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Studies on Organometallic Compounds. III.[1] Reaction of Trimethylstannylazines with Acyl Chlorides. A Novel C-C Bond Formation of Pyridine Nuclei[2]

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Introduction of an acyl group at the α-, β-, and γ-positions of pyridine nuclei was accomplished. 2-Trimethylstannyl-pyridine and -quinoline and 1-trimethylstannylisoquinoline directly reacted with various acyl chlorides to give the corresponding 2-pyridyl, 2-quinolyl, and 1-isoquinolyl ketones, respectively. Reaction of 3-trimethylstannylpyridine, -quinoline, and -isoquinoline with acyl chlorides proceeded smoothly under catalysis by $PdCl_2$ or $PdCl_2(PPh_3)_2$ to afford the corresponding ketones in good yields. Similarly, 4-pyridyl, -quinolyl, and -isoquinolyl ketones were prepared from the corresponding 4-trimethylstannyl derivatives and acyl chlorides.

Keywords——trimethylstannylazine; palladium-catalyzed reaction; acylation; palladium dichloride; dichlorobis(triphenylphosphine)palladium(II)

Application of organostannyl groups as well as organosilyl groups in organic synthesis has attracted increasing attention in recent years. However, relatively little work has been carried out on applications of such organometallic groups in *N*-heteroaromatic chemistry. The preceding paper[1] described a general procedure for preparing trimethylstannylazines. We became interested in the synthetic utility of the trimethylstannyl (TMSn) group for functionalization of π-deficient *N*-heteroaromatics, and initiated a study on the reaction of trimethylstannylazines with acyl chlorides. This paper describes a method for the introduction of an acyl group into the pyridine nuclei of pyridine, quinoline, and isoquinoline through the reaction between trimethylstannylazines (**1a—k**) and various acyl chlorides (**2a—f**). This method is a new means of C-C bond formation in such heteroaromatic ring systems.

The TMSn group the 2-position of pyridine and quinoline and at the 1-position of isoquinoline was found readily to undergo replacement with acyl groups. For example, when 2-TMSn-quinoline (**1a**) was treated with benzoyl chloride (**2f**) in dry benzene at room temperature, an exothermic reaction took place to give phenyl 2-quinolyl ketone (**3f**) in high yield. Table I lists the other chlorides used. 2-TMSn-pyridine (**1b**) and 1-TMSn-isoquinoline (**1c**)

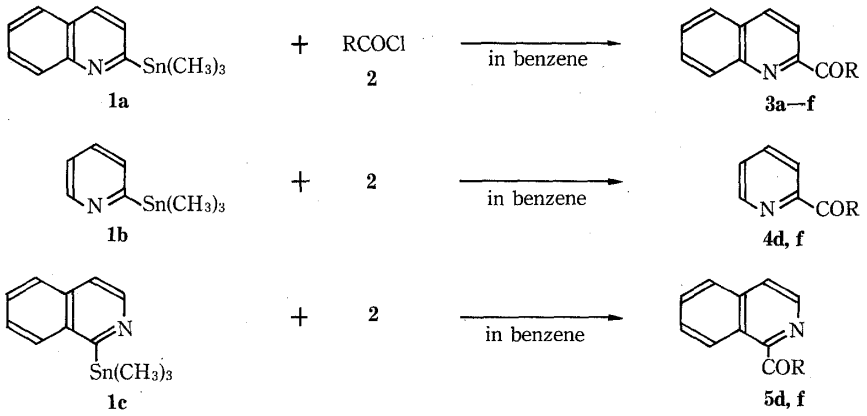

Chart 1

Table I. Synthesis of 2-Pyridyl, 2-Quinolyl, and 1-Isoquinolyl Ketones[a]

Start. compd.	No.	RCOCl R=	RCOCl No.	Temp, time	Product mp, °C	Product bp, °C (Torr)	Yield (%)	Product No.
2-TMSn-Q	**1a**	Me	**2a**	0°C, 2 h—r.t., 3 h	50—52[b]	93— 95(0.45)	39	**3a**
		Et	**2b**	0°C, 2 h—r.t., 3 h	59—60[c]	120—121(1.0)	64	**3b**
		iso-Pr	**2c**	r.t., 5 h		105—108(0.55)	83	**3c**
		C-hex	**2d**	r.t., 5 h	88—90[d]	154—156(0.50)[d]	76	**3d**
		tert-Bu	**2e**	Reflux, 8 h		97—99(0.25)	95	**3e**
		Ph	**2f**	r.t., 3 h	109—110[e]	168—170(0.35)	74	**3f**
2-TMSn-Py	**1b**	C-hex	**2d**	r.t., 3 h		138—140(10.0)[f]	77	**4d**
		Ph	**2f**	r.t., 3 h		166—169(10.0)[g]	68	**4f**
1-TMSn-IQ	**1c**	C-hex	**2d**	r.t., 3 h	66—68[d]	137—138(0.20)[d]	72	**5d**
		Ph	**2f**	r.t., 3 h	75—76[h]	137—138(0.02)	65	**5f**

a) The following abbreviations are used: TMSn=trimethylstannyl; Q=quinoline; Py=pyridine; IQ=isoquinoline; C-hex=cyclohexyl.
b) Ref. 3, mp 52—53°C.
c) Ref. 3, mp 59—60°C.
d) mp or bp was not designated in ref. 4.
e) Ref. 3, mp 111°C.
f) Ref. 5, bp 117—118°C (0.8 Torr).
g) Ref. 3, bp 165°C (7 Torr).
h) Ref. 6, mp 76—77°C.
r.t.=room temperature.

analogously reacted with **2d, f** leading to the corresponding ketones (**4d, f** and **5d, f**), respectively. These results are summarized in Table I.

On the other hand, similar treatment of 3-TMSn derivatives **1d—f** with **2** resulted in quantitative recovery of the starting compounds **1d—f**. Palladium chloride ($PdCl_2$, **6a**) or dichlorobis(triphenylphosphine)palladium(II) [$PdCl_2(PPh_3)_2$, **6b**] was found to catalyze the reaction effectively.[7] Thus, a mixture of **1d** with cyclohexanecarbonyl chloride (**2d**) in dry benzene was heated for 8 h under reflux in the presence of **6b** as a catalyst to give cyclohexyl 3-quinolyl ketone (**7d**) in satisfactory yield together with a small amount of the homo-coupling product 3,3′-biquinoline (**8a**). Table II summarizes the results obtained in the acylation of the 3-TMSn derivatives **1d—f**.

During this investigation, Milstein and Stille[8] reported that benzylchlorobis(triphenylphosphine)palladium(II) (**6c**) catalyzes the reaction of alkyl- and ary-stannane derivatives with

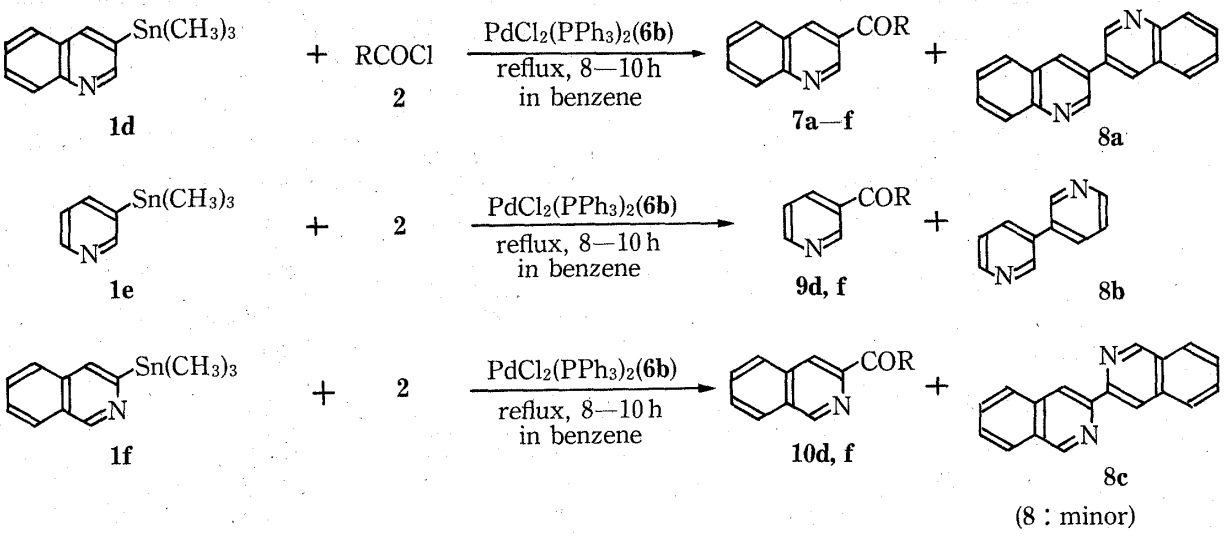

Chart 2

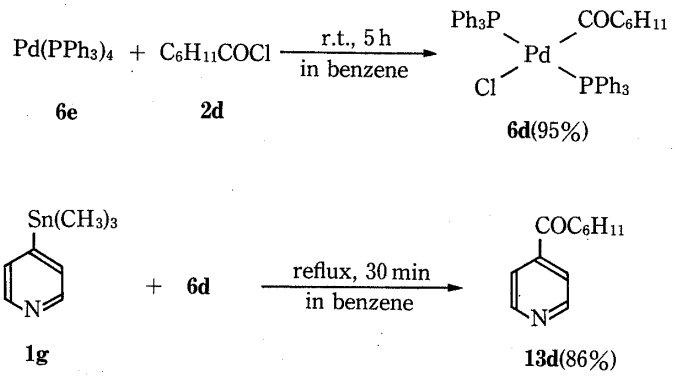

Chart 3

TABLE II. Syntheses of 3- and 4-Acyl-pyridines, -quinolines, and -isoquinolines[a]

Start. compd.	No.	RCOCl No.	Cat. No.	Time	mp (°C)	Product (major) bp, °C (Torr)	Yield (%)	No.	Homo-coupling product (minor) [mp, °C or bp, °C (Torr)]	No.
3-TMSn–Q	**1d**	**2a**	**6b**	8 h	100—102[b]	139—140(1.0)	70	**7a**	3,3′-Biquinoline	**8a**
		2b	**6b**	8 h	83—85[d]	140—142(0.80)	76	**7b**	(271—271.5)[c]	
		2c	**6b**	8 h		131—132(1.0)	82	**7c**		
		2d	**6a**	8 h	72—74	179—180(0.50)	73	**7d**		
			6b				80			
		2e	**6b**	8 h		141—143(0.90)	73	**7e**		
		2f	**6b**	8 h	74—76[e]	165—167(0.25)	71	**7f**		
3-TMSn–Py	**1e**	**2d**	**6b**	8 h		164—165(15.0)[f]	68	**9d**	3,3′-Bipyridine	**8b**
		2f	**6b**	8 h		156—157(7.0)[h]	67	**9f**	[120(bath temp.) (3.5)][g]	
3-TMSn–IQ	**1f**	**2d**	**6b**	10 h	85—87		73	**10d**	3,3′-Biisoquinoilne	**8c**
		2f	**6b**	10 h	79—81		69	**10f**	(194—195)[i]	
2-Methyl-	**1g**	**2d**	**6b**	8 h		156—158(10.0)	67	**11d**	2,2′-Dimethyl-4,4′-	**8d**
4-TMSn–Py		**2f**	**6b**	8 h	43—44[k]	163—165(10.0)[k]	60	**11f**	bipyridine (76—78)[j]	
2,6-Dimethyl-	**1h**	**2d**	**6b**	8 h		160—161(9.0)	73	**12d**	2,2′,6,6′-Tetrame-	**8e**
4-TMSn–Py		**2f**	**6b**	8 h	81—83[m]	158—160(10.0)[m]	70	**12f**	thyl-4,4′-bipyridine (153—154)[l]	
4-TMSn–Py	**1i**	$PdCl(C_6H_{11}CO)(PPh_3)_2$	**(6d)**	30 min		170—175 (bath temp.) (10.0)[n]	86	**13d**		
4-TMSn–Q	**1j**	**2a**	**6a**	4 d		118—121(1.0)[o]	24	**14a**	4,4′-Biquinoline	**8f**
		2b	**6a**	4 d		128—130(1.0)[q]	55	**14b**	(176—178)[p]	
		2c	**6a**	4 d		128—130(1.0)	28.5	**14c**		
		2d	**6a**	4 d	75—77	170—171(1.0)	50	**14d**		
		2e	**6a**	4 d		130—132(1.0)	7	**14e**		
		2f	**6a**	4 d	57—61	163—165(0.25)[r]	47	**14f**		
4-TMSn–IQ	**1k**	**2d**	**6a**	5 d		140—143(0.18)	62	**15d**	4,4′-Biisoquinoline	**8g**
		2f	**6a**	5 d	76—78[t]	157—160(0.30)	49	**15f**	(146—148)[s]	

a) The following abbreviations are used: TMSn=trimethylstannyl; Q=quinoline; Py=pyridine; IQ=isoquinoline. *b*) Ref. 9, mp 97—101°C. *c*) Ref. 10, mp 271°C. *d*) Ref. 11, mp 79—80°C. *e*) Ref. 12, mp 76—77°C. *f*) Ref. 13, bp 100—103°C (0.1 Torr). *g*) Ref. 14, bp 291—292°C (760 Torr). *h*) Ref. 12, bp 154—156°C (2.5—2.7 Torr). *i*) Ref. 15, mp 197—198°C. *j*) Ref. 16, mp 81—83°C. *k*) Ref. 17, mp 42.5—44°C; bp 135—138°C (2 Torr). *l*) Ref. 16, mp 150—152°C. *m*) Ref. 17, mp 79—81°C; bp 155—159°C (9 Torr). *n*) Ref. 18, bp 63—65°C (0.05 Torr). *o*) Ref. 19, bp 105°C (0.5 Torr). *p*) Ref. 20, mp 171°C. *q*) Ref. 21, bp 165°C (13 Torr). *r*) Ref. 19, bp 154°C (0.5 Torr). *s*) Ref. 22, mp 149°C. *t*) Ref. 23, mp 76—78°C.

acid chlorides, and is useful for the synthesis of various ketones. The complex **6c** had the effect of producing the ketone **7d** in about 18% yield in the reaction of **1d** with **2d** in hexamethylphosphoramide (HMPA) at 65°C for 56 h according to Still's procedure.

Reaction of the 4-TMSn derivatives (**1h, i**) of 2-methyl- and 2,6-dimethyl-pyridines with **2** in the presence of **6b** proceeded similarly to afford the corresponding pyridyl ketones (**11d, f** and **12d, f**; major) and the homo-coupling product **8** (minor), respectively, whereas similar treatment of 4-TMSn-pyridine (**1g**) led to a viscous substances. The substance appeared to be a polymer derived from the quaternary salt formed from **1** and **2**, since 4-pyridyl ketone **13d** was quantitatively formed from **1g** and chloro(cyclohexanecarbonyl)bis(triphenylphosphine)palladium(II) (**6d**), which was prepared from tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$, **6e**] and **2d**.

It was found that 4-TMSn-quinoline (**1j**) and -isoquinoline (**1k**) were rather resistant to acylation, and furthermore **6b** did not catalyze the reactions. Similar reaction **1j** with **2d** catalyzed by **6a** required refluxing for **4** d in benzene to give cyclohexyl 4-quinolyl ketone (**14d**)

Table III. Spectral and Analytical Data for New Acylazines[a)]

Product No.	IR $\nu_{max}^{CHCl_3}$ cm^{-1}: (C=O)	NMR[b)] J (Hz)	Formula	Analysis (%) Calcd (Found) C	H	N
3c	1680	1.25 (6H, d; J=7), 4.1—4.7 (1H, m; J=7), 7.2—8.3 (6H, m).	$C_{13}H_{13}NO$	78.37 (78.38	6.58 6.78	7.03 6.96)
3d[a)]	1680	1.1—2.2 (10H, m), 3.8—4.5 (1H, m), 7.4—8.4 (6H, m).	$C_{16}H_{17}NO$	80.30 (80.21	7.16 7.03	5.85 6.05)
3e	1670	1.50 (9H, s), 7.2—8.4 (6H, m).	$C_{14}H_{15}NO$	78.84 (78.98	7.09 7.36	6.57 6.66)
5d[a)]	1680	0.9—2.5 (10H, m), 3.6—4.2 (1H, m), 7.3—8.0 (4H, m), 8.43 (1H, d; J=5), 9.41 (1H, m).	$C_{16}H_{17}NO$	80.30 (80.37	7.16 7.25	5.85 5.90)
7c	1680	1.28 (6H, d; J=7), 3.3—4.0 (1H, m; J=7), 7.4—8.3 (4H, m), 8.67 (1H, d; J=2), 9.42 (1H, d; J=2).	$C_{13}H_{13}NO$	78.37 (78.59	6.58 6.52	7.03 6.81)
7d	1675	1.1—2.3 (10H, m), 3.1—3.7 (1H, m), 7.4—8.3 (4H, m), 8.70 (1H, d; J=2), 9.42 (1H, d; J=2).	$C_{16}H_{17}NO$	80.30 (80.03	7.16 7.03	5.85 5.56)
7e	1670	1.42 (9H, s), 7.4—8.3 (4H, m), 8.54 (1H, d; J=2), 9.27 (1H, d; J=2).	$C_{14}H_{15}NO$	78.84 (79.10	7.09 7.02	6.57 6.61)
10d	1680	0.8—2.4 (10H, m), 3.6—4.4 (1H, m), 7.4—8.2 (4H, m), 8.47 (1H, s), 9.30 (1H, s).	$C_{16}H_{17}NO$	80.30 (80.22	7.16 7.32	5.85 5.81)
10f	1660	7.3—8.4 (9H, m), 8.42 (1H, s), 9.30 (1H, s).	$C_{16}H_{11}NO$	82.38 (82.42	4.75 4.59	6.00 6.16)
11d	1680	1.0—2.2 (10H, m), 2.56 (3H, s), 2.8—3.5 (1H, m), 7.2—7.5 (2H, m), 8.46 (1H, d; J=4.5).	$C_{13}H_{17}NO$	76.81 (76.76	8.43 8.46	6.89 6.86)
12d	1685	1.0—2.2 (10H, m), 2.55 (6H, s), 2.8—3.0 (1H, m), 7.19 (2H, s).	$C_{14}H_{19}NO$	77.38 (77.39	8.81 8.96	6.45 6.30)
14c	1685	1.11 (6H, d; J=7), 2.9—3.4 (1H, m; J=7), 7.2—8.2 (5H, m), 8.77 (1H, d; J=4).	$C_{13}H_{13}NO$	78.37 (78.47	6.58 6.70	7.03 6.74)
14d	1685	0.9—2.3 (10H, m), 2.8—3.4 (1H, m), 7.8—8.3 (5H, m), 8.93 (1H, d; J=4).	$C_{16}H_{17}NO$	80.30 (80.33	7.16 6.87	5.85 6.14)
14e	1685	1.25 (9H, s), 7.09 (1H, d; J=4), 7.3—8.3 (4H, m), 8.80 (1H, d, J=4).	$C_{14}H_{15}NO$	78.84 (78.76	7.09 7.21	6.57 6.36)
15d	1665	1.0—2.5 (10H, m), 2.9—3.6 (1H, m), 7.3—8.1 (3H, m), 8.3—8.6 (1H, m), 8.76 (1H, s), 9.15 (1H, s).	$C_{22}H_{23}N_3$[c)]	80.21 (80.41	7.04 7.14	12.75 12.51)

a) mp or bp of **3d** and **5d** were not designated in ref. 4.
b) $CDCl_3$ was used as a solvent in the cases of **3, 5, 7,** and **10**, while CCl_4 was used in the other cases.
c) **15d** was analyzed as the phenylhydrazone; mp 218—220°C; IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 1600 (C=N). NMR ($CDCl_3$): δ: 0.9—2.9 (11H, m), 6.6—8.2 (10H, m), 8.37 (1H, s), 9.27 (1H, br s).

along with a small amount of 4,4′-biquinoline (**8f**). The acylation reactions of 4-TMSn-azines are also summarized in Table II.

A feasible pathway for acylation at the α-positions of pyridine nuclei would involve the formation of the quaternary salt as an intermediate and subsequent migration of the acyl group to the α-carbon as depicted in Chart 4.

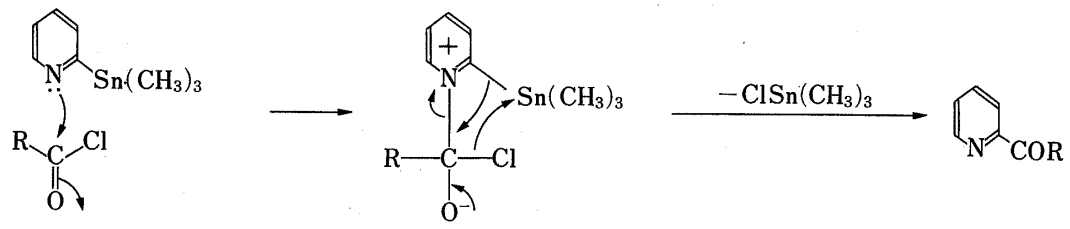

Chart 4

The reaction of **1d** with some palladium complexes provided valuable evidence in relation to the mechanism of acylation of 3- and 4-TMSn-azines. A mixture of **1d** and a half equivalent of **6b** in benzene was refluxed for 2 h to give 3,3′-biquinoline (**8a**) in 82% yield. When a benzene solution of **1d** was refluxed in the presence of bromo(3-quinolyl)bis (triphenylphosphine)palladium(II) [$PdBr(3\text{-Quin})(PPh_3)_2$, **6f**], which was prepared from 3-bromoquinoline (**16**) and **6e**, 3,3′-biquinoline (**8a**) was obtained in 83% yield. In addition, **1d** reacted with **6d** to furnish **7d** in excellent yield.

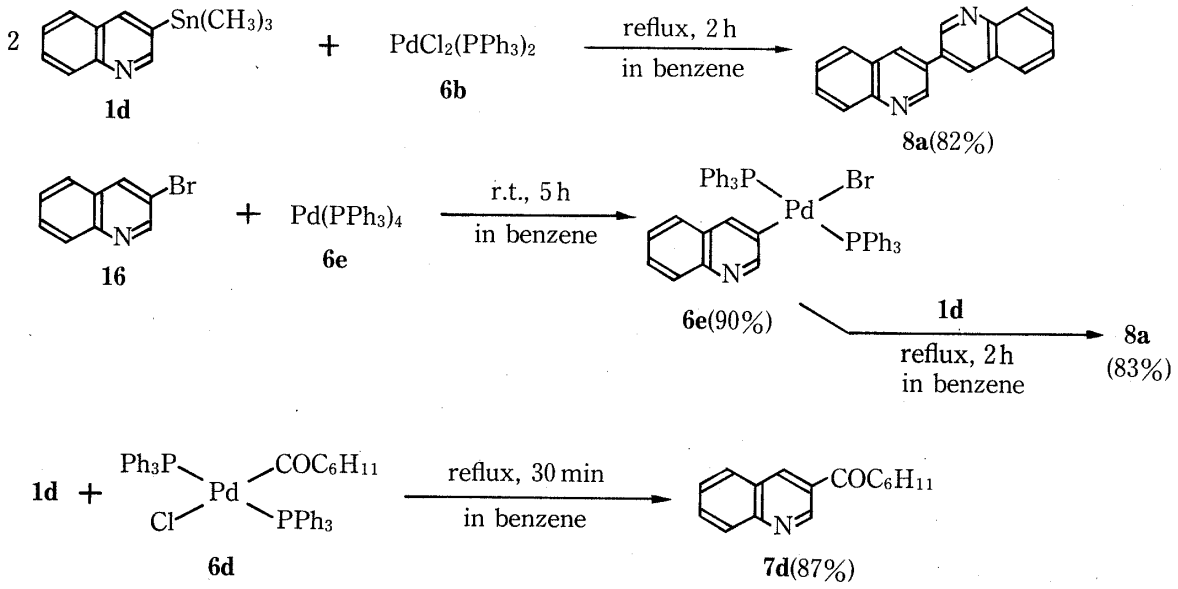

Chart 5

These results suggested that the acylation could be explained by the following sequential steps, as shown in Chart 6: double metathetical replacement of chrloides in **6b** by the 3-quinolyl group with loss of chlorotrimethylstannane, followed by reductive elimination, affords the coupling product **8a** and bis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_2$, **6g**], active catalyst. Next, **2d** adds oxidatively to the resulting **6g** to yield the complex **6d**, which undergoes metathetical replacement of chloride by the 3-quinolyl group accompanied with elimination of chlorotrimethylstannane to form $Pd(C_6H_{11}CO)(3\text{-Quin})(PPh_3)_2$ (**6h**). The ketone **7d** is reductively eliminated from **6h**, and **6g** simultaneously formed serves again as a catalyst in the reaction between **1d** and **2d**. The catalysis of **6a** would be essentially the same as that of **6b**.

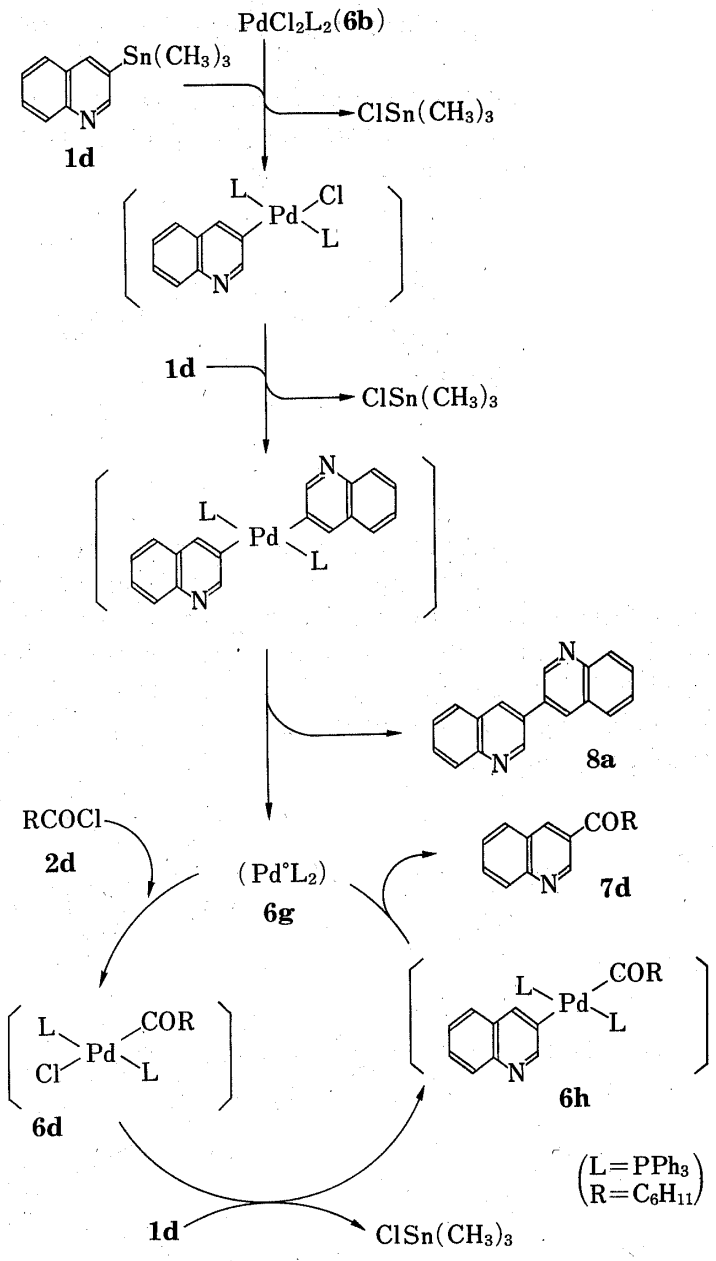

Chart 6

The lower reactivity of **1j, k** than of **1d—i** could be presumed sterically to be related to the hydrogen in the *peri*-position in view of the following evidence, although the mechanistic details are not clear: no reaction of **1j** with the complex **6d** took place. β-TMSn-naphthalene (**1l**) underwent conversion into the corresponding ketone **17** in 80% yield on being refluxed with **2d** in benzene for 5 h in the presence of **6b**. In contrast, α-TMSn-naphthalene (**1m**) required refluxing for 30 h in benzene to give the ketone **18** in only 12% yield.

It is of interest to note that similar reaction of 3-trimethylsilylpyridine, synthesized by the literature procedure,[24] with **2d** in the presence of **6b** resulted in quantitative recovery of the starting silylpyridine.

Experimental[25]

Cyclohexyl 2-Quinolyl Ketone (3d): General Procedure for 3c, d, f——A solution of **2d** (1.76 g, 12 mmol) was added dropwise to a stirred solution of **1a** (2.92 g, 10 mmol) in benzene. The mixture was stirred for 5 h at room temperature, then the solvent was removed *in vacuo*. The residue was extracted

with hot 15% hydrochloric acid (HCl). The HCl layer was allowed to cool at room temperature, then filtered. The filtrate was concentrated *in vacuo*, made alkaline with sodium carbonate, and extracted with chloroform ($CHCl_3$). The $CHCl_3$ layer was dried and concentrated. The residue was distilled under reduced pressure to give **3d**. Yield: 1.82 g (76%).

Methyl 2-Quinolyl Ketone (3a)——A solution of **2a** (0.94 g, 12 mmol) was added dropwise to an ice-salt cooled solution of **1a** (2.92 g, 10 mmol) in benzene with stirring. The reaction mixture was kept at the same temperature for 1.5 h and then at ambient temperature for 3 h. Treatment of the reaction mixture by the method given for **3d** afforded **3a**. Yield: 0.67 g (39%).

Ethyl 2-Quinolyl Ketone (3b)——Ethyl 2-quinolyl ketone (**3b**) was prepared from **1a** (2.92 g, 10 mmol) and propionyl chloride (**2b**, 1.11 g, 12 mmol) by a procedure similar to that described for **3a**.

***tert*-Butyl 2-Quinolyl Ketone (3e)**——A solution of **1a** (2.92 g, 10 mmol) and pivaloyl chloride (**2e**, 1.45 g, 12 mmol) in benzene was refluxed for 8 h. Treatment of the resulting solution by the method described for **3d** afforded **3e**.

Chloro(cyclohexanecarbonyl)bis(triphenylphosphine)palladium (II) (6d)——A mixture of cyclohexanecarbonyl chloride (**2d**, 1.47 g, 10 mmol) and $Pd(PPh_3)_4$ (**6e**, 5.78 g, 5 mmol) in benzene (80 ml) was stirred under an argon stream for 5 h at room temperature, then concentrated *in vacuo*. Anhydrous ether (*ca.* 10 ml) was added to the residue. The insoluble **6d** was collected by filtration, washed with ether, and dried *in vacuo*. The colorless powder **6d** decomposed at 85°C. Yield: 3.7 g (95%). IR ν_{max}^{KBr} cm^{-1}: 1670, 1480, 1435, 1095, 745, 690. NMR ($CDCl_3$) δ: 0.2—0.3 (11H, m), 7.1—8.1 (30H, m). *Anal.* Calcd for $C_{43}H_{41}ClOP_2Pd$: C, 66.42; H, 5.31. Found: C, 66.20; H, 5.54.

Bromo(3-quinolyl)bis(triphenylphosphine)palladium (II) (6f)——A mixture of 3-bromoquinoline (2.08 g, 10 mmol) and **6e** (5.78 g, 5 mmol) in benzene (*ca.* 80 ml) was stirred for 5 h at room temperature. Treatment of the reaction mixture by the method described for **6d** afforded **6f**. Recrystallization from benzene gave colorless prisms of **6f**, mp 183—185° (dec.). Yield: 3.78 g (90%). IR ν_{max}^{KBr} cm^{-1}: 1590, 1480, 1430, 1090, 740, 690. NMR ($CDCl_3$) δ: 6.6—7.8 (35H, m), 8.25 (1H, br s). *Anal.* Calcd for $C_{45}H_{36}BrNP_2Pd$: C, 64.42; H, 4.33; N, 1.67. Found: C, 64.57; H, 4.37; N, 1.73.

Cyclohexyl 3-Quinolyl Ketone (7d)——Method A: A typical procedure for **7**, **9**, **10**, **11**, **12**, **14**, and **15** in Table II is as follows. A solution of **2d** (1.76 g, 12 mmol) in benzene (15 ml) was added to a mixture of **1d** (2.92 g, 10 mmol) and **6b** (0.35 g, 0.5 mmol) in benzene (15 ml). The resulting solution was refluxed for 8 h and treated as in the case of **3d**. Distillation gave **7d**. Yield: 1.92 g (80%). The residual substance was purified by column chromatography on alumina or by recrystallization, giving a homo-coupling product **8**.

Method B: A mixture of **1d** (0.92 g, 10 mmol), **2d** (1.76 g, 12 mmol), and **6a** (89 mg, 0.5 mmol) in benzene was refluxed for 8 h. Treatment of the reaction mixture by the method given for **3d** afforded **7d**. Yield: 1.75 g, (73%). The spectral and analytical data are summarized in Table III.

Stoichiometric Reaction of 3-TMSn-quinoline (1d) with $PdCl(C_6H_{11}CO)(PPh_3)_2$ (6d)——A mixture of **1d** (0.44 g, 1.5 mmol) and **6d** (1.17 g, 1.5 mmol) in benzene (20 ml) was refluxed for 30 min. The reaction mixture was filtered to remove palladium black formed. Treatment of the filtrate by the method given for **3d** afforded **7d**. Yield: 0.31 g (87%).

Reaction of 3-TMSn-quinoline (1d) with $C_6H_{11}COCl$ (2d) in the Presence of $PdCl(C_6H_{11}CO)(PPh_3)_2$ (6d)——A mixture of **1d** (2.92 g, 10 mmol), **2d** (1.76 g, 12 mmol), and **6d** (0.39 g, 0.5 mmol) in benzene (30 ml) was refluxed for 8 h and then treated by a procedure similar to that given for **3d** to afford **7d**. Yield: 2.17 g (91%). 3,3′-Biquinoline (**8a**) was not detected in this reaction.

Reaction of 3-TMSn-quinoline (1d) with $C_6H_{11}COCl$ (2d) in the Presence of $PdBr(3\text{-Quin})(PPh_3)_2$ (6f)——A mixture of **1d** (1.46 g, 5 mmol), **2d** (0.88 g, 6 mmol), and **6f** (0.21 g, 0.25 mmol) in benzene (20 ml) was refluxed for 8 h and then treated by a procedure similar to that given for **3d** to afford **7d** (0.75 g, 62.5%) and **8a** (41 mg, 6.4%).

Reaction of 3-TMSn-quinoline (1d) with $PdCl_2(PPh_3)_2$ (6b)——A mixture of **1d** (146 mg, 0.5 mmol) and **6b** (175 mg, 0.25 mmol) in benzene (15 ml) was refluxed for 2 h, then filtered. The filtrate was concentrated and ether (30 ml) was added to the residue. The precipitate formed was collected and recrystallized from $CHCl_3$ to give 52 mg (82%) of 3,3′-biquinoline (**8a**).

Stoichiometric Reaction of 3-TMSn-quinoline (1d) with $PdBr(3\text{-Quin})(PPh_3)_2$ (6f)——A mixture of **1d** (584 mg, 2 mmol) and **6f** (1.68 g, 2 mmol) in benzene (15 ml) was refluxed for 2 h, and filtered. The filtrate was concentrated and ether (30 ml) was added to the residue. The precipitate formed was collected and recrystallized from $CHCl_3$ to give 426 mg (83%) of **8a**.

Cyclohexyl 4-Pyridyl Ketone (13d) from 4-TMSn-pyridine (1g) and $PdCl(C_6H_{11}CO)(PPh_3)_2$ (6d)——A mixture of **1g** (1.21 g, 5 mmol) and **6d** (4.3 g, 5.5 mmol) in benzene (30 ml) was refluxed for 30 min. The reaction mixture was treated by the procedure given for **3d** to afford 1.63 g (86%) of **13d**.

Cyclohexyl β-Naphthyl Ketone (17)——A mixture of β-TMSn-naphthalene[25] (**1l**, 1.45 g, 5 mmol) and **2d** (0.88 g, 6 mmol) in benzene (20 ml) was refluxed for 5 h in the presence of **6b** (0.18 g, 0.25 mmol). The resulting mixture was concentrated and ether (*ca.* 30 ml) was added. After removal of an insoluble substance by filtration, the ether layer was washed with saturated sodium carbonate solution, dried, and concentrated. Distillation of the residue under reduced pressure gave 0.95 g (80%) of **17**, bp 160—162°C (3.5 Torr), mp 66—68°C (petr. benzine). Picrate: mp 119—121°C (lit. mp 120—123°C).[27]

Cyclohexyl α-Naphthyl Ketone (18)——A mixture of α-TMSn-naphthalene[26] (**1m**, 1.45 g, 5 mmol), **2d** (0.88 g, 6 mmol), and **6b** (0.18 g, 0.25 mmol) was refluxed in benzene for 30 h. The resulting mixture was treated by the procedure given for **17** to afford 1.03 g (71%) of the starting compound **1m** and 0.41 g, (12%) of **18**, bp 152—154°C (2.8 Torr), mp 62—64°C (petr. benzine). Picrate: mp 77—78°C (lit. mp 75—76°C).[27]

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