Regioselective Addition of Trimethylstannylcopper–Dimethyl Sulphide to 1-Alkynes: Synthesis of ω-Substituted 2-(Trimethylstannyl)-1-alkenes

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Treatment of ω-substituted 1-alkynes (**2**) with 2 equiv. of trimethylstannylcopper–dimethyl sulphide (**1**) in tetrahydrofuran (−63 °C) in the presence of 60 equiv. of methanol affords good to excellent yields of the corresponding 2-(trimethylstannyl)-1-alkenes (**3**).

In connection with a research programme[1] aimed at the preparation and use of conjunctive reagents containing both a donor (d)[2] and an acceptor (a)[2] carbon centre, we report herein that, under appropriate conditions, the trimethylstannylcopper reagent (**1**)[3] adds regioselectively to ω-substituted 1-alkynes (**2**) (X = leaving group or potential leaving group) to provide, efficiently, the corresponding 2-(trimethylstannyl)-1-alkenes (**3**).[4] Since transmetallation (RLi) of trialkylvinylstannanes to form vinyl-lithium reagents is a well known transformation and normally occurs readily under mild conditions, the products (**3**) potentially represent convenient precursors of reagents which are formally equivalent to the d,a-synthons (**4**).

When 8-tetrahydropyran-2-yloxyoct-1-yne (**2a**)† was allowed to react with 2 equiv. of reagent (**1**) under the conditions indicated in equation (1) the isolated product mixture (90%) consisted mainly of the starting material (**2a**) and the trimethylstannyl alkene (**3a**) in a ratio of about 3 : 7. Greater amounts of starting material were recovered when shorter reaction times were used, while longer times failed to decrease the ratio of (**2a**) : (**3a**) in the isolated material. Similar results were obtained with other terminal alkynes. In each case, under the reaction conditions indicated in equation (1), the reaction failed to go to completion and the isolated yield of the product was 60% or less. These results indicated that the reactions of substrates (**2**) with the reagent (**1**) are quite slow, that the processes are reversible,‡ and that the equilibrium favours only marginally the intermediate vinylcopper species [see (**5**), equation (2)].

It is known[3,5,6] that trialkylstannylcopper reagents are very weak bases and react only slowly, if at all, with weakly acidic proton donors. On the other hand, vinylcopper species obtained from the addition of reagents such as (**1**) to α,β-acetylenic esters are readily protonated by methanol.[3] Therefore, in the hope of shifting the equilibrium (2) to the right by protonation of the intermediate (**5**), we carried out the reaction of substrates (**2**) with (**1**) in the presence of methanol. Eventually, it was found that a suitable procedure for effecting the efficient conversion of (**2**) into (**3**) involved treatment of the former substances with 2 equiv. of reagent (**1**) (tetrahydrofuran, −63 °C, 12 h) in the presence of 60 equiv. of methanol. Under these conditions, consistently high yields of addition products were formed in most cases (see Table 1).[7]

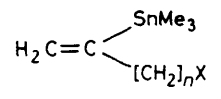
Although the data given in Table 1 are largely self-explanatory, two comments should be made regarding the conversions summarized in entries 9—11. Firstly, the relatively low yields of compounds (**3i**—**k**) were due to the fact that these substances were accompanied by significant amounts (*ca.* 25—30%) of the regioisomeric products (**6**)—(**8**), respectively.§

$Me_3SnCu\cdot Me_2S$

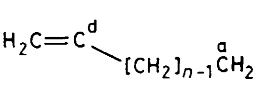
(**1**)

$H{-}C{\equiv}C{-}[CH_2]_n{-}X$

(**2**)



(**3**)

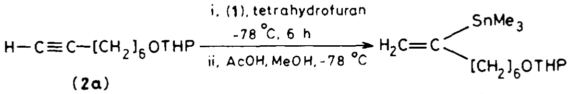


(**4**)

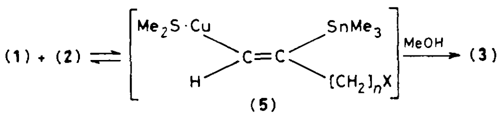
Table 1. Conversion of 1-alkynes (**2**) into 2-(trimethylstannyl)-1-alkenes (**3**).[a]

Entry		Substrate (2) n	X	Product (3) yield, %[b]
1	(**a**)	6	OTHP[d]	(**a**) 84
2	(**b**)	4	OH	(**b**) 85
3	(**c**)	4	Cl	(**c**) 80
4	(**d**)	3	OSi(Bu^t)Me$_2$	(**d**) 82
5	(**e**)	3	OH	(**e**) 88
6	(**f**)	3	Cl	(**f**) 79
7	(**g**)	2	OSi(Bu^t)Me$_2$	(**g**) 81
8	(**h**)	2	OH	(**h**) 82
9	(**i**)	2	Cl	(**i**) 59
10[c]	(**j**)	1	OTHP	(**j**) 58
11[c]	(**k**)	1	OSi(Bu^t)Me$_2$	(**k**) 55

[a] Conditions: reagent (**1**) (2 equiv.), MeOH (60 equiv.), tetrahydrofuran, −63 °C, 12 h. [b] Yields refer to isolated, purified materials. In each case, the desired substance was purified by column chromatography of the product mixture (see text) on silica gel (elution with 1 : 3 ether–light petroleum for entries 2, 5, and 8; 1 : 20 and 1 : 15 ether–light petroleum for entries 1 and 10, respectively; and light petroleum for entries 3, 4, 6, 7, 9, and 11). [c] These conversions were done at −78 °C in the absence of methanol (see text). [d] THP = tetrahydropyran-2-yl.



(**2a**) (**3a**) (1)



(2)

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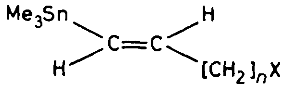
† All compounds reported herein exhibited spectra consistent with assigned structures. Those of the substituted 1-alkynes (**2**) which are not commercially available were prepared *via* standard methods. All new compounds were fully characterized and gave satisfactory molecular mass determinations (high resolution mass spectrometry).

‡ The reversible nature of the reaction of trialkylstannylcopper reagents with α,β-acetylenic esters has been demonstrated (ref. 5), and we have obtained similar evidence for the reversibility of the reaction of (**2**) with (**1**). For example, when the second step given in equation (1) involved treatment of the reaction mixture with iodine (2 equiv., −78 °C, 3 h) instead of with AcOH–MeOH, the starting material (**2a**) was recovered in >90% yield. None of the product (**3a**) could be detected. Details of this and other similar experiments will be given in a full paper.

§ Although the products (**3a**—**h**) were also accompanied by the corresponding regioisomers, the amounts of the latter substances were relatively minor (generally <8%).



(**6**) $n = 2$, X = Cl
(**7**) $n = 1$, X = OTHP
(**8**) $n = 1$, X = $OSi(Bu^t)Me_2$

Secondly, addition of reagent (**1**) to (**2j**) and (**2k**) proceeded essentially to completion even in the absence of methanol. Apparently, when the electron-withdrawing X group is positioned near to the carbon–carbon triple bond, the regioselectivity of the transformation is notably decreased and, at least with substrates (**2j**) and (**2k**), the intermediate vinylcopper species are relatively more stable.

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