Regio- and stereo-specific addition of chlorodibutyltin hydride to prop-2-ynylic ethers

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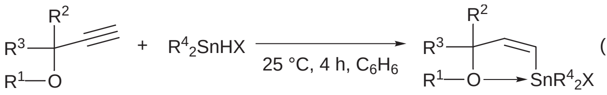
A number of prop-2-ynylic ethers smoothly undergo regio- and stereo-specific hydrostannation with chlorodibutyltin hydride in good to nearly quantitative yield at room temperature in benzene.

The importance of vinyltins in cross-couplings of the Stille–Migita type[1] has recently led to efforts to find new approaches to their preparation. A very useful approach has recently been designed by Yamamoto and co-workers,[2] who used zirconium and hafnium tetrachlorides as Lewis acid catalysts in the hydrostannation of alkynes; a refinement of this procedure[3] involves the *in situ* preparation of the tin hydride from the corresponding chloride and triethylsilane. In all cases reported, the procedure gave single isomers derived from *trans* attack of the tin hydride.

The disadvantage of this methodology is that the Lewis acid centre is blocked when the alkyne contains substituents bearing a lone pair; thus we have found that prop-2-ynylic ethers or amines, which are synthetically much more important than simple alkynes, do not react satisfactorily.

In an attempt to circumvent this problem we had recourse to the long-known but relatively little used chlorodibutyltin hydride,[4] which is readily prepared by mixing the dihydride[5] and dichloride. A hint of the potential of this reagent had been provided relatively recently by Davies,[6] who observed a rapid hydrostannation of a prop-2-ynylic alcohol (2-methylprop-3-yn-2-ol, 2 h at room temperature in toluene), though with the formation of a Z/E isomer mixture. An exothermic reaction occurs when the hydride chloride is mixed with prop-2-ynylic ethers [reaction (1)], but when the two reagents are mixed slowly at room temperature and stirred for 4 h in benzene the hydrostannation occurs in yields which are good to virtually quantitative (63–99%), only one single isomer being detected.



(1)

This is in clear contrast to the behaviour of tributyltin hydride, which gives product mixtures containing predominantly either the *E*- or the *Z*-isomer (depending on the amount of tin hydride used) when allowed to react under free radical conditions with unsubstituted prop-2-ynylic alcohols and ethers;[7] in contrast, a clean reaction does occur (*via* regiospecific *trans* addition) with substituted prop-2-ynylic residues attached to either oxygen[8] or nitrogen,[9] though yields are variable. Table 1 gives details of the ethers used in this work and the respective yields. The reactions are carried out as follows: the dialkyltin dihydride[5] (2.5 mmol) is added at 0 °C during 10 min to the dichloride (2.5 mmol) with constant stirring. The mixture is stirred for 0.5 h at room temperature and a solution of the prop-2-ynyl ether[10] (5 mmol) in benzene (5 ml) is added during 10 min with stirring. The reaction mixture is stirred for 4 h at room temperature, the volatiles removed at the oil pump, and the colourless oil (which solidifies on storing at 5 °C) obtained is characterised by multinuclear NMR spectroscopy.

Table 1 Addition of halodialkyltin hydrides to prop-2-ynyl ethers

	Prop-2-ynyl ether			Halodialkyltin hydride		
	R^1	R^2	R^3	R^4	X	Yield (%)[a]
1a	Allyl	Pr	H	Bu	Cl	93
1b	2-Methylallyl	H	H	Bu	Cl	71
1c	Cyclohex-2-enyl	H	H	Bu	Cl	>91
1d	But-2-enyl	H	H	Bu	Cl	63
1e	Et	Me	Me	Bu	Cl	>98
1f	2-Furyl	H	H	Bu	Br	97
1g	2-Methylallyl	H	H	Bu	Br	>98
1h	2-Furyl	H	H	Et	Cl	>98
1i	2-Furyl	H	H	Me	Cl	>98
1j	Et	Me	Me	Me	Cl	97

[a] From integration of ^1H NMR spectra.

The ^1H NMR spectra confirm that the reaction has occurred in a *trans* manner with attack of the tin at the terminal carbon [$^3J(H,H) = 12–13$ Hz]. In a control experiment with hex-1-yne a mixture of E ($^3J = 18$ Hz) and Z ($^3J = 12.5$ Hz) isomers is observed, clearly demonstrating that the ether oxygen determines the reaction course. The tin resonance occurs at relatively high field [1 to 13 ppm compared with 56 (E) and 67 ppm (Z) in the isomers derived from hex-1-yne], suggesting intramolecular coordination between oxygen and tin in the product. This is confirmed by the carbon-13 data: one-bond tin–carbon coupling constants are of a magnitude expected for pentacoordination at tin (540–664 Hz). Analogous results are obtained using other compounds R_2SnHX (R = Me, Et; X = Cl, Br). Treatment of the vinyltins (**1**) with Grignard reagents lead to the corresponding trialkyltin species: thus, for example, treatment of (**1f**) with EtMgBr leads to a product showing the expected NMR spectroscopic data [$\delta(^{119}Sn)$ -40.5 ppm, vinyl $^1H–^1H$ coupling constant 10.4 Hz].

Notes and References

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1 T. N. Mitchell, in *Metal-catalysed Cross-coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, Berlin, New York, Chichester, Brisbane, Singapore, Toronto, 1998, p. 167.

2 N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4568; N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1995, 2405.

3 V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *Chem. Commun.*, 1998, 37.

4 W. P. Neumann and J. Pedain, *Tetrahedron Lett.*, 1964, 2461; A. K. Sawyer and J. E. Brown, *J. Organomet. Chem.*, 1966, **5**, 438; A. K. Sawyer, J. E. Brown and G. S. May, *J. Organomet. Chem.*, 1968, **11**, 192.

5 G. J. M. Van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, 1957, **7**, 366.

6 A. G. Davies, W. J. Kinart and D. K. Ossei-Kissi, *J. Organomet. Chem.*, 1994, **474**, C11.

7 M. E. Jung and L. A. Light, *Tetrahedron Lett.*, 1982, **23**, 3851.
8 M. Lautens and A. H. Huboux, *Tetrahedron Lett.*, 1990, **31**, 3105; T. Konoike and Y. Araki, *Tetrahedron Lett.*, 1992, **33**, 5093.
9 J. L. Anderson and C. A. Roberts, *Tetrahedron Lett.*, 1998, **39**, 159.
10 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 2nd edn., 1988.

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