Pergamon

Tetrahedron Letters 39 (1998) 6295–6298

TETRAHEDRON
LETTERS

Selective *O*-Acylation of Silyl Enol Ethers with Acid Halides Mediated by a Copper(I) Salt [1]

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Received 15 May 1998; revised 22 June 1998; accepted 26 June 1998

Abstract

A new selective synthetic method of enol esters (*O*-acylated products) from silyl enol ether and acid chloride in the presence of CuCl is described. This reaction proceeds smoothly in DMI (1,3-dimethyl-2-imidazolidinone) but not in a less polar solvent. The silicon-copper exchange reaction pathway is proposed for this transformation as in the cases of hydrosilane and alkynylsilane which were previously reported.

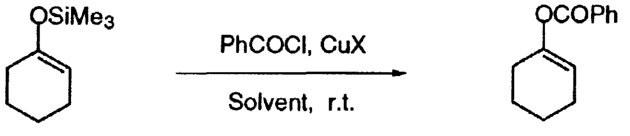
Key Words: Silicon and compounds; Copper and compounds; Enolates; Esterification

There have been numerous reports of the C-C bond formation using silyl enol ether mediated by metal salts [2-4]. However, there are few methods of the C-O bond formation reaction [5]. Recently, we reported that silicon-copper exchange reactions between organosilicon compounds and copper(I) salts occur smoothly in 1,3-dimethyl-2-imidazolidinone (DMI) [6-8]. We report herein a new, convenient procedure for the synthesis of enol esters (*O*-acylated products) from silyl enol ethers by use of a copper(I) salt in a polar solvent.

We already described that the organic group transfer from organosilicon compounds to a copper(I) salt occurred in an aprotic polar solvent such as DMI (1,3-dimethylimidazolidinone) [6-8]. Under the reported conditions, alkynyl-, aryl-, heteroaryl-, and hydro-silanes were smoothly converted to the corresponding organocopper reagents. Then, we tested enolate transfer from a silyl enol ether to a copper(I) salt in DMI. Initial attempts to obtain a metal exchange product between a silyl enol ether and a copper(I) chloride were unsuccessful. Thus, addition of 1-trimethylsiloxycyclohexene to a suspension of dry copper(I) chloride in DMI at room temperature under nitrogen effected no consumption of the silyl enol ether [9]. However, we found that an esterification product of a silyl enol ether was obtained in the

PII: S0040-4039(98)01334-3

presence of an acid chloride under the same conditions. We examined in detail combinations between various solvents and copper(I) salts in order to optimize this transformation (eq. 1). The results are shown in Table 1. In all cases, the *O*-acylated product was obtained selectively and the corresponding *C*-acylated product was not observed at all. The enol ester **3a** was produced in good yield in the presence of CuCl in DMI at room temperature (entry 1). The yield of the enol ester **3a** decreased by use of CuBr or CuI instead of CuCl (entries 2,3). The solvent plays an important role on this reaction (entries 4-6). In a less polar solvent such as THF and CH_2Cl_2, the enol ester was scarcely obtained. The propensity was in good agreement with our previous reports for *Si-Cu* exchange reactions of alkynyl- and hydro-silane [6-8]. Even a catalytic amount of copper(I) chloride gave a desirable result at 70 °C (entry 7). No product was obtained in the absence of CuCl even at elevated temperature (entry 8). This result indicates that a copper(I) salt is necessary for this reaction.



1a **3a** (1)

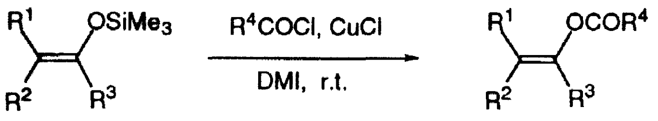
Table 1. Copper(I) Salts Mediated Esterification of Silyl Enol Ether with Acid Chloride[a]

Entry	Copper salt	Equivalent	Solvent	Time / h	Yield of **3a** / %[b]
1	CuCl	1.0	DMI	20	87
2	CuBr	1.0	DMI	20	35
3	CuI	1.0	DMI	20	11
4	CuCl	1.0	DMF	20	2
5	CuCl	1.0	THF	21	0
6	CuCl	1.0	CH_2Cl_2	23	trace
7[c]	CuCl	0.2	DMI	20	92
8[c]	CuCl	—	DMI	18	0

[a]A mixture of a silyl enolate (1.0 mmol), an acyl halide (2.0 mmol) and CuCl was stirred in a solvent (1.0 ml). [b]Isolated yield unless otherwise noted. [c]The reaction was carried out at 70 °C.

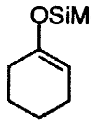
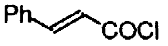
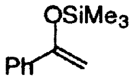
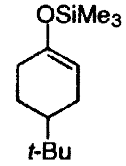
We applied this reaction to various silyl enol ethers and acid chlorides. Representative results are listed in Table 2. In every case, the *C*-acylated product was not found at all. The reaction proceeded smoothly to give the corresponding *O*-acylated enol esters in moderate to high yield. A typical procedure is given as follows. To a mixture of 1-trimethylsiloxycyclohexene **1a** (176 mg, 1.0 mmol) and CuCl (99 mg, 1.0 mmol) in DMI (1.0 mL), benzoyl chloride **2a** (272.5 mg, 2.0 mmol) was added at room temperature. After stirring for 20 h at room temperature, triethylamine (0.28 mL) was added and the reaction mixture was diluted with chloroform. Filtration through a short-column chromatography

(Frolisil®, ethyl acetate : hexane = 1 : 10) followed by purification using column chromatography (SiO_2, ethyl acetate : hexane = 1 : 60) gave 1- cyclohexenyl benzoate **3a** (175 mg, 87% yield).



1 **3** (2)

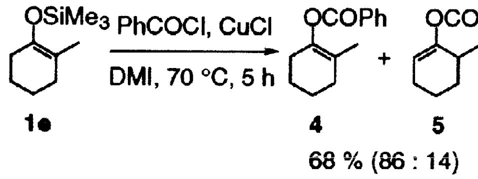
Table 2. Copper(I) Chloride Mediated Esterification of Silyl Enol Ether with Acid Chloride in DMI[a]

Entry	Silyl enolate 1	R^4COCl	2	CuCl / equiv.	Time / h	Yield of 3 / %[b]
1	 **1a**	PhCOCl	**2a**	1	20	**3a**, 87
2	**1a**	*t*-BuCOCl	**2b**	1	27	**3b**, 77
3	**1a**	CH_3COCl	**2c**	3	19	**3c**, 52
4	**1a**	CH_3CH_2COCl	**2d**	3	20	**3d**, 74
5	**1a**	$CH_3(CH_2)_4COCl$	**2e**	3	10	**3e**, 78
6	**1a**		**2f**	3	5	**3f**, 75
7	 **1b**	PhCOCl	**2a**	3	60	**3g**, 52
8	 **1c**	CH_3COCl	**2c**	3	22	**3h**, 65
9[c]	 **1d**[d]	PhCOCl	**2a**	3	8	**3i**, 78[e]

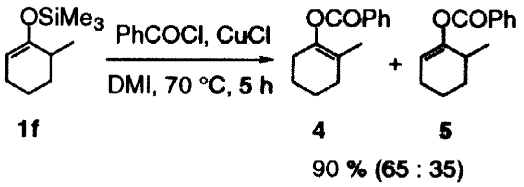
[a]A mixture of a silyl enolate (0.5 mmol), an acid chloride (1.0 mmol) and CuCl was stirred in DMI (0.5 mL) at room temperature. [b]Isolated yield unless otherwise noted. [c]The reaction was carried out at 70 °C. [d]An E/Z mixture (E : Z =57 : 43). [e]An E/Z mixture (E : Z = 34 : 66).

Esterification of 2-methyl-1-trimethylsiloxycyclohexene **1e** with benzoyl chloride promoted by CuCl mainly gave 1-benzoxy-2-methylcyclohexene **4** (eq. 3). However, the major product of 6-methyl-1-trimethylsiloxycyclohexene **1f** was 1-benzoxy-2-methycyclohexene **4** under the same conditions (eq. 4). These results revealed that this esterification reaction was accompanied with transposition of the double bond and favored to form a thermodynamically stable product.

Ketene silyl acetal **1g** was converted to the corresponding keto ester **6** (*C*-acylated product) under similar conditions (eq. 6) [10]. In this case, the *O*-acylated product was not obtained (eq. 5).



(3)



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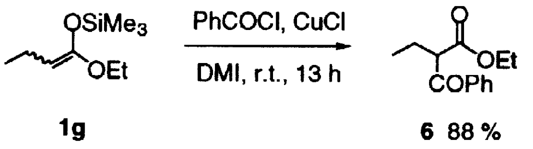
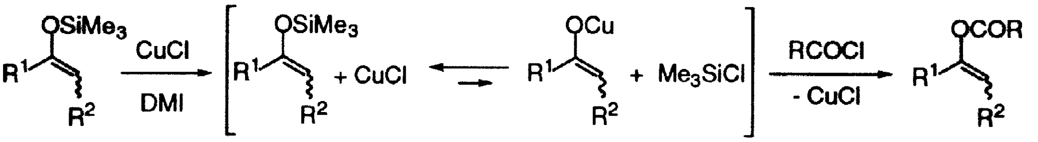


(5)

We propose a plausible mechanism of this reaction as follows (eq. 6). Equilibrium of the silicon-copper exchange should be present in the mixture of silyl enol ether and copper(I) chloride in DMI. Subsequent *O*-acylation of a thermodynamically stable copper(I) enolate with acid chloride produces the corresponding enol ester and copper(I) chloride.



(6)

In conclusion, a copper(I) salt efficiently promotes the esterification reaction between a silyl enol ether and an acid chloride. These results provide not only valuable insight into the chemistry of silyl enol ethers but also a practical method for the synthesis of enol esters under mild conditions. Further characterization of the reaction mechanism and the structure of the active species is under investigation.

Acknowledgments

Financial support for this work is partly provided by Grants-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Japan and Pfizer Pharmaceuticals Inc. We thank Dow Corning Toray Silicone Co. Ltd., Chisso Co. Ltd., and Shin-Etsu Chemical Co. Ltd. for a gift of organosilicon compounds.

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