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A NEW PALLADIUM CATALYZED AROMATIC ACETONYLATION BY ACETONYLTRIBUTYLTIN

Masanori KOSUGI, Mikio SUZUKI, Isao HAGIWARA, Katsuhisa GOTO,
Kyoko SAITOH, and Toshihiko MIGITA*
Department of Chemistry, Faculty of Technology, Gunma Univesity,
Kiryu, Gunma, 376

The reaction of acetonyltributyltin, prepared from tributyltin methoxide and isopropenyl acetate *in situ*, with aryl bromide in the presence of a catalytic amount of $PdCl_2(o\text{-}Tolyl_3P)_2$ was found to give arylacetones in good yields.

The α-arylation of enolates is very difficult in general. A few methods have been recently developed for this purpose. One of the promising methods is Bunnett's photochemical arylation (S_{RN} 1 mechanism),$^{1)}$ and the other is the transition metal catalyzed arylation of enolate and cognate reagents.$^{2)}$ While organotin enolates have been shown to react both with carbonyl compounds to give addition products$^{3)}$ and with alkyl halides to give substitution products,$^{3,4)}$ there is no example of the reaction with aryl halides.

We report here, the first palladium catalyzed acetonylation of aryl bromides with acetonyltributyltin.

$$Bu_3SnCH_2COCH_3 \quad + \quad ArBr \xrightarrow{[Pd]} ArCH_2COCH_3 \quad + \quad Bu_3SnBr$$

After preliminary trials, the best procedure was found to be the "*in situ*" method as follows;

$$Bu_3SnOCH_3 \quad + \quad CH_3CO_2C(CH_3){=}CH_2 \longrightarrow [Bu_3SnCH_2COCH_3] \quad + \quad CH_3CO_2CH_3$$

$$[Bu_3SnCH_2COCH_3] \quad + \quad ArBr \xrightarrow{[Pd]} ArCH_2COCH_3 \quad + \quad Bu_3SnBr$$

A solution of tributyltin methoxide (15 mmol), isopropenyl acetate (15 mmol), aryl bromide (10 mmol), palladium complex (0.1 mmol) in toluene (5 ml) was heated with stirrig under argon atmosphere at 100°C for 5 h. After the evaporation of the solvent and methyl acetate, the residue was subjected to column chromatography (eluted with cyclohexane followed by diethyl ether on Silica gel). Arylacetone was obtained from the ethereal fraction by distillation under reduced pressure. Results were listed in Table.

As shown in Table, the isolated yields were reasonably high irrespective of the substitutent in aryl bromide, indicating that the reaction can be used for the preparation of arylacetones. $PdCl_2(o\text{-}Tolyl_3P)_2$ was the best catalyst among the various complexes examined. Palladium acetate combined with twice molar amounts of

Table Pd-Catalyzed Reactions of Acetonyltributyltin Prepared *in situ* with Various Aryl Bromides

R-C_6H_4Br	Catalyst	Yield* of $ArCH_2COCH_3$	b.p.
H-	$Pd(Ph_3P)_4$	(22) %	
H-	$PdCl_2(Ph_3P)_2$	(15)	
H-	$PdCl_2$(o-Tolyl$_3$P)$_2$	78 (83)	88-92°/15 mmHg
H-	$PdCl_2$(p-Tolyl$_3$P)$_2$	(16)	
H-	$PdCl_2$(o-Cl-phenyl$_3$P)$_2$	(68)	
p-Me_2N-	$PdCl_2$(o-Tolyl$_3$P)$_2$	71 (74)	103-104°/2.5
p-MeO-	$PdCl_2$(o-Tolyl$_3$P)$_2$	51 (66)	88-90°/3
o-Me-	$PdCl_2$(o-Tolyl$_3$P)$_2$	91 (100)	97-99°/16
m-Me-	$PdCl_2$(o-Tolyl$_3$P)$_2$	88 (95)	95-97°/14
p-Me-	$PdCl_2$(o-Tolyl$_3$P)$_2$	80 (84)	122-125°/35
p-Cl-	$PdCl_2$(o-Tolyl$_3$P)$_2$	73 (74)	115-117°/15
p-MeCO-	$PdCl_2$(o-Tolyl$_3$P)$_2$	64 (71)	128-130°/2.5, 43-44°(m.p.)

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

tri-o-tolylphosphine was also an effective catalyst for this reaction. It is interesting that tri-o-chlorophenylphosphine was secondly better ligand.

Among halobenzenes, bromobenzene was the best substrate. Chlorobenzene did not react with this reagent, and iodobenzene which was considered to be more reactive, gave the product in poor yields.

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