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Preliminary communication

SYNTHESIS OF (*Z*)-1,2-BIS(TRIMETHYLSTANNYL)-1-ALKENES BY PLATINUM-CATALYSED ADDITION OF HEXAMETHYLDISTANNANE TO 1-ALKYNES

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Summary

Addition of hexamethyldistannane to 1-alkynes in the presence of tetrakis(triphenylphosphine)palladium yields the title compounds, which can be photochemically isomerised to the corresponding (*E*)-distannylalkenes.

We [1] and others [2] have recently been interested in α-metallated vinyl anionoids of the type $RCH{=}C(M)(M'Me_3)$ (M = Li, MgX, Cu; M' = Sn [1]; M = Li, M' = Si [2]). As a precursor for these we used 1,1-bis(trimethylstannyl)-1-alkenes (I), prepared by hydrostannation of 1-trimethylstannyl-1-alkynes (eq. 1). This

$$RC{\equiv}CSnMe_3 + Me_3SnH \rightarrow \underset{\text{(I)}}{RCH{=}C(SnMe_3)_2} + \underset{(E)\text{-(II)}}{RC(SnMe_3){=}CHSnMe_3} \qquad (1)$$

reaction produced (*E*)-1,2-bis(trimethylstannyl)-1-alkenes (II) as by-products, generally in very low yields but in up to ca. 40% yield when R = $PhOCH_2$ or $MeOCH_2$.

Recent reports on the addition of disilanes [3,4] and stannylcopper reagents [5,6] to alkynes prompted us to attempt the addition of hexamethyldistannane to 1-alkynes in the presence of tetrakis(triphenylphosphine)palladium [3] as a catalyst in the hope that this would provide a route to the hitherto uncharacterised (*Z*)-isomer of the distannylalkenes (II).

We find that such an addition does in fact take place with acetylene itself and with a number of 1-alkynes (eq. 2).

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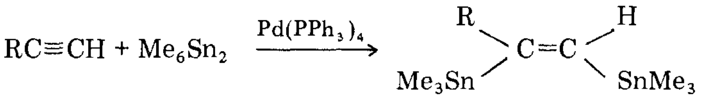
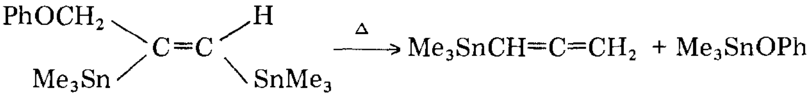


(2)

(Z)-(II)

(R = H, n-Bu, Ph, $PhCH_2$, $MeOCH_2$, $PhOCH_2$)

Two complications have so far been observed: when acetylene is bubbled into hexamethyldistannane at 70°C in the presence of the catalyst, formation of (Z)-1,2-distannylethene is observed, but before the reaction is complete this product isomerises to a large extent to the (E)-isomer. However, the pure (Z)-product is obtained when the reaction is carried out at 25°C. The second complication is that in the case of phenyl propargyl ether use of a reaction temperature above 80°C leads to the formation of large amounts of decomposition products, trimethylstannyl allene and trimethyltin phenoxide (eq. 3).



(3)

However, the other alkynes used so far have given exclusively the required (Z)-isomers in the form of distillable liquids. These were characterised by proton NMR spectroscopy (see Table 1). The observed coupling constant values can be compared to those typical for I: $^3J_{cis}$ 110—120, $^3J_{trans}$ 190—200 Hz.

TABLE 1

REACTION OF ACETYLENES RC≡CH WITH Me_6Sn_2; REACTION CONDITIONS[a], YIELDS, AND PROPERTIES OF THE (Z)-DISTANNYLALKENES

R	Temperature/time (°C/h)	B.p. (°C/mmHg)	Yield[d]	Tin—proton coupling[c,f] ^2J(SnH)	^3J(SnH)
H[b]	25/8	[c]	80	106	217
C_4H_9	85/100	$100/10^{-3}$	29	92	208
Ph	75/4	$92/10^{-3}$	42	86(104)	191(104)
$PhCH_2$	85/63	$100/10^{-3}$	43	88	196
$MeOCH_2$	85/16	$60/10^{-3}$	70	88(104)	196(104)
$PhOCH_2$	65/6	[c]		86	188

[a] Ca. 1 mol% $Pd(PPh_3)_4$ added. [b] ^3J(HH) 17 Hz. [c] Not distilled. [d] After distillation (not R = H). [e] Values in parentheses are for the (E)-isomer. [f] Coupling constants in Hz.

The corresponding (Z)-disilyl alkenes generally undergo only partial isomerisation to the (E)-isomers in the presence of the palladium catalyst [3]; in contrast, the (Z)-distannyl alkenes undergo isomerisation on photolysis in the absence of catalyst, though at greatly differing rates. Thus for R = $MeOCH_2$ the isomerisation is complete after 20 h, and for R = Ph it is 90% complete after 48 h, while other alkenes are isomerised only very slowly and partially even in the presence of catalytic amounts of Me_3SnH.

We are carrying out further studies of this addition of distannanes to alkynes with a view to extending it to internal alkynes and metallated alkynes. The mechanism of the reaction is presumably similar to that involved in the addition of disilanes [3,4]; this would require the presence of the palladium analogues of platinum complexes recently reported by Eaborn and Pidcock [7].

Independent studies in this department have shown that activated distannanes such as *sym*-tetramethyldichlorodistannane undergo addition to alkynes even in the absence of catalysts [8].

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