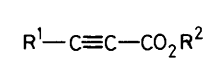
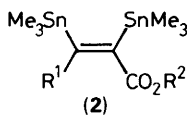
# Concise, Stereoselective Preparation and Synthetic Uses of (*Z*)-4-(Trimethylstannyl)buta-1,3-dienes

**Edward Piers* and Richard D. Tillyer**
*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6*

Two experimentally simple steps [$(Me_3Sn)_2$, $(Ph_3P)_4Pd$; $Ph_3P{=}CH_2$] serve to convert α,β-acetylenic aldehydes and ketones into (*Z*)-4-(trimethylstannyl)buta-1,3-dienes, which are useful intermediates for organic synthesis.

Recently, we reported[1a] that the palladium(0)-catalysed reaction of $(Me_3Sn)_2$ with α,β-acetylenic esters (**1**) provides cleanly and efficiently the corresponding alkyl (*Z*)-2,3-bis-(trimethylstannyl)alk-2-enoates (**2**). The latter compounds are thermally unstable and, upon heating (75—95 °C), undergo smooth isomerisation to the corresponding *E* isomers (**3**).[1a] Subsequently, it was shown[1b] that (**2**) and (**3**) are excellent precursors for the synthesis of functionalised, stereochemically defined tetrasubstituted alkenes.


(**1**)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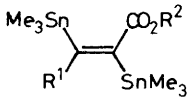
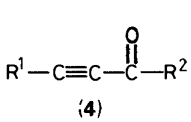
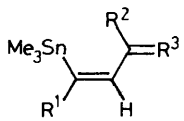
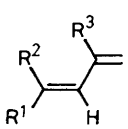

(**3**)


(**4**)


(**5**) $R^3 = O$
(**6**) $R^3 = CH_2$


(**7**)

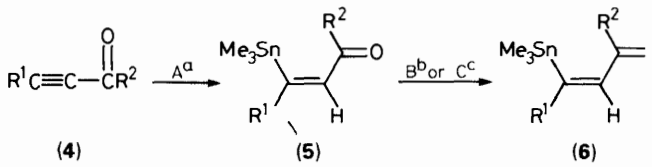
In connection with our continuing interest in the use of novel organotin compounds in organic synthesis, we report here that, unlike substrates (**1**), α,β-acetylenic aldehydes and ketones (**4**) react with $(Me_3Sn)_2$ in the presence of $(Ph_3P)_4Pd$ to afford, *stereoselectively*, products (**5**) that contain only *one* $Me_3Sn$ group. Furthermore, we demonstrate that compounds (**5**) serve as effective synthetic precursors of functionalised, stereochemically homogeneous 1,3-dienes of general structures (**6**) and (**7**).

Reaction [tetrahydrofuran (THF), reflux] of 5-(t-butyldimethylsiloxy)pent-2-ynal (**4a**)†,‡ with $(Me_3Sn)_2$ (1.0 equiv.) in

† The carbonyl compounds (**4**) were prepared by oxidation ($C_5H_5N$–$CrO_3$–HCl, NaOAc, $CH_2Cl_2$) of the corresponding primary or secondary alcohols, which were obtained by reaction of the appropriate lithium acetylide with methanal (**4a**—**c**), ethanal (**4d**—**h**), or heptanal (**4i**).

‡ All compounds reported herein exhibited spectra consistent with structural assignments and new compounds gave satisfactory results in molecular mass determinations (high resolution mass spectrometry).

**Table.** Preparation of the enals and enones (**5**) and the dienes (**6**)



(**4**) (**5**) (**6**)

**a**; $R^1$ = $Bu^tMe_2SiO(CH_2)_2$, $R^2$ = H
**b**; $R^1$ = $Bu^tMe_2SiO(CH_2)_4$, $R^2$ = H
**c**; $R^1$ = $MeOCH_2O(CH_2)_2$, $R^2$ = H
**d**; $R^1$ = $HC{\equiv}C(CH_2)_3$, $R^2$ = Me
**e**; $R^1$ = $Bu^tMe_2SiO(CH_2)_2$, $R^2$ = Me
**f**; $R^1$ = $Bu^tMe_2SiO(CH_2)_4$, $R^2$ = Me
**g**; $R^1$ = $Cl(CH_2)_3$, $R^2$ = Me
**h**; $R^1$ = $Pr^i$, $R^2$ = Me
**i**; $R^1$ = $Bu^t$, $R^2$ = $C_6H_{13}$

| Entry | Starting material | Reaction time (h) | Product, yield (%)[d] | Reaction conditions | Product yield (%)[d] |
|---|---|---|---|---|---|
| 1 | (**4a**) | 2 | (**5a**), 87 | B | (**6a**), 87 |
| 2 | (**4b**) | 2 | (**5b**), 88 | B | (**6b**), 81 |
| 3 | (**4c**) | 4 | (**5c**), 74 | B | (**6c**), 82 |
| 4 | (**4d**) | 4 | (**5d**), 69 | C | (**6d**), 78 |
| 5 | (**4e**) | 2 | (**5e**), 90 | C | (**6e**), 86 |
| 6 | (**4f**) | 2 | (**5f**), 83 | C | (**6f**), 75 |
| 7 | (**4g**) | 3 | (**5g**), 81 | C | (**6g**), 57 |
| 8 | (**4h**) | 5 | (**5h**), 80 | B | (**6h**), 87 |
| 9 | (**4i**) | 24 | (**5i**), 48 | C | (**6i**), 81 |

[a] A: $(Me_3Sn)_2$ (1.0 equiv.), $(Ph_3P)_4Pd$ (0.05 equiv.), THF, reflux. [b] B: $Ph_3P{=}CH_2$ [prepared from $(Ph_3PMe)Br$ and BuLi], THF, room temp. [c] C: $Ph_3P{=}CH_2$ [prepared from $(Ph_3PMe)Br$ and t-PentylONa], PhH, room temp. [d] Yield of purified, distilled product.

the presence of $(Ph_3P)_4Pd$ (0.05 equiv.) gave, after chromatography of the crude product on silica gel, the corresponding (*Z*)-3-(trimethylstannyl)pent-2-enal (**5a**) in 87% yield. In similar fashion, the α,β-acetylenic aldehydes (**4b,c**) and ketones (**4d—i**) were converted, highly regio- and stereo-selectively, into the (*Z*)-β-(trimethylstannyl)-α,β-unsaturated carbonyl compounds (**5b—i**), respectively (see Table).

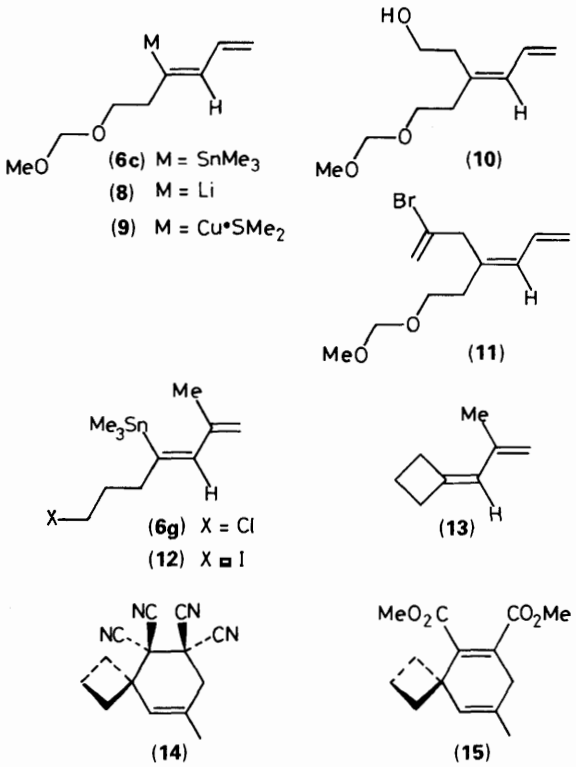
Significantly, the reaction is successful in the presence of a number of different functional groups (Table, entries 1, 3, 4, 7). Furthermore, in most cases, the transformations are clean and efficient and are complete within a reasonable length of time. However, when $R^1$ in the substrate (**4**) is bulky (*e.g.* $Bu^t$, entry 9), the reaction is sluggish and the yield, even after a reaction time of 24 h, is mediocre. Clearly, steric hindrance at the β carbon of the α,β-acetylenic carbonyl compound has a deleterious effect on the rate and efficiency of the process.

In the $^1H$ n.m.r. spectra of the products (**5**), the $^3J_{Sn,H}$ values associated with coupling between the olefinic proton and the $^{117}Sn$ and $^{119}Sn$ isotopes are in the range 113—130 Hz. These coupling constants are typical of alkenes having a proton and a $Me_3Sn$ group in a *trans* relationship[2] and, therefore, the stereochemistry of each of the compounds (**5a—i**) was easily ascertained.

Treatment of the carbonyl compounds (**5**) with $Ph_3P{=}CH_2$ provided the corresponding 4-(trimethylstannyl)buta-1,3-dienes (**6**) (see Table). In each case, the product was conveniently purified by flash chromatography and distillation.

The reactions summarized in the Table show that the readily prepared α,β-acetylenic carbonyl compounds (**4**) can be converted stereoselectively and efficiently into dienes of general structure (**6**). The latter have appreciable potential as versatile intermediates in organic synthesis. For example, transmetalation (MeLi, THF, −78 °C) of (**6c**), followed by reaction (−78 °C to room temperature) of the resultant lithio diene (**8**) with ethylene oxide, resulted in the stereoselective formation of the 1,1-disubstituted buta-1,3-diene (**10**) (77%). On the other hand, treatment (THF, −48 °C) of (**8**) with CuBr·$Me_2S$ (1 equiv.) provided reagent (**9**), which readily coupled (−48 °C) with 2,3-dibromopropene to give the triene (**11**) (69%).

The efficacy of compounds (**6**) in organic synthesis is demonstrated further by the following transformations. Reaction of (**6g**) with NaI in refluxing acetone provided the iodide (**12**) (86%), which, upon treatment with MeLi (THF, −78 °C, 10 min; −48 °C, 20 min) gave, cleanly and efficiently, the novel, volatile diene (**13**). Diels–Alder reactions of (**13**) with tetracyanoethylene and dimethyl acetylenedicarboxylate produced the spiro alkene (**14**) (69%, m.p. 166—167 °C) and the spiro diene (**15**) (70%, m.p. 55—56 °C), respectively.



(**6c**) M = $SnMe_3$
(**8**) M = Li
(**9**) M = $Cu{\bullet}SMe_2$
(**10**)
(**11**)
(**6g**) X = Cl
(**12**) X = I
(**13**)
(**14**)
(**15**)

In summary, the work described above demonstrates that (*Z*)-4-(trimethylstannyl)buta-1,3-dienes of general structure (**6**) are readily prepared from α,β-acetylenic carbonyl compounds, are excellent synthetic precursors for the preparation of substituted, stereochemically defined buta-1,3-dienes, and can be employed to prepare structurally novel, strained-ring systems such as (**13**). Many extensions to this work are possible.

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## References

1 (*a*) E. Piers and R. T. Skerlj, *J. Chem. Soc., Chem. Commun.*, 1986, 626; (*b*) *J. Org. Chem.*, 1987, **52**, 4421.
2 A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, 1967, **9**, 285.

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