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The Solvent Promoted Addition of Tetraallyltin to Aldehydes: A Convenient and Chemoselective Allylation Procedure.

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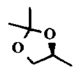
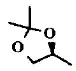
Abstract: Aldehydes **2a - e** react with tetraallyltin (**1**,0.25 equiv.) in methanol or other polar solvent at room temperature (*ca* 30°C, <20 h) to provide the corresponding homoallyl alcohols **3a - e** in 69 - 98% yield. No additional catalysis is required.

The allylation of carbonyl compounds to yield homoallyl alcohols can be achieved with many allylic metal species and is a very useful transformation in organic synthesis.[1] Allylic stannanes have received considerable attention in this respect and addition to aldehydes has been achieved by employing heat, high pressure or Lewis acid promotion. More recently, the chemoselective allylation of carbonyl compounds with tetraallyltin in acidic aqueous media has been reported.[2] This reaction involved the use of 1.0 equiv. of HCl (relative to the tetraallyltin) in aqueous THF and resulted in the transfer of all four allyl groups with a high chemoselectivity towards aldehydes. We now report that this same outcome can be achieved in methanol and some other solvents without the need for acid catalysis, providing an extremely mild and convenient allylation procedure.

The reaction of tetraallyltin (**1**, 0.25 equiv.) with aldehydes **2** in methanol at room temperature (*ca* 30°C) provided the homoallyl alcohols **3** (eq 1) in good yields (Table 1).[3] Reactions required approximately 4 to 20 h to reach completion, depending upon the aldehyde. The product could be isolated either by aqueous workup or by evaporating the solvent and washing the resulting slurry of **3** and tin salts with dichloromethane followed by kugel rohr distillation or filtration through silica gel. This simple workup is in marked contrast to the tedious separation of product from organotin residues often associated with the use of allyltrialkylstannanes.

Table 1 Allylation of Aldehydes **2** with Tetraallytin **1** in Different Solvents.[a]

Entry	carbonyl compound	R	solvent	product	**3** Yield (%)[b]
1	**2a**	i C_3H_7	CH_3OH	**3a**	69
2	**2a**	i C_3H_7	CH_2Cl_2	**3a**	(5)
3	**2b**	c C_6H_{11}	CH_3OH	**3b**	84
4	**2c**	Ph	CH_3OH	**3c**	81
5	**2c**	Ph	$HCONH_2$	**3c**	84
6	**2d**	$PhCH_2$	CH_3OH	**3d**	98
7	**2d**	$PhCH_2$	Me_2SO	**3d**	70[c]
8	**2e**		CH_3OH	**3e**	95
9	**2e**		CH_2Cl_2	**3e**	98

[a]Reactions conducted for *ca* 20 h unless otherwise stated. [b] Isolated yields (unoptimised), the value in parenthesis is a percentage yield determined by ^1H NMR spectroscopy. [c]After 63h at approximately 30°C.

Selected reactions were performed in CD_3OD and monitored by ^1H NMR spectroscopy (eg Figure 1). No intermediate allyl tin species $(allyl)_{4-n}Sn(OR)_n$ (n = 1 - 3) were observed in this study, indicating that transfer of the first allyl group is slower than subsequent transfers. This result is not surprising as each substitution of alkoxide for an allyl group on tin would be expected to yield a more reactive allylating species.[4] Interestingly, the consumption of **1** accelerates during the course of the reaction, presumably due to Lewis acid catalysis provided by the tin (IV) methoxide generated *in situ*. This spectroscopic study also revealed that the aliphatic aldehydes **2a** and **2b** exist primarily as the corresponding hemiacetals in methanol[5] (at 0.8M, 24.0°C) and that in the latter stage of the reaction only hemiacetal is observed, indicating that the hemiacetal to aldehyde interconversion becomes rate determining.

Allylation also occurred in formamide (entry 5) and dimethylsulfoxide (entry 7) although the latter required almost 3 days for complete reaction. The corresponding reactions in dichloromethane were substantially slower (entry 2). Only reactive aldehyde **2e** underwent complete allylation in this solvent and yielded the Cram (*erythro,* d.e. = 70%) addition product[6] predominantly in either dichloromethane (entry 9) or methanol (entry 8). Ketones such as cyclohexanone reacted very slowly with **1** in methanol or formamide under these conditions (<5%, 24 h) and a competitive experiment involving **2b** (1 equiv.) and cyclohexanone (1 equiv.) with **1** (0.25 equiv.) in formamide (36 h) yielded **3b** exclusively. Allyltrimethylstannane also reacted with aldehydes in methanol, but at a much reduced rate relative to **1**. The allylation of benzaldehyde, for example, was 42% complete after 110 h at 30 °C.

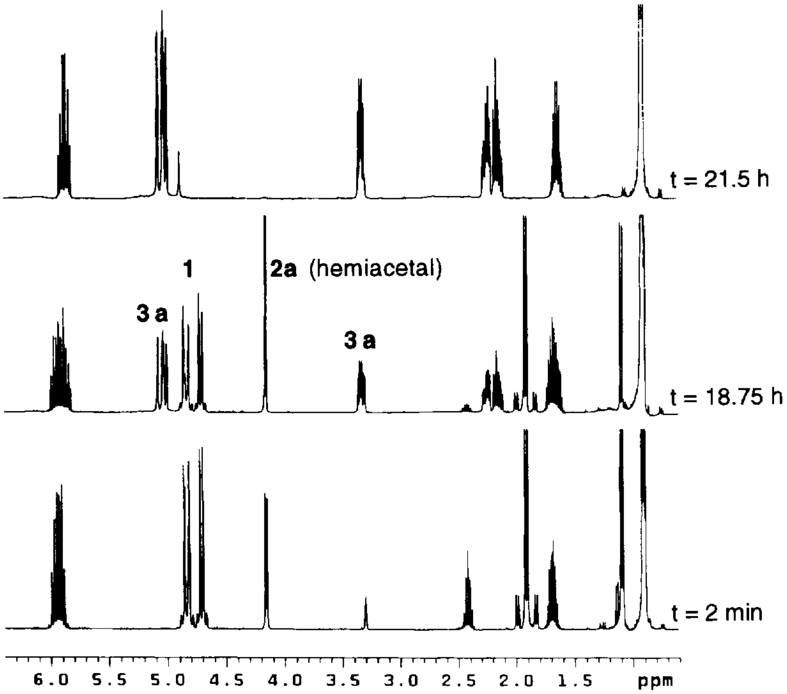


Figure 1 400 MHz ^{1}H NMR spectra acquired during reaction of **2a** (0.8 M) with **1** (0.2 M) in CD_3OD at 24°C.

The allylic isomerisation of allylic, propargylic and indenyl stannanes in methanol and other polar solvents is well documented and has been attributed to the reversible formation of solvent stabilized, ion pair intermediates.[7] The existance of such intermediates could explain this unusual reactivity of allylic stannanes towards aldehydes in polar solvents. From a synthetic perspective, however, it is clear that the use of **1** in methanol or other polar solvents provides an extremely mild, clean and convenient procedure for the chemoselective allylation of aldehydes.

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References and Notes

1. For a review, see: Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.

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3. General experimental procedure: aldehydes (**2**, 10 mmol) and tetraallyltin (**1**, 2.5 mmol) were dissolved in methanol (10 ml) and stirred at room temperature (*ca* 30°C) for 20 h. Water (25 mL) was then added and the resulting white precipitate allowed to settle. The solvent was decanted and the solid washed with dichloromethane. The aqueous methanol was then extracted with dichloromethane (3 x 25 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* . The crude product (**3**) was purified by kugel rohr distillation or filtration through a short bed of silica gel (dichloromethane).

4. For an example of the increased reactivity resulting from substitution of an electron withdrawing group on tin, see: Gambaro, A.; Ganis, P.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1982**, *231*, 307.

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