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SI-THALL REACTION, A METHOD FOR CROSS COUPLING
SILICON COMPOUNDS WITH THALLIUM COMPOUNDS¹

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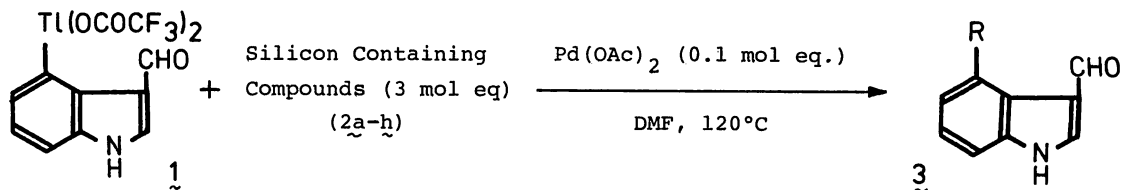
Abstract ————— A new palladium catalyzed regioselective cross coupling reaction between thallium compounds and silicon containing compounds is developed.

The necessity of a regioselective cross coupling reaction which works at the 4-position of indole nucleus led us to create the concept of thallation-palladation method.² The thallation-palladation method, in a broad sense, is defined as a palladium catalyzed reactions of thallium compounds with any type of substrates. In our continuing study to realize the above concept, we have so far succeeded in finding thallation-palladation³ (in a narrow sense), bo-thall,⁴ and tin-thall⁵ reactions. In this communication, we wish to describe si-thall reaction which also belongs to the concept of thallation-palladation method.

The si-thall reaction is a palladium catalyzed cross coupling reaction between thallium compounds and silicon containing compounds, and it works in the presence of air and moisture. Therefore, without any special precautions, the reaction was carried out only by adding silicon containing compounds (3.0 mol eq) and a catalytic amount (0.1 mol eq) of palladium acetate to a solution of thallium compound (1) in *N,N*-dimethylformamide, followed by heating at 120°C with stirring.

Typical examples are summarized in the Table. As can be seen from the Table, the yields are moderate to poor, but this defect is overcome by the simplicity of the reaction and commercial availability of various silicon containing reagents. It is interesting to note that the reactions with potassium organopentafluorosilicates⁶ gave generally superior results to those with organosilanes (compare run 1 with 6, and 8 with 11). The presence of acid scavenger, magnesium oxide, clearly improved the yield (compare run 5 with 1, 9 with 8, and 13 with 12). Further interesting

Table. Typical Results of Si-Thall Reaction



Run	Silicon Containing Compounds (2a-h)		Reaction Conditions		Products (3a-i)	
		(mol eq)	Gas *	Time (h)	(Yield, %)	
1	$\text{K}_2 \text{F}_5\text{Si-Ph}$ (2a)	-	-	4	3a: R=Ph ^{4,5} (48)	+ 3b: R=H (16)
2	2a	MgO (1.0)	-	4	3a (52)	+ 3b (30)
3	2a	-	CO	6	3a (66)	+ 3b (27)
4	2a	H ₂ O (6.0)	CO	12	3a (27) + 3b (23) + 3c: R=PhCO (21)	
5	2a	MgO (2.0)	CO	10	3a (45) + 3b (25) + 3c (6)	
6	$\text{Me}_3\text{Si-Ph}$ (2b)	-	-	5	3a (2)	+ 3b (17)
7	$\text{Me}_3\text{Si-2-furyl}$ (2c)	-	-	2	3b (26) + 3d: R=2-furyl ^{4,5} (28)	
8	$\text{K}_2 \text{F}_5\text{Si-CH=CH}_2$ (2d)	-	-	3	3b (17) + 3e: R=CH=CH ₂ ^{3b} (28)	
9	2d	{ MgO (2.0) MgSO ₄ (4.0)	CO	3	3b (15)	+ 3e (46)
10	2d	"	Ar	3	3b (14)	+ 3e (40)
11	$\text{Me}_3\text{Si-CH=CH}_2$ (2e)	-	-	1	3b (8) + 3e (24) + 3f: R=CH=CH-SiMe ₃ (20)	
12	$\text{Me}_3\text{Si-CH}_2\text{CH=CH}_2$ (2f)	-	-	17	3b (33) + 3g: R=CH ₂ CH=CH ₂ ^{3b} (6)	
13	2f	{ MgO (2.0) MgSO ₄ (4.0)	CO	16	3b (37)	+ 3g (20)
14	2f	"	Ar	16	3b (27)	+ 3g (11)
15	$\text{Me}_3\text{Si-SiMe}_3$ (2g)	-	-	7	3b (47) + 3h: R=SiMe ₃ (25)	
16	2g	-	-	15	3b (44)	+ 3h (17)
17	2g	MgO (2.0)	CO	12	3b (33)	+ 3h (21)
18	$\text{K}_2 \text{F}_5\text{Si-Et}$ (2h)	-	-	17.5	3b (19)	+ 3i: R=Et (4)

* A static gas atmosphere is maintained in the reaction vessel fitted with a balloon filled with an appropriate gas.

phenomenon is the effect of carbon monoxide. Thus, the reactions in an atmosphere of carbon monoxide clearly raised the yields of the desired products (compare run 3 with 1, 9 with 8, 13 with 12, and 17 with 16), and in the case of run 4, formation

of 4-benzoylindole-3-carboxaldehyde (3c, mp 240-241°C) was observed. 4-Trimethylsilylindole-3-carboxaldehyde⁷ (3h, mp 134-137°C), which would be a versatile synthetic intermediate, could be produced for the first time (runs 15-17) by applying the si-thall reaction. On the other hand, an attempt to introduce alkyl group generally gave poor results as a typical example was shown in the run 18, where the desired 4-ethylindole-3-carboxaldehyde (3i, mp 137-139°C) was produced in only 4% yield.

The mechanism of si-thall reaction is uncertain. However, our working hypothesis² about the mechanism of the thallation-palladation method would be useful to understand the si-thall reaction, referring to the fact that aryl substituents of organosilanes are readily transferred to the thallium atom of thallium compounds.⁸ In conclusion, we could add a novel si-thall reaction as the fourth member of thallation-palladation family. Although optimum reaction conditions are not made, the si-thall reaction should find wide application in organic synthesis, since various organosilicon compounds are known. We are currently investigating reactions of thallium compounds with many organometallic compounds as an extension of the thallation-palladation concept.

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