allylic halide **2**	ROCu **3**	Products (yield (%))	
1[bc]					
	1a	**2a**	**3a**	**4a** (21)	**5a** (50)
2	**1a**	**2a**	**3a**	**4a** (80)	
3	**1a**	**2a**	**3a**[d]	**4a** (77)	
4	**1a**	**2a**	**3a**[de]	**4a** (57)	
5[bc]	**1a**				
		2b	**3b**	**4b** (15)	**5b** (47)
6[bc]	**1a**				
		2c	**3b**	**4c** (25)	**5c** (42)
7[f]	**1a**	**2c**	**3b**	**4c** (63)	
8[b]		**2a**	**3a**		
	1b			**4d** (13)	**5d** (68)[g]
9	**1b**	**2a**	**3a**	**4d** (76)	
10[b]	**1b**	**2b**	**3b**		
				4e (16)	**5e** (69)[h]
11[i]	**1b**	**2c**	**3b**		
				4f (65)	**4f′** (4)
12[j]		**2a**	**3b**		
	1c			**4g** (62)	**9** (12)

[a] All reactions were carried out with the method described in the note, unless otherwise noted. [b] The products were isolated without hydrolysis. [c] The reaction was carried out for 1 h. [d] 1.1 equiv. of CuCl and 1.2 equiv. of LiOBu^t were used. [e] 1.1 equiv. of CuI and 1.2 equiv. of LiOBu^t were used. [f] The formal S$_N$2 product was also obtained in 4% yield. [g] The ratio of isomers; 84 : 16. [h] The ratio of isomers; 83 : 17. [i] The products **4f** and **4f′** were obtained as a mixture. The yields were determined by NMR analysis. [j] 3 equiv. of CuCl and 3 equiv. of LiOCEt$_3$ were used.

mixture was stirred for 2 h at the same temperature. A THF (0.1 M) solution of TBAF (0.3 ml) was added and stirring was continued for 15 min at room temperature. The reaction mixture was diluted with NH$_4$Cl aqueous solution (15 ml), and the organic materials were extracted with ether, washed with water, and dried over Na$_2$SO$_4$. After removal of the solvent, the residue was purified by silica gel PTLC (hexane : AcOEt = 9 : 1) to yield 64 mg (80%) of **4a**.

The enol silyl ether **5a** was isolated as a major product by the following work-up and isolation procedure: The reaction mixture was diluted with dry hexane (15 ml). The insoluble materials were filtered off through celite and washed with dry hexane (15 ml). The filtrate was concentrated under reduced pressure. The residue was subjected to column chromatography using alumina gel deactivated with 5% water to give **5a** (51 mg, 50%) and **4a** (27 mg, 21%).

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6 Retro anionic 1,4-silyl migration from enol oxygen to sp^2 carbon was reported, see B. M. Comanita, S. Woo and A. G. Fallis, *Tetrahedron Lett.*, 1999, **40**, 5283.