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Palladium(II)-Catalyzed Michael-Type Addition Reactions Using Aryltin Compounds

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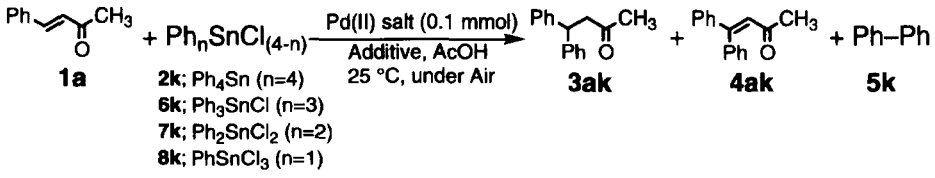
A variety of aryltin compounds can be employed for Michael-type hydroarylation reactions to α,β-unsaturated ketones and aldehydes in the presence of a catalytic amount of palladium(II) salt in acetic acid under air. Each reaction is much accelerated in the presence of a soluble metal chloride such as LiCl, $MgCl_2$, and $CaCl_2$. It is found that slightly fewer than four aryl groups of tetraaryltins can be transferred to the products in this arylation.

Organic transformations using organotin compounds have been powerful tools in the last two decades.[1] Many examples of conversion of C–Sn bond to C–C bond have been reported, such as Pd(0)-catalyzed cross coupling reaction with organic halides or acyl halides (the so-called Stille cross coupling),[1] Lewis acid-mediated or transition metal-catalyzed 1,2-addition reaction to carbonyl compounds and imines,[2] Heck-type dehydroarylation reaction to α,β-unsaturated carbonyl compounds,[3] organic transformations including radical intermediates,[4] and so on. The Michael-type hydroarylation reaction (addition of Ar–H to C=C double bond) to α,β-unsaturated carbonyl compounds is also of interest. Thus, it has been reported that tetraphenyltin reacted with α,β-unsaturated ketones and esters in the presence of a catalytic amount of palladium(II) chloride ($PdCl_2$) in water-dichloromethane biphasic system,[5] while a cationic rhodium(I) complex also catalyzed similar reactions using aryltrimethyltins.[6] In most of these reactions, only one of four organic groups of organotins was consumed. However, it has been revealed recently that almost all of the four organic groups of organotins could be utilized in such reactions as Pd-catalyzed Stille-type coupling reaction of tetraaryltins (Ar_4Sn) with aryl halides[7] and $Sc(OTf)_3$-catalyzed 1,2-addition reaction of tetraallyltins to hydrazones.[8] On the other hand, it has been disclosed in our laboratory that organoborons[9] and organoantimonys[10] reacted with α,β-unsaturated ketones and aldehydes in the presence of a catalytic amount of palladium acetate [$Pd(OAc)_2$] in acetic acid (AcOH) to afford mainly the corresponding Michael-type hydroarylation compounds. As one of our series of studies in organic transformations using organoheteroatom compounds, we attempted to apply aryltins to this Michael-type hydroaryltion reaction from the viewpoint of atom efficiency of aryl groups. As a result, it was disclosed that more than one aryl group, and sometimes almost all of them, were utilized in this reaction in the presence of a catalytic amount of Pd(II) salt together with a suitable soluble metal chloride in AcOH. We report here the details of this catalytic reaction.[11]

Results and Discussion

Pd(II)-Catalyzed Michael-Type Addition of $Ph_nSnCl_{(4-n)}$ to Benzylideneacetone (1a) in AcOH. At first, we selected the catalytic system used so far for the reaction using sodium tetraphenylborate[9] and triarylantimonys.[10] Thus, Ph_4Sn (**2k**, 1 mmol) was treated with benzylideneacetone (4-phenyl-3-buten-2-one, **1a**, 1 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol) and AgOAc (2 mmol) in AcOH under air at 25 °C for 24 h. As a result, the Michael-type product, 4,4-diphenyl-2-butanone (**3ak**), was mainly obtained together with the Heck-type substituted compound, 4,4-diphenyl-3-buten-2-one (**4ak**), and biphenyl (**5k**) (Scheme 1, Table 1). Instead of AgOAc, $Cu(OAc)_2$ (2 mmol) was also effective as an additive. This catalytic system was not effective in the absence of AgOAc or $Cu(OAc)_2$. Here, $PdCl_2$ was revealed to be slightly less effective than $Pd(OAc)_2$.

We have reported that diarylantimony chlorides (Ar_2SbCl) reacted with α,β-unsaturated ketones and aldehydes in the presence of catalytic amounts of $Pd(OAc)_2$ in AcOH to give



Scheme 1.

Table 1. Pd(II)-Catalyzed Michael-Type Addition Reactions of Phenyltin Compounds to Benzylideneacetone (**1a**) under Various Conditions[a]

$Ph_nSnCl_{(4-n)}$ (1 mmol)	Pd(II) salt (0.1 mmol)	Additive (mmol)	AcOH mL	Reaction time/h	GLC yield(%)[b] **3ak**[c]	**4ak**[c]	**5k**[d]
2k	$Pd(OAc)_2$	—	20	24	27	10	7
2k	$Pd(OAc)_2$	AgOAc 2	20	24	69	22	14
2k	$Pd(OAc)_2$	$Cu(OAc)_2$ 2	20	24	68	9	28
2k	$PdCl_2$	$Cu(OAc)_2$ 2	20	24	44	8	4
2k	Na_2PdCl_4	—	10	15	40	17	2
6k	$Pd(OAc)_2$	—	10	15	8	Trace	11
6k	Na_2PdCl_4	—	10	15	83	Trace	18
6k	$PdCl_2$	LiCl 1	10	15	99	Trace	26
7k	$Pd(OAc)_2$	—	10	15	95	3	10
8k[e]	$Pd(OAc)_2$	—	10	15	(96)	(0)	(1)

a) **1a** (1 mmol) was used. b) Isolated yield (%) is in parenthesis. c) Based on **1a**. d) Based on $Ph_nSnCl_{(4-n)}$: $n/2$ mmol of **5k** corresponds to 100% yield. e) Double scale reaction.

the Michael-type products exclusively. Thus, we next examined various phenyltin chlorides [$Ph_nSnCl_{(4-n)}$] as phenylation reagents focusing on the effect of chloro ligand(s) (Scheme 1). Treatment of $Ph_nSnCl_{(4-n)}$ [n = 3 (**6k**), n = 2 (**7k**), n = 1 (**8k**); 1 mmol] with **1a** (1 mmol) in the presence of Pd(II) salt (0.1 mmol) in AcOH under air at 25 °C for 15 h afforded mainly **3ak** together with **5k**. Little of the Heck-type product **4ak** was produced (Table 1). Increasing the number of chloro ligands allowed one to increase the selectivity for Michael-type addition, except for the **6k**–Pd(OAc)$_2$ system where Pd metal precipitated. It was found that the addition of lithium chloride (LiCl) or use of sodium chloropalladate as catalyst was effective in these reactions.

The Effect of LiCl Added. Since we found that the presence of chloro ligand and also the addition of LiCl were effective for these catalytic reactions, the effect of LiCl on the reaction between tetraphenyltin (**2k**) and **1a** was next carefully examined. Treatment of **2k** (1 mmol) with **1a** (1 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol) and LiCl (2 mmol) in AcOH at 25 °C afforded **3ak** in quite high yield together with **5k** (Table 2). In the presence of LiCl, $PdCl_2$ was also revealed to be as effective as $Pd(OAc)_2$. The reaction proceeded even using 0.01 molar amount of Pd(II) salt to **1a**, though a prolonged reaction time was needed. More importantly, the amount of **2k** can be reduced to 0.25 molar amount to **1a**, and yet almost the same or higher yield of product (**3ak**) was obtained than that by use of more amount of **2k**. Actually, in some cases, almost all phenyl groups were transferred to the products by using the appropriate amount of LiCl (2 molar amount to **1a**; 8 molar amount to **2k**). Either the increased (5 molar amount) or the reduced amount (1 molar amount) of LiCl was not effective for this reaction. After the reaction tin(IV) seems to be present in the form of inorganic salts such as $SnCl_4$ and/or $Sn(OAc)_4$ and, actually, the addition of brine to the resulting solution sometimes afforded voluminous white material, probably $Sn(OH)_4$, which is quite soluble in dilute aqueous HCl.

Michael-Type Addition of $Ph_nSnCl_{(4-n)}$ to 1a in $PdCl_2$/LiCl/AcOH System. Since it was revealed that slightly fewer than four phenyl groups of tetraphenyltin (**2k**) were transferred to the products in $PdCl_2$/LiCl/AcOH system, we next examined whether a similar atom efficiency was observed in the case of phenyltin compounds $Ph_nSnCl_{(4-n)}$. Treatment of $Ph_nSnCl_{(4-n)}$ [**6k** (n = 3), **7k** (n = 2), **8k** (n = 1)]

Table 2. Effect of Lithium Chloride Added[a]

Pd(II) salt	molar amount to **1a**	LiCl molar amount to **1a**	Ph_4Sn (**2k**) molar amount to **1a**	Reaction time/h	GLC yield (%)[b] **3ak**[c]	**4ak**[c]	**5k**[d]
$Pd(OAc)_2$[e]	0.1	—	1	24	27	10	7
$Pd(OAc)_2$	0.1	2	1	15	86	1	15
$Pd(OAc)_2$	0.1	2	1	5	80	3	3
$Pd(OAc)_2$	0.1	2	0.5	15	78	0	31
$PdCl_2$	0.1	2	0.5	15	74	0	26
$Pd(OAc)_2$	0.01	2	0.25	15	85	Trace	19
$PdCl_2$	0.01	2	0.25	20	88(81)	1(0)	9(3)
$PdCl_2$	0.01	1	0.25	20	(56)	(0)	(2)
$PdCl_2$	0.01	5	0.25	20	(26)	(0)	(<1)
$PdCl_2$	0.01	—	0.25	20	(5)	(0)	(1)

a) **1a** (1 mmol) and AcOH (10 mL) were used at 25 °C under air. b) Isolated yield (%) is in parenthesis: double scale reaction for isolation. c) Based on **1a**. d) Based on the double molar amount of **2k**. e) AcOH (20 mL) was used.

with **1a** in the presence of $PdCl_2$ and LiCl in AcOH at 25 °C afforded mainly **3ak** together with **5k**, as summarized in Table 3. Here, little formation of **4ak** was observed. Although the reactivity of **6k** in the presence of $PdCl_2$ and LiCl in AcOH was much less than that of **2k**, more than one phenyl group ($0.47\times2/0.67 = 1.40$) was transferred to **3ak** even in this case. Also, in the case of **7k**, more than one phenyl group ($0.68\times2/1 = 1.36$) was transferred.

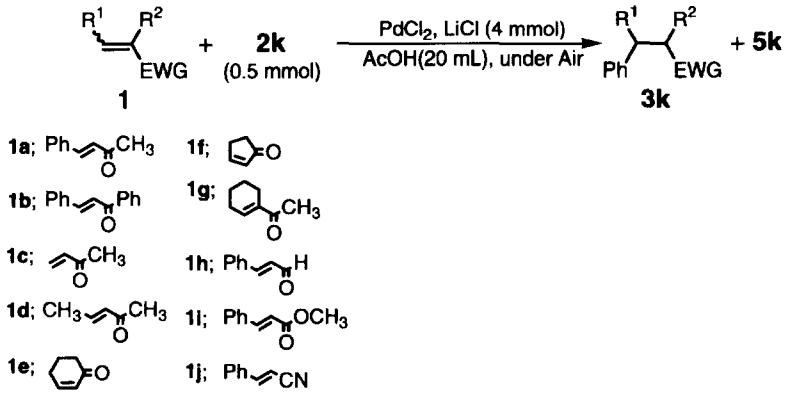
Table 3. Reactions between **1a** and $Ph_nSnCl_{(4-n)}$ in the Presence of LiCl: Atom Efficiency[a]

$Ph_nSnCl_{(4-n)}$	(mmol)	Isolated yield (%)[b]		
		3ak[c]	**4ak**[c]	**5k**[d]
2k	0.5	81 (88)	0 (1)	3 (9)
6k	0.67	47	0	24
7k	1	68	0	5
8k	2	64	0	2

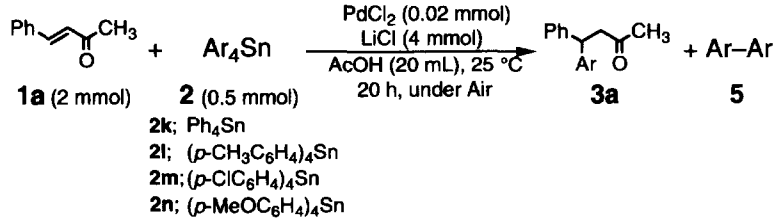
a) **1a** (2 mmol), $PdCl_2$ (0.02 mmol), LiCl (4 mmol), and AcOH (20 mL) were used at 25 °C for 20 h under air. b) GLC yield (%) is in parenthesis. c) Based on **1a**. d) Based on $Ph_nSnCl_{(4-n)}$: 1 mmol of **5k** corresponds to 100 % yield.

The Effect of Solvent. This $PdCl_2$/LiCl catalytic reaction using **1a** and **2k** was carried out in other solvents than acetic acid, such as methanol, ethanol, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), acetonitrile (MeCN), pyridine (C_5H_5N), *N*,*N*-dimethylformamide (DMF), and benzene, but the product yield was quite low or nothing was obtained, except for the case of CH_2Cl_2 where 28% of **3ak** and 7% of **5k** were obtained. The addition of a small amount of AcOH to these solvents did not improve the situation. These results clearly show that acetic acid was the solvent of choice in this catalytic system.

The Effect of Other Chlorides. The effect of other chlorides than LiCl on this catalytic reaction was examined in the reaction of **1a** with **2k** in the presence of a catalytic amount of $PdCl_2$ in AcOH. The yield of the product **3ak** was as follows: NaCl (21%), KCl (2%), CsCl (0%), $MgCl_2$



Scheme 2.

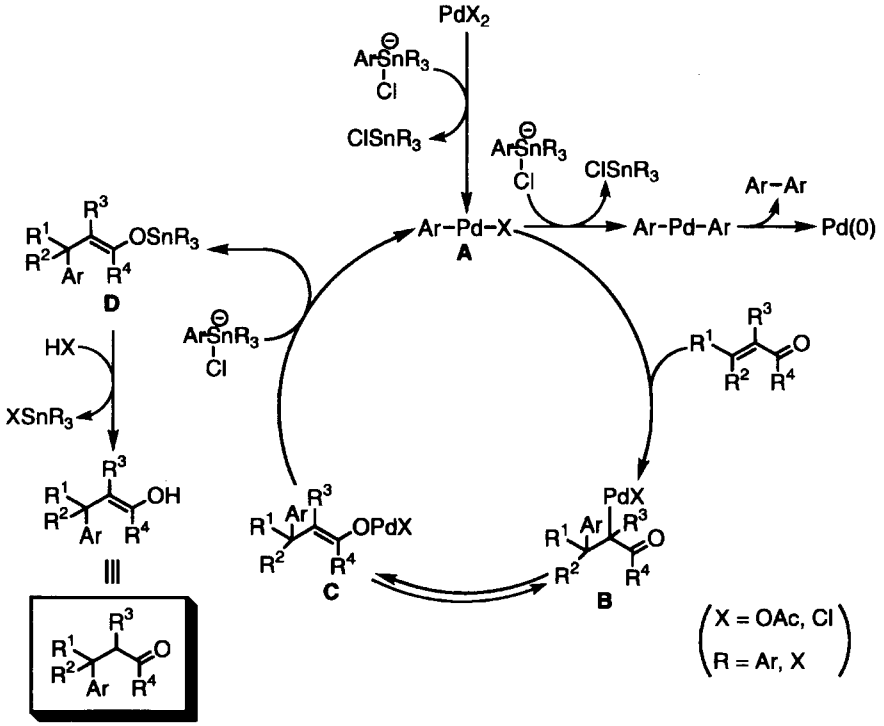


Scheme 3.

Table 4. Reactions between **2k** and Various **1** in $PdCl_2$/LiCl/AcOH Catalytic System

Substrate		$PdCl_2$	Reaction	Reaction	Isolated yield (%)[a]		
1	(mmol)	mmol	temp/°C	time/h	**3k**		**5k**
1a	2.0	0.02	25	20	**3ak**	81	3
1b	2.0	0.02	50	2	**3bk**	56	35
1c	2.4	0.04	50	5	**3ck**	81	10
1d	2.4	0.04	50	5	**3dk**	69	18
1e	2.4	0.04	50	5	**3ek**	63	28
1f	2.4	0.04	50	5	**3fk**	26	55
1g	2.0	0.04	50	5	**3gk**	4	66
1h	2.0	0.04	50	5	**3hk**	28	55

a) Based on Ph (0.5×4 = 2 mmol) of **2k** : 2 mmol of **3k** and 1 mmol of **5k** correspond to 100% yield, respectively. NR with **1i** and **1j**.



Scheme 4. Plausible reaction pathway.

Table 5. Reactions between **1a** and Various **2** in $PdCl_2$/LiCl/AcOH Catalytic System

Ar_4Sn	Isolated yield (%)			
	3a[a]		**5**[b]	
2k	**3ak**	81	**5k**	3
2l	**3al**	77	**5l**	3
2m[c]	**3am**	12—34	**5m**	56—78
2n[c,d]	**3an**	8—13	**5n**	<1

a) Based on **1a**. b) Based on **2**: 1 mmol of **5** corresponds to 100% yield. c) Several runs. d) Anisole (84—89% of GLC yield) was also formed.

(83%), $CaCl_2$ (82%), $SrCl_2$ (47%), and $BaCl_2$ (21%). In the Group 2 element cases, 2 mmol of the salt were used, while 4 mmol of the salt were used in the case of the Group 1 elements. Some of these (i.e. $MgCl_2$ and $CaCl_2$) were revealed to be as effective as LiCl. This reactivity difference seems to be merely due to their solubility to AcOH.[12] The chlorides LiCl, $MgCl_2$, and $CaCl_2$ are very soluble in AcOH, but NaCl, KCl, CsCl, $SrCl_2$, and $BaCl_2$ are quite insoluble.

Michael-Type Addition Reaction to Other Substrates. Since it was revealed that slightly fewer than four phenyl groups of **2k** could react with **1a** under the catalytic system of $PdCl_2$/LiCl/AcOH, the reactions of other α,β-unsaturated substrates were examined. Our choice of substrates was benzylideneacetophenone (**1b**), methyl vinyl ketone (**1c**), 3-penten-2-one (**1d**), 2-cyclohexenone (**1e**), 2-cyclopentenone (**1f**), 1-cyclohexenyl methyl ketone (**1g**), cinnamaldehyde (**1h**), methyl cinnamate (**1i**), and cinnamonitrile (**1j**) (Scheme 2). Since the reaction using these substrates other than **1a** was quite slow at 25 °C, the elevated temperature (50 °C) was applied (Table 4). Among them, **1b**, **1c**, **1d**, and **1e** were revealed to be effective in this catalytic system. Thus, considering the yield of Michael-type product **3** and that of **5k**, slightly fewer than four phenyl groups of **2k** were transferred to the products in many cases. Unfortunately, in the case of **1f**, **1g**, and **1h**, the yield of **3k** was quite low. No reaction occurred in the cases of **1i** and **1j**.

Michael-Type Addition Reaction Using Other Aryltin Compounds. We used the most effective catalytic system ($PdCl_2$/LiCl/AcOH) to examine the atom efficiency of other tetraaryltins in the reaction with **1a**. Our choices of other Ar_4Sn (**2**) were tetra(*p*-tolyl)tin [**2l**, $(p\text{-}CH_3C_6H_4)_4Sn$], tetrakis(*p*-chlorophenyl)tin [**2m**, $(p\text{-}ClC_6H_4)_4Sn$], and tetrakis(*p*-methoxyphenyl)tin [**2n**, $(p\text{-}CH_3OC_6H_4)_4Sn$] (Scheme 3). Treatment of **2k** or **2l** (0.5 mmol) with **1a** (2 mmol) in the presence of $PdCl_2$ (0.02 mmol) and LiCl (4 mmol) in AcOH at 25 °C afforded the hydroarylation compounds **3ak** and **3al**, respectively (Table 5), where almost all phenyl groups were transferred to the products. In the case of **2m**, the aryl-coupling product 4,4′-dichlorobiphenyl (**5m**) became the main product. In the case of **2n**, anisole was the main product by the well-known protodestannylation with AcOH,[13] both 4-(*p*-methoxyphenyl)-4-phenyl-2-butanone (**3an**) and 4,4′-dimethoxybiphenyl (**5n**) being produced in very poor yields. In fact, treatment of only **2n** in AcOH at 25 °C for 20 h afforded anisole almost quantitatively (≈92%).

Since Oi et al. have used aryltrimethyltins for Rh-catalyzed hydroarylation to α,β-unsaturated ketones and esters,[6] we also applied our catalytic system to aryltin compounds such as tributylphenyltin (**9k**, $C_6H_5SnBu_3$), allyltributyltin (**9o**, $CH_2{=}CHCH_2SnBu_3$), and tributyl-2-furyltin

(**9p**, $(2\text{-}C_4H_3O)SnBu_3$). These tin reagents scarcely reacted at all with **1a** at 25 °C. Treatment of **9** (2 mmol) with **1a** (2 mmol) in the presence of $PdCl_2$ (0.02 mmol) and LiCl (4 mmol) in AcOH at 50 °C afforded the C=C double bond-reduced product 4-phenyl-2-butanone (**3ck**) in low yield (13—28%), but almost none of the expected corresponding Michael-type product was produced. It has been reported that tributyltin reagents (i.e. Bu_3SnCl) reduced conjugate enones (particularly α,β-unsaturated γ-diketones and some β-aryl-α,β-unsaturated ketones) in the presence of palladium catalyst [Pd(0) or Pd(II) complex] at high temperature (100 °C) or prolonged reaction time.[14]

Plausible Reaction Scheme. Although the details are not yet known, we propose Scheme 4 for this catalytic Michael-type addition reaction. The transmetallation of Sn(IV) moiety of aryltin(IV) compounds by Pd(II) occurs to give an Ar–Pd(II)–X (X = OAc or Cl) species (**A**), which adds to α,β-unsaturated substrates to afford an alkylpalladium(II) species (**B**). Then, this Pd(II) species might give a palladium(II) enolate (**C**) to which the other organotin(IV) compound attacks to afford a tin(IV) enolate (**D**) regenerating the Ar–Pd(II)–X species. The reaction between the corresponding Rh enolate and arylborons has already been proposed.[15] It is assumed that the role of chloride ion of metal chloride (mainly LiCl) is probably due to coordination to aryltin(IV) compounds[12,16] to make the transmetallation step facile. For the formation of biaryl, the second transmetallation of Sn(IV) moiety of aryltin(IV) compounds by the species **A** occurs to give Ar–Pd(II)–Ar species, followed by the reductive elimination.

Experimental

General Procedure. Melting points were determined on a Yanako MP-J3 micro melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded with JEOL JNM-AL300. GLC analyses were carried out with a Shimadzu GC-14A with flame ionization detectors equipped with an SE-30 or an OV-17 (7 mmϕ × 2 m) column using nitrogen as carrier gas. The GLC yields were determined using appropriate aromatics as internal standards. The isolation of pure products was carried out with column chromatography on SiO_2 (Merck 60, 230—400 mesh, Merck KGaA.).

Materials. Solvents except AcOH were freshly distilled under N_2 prior to use: MeOH was distilled from in situ prepared $Mg(OMe)_2$ (Mg metal + I_2); THF was distilled from sodium diphenylketyl; EtOH, CH_2Cl_2, MeCN, C_5H_5N, and C_6H_6 were distilled from calcium hydride; DMF was distilled twice under reduced pressure, first from phosphorus pentaoxide and next from calcium hydride. Commercially available chlorides of Group 2 metals such as $MgCl_2$, $SrCl_2$, and $BaCl_2$ were dehydrated by thionyl chloride and dried prior to use. Tetraaryltins **2l**, **2m**, and **2n** were prepared from the corresponding Grignard reagents and $SnCl_4$ in THF, followed by recrystallization.[17] The compound **9k** was prepared from phenylmagnesium bromide and Bu_3SnCl in THF, followed by distillation under reduced pressure.[18] Lithium acetate was prepared from $LiOH\cdot H_2O$ and acetic anhydride under reflux, followed by evaporation of unreacted acetic anhydride. The authentic samples such as 4,4-diphenyl-2-butanone (**3ak**)[19] and 4,4-diphenyl-3-buten-2-one (**4ak**)[20] were synthesized by the literature method. Other reagents such as AcOH, $Pd(OAc)_2$, Na_2PdCl_4, $PdCl_2$, AgOAc, $Cu(OAc)_2$, LiCl, $CaCl_2$, NaCl, KCl, CsCl, $LiOH\cdot H_2O$, $SnCl_4$, Bu_3SnCl, **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **2k**, **6k**, **7k**, **8k**, **9o**, and **9p** were commercial products and were used without further purification.

Tetra(*p*-tolyl)tin (2l): Recrystallized from benzene–ethyl acetate, mp 242—242.5 °C (lit, 238 °C[21]); ^{1}H NMR ($CDCl_3$) δ = 2.35 (s, 12H), 7.18—7.21 (d, J = 7.9 Hz, 8H), 7.45—7.49 (d, J = 7.7 Hz, 8H).

Tetrakis(*p*-chlorophenyl)tin (2m): Recrystallized from benzene–petroleum ether, mp 198—201 °C (lit, 199 °C[21]); ^{1}H NMR ($CDCl_3$) δ = 7.36—7.58 (m, 16H).

Tetrakis(*p*-methoxyphenyl)tin (2n): Recrystallized from ethyl acetate, mp 135.5—136. 5 °C (lit, 134.8 °C[21]); ^{1}H NMR ($CDCl_3$) δ = 3.81 (s, 12H), 6.93—6.98 (d, J = 8.6 Hz, 8H), 7.47—7.51 (d, J = 8.4 Hz, 8H).

4,4-Diphenyl-2-butanone (3ak): Obtained as pale yellow oil, bp 210—225 °C (bath temp, 3 mmHg, 1 mmHg = 133.322 Pa); ^{1}H NMR ($CDCl_3$) δ = 2.06 (s, 3H), 3.15—3.19 (d, J = 7.5 Hz, 2H), 4.55—4.61 (t, J = 7.6 Hz, 1H), 7.13—7.29 (m, 10H).

4,4-Diphenyl-3-buten-2-one (4ak): Obtained as yellow oil, bp 205—210 °C (bath temp, 3 mmHg); ^{1}H NMR ($CDCl_3$) δ = 1.88 (s, 3H), 6.58 (s, 1H), 7.15—7.55 (m, 10H).

Tributylphenyltin (9k): Obtained as colorless oil; ^{1}H NMR ($CDCl_3$) δ = 0.80—0.95 (t, J = 7.3 Hz, 9H), 1.00—1.10 (t, J = 8.2 Hz, 6H), 1.25—1.40 (sext, J = 7.2 Hz, 6H), 1.45—1.65 (m, 6H), 7.25—7.35 (m, 3H), 7.35—7.55 (m, 2H).

General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds (For GLC Analysis). A mixture of **1a** (0.146 g, 1 mmol), **2k** (0.427 g, 1 mmol), palladium salt (0.1 mmol), additive (2 mmol), and acetic acid (10 mL) was stirred at 25 °C under air. After stirring for 5—24 h, the mixture was poured into brine (150 mL) and extracted with CH_2Cl_2 (30 mL × 3). The organic layer was washed with dilute HCl (ca. 3 mol dm^{-3}, 50 mL × 2) and saturated $NaHCO_3$ solution (50 mL) and then dried over anhydrous $MgSO_4$. The appropriate internal standard was added to the extract and the products were analyzed and determined by gas chromatography. During the extraction with CH_2Cl_2 white solid material sometimes came out at the interface of CH_2Cl_2 and water, and in that case the addition of dilute aqueous HCl was necessary to obtain two clear phases.

General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds (For Isolation). A mixture of enone (2—2.4 mmol), organotin (0.5—2 mmol), $PdCl_2$ (0.02—0.04 mmol), LiCl (4 mmol), and acetic acid (20 mL) was stirred at 25—50 °C under air. After stirring for 2—20 h, the mixture was poured into brine (150 mL) and extracted with diethyl ether (30 mL × 5). The organic layer was washed with dilute HCl (ca. 3 mol dm^{-3}, 50 mL × 2), water (30 mL), saturated KF solution (25 mL), and saturated $NaHCO_3$ solution (50 mL) and then dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the yellow residue was separated by column chromatography. When diethyl ether-insoluble white solid (**2k**) existed, the residue was mixed with diethyl ether (ca. 5 mL × 2) and hexane (ca. 5 mL) in order to remove **2k**, and the supernatant was decanted and then evaporated in vacuo before column chromatography.

1,3,3-Triphenyl-1-propanone (3bk): Obtained as white solid, mp 86—90 °C (recrystallized from hexane, lit, 95 °C[22]); ^{1}H NMR ($CDCl_3$) δ = 3.72—3.76 (d, J = 7.2 Hz, 2H), 4.80—4.86 (t, J = 7.3 Hz, 1H), 7.15—7.20 (m, 2H), 7.25—7.27 (d, J = 4.6 Hz, 6H), 7.37—7.70 (m, 5H), 7.91—7.95 (d, J = 7.2 Hz, 2H).

4-Phenyl-2-butanone (3ck): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 2.14 (s, 3H), 2.72—2.83 (d, J = 7.2 Hz, 2H), 2.83—2.95 (t, J = 7.3 Hz, 2H), 7.12—7.37 (m, 5H).

4-Phenyl-2-pentanone (3dk): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 1.25—1.28 (d, J = 7.0 Hz, 3H), 2.06 (s, 3H), 2.61—2.70 (dd, J = 7.8 and 16.7 Hz, 1H), 2.71—2.80 (dd, J = 6.5 and 16.2 Hz, 1H), 3.22—3.38 (sext, J = 7.1 Hz, 1H), 7.14—7.35 (m, 5H).

3-Phenylcyclohexanone (3ek): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 1.54—1.90 (m, 2H), 1.95—2.20 (m, 2H), 2.20—2.60 (m, 4H), 2.85—3.10 (m, 1H), 7.00—7.50 (m, 5H).

3-Phenylcyclopentanone (3fk): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 1.80—2.20 (m, 1H), 2.20—2.55 (m, 4H), 2.55—2.80 (dd, J = 7.7 and 18.2 Hz, 1H), 3.30—3.60 (m, 1H), 7.10—7.50 (m, 5H).

1-(2-Phenylcyclohexyl)-1-ethanone (3gk): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 1.25—1.50 (m, 1H), 1.65—1.75 (m, 3H and s, 3H), 1.75—1.90 (m, 2H), 1.90—2.00 (m, 1H), 2.25—2.45 (dq, J = 3.3 and 11.3 Hz, 1H), 2.80—3.00 (dt, J = 11.2 and 4.2 Hz, 1H), 3.00—3.10 (t, J = 4.1 Hz, 1H), 7.10—7.45 (m, 5H).

4-Phenyl-4-(*p*-tolyl)-2-butanone (3al): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 2.06 (s, 3H), 2.28 (s, 3H), 3.13—3.16 (d, J = 7.5 Hz, 2H), 4.51—4.57 (t, J = 7.6 Hz, 1H), 7.00—7.33 (m, 9H).

4-(*p*-Chlorophenyl)-4-phenyl-2-butanone (3am): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 2.07 (s, 3H), 3.12—3.15 (d, J = 7.5 Hz, 2H), 4.52—4.58 (t, J = 7.5 Hz, 1H), 7.10—7.30 (m, 9H).

4-(*p*-Methoxyphenyl)-4-phenyl-2-butanone (3an): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 2.05 (s, 3H), 3.11—3.14 (d, J = 7.7 Hz, 2H), 3.72 (s, 3H), 4.49—4.55 (t, J = 7.5 Hz, 1H), 6.76—6.85 (d, J = 8.7 Hz, 2H), 7.05—7.40 (m, 7H).

3,3-Diphenylpropanal (3hk): Obtained as yellow oil; ^{1}H NMR ($CDCl_3$) δ = 3.10—3.20 (dd, J = 1.9 and 7.8 Hz, 2H), 4.55—4.66 (t, J = 7.8 Hz, 1H), 7.10—7.35 (m, 10H), 9.71—9.75 (t, J = 1.9 Hz, 2H).

4,4′-Dichlorobiphenyl (5m): Obtained as white crystal; ^{1}H NMR ($CDCl_3$) δ = 7.35—7.55 (m, 8H).

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