Pergamon

Tetrahedron Letters 39 (1998) 6419–6420

TETRAHEDRON
LETTERS

Improved Cr(II)-mediated synthesis of *E*-alkenylstannanes from aldehydes using Bu_3SnCHI_2 in DMF

David M. Hodgson,*[a] Anne M. Foley[a] and Peter J. Lovell[b]

[a] Dyson Perrins Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QY, UK
[b] SmithKline Beecham Pharmaceuticals, New Frontiers Science Park, Third Avenue, Harlow, Essex, CM19 5AW, UK

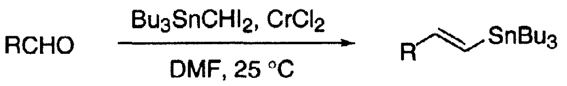
Received 21 May 1998; accepted 23 June 1998

Abstract

An improved chromium(II)-mediated synthesis of *E*-alkenylstannanes from aldehydes using Bu_3SnCHI_2 in DMF is described.

Keywords: Alkenes; Alkenylation; Chromium and compounds; Tin and compounds

Alkenylstannanes are finding increasing application in organic synthesis [1]. We recently developed mild, chemoselective chromium(II)-based chemistry for preparing *E*-alkenylstannanes in one step from aldehydes using $Bu_3SnCHBr_2$ in THF with LiI and DMF as additives [2]. Although this method has found utility in synthesis [3], it suffers from the fact that the stannanes are produced in *ca.* 60% yield along with substantial quantities of the simple methylenated aldehydes. Here we communicate our results concerning an improved procedure (eq. 1).



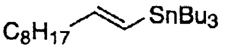
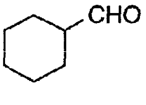
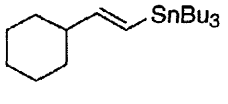
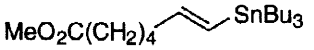
(1)

As stated previously [2*a*], our initial studies with benzaldehyde originally led to the adoption of $CrCl_2/Bu_3SnCHBr_2$ in THF with LiI and DMF as additives as the preferred method for aldehyde homologation since this led exclusively to the *E*-alkenylstannane, whereas $CrCl_2/Bu_3SnCHBr_2$ in DMF was less stereoselective (*E* : *Z* = 87 : 13, by ^1H NMR); however, styrene was only observed as a byproduct in the former reaction. We now find that reaction of nonanal (as a representative aliphatic aldehyde) with $CrCl_2/Bu_3SnCHBr_2$ in DMF (25 °C, 2.5 h) gives *only* *E*-alkenylstannane (78%) [4]; addition of LiI did not lead to an improvement in yield (75%), however further improvement (85-89%, two runs) was observed using Bu_3SnCHI_2 [5] in DMF. Bu_3SnCHI_2 in THF or THF with DMF as an additive was less effective. Compared with our previous results [2*a*], the use of Bu_3SnCHI_2 in DMF resulted in shorter reaction times and gave significantly improved yields of *E*-

PII: S0040-4039(98)01325-2

alkenylstannanes for a selection of aldehydes (Table 1). Cyclododecanone was recovered unchanged (96%) under the new conditions [6]. This modified method should be particularly useful with synthetically valuable aldehydes in complex molecule synthesis.

Table 1. Improved preparation of *E*-alkenylstannanes from aldehydes.

Entry	Aldehyde	Alkenylstannane	Yield, %
1.	$C_8H_{17}CHO$		85-89
2.			80
3.	$MeO_2C(CH_2)_4CHO$		82

The following procedure is representative: dry, deoxygenated DMF (7ml) was added dropwise to well-stirred $CrCl_2$ (0.527 g, Aldrich 99.9% w/w pure, 4.3 mmol) in a flask under argon in an ice-bath. After allowing the flask to warm to room temperature over 15 min it was surrounded by aluminium foil to exclude light and then a mixture of nonanal (61 mg, 0.43 mmol) and Bu_3SnCHI_2 (478 mg, 0.86 mmol) in dry, deoxygenated DMF (2 ml) was added dropwise to the reaction mixture. After 2.5 h at 25 °C water (14 ml) was added and the mixture extracted with ether (3 x 10 ml). The combined organic layers were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification by reversed-phase column chromatography (30% CH_2Cl_2/MeCN) gave a colourless oil, (*E*)-tributyl(1-decenyl)stannane (157 mg, 85%) [2*a*].

Acknowledgements

We thank SmithKline Beecham Pharmaceuticals and the EPSRC for an Industrial CASE award (to A. M. F.), Zeneca (Strategic Research Fund) and Pfizer for additional financial support, and the EPSRC Mass Spectrometry Service Centre for mass spectra.

References

[1] Davies AG. Organotin chemistry. Weinheim: VCH, 1997; Mitchell TN. Organotin reagents in cross-coupling. In: Diederich F, Stang PJ, editors. Metal-catalyzed cross-coupling reactions. Chichester: Wiley-VCH, 1997:167-202; Farina V, Krishnamurthy V, Scott WJ. Org. React. 1997;50:1-652.

[2] (*a*) Hodgson DM, Boulton LT, Maw GN. Tetrahedron 1995;51:3713-3724; (*b*) Recent reviews: Hodgson DM, Boulton LT. Chromium- and titanium-mediated synthesis of alkenes from carbonyl compounds. In: Williams JMJ, editor. Preparation of alkenes: a practical approach. Oxford: OUP, 1996:81-93; Hodgson DM, Comina PJ. Chromium-mediated C-C coupling reactions. In: Beller M, Bolm C, editors. Transition metals for organic synthesis. Chichester: Wiley-VCH, 1998:418-424.

[3] Hodgson DM, Boulton LT, Maw GN. Synlett 1995:267-268; Boyce RJ, Pattenden G. Tetrahedron Lett. 1996;37:3501-3504; Smith III AB, Ott GR. J. Am. Chem. Soc. 1998;120:3935-3948.

[4] Chong JM, Park SB. J. Org. Chem. 1993;58:523-527.

[5] Bu_3SnCHI_2 was obtained from $Bu_3SnCHBr_2$ (ref. 2*a*) [NaI, acetone, 25 °C, 24 h (quant.)] and used without further purification.

[6] The present observations together with our earlier studies are consistent with the methylenated material observed in THF with DMF as an additive arising from competitive formation of $CH_2(CrHal_2)_2$ which would be anticipated to be a selective reagent for aldehydes, but also able to react with ketones [cyclododecanone/CH_2I_2/$CrCl_2$/DMF in THF gives methylenecyclododecane (59%, 85% based on recovered ketone), see also ref. 7], unlike $Bu_3SnCH(CrHal_2)_2$ or $Me_3SiCH(CrHal_2)_2$ (ref. 8); this would explain why cyclododecanone is methylenated using $Bu_3SnCHBr_2$ in THF with DMF as an additive (ref. 2*a*) to approximately the same level (45%, 73% based on recovered ketone) as an aldehyde but with no alkenylstannane observed; it is possible that some $CH_2(CrHal_2)_2$ *is* also formed from $Bu_3SnCHHal_2$ in DMF but has too short a lifetime in this solvent to react with a carbonyl compound (cyclododecanone/CH_2I_2/$CrCl_2$ in DMF gives recovered ketone (quant.), see also ref. 7).

[7] Okazoe T, Takai K, Utimoto K. J. Am. Chem. Soc. 1987;109:951-953.

[8] Takai K, Kataoka Y, Okazoe T, Utimoto K. Tetrahedron Lett. 1987;28:1443-1446.