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REACTIONS OF TERTIARY PHOSPHINES WITH $(CH_3)_3SnCH_2I$

R.L. KEITER * and E.W. ABEL *

Department of Chemistry, University of Exeter, Exeter EX4 4QD (Great Britain)

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Summary

The reactions of $(OC)_5WPPh_2CH_2CH_2PPh_2$, $(OC)_5MoPPh_2CH_2CH_2PPh_2$, PPh_3, $MePh_2P$ and Me_2PhP with $(CH_3)_3SnCH_2I$ have been studied with ^1H NMR spectroscopy. The quaternary phosphonium cations, $[\geqslant PCH_2Sn(CH_3)_3]^+$, formed initially in each reaction, are unstable in chloroform, acetone and methanol but stable in DMSO at ambient temperature. The cations are presumed to interact with I^- to give an adduct which dissociates into trimethyltin iodide and an ylid which reacts further to give $[\geqslant PMe]^+$.

Introduction

Previously complexes of the type $(OC)_5MPPh_2CH_2CH_2PPh_2$ (M = Mo, W) have been shown to undergo reactions characteristic of tertiary phosphines including quaternization by various alkylating agents [1—3]. To continue studies of these complexes, attempts were made to prepare quaternary phosphonium salts such as $[(OC)_5MPPh_2CH_2CH_2PPh_2CH_2Sn(CH_3)_3]I$ from the reactions of $(OC)_5MPPh_2CH_2CH_2PPh_2$ with $(CH_3)_3SnCH_2I$. Contamination of the desired product with $[(OC)_5MPPh_2CH_2CH_2PPh_2Me]I$ led us to investigate reactions of $(CH_3)_3SnCH_2I$ with the simpler phosphines, PPh_3, $PMePh_2$ and PMe_2Ph.

Seyferth and Singh have reported the reaction of PPh_3 with $(CH_3)_3SiCH_2Br$ and obtained a 98% yield of $[Ph_3PCH_2Si(CH_3)_3]Br$ when the two reactants were heated at reflux temperature for 2 h [4]. However, as shown by Schmidbaur and Tronich, when PPh_3 and $(CH_3)_3SiCH_2Cl$ are heated at 90°C for 5 d, the quaternary salt first formed establishes an equilibrium with Ph_3PCH_2 and $(CH_3)_3SiCl$ and undergoes transylidation [5].

* On sabbatical leave from the Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920 (U.S.A.)

TABLE 1

PROTON NMR DATA FOR VARIOUS PHOSPHONIUM SALTS

Cation	^2J(Sn—CH$_2$)	^2J(P—CH$_3$)	^2J(P—CH$_2$)	^2J(Sn—CH$_3$)	τ(CH$_2$)	τ(Sn—CH$_3$)	τ(P—CH$_3$)	Solvent
$[Ph_3PCH_2Sn(CH_3)_3]^+$	48.2		15.9	55.5	6.99	9.76		$CDCl_3$ [a]
	47.6		16.0	57.2, 59.0	6.98	9.83		$(CD_3)_3CO$
	45.8		16.2	57.4, 59.5	7.01	9.86		$(CD_3)_2SO$
$[Ph_2MePCH_2Sn(CH_3)_3]^+$	47.4	13.1	16.1	54.0, 56.4	7.35	9.78	7.32	$CDCl_3$
$[PhMe_2PCH_2Sn(CH_3)_3]^+$	49.2	13.7	16.4	55.6	7.68	9.76	7.56	$CDCl_3$ [a]
$[Ph_3PCH_2Si(CH_3)_3]^+$			18.0		6.82	9.94		$CDCl_3$ [b]
			18.4		6.81	9.93		$CDCl_3$ [c]
$[(OC)_5MoPPh_2CH_2CH_2PPh_2CH_2Sn(CH_3)_3]^+$			16.9	55.5	7.36	9.93		$CDCl_3$ [a]
$[(OC)_5]_5WPPh_2CH_2CH_2PPh_2CH_2Sn(CH_3)_3]^+$			16.9	55.2	7.35	9.92		$CDCl_3$ [a]

[a] Average coupling of ^{119}Sn and ^{117}Sn. [b] Ref. 5. [c] Ref. 4.

$[Ph_3PCH_2Si(CH_3)_3]Cl \rightleftharpoons Ph_3PCH_2 + (CH_3)_3SiCl$

$[Ph_3PCH_2Si(CH_3)_3]Cl + Ph_3PCH_2 \rightarrow Ph_3PCHSi(CH_3)_3 + [Ph_3PCH_3]I$

The reaction of PPh_3 with $(CH_3)_3SnCH_2I$ has not been investigated previously. Only one example of a quaternary phosphonium cation of the type reported in this paper appears in the literature. Seyferth and Grim isolated $[Ph_3PCH_2Sn(CH_3)_3][(CH_3)_3SnBr_2]$ from the reaction of Ph_3PCH_2 and $(CH_3)_3SnBr$ [6]. That these reactions are complex is illustrated by the fact that Schmidbaur and Tronich isolated only $[(CH_3)_3Sn]_2CPPh_3$ from the similar reaction of Ph_3PCH_2 and $(CH_3)_3SnCl$ [5].

Results and discussion

Tertiary phosphines react with $(CH_3)_3SnCH_2I$ at a rate which allows the reactions to be followed by ^1H NMR. Initially in each reaction, the expected quaternary phosphonium salt was formed.

$\geqslant P + (CH_3)_3SnCH_2I \rightarrow [\geqslant PCH_2Sn(CH_3)_3]I$

Proton NMR data for the phosphonium cations of this study are shown in Table I. Integration ratios were consistent with those predicted for the cations, and the observed coupling of the methylene protons to both phosphorus and tin support the assignment. Furthermore the data recorded for $[Ph_3PCH_2Sn(CH_3)_3]^+$ are very similar to the data for the known $[Ph_3PCH_2Si(CH_3)_3]^+$ [4,5].

Attempts to isolate the quaternary salts in pure form from chloroform, acetone, hexane, benzene and DMSO were unsuccessful. Invariably some contamination of the desired product with a methyl phosphonium salt was noted.

The rates of formation of the phosphonium cations at ambient temperature, as shown by repetitive NMR scans, increase in the series $(OC)_5MPPh_2CH_2CH_2PPh_2 < PPh_3 < MePh_2P < Me_2PhP$. The complete conversion of 0.09 g of $(CH_3)_3SnCH_2I$ by a stoichiometric quantity of PPh_3 in 2 ml of chloroform required approximately 2 h. The reaction of PPh_3 with $(CH_3)_3SiCH_2I$ under similar conditions proceeded much slower than the analogous tin reaction. After 3 d only 20% of $(CH_3)_3SiCH_2I$ had been converted to the corresponding phosphonium salt. Thus it is clear that $(CH_3)_3SnCH_2I$ is much more reactive toward PPh_3 than is $(CH_3)_3SiCH_2I$.

While $[Ph_3PCH_2Si(CH_3)_3]I$ is stable in chloroform at ambient temperature, $[Ph_3PCH_2Sn(CH_3)_3]I$ is unstable, decomposing nearly as rapidly as it is formed. Likewise the other tin cations of this study are unstable in chloroform. At elevated temperatures $[Ph_3PCH_2Si(CH_3)_3]Cl$ is known to establish an equilibrium with Ph_3PCH_2 and $(CH_3)_3SiCl$ which is followed by transylidation. It appears that the more reactive tin salts dissociate under much milder conditions. When the reaction of PPh_3 with $(CH_3)_3SnCH_2I$ is carried out in deuteriochloroform one can follow the decomposition of $[Ph_3PCH_2Sn(CH_3)_3]^+$ with ^1H NMR. As the signal for $(CH_3)_3Sn$ and the doublet for CH_2 diminish in intensity, a phosphorous-methyl doublet for $[Ph_3PMe]^+$ and a signal for $(CH_3)_3Sn$ of a new compound ($\tau = 9.44$; $J(Sn—CH_3) = 56$ Hz) appear. The new tin compound is also unstable and as the signal at $\tau = 9.44$ diminishes, a new signal at $\tau = 9.48$

appears ($J(Sn{-}CH_3) = 56$ Hz). Unfortunately, attempts to isolate these tin products have not been successful.

The instability of $[Ph_3PCH_2Sn(CH_3)_3]^+$ in various solvents almost certainly stems from the formation of the ylid, Ph_3PCH_2.

$$[Ph_3PCH_2Sn(CH_3)_3]I \rightleftharpoons Ph_3PCH_2 + (CH_3)_3SnI$$

Several lines of evidence support this conclusion. First, $[Ph_3PCH_3]I$ was isolated from the reaction mixture. Secondly, when the reaction was carried out in deuteriochloroform, the methyl protons of $[Ph_3PCH_3]I$ exchanged with the deuterium of the solvent until the phosphorus-methyl doublet disappeared from the NMR spectrum. As the phosphorus-methyl doublet disappeared, a signal for $HCCl_3$ appeared. Whether or not Ph_3PCH_2 reacts directly with deuteriochloroform as

$$Ph_3PCH_2 + DCCl_3 \rightleftharpoons [Ph_3PCH_2D]^+ + CCl_3^-$$

or first participates in transylidation

$$Ph_3PCH_2 + [Ph_3PCH_2Sn(CH_3)_3]^+ \rightleftharpoons [Ph_3PCH_3]^+ + Ph_3PCHSn(CH_3)_3$$

$$Ph_3PCHSn(CH_3)_3 + DCCl_3 \rightleftharpoons [Ph_3PCHDSn(CH_3)_3]^+ + CCl_3^-$$

is uncertain. Finally, if the reaction is carried out in DMSO, a solvent in which ylids are stable, the $[Ph_3CH_2Sn(CH_3)_3]^+$ which forms appears to be stable. After an initial conversion of a small amount of $[Ph_3PCH_2Sn(CH_3)_3]^+$ to $[Ph_3PCH_3]^+$, the $[Ph_3PCH_2Sn(CH_3)_3]^+$ which remained was stable during the 3 d of observation.

The tin phosphonium cations decomposed rapidly when methanol was added to solution in which they were dissolved.

The concentration of Ph_3PCH_2 in solution was not sufficient to detect its proton signals with certainty. Positive identification is hampered by absorption of trimethyltin protons in the region of interest and by possible exchange processes which have been described by Bestmann [7,8].

Experimental

Iodomethyltrimethyltin was prepared from trimethyltin chloride, diiodomethane, and a zinc/copper couple as described previously [9]. Commercial triphenylphosphine, diphenylmethylphosphine and phenyldimethylphosphine were used, after purification, in all reactions. The metal carbonylphosphines were prepared by cited procedures [1].

NMR spectra were recorded with a Jeol JNM-MH 100 100 MHz spectrometer.

Reactions were carried out under an atmosphere of dry nitrogen, solvents were dried, and traces of ethanol were removed from chloroform prior to use.

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