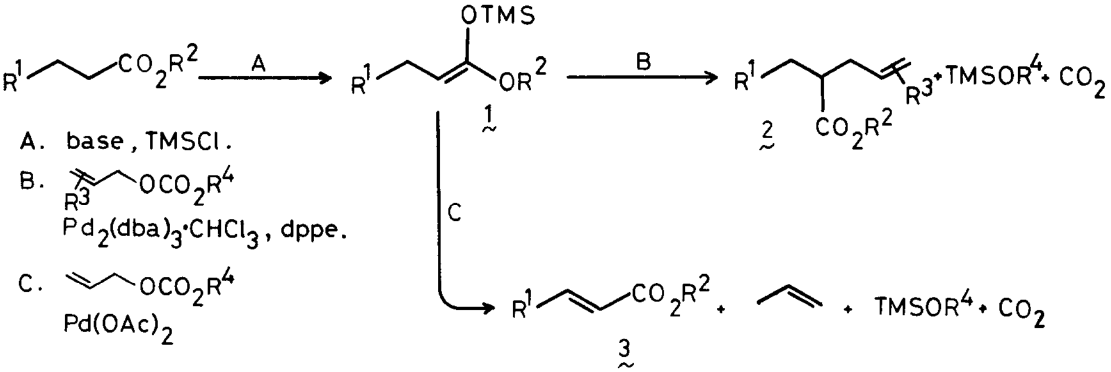
Tetrahedron Letters,Vol.25,No.42,pp 4783-4786,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

PALLADIUM-CATALYZED PREPARATION OF α-ALLYL ESTERS AND α,β-UNSATURATED ESTERS FROM SATURATED ESTERS VIA THEIR KETENE SILYL ACETALS

Jiro Tsuji,* Kazuhiko Takahashi, Ichiro Minami, and Isao Shimizu
Tokyo Institute of Technology, Meguro, Tokyo 152, JAPAN

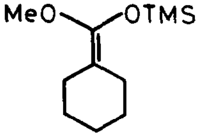
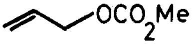
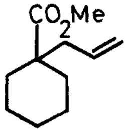
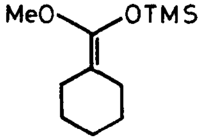
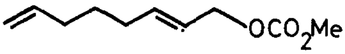
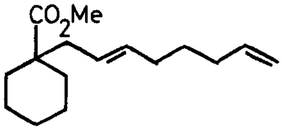
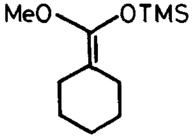
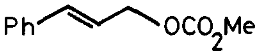
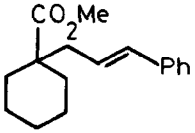
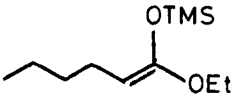
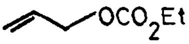
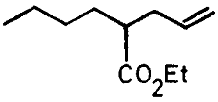
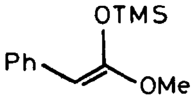
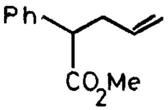
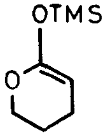
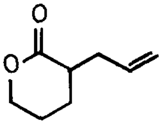
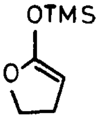
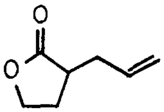
Summary: Reaction of ketene silyl acetals with allylic carbonates in the presence of palladium-phosphine catalyst in dioxane gives α-allyl esters in high yields. When the reaction is carried out with phosphine-free palladium catalyst in nitriles, α,β-unsaturated esters are obtained in good yields.

We have reported an efficient method for allylation of ketones and aldehydes by the palladium-catalyzed reaction of silyl enol ethers with allylic carbonates.[1)] Also α,β-unsaturated ketones and aldehydes are prepared by using nitriles as the solvents.[2)] Unlike silyl enol ethers which are used extensively in organic synthesis, ketene silyl acetals have rather limited use because they are more sensitive to various reagents than silyl enol ethers.[3)] The usefulness of ketene silyl acetals would be more enhanced if they could be converted to various ester derivatives under mild conditions. We now wish to report the facile palladium-catalyzed allylation and dehydrogenation of saturated esters via their ketene silyl acetals as shown by the following scheme.



α-Monoalkylation of esters is an important synthetic operation, but the reaction requires well-controlled reaction conditions to achieve selective monoalkylation.[4)] Also, efficient conversion of saturated esters to α,β-unsaturated ones is highly desirable. The known methods are based on introduction of hetero atoms (Se[5)] and S[6)]), followed by their elimination with β-hydrogen. We have found that these conversions can be done very efficiently via ketene silyl acetals using palladium catalysts.

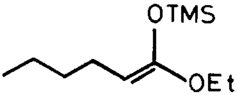
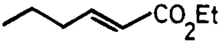
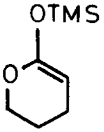
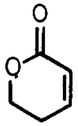
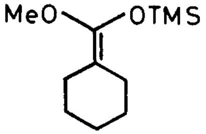
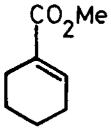
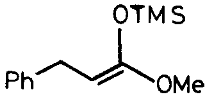
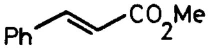
Table 1. Synthesis of Various α-Monoallyl Esters

Run	Ketene Silyl Acetal	Allylic Carbonate	Product	Yield(%)
1		 4		75
2				74
3				91
4				79
5		4		64
6		4		48
7		4		51

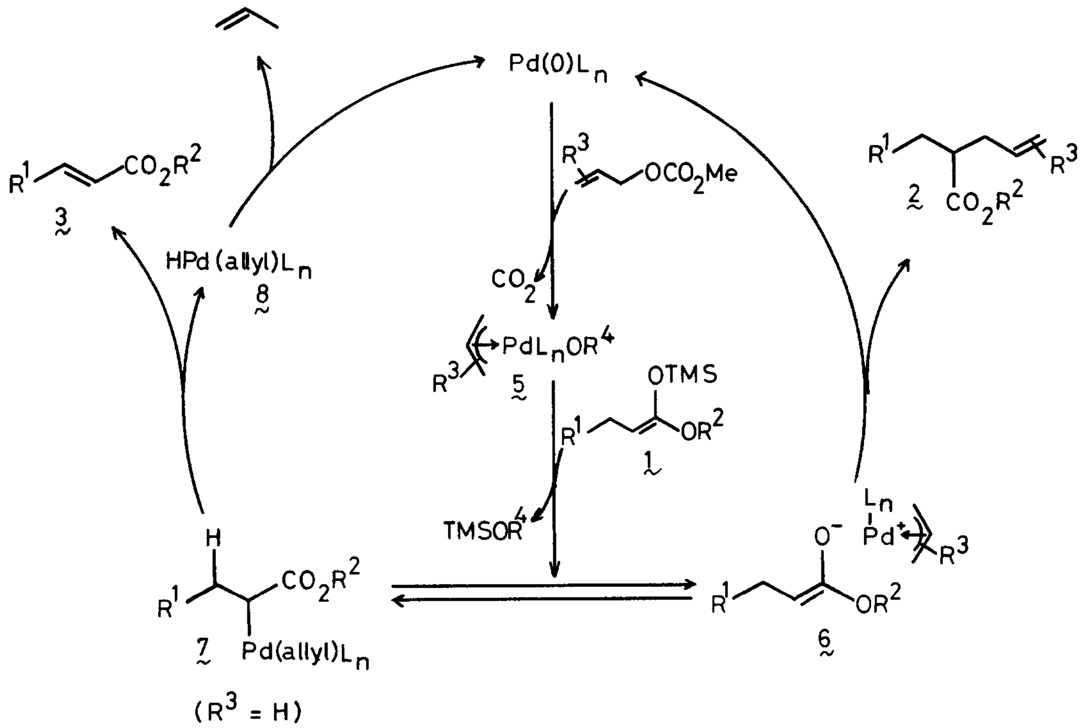
At first we carried out the allylation reaction using Pd-dppe (diphenylphosphinoethane). Examples of satisfactory allylation of various ketene silyl acetals are shown in Table 1. The allylation is carried out simply by refluxing a solution of ketene silyl acetal (1.0 mmol), allylic carbonate (2.0 mmol), $Pd_2(dba)_3CHCl_3$ (0.025 mmol) and dppe (0.1 mmol) in dioxane (5 mL) under argon. Progress of the reaction was monitored by GLC, and the allylated esters were isolated by column chromatography on silica gel or preparative GLC.

Then we discovered that the dehydrogenation to give α,β-unsaturated esters rather than allylation takes place when the reaction is carried out in nitriles as the solvent and using phosphine-free palladium catalyst. We have confirmed that the phosphine-free palladium catalyst is most effective for the dehydrogenation of ketones via their enolate equivalents.7) Various α,β-unsaturated esters are prepared in good yields with high selectivities as shown in Table 2. In some cases, PhCN rather than MeCN gave better results. The reaction can be carried out easily by heating the solution of ketene silyl acetal (1.0 mmol), allyl methyl carbonate (2.0 mmol) and $Pd(OAc)_2$ (0.1 mmol) in MeCN (5 mL) or PhCN (1 mL) under argon. After the reaction was judged to complete (GLC analysis), the α,β-unsaturated esters were isolated by column chromatography or preparative GLC.

Table 2. Preparation of Various α,β-Unsaturated Esters

Run	Ketene Silyl Acetal	Solvent	Product	Yield(%)
1		MeCN		79
2		MeCN		70
3		PhCN		75
4		PhCN		69

These reactions can be explained by the following mechanism. The first step is the formation of π-allylpalladium alkoxide complex **5** by the oxidative addition of allylic carbonate, followed by decarboxylation.8,9) Then Pd-Si transmetallation takes place between **5** and **1** to give allylpalladium enolate complex **6**, which is in equilibrium with the carbon-bonded complex **7**. Then the α-allyl ester is formed by intramolecular nucleophilic substitution of the complex **6**. α,β-Unsaturated ester formation is explained by the β-elimination to give palladium hydride species **8** from the complex **7**. These mechanisms are closely related to those of the palladium catalyzed allylation and dehydrogenation of silyl enol ethers to give α-allyl ketones or α,β-unsaturated ketones respectively.1,2)



Acknowledgement: This research was financially supported by the Grant-in-Aids for Scientific Research, A, No. 57430030, and Encouragement of Young Scientist, No. 58750681 from the Ministry of Education, Science and Culture.

References:

1) J. Tsuji, I. Minami, I. Shimizu, Chem. Lett., **1983**, 1325.

2) J. Tsuji, I. Minami, I. Shimizu, Tetrahedron Lett., **24**, 5635 (1983).

3) For representive reactions of ketene silyl acetals, see;
   a) K. Saigo, M. Osaki, T. Mukaiyama, Chem. Lett., **1975**, 989.
   b) K. Saigo, M. Osaki, T. Mukaiyama, Chem. Lett., **1976**, 163.
   c) M. T. Reetz, K. Schwellnus, Tetrahedron Lett., **1978**, 1455.

4) R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Gichman, R. H. Schessinger, Tetrahedron Lett., **1973**, 2425.

5) a) H. J. Reich, I. L. Reich, J. M. Renga, J. Am. Chem. Soc., **95**, 5813 (1973).
   b) K. B. Sharpless, R. F. Lauer, A. Y. Teranishi, J. Am. Chem. Soc., **95**, 6137 (1973).

6) B. M. Trost, T. N. Salzmann, K. Hiroi, J. Am. Chem. Soc., **98**, 4887 (1976).

7) J. Tsuji, I. Minami, I. Shimizu, H. Kataoka, Chem. Lett., **1984**, 1133.

8) F. Guibe, Y. S. M'Leux, Tetrahedron Lett., **22**, 3591 (1981).

9) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, Tetrahedron Lett., **23**, 4809 (1983).

(Received in Japan 30 June 1984)