

Michael Reactions of Silylated Nucleophiles with Conjugated Enones accompanied by Silyl Group Transfer catalysed by Copper(I) Chloride under Photoirradiation

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Photoreaction of conjugated enones with silylated nucleophiles such as silyl acetals, silyl enol ethers and even an allyl silane resulted in the formation of Michael adducts accompanied by transfer of the silyl group.

The Michael reaction is one of the most actively explored reactions as a carbon-carbon bond forming process.¹ Although the addition of nucleophiles to α,β -unsaturated ketones under basic conditions is well known as the prototype, Lewis-acid promoted reactions² or reaction *via* photocycloaddition³ of silyl enol ethers has been recently actively investigated to overcome some disadvantages of the prototype process such as self-condensation of substrates. Further functionalization of the Michael products *via* their enolates is often complicated due to equilibria between α and α' forms. Methodologies to overcome this problem include use of special Lewis acids such as trityl salts⁴ or [1,2-benzenediolate(2-)-*O,O'*]oxotitanium⁵ which are reported to catalyse the Michael reaction with silyl enol ethers in conjunction with silyl group transfer; an organocopper-halotrimethylsilane system yields silyl enol ethers from 1,4-addition to conjugated enones.⁶ We wish to present herein our results with copper(I) chloride, an easily available and mild salt, which promotes the reaction of α,β -unsaturated carbonyl compounds with silylated nucleophiles such as ketene silyl acetals, silyl enol ethers and even an allyl silane to form regioselectively the new silyl enol ethers from Michael adducts.

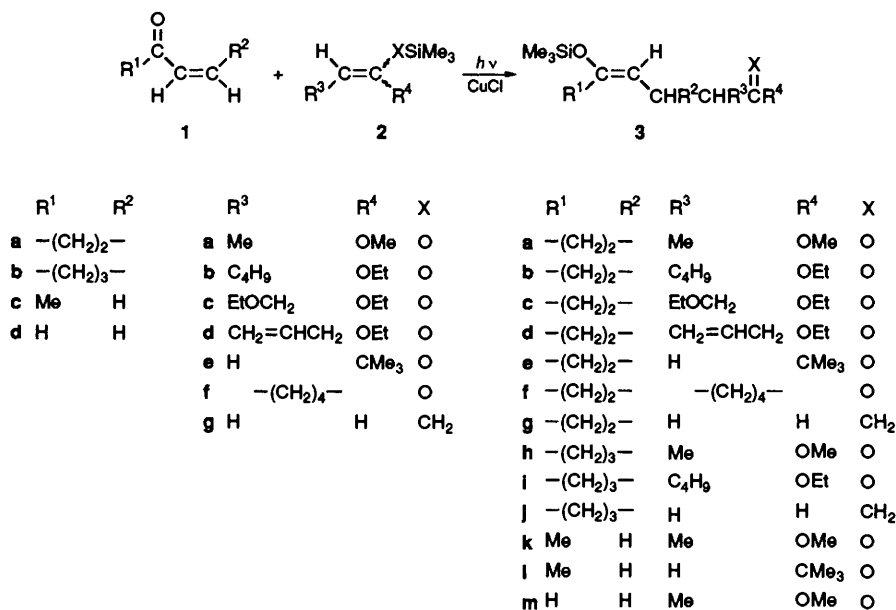
A solution of cyclopent-2-en-1-one **1a** (2 mmol), methyl propionate ketene silyl acetal **2a** (4 mmol), copper(I) chloride (0.4 mmol) and acetonitrile (5 ml) was irradiated using a high-pressure Hg lamp (200 W) for 20 h at ambient temperature under a nitrogen atmosphere to afford the silyl enol ether **3a** in 81% yield with no trace of its regioisomer. Use of DMSO instead of acetonitrile furnished an almost comparable yield of **3a** (78%). The reaction in the presence of a stoichiometric amount of copper(I) chloride in acetonitrile diminished the yield of **3a** to 60%. No product was obtained in a control experiment in the dark at ambient or even at reflux temperature.† Photoreaction in the absence of copper(I) chloride furnished only the [2 + 2] cycloadduct **4**, 5-methoxy-6-methyl-

5-trimethylsilyloxybicyclo[3.2.0]heptan-2-one. Thus, photoirradiation in the presence of copper(I) chloride was essential for the formation of **3a**. As to the reaction mechanism, the pathway by way of intermediate **4** is ruled out since photoirradiation of **4** in acetonitrile containing copper(I) chloride failed to give **3a**. One could envisage a pathway *via* the intermediate formation of 6-methoxy-5-methyl-6-trimethylsilyloxybicyclo[3.2.0]heptan-2-one **5**, the regioisomer of **4**, followed by desilylative ring opening under the action of copper(I) chloride. This pathway, however, seems to be also excluded because the regiochemistry of **5** is opposite to that deduced from the photoadducts of conjugated enones with vinyl ethers⁸ and even photoreaction in the presence of the triplet sensitizers such as acetophenone did not yield **5**. Thus,

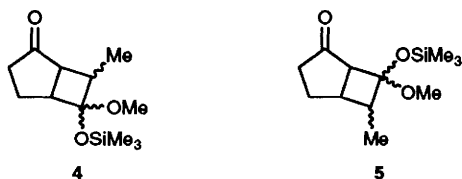
Table 1 Silyl-group transfer Michael reaction of enones **1** with silylated nucleophiles **2**

	1	2	3 Yield (%) ^a
	a	a	a 81
	a	b	b 73
	a	c	c 76
	a	d	d 80
	a	e	e 58
	a	f	f 44
	a	g	g 61
	b	a	h 70
	b	b	i 61
	b	g	j 53
	c	a	k 54
	c	e	l 36
	d	a	m 50

^a Determined by vapour phase chromatography



Scheme 1



the possibility of reaction *via* [2 + 2] cycloaddition is diminished. At this stage therefore, no definite mechanism is proposed. Other cyclic and acyclic enones **1b–d** also undergo similar reactions with **2a** but with rather lower yields of products **3** being formed.

It is worth noting that, besides ketene silyl acetals **2a–d**, silyl enol ethers **2e–f** and even an allyl silane **2g** reacted to give products **3**; results are collected in Table 1.

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Footnote

† Tamura and coworkers have reported that the thermal reaction of conjugated enones with some special ketene silyl acetals in acetonitrile

yields Michael adducts accompanied by transfer of the silyl group.⁷ However, for our system containing copper(I) chloride and substrates at lower concentrations, the Michael reaction was not observed to occur.

References

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