CHEMISTRY LETTERS, pp. 829-830, 1981.

# PALLADIUM CATALYZED REACTION OF HEXABUTYLDITIN WITH ARYL BROMIDES: PREPARATION OF NEGATIVELY SUBSTITUTED ARYLTRIBUTYLTIN

Masanori KOSUGI, Kohji SHIMIZU, Atsushi OHTANI, and Toshihiko MIGITA
Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376

Reaction of hexabutylditin with aryl bromides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium was found to be a promising tool to prepare aryltributyltins, particularly negatively substituted ($-NO_2$, -COMe, -CN) phenyltin compounds.

Aryltin compounds in which the aryl groups bear reactive functional substituents (e.g. $-NO_2$, -COR, -CN, etc.) are difficult to be prepared by ordinary methods. In 1976, Eaborn and his colleagues showed that hexabutyl- and hexamethylditin reacted with some aryl bromides to give aryltrialkyltin, but p-nitrophenyltin compounds could not be prepared by the reaction, which gave only biaryl.$^{1)}$ These results are striking contrast to the corresponding reaction of silane.$^{2)}$ To avoid the formation of biaryl, we reinvestigated the reaction of hexabutylditin with aryl bromides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium under various mild conditions, and found the reaction to be useful to prepare aryltin compounds bearing such functional substituents as nitro, cyano and acyl groups.

$$Bu_3SnSnBu_3 + ArBr \xrightarrow{Pd(PPh_3)_4} ArSnBu_3 + Bu_3SnBr + ArAr$$

Reactions were carried out as follows; a solution of hexabutylditin(12 mmol), aryl bromide(10 mmol), and tetrakis(triphenylphosphine)palladium(0.1 mmol) in tolutne(20 ml) was heated at 80°C with stirring under argon atmosphere. The reaction was completed when the color of the solution turned to black. At this point, the aryl bromide was almost completely consumed. After evaporation of the solvent, the solid material, identified as corresponding biaryl after recrystallization from ethanol was filtered. The filtrate was washed with aqueous potassium fluoride to remove the tributyltin bromide as the insoluble tin fluoride. The organic layer was extracted with benzene and dried over sodium salfate. Purification was performed by column chromatography (benzene, petrolim ether on Silica gel). Satisfactory results of elemental analysis were obtained for aryltin compounds thus obtained.

The results are presented in Table 1. As shown in the Table, nitrophenyl-, cyanophenyl-, and acetylphenyl-tributyltins together with substantial amounts of biaryls are obtained. It is interesting to note that in the reactions of o-substituted aryl bromides, no biaryl was obtained, probably due to the steric effect, and the yields of aryltin compounds were rather high. Since biaryls can be considered to be formed through the reaction of aryltin compound once produced with aryl bromide in the presence of tetrakis(triphenylphosphine)palladium,$^{3,4)}$ usage of excess amounts of ditins may prevent the biaryl formation. The trend was actually observed as shown in Table 2.

The yield of phenyltributyltin was increased at the expense of biphenyl by increasing the concentration of the ditin. It seems likely that the use of about three molar excess of hexabutylditin makes the reaction more promising for synthetic purpose.$^{5)}$ At present, the reactions are considered to proceed through the oxidative addition of aryl bromides to the palladium, followed by metathesis by the ditins, and finally the reductive elimination gives the products. As the reaction proceeds, the product aryltins take part in the metathesis with the oxidative adducts if the concentration of the ditins are low. Further works are in progress.

Table 1. Reaction of $Bu_3SnSnBu_3$ with ArBr in the Presence of $Pd(PPh_3)$ at 80°C

| Aryl Bromides | Products and Yield (%)* | | | |
|---|---|---|---|---|
| X-$C_6H_4$Br | X-$C_6H_4SnBu_3$ | (%) | Symmetrical biaryls | |
| p-$NO_2$- | p-$NO_2$- | 38 (58) | p,p'-di-$NO_2$ | 13 |
| m-$NO_2$- | m-$NO_2$- | 23 (33) | m,m'-di-$NO_2$ | 11 |
| o-$NO_2$- | o-$NO_2$- | 59 (67) | o,o'-di-$NO_2$ | 0 |
| p-CN- | p-CN- | 22 (39) | p,p'-di-CN | 16 |
| m-CN- | m-CN- | 31 (40) | m,m'-di-CN | 18 |
| o-CN- | o-CN- | 42 (52) | o,o'-di-CN | 0 |
| p-$CH_3$CO- | p-$CH_3$CO- | 21 (34) | p,p'-di-$CH_3$CO | 14 |
| o-$CH_3$CO- | o-$CH_3$CO- | 25 (50) | o,o'-di-$CH_3$CO | 0 |

* Isolated yield based on aryl bromides. In parenthesis GLC yield.

Table 2. Reaction of $Bu_3SnSnBu_3$ with PhBr in the Presence of $Pd(PPh_3)_4$ at 80°C

| Reactants | | | Yield of Products (%) | |
|---|---|---|---|---|
| $Bu_3SnSnBu_3$ | PhBr | $Pd(PPh_3)_4$ | $PhSnBu_3$ | PhPh |
| 1.1 mmol | 1 mmol | 0.01 mmol | 58 | 11 |
| 3 | 1 | 0.01 | 85 | 4 |
| 8 | 1 | 0.01 | 89 | 1 |

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(Received April 17, 1981)