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FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

I. PREPARATION AND HYDROSTANNATION OF STANNYLATED ALLYLIC ALCOHOLS AND RELATED COMPOUNDS

A. AMAMRIA and T.N. MITCHELL*

Abteilung Chemie der Universität Dortmund, Postfach 50 05 00, D-4600 Dortmund (F.R.G.)

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Summary

Hydrostannation of 1-alkynols leads to the formation of the corresponding triorganostannylalkenols in good yields. The main product is the *trans*-isomer, while *cis*- and α-products are formed in lower yields. In some cases the stannyl alkenols can be further hydrostannated to give distannyl alkanols. ^{13}C and ^{119}Sn NMR data for the organotin compounds are presented and discussed.

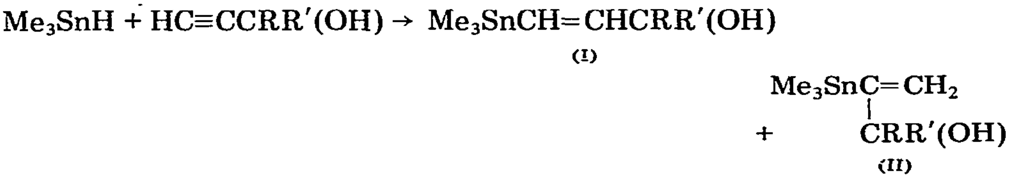
Introduction

Though the hydrostannation of 1-alkynes and some derivatives thereof has been studied in some detail by various workers [1—5], including some mechanistic studies [6—9], the reaction has not previously been applied to alkynols. Our observations [10] that compounds $Me_3SnCH{=}CHR$ (R = Me, Et, Ph) are hydrostannated by Me_3SnH to give exclusively the corresponding 1,1-distannylalkanes $(Me_3Sn)_2CHCH_2R$, while when R = t-Bu or Me_3Sn no reaction is observed, prompted us to prepare and investigate the hydrostannation of further stannyl alkenes; the ready availability of 1-alkynols suggested their use as a source of such alkenes.

Results and discussion

a) Hydrostannation of alkynols and alkyne ethers

In general, hydrostannation of 1-alkynols leads to formation of *trans*- (main product) and *cis*-1-trimethylstannyl-1-alkenols (I), though NMR-spectroscopic analysis (^{13}C and ^{119}Sn) shows the presence of small amounts of the α-adducts (II).



$$Me_3SnH + HC\equiv CCRR'(OH) \rightarrow \underset{(I)}{Me_3SnCH{=}CHCRR'(OH)} \quad + \quad \underset{(II)}{Me_3Sn\underset{\displaystyle CRR'(OH)}{\overset{}{C}}{=}CH_2}$$

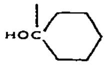
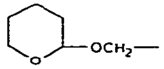
The alkynols studied are listed in Table 1, together with yields, boiling-points and data on *cis*/*trans* ratios. The latter were obtained by direct comparison of integrals in ^{119}Sn NMR and by taking a mean of the integral intensities for the various ^{13}C NMR signals: the latter method should be more reliable, and the ^{13}C values corresponded to those indicated from the proton spectra (not tabulated because of line overlapping). We attempted to obtain further values from gas chromatography, but our results indicated that a number of compounds decomposed on the column. Though yields were normally good, we were not able to obtain the required product from the simplest alkynol, propargyl alcohol, which in our hands polymerised. Previous authors had been able to carry out its hydrostannation using Et_3SnH, Pr_3SnH and Ph_3SnH [11,12]. Propargyl ethers, however, could successfully be reacted with Me_3SnH. The stannyl alkenols were characterised by ^1H NMR and IR, and in addition by ^{119}Sn and ^{13}C NMR: selected data for the latter methods are presented in Tables 2 and 3, which for the purposes of comparison also contain data [14] for the corresponding propenyltins.

Table 2 shows clearly that the nature of R in compounds 1—8 (which are of the general type $Me_3SnCH{=}CHR$ and $Me_3SnCR{=}CH_2$) has little influence on the tin chemical shift: the value for $Me_3SnCH{=}CH_2$ is —40 ppm. The total chemical shift ranges are only 8 (*trans*- and *cis*-) and 5 ppm (α-adducts): within the range of compounds studied, increasing bulk of R causes a small low-field shift for the *trans*-compounds and high-field shifts for the *cis*- and α-adducts.

The chemical shifts of the olefinic carbons (Table 3) are more clearly influ-

TABLE 1

TRIMETHYLSTANNYL ALKENOLS AND ALKENE ETHERS OBTAINED BY HYDROSTANNATION OF COMPOUNDS $RC\equiv CH$

Compound [a]	R	b.p. (°C/mmHg)	Yield (%)	Percent	*trans*
				from ^{13}C NMR	from ^{119}Sn NMR
1	$HOCH_2CH_2$-	37/0.005	72	75	87
2	$HOCMe_2$	40/0.01	82	93	98
3	HOC(Me)Et	50/0.001	85	87	97
4		66/0.2	76	67	94
5	$HOCH(C_3H_7)$	70/0.01	43	81	96
6	$MeOCH_2$	67/0.04	47	64	79
7	$PhOCH_2$	38/0.02	72	62	72
8		55/0.02	61	71	77

[a] Satisfactory elemental analyses were obtained for these compounds.

TABLE 2

^{119}Sn NMR DATA FOR TRIMETHYLSTANNYL ALKENOLS AND ALKENE ETHERS

Compound	δ(*trans*)	δ(*cis*)	δ(α)
Propenyl	−42 [a]	−58 [a]	−34 [b]
1	−41	−57	−34
2	−33	−61	−38
3	−34	−62	−38
4	−33	−60	−37
5	−36	−57	−38
6	−38	−58	−35
7	−36	−54	−33
8	−37	−56	−35

Shifts are given with respect to internal Me_4Sn; $CDCl_3$ was used as internal lock. [a] $Me_3SnCH{=}CHMe$. [b] $Me_3SnC(Me){=}CH_2$.

enced by the size of R: increasing bulk causes a high-field shift of up to 10 ppm for C(1) and a lowfield shift of the same magnitude for C(2). The tin—carbon coupling constants show no similar effect: the values of ^1J(Sn—C(1)) indicate little variation in carbon—tin bond length, while the values of the vicinal coupling do not appear to depend on whether C(3) is a methylene, methine or quaternary carbon, though the values are consistently larger for ethers than for alkenols. Unfortunately, the relatively low percentages of *cis*-products did not permit us to determine the values of *cis*-^3J(Sn—C) except in one case, where the value is of the expected low magnitude. We hope to obtain more data from low-temperature photochemical addition reactions.

b) Hydrostannation of stannyl alkenols and alkene ethers

We attempted to hydrostannate compounds **1**—**8**, but met with limited success: the reaction occurred only with compounds **1** and **6**—**8**. (It should be mentioned that $BuCH{=}CHSnMe_3$ can also be readily hydrostannated.) Thus the reaction can be carried out only with compounds of the type $Me_3SnCH{=}CHCH_2R$, which appears to indicate that steric effects are responsible for the

TABLE 3

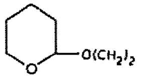
SELECTED ^{13}C NMR DATA [a] FOR TRIMETHYLSTANNYL ALKENOLS AND ALKENE ETHERS

Compound	δ(Me_3Sn)	δ(C(1))	δ(C(2))	^1J(Sn—CH_3)	^1J(Sn—C(1))	^3J(Sn—C(3))
1	−9.9(−8.7)	131.2(132.0)	144.7(144.7)	352(348)	462	66
2	−9.7(−7.8)	121.5	155.4	355	458	66
3	−9.7(−7.8)	124.2(127.2)	154.3(151.6)	354	439	62
4	−9.7(−7.6)	123.9(127.6)	155.5(153.1)	352	460	[b]
5	−9.8(−7.8)	127.4(130.1)	151.2(150.2)	353	456	72
6	−9.8(−7.8)	131.1(132.0)	144.3(143.4)	357	430	78(39)
7	−9.8(−8.3)	131.7(133.0)	142.6(142.6)	355(357)	[b]	78
8	−9.8(−8.3)	130.7(132.6)	144.3(144.3)	354	[b]	76
Propenyl	−9.9(−8.9)	129.9(129.7)	143.5(142.9)	352(347)	478(465)	78(49)

Shifts are given with respect to internal TMS: $CDCl_3$ was used as internal lock. *J* values in Hz. [a] Values in parentheses are for *cis*-adducts. [b] Not observed due to line overlapping.

TABLE 4

BOILING POINTS, YIELDS AND NMR-SPECTROSCOPIC DATA FOR 1,1-DISTANNYLALKANE DERIVATIVES $(Me_3Sn)_2CHR$

Compound	R	B.p. (°C/mmHg)	Yield (%)	$\delta(^{119}Sn)$	$^2J(Sn—C—Sn)$ [a]	$\delta(SnMe)$	$^1J(Sn—CH_3)$	$^1J(Sn—C)$
9	$n\text{-}C_5H_{11}$	148/0.1	79	20.0	156	−8.6	310	302
10	$HO(CH_2)_3$	102/0.02	50	20.6	157	−8.6	313	300
11	$MeO(CH_2)_2$	55/0.03	56	21.1	159	−8.3	316	288
12	$PhO(CH_2)_2$	106/0.02	59	22.4	177	−8.3	318	293
13		94/0.02	60	22.6	165	−8.5	314	296

[a] $^2J(^{119}Sn—C—^{117}Sn)$.

Data given and recorded as in Table 3.

difference in reactivity. However, though no hydrostannation occurs with the remaining compounds, reversible addition of a stannyl radical does occur: for example, when compound 2 is heated with Bu_3SnH, Me_3SnH and the corresponding butylstannylalkenol are formed (as shown by IR and ^1H NMR) in an equilibrium process:

$$Me_3SnCH{=}CHCMe_2OH + Bu_3SnH \rightleftharpoons Bu_3SnCH{=}CHCMe_2OH + Me_3SnH$$

Thus the important factor appears to be the stability of the intermediate radical of the type $Sn_2CH{-}\dot{C}HR$ which, when R is too large, loses a stannyl radical rather than abstracting a hydrogen from a further hydride molecule. Data for the 1,1-distannyl compounds obtained are given in Table 4: these do not include those for the 1,2-distannyl compounds formed by hydrostannation of the α-adducts, since these were present in only small amounts.

It will be seen from Table 4 that all NMR parameters recorded are insensitive to variations in R: this is perhaps not surprising, however, since what we are in fact varying is the substituent on the γ-carbon of the group R. The geminal and vicinal couplings $^nJ(Sn{-}C)$ ($n = 2, 3$) are also virtually constant at 21—23 and 43—46 Hz, respectively.

We are at present carrying out studies on the hydrostannation of silyl and stannyl alkynes and intend to report on these shortly [13].

Experimental

Starting materials were either commercial products or were prepared according to literature procedures: propargyl pyranyl ether (b.p. 80° /14 mm) is apparently a new compound, and was characterised by NMR spectroscopy as well a as elemental analysis. All manipulations were carried out in an argon atmosphere.

Carbon-13 and tin-119 NMR spectra were obtained as described in earlier papers by us [14].

General procedure for hydrostannation of alkynols and stannyl alkenols

Equimolar amounts of Me_3SnH and the appropriate alcohol are heated at 60° C (reflux temperature of Me_3SnH) in the presence of a small amount of azobis(isobutyronitrile) as radical starter. The reaction is complete when reflux of the hydride ceases, in general after 1—2 h. The reaction product is distilled in vacuo. Yields quoted in the tables are for distilled products: amounts of starting materials were generally 30—50 mmol, so that somewhat higher yields can be expected when reactions are carried out on a larger scale. By-products other than those referred to in the text were not observed.

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References

1 G.J.M. van der Kerk, J.G.A. Luijten and J.G. Noltes, Chem. Ind. (1956), 352; idem, J. Appl. Chem., 9 (1959) 106.
2 J.G. Noltes and G.J.M. van der Kerk, Functionally Substitutional Organotin Compounds, Tin Research Institute, Greenford, England, 1958.
3 A.J. Leusink and J.W. Marsmann, Rec. Trav. Chem. Pays-Bas, 84 (1965) 1123.
4 A.J. Leusink, J.W. Marsmann, H.A. Budding, J.G. Noltes and G.J.M. van der Kerk, Rec. Trav. Chim. Pays-Bas, 84 (1965) 567.
5 A.J. Leusink and H.A. Budding, J. Organometal. Chem., 11 (1968) 533.
6 G.J.M. van der Kerk, J.G.A. Luijten and J.G. Noltes, J. Appl. Chem., 7 (1957) 356.
7 J.G. Noltes and G.J.M. van der Kerk, Chimia, 16 (1962) 122.
8 R.F. Fulton, Ph.D. Thesis, Purdue University, 1960.
9 W.P. Neumann and R. Sommer, Liebigs. Ann. Chem., 675 (1964) 10.
10 T.N. Mitchell and M. el-Behairy, J. Organometal. Chem., 172 (1979) 293; idem, unpublished results.
11 G.J.M. van der Kerk, J. Appl. Chem., 9 (1959) 106.
12 A.J. Leusink, J.W. Marsmann and H.A. Budding, Rec. Trav. Chim. Pays-Bas 84 (1965) 689.
13 T.N. Mitchell and A. Amamria, in preparation
14 T.N. Mitchell and C. Kummetat, J. Organometal. Chem., 157 (1978) 275.