## Peterson Allenation Using (Z)-(1-Lithio-1-alkenyl)trimethylsilanes

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Abstract: Lithium alkoxides of β-silylallylic alcohols underwent the Peterson elimination in DMF to give allenes. Allenes were also directly obtained by a Peterson allenation reaction from carbonyl compounds using (Z)-(1-lithio-1-alkenyl)trimethylsilanes in one pot.

Key words: alcohols, allenes, carbonyl, elimination, silicon

The Peterson elimination has been widely used for the preparation of alkenes from  $\beta$ -hydroxysilanes.<sup>1</sup> It has been shown that the elimination proceeds readily from the alkoxides of β-hydroxysilanes that have considerable ionic character on the oxygen atom, such as with a sodium or potassium counterion.<sup>2</sup> The alkenes were also obtained in one pot from carbonyl compounds by condensation with  $\alpha$ -silyl carbanions stabilized by an electron-withdrawing group at the anionic carbon; the overall transformation is called the Peterson olefination.

If the Peterson elimination is applied to β-silylallylic alcohols 1, allenes 2 should be obtained. In this regard, several researchers investigated sodium or potassium hydridemediated Peterson elimination of 1 in THF or HMPA solutions (Scheme 1). However, allyl silyl ethers 3 were produced as the sole products via a 1,3 C(sp<sup>2</sup>)-to-O silyl migration in these cases.<sup>3,4</sup> Tius et al. observed the formation of 1-(4-methoxyphenyl)-1,2-nonadiene from the corresponding  $\beta$ -(triethylsilyl)allylic alcohol by treatment with potassium hydride in THF in low yield (10%) with the allyl silvl ether **3** as a predominant product.<sup>5</sup> These results suggest to us that intermediates proposed for the Peterson elimination (cyclic silicates 4, or vinyl anion species 5 generated by the 1,3-silyl migration of 4) may be rapidly protonated with the as yet unreacted alcohol 1, leading to allyl silyl ethers in preference to the elimination product.

We expected that this problem would be circumvented based on the following thesis: after the complete formation of the lithium alkoxides 6, inactive for the Peterson elimination in a low polar solvent due to the covalent character of the Li-O bond,<sup>6</sup> the elimination would be initiated by increase in the solvent polarity by addition of an aprotic polar solvent.7 We have thus studied the

SYNLETT 2006, No. 16, pp 2577-2580 Advanced online publication: 22.09.2006 DOI: 10.1055/s-2006-951474; Art ID: U08206ST © Georg Thieme Verlag Stuttgart · New York





Peterson elimination along this line and here describe the first one-pot Peterson allenation.

The (Z)- $\beta$ -(trimethylsilyl)allylic alcohols 1 were treated with butyllithium (1.2 equiv) in ether at 0  $^{\circ}$ C to form the alkoxides 6, which were then treated with DMF and warmed to 50 °C to produce the allenes 2 in good yields (Scheme 2, Table 1).<sup>8</sup> It is noteworthy that better yields of 2 were obtained when ether rather than THF was used for the preparation of 6 (Table 1, entry 2) and that HMPA was also effective for the elimination (Table 1, entry 3).

1 
$$\xrightarrow{\text{BuLi}}$$
  $R^1$   $\xrightarrow{\text{SiMe}_3}$   $R^2$   $\xrightarrow{\text{DMF}}$  2  
6  $OLi$ 

Scheme 2

The conventional transformation of silvl alcohols 1 into allenes 2 requires a two-step procedure. The alcohols 1 are first transformed into chlorides, acetates, or trifluoroacetates, which are then treated with fluoride ion to give allenes.<sup>5,6,9</sup> Compared with these two-step procedures, our method enjoys an advantage that it does not require an extra transformation.

The present method was successfully extended to a direct transformation of carbonyl compounds 7 to allenes 2 (Z)-(1-lithio-1-alkenyl)trimethylsilanes utilizing 8 (Scheme 3).<sup>10</sup> The halogen–lithium exchange reaction of (1-halo-1-alkenyl)silanes with tert-butyllithium in ether at -78 °C was used to generate the corresponding organolithium species (1.5 equiv) which were allowed to react with ketones or aldehydes 7 to provide the lithium

 Table 1
 Formation of Allenes 2 from (Z)-β-Silylallylic Alcohols 1



<sup>a</sup> Reaction time after addition of DMF.

<sup>b</sup> Treated with BuLi at -78 °C in THF for 1 h.

<sup>c</sup> The silyl ether **3** was also obtained (25%).

<sup>d</sup> HMPA was used as a co-solvent.

alkoxides **6** in situ. DMF was then added to the solutions of **6** at 0 °C and the mixtures were warmed to 50 °C. The various allenes **2** were obtained in good to high yields when using (1-bromo-1-alkenyl)silanes **9**<sup>11</sup> as precursors of **8**<sup>6</sup> (Table 2). Whereas, the similar reaction using the corresponding iodides **10**<sup>12</sup> resulted in the formation of **2** in poor yields.<sup>13</sup> In some cases a higher reaction temperature (80 °C) was required to attain satisfactory yields.

The vinylallenes **2m** and **2n** were produced by reaction of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds **7g** and **7h** with **9b** (Table 2, entries 11 and 12). Since little is known about the preparation of vinylallenes by carbonyl olefination,<sup>14</sup> the present reaction provides a useful method for the synthesis of vinylallenes.



Scheme 3

In conclusion, we have developed the Peterson allenation using (Z)-(1-lithio-1-alkenyl)trimethylsilanes. Its success results from the appropriate choice of the metal cation of the alkoxides and the control of solvent polarity. Further study on the synthetic application of this new carbonyl allenation is currently underway.

## Acknowledgment

This work was carried out under the 21st Century COE program of 'Future Nano-Materials' in Tokyo University of Agriculture & Technology.

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- (10) Typical Procedure for the Allenation of Carbonyl Compounds 7: A solution of 9c (115 mg, 0.45 mmol) in Et<sub>2</sub>O (0.6 mL) was placed in a flask under argon and *t*-BuLi (1.5 M in pentane, 0.35 mL, 0.53 mmol) was added dropwise

Entry	Vinyl bromide <b>9</b>	Carbonyl compound 7	Temp (°C)	Product	Yield (%)
1	SiMe <sub>3</sub> Br	Ph Ph	50	2e	62
2	9a 9a	7a 7a	80	2e	73
3	Ph SiMe <sub>3</sub> Br 9b	7a	80	Ph Ph 2f	88
4	9b	0 <b>≕</b> ← Ph 7b	50	Ph Ph 2g	77
5	SiMe <sub>3</sub> Ph Br 9c	7a	50	Ph Ph Ph	91
6	9c	Ph Me 7c	50	Ph Ph	64
7	SiMe <sub>3</sub> Hex Br	Ph H	50	2a	49
8	9u 9b	Ph H Ph H	80	Ph Ph 2j	74
9	9b	Ph H 7f	80	Ph Ph 2k	64
10	9c	7e	50	Ph Ph Ph	74
11	9b	0=√) 7g	50	Ph 2m	84
12	9b	о 7h	50	Ph 2n	48

 Table 2
 Formation of Allenes 2 by Carbonyl Allenation

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at -78 °C. After stirring for 2 h at -78 °C, a solution of **7a** (72 mg, 0.30 mmol) in Et<sub>2</sub>O (0.3 mL) was added dropwise. The mixture was slowly warmed to 0 °C and DMF (4.2 mL) was added in one portion. The mixture was heated at 50 °C for 2 h, and the reaction was quenched by addition of H<sub>2</sub>O. The usual work-up and purification gave **2h** (89 mg, 91%). IR (neat): 3061, 3027, 2921, 1947, 1601, 1496, 1453, 745, 694 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.35–2.54 (m, 4 H), 2.73–2.88 (m, 4 H), 6.18 (quin, *J* = 3.0 Hz, 1 H), 7.11–7.30 (m, 15 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 33.9, 34.6, 96.5, 107.5, 125.8, 126.48, 126.53, 128.3, 128.40, 128.44, 135.5, 141.9, 202.4; Anal. Calcd for C<sub>25</sub>H<sub>24</sub>: C, 92.54; H, 7.46. Found: C, 92.28; H, 7.59.

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