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FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

II *. IODODESTANNYLATION OF 1,1-BIS(TRIMETHYLSTANNYL)-1-ALKENES

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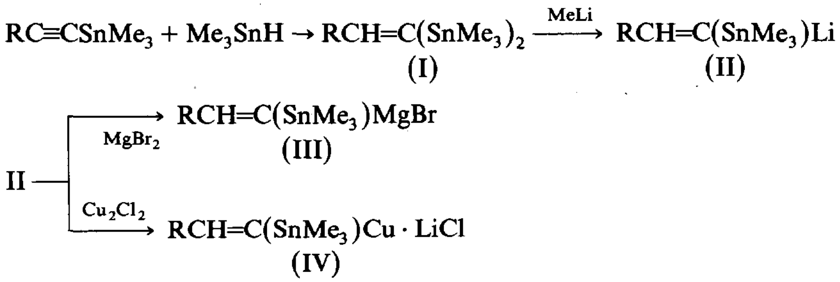
Summary

Treatment of 1,1-bis(trimethylstannyl)-1-alkenes with iodine gives mixtures of (*E*)- and (*Z*)-1-iodo-1-trimethylstannyl-1-alkenes, the ratio depending on the temperature used. Thermal and photochemical interconversion of these vinylic iodides has been observed. They cannot be used as precursors for the corresponding vinyl Grignard reagents, but undergo bromodestannylation to give the corresponding 1-bromo-1-iodo-1-alkenes.

Introduction

The following series of reactions leads to the formation of α-stannylvinyl carbanionoids which show some potential for organic synthesis [2]



$$RC{\equiv}CSnMe_3 + Me_3SnH \rightarrow \underset{(I)}{RCH{=}C(SnMe_3)_2} \xrightarrow{MeLi} \underset{(II)}{RCH{=}C(SnMe_3)Li}$$

$$II \begin{cases} \xrightarrow[MgBr_2]{} \underset{(III)}{RCH{=}C(SnMe_3)MgBr} \\ \xrightarrow{Cu_2Cl_2} \underset{(IV)}{RCH{=}C(SnMe_3)Cu \cdot LiCl} \end{cases}$$

The preparation of the vinyl Grignard and copper reagents III and IV has the disadvantage that it proceeds via the thermally labile vinyllithiums. A possible

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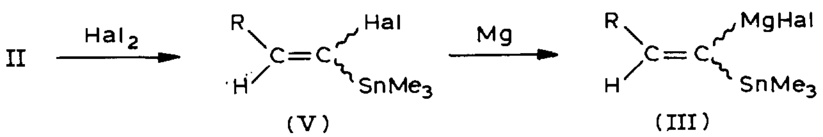
[*] For part I see Ref. 1.

alternative route involves halogenation of II followed by reaction with magnesium:



This paper describes the results of halodestannylation of II and the behaviour of the vinylic iodides obtained.

Results and discussion

Even at −78°C, bromine cleaves both tin–carbon bonds of I, leading to the formation of 1,1-dibromo-1-alkenes. Iodine, however, is more selective: while in most cases mixtures of similar amounts of (*E*)- and (*Z*)-isomers are formed at room temperature (see Table 1), at −78°C (*E*)-1-iodo-1-trimethylstannyl-1-alkene predominates. Small amounts of 1,1-diiodoalkanes are also formed. The stereochemistry of the reaction can be clearly determined from proton NMR spectra on the basis of the values of the coupling constant between tin and the vinylic proton. Selected NMR spectroscopic data are given in Tables 2 and 3.

Attempts to purify the vinylic iodides met with only limited success: distillation of the product mixtures with R = Me and t-Bu led to partial isomerisation in favour of the (*Z*)-isomer, while with R = Ph partial decomposition occurred with formation of trimethylstannyl iodide and phenyl acetylene: presumably this involves α-elimination followed by rearrangement of the initially-formed carbene [3].

UV irradiation of isomer mixtures also leads to isomerisation accompanied by decomposition; in cyclohexene solution no carbene adducts were formed, perhaps not surprisingly in view of the results of Cunico and Han [4].

When the iodides were heated with magnesium in THF as solvent at 65°C, no formation of Grignard reagents was observed, but isomerisation of the (*E*)- to the (*Z*)-isomers again occurred. Prolonged heating led to quantitative formation of the (*Z*)-isomer, which was reproducible in the absence of magnesium.

The exact mechanism of this isomerisation, which in the thermal case occurs at a particularly low temperature, is not known; the fact that the thermal isomerisation

TABLE 1

PRODUCTS OF IODODESTANNYLATION OF 1,1-BIS(TRIMETHYLSTANNYL)-1-ALKENES $RCH{=}C(SnMe_3)_2$ AT 20 AND −78°C (%) (c-Hex = cyclohexyl)

R	(*E*)-$RCH{=}CISnMe_3$		(*Z*)-$RCH{=}CISnMe_3$		$RCH{=}CI_2$	
	20°C	−78°C	20°C	−78°C	20°C	−78°C
CH_3	44	63	47	23	9	14
n-Bu	35	68	46	22	19	10
c-Hex	[a]	67	[a]	30	[a]	3
t-Bu	85	91	9	5	6	4
Ph	50	84	43	4	7	12
$PhCH_2$	48	78	52	22	[b]	[b]

[a] Not determined. [b] Not calculated because of line overlapping.

TABLE 2

SELECTED COUPLING CONSTANT DATA FOR (*E*)- AND (*Z*)-1-IODO-1-TRIMETHYLSTANNYL-1-ALKENES $RCH{=}CISnMe_3$ (Hz)

R	$^3J_{cis}$(SnH) ^{b}	$^3J_{trans}$(SnH) ^{c}	$^3J_{cis}$(SnC) ^{c}	$^3J_{trans}$(SnC) ^{b}
D	50	112	–	–
CH_3	48	112	32	41
n-Bu	46	103	^{d}	^{d}
c-Hex	48	104	30	43
t-Bu	54	120	13	^{a}
Ph	^{a}	100	21	50
$PhCH_2$	44	100	21	30

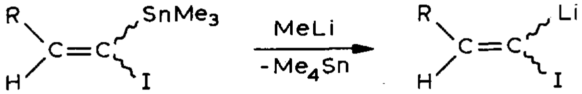
^{a} Not observed. ^{b} (*Z*)-isomer. ^{c} (*E*)-isomer. ^{d} Not measured.

occurs in the presence of magnesium presumably precludes the involvement of iodine atoms.

These results must be compared with those of Ottolenghi [5], who was able to prepare α-trimethylsilylvinylmagnesium bromide from the corresponding bromide in THF.

The direction of isomerisation observed in the present work corresponds to that observed by Zweifel for the corresponding silylated alkenyl halides; his isomerisation method involved UV irradiation in the presence of catalytic amounts of bromine [6] (for chlorides and bromides) or catalysis by means of t-butyllithium (for iodides) [7].

Reaction of the silylated alkenyl halides $RCH{=}C(Hal)SiMe_3$ with organolithium reagents leads to replacement of halogen by lithium [7]. We expected that the stannylated alkenyl iodides would however react in the alternative manner, involving replacement of tin by lithium:



This appears to be the case: treatment of (*E*)-V (R = Ph) with methyllithium at −78°C followed by addition of methyl iodide led to the formation of 1-phenyl-1-

TABLE 3

SELECTED PROTON AND TIN-119 CHEMICAL SHIFT DATA FOR (*E*)- AND (*Z*)-1-IODO-1-TRIMETHYLSTANNYL-1-ALKENES $RCH{=}CISnMe_3$ (in ppm vs. internal TMS or Me_4Sn) (Values in parentheses refer to the (*Z*)-isomer)

R	$\delta(CH_3Sn)$	δ(CH=)	δ(R)	$\delta(^{119}Sn)$
D	0.3 (0.3)	6.9 (6.8)	–	^{d}
CH_3	0.3 (0.2)	7.3 (6.2)	1.7 (1.9)	^{d}
n-Bu	0.3 (0.2)	7.2 (6.1)	^{b}	^{d}
c-Hex	0.3 (0.2)	7.0 (5.8)	^{b}	^{d}
t-Bu	0.2 (0.1)	7.6 (6.5)	1.0 (1.0)	^{d}
Ph	0.4 (0.3)	8.4 (^{a})	^{b}	−1.7 (12.5)
$PhCH_2$	0.3 (0.2)	7.3 (6.2)	3.2 (3.5) ^{c}	−10.7 (4.4)

^{a} Resonance hidden. ^{b} Not characteristic. ^{c} CH_2 resonance. ^{d} Not determined.

propyne as the major product isolated. In view of the results obtained by Schlosser [8] in his study of ω-chloro-ω-lithiostyrenes it can be assumed that lithium phenylacetylide is formed as an intermediate which is methylated by methyl iodide.

The stannylated alkenyl iodides provide an alternative route to unsymmetrical 1,1-dihalo-1-alkenes, since they can readily be subjected to bromodestannylation on treatment with bromine. Alkenyl dihalides of this type have been previously prepared by Zweifel from 1-chloro-1-alken-1-ylboranes [9] and 1-halo-1-alken-1-ylsilanes [10].

The chemistry of the α-stannylated vinylic iodides is at present under further study in our laboratory.

Experimental

All manipulations involving organotin compounds were carried out under argon. The distannyl alkenes were prepared as described previously [2].

Iododestannylation of 1,1-bis(trimethylstannyl)-1-alkenes

The procedure was as follows: to 20 mmol of the distannyl alkene, dissolved in 5 ml chloroform, was added dropwise a solution of 20 mmol iodine in ca. 200 ml chloroform. The iodine was immediately decolorised. The mixture was stirred for 1 h at room temperature and the solvent distilled off under atmospheric pressure. The trimethyltin iodide was then removed under reduced pressure (ca. 0.01 mmHg) at 70°C (bath temperature), leaving a viscous yellow oil.

In the cases where R = Me and t-Bu the product was distilled under reduced pressure (Me: b.p. 87°C/14 mmHg; t-Bu: b.p. 47°C/0.001 mmHg); partial isomerisation occurred. With R = Ph, isomerisation and partial decomposition were observed. In the remaining cases distillation was not attempted.

The yields of isolated product were as follows: R = Me, 50%; R = n-Bu, 71%; R = Ph, 76%; R = $PhCH_2$, 63%.

Satisfactory elemental analysis values could not be obtained for the vinylic iodides because of contamination by the diiodides: however, the values for the t-butyl compound show it to have the correct elemental composition. Found: C, 28.57; H, 4.72. $C_9H_{19}ISn$ calcd.: C, 28.98; H, 5.10%. Carbon-13 NMR data and mass spectra confirmed the structure of the compounds.

Isomerisation of α-stannyl alkenyl iodides

The following reaction conditions are typical:

(i) Thermal isomerisation. A solution of 20 mmol t-BuCH=$CISnMe_3$ (E/Z ratio 85/9) in 10 ml THF was heated for 20 h at 70°C in the presence of magnesium filings. Proton NMR analysis showed that only the (Z)-isomer was present. Similar results were obtained with other alkenyl iodides and in the absence of magnesium.

(ii) Photochemical isomerisation. A solution of 2 g (5.1 mmol) PhCH=$CISnMe_3$ (E/Z ratio 54/46) in 75 ml cyclohexane was irradiated using a 150 W mercury high pressure lamp (TQ 150, Hanau). The reaction was followed by proton NMR spectroscopy, which showed that the prior $E \rightarrow Z$ isomerisation was followed by decomposition. After 12 h no vinyl iodide could be detected. Removal of solvent at atmospheric pressure left a residue which was identified as a mixture of phenyl acetylene and trimethyltin iodide.

Irradiation in cyclohexene solution gave the same products, though the total reaction time was increased. No products of carbene addition to the cyclohexene could be detected.

Lithiation of (E)-PhCH=CISnMe$_3$ and reaction of the vinyl carbanion with methyl iodide

A solution of (*E*)-PhCH=CISnMe$_3$ (3.7 g, 9.4 mmol) in THF (5 ml) was cooled to −78°C and treated with a solution of methyllithium (9.4 mmol) in THF. After stirring for 1 h, methyl iodide (1.3 g, 9.4 mmol) was added; the red-brown solution was immediately decolorised. The reaction mixture was allowed to warm to room temperature, and tetramethyltin (the sole organotin product) and THF distilled off at atmospheric pressure. The residue was distilled at the water-pump: the main fraction boiled at 70–75°C/14 mmHg and was identified as 1-phenyl-1-propyne contaminated with several other compounds; phenylacetylene was not detected.

Bromodestannylation of (E)-1-iodo-1-trimethylstannyl-3,3-dimethyl-1-butene

The alkenyl iodide (6.7 g, 17.9 mmol) was dissolved in THF and treated at −78°C with one molar equivalent of bromine. Proton NMR spectroscopy indicated quantitative formation of trimethyltin bromide. This was distilled off along with THF, and the residue distilled at the water pump to give 2.7 g (53%) 1-bromo-1-iodo-1-alkene as a reddish liquid, b.p. 77–82°C/14 mmHg; the product was treated with 2,6-di-t-butyl-*p*-cresol to stabilise it. The PMR spectrum showed only one vinyl proton resonance at 7.3 ppm and a t-butyl signal at 1.0 ppm; however, GLC (30 m, quarz DB-1) indicated the presence of (*E*)- and (*Z*)-isomers in a ratio of 3/1. Similar behaviour has been observed [10] for the corresponding bromochloroalkenes.

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