Journal of Organometallic Chemistry, 368 (1989) 167–172
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09708

Stannylated phosphines

I. Preparation of (β-trimethylstannyl)-alkyldiphenylphosphines *

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(Received November 28th, 1988)

Abstract

(β-Trimethylstannyl)alkyldiphenylphosphines can be readily prepared by addition of diphenylphosphine to the corresponding vinyltrimethyltin $Me_3SnCR{=}CH_2$ under free radical conditions. In contrast, free radical hydrostannation of the corresponding phosphines $Ph_2PCR{=}CH_2$ is a more complex process, and is apparently of little synthetic value. The title compound can be easily oxidised by potassium permanganate to give the corresponding phosphine oxides in good yields. Hydrostannation of model alkynyldiphenylphosphines ($RC{\equiv}CPPh_2$, R = H, Me_3Sn) occurs regiospecifically.

Introduction

Though functionalised organotin compounds have recently attracted considerable interest [1], very few reports of functionalisation by introduction of a phosphine residue have appeared in the literature. Several years ago, Weichmann et al. [2] described the preparation of (β-triorganostannyl)ethyldiphenylphosphines by addition either of triorganotin hydrides to vinyldiphenylphosphine or of diphenylphosphine to vinyltriorganotins (eq. 1).

$$R_3SnH + H_2C{=}CHPPh_2 \rightarrow R_3SnCH_2CH_2PPh_2 \leftarrow R_3SnCH{=}CH_2 + HPPh_2 \qquad (1)$$

They extended these reactions to include diethyl- and dibutyl-phosphine residues, but there have been no reports of the further extension to include substituted vinyl residues. We therefore felt it of interest to investigate the scope of these two reactions for the preparation of (β-trialkylstannyl)alkyldiphenylphosphines.

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* Dedicated to Professor F. Huber, on the occasion of his 60th birthday on 4th June 1989.

0022-328X/89/$03.50

Results and discussion

In order to facilitate NMR-spectroscopic characterisation of the reaction products we restricted our work to trimethylstannyl derivatives.

1. Preparation of compounds $Me_3SnCR{=}CH_2$ and their reaction with diphenylphosphine

Compounds with R = Me, Ph, t-Bu and $SiMe_3$ were prepared by treating the corresponding vinyl Grignard reagents (in THF) with trimethyltin chloride. The reaction of ethyl vinyl ether with (in sequence) t-butyllithium and trimethyltin chloride yielded the compound with R = OEt.

Addition of the phosphorus–hydrogen bond to alkenes is catalysed by acids [3] and bases [4] as well as by radical initiators (e.g. AIBN) [5]; it can also occur when the reaction mixture is subjected to UV-irradiation [6] or is heated [7]. When an equimolar mixture of a secondary phosphine and a vinyltriorganotin is heated in the presence of AIBN, a mixture containing ca. 60% of the required product, 20% 1,2-bis(bis(triorganostannyl)ethane and 20% 1,2-bis(diorganophosphinyl)ethane is obtained; the by-products are thought to be formed in free radical side reactions [2]. We found the product distribution to be identical when the addition was promoted by UV light, and decided to use UV-irradiation to promote further addition reactions of the type shown in eq. 2.

$$Ph_2PH + Me_3SnCR{=}CH_2 \rightarrow \underset{\textbf{(A)}}{Ph_2PCH_2CHRSnMe_3} \qquad (2)$$

The expected "anti-Markovnikov" product of type **A** was formed in 79% yield from diphenylphosphine and isopropenyltrimethyltin; no by-products containing two organotin or organophosphorus moieties were detected. The same was true for R = Ph (yield 91%, reaction time 1 h, compared with 12–24 h in other reactions), OEt (yield 75%) and $SiMe_3$ (yield 81%). Except for R = Ph, where small amounts of two phosphorus-free organotin by-products (one of which was apparently $Me_3SnCHMePh$) were formed, the only impurities observed were the corresponding phosphine oxides formed when compounds **A** were allowed to come into contact with air. No reaction was observed when R was t-Bu.

3. Preparation of vinyldiphenylphosphines $Ph_2PCR{=}CH_2$ and their hydrostannation

The vinyldiphenylphosphines with R = Me, Ph, t-Bu and $SiMe_3$ were prepared from the corresponding vinyl Grignard reagents and diphenylchlorophosphine. The hydrostannation reaction shown in eq. 3 was also carried out under the influence of UV light. The AIBN-catalysed reaction of trimethyltin hydride with vinyldiphenylphosphine affords the required "anti-Markovnikov" adduct (**B**, R = H) in 78% yield [2], and the yield is almost identical when UV irradiation is used.

$$Me_3SnH + Ph_2PCR{=}CH_2 \rightarrow \underset{\textbf{(B)}}{Ph_2PCHRCH_2SnMe_3} \qquad (3)$$

For R = Me the yield of **B** is 59%, but for R = t-Bu no reaction is observed. No addition product is formed when R = Ph; the only identified product (41%) is $PhCH_2CH_2SnMe_3$. Identical behaviour is observed when AIBN is used to catalyse this reaction. When R = $SiMe_3$, the crude product mixture is very complex (9 signals between −40 and +50 ppm in the ^{31}P NMR spectrum). Distillation affords a product of type **B**, which, as shown by NMR spectroscopy, is only slightly contaminated with impurities; one of these is Me_3SnPPh_2, which is formed in an unknown manner.

3. *Oxidation of (β-trimethylalkyl)diphenylphosphines by $KMnO_4$*

Weichmann et al. [2] reported the oxidation of three (β-triorganostannyl)ethyldiorganophosphines to the corresponding phosphine oxides using $KMnO_4$ in acetone. We found that, as indicated by the presence of phosphine oxide impurities noted above, this is indeed a general reaction, which is not influenced by the nature of the substituents R; the phosphine oxides were obtained in good yields.

4. *Hydrostannation of alkynyl phosphines*

We felt it of interest to carry out preliminary experiments involving the hydrostannation of alkynylphosphines, and chose as our examples ethynyldiphenylphosphine and (2-trimethylstannyl)ethynyldiphenylphosphine. The former gave a mixture of *Z*- and *E*-isomers (eq. 4) contaminated with very small amounts

$$Ph_2PC{\equiv}CH + Me_3SnH \rightarrow \underset{(73\%,\ Z/E\ 1/5)}{Ph_2PCH{=}CHSnMe_3} \qquad (4)$$

of unidentified impurities. In addition, $Ph_2PCH_2CH(SnMe_3)_2$, the product of double hydrostannation, was isolated in 11% yield; the reaction of two equivalents of trimethyltin hydride with ethynyldiphenylphosphine gave this product in 90% yield. The hydrostannation of $Me_3SnC{\equiv}CPPh_2$ gave $Ph_2PCH{=}C(SnMe_3)_2$ in 69% yield, as well as a number of by-products, one of which was clearly identified as $Ph_2PCH_2CH(SnMe_3)_2$.

Experimental

Manipulations involving organotin compounds were carried out under argon. Diphenylphosphine was prepared by a published procedure [8] from lithium aluminium hydride and diphenylchlorophosphine. New compounds were characterised by elemental analysis and by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, ^{119}Sn): while proton data are given below for vinyltins and vinylphosphines, the proton spectra of the title compounds were in some cases extremely complex even at 300 MHz, and spectral parameters could only be obtained by lengthy computer simulation and iteration routines; phosphorus-decoupled spectra were recorded in some cases. Since the compounds were completely characterised by the ^{31}P and ^{119}Sn data, only these are given below (the complete data will form part of a forthcoming paper dealing with the dependence of ^3J(Sn,P) on molecular geometry). Spectra were recorded with a Bruker AM-300 spectrometer operating at 300 MHz for 1H and 59.60 MHz for ^{29}Si (standard: internal TMS), 111.93 MHz for ^{119}Sn (standard: internal Me_4Sn) and 121.50 MHz for ^{31}P (standard: external 85% H_3PO_4).

Preparation of vinyltriorganotins

Vinyltriorganotins $Me_3SnCR{=}CH_2$, with R = Me [9], Ph [10], and $SiMe_3$ [11] were prepared as previously described. The compound with R = t-Bu was, as described in ref. 1, prepared analogously from the corresponding alkenyl Grignard reagent and Me_3SnCl in 56% yield as a colourless oil, b.p. 56–60 °C/15 mmHg. Found: C, 42.8; H, 7.9. $C_9H_{20}Sn$ calc.: C, 43.7; H, 8.2%. ^1H NMR ($CDCl_3$): 0.20 (s, 9H, $SnMe_3$), 1.13 (s, 9H, t-Bu), 5.14 (d, 1H, =CH), 5.73 (d, 1H, =CH).

The compound with R = OEt was prepared by a modification of the procedure described in ref. 12: the organolithium intermediate was treated with Me_3SnCl instead of Me_3SiCl, to give the product as a colourless liquid, b.p. 54–60 °C/18 mmHg. Yield 8.4 g (71%). Found: C, 36.1; H, 7.0. $C_7H_{16}OSn$ calc.: C, 35.8; H, 6.9%. ^1H NMR ($CDCl_3$): 0.18 9s, 9H, $SnMe_3$), 1.33 (t, 3H, CH_3), 3.77 (q, 2H, OCH_2), 4.10 (d, 1H, =CH), 4.77 (d, 1H, =CH).

Reactions of vinyltriorganotins with diphenylphosphine

An equimolar mixture of diphenylphosphine and the vinyltrimethyltin (12–25 mmol of each) was placed in a quartz Schlenk tube and irradiated under argon using a high-pressure mercury lamp (Heraeus TQ-150). The product was purified by distillation. Distilled products were shown to be pure by multinuclear NMR, but on standing in contact with air they underwent slow oxidation to the phosphine oxides (see below).

Reaction times and product data were as follows:

R = Me, 12 h; b.p. 150 °C/0.3 mmHg; yield 79%. Found, C, 55.1; H, 6.2. $C_{18}H_{25}PSn$ calc.: C, 55.3; H, 6.4%. $\delta(^{119}Sn)$ 8.7, $\delta(^{31}P)$ -19.1 ppm, $^3J(^{119}Sn,^{31}P)$ 80.1 Hz.

R = Ph, 1 h; b.p. 160–170 °C/0.01 mmHg; yield 91%. Found, C, 60.3; H, 6.3. $C_{23}H_{27}PSn$ calc.: C, 60.9; H, 6.0%. $\delta(^{119}Sn)$ 14.7, $\delta(^{31}P)$ -18.7 ppm, $^3J(^{119}Sn,^{31}P)$ 70.7 Hz.

R = OEt, 15 h; b.p. 98 °C/0.05 mmHg; yield 75%. Found, C, 53.8; H, 6.2. $C_{19}H_{27}OPSn$ calc.: C, 54.2; H, 6.5%. $\delta(^{119}Sn)$ -15.3, $\delta(^{31}P)$ -20.6 ppm, $^3J(^{119}Sn,^{31}P)$ 66.2 Hz.

R = $SiMe_3$, 15 h; b.p. 113–116 °C/0.1 mmHg; yield 81%. Found, C, 53.3; H, 6.8. $C_{20}H_{31}PSiSn$ calc.: C, 53.3; H, 6.9%. $\delta(^{29}Si)$ 4.7, $\delta(^{119}Sn)$ 10.5, $\delta(^{31}P)$ -12.0 ppm, $^2J(^{29}Si,^{119}Sn)$ 15.0, $^3J(^{29}Si,^{31}P)$ 20.4, $^3J(^{119}Sn,^{31}P)$ 52.5 Hz.

R = t-Bu, 144; no reaction.

Preparation of vinyldiphenylphosphines $Ph_2PCR{=}CH_2$

The compounds with R = Me [13] and Ph [14] were prepared by a published procedure from the corresponding vinylmagnesium bromide and diphenylchlorophosphine in THF. The following compounds were prepared analogously:

R = t-Bu, b.p. 127–130 °C/0.3 mmHg, yield 57%. Found, 80.1; H, 7.4. $C_{18}H_{21}P$ calc.: C, 80.6; H, 7.8%. ^1H NMR ($CDCl_3$): 1.23 (s, 9H, t-Bu), 4.85 (d, 1H, =CH), 5.87 (d, 1H, =CH), 7.3 (m, 10H, Ph).

R = $SiMe_3$, b.p. 118 °C/0.1 mmHg, yield 48%. Found, C, 71.2; H, 7.2. $C_{17}H_{21}PSi$ calcd.: C, 71.6; H, 7.4%.. ^1H NMR ($CDCl_3$): 0.10 (s, 9H, $SiMe_3$), 5.54 (d, 1H,=CH), 6.26 (d, 1H, =CH), 7.4 (m, 10H, Ph).

Hydrostannation of vinyldiphenylphosphines

Equimolar mixtures of the reactants (10–25 mmol of each) in a quartz Schlenk tube were irradiated as above, and the product mixtures distilled under reduced pressure. Reaction times and product yields were as follows:

Table 1

Yields and product data for (β-trimethylstannyl)ethyldiphenylphosphine oxides

R	Yield (%)	M.p. (°C)	Formula	Analysis (Found (calc.) (%))		$\delta(^{119}Sn)$ (ppm)	$\delta(^{31}P)$ (ppm)	$^3J(Sn,P)$ (Hz)
				C	H			
(a) $Me_3SnCHRCH_2P(O)Ph_2$								
Me	70	65–70	$C_{18}H_{25}OPSn$	52.8 53.1	5.9 6.1	15.2	32.1	147.9
Ph	72	121	$C_{23}H_{27}OPSn$	58.2 58.8	5.7 5.8	21.2	14.7	96.2
OEt	73	71–75	$C_{19}H_{27}O_2PSn$	51.7 52.3	6.2 6.2	−7.1	33.4	177.0
$SiMe_3$	65	[a]	$C_{20}H_{31}OPSiSn$	51.6 51.7	6.8 6.7	15.1	33.0	36.7
(b) $Me_3SnCH_2CHRP(O)Ph_2$								
Me	75	134	$C_{18}H_{25}OPSn$	54.0 53.1	6.5 6.1	5.0	37.9	211.6
$SiMe_3$	61	102	$C_{20}H_{31}OPSiSn$	52.3 51.7	7.2 6.7	12.9	36.8	120.0

[a] Viscous oil.

R = Me, 24 h; b.p. 132°C/0.5 mmHg, yield 59%. Found, C, 54.7; H, 6.3. $C_{18}H_{25}PSn$ calc.: C, 55.3; H, 6.4%. $\delta(^{119}Sn)$ −0.7, $\delta(^{31}P)$ 3.6 ppm, $^3J(^{119}Sn,^{31}P)$ 182.7 Hz.

R = $SiMe_3$, 12 h; b.p. 105–107°C/0.05 mmHg, yield 35%. $\delta(^{29}Si)$ 4.6, $\delta(^{119}Sn)$ 7.1, $\delta(^{31}P)$ −2.8 ppm, $^2J(^{29}Si,^{31}P)$ 17.3, $^3J(^{29}Si,^{119}Sn)$ 13.4, $^3J(^{119}Sn,^{31}P)$ 102.4 Hz.

R = Ph, 12 h (benzene as solvent); product with b.. 80°C/0.5 mmHg identified from NMR spectra as $PhCH_2CH_2SnMe_3$ (lit. [15] b.p. 74°C/0.4 mmHg); yield 41%. The same product was formed when the reactants were heated for 6 h at 100°C without solvent in the presence of AIBN (3 mol%).

R = t-Bu, 168 h; no reaction.

Oxidation of (β-trimethylstannyl)alkyldiphenylphosphines (A) and (B)

The general procedure was as follows. The stannyl-substituted phosphine (10 mmol) was dissolved in acetone (15 ml) and treated with a saturated solution of potassium permanganate in acetone until no further permanganate was consumed (the solution remaining pale pink). Manganese dioxide was filtered off and the solvent removed in a rotary evaporator, leaving a residue which crystallized on standing. Purification was carried out by recrystallisation from 5 ml of a mixture of methylene chloride and n-hexane (1/9). Yields and product data are given in Table 1.

Preparation and hydrostannation of alkynyldiphenylphosphines

Ethynyldiphenylphosphine [16] and (2-diphenylphosphinoethynyl)trimethyltin were prepared as previously described [14].

The hydrostannations were carried out as follows. Equimolar mixtures of trimethyltin hydride and the alkynylphosphine $RC{\equiv}CPPh_2$ (10 mmol of each) were irradiated in a quartz Schlenk tube, and the products were purified by distillation.

Reaction times and product data as follows:
R = H, 12 h; b.p. 141–146 °C/0.01 mmHg; yields 73% (*Z*/*E* 1/5). Found, C, 53.9; H, 5.4.$C_{17}H_{21}PSn$ calc.: C, 54.4; H, 5.6%. *E*-isomer: $\delta(^{119}Sn)$ −38.7 ppm, $\delta(^{31}P)$ −3.9 ppm, $^3J(^{119}Sn,^{31}P)$ 130.6 Hz; *Z*-isomer: $\delta(^{119}Sn)$ −54.7, $\delta(^{31}P)$ −10.8 ppm, $^3J(^{119}Sn, ^{31}P)$ 84.2 Hz.
R = Me_3Sn, 12 h; b.p. 153–158 °C/0.01 mmHg; yield 69%. Found, C, 44.4; H, 5.7. $C_{20}H_{29}PSn_2$ calc.: C, 44.6; H, 5.4%. $\delta(^{119}Sn)$ −18.7, −44.4, $\delta(^{31}P)$ −8.2 ppm, $^2J(^{119}Sn,^{119}Sn)$ 618.0, $^3J(^{119}Sn,^{31}P)$ 139.2 (*cis*), 317.8 Hz (*trans*).

The double hydrostannation of ethynyltrimethyltin required irradiation for 20 h. $Ph_2PCH_2CH(SnMe_3)_2$ was obtained on distillation as a colourless oil, b.p. 186 °C/0.4 mmHg, yield 90%. Found, C, 44.6; H, 6.3. $C_{20}H_{31}PSn_2$ calc.: C, 44.5; H, 5.8%. $\delta(^{119}Sn)$ 22.2, $\delta(^{31}P)$ −11.8, $^2J(^{119}Sn,^{119}Sn)$ 153.5, $^3J(^{119}Sn,^{31}P)$ 147.2 Hz.

Acknowledgement

This work was supported by the "Fonds der Chemischen Industrie".

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