Journal of Organometallic Chemistry, 405 (1991) 195–199
Elsevier Sequoia S.A., Lausanne
JOM 21490

Free radical and palladium-catalysed hydrostannation of allenes: a comparison

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(Received August 16th, 1990)

Abstract

While free radical hydrostannation of monosubstituted allenes with Me_3SnH affords mixtures of varying composition, cyclohexylidene allene is attacked by the stannyl radical preferentially at the central carbon atom. In contrast, palladium-catalysed hydrostannation involves a regioselective attachment of the organotin moiety to the less highly substituted terminal carbon atom of the allene framework.

Introduction

The "classical" (free radical) hydrostannation of unsaturated systems has been the subject of many studies [1]. Its application to allenes, however, has been little studied. An early publication by Kuivila [2] dealt with the free radical addition of Me_3SnH to various allenes, and more recent studies were concerned with reactions between Ph_3GeH or Ph_3SnH and allenes in the presence of a palladium(0) catalyst [3]. The increasing interest in palladium-catalysed hydrostannation reactions [4–6] has prompted us to make a direct comparison of free radical and palladium-catalysed reactions between Me_3SnH and a number of allenes in order to determine the relative efficacy of these procedures in producing synthetically useful species.

Results and discussion

Table 1 contains a summary of the results of the reactions carried out. Starting from an allene $RR'C{=}C{=}CH_2$, a total of six products can be obtained, three vinyl- and three allyl-tins:

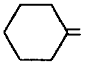
E/Z $RR'C{=}C(Me)SnMe_3$ (I)
$H_2C{=}C(SnMe_3)CHRR'$ (II)
E/Z $RR'C{=}CHCH_2SnMe_3$ (III)
$H_2C{=}CHCRR'SnMe_3$ (IV)

Compounds I and II result from attachment of the organotin moiety to the central allene carbon and in the light of Kuivila's results [2] these should be favoured in the

0022-328X/91/$03.50

Table 1

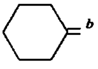
Yields and product distribution in reactions of Me_3SnH with allenes $RR'C{=}C{=}CH_2$

R	R′	Method [a]	Allene consumption (%)	Total adduct yield (%)	Relative product distribution						Me_6Sn_2 (%)
					E-I	*Z*-I	II	*E*-III	*Z*-III	IV	
Bu	H	C	100	87	8	4	6	32	50	0	4
Ph	H	C	100	70	3	0	1	83	13	0	11
${}^tBu$	H	A	96	89	25	9	15	48	3	0	3
		B	100	80	13	7	6	74	0	0	5
		C	0	0							100
${}^cHex$	H	A	100	88	17	23	8	41	11	0	4
		C	100	63	4	4	2	27	63	0	12
CH_2CO_2Et	H	A	100	84	18	16	15	30	21	0	1
		C	10	0							11
MeO	H	A	100	70	10	46	0	37	7	0	3
		B	100	66	33	36	0	22	9	0	10
		C	100	75	12	0	0	12	76	0	15
Me_3Sn	H	C	100	74	0	0	6	7	26	59	22
		A	100	87	55		26	19		0	5
		B	100	78	50		12	21		0	8
		C	100	76				100			15

[a] See Experimental for details.

Table 2

Tin-119 chemical shifts [a] for compounds of type I–IV derived from allenes $RCH{=}C{=}CH_2$ and Me_3SnH

R	δ (Sn)					
	E-I	*Z*-I	II	*E*-III	*Z*-III	IV
Bu	−31.0	−49.9	−35.6	−5.0	−3.3	
Ph	−22.5		−32.6	0.3	−0.2	
ᵗBu	−25.7	−49.3	−32.9	−5.6	−0.7	
ᶜHex	−30.0	−49.6	−35.5	−6.2	−6.7	
CH_2CO_2Et	−27.5	−46.3	−32.5	−0.8	−1.7	
MeO	−19.2	−39.2		−4.9	−5.6	
Me_3Sn			−44.9	−7.3	−6.9	11.0
 [b]	−46.4		−35.8	−4.5		

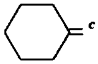
[a] In ppm vs. internal Me_4Sn. [b] Product derived from cyclohexylidene allene.

free radical reaction. We have obtained these compounds independently [7] by hydrolysis of adducts between Me_6Sn_2 and the corresponding allenes, and so their identification as products of hydrostannation was simple.

Isomer identification was based on multinuclear NMR data, and selected structure-relevant NMR parameters are listed in Tables 2–4. Tin-119 chemical shifts (Table 2) permit a ready distinction between compounds I and II in which the tin moiety is vinylic and III and IV in which it is allylic. Isomers *E*- and *Z*-I are immediately distinguished because of the relative high-field shift of the *Z* isomer. Proton coupling data are also useful: *E*- and *Z*-I can also be distinguished by use of the $^3J(SnC{=}CH)$ values , while II has two vinylic protons, each of which shows the appropriate value for $^3J(Sn,H)$. The relevant data are listed in Table 3. *E*- and *Z*-III bear two vinylic protons, the values of $^3J(H,H)$ indicating their geometry (coupling patterns are only clearly analysable at 300 MHz); tin-proton couplings are of no help here. Table 4 gives details. The only product of type IV can be recognised from the presence of a single tin-119 signal which is shifted to low field and shows the coupling $^2J(Sn,Sn)$ (Table 2); it bears three vinylic protons (Table 4).

Table 3

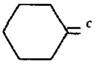
Vinylic proton chemical shifts [a] and coupling constants [b] $^3J(SnC{=}CH)$ in compounds *E*/*Z*-I and II

R	δ (=CH) [$^3J(SnC{=}CH)$]		
	E-I	*Z*-I	II
Bu	5.54 [77.4]		5.11 [70.9], 5.63 [154.8]
Ph	6.62 [80.1]		5.26 [67.6], 5.75 [146.3]
ᵗBu	5.44 [91.2]		5.29 [71.6], 5.63 [154.9]
ᶜHex	5.35 [81.4]	5.83 [143.8]	5.13 [71.5], 5.58 [154.9]
CH_2CO_2Et			5.15 [87.3], 5.65 [147.0]
MeO	5.65 [39.7]	6.37 [97.1]	
Me_3Sn	6.11 [104.4]		
 [c]			5.07 [74.8], 5.63 [156.2]

[a] In ppm w.r.t. TMS. [b] In Hz. [c] Product derived from cyclohexylidene allene.

Table 4

Vinylic proton chemical shifts [a] and coupling constants [b] $^3J(HC{=}CH)$ in compounds *E*/*Z*-III and IV

R	δ (=CH) [$^3J(HC{=}CH)$]		
	E-III	*Z*-III	IV
Bu	5.20, 5.48 [15.1]	5.10, 5.50 [10.5]	
Ph	6.22, 6.36 [15.7]		
^{t}Bu	5.26, 5.44 [15.4]		
^{c}Hex	5.11, 5.40 [15.1]	4.90, 5.36 [9.4]	
MeO	6.18, 4.90 [12.5]	5.73, 4.52 [6.2]	
Me_3Sn			4.63, 4.52, 5.90 [16.4, 9.5]
 [c]	5.21		

[a] In ppm w.r.t. TMS. [b] In Hz. [c] Product derived from cyclohexylidene allene.

Kuivila [2] finds that under free radical conditions only for allene itself is there relatively little difference in reactivity between the central and terminal carbons (though after correction for the statistical factor the central carbon is clearly preferred). For methylallene 87% of the products are derived from attack at the central carbon, while for 1,1- and 1,3-dimethyl- as well as trimethyl-allene all the products are derived from non-terminal attack. The very limited information available on Pd-catalysed hydrostannation with Ph_3SnH [3] does not permit the recognition of regiochemical trends.

Our results (see Table 1 for details) can be summarised as follows:

(a) There are differences between the product ratios for the two sets of free radical conditions used (AIBN-initiation, method A and UV-irradiation, method B), though these do not affect the overall trends.

(b) Under free radical conditions the regiochemistry of attack is not defined as clearly as expected on the basis of Kuivila's [2] results: the ratio of products derived from central and terminal attack varies in monosubstituted allenes between ca. 30 : 70 and ca. 70 : 30, whereas for cyclohexylidene allene it is ca. 80 : 20. *E* isomers are generally formed preferentially.

(c) In the palladium-catalysed reaction terminal attack is preferred: 82–100% of the hydrostannation products are (with one exception) of type III.

(d) Only in one case is a product of type IV obtained [$Me_3SnCH{=}C{=}CH_2/Pd^0$].

(e) Under both sets of reaction conditions small amounts of hexamethylditin are formed. This is the sole product when t-butylallene is subjected to palladium-catalysed reaction with Me_3SnH.

(f) Cyclohexylidene allene gives a small amount of a 1 : 2 allene : tin hydride adduct under UV-irradiation; this adduct has the structure c-$C_6H_{11}CH(SnMe_3)$-CH_2SnMe_3, and it is apparently formed by hydrostannation of II, as shown by the considerable decrease in the yield of this product when 2 equivalents of Me_3SnH are used.

(g) Two allenes fail to react in the presence of Pd^0 catalysts, but do undergo reaction under free radical conditions; steric factors are probably involved here.

Experimental

All manipulations involving organotin compounds were carried out under argon. Allenes were prepared by published procedures [8]. NMR spectra were recorded on a Bruker AM-300 spectrometer; NMR parameters are listed in Tables 2–4. Reactions were carried out by mixing the allene (7.5 mmol) and Me_3SnH (9.0 mmol). This mixture was allowed to react under the conditions of either method A (heating for 20 h at 80 °C in the presence of a catalytic amount of AIBN), method B (irradiating for 15 h with a high-pressure mercury lamp (TQ 150, Heraeus GmbH, Hanau)), or method C (stirring for 48 h at room temperature with THF (30 mL) and a catalyst amount of $Pd(PPh_3)_4$). Any remaining Me_3SnH and (method C) the solvent were removed at the oil pump, and product mixtures were analysed by GLC (column: 30m DB1-(5)-CB quartz) and multinuclear NMR spectroscopy. Product ratios were determined from the GLC traces in combination with tin-119 NMR spectra.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie and the Volkswagen Foundation.

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