

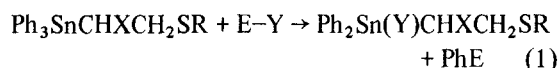
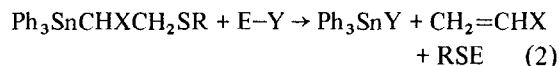
Reactions of $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{NMe}_2$ with Electrophilic Reagents

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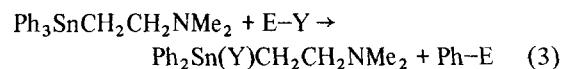
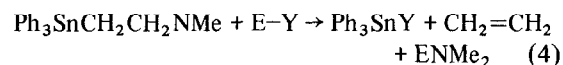
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For many tetraorganostannanes, the site of reaction with electrophilic species is independent of the specific electrophile. However, for the β -sulphides, $\text{Ph}_3\text{SnCHXCH}_2\text{SR}$ ($\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{SCN}$), two distinct electrophilic reactions were observed [1] (equations 1 and 2):

 $\text{R} = p\text{-MeC}_6\text{H}_4$; $\text{X} = \text{H}$; $\text{E-Y} = \text{I-I}; \text{ClHg-Cl}$ $\text{R} = o\text{-NO}_2\text{C}_6\text{H}_4$; $\text{X} = \text{Cl}$; $\text{E-Y} = \text{I-I}; \text{Br-Br}; \text{ClHg-Cl}$  $\text{R} = p\text{-MeC}_6\text{H}_4$; $\text{X} = \text{H}$; $\text{E-Y} = \text{Br-Br}; \text{Me-I}$; $o\text{-NO}_2\text{C}_6\text{H}_4\text{S-Cl}$ $\text{R} = o\text{-NO}_2\text{C}_6\text{H}_4$; $\text{X} = \text{Cl}$; $\text{E-Y} = o\text{-NO}_2\text{C}_6\text{H}_4\text{S-Cl}$

The report by Sato *et al.* [2] that another β -substituted tetraorganostannane, $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{NMe}_2$, on reaction with MeI produced ethylene led us to investigate further electrophilic reactions of this compound. We now wish to report our preliminary findings.

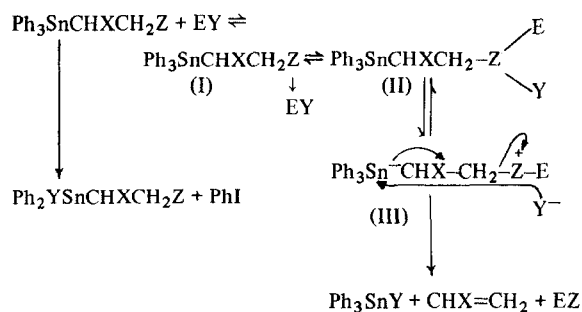
As with the β -sulphides, $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{NMe}_2$ reacted in two distinct ways (equations 3 and 4).

 $\text{E-Y}(\text{solvent}) = \text{ClHg-Cl}(\text{EtOH}); \text{Br-Br}(\text{CCl}_4); \text{I-I}(\text{CCl}_4)$  $\text{E-Y}(\text{solvent}) = p\text{-MeC}_6\text{H}_4\text{SO}_2\text{-Cl}(\text{CDCl}_3); o\text{-NO}_2\text{C}_6\text{H}_4\text{S-Cl}(\text{CCl}_4); \text{MeCO-Cl}(\text{CCl}_4); \text{Me-I}$

Each electrophile reacted predominantly, if not exclusively, *via* one of these reactions. The products of the reactions (all 1:1 except for MeI in which an excess was used) were either isolated (>80%) and correctly analysed or identified by comparison with

authentic samples (using n.m.r. and i.r. spectroscopy, g.l.c., *etc.*).

The reactions of $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{NMe}_2$, and also of $\text{Ph}_3\text{SnCHXCH}_2\text{SR}$, indicate that the major factor for alkene elimination is the development of a charged species, *i.e.* represented as III in the Scheme, or a related ion-pair at some point along the reaction pathway. Which of the two reactions occurs for each

 $\text{Z} = \text{SR} \text{ and } \text{NR}_2$ $\text{E-Y} = \text{Br-Br}, \text{I-I}, \text{ClHg-Cl}, \text{ArS-Cl}, \text{Me-I} \text{ etc.}$

Scheme

$\text{Ph}_3\text{SnCHXCH}_2\text{Z}/\text{EY}$ combination depends on the relative ease of phenyl-tin bond cleavage and charge development on the β -substituent. For example, HgCl_2 is able to cleave a Ph-Sn bond [3] and although it readily forms complexes with amines and sulphides, charged species (III) are most unlikely [4]. Thus, Ph-Sn bond cleavage by HgCl_2 is expected with the neutral HgCl_2 complexes merely appearing as cul-de-sacs in the reaction scheme. On the other hand, MeI , shown to be insufficiently reactive towards a Ph-Sn bond but capable of producing ammonium and sulphonium iodides, will react with $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{Z}$ ($\text{Z} = \text{NMe}_2$ and $\text{S-C}_6\text{H}_4\text{Me-}p$) to produce ethylene. The lability of a positive charged β -substituent can also be ascertained from the fact that both $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{NMe}_3^+$, I^- and $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{-CH}_2\text{NMe}_3^+$, I^- can be isolated from MeI reactions with the appropriate aminoalkylstannane.

References

- (a) J. L. Wardell, *J. Chem. Soc. Dalton*, 1786 (1975);
(b) R. D. Taylor and J. L. Wardell, *J. Organometal. Chem.*, 94, 15 (1975).
- Y. Sato, Y. Ban and H. Shirar, *J. Org. Chem.*, 38, 4373 (1973).
- R. C. Poller, "Chemistry of Organotin Compounds", Logos, London (1970).
- P. Biscarini, L. Fusina and G. D. Nivellini, *Inorg. Chem.*, 10, 2564 (1971).