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STEREOSPECIFIC SYNTHESIS OF VINYLSTANNANES USING TRIPHENYLSTANNYLCOPPER(I) SPECIES PREPARATION OF THE *cis* - ISOMER OF THE PRESUMED SEX ATTRACTANT OF *ACANTHOSCELIDES OBTECTUS.*

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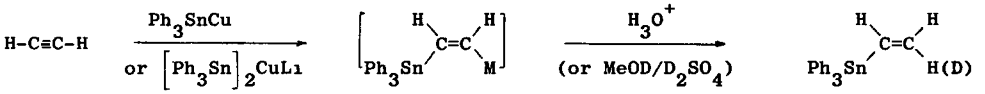
Summary *Triphenylstannylcopper(I) species add to acetylene, the produced (Z)-β-triphenylstannylvinylcopper(I) intermediates smoothly react with carbon electrophiles.The method has been applied to the preparation of the cis-isomer of the presumed sex attractant of Acanthoscelides obtectus.*

Vinylstannanes have been converted with retention of configuration into vinyllithium compounds by transmetalation with organolithium compounds[1] Vinylstannanes can be prepared by hydrostannation of alkynes Unfortunately,this hydrostannation reaction is not always stereospecific [1b,2] It was therefore of interest to develop other,stereospecific routes to vinylstannanes From organocopper chemistry it is known that organocopper reagents may convert 1-alkynes into vinylcopper species with high stereo- and regio-selectivity [3] It was therefore decided to investigate the behaviour of stannylcopper(I) species in this reaction In a recent paper Piers et al showed that stannylcopper(I) compounds add to the activated triple bond of 2-alkynoic esters [4] We anticipated that also less reactive alkynes could undergo addition of stannylcopper compounds In this paper we wish to report that such an addition is indeed possible for acetylene Thus reaction of acetylene with triphenylstannylcopper(I)[5,6] in tetrahydrofuran, at -55°C, gives the cis-adduct 1a (see eq 1) in excellent yield within 15 min A similar result has been obtained for the reaction of acetylene with $[Ph_3Sn]_2CuLi$ [5,7] In this case both Ph_3Sn groups have been transferred with formation of adduct 1b (eq 1) The vinylstannane 2 obtained after protolysis of 1 was identical to the vinylstannane prepared from vinylmagnesium bromide and Ph_3SnCl Some characteristic ^1H NMR data for this compound as well as for its deuterated analog are given in ref 8

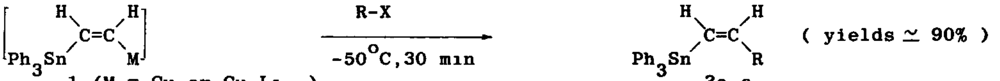


1a M = Cu
1b M = $Cu_{\frac{1}{2}}Li_{\frac{1}{2}}$

2 (yield≃ 90%)

(1)

For synthetic purposes it is important that adducts 1 easily react with various carbon electrophiles such as methyl iodide, allyl bromide and 1-iodo-trimethylsilylacetylene to give,with retention of configuration and in high yields, vinylstannanes 3a,[9] 3b, [10] and 3c, [11] respectively



1 (M = Cu or $Cu_{\frac{1}{2}}Li_{\frac{1}{2}}$)

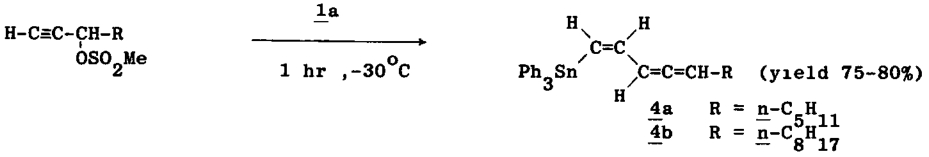
3a-c

(yields ≃ 90%)

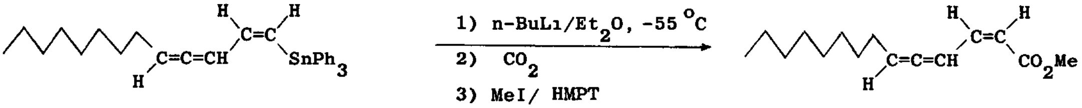
(2)

3a R = Me, 3b R = $H_2C{=}CH{-}CH_2$, 3c R = $Me_3SiC{\equiv}C$

The reaction of 1 with methyl iodide was performed in the presence of 3 0 mole equivalents of $P(OMe)_3$ in order to enhance the rate of this reaction Another interesting application is the synthesis of vinylallenes 4[12] by reaction of 1a with propargylic esters During this S_N2' reaction the Z-configuration of the vinylic unit is retained


(3)

Vinylallenes 4 bear the Ph_3Sn-group in a strategical position For instance,the transmetalation of 4b with n-butyllithium followed by reaction of the produced lithiated vinylallene with carbon dioxide and subsequent methylation of the obtained acid gives vinylallene 5,[12] the cis-isomer of the presumed sex attractant of *Acanthoscelides obtectus*,[14] in ca 90 % yield This result shows that our method is of potential interest for natural product synthesis


(4)

Currently the scope of this interesting reaction is under active investigation

References and notes

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2. P.W.Collins,C.J.Jung,A.Gasiecki,R.Pappo, *Tetrahedron Lett.* ,3187(1978)
3. See for a recent review J F.Normant,A Alexakis, *Synthesis* ,841(1981).
4. E Piers,J.M.Chong,H E.Morton, *Tetrahedron Lett.*, 22(1981)4905
5 See our procedure described in *Recl.Trav.Chim Pays-Bas* ,95(1976)299
6 The reagent was prepared from Ph_3SnLi and CuBr.The addition reaction was performed in the presence of 3 0 mole equivalents of hexamethylphosphoric triamide (HMPT)in order to prevent the formation of side products.
7. The cuprate was prepared from Ph_3SnLi and the THF-soluble complex $LiCuBr_2$
8 ^{1}H NMR data (CCl_4,Me_4Si) for Ph_3Sn-CH^1=CH^2H^3 $\delta(H^1)$6.73, $\delta(H^2)$6.35, $\delta(H^3)$5 88, $^3J(H^1,H^2)$13.8Hz, $^3J(H^1,H^3)$19.8Hz Within experimental error the same δ-values for H^1 and H^2 and the same size of $^3J(H^1,H^2)$ is found for the compound in which D is substituted for H^3.
9. ^{1}H NMR data (CCl_4,Me_4Si) for Ph_3SnCH^1=CH^2-CH^3_3 δ((H^1)6 10, $\delta(H^2)$6.84, $\delta(H^3)$1 78 , $^3J(H^1,H^2)$12.3 Hz.
10. ^{1}H NMR data (CCl_4,Me_4Si) for Ph_3SnCH^1=$CH^2CH^3_2$-CH^4=CH^5H^6 $\delta(H^1)$6 15, $\delta(H^2)$6 74 , $\delta(H^3)$2 82, $\delta(H^4)$5.62, $\delta(H^5)$4.89 , $\delta(H^6)$4 80, $^3J(H^1,H^2)$12.0Hz, $^3J(H^4,H^5)$9.0Hz, $^3J(H^4,H^6)$18 3 Hz , Mass spectrum ,m/z 418 ($M^{+\cdot}$for ^{118}Sn)
11. ^{1}H NMR data (CCl_4,Me_4Si) for Ph_3Sn-CH^1=CH^2-C≡C-$SiMe^3_3$ $\delta(H^1)$ and $\delta(H^2)$ 6 67 and 6 88 , $\delta(H^3)$-0.17 $^3J(H^1,H^2)$13.5 Hz , Mass spectrum ,m/z 474 ($M^{+\cdot}$for ^{118}Sn).
12 ^{1}H NMR data (CCl_4,Me_4Si) for Ph_3Sn-CH^1=CH^2-CH^3=C=CH^4-R.
compound 4a (R = n-C_5H_{11}) $\delta(H^1)$6 10, $\delta(H^2)$7 10, $\delta(H^3)$5.80, $\delta(H^4)$5.22, $^3J(H^1,H^2)$12 3 Hz , $^3J(H^2,H^3)$9 6 Hz, $^3J(H^3,H^4)$6 3 Hz, Mass spectrum,m/z 484 ($M^{+\cdot}$ for ^{118}Sn)
compound 4b (R = n- C_8H_{17}) $\delta(H^1)$6.10, $\delta(H^2)$7.10, $\delta(H^3)$5 82, $\delta(H^4)$5.22, $^3J(H^1,H^2)$12 3 Hz , $^3J(H^2,H^3)$9 6 Hz, $^3J(H^3,H^4)$6 3 Hz
13 ^{1}H NMR data (CCl_4,Me_4Si) for n-C_8H_{17}-CH^1=C=CH^2-CH^3=CH^4-CO_2Me^5
$\delta(H^1)$ 5.30 , $\delta(H^2)$7.19 , $\delta(H^3)$6 39 , $\delta(H^4)$ 5 52 , $\delta(H^5)$ 3 62 , $^3J(H^1,H^2)$ 6 8 Hz, $^3J(H^2,H^3)$11 4 Hz, $^3J(H^3,H^4)$11 1 Hz
14. The natural occurring sex attractant possesses the *trans* configuration
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