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Reactions of $Ph_3SnCH_2CH_2NMe_2$ with Electrophilic Reagents

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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, $Ph_3SnCHXCH_2SR$ (X = H, Cl, Br, SCN), two distinct electrophilic reactions were observed [1] (equations 1 and 2):

$$Ph_3SnCHXCH_2SR + E{-}Y \rightarrow Ph_2Sn(Y)CHXCH_2SR + PhE \quad (1)$$

$R = p\text{-}MeC_6H_4$; $X = H$; $E{-}Y = I{-}I$; $ClHg{-}Cl$

$R = o\text{-}NO_2C_6H_4$; $X = Cl$; $E{-}Y = I{-}I$; $Br{-}Br$; $ClHg{-}Cl$

$$Ph_3SnCHXCH_2SR + E{-}Y \rightarrow Ph_3SnY + CH_2{=}CHX + RSE \quad (2)$$

$R = p\text{-}MeC_6H_4$; $X = H$; $E{-}Y = Br{-}Br$; $Me{-}I$; $o\text{-}NO_2C_6H_4S{-}Cl$

$R = o\text{-}NO_2C_6H_4$; $X = Cl$; $E{-}Y = o\text{-}NO_2C_6H_4S{-}Cl$

The report by Sato *et al.* [2] that another β-substituted tetraorganostannane, $Ph_3SnCH_2CH_2NMe_2$, 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, $Ph_3SnCH_2CH_2NMe_2$ reacted in two distinct ways (equations 3 and 4).

$$Ph_3SnCH_2CH_2NMe_2 + E{-}Y \rightarrow Ph_2Sn(Y)CH_2CH_2NMe_2 + Ph{-}E \quad (3)$$

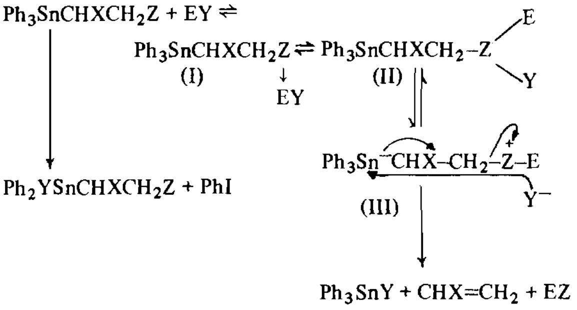
$E{-}Y(\text{solvent}) = ClHg{-}Cl(EtOH)$; $Br{-}Br(CCl_4)$; $I{-}I(CCl_4)$

$$Ph_3SnCH_2CH_2NMe + E{-}Y \rightarrow Ph_3SnY + CH_2{=}CH_2 + ENMe_2 \quad (4)$$

$E{-}Y(\text{solvent}) = p\text{-}MeC_6H_4SO_2{-}Cl(CDCl_3)$; $o\text{-}NO_2C_6H_4S{-}Cl(CCl_4)MeCO{-}Cl(CCl_4)$; $Me{-}I$

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 $Ph_3SnCH_2CH_2NMe_2$, and also of $Ph_3SnCHXCH_2SR$, 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 $Ph_3SnCHXCH_2Z/EY$ 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 $Ph_3SnCH_2CH_2Z$ (Z = NMe_2 and $S{-}C_6H_4Me\text{-}p$) to produce ethylene. The lability of a positive charged β-substituent can also be ascertained from the fact that both $Ph_3SnCH_2\overset{+}{N}Me_3$, I^- and $Ph_3SnCH_2CH_2CH_2\overset{+}{N}Me_3$, I^- can be isolated from MeI reactions with the appropriate aminoalkylstannane.



Z = SR and NR_2

E–Y = Br–Br, I–I, ClHg–Cl, ArS–Cl, Me–I *etc.*

Scheme

References

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