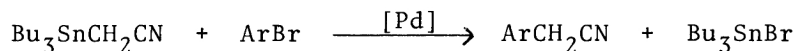


PALLADIUM CATALYZED REACTION OF ARYL BROMIDES WITH CYANOMETHYL-
TRIBUTYLTIN. AROMATIC CYANOMETHYLATIONMasanori KOSUGI, Masahiro ISHIGURO, Yoshikazu NEGISHI, Hiroshi SANNO,
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Palladium catalyzed reaction of aryl bromides with cyanomethyltributyltin gave arylacetonitriles in moderate yields. Aryl bromides having strong electron-withdrawing groups (such as acyl, cyano, nitro, etc.) cannot be applied to the reaction.

Palladium catalyzed cross-coupling between organic halides and organometallics is useful for carbon-carbon bond formation.¹⁾ Among these organometallics, organotin compounds are worthy to notice, since many kinds of functional organotin (allyl, vinyl, aryl, acetyl, methoxymethyl, etc.) can be prepared easily and be applied to the cross-coupling, providing new tools for nucleophilic C-C bond formation toward aryl bromides.²⁾ In this letter, we wish to report the palladium catalyzed reaction of aryl bromides with cyanomethyltributyltin. To our knowledge, there have been few reports on the direct cyanomethylation of aryl halides.³⁾



The reaction was carried out as follows: a mixture of aryl bromide (3.0 mmol), cyanomethyltributyltin (4.5 mmol), $\text{PdCl}_2[\text{P}(\text{o-tolyl})_3]_2$ (0.03 mmol), and m-xylene (4 ml) as a solvent was degassed and heated at 120 °C until the color of the mixture turning to black. After evaporation of the solvent, column chromatography of the residue (silica gel; cyclohexane followed by ether as an eluent) provided the arylacetonitrile in the ethereal eluate, from which the products were isolated by distillation under reduced pressure. Results are shown in Table 1.

Table 1. Cyanomethylation of Aryl Bromides by Means of Cyanomethyltributyltin

R-C ₆ H ₄ Br	Time h	Solvent	Catalyst	Yield of ArCH ₂ CN	Bp/°C
				% ^{a)}	(mmHg) ^{b)}
H-	3	xylene	none	0	
	3		PdCl ₂ (PPh ₃) ₂	(22)	
	3		PdCl ₂ [P(o-toly) ₃] ₂	72	38(0.15)
	3	CHCl ₃	(33)		
	3	HMPA	(26)		
	3	THF	(55)		
	3	dioxane	(45)		
o-CH ₃ -	3	xylene		74	43(0.2)
m-CH ₃ -	3			74	44(0.2)
p-CH ₃ -	3			78	55(0.5)
o-CH ₃ O-	3			70	48(0.4)
p-CH ₃ O-	3			77	55(0.6)
o-Cl-	24			67	45(0.2)
p-Cl-	24			66	64(0.8)
p-CH ₃ CO-	20		trace		
p-CN-	20		trace		
p-NO ₂ -	3		trace		

a) Isolated yield (GLC yield in parentheses). b) Uncorrected value by Kugelrohr.

As Table 1 shows, the proper catalysts and applicable aryl bromides are quite similar to those used in the reaction of aryl bromides with acetyltributyltin.⁴⁾ Again PdCl₂[P(o-tolyl)₃]₂ was the best catalyst, and xylene was the best solvent, and aryl bromides having strong electron-withdrawing group could not give satisfactory results. Nevertheless, the present method may be useful for cyanomethylation of ordinary aryl bromides.

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