Reactions of 2-(Tributylstannyl)-4,4-dimethyl-2-oxazoline with Organic Halides. Unusual Product from Aroyl Halide

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2-(Tributylstannyl)-4,4-dimethyl-2-oxazoline (1) reacted with aroyl chloride smoothly without any palladium catalyst to give the unusual product, bis(N-aroyl-4,4-dimethyl-2-oxazolinylidene) in good yields. The reaction of 1 with other types of halide needed a palladium catalyst, and gave the corresponding 2-substituted-4,4-dimethyl-2-oxazoline in good yields.

Oxazoline is an important synthetic intermediate which is easily converted into carboxylic acid, ketone, nitrile etc.¹⁾ Recently, 2-(trimethylstannyl)-4,4-dimethyl-2-oxazoline was reported to react with aryl bromides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium giving the corresponding 2-aryl-4,4-dimethyl-2-oxazoline in good yields.²⁾ From the view of our series of investigation about the palladium-catalyzed reactions of organo-tin reagents, this behavior of stannyl oxazoline is interesting, because C-stannyl imines except stannyl aromatics such as 2-stannyl-benzoxazole, -thiazole, and -imidazole have been found not to react with organic halides.³⁾

So we clarify the scope and limitation of the coupling reaction of 2-(tributylstannyl)-4,4-dimethyl-2-oxazoline (1) with various types of halide,

$$Bu_{3}Sn \swarrow_{O}^{N} \downarrow^{+} RX \xrightarrow{[Pd]} R \swarrow_{O}^{N} \downarrow^{+} Bu_{3}SnX$$

and found that the unusual reaction took place with aroyl halide.

As shown in Table 1, the reaction of 1 with aroyl chloride which was carried out being expected to form the α -keto acid equivalents, proceeded smoothly without a catalyst to give the crystalline product in good yields. The result of elemental analysis of the crystal was consistent with that of the expected 2-benzoyl-4,4-dimethyl- 2-oxazoline. Its ¹H NMR spectra, however, showed the signal of methylene proton at 3.00 ppm which was different from that of the ordinary oxazoline (3.8-3.9 ppm). MS spectra showed that the molecular weight of the product corresponded to a dimer of the expected compound. A single crystal X-ray analysis showed the molecular structure being bis(Nbenzoyl-4,4-di-methyl-2-oxazolinylidene) (2-A) (Fig. 1). Such type of the product was so far reported to be formed from the reaction with 2-trimethylstannylbenzothiazole with acetyl chloride only in low yields, and not with 2trimethylstannylbenzoxazole.⁴)

Table 1. Reaction of 1 with Acid Chloride						
2 1 + 2	2 ArCOCl in	.t. hexane		$\frac{1}{2}$ + 2 Bu ₃ SnCl		
Ar- Yi	eld of 2 ^{a)} /%	Mp/°C	MS: M ⁺	$\frac{2}{1}$ H NMR δ		
Ph-	84, 2-A	302-303	406	1.36(s,6H), 3.00(s,2H),		
				7.20-7.78(m,5H)		
p-MeC ₆ H ₄ -	75, 2-в	286-287	434	1.34(s,6H), 2.40(s,3H),		
				3.30(s,2H), 6.98-7.70(m,4H)		
p-MeOC ₆ H ₄ -	73, 2-C	251-253	466	1.40(s,6H), 3.17(s,2H),		
				3.90(s,3H), 6.80-7.83(m,4H)		
p-ClC ₆ H ₄ -	82, 2-D	297-298	474	1.41(s,6H), 3.20(s,2H),		
				7.16-7.72(m,4H)		
p-NO ₂ C ₆ H ₄ -	85, <u>2</u> -Е	297-298	496	b)		
	76, 2-F	280-282	418	1.41(s,6H), 3.40(s,2H),		
s s s				6.82-7.88(m,3H)		
cyclo-C ₆ H ₁₁ -	17, 2-G	195-196	418	0.72-2.10(m,16H), 2.31-2.82		
	-			(m,1H), 3.71(s,2H)		

a) Elemental analyses gave satisfactory results.⁵) b) Insoluble in CDCl₃.

It should be noted here again that $2 \\ \sim 2 \\ \sim$



Fig.1. Computer-generating drawing of 2-A as determined by X-ray crystallographic analysis.⁶)

The reaction of 1 with other types of organic halide needed a palladium catalyst like the reaction with aryl bromide reported by Dondori et al.,²) but the most effective catalyst was dichloro-bis(triphenylphosphine)palladium in place of tetrakis(triphenylphosphine)palladium as shown in Table 2.

Table 2. Palladium-Catalyzed Reaction of 1 with Other Type of Halides

RX	[Pd](mol%)	Isolated yield of 3/%
PhBr	Pd(PPh ₃) ₄ (1)	(25)a)
PhBr	$Pd(PPh_3)_4$ (5)	(81)
PhBr	$PdCl_2(PPh_3)_2$ (1)	(73), 70
PhBr	$PdCl_2[P(o-tolyl)_3]_2$ (1)	trace
PhCH ₂ Cl	$PdCl_2(PPh_3)_2$ (1)	58
Me ₂ C=CHBr	$PdCl_2(PPh_3)_2$ (1)	51
Me ₂ C=CMeBr	$PdCl_2(PPh_3)_2$ (1)	65
PhCH=CHBr (E)	$PdCl_2(PPh_3)_2$ (1)	77 (E)
PhCH=CHBr (Z>90%)	$PdCl_2(PPh_3)_2$ (1)	95 (Z/E= 1/1)
CH2=CMeCH2Cl	$PdCl_2(PPh_3)_2$ (1)	47
Me ₂ C=CHCH ₂ Br	$PdCl_2(PPh_3)_2$ (1)	51

 $RX + 1 \longrightarrow Bu_3SnX$

a) In parentheses GLC yield.

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5) 2-A, Found: C, 70.98; H, 6.42; N, 6.98%. Calcd for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45; N, 6.89%. 2-B, Found: C, 71.68; H, 6.85; N, 6.45%. Calcd for $C_{13}H_{15}O_2N$: C, 71.86; H, 6.96; N, 6.45%. 2-C, Found: C, 66.62; H, 6.61; N, 6.19%. Calcd for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01%. 2-D, exact MS, Found: m/e 474.1090. Calcd for $C_{24}H_{24}O_4N_2Cl_2$: 474.1113. 2-E, Found: C, 57.73; H, 4.87; N, 11.29%. Calcd for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.87; N, 11.29%. 2-F, exact MS, Found: m/e 418.1075. Calcd for $C_{20}H_{22}O_4N_2S_2$: 418.1021. 2-G, Found: C, 69.06; H, 8.95; N, 6.64%. Calcd for $C_{12}H_{19}O_2N$: C, 68.87; H, 9.15; N, 6.69%.

6) Crystal data of 2-A: $C_{24}H_{26}O_{4}N_{2}$, Fw 406.2, space group P_{21}/n , a=10.687 (8), b=16.999 (9), c=5.818 (1) Å, β =93.14°(4), V=1055.3 (9) Å³, Z=2, d_{calcd}=1.28 g cm⁻³, the final R factor 0.0903, number of unique reflections ($|F_{0}|_{2}3\sigma|F_{0}|$) 3075.

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