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Highly Stereoselective Preparation of Tri- and Tetra-substituted Olefins via β-Tributylstannyl-α,β-unsaturated Ketones

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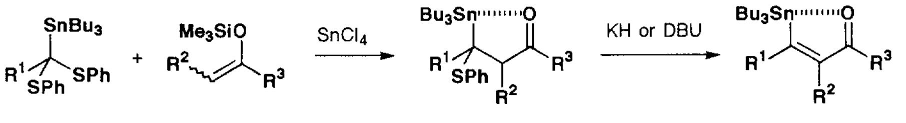
Abstract: The palladium(0)-catalyzed reactions of β-tributylstannyl-α,β-unsaturated ketones **3** with benzyl or aryl halides in the presence of copper(I) iodide gave the tri- and tetra-substituted olefins **4** or **5** with high stereoselectivity, respectively. It was found that the yields of **5** were remarkably improved by the use of triethylamine as an additive. The starting materials **3** were easily prepared by the tin(IV) chloride-promoted coupling reaction of α-tributylstannylthioacetals with enol silyl ethers followed by the treatment with potassium hydride or DBU in good yields.

Since some classes of natural products have tri- and tetra-substituted olefin moieties, the construction of such structural units has extensively studied.1) The reactions of vinylmetal species with electrophiles would be the one of the most useful methods for this purpose. Vinylstannanes are thermally stable, not moisture-sensitive, and handled by all the usual chromatographic and spectroscopic techniques. It is well known that the treatment of vinylstannanes with butyllithium gives the corresponding vinyllithium with retention of configuration.2) Furthermore, a trialkylstannyl group in vinylstannanes can be easily substituted by free radical3) or transition metal catalyzed reactions,4) the latter having been known to proceed with retention of configuration. Therefore vinylstannanes seem to be useful vinylmetal reagents for preparation of highly substituted olefins. Although several methods for the stereoselective preparation of vinylstannanes have been reported,5) there still remains the problems of stereoselectivity and applicability.

Recently, we showed that β-tributylstannyl-α,β-unsaturated ketones **3** were easily prepared by the reaction of α-tributylstannylthioacetals **1** with enol silyl ethers in the presence of tin(IV) chloride, followed by the treatment with potassium hydride or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Eq. 1).6)

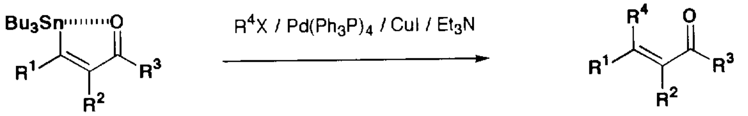


(1)

1 **2** **3**

Although the exact stereoisomeric purity of β-stannyl ketones **3** thus obtained was uncertain, we presumed that the *Z*-isomers predominate in this reaction on the basis of the IR data of the β-bromodibutylstannyl-α,β-unsaturated ketones formed by the treatment of **3** with copper(II) bromide or bromine-dioxane complex.

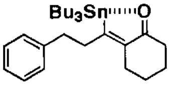
Since the stereocontrolled synthesis of highly substituted olefins is still a problem to be solved, it is obvious that the β-stannyl ketones **3** hold great promise for the construction of highly substituted olefins including exocyclic ones.7) We wish to describe here the highly stereoselective preparation of olefins by the palladium(0)-catalyzed coupling reaction of **3** with benzyl or aryl halides (Eq. 2). Although the similar approach to exocyclic olefins using the γ-oxovinyltrimethylsilane has been recently reported,8) the palladium-catalyzed coupling reaction with iodobenzene was performed after reduction of the γ-oxovinylsilane to γ-hydroxy derivative owing to the low reactivity of vinylsilane.



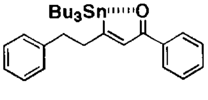
(2)

3

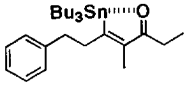
4; R^4 = $PhCH_2$
5; R^4 = Aryl



3a



3b



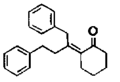
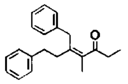
3c

RESULTS AND DISCUSSION

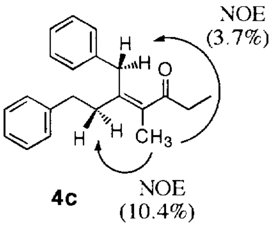
Since the vinyl-tin bond of β-stannyl ketones **3** is stabilized by the intramolecular coordination of carbonyl group to tin atom,6) we expected that **3** is not so reactive as common vinylstannanes toward transition metal-catalyzed coupling reaction. In fact, the formation of only a trace amount of benzylation product **4a** was observed when 2-(3-phenyl-1-tributylstannylpropylidene)cyclohexanone (**3a**) was treated with benzyl bromide in the presence of 4 mol% of tetrakis(triphenylphosphine)palladium(0) in DMF at room temperature. Although the coupling product **4a** was produced in a moderate yield at the elevated temperature, it was found that the product was a mixture of stereoisomers (run 1, Table 1). Furthermore, the ratio of stereoisomers is apparently dependent on the reaction temperature employed. This fact may indicate that the isomerization of **4a** readily proceeds under the reaction conditions. Recently it has been reported that copper(I) iodide is effective co-catalyst in some Stille reactions.9) Then we examined the use of copper(I) salts, and found that copper(I) iodide remarkably accelerated the present reaction to give Z-**4** as the sole products at room temperature (runs 8 and 9). Unlike precedents, however, the use of more than 0.5 equiv. of copper(I) salt was essential to complete the present reaction within a reasonable reaction time.

The configuration of **4a** was determined to be Z on the basis of the chemical shift of the methylene protons of introduced benzyl group. In the NMR spectrum of **4a** obtained by the reactions carried out at high temperature, the signals corresponding to the protons of benzyl group occurs as two singlets at δ 3.64 and 3.52, respectively. It is rational to assume that the protons due to the Z-isomer is found further down field because of the deshielding effect of carbonyl group. The stereochemisty of **4c** was determined by the NOE experiment (Fig. 1). Considering the fact that the palladium(0)-catalyzed coupling reactions of vinylstannanes proceed with

Table 1. The Reaction of β-Tributylstannyl-α,β-unsaturated Ketones **3** with Benzyl Bromide.[a)]

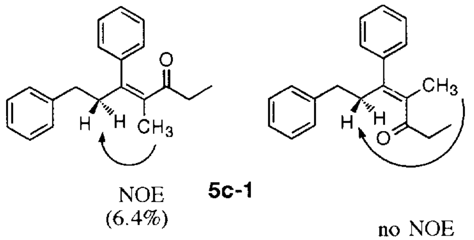
Run	3	CuX (equiv.)	Solvent	Temp °C	Time h	Product	Yield %	E : Z[b)]
1	**3a**	-	DMF	120	0.5	 **4a**	44	38 : 62
2	**3a**	-	toluene	111	3	**4a**	65	21 : 79
3	**3a**	-	THF	67	27	**4a**	46	8 : 92
4	**3a**	-	CH_2Cl_2	40	41	**4a**	39	3 : 97
5	**3a**	CuBr (1.0)	DMF	room temp	11	**4a**	23	0 : 100
6	**3a**	CuI (0.1)	DMF	room temp	20	**4a**	10	0 : 100
7	**3a**	CuI (0.5)	DMF	room temp	16	**4a**	84	0 : 100
8	**3a**	CuI (1.0)	DMF	room temp	12	**4a**	88	0 : 100
9	**3c**	CuI (1.0)	DMF	room temp	7	 **4c**	92	0 : 100

a) All the reactions were performed using $Pd(Ph_3P)_4$ (4 mol%) and benzyl bromide (2 equiv.), unless otherwise noted. b) The ratio of stereoisomers was determined by NMR analysis.



4c

Fig. 1



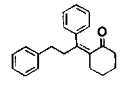
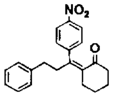
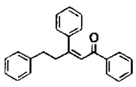
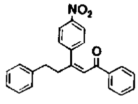
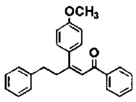
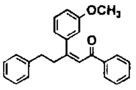
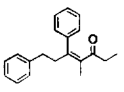
5c-1

Fig. 2

retention of configuration, the stereochemical result of the present reaction well agrees with presumed Z-configuration of **3**.

Next the arylation of **3** with aryl iodides under the similar reaction conditions was studied. As was distinct from the reaction with benzyl bromide, the palladium(0)-catalyzed reaction of **3a** with iodobenzene at 120 °C for 3 h gave the arylation product **5a-1** with high stereoselectivity (E : Z = 3 : 97) in 36% yield. However, the yield of **5a-1** was only moderate even when an equimolar amount of copper(I) salts were used. Then we turned our attention to activation of vinylstannanes **3** by forming the higher coordinated complexes with appropriate ligands. After several attempts, it was found that the use of tertiary amine as an additive largely improved the yield of **5** (Table 2). Using an equimolar amount of triethylamine, **5a-1** was obtained with high

Table 2. The Coupling Reaction of β-Tributylstannyl-α,β-unsaturated Ketones **3** with Aryl Iodides in the Presence of Copper(I) Halides and Tertiary Amines.[a)]

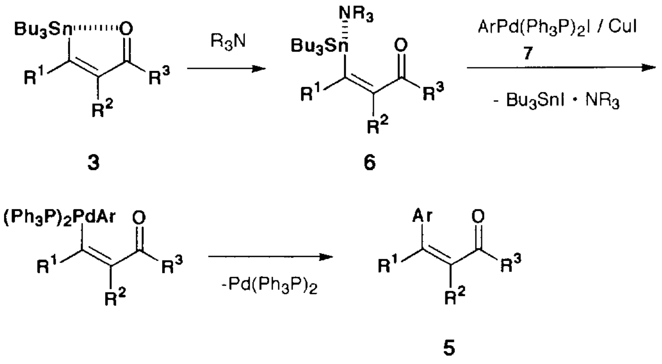
Run	3	CuX	Amine	Aryl Iodide	Time h	Product	Yield %	*E* : *Z*[b)]
1	**3a**	CuI	-	PhI	38	 **5a-1**	45	5 : 95
2	**3a**	CuI[c)]	Et_3N	PhI	38	**5a-1**	54	5 : 95
3	**3a**	CuI	Et_3N	PhI	38	**5a-1**	72	6 : 94
4	**3a**	CuI	-	*p*-NO_2PhI	14	 **5a-2**	82	3 : 97
5	**3b**	CuI	-	PhI	22	 **5b-1**	51	1 : 99
6	**3b**	CuI	DBU[c)]	PhI	12	**5b-1**	85	3 : 97
7	**3b**	CuI	Et_3N[c)]	PhI	22	**5b-1**	81	2 : 98
8	**3b**	CuI	Et_3N	PhI	16	**5b-1**	92	1 : 99
9	**3b**	CuCl	Et_3N	PhI	3	**5b-1**	74	2 : 98
10	**3b**	CuBr	Et_3N	PhI	4	**5b-1**	85	2 : 98
11	**3b**	-	Et_3N	PhI	20	-	- (90)[d)]	-
12	**3b**	CuI	-	*p*-NO_2PhI	15	 **5b-2**	86	2 : 98
13	**3b**	CuI	Et_3N	*p*-NO_2PhI	20	**5b-2**	84	3 : 97
14[e,f)]	**3b**	CuI	Et_3N	*p*-CH_3OPhI	40	 **5b-3**	73	1 : 99
15[e)]	**3b**	CuI	Et_3N	*m*-CH_3OPhI	19	 **5b-4**	87	1 : 99
16	**3c**	CuI	Et_3N	PhI	39	 **5c-1**	89	1 : 99

a) All the reactions were performed using $Pd(Ph_3P)_4$ (4 mol%), CuX (1 equiv.), amine (1 equiv.), and aryl iodide (2 equiv.) in DMF, unless otherwise noted. b) The ratio of stereoisomers was determined by HPLC analysis. c) 0.5 equiv. of the reagent used. d) Recovered starting material. e) Carried out in the dark. f) When the reaction was carried out in an usual manner for 38 h, it was complicated and **5b-3** was obtained in 44% yield.

stereoselectivity in 72% yield (run 3). Among various amines examined, DBU was also effective for the present reaction (run 6). On the contrary, 1,4-diazabicyclo[2.2.2]octane largely retarded the reaction, and the yield of **5** was decreased by addition of N,N-dimethylaniline. No appreciable effect of the additive was observed in the reactions of 1-iodo-4-nitrobenzene, which is known to be highly reactive in the Stille reaction (runs 12 and 13).10) In a similar manner, the coupling reactions of several vinylstannanes **3** with aryl halides were performed, and the corresponding tri- and tetra-substituted olefins **5** were isolated in good to high yields.

In all the cases examined, olefins **5** were obtained with high stereoselectivity (>94%). The configuration of main isomers was determined to be *Z* on the basis of the chemical shifts of methylene protons attached to the carbon atom γ to carbonyl group. The minor isomers were prepared by photoisomerization of the coupling products **5** in considerable quantities for NMR analysis. In the cases of **5a** and **5b**, the γ-protons of one isomer are found at further downfield from those of another isomer (Table 3). Since the γ-protons of *E*-isomer are located in the deshielding zone of carbonyl group, the former should have *E*-configuration. The stereochemistry of **5c-1** was assigned by the NOE experiment. The main isomer showed NOE (6.4%) between α-methyl and γ-methylene protons. On the other hand, no NOE was observed between those of the other isomer (Fig. 2). These results clearly show that the former is *Z*- and the latter is *E*-isomer.

The roles of copper(I) salt and tertiary amine are uncertain at present. As for the beneficial effects of adding copper(I) salts in the palladium-catalyzed cross-coupling reactions of organotin compounds with aryl halides or triflates, several authors indicated that copper(I) salt may facilitate the transmetallation step.9b,i,j) Recently, Liebeskind *et al.* noted that the effect of copper(I) salt in Stille coupling using a palladium catalyst with triphenylphosphine is to scavenge free ligand which is inhibitory to the transmetalation.11) We tentatively assume that the present reaction proceeds through the five-coordinated vinylstannane **6** as illustrated in Eq. 3. The complex **6** would be more reactive toward arylpalladium iodide **7** in the transmetallation step than **3** which is deactivated by the intramolecular coordination.



(3)

Table 3. The Chemical Shifts (δ) of Protons Attached to the Carbon γ to Carbonyl Group of Arylation Products **5**.

5	*Z*	*E*	**5**	*Z*	*E*
5a-1	2.68 - 2.79	2.78 - 2.89	**5b-3**	2.83 - 2.95	3.29 - 3.44
5a-2	2.69 - 2.82	2.79 - 2.91	**5b-4**	2.82 - 2.95	3.29 - 3.39
5b-1	2.83 - 2.99	3.26 - 3.47	**5c-1**	2.69 - 2.89	2.64 - 2.77
5b-2	2.85 - 2.98	3.29 - 3.41			

CONCLUSION

The palladium(0)-catalyzed coupling reactions of β-tributylstannyl-α,β-unsaturated ketones **3** with benzyl bromide or ary iodides proceed in the presence of copper(I) salt to give (*Z*)-tri- and tetra-substituted olefins with high stereoselectivity. These results turn out to support the assumption that the configuration of **3** is *Z*. In addition, the use of triethylamine or DBU in the coupling reactions of **3** with aryl iodides remarkably increased the yields of arylation products **5**. Since the various vinylstannanes **3** can be prepared using easily accessible thioacetals and enol silyl ethers, it should be noted that the present series of reactions provides a facile method for the highly stereoselective preparation of not only acyclic but also exocyclic olefins.

EXPERIMENTAL SECTION

General. All the reactions were carried out in a dry reaction vessel under argon. All melting points were determined with a YANACO MP-S3 micromelting point apparatus. ^{1}H NMR spectra were measured for a $CDCl_3$ solution on JEOL FX-200 and GX-270 instruments and are reported in parts per million from internal tetramethylsilane. IR spectra were recorded on a JASCO A-100; absorptions are reported in cm^{-1}. Elemental analyses were performed by Perkin Elmer 2400II. HPLC analyses were carried out with an UV detector (monitored at 254 nm) on a Merck Si 60 column (4.6 mm inside diameter, 25 cm length) using hexane-AcOEt (9 : 1) as eluent. A Riko UVL-400HA 400 W high-pressure mercury lamp was used in the irradiation.

Materials. Methylene chloride was distilled from calcium hydride under argon immediately before use. THF was distilled from benzophenone ketyl under argon immediately before use. Copper(I) iodide was purified by washing with THF and dried *in vacuo*. All commercially available reagents were either distilled or recrystallized before use.

Preparation of 1-Phenyl-3,3-bis(phenylthio)-3-tributylstannylpropane (1). To a THF (4 ml) solution of 1-phenyl-3,3-bis(phenylthio)propane (1.01 g, 3 mmol) was added butyllithium (1.61 M in hexane, 3 mmol) at -40 °C, and the reaction mixture was stirred for 1 h. Then tributyltin chloride (1.07 g, 3.3 mmol) was added at the same temperature. After being stirred for 1 h, the reaction was quenched by addition of saturated aqueous NH_4Cl. The organic materials were extracted with hexane, dried (Na_2SO_4), and condensed under reduced pressure. The residue was purified by silica-gel chromatography (hexane) to give **1** (1.82 g, 97%). IR (neat) 2921, 1583, 1457, 745, 693; ^{1}H NMR δ 7.74-7.53 (m, 4H), 7.42-7.07 (m, 9H), 7.07-6.94 (m, 2H), 2.92-2.70 (m, 2H), 2.29-2.11 (m, 2H), 1.71-1.17 (m, 6H), 1.30 (tq, *J*= 7, 7 Hz, 6H), 1.17-0.71 (m, 6H), 0.89 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{33}H_{46}S_2Sn$: C, 63.36; H, 7.41. Found: C, 63.10; H, 7.19.

Preparation of 2-(3-Phenyl-1-phenylthio-1-tributylstannylpropyl)cyclohexanone (2a). To a CH_2Cl_2 (15 ml) solution of **1** (3.08 g, 4.93 mmol) and 1-trimethylsiloxy-1-cyclohexene (1.26 g, 7.40

mmol) was added a CH_2Cl_2 (4.83 ml) solution of tin(IV) chloride (4.93 mmol) at -78 °C, and the reaction mixture was stirred for 3 h. After addition of water, the organic materials were extracted with CH_2Cl_2, dried (Na_2SO_4), and condensed under reduced pressure. The residue was purified by silica-gel chromatography (hexane : AcOEt = 98 : 2) to give **2a** (2.73 g, 90%). In a similar manner, 1,5-diphenyl-3-phenylthio-3-tributylstannylpentan-1-one (**2b**) and 4-methyl-7-phenyl-5-phenylthio-5-tributylstannylheptan-3-one (**2c**) were obtained in 92% and 69% yields, respectively.

Physical Properties of β-Phenylthio-β-tributylstannyl Ketones 2. 2-(3-Phenyl-1-phenylthio-1-tributylstannylpropyl)cyclohexanone (2a): mp 64-65 °C; IR (KBr) 2919, 1695, 1600, 1454, 747, 702; ^1H NMR δ 7.58-7.46 (m, 2H), 7.36-7.04 (m, 8H), 3.30 (dt, *J*= 4, 13 Hz, 1H), 3.20-2.94 (m, 1H), 2.55 (dt, *J*= 4, 13 Hz, 2H), 2.42-1.81 (m, 5H), 1.81-1.28 (m, 10H), 1.38 (tq, *J*= 7, 7 Hz, 6H), 1.14-0.81 (m, 6H), 0.93 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{33}H_{50}OSSn$: C, 64.60; H, 8.21. Found: C, 64.51; H, 8.27.

1,5-Diphenyl-3-phenylthio-3-tributylstannylpentan-1-one (2b): mp 50-52 °C; IR (KBr) 2916, 1676, 1596, 1448, 752, 688; ^1H NMR δ 7.86-7.73 (m, 2H), 7.64-7.09 (m, 13H), 3.52 (d, *J*= 18 Hz, 1H), 3.33 (dt, *J*= 4, 13 Hz, 1H), 3.26 (d, *J*= 18 Hz, 1H), 2.58 (dt, *J*= 5, 13 Hz, 1H), 2.38 (tq, *J*= 7, 7 Hz, 6H), 2.13 (dt, *J*= 4, 13 Hz, 1H), 1.84-0.85 (m, 13H), 0.92 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{35}H_{48}OSSn$: C, 66.15; H, 7.61. Found: C, 66.02; H, 7.54.

4-Methyl-7-phenyl-5-phenylthio-5-tributylstannylheptan-3-one (2c): IR (neat) 2970, 1706, 1600, 1454, 738, 693; ^1H NMR δ 7.61-7.46 (m, 2H), 7.42-7.05 (m, 8H), 5.47 (dt, *J*= 5, 13 Hz, 1H), 2.67-2.01 (m, 4H), 1.85-0.87 (m, 14H), 1.39 (tq, *J*= 7, 7 Hz, 6H), 1.36 (d, *J*= 7 Hz, 3H), 0.94 (t, *J*= 7 Hz, 9H), 0.93 (t, *J*= 7 Hz, 3H). Anal. calcd for $C_{32}H_{50}OSSn$: C, 63.90; H, 8.38. Found: C, 64.19; H, 8.55.

Preparation of (Z)-2-(3-Phenyl-1-tributylstannylpropylidene)cyclohexanone (3a). To a suspension of potassium hydride (35 wt. % dispersion in mineral oil; 4.75 g, 41.5 mmol) in THF (10 ml) was added a THF (40 ml) solution of **2a** (5.09 g, 8.3 mmol) and HMPA (17 ml) successively at 0 °C with vigorous stirring. After being stirred for 3 h, the reaction mixture was carefully poured over crashed ice. The organic materials were extracted with ether, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the crude product by silica-gel chromatography (hexane : AcOEt = 98 : 2) gave (*Z*)-**3a** (3.57 g, 85%).

Preparation of (Z)-4-Methyl-7-phenyl-5-tributylstannyl-4-hepten-3-one (3c). To a THF (7 ml) solution of **2c** (674 mg, 1.1 mmol) was added DBU (0.5 ml, 3.4 mmol), and the reaction mixture was refluxed for 10 h. After addition of water, the organic materials were extracted with hexane, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica-gel chromatography (hexane) to give (*Z*)-**3c** (308 mg, 57%). (*Z*)-1,5-Diphenyl-3-tributylstannyl-2-penten-1-one (**3b**) was also prepared by the similar treatment of **2b** with 2 equiv. of DBU at 0 °C for 3 h in 88% yield.

Physical Properties of (Z)-β-Tributylstannyl-α,β-unsaturated Ketones 3. (Z)-2-(3-Phenyl-1-tributylstannylpropylidene)cyclohexanone (3a): IR (neat) 2950, 1662, 1541, 745, 697; ^1H NMR δ 7.36-7.12 (m, 5H), 2.78-2.60 (m, 2H), 2.60-2.39 (m, 4H), 2.46 (t, *J*= 7 Hz, 2H), 1.91-1.14 (m, 10H), 1.30 (tq, *J*= 8, 7 Hz, 6H), 0.99-0.72 (m, 6H), 0.88 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{27}H_{44}OSn$: C, 64.43; H, 8.81. Found: C, 64.36; H, 8.77.

(Z)-1,5-Diphenyl-3-tributylstannyl-2-penten-1-one (3b): IR (neat) 2936, 1646, 1561, 778, 694; ^1H NMR δ 7.98-7.85 (m, 2H), 7.60-7.38 (m, 4H), 7.38-7.12 (m, 5H), 2.94-2.70 (m, 4H), 1.79-1.11 (m, 6H), 1.31 (tq, *J*= 7, 7 Hz, 6H), 1.11-0.96 (m, 6H), 0.87 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{29}H_{42}OSn$: C, 66.30; H, 8.06. Found: C, 66.29; H, 8.05.

(Z)-4-Methyl-7-phenyl-5-tributylstannyl-4-hepten-3-one (3c): IR (neat) 2932, 1670, 1559, 750, 700; ^1H NMR δ 7.37-7.13 (m, 5H), 2.76-2.45 (m, 4H), 2.62 (q, *J*= 7 Hz, 2H), 1.96 (s, 3H), 1.68-1.18 (m, 6H), 1.30 (tq, *J*= 7, 7 Hz, 6H), 1.09 (t, *J*= 7 Hz, 3H), 0.99-0.69 (m, 6H), 0.88 (t, *J*= 7 Hz, 9H). Anal. calcd for $C_{26}H_{44}OSn$: C, 63.56; H, 9.03. Found: C, 63.37; H, 8.93.

A Typical Procedure: Reaction of (Z)-4-Methyl-7-phenyl-5-tributylstannyl-4-hepten-3-one (3c) with Benzyl Bromide. To a flask charged with tetrakis(triphenylphosphine)palladium(0) (14 mg, 0.012 mmol) and copper(I) iodide (57 mg, 0.3 mmol) was added a DMF (3 ml) solution of **3c** (147 mg, 0.3 mmol) and benzyl bromide (103 mg, 0.6 mmol) at room temperature. After being stirred for 7 h, the reaction mixture was diluted with ether (25 ml) and washed with saturated NH_4Cl and $NaHCO_3$ aqueous solutions successively. The organic layer was dried (Na_2SO_4) and condensed. The residue was purified by silica-gel chromatography (hexane : AcOEt = 98 : 2) to give 5-benzyl-4-methyl-7-phenyl-4-hepten-3-one (**4c**) (81 mg, 92%).

Physical Properties of Benzylation Products 4. (*Z*)-2-(1-Benzyl-3-phenylpropylidene)-cyclohexanone (4a): IR (neat) 2948, 1676, 1603, 738, 693; ^{1}H NMR δ 7.42-7.04 (m, 10H), 3.64 (s, 2H), 2.63-2.41 (m, 6H), 2.38-2.23 (m, 2H), 2.00-1.81 (m, 2H), 1.78-1.57 (m, 2H). Anal. calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.96. Found: C, 86.60; H, 8.13.

(*Z*)-5-Benzyl-4-methyl-7-phenyl-4-hepten-3-one (4c): IR (neat) 2959, 1685, 1603, 741, 695; ^{1}H NMR δ 7.36-7.02 (m, 10H), 3.43 (s, 2H), 2.66-2.48 (m, 2H), 2.56 (q, *J*= 7 Hz, 2H), 2.33-2.20 (m, 2H), 1.80 (s, 3H), 1.09 (t, *J*= 7 Hz, 3H). Anal. calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.25; H, 8.31.

A Typical Procedure: Reaction of (*Z*)-4-Methyl-7-phenyl-5-tributylstannyl-4-hepten-3-one (3c) with Iodobenzene. To a flask charged with tetrakis(triphenylphosphine)palladium(0) (23 mg, 0.02 mmol) and copper(I) iodide (95 mg, 0.5 mmol) was added a DMF (4.5 ml) solution of **3c** (246 mg, 0.5 mmol), iodobenzene (204 mg, 1.0 mmol), and triethylamine (51 mg, 0.5 mmol) at room temperature. After being stirred for 39 h, the reaction mixture was diluted with ether (25 ml). The usual work-up and purification by silica-gel chromatography (hexane : AcOEt = 95 : 5) gave 4-methyl-5,7-diphenyl-4-hepten-3-one (**5c-1**) (124 mg, 89%).

Physical Properties of Arylation Products 5. (*Z*)-2-(1,3-Diphenylpropylidene)cyclohexanone (5a-1): mp 42-43 °C; IR (KBr) 2945, 1686, 1621, 743, 698; ^{1}H NMR δ 7.37-7.05 (m, 10H), 2.79-2.68 (m, 2H), 2.65-2.54 (m, 2H), 2.48 (t, *J*= 6 Hz, 2H), 2.38 (t, *J*= 7 Hz, 2H), 1.93-1.77 (m, 2H), 1.67-1.51 (m, 2H). Anal. calcd for $C_{21}H_{22}O$: C, 86.86; H, 7.64. Found: C, 86.73; H, 7.63.

(*Z*)-2-[1-(4-Nitrophenyl)-3-phenylpropylidene]cyclohexanone (5a-2): mp 100 °C; IR (KBr) 2944, 1684, 1596, 1510, 1339, 821, 754, 702; ^{1}H NMR δ 8.21-8.12 (m, 2H), 7.36-7.07 (m, 7H), 2.82-2.69 (m, 2H), 2.66-2.48 (m, 2H), 2.53 (t, *J*= 6 Hz, 2H), 2.36 (t, *J*= 7 Hz, 2H), 1.96-1.78 (m, 2H), 1.74-1.53 (m, 2H). Anal. calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.20; H, 6.30; N, 4.19.

(*Z*)-1,3,5-Triphenyl-2-penten-1-one (5b-1): mp 63-64 °C; IR (KBr) 3023, 1664, 1626, 1600, 741, 698; ^{1}H NMR δ 7.68-7.56 (m, 2H), 7.48-7.04 (m, 13H), 6.51 (s, 1H), 2.99-2.83 (m, 2H), 2.83-2.69 (m, 2H). Anal. calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.09; H, 6.40.

(*Z*)-3-(4-Nitrophenyl)-1,5-diphenyl-2-penten-1-one (5b-2): mp 89-90 °C; IR (KBr) 2946, 1663, 1625, 1599, 1520, 1351, 780, 755, 705; ^{1}H NMR δ 8.17-8.08 (m, 2H), 7.70-7.10 (m, 12H), 6.73 (s, 1H), 2.98-2.85 (m, 2H), 2.85-2.71 (m, 2H). Anal. calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.11; H, 5.30; N, 3.96.

(*Z*)-3-(4-Methoxyphenyl)-1,5-diphenyl-2-penten-1-one (5b-3): mp 74-75 °C; IR (KBr) 2926, 1633, 1629, 1597, 1247, 839, 764, 712; ^{1}H NMR δ 7.71-7.56 (m, 2H), 7.50-7.04 (m, 10H), 6.83-6.74 (m, 2H), 6.45 (s, 1H), 3.76 (s, 3H), 2.95-2.83 (m, 2H), 2.83-2.70 (m, 2H). Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.14; H, 6.51.

(*Z*)-3-(2-Methoxyphenyl)-1,5-diphenyl-2-penten-1-one (5b-4): IR (neat) 2948, 1665, 1599, 1581, 1256, 783, 751, 701; ^{1}H NMR δ 7.67-7.58 (m, 2H), 7.47-7.10 (m, 9H), 6.79-6.67 (m, 3H), 6.47 (s, 1H), 3.68 (s, 3H), 2.95-2.82 (m, 2H), 2.82-2.71 (m, 2H). Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.03; H, 6.51.

(*Z*)-4-Methyl-5,7-diphenyl-4-hepten-3-one (5c-1): IR (neat) 2954, 1677, 1601, 741, 694; ^{1}H NMR δ 7.40-7.02 (m, 10H), 2.89-2.69 (m, 2H), 2.68-2.52 (m, 2H), 1.90 (q, *J*= 7 Hz, 2H), 1.87 (s, 3H), 0.74 (t, *J*= 7 Hz, 3H). Anal. calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.61; H, 8.04.

A Typical Procedure: Photoisomerization of (*Z*)-2-(1,3-Diphenylpropylidene)cyclohexanone (5a-1). A hexane (5 ml) solution of (*Z*)-**5a-1** (41 mg, 0.14 mmol) in a pyrex test tube was irradiated with high pressure mercury lamp at 20 °C for 1.5 h. After evaporation of the solvent, the residue was purified by silica-gel chromatography (hexane : AcOEt = 9 : 1) to give (*E*)-**5a-1** (10 mg, 24%), and (*Z*)-**5a-1** (18 mg, 44%) was recovered.

Physical Properties of (*E*)-5. (*E*)-5a-1: mp 87-89 °C; IR (KBr) 2941, 1669, 1602, 768, 706; ^{1}H NMR δ 7.46-7.06 (m, 10H), 2.89-2.78 (m, 2H), 2.68-2.56 (m, 2H), 2.33 (t, *J*= 7 Hz, 2H), 2.30 (t, *J*= 6 Hz, 2H), 1.93-1.76 (m, 2H), 1.70-1.51 (m, 2H). Anal. calcd for $C_{21}H_{22}O$: C, 86.86; H, 7.64. Found: C, 86.57; H, 7.67.

(*E*)-5a-2: mp 128-129 °C; IR (KBr) 2941, 1673, 1589, 1516, 1346, 823, 752, 706; ^{1}H NMR δ 8.32-8.21 (m, 2H), 7.36-7.06 (m, 7H), 2.91-2.79 (m, 2H), 2.68-2.56 (m, 2H), 2.36 (t, *J*= 6 Hz, 2H), 2.25 (t, *J*= 6 Hz, 2H), 1.97-1.79 (m, 2H), 1.73-1.54 (m, 2H). Anal. calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 74.92; H, 6.39; N, 4.40.

(*E*)-5b-1: IR (neat) 3027, 1655, 1598, 1573, 758, 697; ^{1}H NMR δ 8.05-7.87 (m, 2H), 7.72-7.36 (m, 8H), 7.33-7.03 (m, 5H), 7.09 (s, 1H), 3.47-3.26 (m, 2H), 2.89-2.69 (m, 2H). Anal. calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.35; H, 6.51.

(*E*)-5b-2: mp 75-76 °C; IR (KBr) 2927, 1649, 1596, 1585, 1511, 1344, 784, 740, 686; ^{1}H NMR δ 8.34-8.20 (m, 2H), 7.99-7.86 (m, 2H), 7.69-7.41 (m, 5H), 7.28-7.04 (m, 5H), 7.07 (s, 1H), 3.41-3.29 (m, 2H), 2.85-2.73 (m, 2H). Anal. calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.21; H, 5.44; N, 4.15.

(*E*)-5b-3: IR (neat) 2965, 1648, 1586, 1563, 1248, 825, 743, 694; ^{1}H NMR δ 8.03-7.88 (m, 2H), 7.67-7.39 (m, 5H), 7.39-7.08 (m, 5H), 7.10 (s, 1H), 7.02-6.91 (m, 2H), 3.86 (s, 3H), 3.44-3.29 (m, 2H), 2.89-2.74 (m, 2H). Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.36; H, 6.57.

(*E*)-5b-4: mp 72-73 °C; IR (KBr) 2937, 1643, 1599, 1564, 1228, 777, 751, 701; ^{1}H NMR δ 7.99-7.89 (m, 2H), 7.62-6.91 (m, 13H), 3.86 (s, 3H), 3.39-3.29 (m, 2H), 2.86-2.74 (m, 2H). Anal. calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.09; H, 6.63.

(*E*)-5c-1: IR (neat) 2937, 1686, 1599, 738, 693; ^{1}H NMR δ 7.47-7.01 (m, 10H), 2.77-2.64 (m, 2H), 2.64-2.31 (m, 2H), 2.44 (q, *J*= 7 Hz, 2H), 1.70 (s, 3H), 1.07 (t, *J*= 7 Hz, 3H). Anal. calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.55; H, 8.03.

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