$TiCl_4$-mediated Conjugate Addition Reactions of Stannylallenes to α,β-Unsaturated Carbonyl Compounds

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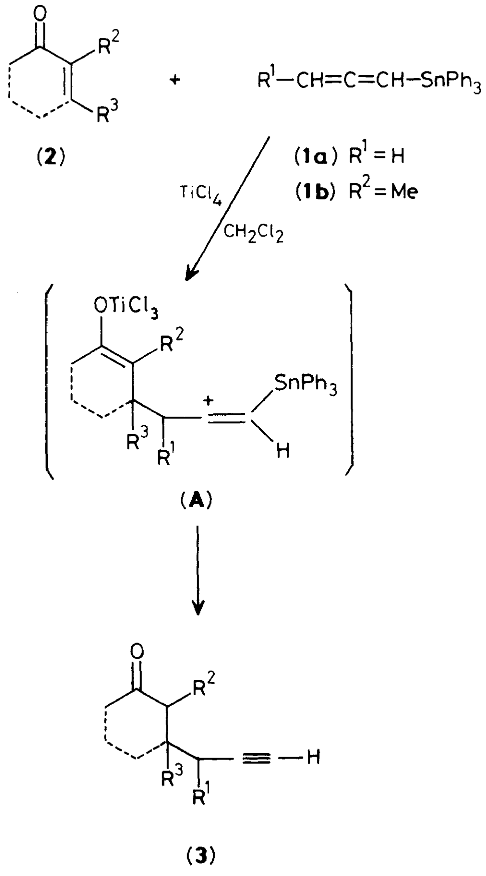
Stannylallene reacted with α,β-unsaturated carbonyl compounds in the presence of $TiCl_4$ to give the corresponding conjugate addition products, β-prop-2-ynylic carbonyl compounds.

Conjugate addition of allylic metal reagents to α,β-unsaturated carbonyl compounds is well established[1] and has been widely used as a synthetic method for carbon–carbon bond formation. In contrast to extensive studies on conjugate allylation, the study of conjugate propynylation of propynylic or allenic metal reagents to α,β-unsaturated carbonyl compounds[2] has been limited to a few examples in spite of the synthetic utility of the propynylic moiety.[3] It is difficult to introduce the propynylic moiety selectively to the β-position of α,β-unsaturated carbonyl compounds using metal reagents because of problems in controlling their ambident behaviour. They usually combine with electrophiles to give a mixture of propynylic and allenic products,[4] and show low regioselectivity of their manner of addition (1,2- or 1,4-addition).[2] Corey *et al.* reported a single example of selective conjugate propynylation using lithio(1-tri-isopropylsilyl)propyne in tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA) and cyclohex-2-enone.[5] Here we report a novel and general conjugate propynylation of α,β-unsaturated carbonyl compounds using triphenylstannylallenes (Scheme 1).

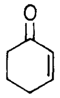
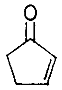
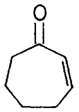
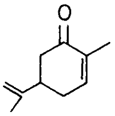
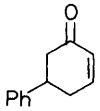
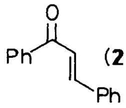
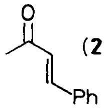
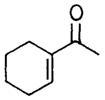
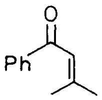
Treatment of cyclohex-2-enone (**2a**) with triphenylstannylallene (**1a**) in CH_2Cl_2 in the presence of $TiCl_4$ gave the conjugate addition product 3-prop-2-ynylcyclohexanone (**3a**) in 78% yield. Neither the 1,2-adduct nor 3-allenylcyclohexanone was detected in the crude reaction mixture (checked by t.l.c., i.r., and 500 MHz ^1H n.m.r. spectra). Other Lewis acids such as $SnCl_4$, $AlCl_3$, $AlEtCl_2$, $ZrCl_4$, $BF_3{\cdot}Et_2O$, Cl–$SiMe_3$, and $Me_3SiOSO_2CF_3$ were ineffective for the reaction and the best result was obtained by the use of $TiCl_4$. The use of ZnI_2 as a Lewis acid resulted in reversal of the regioselectivity, producing the 1,2-addition product homopropynylcyclohexanol in 72% yield, although the reason for this is not yet clear.

A series of the α,β-unsaturated carbonyl compounds (**2a—i**) was similarly treated with the stannylallenes (**1a,b**) to give the corresponding β-propynylic carbonyl compounds



Scheme 1

Table 1. Propynylation of α,β-unsaturated carbonyl compounds (**2a**—**i**) using stannylallenes (**1a**,**b**).[a]

Entry	Enone (2)	Reagent (1)	Product (3)	% Yield[b]
1	 (**2a**)	(**1a**)	(**3a**) $R^1 = H$	78
2	(**2a**)	(**1b**)	(**3b**) $R^1 = Me$	86
3	 (**2b**)	(**1a**)	(**3c**) $R^1 = H$	59
4	 (**2c**)	(**1a**)	(**3d**) $R^1 = H$	60
5	 (**2d**)	(**1a**)	(**3e**) $R^1 = H$	86
6	(**2d**)	(**1b**)	(**3f**) $R^1 = Me$	81
7	 (**2e**)	(**1a**)	(**3g**) $R^1 = H$	67
8	 (**2f**)	(**1a**)	(**3h**) $R^1 = H$	86
9	(**2f**)	(**1b**)	(**3i**) $R^1 = Me$	88
10	 (**2g**)	(**1a**)	(**3j**) $R^1 = H$	68
11	 (**2h**)	(**1a**)	(**3k**) $R^1 = H$	54
12	 (**2i**)	(**1a**)	(**3l**) $R^1 = H$	59

[a] A typical experimental procedure (entry 5) is as follows: To a CH_2Cl_2 solution (2 ml) of carvone (**2d**) (1 mmol) was added a CH_2Cl_2 solution of $TiCl_4$ (1 M; 1.2 mmol) at −40 °C. After 10 min, a CH_2Cl_2 solution (2 ml) of triphenylstannylallene (**1a**) (2 mmol) was added, and the mixture was allowed to warm to 0 °C over 1 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extract was concentrated and the residue was diluted with ether, and added to saturated aqueous KF. Vigorous stirring was continued for 1 h and the precipitate was filtered off. The usual work-up, followed by silica gel column chromatography gave (**3e**) in 88% yield.
[b] Yields of chromatographically purified products.

(**3a**—**l**). The results are summarised in Table 1.† The present procedure was found to be effective for the conjugate propynylation of both cyclic (entries 1—7) and acyclic (entries 8—12) α,β-unsaturated carbonyl compounds.

It is presumed that the stannylallene (**1**) reacts initially with (**2**) in the γ-position[6] to give a vinyl cation intermediate (**A**), stabilised through hyperconjugation with the C–Sn bond,[7] and removal of the stannyl group occurs readily[8] to afford (**3**) selectively (Scheme 1).[9]

In conclusion, stannylallene (**1**) was found to behave as a propynylic anion equivalent in the conjugate addition of α,β-unsaturated carbonyl compounds. The application of the present propynylation using stannylallene to the other conjugate systems is in progress.

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† All compounds (**3a**—**l**) gave satisfactory spectral and analytical data. Selected data for (**3a**): i.r. ($CHCl_3$) ν 3310, 1710 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.2—2.7 (11H, m), 2.01 (1H, t, *J* 2.5 Hz, C≡CH). High resolution m.s., found M^+ 136.0885; $C_9H_{12}O$ requires 136.0886. (**3e**): i.r. ($CHCl_3$) ν 3310, 1705 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.02 and 1.08 (3H, d × 2, *J* 7 Hz, CH*Me*), 1.76 [3H, s, =C(Me)–], 1.5—2.9 (10H m), 4.6—4.9 (2H, m, CH_2=C–). High resolution m.s., found M^+ 190.1364; $C_{13}H_{18}O$ requires 190.1358. (**3h**): i.r. ($CHCl_3$) ν 3310, 1685 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.96 (1H, t, *J* 2.5 Hz, C≡CH), 2.61 (2H, dd, *J* 6, 2.5 Hz, –CH_2–C–C), 3.1—3.8 [3H, m, COC*H*$_2$C*H*(Ph)], 7.0—8.0 (10H, m, ArH). High resolution m.s., found M^+ 248.1198; $C_{18}H_{16}O$ requires 248.1198.