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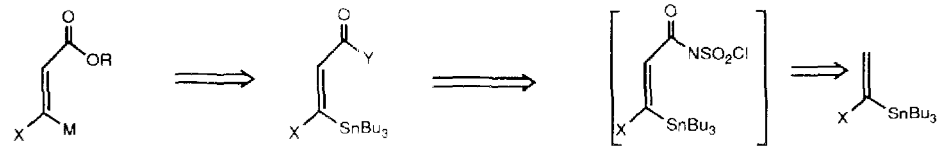
Preparation and Reactivity of ß-(tri-n-butylstannyl)acrylates

Colin Booth, Hussein Imanieh, Peter Quayle*, and Lu Shui-Yu.

Department of Chemistry
Victoria University of Manchester
Manchester M13 9PL. U.K.

Abstract:*.The reaction of heterofunctionalised vinyl stannanes with trichloroacetyl chloride occours without ipso-substitution, and provides easy access to a variety of β-(tri-n-butylstannyl)acrylates.*

Whilst there exist in the literature a number of elegant approaches to reactive intermediates[1] of the type (**1**), our previous interest in this area[2] led us to investigate the transmetallation chemistry of ß-(tri-n-butylstannyl)acrylates (**2**). Initially, it was envisaged[3a] that the acrylates (2) could be prepared *via in situ* trapping of an N-chlorosulphonamide (**3**) derived from reaction of a suitable vinylstannane (**4**) with chlorosulphonyl isocyanate, CSI (Scheme 1). However, reaction of the stannane (**5**) with CSI (1 equivalent) at low temperature (-78°C to 0°C) followed by a methanol/pyridine quench merely gave rise to isolation of the acrylamide (6), 22 % and the sulphonamide (7), 32 %.



X = OR'; SR' etc.
M = Li etc.
(1)

(2) X = OR'; SR' etc.; Y = NR$_2$'', OR'' etc
(6) X = PhS; Y = NH$_2$
(7) X = PhS; Y = NHSO$_2$OMe

(3)

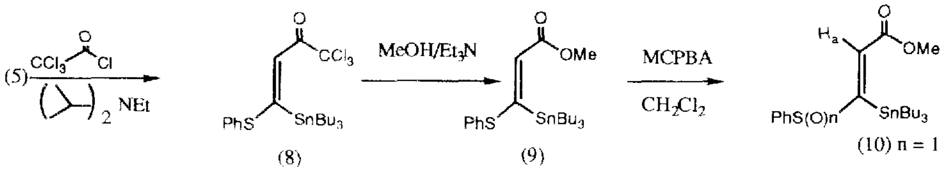
(4) X = OR'; SR' etc
(5) X = SPh

Scheme 1

Fortunately, after some experimentation, it was shown that reaction of the stannane (**5**) with trichloroacetyl chloride (1 equivalent) in the presence of Hunig's base (0.1 equivalent) in anhydrous dichloromethane at ambient temperature[3b] for one hour resulted in the disappearance of starting material (^{1}H nmr) and the formation of the trichloro-ketone (**8**), apparently without *ipso-* substitution of the tin moiety[4]. After an aqueous work-up (10% aq. K_2CO_3), column chromatography afforded the ketone (**8**) in 50% isolated yield as the only identifiable product (Scheme 2). Allowing this reaction to proceed for extended periods (> 12 hours) resulted in protodestannylation to the acrylate (22) as a competing process. The acylation reaction proceeds in a highly stereoselective manner, affording the Z-isomer (**8**) with > 95:1 selectivity, as judged from spectroscopic evidence[5] (^{1}Hnmr, $J_{117/119\,Sn-Ha}$ = 80 Hz) and subsequent chemical manipulations.

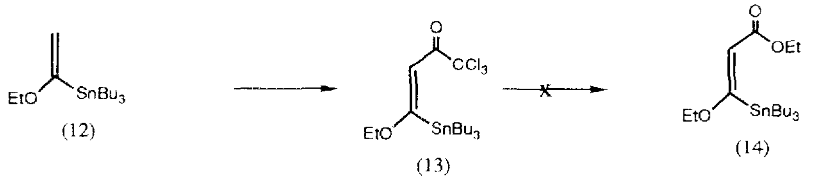
Dissolution of the trichloro-ketone (**8**) in methanolic triethylammine (10% Et_3N-90% MeOH) for 12 hours at ambient temperature cleanly led to the formation of the ester (**9**) in 58% isolated yield[6]. This transformation proceeds in a highly stereoselective manner (Z:E >95:1), as indicated by the relatively large Sn-Ha coupling constant ($J_{Sn117/119-Ha}$ = 80

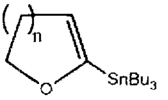
Hz). Moreover, sequential oxidation of the thioether (**9**) to the sulphoxide (**10**), (1 eq. MCPBA, CH_2Cl_2, rt, 12 hrs.; 58%) and then to the sulphone (**11**), (1 eq. MCPBA, CH_2Cl_2, rt, 12 hrs.; 55%) resulted in a downfield shift of the Ha proton from 5.68 ppm to 7.40 ppm (J $_{Sn117/119}$ - Ha = 72, 73 Hz) and 6.59 ppm (J $_{Sn\ 117/119}$ - Ha = 59, 62 Hz) respectively, indicative[2] of a *cis* relationship between the sulphur substituent at C_β and H_a.



Scheme 2

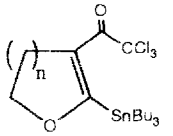
Similarly, reaction of the stannane (**12**) with trichloroacetyl chloride afforded the trichloroketone (**13**) in 89 % yield as a single geometric isomer (stereochemistry by analogy with (**8**); H_a at 6.56 ppm (J $_{Sn\ 117/119}$ - Ha = 63, 66 Hz)). Curiously, dissolution of the ketone (**13**) in ethanolic triethylammine afforded none of the desired ester (**14**), only starting material being isolated from the reaction mixture.





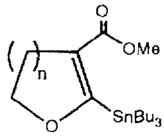
(15) n = 1

(16) n = 2



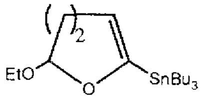
(17) n = 1

(18) n = 2



(19) n = 1

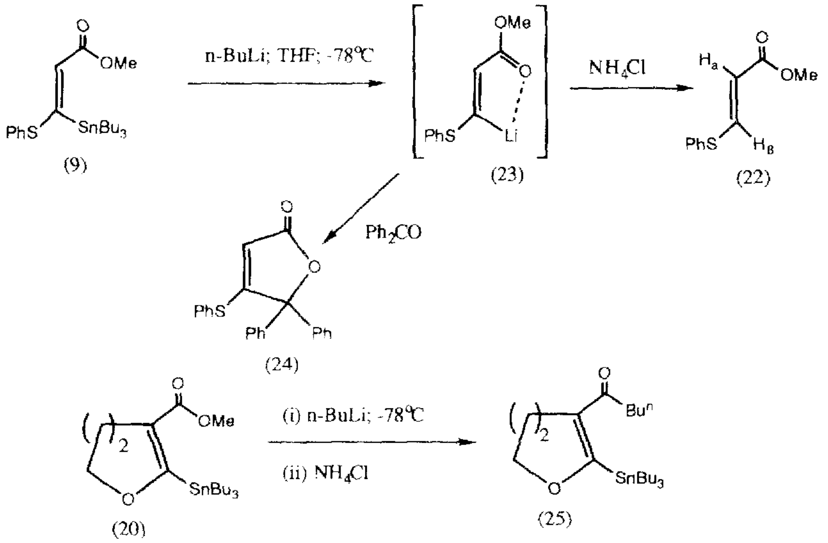
(20) n = 2



(21)

However, reaction of the heterocyclic vinylstannanes (**15**) and (**16**) with trichloroacetyl chloride in the presence of Hunig's base cleanly afforded the vinylogous esters (**17**) and (**18**) in good yield (65% and 60% respectively), which upon exposure to methanolic triethylammine afforded the desired esters (**19**) and (**20**) as colourless, mobile oils (both in 65% yield). Unfortunately, reaction of the stannane (**21**) as above led to the disruption of the the pyran ring, affording a number of unidentifiable products.

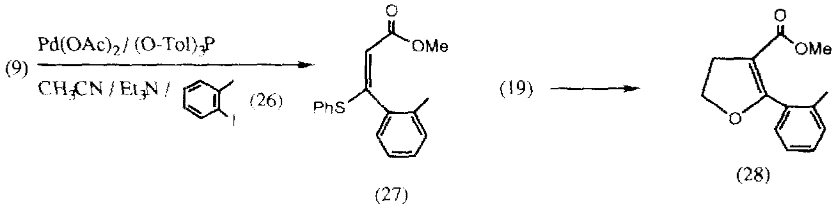
Having established a viable route to a variety of functionalised vinylstannanes their transmetallation chemistry is currently under investigation. The results of our initial studies are reported below. Treatment of the ester (**9**) with n-BuLi (1.1 equivalent) at -78°C in THF for 30 minutes, followed by an aqueous quench (satd. NH_4Cl soln.) afforded the *E* - thioether (**22**); (J H_a-H_β = 15Hz) in moderate yield (52%). Presumably this reaction proceeds *via* the generation of a relatively stable chelated[7] vinyl anion (**23**). Similarly, sequential treatment of the ester (**9**) with n-BuLi (1.1 equivalent) and benzophenone (1 equivalent) at -78°C afforded, after aqueous work-up and chromatography, the butenolide (**24**) in 46% overall yield. In contrast, reaction of the vinylstannane (**20**) with n-BuLi as above afforded the ketone (**25**) in low yield (12%) as the only identifiable product. Clearly, the transmetallation reactions of these functionalised vinylstannanes are highly substrate dependent (Scheme 3).



Scheme 3

The use of vinylstannanes in palladium-catalysed carbon - carbon bond forming reactions has been the subject of much interest[8]. The use of α-heterofunctionalised vinylstannanes in such reactions, has however received scant attention[8a]. We were pleased to observe therefore that reaction of the vinylstannanes (**9**) and (**19**) with the aryl iodide (**26**) in the presence of 15 mol% Pd(OAc)$_2$, (O-Tol)$_3$P and excess triethylammine[9] in refluxing acetonitrile (3 hours) afforded the coupled products (**27**) and (**28**) in good yield (62% and 82% respectively) (Scheme 4).

In conclusion, we have shown that a number of α-hetero functionalised (i.e. electron rich) vinylstannanes undergo acylation reactions rather than *ipso* - substitution[10]. The reaction of electron rich vinylstannanes with other electrophilic species is currently under investigation. Additionally, the ß-stannylacrylates, accessible *via* this sequence, appear to be useful intermediates for the generation of ß- lithioacrylates and also undergo clean palladium catalysed coupling reactions with vinyl (or aryl) halides. The generality of these coupling reactions is now under active investigation and will be the subject of future reports.



Scheme 4

General experimental procedure

To a solution of the stannane (**15**) (11.2 g, 30 mmol) and N,N-diisopropyl - ethylamine (0.4 g, 3 mmol) in methylene chloride (100 ml) at 0^{o}C was added trichloroacetyl chloride (5.7 g, 30 mmol) portionwise over a period of 5 minutes. Upon allowing to warm up to room temperature, reaction was continued for a further period of 12 hours, after which time it was quenched by pouring into water (kept at slightly basic pH by the addition 5% aq. $NaHCO_3$). The organic layer was separated, washed (water, 2 x 50 ml), dried and concentrated *in vacuo*. Chromatography of the residue afforded the *ketone (17)* as mobile oil. Yield 10.2 g (65%). ^{1}H nmr (300 MHz, $CDCl_3$) ∂ 4.69 (2H, tr, J = 9 Hz), 3.17 (2H, tr, J = 9 Hz), 1.52 (6H, m), 1.32 (6H, m), 1.11 (6H, m), 0.9 (9h, tr, J = 9Hz); i.r. ν_{max} 2958, 2873, 1660, 1498 cm^{-1}; m/e 448 (M$^+$- Bu, 100%). Mass measurement $C_{14}H_{22}{}^{35}Cl_2{}^{37}ClO_2{}^{120}Sn$ requires 448.9678; found 448.9681.

A solution of the ketone (**17**) (10.2 g) in 10% methanolic triethylammine (2L) was stirred at ambient temperature for 24 hours. The solvent was removed *in vacuo* and the residue washed (1M HCl, 150 mls and then water). Chromatography of the crude product (silica, eluent CH_2Cl_2 : petrol (2:8)) afforded the *ester (19)* as a mobile oil. Yield 5.73g (65%). ^{1}H nmr (300 MHz, $CDCl_3$) ∂ 4.48 (2H, tr, J = 10 Hz), 3.68 (3H, s), 2.77 (2H, tr, J = 10 Hz), 1.55 (6H, m), 1.35 (6H, m), 1.1 (6H, m), 0.9 (9h, tr, J = 9 Hz); i.r. ν_{max} 2958, 2872, 1692, 1574 cm^{-1}; m/e 361 (M$^+$- Bu, 100%). Mass measurement $C_{14}H_{25}O_3{}^{120}Sn$ requires 361.0826; found 361.0824.

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