Convenient Synthesis of Alkyl (*Z*)- and (*E*)-2,3-Bis(trimethylstannyl)alk-2-enoates and *N,N*-Dimethyl (*E*)-2,3-Bis(trimethylstannyl)alk-2-enamides

Edward Piers* and Renato T. Skerlj

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Palladium(0)-catalysed addition of $(Me_3Sn)_2$ to the α,β-acetylenic esters (**1a—n**) and amides (**4a—d**) provides the (*Z*)-2,3-bis(trimethylstannyl)alk-2-enoates (**2a—n**) and the (*E*)-2,3,-bis(trimethylstannyl)alk-2-enamides (**6a—d**), respectively; thermolysis of (**2a—h**) transforms these substances into the corresponding (*E*)-isomers (**3a—h**).

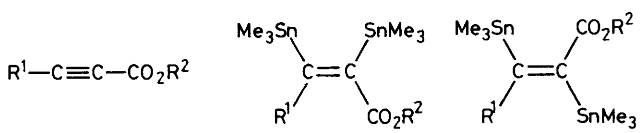
In connection with our interest in the preparation and chemistry of alkyl 2,3-bis(trimethylstannyl)alk-2-enoates[1] and related substances, we report herein (i) that $(Ph_3P)_4Pd$-catalysed addition of $(Me_3Sn)_2$ to α,β-acetylenic esters (**1**) provides smoothly and efficiently alkyl (*Z*)-2,3-bis(trimethylstannyl)alk-2-enoates (**2**), (ii) that the latter compounds are thermally unstable and, upon warming to 75—95 °C, rearrange cleanly to the corresponding (*E*)-isomers (**3**), (iii) that similar results are obtained using *N,N*-dimethyl α,β-acetylenic amides (**4**) as substrates, although in these cases the (*Z*)-addition products (**5**) rearrange [to (**6**)] under the conditions necessary to effect the initial addition, and (iv) transmetallation of certain addition products containing ω-halogeno substituents [*e.g.* (**2k—m**), (**3i**), (**6d**)] affords cyclic compounds [*e.g.* (**7**)—(**10**)].

When a solution of ethyl but-2-ynoate (**1a**), $(Me_3Sn)_2$ (1 equiv.), and $(Ph_3P)_4Pd$ (0.01 equiv.) in dry tetrahydrofuran (THF) was stirred at room temperature for 24 h,[2] ethyl (*Z*)-2,3-bis(trimethylstannyl)but-2-enoate (**2a**)† was produced in 82% yield. Similarly, addition of $(Me_3Sn)_2$ to the acetylenic esters (**1b—n**)‡ provided the bis(trimethylstannyl) products (**2b—n**), respectively. Since, in many cases, the room temperature reactions were quite sluggish, most of the additions were performed in refluxing THF (reaction times 4—6 h). In general, the reactions were clean and efficient (yields 66—90%).

Interestingly, the (*Z*)-2,3-bis(trimethylstannyl)alk-2-enoates (**2**) are thermally unstable. For example, when substances (**2a—h**) were warmed (neat) to 75—95 °C for 6—48 h, the corresponding (*E*)-isomers (**3a—h**) were obtained in high yields (81—98%). Thus, both alkyl (*Z*)- and (*E*)-2,3-bis(trimethylstannyl)alk-2-enoates are readily available *via* experimentally straightforward reactions.

Evidence for the stereochemistry of compounds (**2**) and (**3**) could be derived from ^1H n.m.r. nuclear Overhauser enhancement (n.O.e.) difference experiments. For example, irradiation at δ 3.70 (CO_2Me signal) in the ^1H n.m.r. spectrum of (**3i**) caused enhancement of both signals (δ 0.17, 0.26) due to the Me_3Sn groups, while a similar experiment with (**2i**) resulted in enhancement of only one of the Me_3Sn singlets.

Palladium(0)-catalysed additions of $(Me_3Sn)_2$ to the α,β-acetylenic amides (**4**)‡ are considerably slower and generally less efficient than the corresponding reactions involving the esters (**1**). Furthermore, the initially formed (*Z*)-products (**5**) are notably less stable than the (*Z*)-esters (**2**). Thus, reaction of (**4a**) with $(Me_3Sn)_2$–$(Ph_3P)_4Pd$ in THF at room temperature

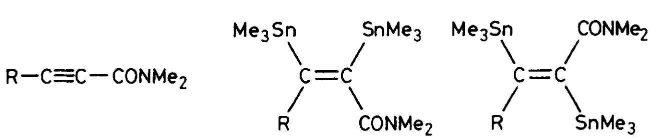


(**1a-n**) (**2a-n**) (**3a-h**)

a; $R^1 = Me$
b; $R^1 = Pr^i$
c; R^1 = cyclopropyl
d; R^1 = cyclohex-3-enylmethyl
e; R^1 = 2-cyclopent-2-enylethyl
f; $R^1 = Bu^tMe_2SiOCH_2$
g; $R^1 = Bu^tMe_2SiO[CH_2]_4$
h; $R^1 = THP{\cdot}O[CH_2]_3$
i; $R^1 = Cl[CH_2]_3$
j; $R^1 = Cl[CH_2]_2$
k; $R^1 = Br[CH_2]_5$
l; $R^1 = Br[CH_2]_4$
m; $R^1 = Br[CH_2]_3$
n; $R^1 = Br[CH_2]_2$

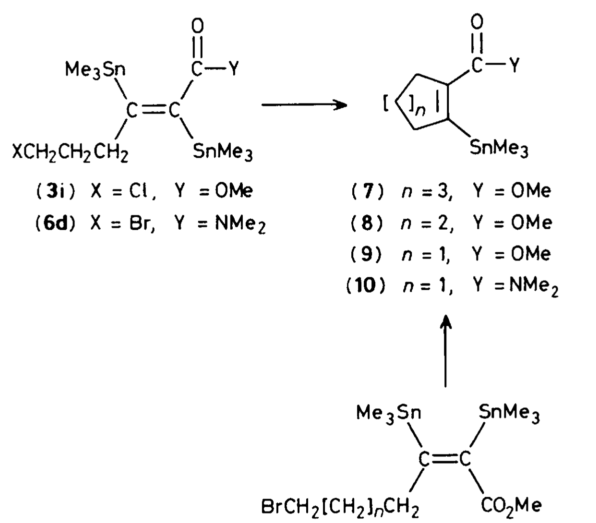
R^2 = Et for **a**, **f**, **j**, and **n**
R^2 = Me for **b—e**, **g—i**, and **k—m**

THP = tetrahydropyran-2-yl



(**4a-d**) (**5a-d**) (**6a-d**)

a; R = Me
b; R = Et
c; $R = Bu^tMe_2SiO[CH_2]_3$
d; $R = Br[CH_2]_3$



(**3i**) X = Cl, Y = OMe
(**6d**) X = Br, Y = NMe_2

(**7**) *n* = 3, Y = OMe
(**8**) *n* = 2, Y = OMe
(**9**) *n* = 1, Y = OMe
(**10**) *n* = 1, Y = NMe_2

(**2k**) *n* = 3
(**2l**) *n* = 2
(**2m**) *n* = 1

† All compounds reported herein exhibit spectra consistent with assigned structures. New compounds gave satisfactory molecular mass determinations (high-resolution mass spectrometry).

‡ The α,β-acetylenic esters (**1**) and amides (**4**) were readily prepared by reaction of appropriate lithium acetylides with an alkyl chloroformate or *N,N*-dimethylcarbamoyl chloride, followed by any necessary functional group interconversions.

(48 h) gave, in 66% yield, a 4:1 mixture of the geometric isomers (**5a**) and (**6a**).§ Similar reactions involving substrates (**4b**) (room temperature, 72 h), (**4c**) (reflux, 48 h), and (**4d**) (reflux, 26 h) provided, directly, only the (*E*)-products (**6b—d**) (48, 63, and 75%, respectively).

Compounds (**2**), (**3**), and (or) (**6**), in which the R group is an appropriate ω-halogeno-alkyl group, can serve as convenient synthetic precursors of 2-trimethylstannylcycloalk-1-enecarboxylic acid derivatives. For example, treatment of (**3i**) with 1.2 equiv. of MeLi in THF–hexamethylphosphoramide (2 equiv.) at −98 °C, followed by continued stirring for 20 minutes, afforded compound (**9**) (69%). The latter substance could also be obtained (71% yield) by transmetallation–cyclisation of (**2m**), thus showing that the configuration of the substrate is of no consequence in the cyclisation process.¶ In similar fashion, substrates (**2k**), (**2l**), and (**6d**) were transformed into the cyclic compounds (**7**), (**8**), and (**10**), respectively.

We gratefully acknowledge Merck Frosst Canada, Inc., Merck and Co., Inc., and the Natural Sciences and Engineering Research Council of Canada for financial support.

Received, 6th January 1986; Com. 028

§ Compounds (**5a**) and (**6a**) could be separated readily by column chromatography. Interestingly, (**5a**) isomerised (slowly) to (**6a**) even when stored (neat) at 0 °C. When a solution of (**5a**) in THF was heated at reflux for 1—2 h, (**6a**) was produced nearly quantitatively.

¶ Presumably, selective transmetallation of the α-trimethylstannyl group in (**3i**) or (**2m**) leads, in each case, to an allenoate anion intermediate, which then undergoes ring closure.

References

1 E. Piers and J. M. Chong, *J. Org. Chem.*, 1982, **47**, 1602.

2 *Cf.* T. N. Mitchell, A. Amamria, H. Killing, and D. Rutschow, *J. Organomet. Chem.*, 1983, **241**, C45.