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ALKYLATION OF ARALKYL BROMIDES WITH TETRA ALKYL TIN COMPOUNDS IN PRESENCE OF (2,2'-BIPYRIDINE)FUMARONITRILE PALLADIUM(0)

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Abstract: (2,2'-bipyridine)fumaronitrile palladium(0) acts catalytically in the alkylation of benzylic halides with tetra alkyl tin even for an alkyl halide with hydrogen atoms on a sp^3 carbon *β* to the leaving group.

Recently we discovered that reductive elimination from (2,2'-bipyridine) *diethylpalladium(II) in the presence of electron deficient olefins gives n*-butane in high yield[1]. With olefins, being better electron acceptors than methyl acrylate, as for instance fumaronitrile, one isolates as organometallic reaction product (2,2'-bipyridine)olefin palladium(0) complexes[2]. It was also shown that the olefin takes part in the rate limiting step of the CC-coupling reaction[3]. We now demonstrate that these observations can be utilized for reactions in which palladium(0) acts catalytically in CC-bond formation. Our particular goal are reactions in which CC-bond formation occurs between alkyl groups with *β*-hydrogen atoms on a sp^3 carbon.

Palladium catalyzed CC-coupling reactions are of great synthetic utility in Organic Chemistry[4]. One of the more recent applications deals with the reaction of organic halides with tetra alkyl tin compounds (eq.1)[5]. This reaction is, however, limited to alkyl halides without hydrogen atoms on a sp^3 carbon *β* to the carbon atom bearing the leaving group. In the latter case olefin formation overrides the CC-coupling reaction. We chose this particular reaction for a first test of the catalytic activity of (2,2'-bipyridine)-fumaronitrile palladium(0) (1).

$$R-X \ + \ R'_4Sn \ \xrightarrow[\text{HMPTA}]{\text{Pd (0) } L_n} \ R-R' \ + \ R'_3SnX \qquad (1)$$

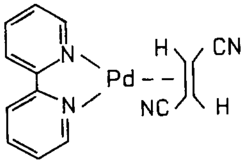
$$R = C_6H_5CH_2- \ , \ H_2C=CH-CH_2- \ , \ H_2C=CH- \ , \ C_6H_5- \ , \ R''CO-$$

$$R' = \text{alkyl}$$

Table 1: Reactions of benzyl bromide and α-phenyl ethyl bromide with tetra alkyl tin compounds in the presence of palladium complexes[a]

No.	R-Br	R'_4Sn	t (h)	T (^oC)	molar ratio Kat/RBr/R'_4Sn	fumaronitrile (Mol)	R-R'[b] (%)	conversion[b] (%)	catalyst
1.	$PhCH_2Br$	Me_4Sn	15	60	1/ 70/140	-	94	100	(FMD)Pd(bpy)
2.	$PhCH_2Br$	Me_4Sn	20	60	1/200/460	-	93	100	(FMD)Pd(bpy)
3.	$PhCH_2Br$	Me_4Sn	24	60	1/ 70/140	$1.0 x 10^{-4}$	76	88	(FMD)Pd(bpy)
4.	$PhCH_2Br$	Me_4Sn	76	20	1/ 70/140	-	76	97	$(Et_2)Pd(bpy)$
5.	$PhCH_2Br$	Me_4Sn	70	20	1/ 70/140	-	82	97	$(Et_2)Pd(bpy)$
6.	$PhCH_2Br$	Me_4Sn	24	60	1/ 70/140	$2.0 x 10^{-4}$	85	93	$(Et_2)Pd(bpy)$
7.	$PhCH_2Br$	Me_4Sn	40	60	-/ 1/ 2	-	0	0	-
8.	$PhCH_2Br$	Me_4Sn	20	60	-/ 1/ 2	-	0	0	-
9.	$PhCHBrCH_3$	Me_4Sn	26	60	1/107/170	-	34	42	(FMD)Pd(bpy)
10.	$PhCHBrCH_3$	Me_4Sn	66	60	1/ 70/140	$1.5 x 10^{-4}$	61	71	$(Et_2)Pd(bpy)$
11.	$PhCHBrCH_3$	Me_4Sn	113	60	1/ 70/140	$2.0 x 10^{-4}$	77	89	$(Et_2)Pd(bpy)$
12.	$PhCHBrCH_3$	Me_4Sn	114	60	1/ 70/140	$4.3 x 10^{-5}$	23	97	$(Et_2)Pd(bpy)$
13.	$PhCHBrCH_3$	Me_4Sn	25	60	1/ 70/140	$4.0 x 10^{-5}$	22	54	$(Et_2)Pd(bpy)$
14.	$PhCHBrCH_3$	Me_4Sn	42	60	1/ 70/140	-	2	36	$(Et_2)Pd(bpy)$
15.	$PhCHBrCH_3$	Me_4Sn	42	20	1/ 70/140	-	0	0	$(Et_2)Pd(bpy)$
16.	$PhCHBrCH_3$	Et_4Sn	27	60	1/106/212	-	37	41	(FMD)Pd(bpy)
17.	$PhCHBrCH_3$	Et_4Sn	22	60	-	-	0	0	-

a) ca. 2.0 mmol aralkyl bromide in 3.0 ml hexamethyl phosphorous triamide (HMPTA) were reacted in presence of 3.0×10^{-5} mol palladium complex; b) determined by GLC with a 10 % SE-30 glass column.



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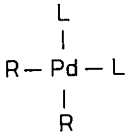

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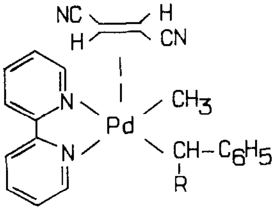
In Stille's work[5], where tetrakis triphenyl phosphane is used as source of palladium(0), a dialkyl ligand palladium(II) intermediate 2 is formulated in the catalytic cycle. Reductive elimination from this complex leads to CC-bond formation. In our study[1] we had shown that this elementary step can be influenced by the presence of olefins.

Table 1 reports results for reactions of benzyl bromide and α-phenyl ethyl bromide mainly with tetra methyl tin. Benzyl bromide was chosen to test principally the catalytic capability of (2,2'-bipyridine)fumaronitrile palladium(0) in this reaction, α-phenyl ethyl bromide should demonstrate whether the presence of hydrogen atoms on a sp^3 carbon β to the leaving group in the alkyl halide alters the course of the reaction.

Experiments 1 and 2 demonstrate that a catalytic activity is found for the alkylation of benzyl bromide with tetra methyl tin if (2,2'-bipyridine)-fumaronitrile palladium(0) is added. Quantitative conversion of benzyl bromide leads in almost quantitative yield to ethyl benzene. Addition of fumaronitrile does not show a significant change (experiment 3). Instead of using 1 as precursor of the catalytic species one may take (2,2'-bipyridine)diethyl palladium(II) (experiments 4 and 5) or one may add fumaronitrile to the solution which contains the diethyl palladium complex (experiment 6). The latter procedure leads to an in situ formation of the (2,2'-bipyridine)fumaronitrile palladium(0) complex with liberation of n-butane. Experiments 7 and 8 were run in order to show that no conversion of benzyl bromide takes place in the absence of the palladium complexes. Thus we have shown that either (2,2'-bipyridine)fumaronitrile palladium(0) or (2,2'-bipyridine)diethyl palladium-(II) may act catalytically in the coupling reaction.

The crucial experiments are those with α-phenyl ethyl bromide which offers three hydrogen atoms in β-position to the halogen atom on a sp^3 carbon. Cumene is, indeed, formed in the reaction (experiment 9). Experiments 14 and 15 prove that fumaronitrile is essential for this CC-bond formation. In contrast to the reaction with benzyl bromide (2,2'-bipyridine)diethyl palladium-(II) alone is not sufficient for the success of the reaction. The product of β-H-elimination, styrene, is produced under these conditions. Similarly experiments 10-13 underline the necessary presence of fumaronitrile. With decreasing olefin concentration one finds lower yields of cumene even though the conversion of α-phenyl ethyl bromide is high. In these cases styrene is formed as main product. Experiments 16 and 17 were carried out to widen the scope of the transformations to other tetra alkyl tin compounds.



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R = H, CH3

(2,2'-bipyridine)fumaronitrile-palladium(0) seems to be the first palladium complex which enables the coupling of alkyl halides with hydrogen atoms on a sp^3 carbon atom β to the leaving group. From the result that the olefin is essential for this reaction we conclude that the final reductive elimination to form ethyl benzene or cumene occurs in a species to which fumaronitrile is coordinated. The absence of β-hydrogen elimination must, in fact, be the consequence of the coordination of the olefin. One mechanistic description of β-hydrogen elimination requires a free coordination site in order to transfer a hydrogen atom from the ligand to the central metal atom prior to the departure of the olefin. In view of our studies on (2,2'-bipyridine)diethyl palladium(II)[1,3] we thus suggest that a fivefold coordinated palladium-(II) complex 3 is involved in the product forming step.

The variability of this catalytic reaction is presently explored.

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