Tetrahedron Letters,Vol.27,No.14,pp 1599-1602,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

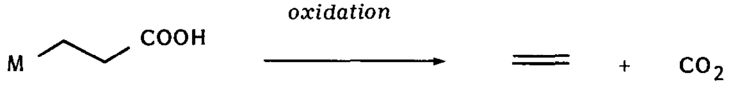
Silicon- and Tin-Directed Oxidative Decarboxylation: Regioselective Formation of Olefins from β-Silyl and β-Stannyl Carboxylic Acids

Hisao Nishiyama,* Makoto Matsumoto, Hiroyuki Arai, Hisao Sakaguchi, and Kenji Itoh

School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 440, Japan

Abstract: Oxidative decarboxylation of β-silyl and β-stannyl carboxylic acids with lead tetra-acetate (LTA) can be controlled by the silyl and stannyl functions to give the corresponding olefins under the mild conditions.

We have already investigated the metal-directed cleavage reactions in cationic[1] and homolytic[2] systems. We report here a new metal-directed oxidative decarboxylation of carboxylic acids with LTA giving olefins.



M = Me_3Si, Me_2PhSi, n-Bu_3Sn

Although the oxidative decarboxylation of carboxylic acids with LTA has been used for the preparation of olefins, the reaction is not always efficient and versatile as a transformation method.[3] The reaction needs thermal or photochemical activation and is influenced by solvents and other additives.[4] Therefore we have intrigued to refine the decarboxylation by introduction of silyl and stannyl functions as leading groups in order to improve the regioselectivity and the yields for the olefin formation.

We have obtained the starting β-silyl and β-stannyl carboxylic acids **1-14** by hydrolysis[5] of the corresponding esters, which were synthesized by the conjugate addition[6] of the silyl or the stannyl lithium reagents to α,β-unsaturated esters and by silyl- or stannyl-methylation[7] of the ester enolates with iodomethyl(trimethyl)silane or iodomethyl(tri-n-butyl)stannane.

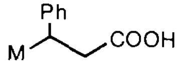
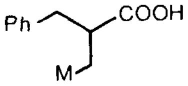
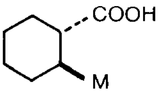
Treatment of the β-stannyl acids **1** and **4** with LTA (2.0 eq) in dichloromethane for 2 h gave styrene and allylbenzene in 47% and 70% yields, respectively (Table; run 1 and 10). Addition of cupric acetate (0.2 eq) as a co-catalyst improved the yields (run 2 and 11). Thus the regio-controlled decarboxyl-destannylation is successfully carried out under the mild conditions.

On the other hand, the β-silyl acid **2** was recovered by treatment with LTA in dichloromethane and in acetonitrile at room temperature. Decarboxylation of **2** was observed with LTA and NaOAc in acetonitrile under the heating condition (at 70°C) for 1 h to give styrene in high yield; conversion, 60% (run 7). We found that the use of N,N-dimethylformamide (DMF) in the presence of a catalytic amount of cupric acetate (2 mol%) is effective to give the olefins from **2**, **3**, **5**, **6**, **7**, and **8** in high yields (run 5, 8, 12-16; condition (B)).

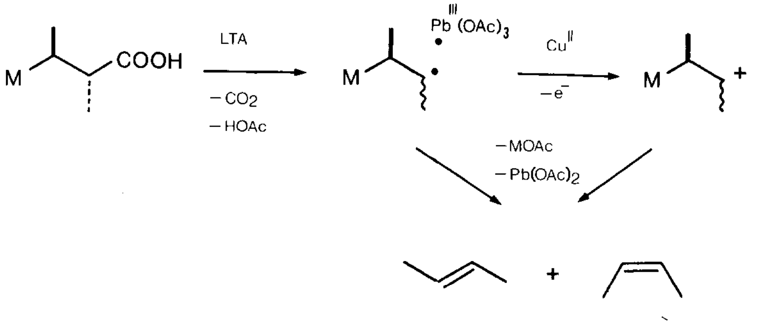
It is quite interesting that the oxidative desilylation forming olefins can be achieved, since the efficient elimination of a silyl group in oxidation media is a fairly difficult problem.[8]

The stereochemical course of the decarboxyl-demetalation was then examined (run 17-26). However, the stereospecificity for the reaction could not be observed. Trans-β-methylstyrene was obtained as a major product from **9-12** in any case. While, the mixture of trans- and cis-2-butene was obtained from **13** and **14** (run 25 and 26).

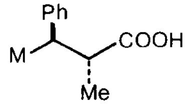
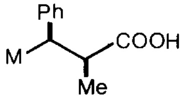
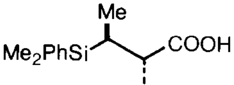
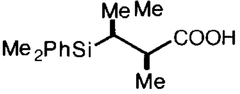
Table 1. Oxidative decarboxylation of β-silyl and β-stannyl carboxylic acids.

run	carboxylic acid		M	condition[a]	temp. (°C)	time (h)	product	yield[b] (%)
1		**1**	n-Bu$_3$Sn	LTA(1.4 eq), CH$_2$Cl$_2$	0	2	styrene	(47)
2				(A)	0	0.5		(86)
3				(B)	0	0.5		(83)
4		**2**	Me$_3$Si	(A)	rt	120		(trace)
5				(B)	rt	2		(87)
6				(C)	rt	120		(74)[c]
7				(C)	70	1		(82)[c]
8		**3**	Me$_2$PhSi	(B)	rt	3		(84)
9				(C)	70	1		(83)[c]
10		**4**	n-Bu$_3$Sn	LTA(1.5 eq), CH$_2$Cl$_2$	rt	2	allyl-benzene	(70)
11				(A)	0	6		(89)
12				(B)	rt	4		(81)
13		**5**	Me$_3$Si	(B)	rt	3		(84)
14		**6**	Me$_2$PhSi	(B)	rt	9		(81)
15		**7**	Me$_3$Si	(B)	rt	3	cyclo-hexene	(72)
16		**8**	Me$_2$PhSi	(B)	rt	6		(71)

These facts could be accounted for formation of the free radical or the free cationic species causing loss of stereospecificity. In the case of the stannyl acids, the decarboxylation may proceed via transmetalation by the lead species involving both retention and inversion process of the C-Sn bond.[9]



(continued)

run	carboxylic acid	M	condition[a]	temp. (°C)	time (h)	product	yield[b] (%)t : c
17		**9** n-Bu$_3$Sn	(A)	0	1.5	β-methyl-styrene	(87)97: 3
18		**10** Me$_2$PhSi	(A)	rt	144		(90)95: 5[c]
19			(B)	rt	2		(93)96: 4
20			(C)	rt	72		(78)93: 7
21		**11** n-Bu$_3$Sn	(A)	0	0.5	β-methyl-styrene	(78)99: 1
22		**12** Me$_2$PhSi	(A)	rt	120		(84)76:24[c]
23			(B)	rt	2		(97)95: 5
24			(C)	rt	48		(58)67:33
25		**13**	(B)	rt	3	2-butene	(74)54:46
26		**14**	(B)	rt	4		(72)54:46

[a] (A); LTA (2.0 eq), Cu(OAc)$_2$·H$_2$O (0.2 eq), pyridine (1.0 eq), CH$_2$Cl$_2$ (0.2 M). (B); LTA (1.2 eq), Cu(OAc)$_2$·H$_2$O (0.02 eq), DMF-AcOH (10:1, 0.4 M). (C); LTA (5.0 eq), NaOAc (2.0 eq), CH$_3$CN (0.2 M). [b] GLPC. Identification was performed by ^{1}H NMR. [c] Conversion; run 6, 62%; run 7, 60%; run 9, 77%; run 18, 69%; run 22, 73%.

References and Notes.

(1) (a) H. Nishiyama, K. Sakuta, N. Osaka, and K. Itoh, Tetrahedron Lett., **1983**, 24, 4021.
(b) H. Nishiyama, K. Sakuta, and K. Itoh, Ibid., **1984**, 25, 223.

(2) (a) H. Nishiyama, H. Arai, T. Ohki, and K. Itoh, J. Am. Chem. Soc., **1985**, 107, 5310.
(b) H. Nishiyama, H. Arai, Y. Kanai, H. Kawashima, and K. Itoh, Tetrahedron Lett., in press.

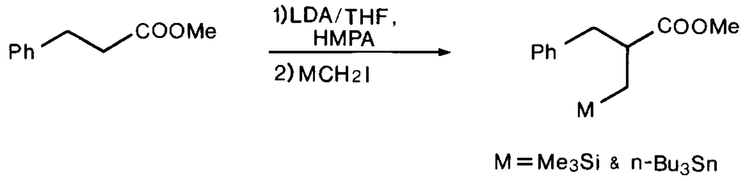
(3) R. A. Sheldon and J. K. Kochi, "Organic Reactions"; John Wiley & Sons, Inc.: New York, 1972; Vol 19, p 279.

(4) J. D. Bacha and J. K. Kochi, J. Org. Chem., **1968**, 33, 83; **1968**, 33, 2746. J. D. Bacha and J. K. Kochi, Tetrahedron, **1968**, 24, 2215.

(5) The hydrolysis was performed by treatment of the corresponding esters with NaOH (3 eq) and n-Bu_4N·Br (a catalytic amount) in MeOH-H_2O at 50°C for 2-24 h. The reaction was monitored by TLC examination. The yields of the acids were 90-96%. Purification was performed by silica gel column chromatography. Structural identification was carried out on the basis of ^{1}H NMR and IR.

(6) For the esters of **10**, **12**, **13**, and **14**, see (a) W. Bernhard, I. Fleming, and D. Waterson, J. Chem. Soc., Chem. Commun., **1984**, 28. For the esters of **9** and **11**, see (b) I. Fleming and C. J. Urch, J. Organomet. Chem., **1985**, 285, 173. The esters of **1**, **2**, **3**, **6**, **7**, and **8** were prepared by using n-Bu_3SnLi, Me_3SiLi, and Me_2PhSiLi with methyl cinnamate, methyl acrylate, and methyl 1-cyclohexenecarboxylate.

(7) The esters of **4** and **5** were prepared from methyl 3-phenylpropionate as follows:
Treatment of methyl 3-phenylpropionate (3.0 mmol) with lithium di-isopropylamide (3.6 mmol) in THF (12 mL) and HMPA (2.0 mL) at -78°C for 30 min and then at -10°C for 10 min. The temperature was again lowered. Iodomethyl(trimethyl)silane (4.5 mmol) was added at -78°C. The mixture was stirred for 1 h, when the temperature was gradually raised to ca. -10°C. Stirring was continued for an additional hour. After usual work up, 2-(trimethylsilylmethyl)-3-phenylpropionate was obtained in 71% yield. By the same manner, 2-(tri-n-butylstannylmethyl)-3-phenylpropionate was obtained in 53% yield with iodomethyl(tri-n-butyl)stannane (4.5 mmol).



(8) S. R. Wilson, P. A. Zucker, C. Kim, and C. A. Villa, Tetrahedron Lett., **1985**, 26, 1969.

(9) (a) H. Nishiyama, M. Matsumoto, T. Matsukura, R. Miura, and K. Itoh, Organometallics, **1985**, 4, 1911. (b) W. R. Baker, J. Org. Chem., **1985**, 50, 3943.

(Received in Japan 23 January 1986)