

DEHYDROGENATIVE SILYLATION OF KETONES WITH HYDROSILANES.
A CLEAN AND CONVENIENT METHOD OF PREPARING SILYL ENIOL ETHERS¹

Hideki Sakurai*, Kazuhito Miyoshi and Yasuhiro Nakadaira
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 JAPAN

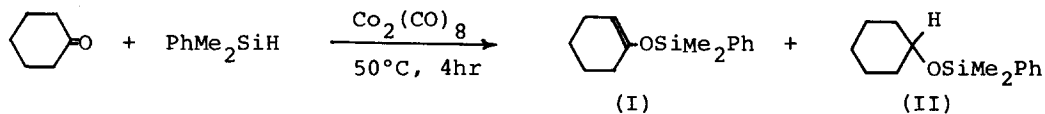
(Received in Japan 23 May 1977; received in UK for publication 14 June 1977)

Silyl enol ethers have been recognized as an important intermediate in the organic synthesis.² A standard method for the preparation of silyl enol ethers has been the silylation of ketones with the combination of base and chlorosilane.³ Although the yield of the reaction itself is high, separation of moisture-sensitive products from a large amount of inorganic or amine salt is the drawbacks of the method.

Recently Kuwajima et al. have reported an improved method of silylation of ketones with ethyl trimethylsilylacetate-tetrabutylammonium fluoride, in which relatively volatile ethyl acetate is the by-product.⁴ Nevertheless, the catalytic dehydrogenation from ketone and hydrosilane would be the most clean and convenient method of preparing silyl enol ether, if a suitable catalyst could be found.

The catalytic dehydrogenation from ketone and hydrosilane is not unprecedented. Reactions catalyzed by palladium salts,⁵ rhodium complexes⁶ and nickel salts⁷ have been reported. However, these catalysts are not always very satisfactory because of side reactions and/or the scope of the reaction.

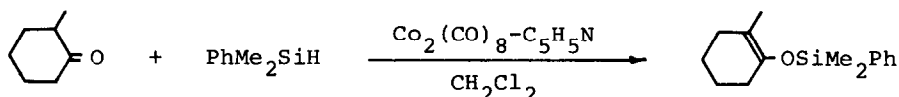
We have found that dicobalt octacarbonyl is an excellent catalyst for the purpose, provided a certain cocatalyst is added to the system. For example, the reaction of cyclohexanone and phenyldimethylsilane gave a 40:60 mixture of dimethylphenyl(1-cyclohexenyloxy)silane (I) and dimethylphenyl(cyclohexyloxy)silane (II) in the presence of a catalytic amount (2-4 mol %) of dicobalt octacarbonyl.



However, addition of a small amount (2-4 mole %) of an amine such as triethylamine and pyridine changes the product distribution dramatically. Thus, the reaction with a combined catalyst of dicobalt octacarbonyl (2 mole %) and triethylamine (2 mole %) afforded only (I) in the yield more than 99%(vpc).

Besides amines, certain other bases such as potassium t-butoxide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), phosphines, phosphites, and even sodium acetate are effective cocatalysts in the reaction. However, addition of an excess amount of triethylamine, on the contrary, retards the rate of the reaction and changes the product distribution again in favor of silyl ether (reduction). The optimum ratio of the base to dicobalt octacarbonyl ranges from 0.5 to 2.0.

The silyl enol ether obtained in this reaction, where two isomeric enols are possible for a ketone, arises always from the thermodynamically stable one as shown in the following example.



Thus, dimethyl-phenyl(2-methylcyclohex-1-enyloxy)silane was obtained in 89% yield. The ratio of this isomer to the thermodynamically less stable one is 92:8.

A typical example of the experimental procedure is shown for methyl isopropyl ketone. A dry 50ml-two necked flask, equipped with a reflux condenser, a glass stopper, a magnetic stirring bar and a nujor bubbler, is maintained under a constant pressure of nitrogen. The flask is charged with 7.50g(55.0 mmol) of dimethylphenylsilane, 4.30g(50.0mmol) of methyl isopropyl ketone and 0.11g(1.42mmol, 2.8mol%) of pyridine. To the stirred mixture, a solution of dicobalt octacarbonyl (2 mol%) in dichloromethane is added, and warmed in an oil bath for 2 hours. After the condenser is replaced with a distillation apparatus equipped with a Vigreux column, the expected silyl enol ether, dimethylphenyl-(1,2-dimethyl-1-propenyloxy)silane, is distilled under reduced pressure directly from the flask in 94% yield, b.p. 96-117°C/8mmHg.

Table 1 shows the results of the dehydrogenative silylation of cyclohexanone with various kinds of hydrosilanes. Phenylmethylsilane (PhMeSiH_2) was most reactive among hydrosilanes examined, but at the same time, least selective in the product distribution.

Trimethylsilane (b.p. 6.7°C) is one of the best hydrosilanes from the synthetic point of view and may be conveniently obtained from commercially available trimethylchlorosilane. Thus, about 4 molar excess amount of trimethylchlorosilane is added to a suspension of lithium aluminum hydride in dibutyl ether placed in another flask. Trimethylsilane is transferred directly into the reaction flask, equipped with a Dry Ice trap on the top of the condenser, with a slow stream of nitrogen through a short column packed with soda lime. The latter is essential to remove acidic chlorosilane or hydrogen chloride and otherwise dicobalt octacarbonyl may be destroyed.

Table 1 Reaction of cyclohexanone with hydrosilanes in the presence of $\text{Co}_2(\text{CO})_8$ (2 mol%)-pyridine (2 mol%) at 50°C.

Hydrosilane	Time (hr)	Yield of the isolated product (%)	Product ratio	
			(I)	(II)
PhMe_2SiH	2	85	100	0
Et_3SiH	4	72	100	0
$(\text{EtO})_3\text{SiH}$	6	55	100	0
Me_3SiH	2	84	100	0
PhMeSiH_2	1 ^{a)}	(100) ^{b)}	90 ^{b)}	10 ^{b)}

a) At room temperature.

b) Determined by vapor phase chromatography.

The study on the scope and limitations of the reaction is under way, but it will be pertinent to show the results for various ketones in Table 2 in the last page.

Acknowledgment.


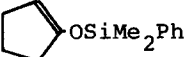



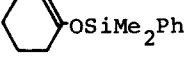

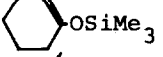

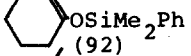
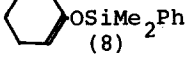
We thank Toshiba Silicon Co., Ltd., for gifts of chlorosilanes.

References

- (1) Chemistry of Organosilicon Compounds 101.
- (2) For recent reviews, see
 - (a) A.Hosomi, *Kagaku no Ryoiki*, **29**, 528 (1975);
 - (b) R.F.Hudrilik, "New Applications of Organometallic Reagents in Organic Synthesis" D.Seyferth ed., Elsevier, Amsterdam, 1976, p.127.
- (3) G.Stork and P.F.Hudrilik, *J.Amer.Chem.Soc.*, **90**, 4462 (1968); H.O.House, L.J.Czuba, M.Gall and H.D.Olmstead, *J.Org.Chem.*, **34**, 2324 (1969).
- (4) I.Kuwajima, E.Nakamura, T.Murofushi and M.Shimizu, *J.Amer.Chem.Soc.*, **98**, 2346 (1976).
- (5) Y.Nagai, K.Uetake, T.Yoshikawa and H.Matsumoto, *J.Syn.Org.Chem.Japan*, **31**, 759 (1973).
- (6) I.Ojima and Y.Nagai, *J.Organometal.Chem.*, **57**, C42 (1973).
- (7) E.Frainnet, Y.Martel-Siegfried, E.Brousse and J.Dedier, *J.Organometal.Chem.*, **85**, 297 (1975).

Table 2

Preparation of silyl enol ethers by the reaction of ketones with hydrosilane in the presence of $\text{Co}_2(\text{CO})_8$ (2 mol%)-pyridine (2 mol%) at 50°C.

Ketone	Hydrosilane	Time (hr)	Product (yield %)	Product (ratio %) ^{a)}	
				Silyl enol ether (E/Z)	Silyl ether
MeCO^tBu	PhMe_2SiH	1	81	$\text{CH}_2=\text{C}(^t\text{Bu})\text{OSiMe}_2\text{Ph}$	
MeCOiPr	PhMe_2SiH	2	94	$\text{Me}_2\text{C}=\text{C}(\text{Me})\text{OSiMe}_2\text{Ph}$	
MeCOEt	PhMe_2SiH	2	87	$\text{MeCH}=\text{C}(\text{Me})\text{OSiMe}_2\text{Ph}$ (20/63)	
				$\text{CH}_2=\text{C}(\text{Et})\text{OSiMe}_2\text{Ph}$ (17)	
MeCOMe	PhMe_2SiH	3	71	$\text{CH}_2=\text{C}(\text{Me})\text{OSiMe}_2\text{Ph}$ (93)	$\text{Me}_2\text{CHOSiMe}_2\text{Ph}$ (7)
EtCOEt	PhMe_2SiH	2	87	$\text{MeCH}=\text{C}(\text{Et})\text{OSiMe}_2\text{Ph}$	
$\text{EtCOEt}^b)$	Me_3SiH	4	80	$\text{MeCH}=\text{C}(\text{Et})\text{OSiMe}_3$	
	PhMe_2SiH	2	90		
 ^{b)}	Me_3SiH	20	52		
	PhMe_2SiH	2	85		
 ^{b)}	Me_3SiH	2	84		
	PhMe_2SiH	2	89	 (92)	
				 (8)	
PhCH_2COMe	PhMe_2SiH	3	93	$\text{PhCH}=\text{C}(\text{Me})\text{OSiMe}_2\text{Ph}$ (15/82)	
PhCOEt	PhMe_2SiH	2.5	82	$\text{MeCH}=\text{C}(\text{Ph})\text{OSiMe}_2\text{Ph}$ (8/92)	
PhCOMe	PhMe_2SiH	2	88	$\text{CH}_2=\text{C}(\text{Ph})\text{OSiMe}_2\text{Ph}$ (35)	$\text{PhCH}(\text{Me})\text{OSiMe}_2\text{Ph}$ (65)

a) Product ratio determined by either nmr spectrum or vapor phase chromatography.

b) At ca. 40°C by using methylene chloride as a solvent.