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Allyltin Chlorides in Chemical Synthesis. Insertion Reaction of Dibutylallyl- and Triallyltin Chlorides with Methyl-*i*-propyl-ketone

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Additions of tin–carbon bonds across a carbonyl function have been reported [1–5]. Representative of these are the insertions of several perhaloketones into the tin–allyl bond of trialkylallyltins [4, 5]. We now describe the preparation of dibutylallyl- and triallyltin chloride and their insertion reactions with methyl-*i*-propyl-ketone.

Experimental

Equimolecular amounts of dibutylallyltin (10 g) and dibutyltin dichloride (9.64 g, 31.7 mmol) were heated at 80 °C under stirring for 1 h. Distillation under reduced pressure of the crude liquid gave a product (15 g, 76% yield) boiling at 97–98 °C, 0.5 mm Hg. *Anal.* $C_{11}H_{23}ClSn$. Calcd.: C 42.69, H 7.49, Cl 11.45. Found: C 42.35, H 7.24, Cl 11.62%. MW in $CHCl_3$: calcd.: 309.44, found 313.

Dibutylallyltin chloride rapidly hydrolyzes in water–acetone mixture to form quantitatively a white precipitate of tetrabutyl-1,3-dichloro-distannoxane melting at 110 °C (Lit. [6] 110–112 °C).

Protolysis of the tin–allyl bond, as has already been shown for allyltins [7], takes place:

$$2Bu_2(CH_2{=}CHCH_2)SnCl + H_2O \rightarrow [Bu_2SnCl]_2O + 2CH_3CH{=}CH_2$$

Triallyltin chloride was prepared by adding dropwise tin tetrachloride (4.6 g, 17.6 mmol) to tetraallyltin (15 g, 53 mmol) at –25 °C. Then the mixture was allowed to react for 4 h at room temperature. Distillation under reduced pressure gave 15.6 g (about 80%) of a liquid boiling at 100 °C, 0.5 mm Hg. *Anal.* $C_9H_{15}ClSn$. Calcd.: C 38.97, H 5.45, Cl 12.78. Found: C 39.02, H 5.33, Cl 12.64%.

Hydrolysis of the triallyltin chloride in wet methanol leads to tetrallyl-1,3-dichlorodistannoxane, which is recovered as a solid by evaporating the solvent. Crystallization from n-hexane–$CHCl_3$ mixture gives a product melting at 109 °C.

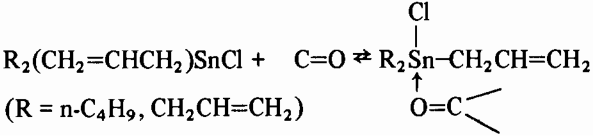
Hydrolysis in water–acetone medium (50/50, v/v) takes place more rapidly and more than one Sn–allyl bond are cleaved giving a mixture of tin and organotin oxides.

Addition Reactions

The following experiments have been carried out:
(1) Dibutylallyltin chloride (7.35 g, 23.7 mmol) was stirred with methyl-*i*-propyl-ketone (1.84 g, 21.33 mmol) at 80 °C. The reaction was followed at intervals by means of infrared spectra on a thin film (KBr discs). These indicate that the reaction goes to completion after about 7 h. The final spectrum reveals the disappearance of both the strong bands due to the C=O (1710 cm^{-1}) and to the C=C stretching vibrations of the allyl group linked to the tin atom (1625 cm^{-1}). In addition a new band centered at 1640 cm^{-1} attributable to the C=C stretch of a terminal alkenyl linkage removed from tin is observed [5]. After distillation under reduced pressure (1 mm Hg) to remove excess of the reagents, the insertion product remained as an oil. This was hydrolyzed with water. The reaction is very rapid: tetrabutyl-1,3-dichlorodistannoxane (5.8 g) was separated as precipitate. Then the filtrate was extracted with n-pentane and 2.1 g of 2,3-dimethyl-5-hexen-3-ol (76%) was recovered by distillation of the organic layer. B.p. 149 °C, lit. 151–153 °C [8].
(2) Following the same procedure, triallyltin chloride (10 g, 36 mmol) was allowed to react with the ketone (2.8 g, 32.6 mmol) at room temperature. The reaction was followed as above by monitoring IR spectra. It was completed after 2 h. The insertion product recovered as an oil hydrolyzed in water to yield hexenol (65%) and tin–organotin oxides.

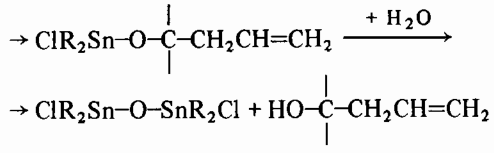
Conclusion

It seems to us that the previously reported insertion reactions involving a tin–allyl bond and a carbonyl function [4, 5] have been successful with trialkylallyltin derivatives since ketones bearing strong electron withdrawing groups were used. In our cases it is to be noted that the activated reagent is the organotin chloride since in this kind of compounds the carbonyl function can better coordinate to the tin center [9]. A coordination step may facilitate the overall reaction as is visualized in the following scheme:



$$R_2(CH_2{=}CHCH_2)SnCl + \; C{=}O \rightleftarrows R_2\overset{\displaystyle Cl}{\underset{\displaystyle \uparrow \atop O{=}C\!<}{Sn}}{-}CH_2CH{=}CH_2$$

$(R = n\text{-}C_4H_9, CH_2CH{=}CH_2)$



$$\rightarrow ClR_2Sn{-}O{-}\overset{|}{\underset{|}{C}}{-}CH_2CH{=}CH_2 \xrightarrow{+\ H_2O}$$

$$\rightarrow ClR_2Sn{-}O{-}SnR_2Cl + HO{-}\overset{|}{\underset{|}{C}}{-}CH_2CH{=}CH_2$$

Further studies involving allyltin derivatives and unsaturated substrates are now in progress.

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