BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 1241—1242 (1979)

The Silver(I) Salt-promoted Benzylation of Silyl Enol Ethers

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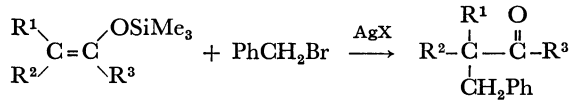
(Received September 1, 1978)

Synopsis. Various silyl enol ethers gave the corresponding mono benzyl products in moderate to good yields by the reaction with benzyl bromide in the presence of silver perchlorate in dichloromethane at −78—0 °C.

Silyl enol ethers are known to be useful intermediates for the alkylation of carbonyl compounds; the alkylation is usually performed through the enolate anion generated by the treatment with MeLi[1] or $R_4N^+F^-$.[2] On the other hand, the *t*-butylation of silyl enol ethers was recently accomplished by the use of Lewis-acid catalysts.[3]

Silver(I) salts are well known to activate the halogenated compounds. Therefore, it seemed possible to alkylate the silyl enol ethers with alkyl halides activated by silver(I) salt. In this paper, we will describe the silver(I) salt-promoted benzylation of silyl enol ethers.[4]



Results and Discussion

First, we examined the reaction of 1-trimethylsiloxycyclohexene and benzyl bromide in dichloromethane as a model reaction. When the reaction was carried out in the presence of silver(I) oxide or silver(I) nitrate, no alkylated product was obtained. However, 2-benzylcyclohexanone was obtained in 9% (Ag_2O) or 15% ($AgNO_3$) yield by the addition of a catalytic amount of zinc chloride to the reaction mixture. Therefore, in order to ascertain the best conditions for the reaction, various silver(I) salts, Lewis acids, and reaction temperatures were examined. These results are summarized in Table 1.

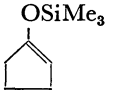
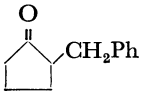
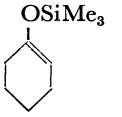
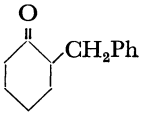
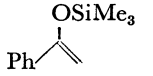
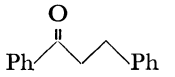
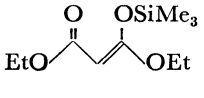
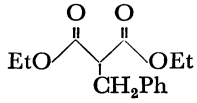
Table 1. Reaction of 1-trimethylsiloxycyclohexene with benzyl bromide in dichloromethane

Silver(I) salt (1 equiv)	Catalyst[c]	Temp/°C	Time/h	Isolated yield/%
Ag_2O	$ZnCl_2$	room temp	20	9[a]
$AgNO_3$	$ZnCl_2$	room temp	20	15[a]
$AgClO_4$	$ZnCl_2$	room temp	20	21[a]
$AgNO_3$	$ZnCl_2$	−78—0	14	11[b]
$AgNO_3$	$TiCl_4$	−78—0	14	14[b]
$AgNO_3$	$SnCl_4$	−78—0	14	22[b]
$AgNO_3$	$BF_3\cdot Et_2O$	−78—0	14	49[b]
$AgClO_4$	$BF_3\cdot Et_2O$	−78—0	14	82[b]
$AgClO_4$	—	−78—0	14	64[b]
$AgBF_4$	$BF_3\cdot Et_2O$	−78—0	14	32[b]
$AgBF_4$	—	−78—0	14	51[b]

a) 1-Trimethylsiloxycyclohexene (1 equiv) and benzyl bromide (1.1 equiv) were used. b) 1-Trimethylsiloxycyclohexene (1.2 equiv) and benzyl bromide (1 equiv) were used. c) A catalytic amount of Lewis acid was used.

As shown in Table 1, a combination of silver perchlorate and boron trifluoride etherate was the best one. Moreover, it was found that the reaction could proceed without a Lewis-acid catalyst when silver perchlorate or silver tetrafluoroborate was used. In the case of the reaction of 1-phenyl-1-trimethylsiloxyethene and benzyl bromide, silver perchlorate alone gave the best result (44%), although the addition of boron trifluoride etherate, zinc chloride, or magnesium chloride gave the corresponding benzylated product in 21, 41, or 34% yield respectively. The reaction of several silyl enol ethers and benzyl bromide in the presence of silver perchlorate was also examined; the results are listed in Table 2.

Table 2. Benzylation of various silyl enol ethers[a]

Silyl enol ether	Product[6]	Isolated yield/%
		69
		82[b]
		44
		35

a) Silyl enol ether (1.2 equiv) and benzyl bromide (1 equiv) were used in dichloromethane at −78—0 °C for 14 h in the presence of $AgClO_4$ (1 equiv). b) A catalytic amount of $BF_3\cdot Et_2O$ was used.

These yields are well in accordance with the order of the electron density of the carbon-carbon double bond of silyl enol ethers. Therefore, it is reasonable to assume that the reaction is an electrophilic one. Under similar reaction conditions, we examined the alkylation of 1-phenyl-1-trimethylsiloxyethene using other alkyl halides. However, all attempts failed in the cases of isopropyl iodide, allyl brimide, and butyl iodide. The only successful case except for benzyl bromide was that of methyl iodide (51%).

To ascertain the regioselectivity of the reaction, we also examined the reaction of 6-methyl-1-trimethylsiloxycyclohexene with benzyl bromide. However, the reaction was found not to be regioselective even under rather basic conditions.

Table 3. Reaction of 6-methyl-1-trimethylsiloxycyclohexene with benzyl bromide[a)]

Additive	Product[6)] Yield(%)[b)] *cis*	*trans*	Yield/%[b)]	Total yield/%
—	34	14	22	70
2,4,6-Collidine (1 equiv)	28	22	14	64

a) 6-Methyl-1-trimethylsiloxycyclohexene (1.1 equiv) and benzyl bromide (1 equiv) were used in dichloromethane at −78—0 °C for 14 h in the presence of $AgClO_4$ (1 equiv). b) Isolated yield.

Experimental

A typical procedure for the benzylation of silyl enol ethers[5)] was as follows.

2-Benzylcyclohexanone. A dichloromethane solution (2 ml) of 1-trimethylsiloxycyclohexene (204 mg, 1.2 mmol) and benzyl bromide (171 mg, 1 mmol) was added to silver perchlorate (208 mg, 1 mmol) at −78 °C under argon atmosphere. The mixture was then allowed to warm to 0 °C over about 14 h. The silver salts were filtered off, and water was added. The solution was then extracted with ether, and the organic layer was dried over sodium sulfate and evaporated. 2-Benzylcyclohexanone was obtained by using TLC (hexane: ether = 10: 1, R_f = 0.4); 119 mg (64%).

References

1) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462 (1968).

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3) T. H. Chan, I. Paterson, and J. Pinsonnault, *Tetrahedron Lett.*, **1977**, 4183; M. T. Reetz and W. F. Maier, *Angew. Chem.*, **90**, 50 (1978).

4) The oxidative coupling reaction of silyl enol ethers using silver(I) oxide in DMSO was previously reported; Y. Ito, T. Konoike, and T. Saegusa, *J. Am. Chem. Soc.*, **97**, 649 (1975).

5) The silyl enol ethers were prepared according to the procedures of H. O. House, L. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971).

6) These products were confirmed by their spectral data, by elemental analyses, and by comparison with authentic samples prepared according to I. Kuwajima and E. Nakamura, *J. Am. Chem. Soc.*, **97**, 3257 (1975).