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The Transfer of the Allyl Group from Allyl-di-alkyl-carbinols to Organotin Substrates

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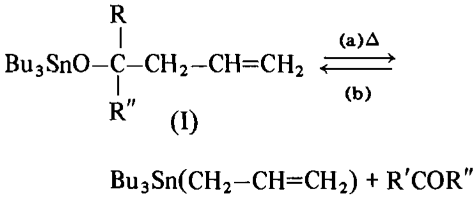
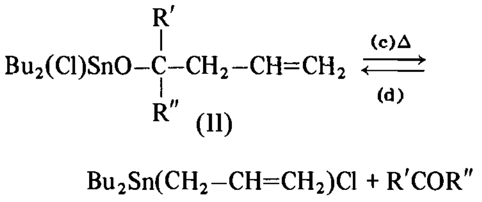
We wish to refer that allyl-dialkyl-carbinols react with $[Bu_3Sn]_2O$ and $[Bu_2SnCl]_2O$ giving the transfer of the allyl group from the organic substrate to the tin atom. Thus, the main products are water, the corresponding ketones and mixed allyltins: $Bu_3Sn(CH_2{-}CH{=}CH_2)$ and $Bu_2Sn(CH_2{-}CH{=}CH_2)Cl$ respectively.

The results can be based on the "reversibility" of the following reactions:



$$\underset{(I)}{\mathrm{Bu_3SnO{-}\overset{R}{\underset{R''}{C}}{-}CH_2{-}CH{=}CH_2}} \underset{(b)}{\overset{(a)\Delta}{\rightleftarrows}} \mathrm{Bu_3Sn(CH_2{-}CH{=}CH_2) + R'COR''} \qquad (1)$$



$$\underset{(II)}{\mathrm{Bu_2(Cl)SnO{-}\overset{R'}{\underset{R''}{C}}{-}CH_2{-}CH{=}CH_2}} \underset{(d)}{\overset{(c)\Delta}{\rightleftarrows}} \mathrm{Bu_2Sn(CH_2{-}CH{=}CH_2)Cl + R'COR''} \qquad (2)$$

since the organotin alkoxides (I) and (II) seem to be the intermediates of the reactions between the organotin oxides and the examined alcohols.

Paths (b) and (d) of reactions (1) and (2) have been previously established for some unsaturated organic compounds by different authors [1–5] and by us [6] respectively; no mention of paths (a) and (c) has been made hitherto.

Reaction of Bis-tri-n-butyltin Oxide and Methyl-isobutyl-allyl-carbinol (2,4-dimethyl-6-hepten-4-ol)

In a three necked flask (50 ml) equipped with a Vigreux column (12 cm) and a condenser, a thermometer and a separator funnel, bis-tri-n-butyltin oxide (23.4 g), commercially available from Schuchardt (München), and 11.6 g of methyl-isobutyl-allyl-carbinol (prepared as the Barbier–Grignard procedure [7]) were kept at 220 °C for 10 hours. During this time an equal amount of carbinol (11.6 g) was added dropwise and a liquid sample (16.04 g) was condensed and collected at a rate of about one drop every two minutes.

The infrared spectrum of the collected sample registered as a thin film (NaCl discs) showed the presence of the following relevant bands at: 3500 cm^{-1} (OH stretching vibration) and 1642 cm^{-1} (C=C stretching of an allyl group linked to the carbon atom), which refer to the original carbinol; and 1710 cm^{-1} dealing with the C=O stretching vibration of a carbonyl group.

Fractionation of this sample by the Auto Annular Still 251 (Perkin-Elmer) gave 0.8 g of water and 7.2 g of methyl-isobutyl-ketone boiling at 119–120 °C. The remainder was checked to be unreacted carbinol.

The infrared spectrum registered as a thin film (NaCl discs) on the residue showed the appearance of a band centered at 1625 cm^{-1} which is related with the C=C stretching vibration of the allyl group bonded to the tin atom [5, 6]. Thus distillation under reduced pressure of the residue gave 11.5 g of allyl-tri-n-butyltin boiling at 92–93 °C/0.3 mm (Lit. 89 °C/0.3 mm [8]).

Reaction of Tetra-n-butyl-1,3-dichlorodistannoxane and Methyl-isopropyl-allyl-carbinol (2,3-dimethyl-5-hexen-3-ol)

Similarly a mixture of tetra-butyl-1,3-dichlorodistannoxane (20 g) and methyl-isopropyl-allyl-carbinol (16 g) prepared by the Barbier–Grignard procedure [7] were heated at 200 °C for 12 hours. During this time a liquid sample (7.53 g) was collected. Its IR spectrum showed a strong band centered at 1710 cm^{-1} (C=O stretching vibration). Bands centered at 3500 and 1642 cm^{-1} which refer to the carbinol were absent. The sample resulted to be methyl-isopropyl-ketone (b.p. 95 °C) free from the parent carbinol.

The infrared spectrum registered on the residue presented the characteristic band centered at 1625 cm^{-1} dealing with an allyl group linked to the tin atom. Distillation under reduced pressure of the residue gave 9 g of allyl-di-n-butyltin chloride boiling at 110–115 °C/0.5 mm.

Reaction of Tetra-n-butyl-1,3-dichlorodistannoxane and Dimethyl-allyl-carbinol (2-methyl-4-penten-2-ol)

Following the same procedure a mixture of tetra-n-butyl-1,3-dichlorodistannoxane (23.5 g) and dimethyl-allyl-carbinol (16.6 g) were heated for 6 h at 200 °C. During this time acetone with a small amount of water was formed.

Distillation under reduced pressure of the residue gave 6.1 g of allyl-di-n-butyltin chloride boiling at 112–113 °C/0.7 mm.

In the two runs where $[Bu_2SnCl]_2O$ has been used, small amounts of Bu_2SnCl_2 and Bu_3SnCl have been found to be present in the residues.

Preparation of Allyl-tri-n-butyltin Chloride Through the Adduct (II) Having $R' = R'' = CH_3$

Adduct (II) ($R' = R'' = CH_3$) has been prepared following the previously described procedure for organotin alkoxides [9]. Metallic sodium (1.15 g) was added to 12 g of dimethyl-allyl-carbinol at room temperature. Then the mixture was kept at 70 °C. After 5 hours, 13.2 g of n-Bu_2SnCl_2 dissolved in 20 ml of carbinol were added dropwise during the course of two hours. Sodium chloride was formed as a precipitate.

Distillation under reduced pressure of the resulting slush gave the following products: unreacted carbinol (18 g), acetone (1.2 g) and allyl-di-n-butyltin chloride (7.8 g) boiling at 102–103 °C/0.3 mm.

The reaction may be explained as the following scheme:

$$CH_2{=}CH{-}CH_2(CH_3)_2C{-}ONa + Bu_2SnCl_2 \xrightarrow{-NaCl}$$

$$Bu_2(Cl)Sn{-}O{-}C(CH_3)_2CH_2{-}CH{=}CH_2 \xrightarrow{\Delta}$$

$$Bu_2Sn(CH_2{-}CH{=}CH_2)Cl + (CH_3)_2CO$$

On the basis of these findings at present it seems to us reasonably established that the reactions between allyl-dialkyl-carbinols and the two used organotin oxides go through the formation of the alkoxides (I) and (II). These, on heating, arrange themselves with transfer of the allyl group to give ketones and mixed allyltins. Other systems are now under consideration.

Acknowledgments

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