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

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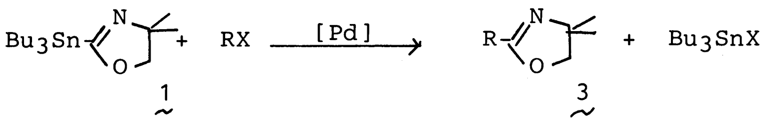
2-(Tributylstannyl)-4,4-dimethyl-2-oxazoline (**1**) reacted with aroyl chloride smoothly without any palladium catalyst to give the unusual product, bis(N-aroyl-4,4-dimethyl-2-oxazolinylidene) in good yields. The reaction of **1** with other types of halide needed a palladium catalyst, and gave the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

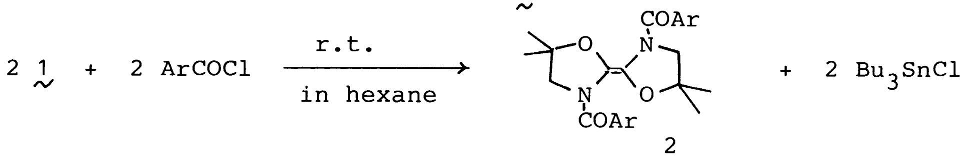
So we clarify the scope and limitation of the coupling reaction of 2-(tributylstannyl)-4,4-dimethyl-2-oxazoline (**1**) with various types of halide,

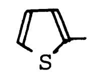


and found that the unusual reaction took place with aroyl halide.

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 ^{1}H 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(N-benzoyl-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-trimethyl-stannylbenzothiazole with acetyl chloride only in low yields, and not with 2-trimethylstannylbenzoxazole.[4]

Table 1. Reaction of **1** with Acid Chloride



Ar-	Yield of **2**$^{a)}$/%	Mp/°C	MS: M$^+$	^{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_6H_4-	75, **2**-B	286-287	434	1.34(s,6H), 2.40(s,3H), 3.30(s,2H), 6.98-7.70(m,4H)
p-$MeOC_6H_4$-	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_6H_4-	82, **2**-D	297-298	474	1.41(s,6H), 3.20(s,2H), 7.16-7.72(m,4H)
p-$NO_2C_6H_4$-	85, **2**-E	297-298	496	b)
	76, **2**-F	280-282	418	1.41(s,6H), 3.40(s,2H), 6.82-7.88(m,3H)
cyclo-C_6H_{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 $CDCl_3$.

It should be noted here again that 2 could be obtained in good yields from the reaction of 1 only with aroyl halides, but not with aliphatic acid chlorides, such as acetyl, pentanoyl, and 2,2-dimethylpropanoyl chloride etc.

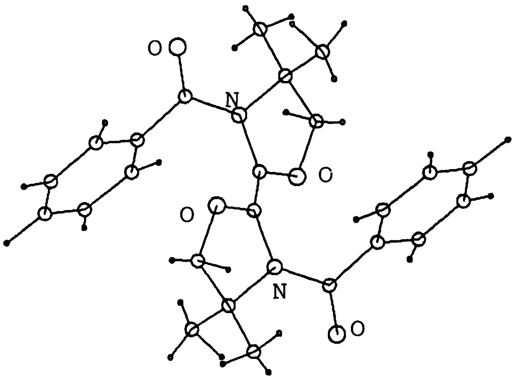


Fig.1. Computer-generating drawing of 2-A as determined by X-ray crystallographic analysis.[6)]

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

$$\mathrm{RX} + \mathbf{1} \xrightarrow{[\mathrm{Pd}]} \mathbf{3} + \mathrm{Bu_3SnX}$$

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	$PdCl_2[P(o\text{-tolyl})_3]_2$ (1)	trace
$PhCH_2Cl$	$PdCl_2(PPh_3)_2$ (1)	58
$Me_2C{=}CHBr$	$PdCl_2(PPh_3)_2$ (1)	51
$Me_2C{=}CMeBr$	$PdCl_2(PPh_3)_2$ (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)
$CH_2{=}CMeCH_2Cl$	$PdCl_2(PPh_3)_2$ (1)	47
$Me_2C{=}CHCH_2Br$	$PdCl_2(PPh_3)_2$ (1)	51

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: $C_{24}H_{26}O_4N_2$, Fw 406.2, space group $P2_1/n$, a=10.687 (8), b=16.999 (9), c=5.818 (1) Å, β=93.14°(4), V=1055.3 (9) $Å^3$, Z=2, d_{calcd}=1.28 g cm^{-3}, the final R factor 0.0903, number of unique reflections ($|F_o| \geq 3\sigma|F_o|$) 3075.

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