Journal of Organometallic Chemistry, 51 (1973) 167–171
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THE PREPARATION AND REACTIONS OF {[α-(TRIMETHYL- AND TRIPHENYL)STANNYL]PHENACYL} TRIPHENYLPHOSPHONIUM SALTS AND YLIDES

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(Received September 9th, 1972)

SUMMARY

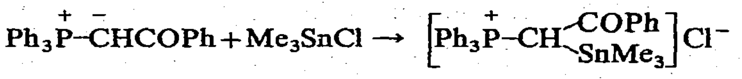
Several {*p*-substituted [α-(trimethyl- or triphenyl)stannyl]phenacyl} triphenylphosphonium salts, $[\mathrm{Ph_3\overset{+}{P}CH(SnR_3)COPh}]\mathrm{Cl^-}$ (R = Me and Ph), have been prepared by the reaction of *p*-substituted phenacylidenetriphenylphosphoranes with trimethyl- or triphenyltin chlorides. Extremely low carbonyl stretching frequencies in the infrared spectrum of these compounds suggested strong coordination of the carbonyl oxygen to the trimethyltin moiety. [α-(Trimethylstannyl)phenacyl]triphenylphosphonium chloride gave the corresponding ylide by reaction with n-butyllithium.

INTRODUCTION

In a previous paper[1], the isolation of a crystalline tetramethylene[α-(trimethylstannyl)phenacyl]sulfonium salt was reported. We describe below the preparations and reactions of {[α-(trimethyl- or triphenyl)stannyl]phenacyl}triphenylphosphonium salts and ylides.

RESULTS AND DISCUSSION

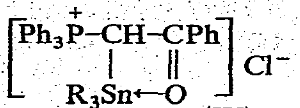
When a dichloromethane solution of phenacylidenetriphenylphosphorane (0.01 mol) was treated with an equimolar amount of chlorotrimethyltin, [α-(trimethylstannyl)phenacyl]triphenylphosphonium chloride (IIa) was readily obtained in 76% yield as colorless crystals. The structure of (IIa) was confirmed by means of



$$\mathrm{Ph_3\overset{+}{P}\text{–}\overset{-}{C}HCOPh + Me_3SnCl} \longrightarrow \left[\mathrm{Ph_3\overset{+}{P}\text{–}CH}\begin{smallmatrix}\mathrm{COPh}\\ \mathrm{SnMe_3}\end{smallmatrix}\right]\mathrm{Cl^-} \qquad (1)$$

(Ia) (IIa)

elemental analysis and spectral data. Thus, the NMR spectrum showed peaks at τ 2.52 (C_6H_5, m, 20H), 5.83 (CH, s, 1H) and 9.67 ppm [$SnCH_3$ (m, 9H) with $J(^{119}\mathrm{Sn{-}C{-}H})$ 68.1, and $J(^{117}\mathrm{Sn{-}C{-}H})$ 64.5 Hz]. In the IR spectrum, a very intensive absorption band at 1480 cm^{-1} due to ν(C=O) was observed. Such a large shift of the carbonyl stretching frequency to a lower wave number indicates a structure, (IV);



(IV)

TABLE 1

PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF PHOSPHONIUM SALTS
$[(Ph_3\overset{+}{P}{-}CH\genfrac{}{}{0pt}{}{COPh{-}X(p)}{SnR_3})Cl^-$; (II) R = CH_3; (III) R = C_6H_5]

No.	*X*	*R*	*M.p.* (°C)	*Yield* (%)	*ν(C=O)*[a] (*cm*$^{-1}$)	*NMR (CDCl*$_3$*) τ (ppm)*	
						C$_6$*H*$_5$*, m*	*CH or CH*$_3$*, s*
(IIa)	H	CH_3	188.0–189.2	76	1480	2.52, 20H	5.83 (CH), 1H
(IIb)	CH_3	CH_3	183.0–185.0	83	1470	2.54, 19H	7.66 (CH_3), 3H
(IIc)	OCH_3	CH_3	110.0–113.0	67	1475	2.54, 19H	6.20 (CH_3), 3H
(IId)	Cl	CH_3	199.0–200.5	69	1495	2.51, 19H	5.60 (CH), 1H
(IIe)	Br	CH_3	202.0–203.0	69	1490	2.50, 19H	5.80 (CH), 1H
(IIIa)	H	C_6H_5	177.5–178.5	80	1470	2.52	? (CH)
(IIIb)	CH_3	C_6H_5	172.0–174.5	75	1470	2.54, 33H	7.66 (CH_3), 3H
(IIIc)	OCH_3	C_6H_5	174.2–175.2	75	1470	2.53, 33H	6.20 (CH_3), 3H
(IIId)	Cl	C_6H_5	138.0–139.0	50	1470	2.51	? (CH)
(IIIe)	Br	C_6H_5	146.5–147.0	88	1472	2.50	? (CH)

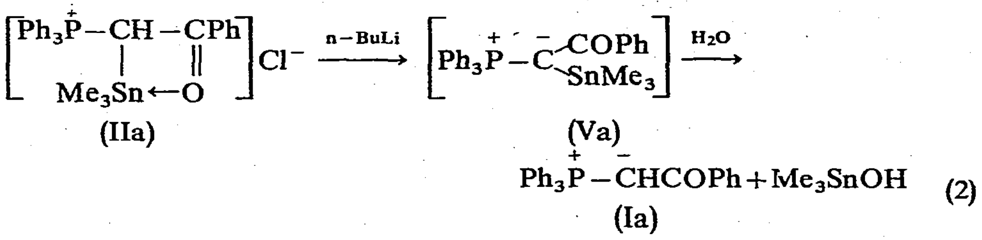
[a] In KBr.

NMR (CDCl$_3$*) τ (ppm)*	*J(Hz)*		*Formula*	*Analysis found (calcd.) (%)*			
Sn–C–H, s	^{119}*Sn–C–H*	^{117}*Sn–C–H*		*C*	*H*	*Cl*	*Br*
9.67, 9H	68.1	64.5	$C_{29}H_{30}ClOPSn$	60.10 (60.09)	5.23 (5.22)	6.34 (6.12)	
9.63, 9H	67.5	64.5	$C_{30}H_{32}ClOPSn$	60.76 (60.69)	5.50 (5.43)	5.99 (5.97)	
9.58, 9H	67.5	68.9	$C_{30}H_{32}ClO_2PSn$	59.44 (59.10)	5.32 (5.29)	5.88 (5.81)	
9.57, 9H	69.3	65.1	$C_{29}H_{29}Cl_2OPSn$	56.68 (56.72)	4.77 (4.76)	11.63 (11.55)	
9.59, 1H	70.1	65.4	$C_{29}H_{29}BrClOPSn$	52.88 (52.89)	4.44 (4.44)	5.39 (5.38)	12.11 (12.14)
			$C_{44}H_{35}ClOPSn$	69.31 (69.09)	4.60 (4.58)	4.69 (4.65)	
			$C_{45}H_{37}ClOPSn$	69.53 (69.39)	4.78 (4.75)	4.56 (4.56)	
			$C_{45}H_{37}ClO_2PSn$	67.92 (67.99)	4.67 (4.66)	4.48 (4.47)	
			$C_{44}H_{34}Cl_2OPSn$	66.21 (66.11)	4.28 (4.26)	8.96 (8.89)	
			$C_{44}H_{34}BrClOPSn$	62.65 (62.62)	4.09 (4.03)	4.27 (4.21)	9.58 (9.49)

in which there is strong coordination of the oxygen to the trimethyltin moiety, as in tetramethylene[α-(trimethylstannyl)phenacyl]sulfonium salts. By analogous treatment of other *para*-substituted phenacylidenetriphenyl phosphorane with chlorotrimethyl or -triphenyltin, the corresponding phosphonium salts [(II) and (III)] containing triorganotin group were obtained in excellent yields (Table 1).

These phosphonium salts were fairly stable crystalline materials. For example, (IIa) did not change in air for over one month and even on refluxing in methanol for 48 h. However, heating of (IIa) above its melting point gave the corresponding phenacylidenetriphenylphosphorane and chlorotrimethyltin. The stability of these salts towards hydrolysis and methanolysis can be attributed to the coordination described above.

Attempts to isolate [α-(trimethylstannyl)phenacylidene]triphenylphosphorane (Va) by treatment of the salts (IIa) with n-butyllithium in petroleum ether or tetrahydrofuran were carried out unsuccessfully under various conditions. However, hydrolysis of the yellowish solution obtained by the treatment of the salts (IIa) in THF with n-butyllithium gave the parent phenacylidenetriphenylphosphorane and trimethyltin hydroxide in good yields [eqn. (2)]. Furthermore, addition of phenyl isocyanate to the yellowish tetrahydrofuran solution of (IIa) resulted in trimeric cyclization of isocyanate, to give triphenyl isocyanurate*. These results suggest that the ylide (Va) is formed as an intermediate in the treatment of the salts (IIa) with n-butyllithium.



(IIa) (Va) (Ia) (2)

$$\left[Ph_3\overset{+}{P}-CH-CPh\ \cdots\ Me_3Sn\leftarrow O\right]Cl^- \xrightarrow{n\text{-BuLi}} \left[Ph_3\overset{+}{P}-\overset{-}{C}\begin{smallmatrix}COPh\\SnMe_3\end{smallmatrix}\right] \xrightarrow{H_2O} Ph_3\overset{+}{P}-\overset{-}{C}HCOPh + Me_3SnOH \quad (2)$$

The salts (IIa) did not react with methyl iodide, whereas tetramethylene-[α-(trimethylstannyl)phenacyl]sulfonium chloride gave 1,2,3-tribenzoylcyclopropane in good yield[2].

EXPERIMENTAL**

Materials

Para-substituted phenacylidenetriphenylphosphoranes were prepared by the method described in the literature[3]. Their physical properties were summarized in Table 2. Chlorotrimethyltin (b.p. 153–157°, lit.[4] 154–156°) and chlorotriphenyltin

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* The ylide (Va) would be expected to undergo the insertion reaction as aminostannanes do, because the electronic structure of the $\equiv Sn-C<$ linkage in the ylide (Va) is isoelectronic with that of the $\equiv Sn-N<$ linkage of aminostannanes.

** All melting points were uncorrected. The IR spectra were measured on a JASCO grating infrared spectrophotometer IR-G. The NMR spectra were recorded on a JEOL C-60 HL, with tetramethylsilane as internal standard.

TABLE 2

PHYSICAL PROPERTIES OF *p*-SUBSTITUTED PHENACYLIDENETRIPHENYLPHOSPHORANES, $Ph_3\overset{+}{P}$–CHCOPh–X(*p*)

No.	*X*	*M.p. (°C)*	*Yield (%)*	*ν(C=O)*[a] *(cm⁻¹)*	*NMR (CDCl₃) τ (ppm)*		
					C_6H_5, *m*	*CH, s*	CH_3, *s*
Ia	H	185.2–186.5	66	1525 (1645)[b]	2.50, 20H	5.63, 1H	
Ib	CH_3	183.5–185.0	30	1512 (1650)[b]	2.50, 19H	5.67, 1H	8.67, 3H
Ic	OCH_3	150.0–151.3	44	1502 (1648)[b]	2.35, 19H	5.53, 1H	6.19, 3H
Id	Cl	200.0–202.0	60	1515 (1670)[b]	2.43, 19H	5.71, 1H	
Ie	Br	203.0–205.0	58	1515 (1660)[b]	2.43, 19H	6.01, 1H	
If	NO_2	157.0–158.0	43	1528 (1665)[b]			

[a] In KBr. The corresponding phenacyltriphenylphosphonium bromide. [b] In KBr.

(m.p. 102–104°, lit.[4] 104–107°) were prepared according to procedures described by Kozeschkow.

Typical procedures are described, and physical properties are summarized in Table 1.

Preparation of [α-(trimethylstannyl)phenacyl]phosphonium chloride (IIa)

Chlorotrimethyltin (0.5 g, 0.0025 mol) was added to a dichloromethane solution of (Ia) (0.95 g, 0.0025 mol) and the mixture was stirred for 30 min at room temperature. After removal of the dichloromethane under reduced pressure, the crystalline product was obtained by addition of small portions of acetone/petroleum ether (b.p. 30–40°) (1/1). Filtration of the reaction product gave [α-(trimethylstannyl)-phenacyl]triphenylphosphonium chloride (IIa).

Thermolysis of (IIa)

(*a*). Phosphonium chloride [(IIa), 1.0 g, 0.0017 mol] was heated at 190° for 5 h in glass ampoule filled with nitrogen. Distillation of the decomposition products and fractional crystallization of the distillation residue from dichloromethane, ether and petroleum ether (b.p. 30–40°) gave chlorotrimethylstannane in a 68.2% (0.23 g) yield, and phenacylidenetriphenylphosphorane in a 76.4% (0.50 g) yield. These compounds were identified by comparison of their melting points and infrared spectra with those of the authentic samples.

(*b*). A methanol solution (10 ml) of (IIa) (1.0 g, 0.0017 mol) was refluxed for 48 h. After removal of the methanol under reduced pressure, the recrystallization of the residue from dichloromethane/petroleum ether (b.p. 30–40°) gave 0.95 g of the starting phosphonium salts.

Hydrolysis of [α-(trimethylstannyl)phenacyl]triphenylphosphonium ylide (Va) in THF

The phosphonium salt [(IIa), 1.16 g, 0.002 mol] in THF (10 ml) was stirred with an equimolar amount of 1.2 *M* n-butyllithium at room temperature for 1 h. After removal of lithium chloride by filtration, the filtrate was stirred at room temperature overnight in air. Removal of the solvent under reduced pressure, and subsequent washing of the crystalline residues with small amount of dry acetone gave trimethyltin hydroxide in 33% (0.12 g) yield. The evaporation of the acetone from the washings combined gave phenacylidenetriphenyl phosphorane in a 71% (0.58 g) yield.

Reaction of the ylide (Va) in THF with phenyl isocyanate

Phenyl isocyanate (1.44 g, 0.12 mol) was added to a THF solution (10 ml) of the ylide [(Va), 0.002 mol] and stirred overnight at room temperature. After removal of the solvent, the residue was washed with small portions of water, and recrystallization of the solids from hot benzene gave phenyl isocyanurate in 82% yield (1.19 g), which was identified by comparison of its melting point and infrared spectrum with those of an authentic sample prepared by an established method[5].

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