Rhodium-Catalyzed Reaction of Aromatic Carboxylic Acid Derivatives or Aldehydes with Unsaturated Compounds

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Graduate School of Engineering
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（ロジウム触媒を用いる芳香族カルボン酸誘導体あるいはアルデヒドと不飽和化合物との反応）

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Preface

The work of this thesis has been carried out under the guidance of Professor Masakatsu Nomura of the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

The objective of this thesis is to develop novel synthetic methods for coupling reaction of aromatic carbonyl compounds with unsaturated compounds by means of rhodium catalysis, forming carbon–carbon bonds. The author hopes that the findings obtained in this work can to some extent contribute to further development in the area of organic synthesis using transition metal catalysts.

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Contents

Chapter 3. Rhodium-Catalyzed Hydroacylation of Alkynes with Salicylaldehydes via Cleavage of Aldehyde C–H Bond

General Introduction

In connection with increasing interest in synthesis of aromatic fine chemicals and their synthetic intermediates, including biologically active compounds for medicines or agricultural chemicals and functionalized organic materials, such as liquid crystals, pigment, and engineering plastics,[1] further development of efficient and selective synthetic methods for them is currently required. One of the most useful tools for the purpose appears to be transition-metal catalysis, especially in cases that involve carbon-carbon bond formation.[2]

One of the most useful arylation reaction of unsaturated compounds including alkenes and alkynes is the Heck reaction which is catalyzed by palladium complexes.[3] Since the reaction was first reported in 1971, a variety of arylation reactions as well as aroylation reactions using palladium catalysts have been developed. Recently, significant ruthenium-catalyzed arylation reactions of unsaturated compounds involving aromatic C–H bond activation as the key step have been developed by Murai et al.[4] In contrast to these palladium and ruthenium catalyses, rhodium-catalyzed arylation or aroylation reactions have been so far less explored,[5] while the position of rhodium in the periodic table of elements is between ruthenium and palladium.

In the light of these results, this work has focused on the subject to develop novel arylation or aroylation reactions of unsaturated compounds with aromatic carbonyl compounds, including acid anhydrides, acid chlorides, and aldehydes by means of rhodium catalysis. The results obtained are described in this thesis.

Chapter 1 is concerned with a novel synthetic method for aromatic ketones. It has been found that styrenes undergo intermolecular hydroacylation by aromatic acid anhydrides under a normal pressure of molecular hydrogen in the presence of a tertiary amine and a catalytic amount of $[RhCl(cod)]_2$ and a phosphite ligand to give 1,2-diaryl-1-propanones together with their 1,3-diaryl isomers.

In chapter 2, three unprecedented and synthetically useful reactions of aroyl chlorides with alkynes are described. In the first reaction, aroyl chlorides react with terminal alkynes accompanied by decarbonylation in the presence of a catalytic amount of $[RhCl(cod)]_2$ and PPh_3 to give the corresponding vinyl chloride derivatives regio- and stereo-selectively in good yields. In the second reaction, in contrast to the reaction with terminal alkynes, that with some internal ones proceeds without decarbonylation to produce 2,3-disubstituted-1-indenones as the predominant products. In the third reaction, internal alkynes effectively undergo aroylarylation, that is 1,2-addition of aroyl and aryl groups, on treatment with aroyl chlorides in the presence of a catalytic amount of $[RhCl(cod)]_2$ and PPh_3 using hexamethyldisilane as a reducing agent to produce the corresponding 1,3-diaryl-2-propen-1-one derivatives in good yields.

Chapter 3 deals with intermolecular hydroacylation of alkynes with aromatic aldehydes: Salicylaldehydes have been found to smoothly and efficiently react with both internal and terminal alkynes accompanied by cleavage of the aldehyde C-H bond by using a rhodium-based catalyst system of $[RhCl(cod)]_2$ / dppf / Na_2CO_3 to give the corresponding 2-alkenoylphenols in good to excellent yields.

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List of Publications

1) Rhodium-Catalyzed Reaction of Benzoic Anhydride with Styrene under Molecular Hydrogen

Ken Kokubo, Masahiro Miura, and Masakatsu Nomura

Organometallics, **1995**, *14*, 4521.

2) Rhodium-Catalyzed Reaction of Aroyl Chlorides with Alkynes

Ken Kokubo, Kenji Matsumasa, Masahiro Miura, and Masakatsu Nomura

J. Org. Chem., **1996**, *61*, 6941.

3) Rhodium-Catalyzed Coupling Reaction of Salicyl Aldehydes with Alkynes via Cleavage of the Aldehyde C-H Bond

Ken Kokubo, Kenji Matsumasa, Masahiro Miura, and Masakatsu Nomura

J. Org. Chem., **1997**, *62*, 4564.

4) Rhodium-Catalyzed Reaction of Aroyl Chlorides with Alkynes or Alkenes in the Presence of Disilanes

Ken Kokubo, Kenji Matsumasa, Masahiro Miura, and Masakatsu Nomura

in contribution.

Supplementary Publication

1) Effect of Copper and Iron Cocatalysts on the Palladium-Catalyzed Carbonylation Reaction of Iodobenzene

Tetsuya Satoh, Ken Kokubo, Masahiro Miura, and Masakatsu Nomura

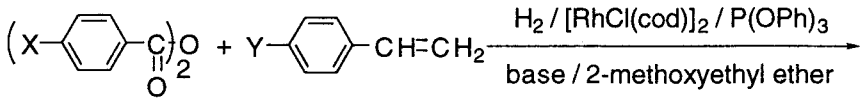
Organometallics, **1994**, *13*, 4431.

Chapter 1. Rhodium-Catalyzed Hydroacylation Reaction of Alkenes with Acid Anhydrides and Molecular Hydrogen

1-1. Introduction

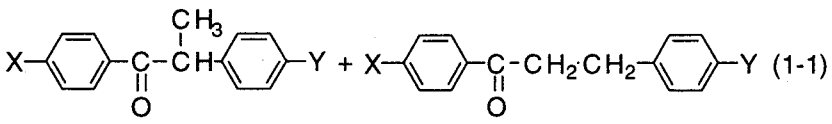
Transition metal complex catalyzed hydroacylation of alkenes may provide an attractive tool for preparation of ketones. One of the most effective metals for the reaction with aldehydes as both the acyl and hydrogen moieties has appeared to be rhodium, and the intramolecular reaction of 4-pentenals to produce cyclopentanones,[1] especially using its cationic complexes,[2] has been successfully developed. However, the intermolecular reaction has been so far less explored,[3,4] while an catalytic example for the reaction of benzaldehyde with ethylene using an indenylrhodium complex has been described.[5] One of the major reasons for this may be due to formation of catalytically inactive carbonylrhodium species.

On the other hand, it has been reported that hydroacylation of ethylene takes place by using acyl halides and a stoichiometric amount of $HRh(CO)(PPh_3)_3$.[6] We conceived that such a reaction could be made catalytic when it is performed in the presence of an appropriate hydrogen source and a base. Indeed, it has been observed that hydroaroylation of 4-substituted styrenes with 4-substituted benzoic anhydrides as the acyl moieties efficiently proceeds in the presence of $[RhCl(cod)]_2$ and a phosphorous ligand using a tertiary amine under a normal pressure of hydrogen (eq 1-1), while aroyl halides were ineffective.[7,8] Consequently, it has been carried out a detailed investigation to elucidate the factors affecting the reaction. The results are described herein.



1a: X = H
1b: X = Cl
1c: X = Me
1d: X = OMe

2a: Y = H
2b: Y = Cl
2c: Y = Me
2d: Y = OMe



(1-1)

3a : X = H, Y = H
3b : X = H, Y = Cl
3c : X = H, Y = Me
3d : X = H, Y= OMe
5 : X = Cl, Y = H
7 : X = Me, Y = H
9 : X = OMe, Y = H

4a : X = H, Y = H
4b : X = H, Y = Cl
4c : X = H, Y = Me
4d : X = H, Y= OMe
6 : X = Cl, Y = H
8 : X = Me, Y = H
10 : X = OMe, Y = H

1-2. Results and Discussion

Reaction of Benzoic Anhydride with Styrene. The reaction of benzoic anhydride (**1a**; 2 mmol), with styrene (**2a**; 8 mmol) in the presence of $[RhCl(cod)]_2$ (0.01 mmol), triphenylphosphine (0.04 mmol), and diisopropylethylamine (4 mmol) in 2-methoxyethyl ether at 100 °C for 20 h under 1 atm of hydrogen gave 1,2-diphenyl-1-propanone (**3a**) as the major product along with 1,3-diphenyl-1-propanone (**4a**) in a total ketone yield of 17 % based on **1a** used (eq 1-1 and Table 1-1). When the ligand employed was varied, the product yield as well as the product composition were significantly affected. Among the phosphorus ligands examined, $P(OPh)_3$ gave the most favorable result with respect to the product yield. The ratios of $P(OPh)_3$/Rh and **2a/1a** and the reaction temperature were found to be also important functions; favorable results were obtained at approximately $P(OPh)_3$/Rh=2, **2a/1a**=4, and 60–80 °C (Table 1-1). A reasonable ketone yield of 66 % was attained by using 0.02 mmol of $[RhCl(cod)]_2$ at 65 °C. It has been reported that in the rhodium-catalyzed hydroformylation of alkenes using phosphite ligands, hindered phosphites enhance

Table 1-1. Reaction of 1a with 2a using Various Phosphorus Ligands[a]

ligand	temp (°C)	yield of **3a** + **4a** (%)[b]	**3a** : **4a**
PPh_3	100	17	92 : 8
$P(n\text{-}Bu)_3$	100	8	54 : 46
$P(OEt)_3$	100	11	80 : 20
$P(OPh)_3$	100	46	68 : 32
$P(OPh)_3$[c]	100	26	50 : 50
$P(OPh)_3$[d]	100	25	68 : 32
$P(OPh)_3$[e]	100	28	68 : 32
$P(OPh)_3$[f]	100	39	67 : 33
$P(O\text{-}o\text{-}MePh)_3$	100	43	65 : 35
$P(O\text{-}o\text{-}t\text{-}BuPh)_3$	100	36	64 : 36
$P(OPh)_3$	80	52	73 : 27
$P(OPh)_3$	65	59	75 : 25
$P(OPh)_3$[g]	65	66	72 : 28
$P(OPh)_3$	50	40	73 : 27

[a]The reaction was carried out in 2-methoxyethyl ether for 20 h under H_2 (1 atm). $[[RhCl(cod)]_2]$:[ligand]:[**1a**]:[**2a**]:[$Et(i\text{-}Pr)_2N$] = 0.01:0.04: 2 : 8 : 4 (in mmol). [b]GC yield based on **1a** used. [c][ligand]=0.02. [d][ligand]=0.06. [e][**2a**]=4. [f][**2a**]=16. [g]$[[RhCl(cod)]_2]$: [ligand]:[**2a**] = 0.02:0.08: 16 (in mmol).

the reaction.[9] Consequently, $P(O\text{-}o\text{-}MePh)_3$ and $P(O\text{-}o\text{-}t\text{-}BuPh)_3$ were tested; however, no considerable influence on the reaction was observed.

The effect of base employed is indicated in Table 1-2. While tertiary amines and inorganic carbonates could be used, the hindered organic base $Et(i\text{-}Pr)_2N$ was found to be favorably used. More strong and weak nitrogen-bases, DBU and pyridine, were almost ineffective. Although solvent effect for this reaction was examined using heptane, toluene, acetonitrile, and DMF, none of them was superior to 2-methoxy-

Table 1-2. Reaction of 1a with 2a using Various Bases[a]

base	yield of **3a** + **4a** (%)[b]	**3a** : **4a**
Et_3N[c]	31	71 : 29
$Et(i\text{-}Pr)_2N$	46	68 : 32
$(n\text{-}Bu)_3N$	21	57 : 43
K_2CO_3[d]	28	75 : 25
Li_2CO_3[d]	20	60 : 40
Pyridine	3	67 : 33
DBU	0	-

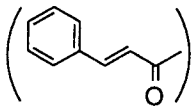
[a]The reaction was carried out in 2-methoxyethylether at 100 °C for 20 h under H_2 (1 atm).[[RhCl(cod)]$_2$]:[$P(OPh)_3$]:[**1a**]:[**2a**]:[base]=0.01:0.04:2:8:4 (in mmol). [b]GC yield based on **1a** used. [c]Reaction at 65 °C. [d][base]=2 (in mmol).

ethyl ether.

Reaction of Various Acid Anhydrides with Alkenes. The reactions of 4-substituted benzoic anhydrides (**1b–d**) with **2a** and **1a** with 4-substituted styrenes (**2b–d**) gave 1,2-diaryl-1-propanones together with the corresponding 1,3-diaryl isomers in good yields (eq 1-1 and Table 1-3). Cinnamic anhydride (**1e**) and acetic anhydride (**1f**) could also be reacted with **2a**, although the product yields were reduced. The anhydride **1a** reacted with triethoxy-vinylsilane (**2e**), 2-norbornene (**2f**), cyclopentene (**2g**) to give ketones **15–17**, whereas with 1-octene only a few percent of the corresponding products was detected by GC-MS. It is noted that the reaction with **2e** gave 1-phenyl-3-(triethoxysilyl)-1-propanone (**15**) as the single detectable hydrobenzoylated product.

Reaction Scheme. To obtain insight into the mechanism of the present reaction, the reaction of **1a** with **2a** was carried out under deuterium. The numbers of D atoms introduced into products **3a** and **4a** determined by ^1H NMR are indicated in eq 1-2.

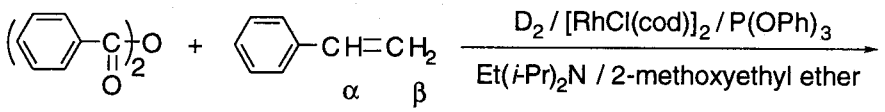
Table 1-3. Reaction of Various Acid Anhydrides 1 with Alkenes 2[a]

substrates		
1	**2**	ketone yield (%)[b]
1a	**2a**	66 (**3a/4a** = 73:27)
1b	**2a**	54 (**5 / 6** = 67:33)
1c	**2a**	47 (**7 / 8** = 68:32)
1d	**2a**	52 (**9 /10** = 71:29)
 : **1e**	**2a**	21 (**11/12** = 62:38)[c]
Ac_2O : **1f**	**2a**	18 (**13/14** = 39:61)[d]
1a	**2b**	47 (**3b/4b** = 71:29)
1a	**2c**	71 (**3c/4c** = 68:32)
1a	**2d**	58 (**3d/4d** = 74:26)
1a[e]	$(EtO)_3Si$  : **2e**	27 (**15**)[f]
1a[e]	 : **2f**	23 (**16**)[g]
1a[e, h]	 : **2g**	20 (**17**)[i]

[a]The reaction was carried out in 2-methoxyethyl ether at 65 °C for 20 h under H_2 (1 atm). $[[RhCl(cod)]_2]$:$[P(OPh)_3]$:[**1**]:[**2**]:$[Et(i\text{-}Pr)_2N]$=0.02:0.08: 2 : 16 : 4 (in mmol). [b]GC yield based on **1** used. [c]**11**: 1,4-diphenyl-1-penten-3-one; **12**: 1,5-diphenyl-1-penten-3-one. [d]**13**: 3-phenyl-2-butanone; **14**: 4-phenyl-2-butanone. [e]Reaction at 100 °C. [f]**15**: 1-phenyl-3-(triethoxysilyl)-1-propanone. [g]**16**: *exo*-2-benzoylnorbornane. [h]Under 5 atm of H_2. [i]**17**: cyclopentyl phenyl ketone

The reaction may be considered to involve initial styrene insertion to a hydridorhodium species generated in situ to form 1- and 2-phenethylrhodium complexes. The incorporation of deuterium in both the olefinic carbons in styrene may indicate that the insertion is reversible, as is the usual rhodium-catalyzed

hydroformylation of alkenes.[10] The fact that (a) the numbers of deuterium incorporated into both **3a** and **4a** were more than unity and (b) the recovered styrene



3a + **4a** (1-2)

D(α) = 0.3, D(β) = 1.2 D(α) = 0.8, D(β) = 0.8

was estimated to contain 1.7 deuterium atoms by GC-MS may suggest that the coordination of the alkene to the hydridorhodium species is also reversible.

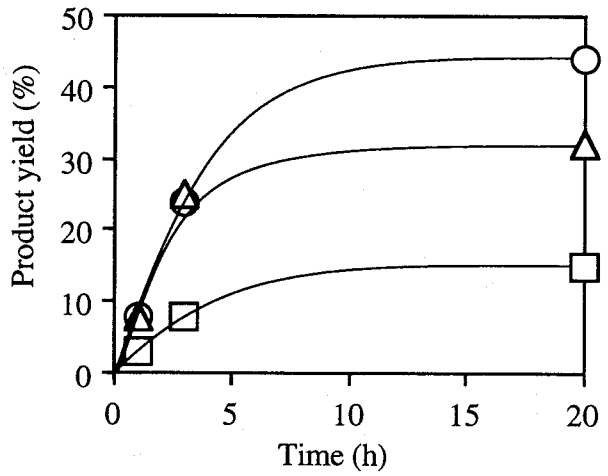


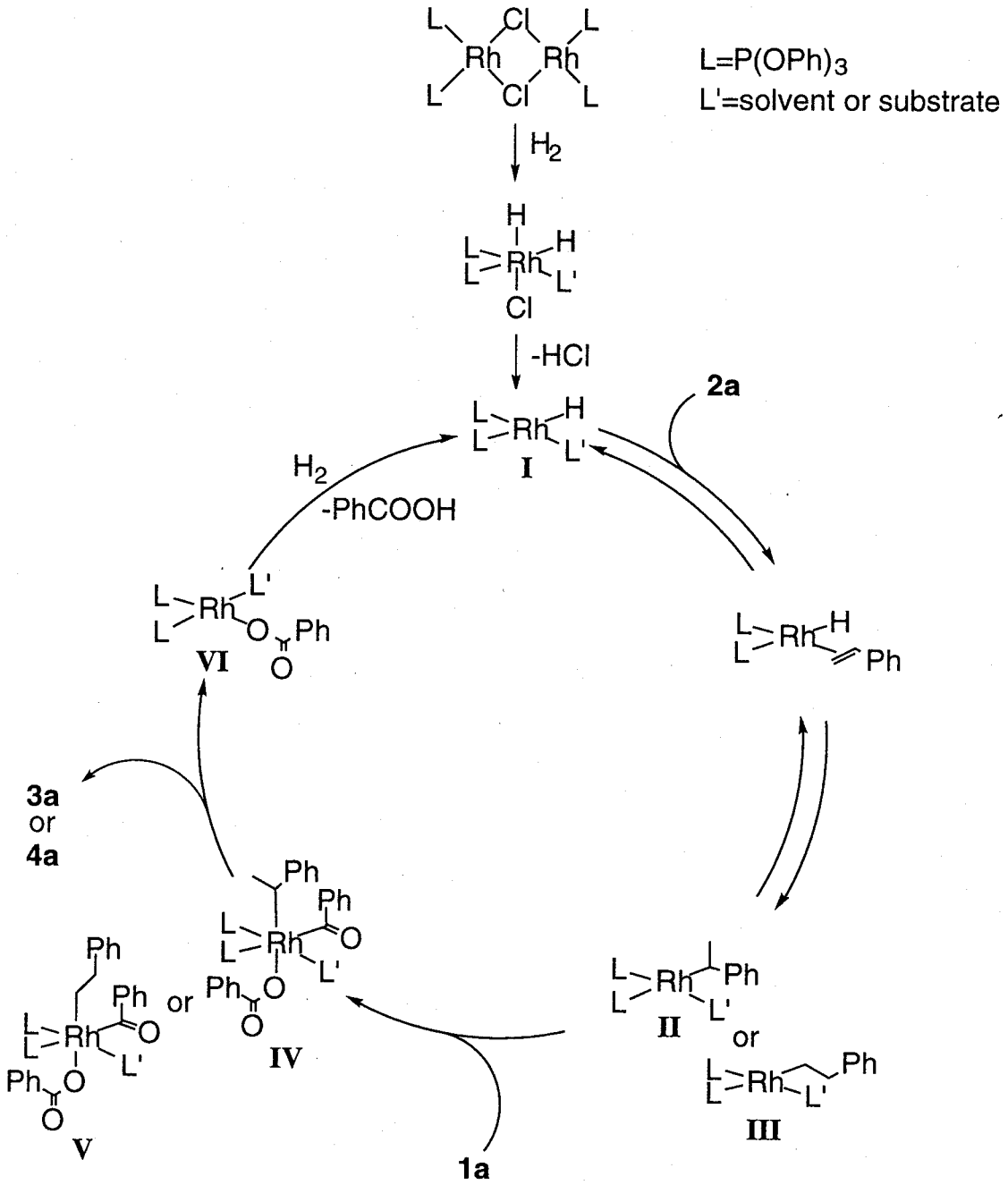
Figure 1-1. Time course of the reaction of **1a** with **2a** showing yields of **3a** (○), **4a** (□), and ethylbenzene (△, yield based on **2a** used). Reaction conditions: $[RhCl(cod)]_2$ (0.01 mmol), $P(OPh)_3$ (0.04 mmol), **1a** (2 mmol), **2a** (8 mmol), $Et(i\text{-}Pr)_2N$ (4 mmol), in 2-methoxyethyl ether under H_2 (1 atm) at 65 °C.

It should also be noted that (a) during the reaction of **1a** with **2a**, the product ratio of **3a** to **4a** was essentially constant and (b) ethylbenzene was formed as the predominant byproduct whose amount increased as the hydrobenzoylation proceeded (Figure 1-1).

Based on the above results, a plausible catalytic cycle for the reaction of **1a** with **2a** is illustrated in Scheme 1-1. Reaction of $[RhCl(cod)]_2$ with hydrogen in the presence of $P(OPh)_3$ and a base may generate a catalytically active hydridorhodium species (**I**). Insertion of styrene to **I** affords either 1- (**II**) or 2-phenethylrhodium complex (**III**) and the successive oxidative addition of **1a** may produce benzoyl (1- or 2-phenethyl) rhodium species (**IV** or **V**). Reductive elimination of product **3a** or **4a** gives benzoyloxyrhodium species (**VI**) which may react with hydrogen to regenerate the hydridorhodium complex **I**. Requirement of a base more than a stoichiometric amount may imply that it acts as a trap of benzoic acid as well as that of HCl in the initial generation of **I**. The hindered base $Et(i\text{-}Pr)_2N$ appears to be less ligative, and hence, the coordination of the substrates to the metal may be less prevented. The fact that **3a** was the major product may suggests that the formation of complex **II** is relatively more favorable than that of **III**.[9b] The deuterium distribution in **3a** could also indicate that **II** is the kinetically major intermediate and therefore, deuterium is preferentially introduced into the methyl group. On the other hand, the comparable incorporation of deuterium in the two methylene groups in **4a** may imply that a significant part of **III**, which reacts with **1a** to give **4a**, comes via **II**. The byproduct ethylbenzene may be produced via oxidative addition of hydrogen to intermediate **II** or **III**, competitively with that of **1a**. Although the reason why $P(OPh)_3$ is significantly superior to PPh_3 for this reaction is not definitive at the present stage, the better π-acceptor property of the phosphite ligand would ease the coordination of **1a** to **I** to enhance the reaction.[9b]

When the reaction of benzoyl chloride in place of **1a** was carried out with **2a**, benzoyl chloride was gradually consumed to give benzoic anhydride (possibly by

Scheme 1-1


L=P(OPh)3
L'=solvent or substrate
H2
-HCl
2a
I
H2
-PhCOOH
VI
II
or
III
1a
IV
or
V
3a
or
4a

participation of adventitious water) together with small amounts of benzaldehyde, benzophenone, and other minor unidentified products. After the complete disappearance of the chloride, the formation of **3a** and **4a** was observed. This would imply that benzoyl chloride reacts with **I** more faster than **2a**. In turn, the reason why the tandem reaction of hydrogen, **1a**, and **2a** around the rhodium species proceeds smoothly may be largely owing to the reactivity order toward **I**.[6]

1-3. Experimental Section

^{1}H NMR spectra were recorded at 400 MHz for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicone OV-17 glass column (ϕ 2.6 mm x 1.5 m) or a CBP-1 capillary column (ϕ 0.5 mm x 25 m). Benzoic anhydrides **1b–d**[11] and **1e**[12] were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of Benzoic Anhydride (1a) with Styrene (2a). To a flask containing $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) under hydrogen (with a balloon) was added a solution of **1a** (452 mg, 2 mmol), **2a** (832 mg, 8 mmol), $P(OPh)_3$ (12.4 mg, 0.04 mmol), $Et(i\text{-}Pr)_2N$ (516 mg, 4 mmol), and 1-methylnaphthalene (ca. 100 mg) as an internal standard in 2-methoxyethyl ether (5 mL) and the resulting mixture was stirred at 65 °C for 20 h. GC and GC-MS analyses of the mixture confirmed formation of **3a** (185 mg, 44 %) and **4a** (63 mg, 15 %). Products **3a** and **4a** were also isolated by column chromatography on silica gel using hexane-dichloromethane as eluent. Compound **3a**: mp 49–50 °C (lit.[13] 52–53 °C); ^{1}H NMR δ1.53 (d, 3H, J = 6.8 Hz), 4.68 (q, 1H, J = 6.7 Hz), 7.18–7.30 (m, 5H), 7.37 (t, 2H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.3 Hz), 7.95 (d, 2H, J = 7.3 Hz); MS *m/z* 210 (M^+). Compound **4a**: mp 71–71.5 °C (lit.[14] 70–71 °C); ^{1}H NMR δ3.07 (t, 2H, J = 7.6 Hz), 3.30 (t, 2H, J = 7.6 Hz), 7.20–7.32 (m, 5H), 7.45 (t,

2H, J = 7.6 Hz), 7.55 (t, 1H, J = 7.3 Hz), 7.96 (d, 2H, J = 6.8 Hz); MS m/z 210 (M^+).

Other products **3b**,[15] **4b**,[16] **3c**,[17] **4c**,[18] **3d**,[19] **4d**,[18] **5**,[15] **6**,[20] **7**,[15] **8**,[16] **9**,[20] **10**,[21] **11**,[22] **12**,[23] **13**,[24] **14**,[25] **15**,[26] **16**[27] and **17**[28] are also known and were compared with those authentic specimens.

1-4. References and Notes

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Chapter 2. Rhodium-Catalyzed Coupling Reaction of Aroyl Chlorides with Alkynes

2-1. Introduction

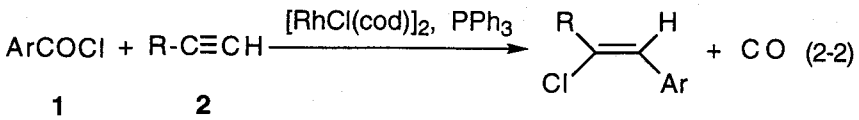
Aroyl chlorides are known to smoothly react with low-valent transition-metal species, including rhodium and palladium complexes, to produce the corresponding aroylchlorometal complexes which may be further transformed into arylchlorometal complexes by decarbonylation at somewhat elevated temperatures.[1] The aroyl- and aryl-metal species may be expected to be synthetically versatile, and indeed, catalytic aroylation of alkenes[2] and alkynes[3] and arylation of alkenes[4] and dienes[5] with aroyl chlorides using palladium complexes have been successfully developed. While such catalytic reactions could also be realized by using rhodium species, they have been so far unexplored.

As described in chapter 1, it has been found that benzoic anhydride smoothly reacts with styrene under a normal pressure of hydrogen in the presence of a tertiary amine and catalytic amounts of $[RhCl(cod)]_2$ and a phosphorus ligand to give 1,2-diphenyl-1-propanone together with its 1,3-diphenyl isomer (eq 2-1);[6] however, benzoyl chloride is ineffective for this reaction.

$$(ArCO)_2O + R\text{-}CH{=}CH_2 \xrightarrow[H_2,\ base]{[RhCl(cod)]_2,\ P(OPh)_3} Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{CH_3}{CH}\text{-}R + Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2CH_2\text{-}R \quad (2\text{-}1)$$

In the context of the above investigation, in connection with our study of arylation and aroylation of unsaturated compounds by means of homogeneous catalysis,[7] it has been observed that aroyl chlorides can effectively react with terminal alkynes accompanied by decarbonylation in the presence of $[RhCl(cod)]_2$

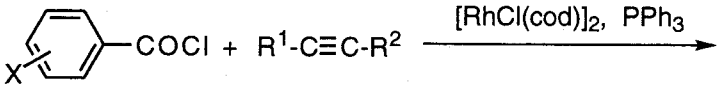
and PPh_3 to give the corresponding vinyl chloride derivatives regio- and stereo-selectively with good product yields (eq 2-2).



1 **2** **3**

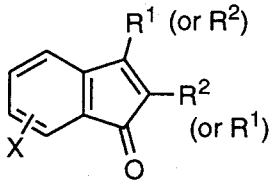
1a: Ar= Ph **2a**: R= Ph
1b: Ar= 4-ClC_6H_4 **2b**: R= $CH_3(CH_2)_5$
1c: Ar= 4-MeC_6H_4 **2c**: R= 1-cyclohexenyl
1d: Ar= PhCH=CH **2d**: R= $BuOCH_2$
1e: Ar= MeCH=CH **2e**: R= 5-hexynyl

Moreover, the reaction of aroyl chlorides with some internal alkynes in place of terminal ones has been found to proceed without decarbonylation to produce 2,3-disubstituted-1-indenones (eq 2-3).[8]



1 **2**

2f: $R^1 = R^2 =$ Pr
2g: $R^1 = R^2 =$ Et
2h: $R^1 = R^2 =$ Ph
2i: R^1= Ph, R^2= Me
2j: R^1= Bu, R^2= Me
2k: R^1= Ph, R^2= $SiMe_3$



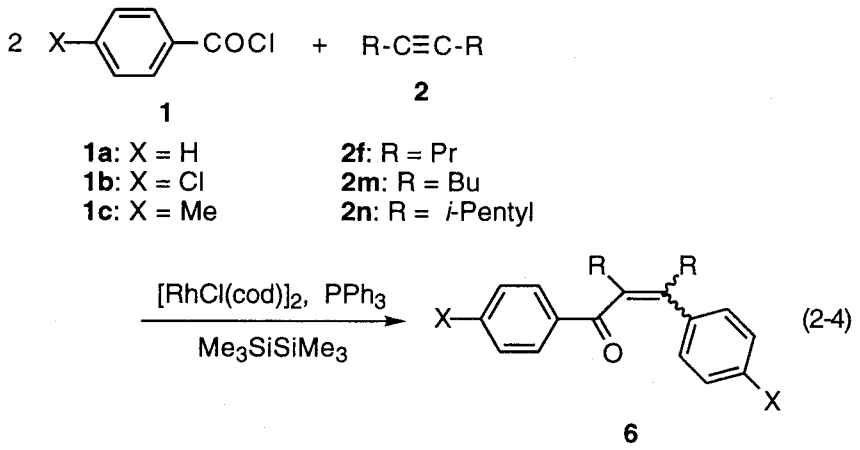
+ HCl (2-3)

4

On the other hand, hydrosilanes[9] or disilanes[10] are known to be capable of using for the rhodium- or palladium-catalyzed reductive reactions of aroyl chlorides to produce benzophenones, benzaldehydes, aroylsilanes, silylbenzenes, and biaryls. The reaction using disilanes also was aptly extended to the palladium-catalyzed decarbonylative 1,4-arylsilylation of dienes.[5]

Thus, the reaction in eqs 2-2 and 2-3 in the presence of disilanes was examined; it was found that by addition of hexamethyldisilane to the reaction using internal alkynes in eq 2-3 as well as using alkenes such as norbornenes, novel aroylarylation,

that is 1,2-addition of aroyl and aryl groups to the unsaturated bonds, can take place (eq 2-4), and with a terminal alkyne, phenylacetylene, aroylsilylation also occurs.[11]



Consequently, a detailed investigation has been carried out to elucidate the factors affecting the reactions in eqs 2-2–2-4.

2-2. Results and Discussion

2-2-1. Arylchlorination Reaction of Terminal Alkynes with Aroyl Chlorides

Reaction of Benzoyl Chloride (1a) with Phenylacetylene (2a). When the reaction of **1a** (2 mmol) with **2a** (2 mmol) in the presence of $[RhCl(cod)]_2$ (0.01 mmol, 1 mol%) and PPh_3 (0.02 mmol; P/Rh = 1.0) was carried out in octane at 140 °C (bath temperature) for 20 h under nitrogen, (*Z*)-1-chloro-1,2-diphenylethene (**3a**) was obtained in a yield of 71 % (Table 2-1 and eq 2-2; Ar = R = Ph). The product yield was increased up to 92 % (based on amount of **1a** used) by using 3 mmol of **2a**. Analysis of the reaction mixture by ^1H NMR and GC-MS confirmed that no (*E*)-1-chloro-1,2-diphenylethene was formed. The reaction was found to be very sensitive to the amount of the ligand added; the product yield was very low, when the PPh_3/Rh ratio was ≥2 or 0. Other phosphorus compounds, PBu_3, $P(OPh)_3$, dppb

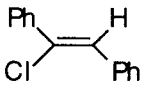
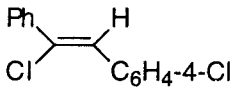
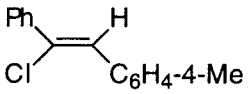
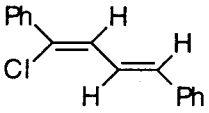
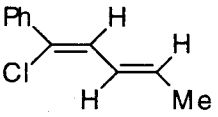
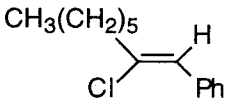
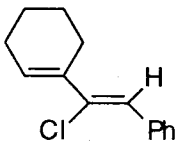
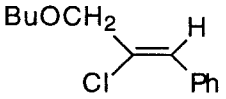
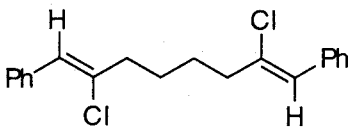
Table 2-1. Effect of Ligands on the Reaction of Benzoyl Chloride 1a with Phenylacetylene 2a[a]

entry	ligand (equiv.)[b]		% yield[c]
1	PPh_3	(1)	71
2[d]	PPh_3	(1)	92
3	PPh_3	(0)	2
4	PPh_3	(2)	7
5	PPh_3	(6)	1
6	PBu_3	(1)	17
7	$P(OPh)_3$	(1)	21
8	dppb	(1)	5
9	dppb	(0.5)	10
10	dppp	(0.5)	23
11[e]	PPh_3	(1)	23
12[f]	PPh_3	(1)	57
13[g]	PPh_3	(1)	68
14[h]	PPh_3	(1)	47
15[i]	PPh_3	(1)	33

[a]The reaction was carried out in octane at 140 °C for 20 h under N_2. $[[RhCl(cod)]_2]$:[ligand]:[**1a**]:[**2a**]=0.01:0.02: 2 : 2 (in mmol). [b]Relative to Rh metal. [c]GC yield based on **1a** used. [d][**2a**]=3 mmol. [e]Reaction at 100 °C. [f]Reaction at 120 °C. [g]Reaction in *o*-xylene. [h]Reaction in 2-methoxyethyl ether. [i]$[[RhCl(cod)]_2]$=0.001 mmol, [**2a**]= 3 mmol.

($Ph_2P(CH_2)_4PPh_2$), and dppp ($Ph_2P(CH_2)_3PPh_2$) were examined as ligands; however, none of them was superior to PPh_3. At a lower reaction temperature of 100 or 120 °C, the product yield was considerably decreased. While *o*-xylene could be used as well as octane as solvent, $(CHCl_2)_2$, 2-methoxyethyl ether, and PhCN were less effective.

Table 2-2. Reaction of Various Acid Chlorides 1 with Terminal Alkynes 2[a]

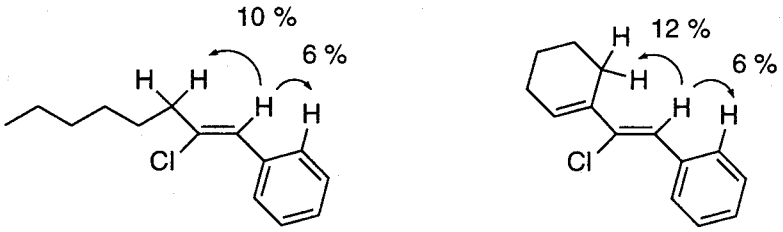
substrates 1	substrates 2	product 3, % yield[b]		
1a	**2a**		**3a**	91
1b	**2a**		**3b**	94
1c	**2a**		**3c**	76
1d	**2a**		**3d**	91
1e	**2a**		**3e**	84
1a	**2b**		**3f**	74
1a	**2c**		**3g**	81
1a	**2d**		**3h**	(27)[c, d]
1a	**2e**		**3i**	(60)[d, e]

[a]The reaction was carried out in octane at 140 °C for 20 h under N_2.[$[RhCl(cod)]_2$]:[PPh_3]:[**1**]:[**2**]=0.01:0.02: 2 : 3 (in mmol). [b]Isolated yield based on **1** used. Value in parentheses was determined by GC. [c]$[[RhCl(cod)]_2]$:$[PPh_3]$=0.02:0.04. [d]The corresponding stereoisomer (≤5 %) was contaminated. [e][**1**]:[**2**]=6:2.

Reaction of Various Acid Chlorides with Terminal Alkynes. The reactions of 4-chloro- and 4-methylbenzoyl chlorides (**1b** and **1c**) with **2a** gave the correspond-

ing vinyl chloride derivatives **3b** and **3c** in good yields, as did that of **1a** (Table 2-2). Cinnamoyl chloride (**1d**) and crotonoyl chloride (**1e**) also reacted with **2a** smoothly to afford chlorodienes **3d** and **3e**. 1-Octyne (**2b**), 1-ethynylcyclohexene (**2c**), and butyl propargyl ether (**2d**) could be used in place of **2a**, giving compounds **3f–h**. Reaction of **1a** (6 mmol) with 1,7-octadiyne (**2e**; 2 mmol) gave compound **3i**.

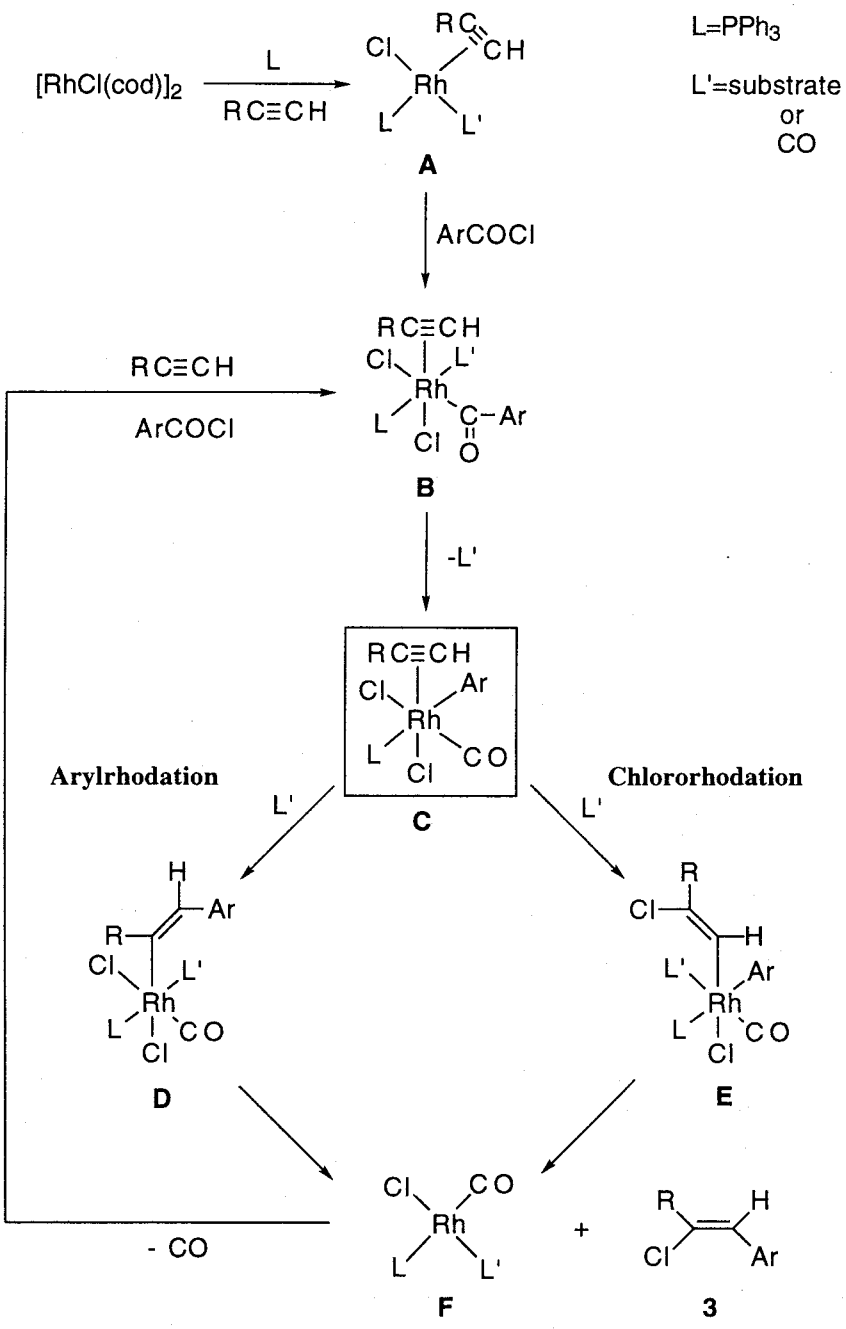
The configuration of each product was determined by ^{1}H NMR with the aid of NOE experiments. For example, NOE peak enhancements observed for products **3f** and **3g** were as follows. It should be noted that each product, with the exception of **3h** and **3i**, did not accompany other regio- and stereoisomers, which was confirmed by ^{1}H NMR and GC-MS. In the case of **3h** and **3i**, small amounts (≤5 %) of the corresponding (*E*) and (*Z, E*) isomers, respectively, were contaminated. Reaction of benzoyl bromide (**1g**) with **2a** gave (*Z*)-1-bromo-1,2-diphenylethene (**3j**) (73 %) along with its (*E*)-isomer **3j'** (3 %) (Table 2-3).



3f **3g**

Reaction Scheme for the Formation of 3. A plausible reaction mechanism, which may rationalize the regio- and stereoselective formation of **3** from **1** and **2**, is illustrated in Scheme 2-1. The reaction may be considered to involve initial oxidative addition of aroyl chloride to a catalytically active rhodium(I) species **A** generated from $[RhCl(cod)]_2$ in the presence of PPh_3 and a terminal alkyne to form an aroylrhodium complex **B**. The subsequent decarbonylation gives intermediate **C**. Then, there may exist two possible pathways; the one is arylrhodation where the aryl moiety migrates to the coordinated alkyne in **C** to give complex **D**, and the other is chlororhodation where the chlorine migrates to the alkyne to give complex **E**.

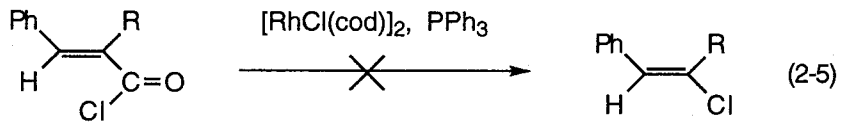
Scheme 2-1



Whichever arylrhodation or chlororhodation, reductive elimination affords product **3** along with carbonylrhodium(I) species **F**. While the catalytic cycle proceeds, ligand L' is possibly CO, since it is known that complete removal of CO from rhodium(I)

species is rather difficult.[1,12] However, the second CO seems to be capable of being replaced by alkyne **2**. It should be noted that carbon monoxide exchange reaction in benzoyl chloride with ^{13}CO has been reported to occur in the presence of $RhCl(CO)(PPh_3)_2$ even at 90 °C.[13]

If the reaction proceeds *via* arylrhodation, it has to involve reductive elimination of the vinyl moiety with chlorine from **D**. Generally, reductive elimination of organic halides from haloorganometals usually requires high temperatures over 200 °C.[1,12,14] It is noted that decarbonylation of α,β-unsaturated acyl chlorides with a stoichiometric amount of $RhCl(PPh_3)_3$ has been reported to produce vinyl triphenylphosphonium salts, giving no vinyl chlorides.[15] It was also confirmed that treatment of cinnamoyl chloride (**1d**) and its α-phenyl derivative **1f** under the present catalytic conditions gave no trace of β-chlorostyrenes (eq 2-5). In the light of these results, the reaction sequence **C** → **D** → **F** seems to be unlikely involved.



(2-5)

1d: R=H
1f: R=Ph

While chlororhodation to alkynes is less common, a number of reactions, which involve chloropalladation to them, are known.[16,17] It has been recently reported that stereochemistry of alkyne chloropalladation is dependent on chloride ion concentration; at a low chloride concentration, *cis*-chloropalladation predominates, whereas at a high chloride concentration, *trans*-chloropalladation becomes to be favorable.[17] Consequently, we examined effect of addition of a quaternary ammonium chloride or bromide on the present reaction. When $PhCH_2NEt_3Cl$ (2 mmol) was added to the reaction of **1a** (2 mmol) with **2a** (3 mmol), a mixture of **3a** and its (*E*)-isomer **3a'** in a ratio of 19:13 was formed (eq 2-6 and Table 2-3). This is in marked contrast to the fact that without the chloride, the (*Z*)-isomer **3a** is exclusively

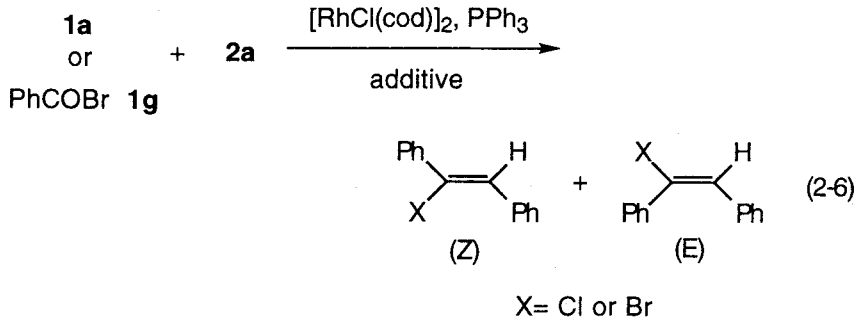


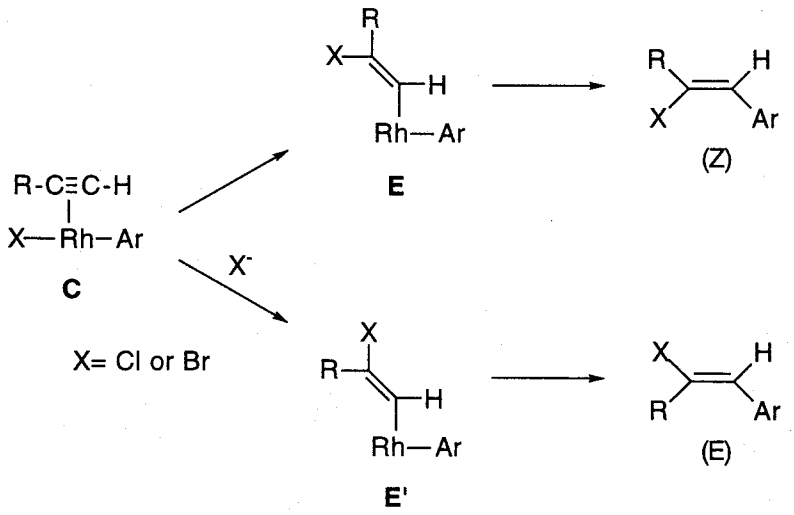
Table 2-3. Effect of Addition of Ammonium Halide on the Reaction of 1a or 1g with 2a[a]

1	additive	3, % yield	
		(Z)	(E)
1a	none	92	0
1a	$PhCH_2NEt_3Cl$	19	13
1g	none	73	3
1g	Bu_3NMeBr	41	12

[a]The reaction was carried out in octane at 140 °C for 20 h under N_2. $[[RhCl(cod)]_2]$:[ligand]: [**1**]:[**2a**]:[additive]=0.01:0.02: 2 : 3 : 2 (in mmol).

produced. Addition of Bu_3NMeBr to the reaction of **1g** with **2a** also increased the product (*E*)/(*Z*) ratio. These results led us to deduce that the present haloarylation of terminal alkynes predominantly involves halorhodation reaction. The formation of the (*E*)-isomers **3a'** and **3f'** is attributable to the *anti*-addition of chloride and bromide added in intermediate **C** as shown in Scheme 2-2.

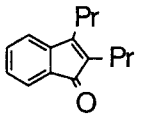
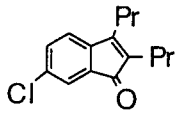
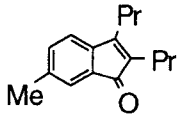
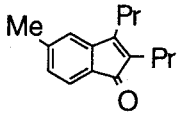
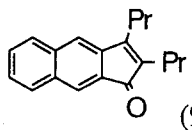
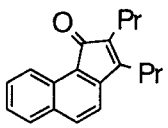
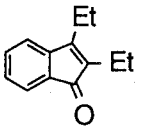
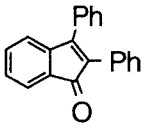
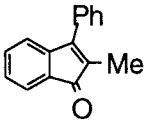
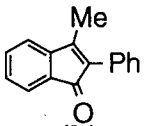
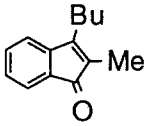
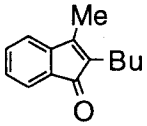
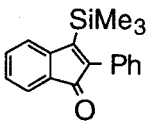
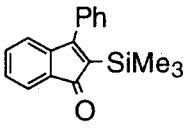
Scheme 2-2



2-2-2. Cycloaddition Reaction of Internal Alkynes with Aroyl Chlorides

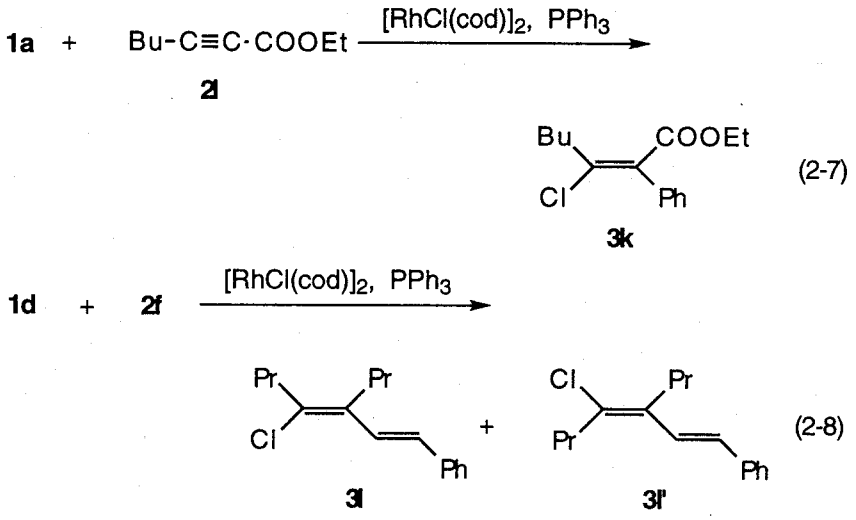
Reaction of Aroyl Chlorides with Internal Alkynes. In order to examine applicability of internal alkynes to the present reaction, reaction of **1a** with 4-octyne (**2f**) was first carried out as the representative in *o*-xylene under the same conditions with those employed for the reactions with terminal alkynes. It was somewhat surprising that 2,3-dipropyl-1-indenone (**4a**) was produced in 34 % yield (14 % in octane) as the single major product, no vinyl chloride derivative being detected (eq 2-3; X = H, R = Pr). By adding Na_2CO_3 as base to trap hydrogen chloride evolved and some modifications of the reaction conditions using 2 mol% of $[RhCl(cod)]_2$, the yield of **4a** was increased up to 76 % based on amount of **2f** used (Table 2-4). The reactions of 4-substituted benzoyl chlorides **1b**, **c** and 3-methylbenzoyl chloride (**1h**) with **2f** also gave indenones **4b–d**. It was of quite interest that the carbonyl moiety in these products was found to be sifted to the neighboring position in the starting aroyl chlorides. The reaction of 2-naphthoyl chloride (**1i**) with **2f** predominantly gave 2,3-fused compound **4e** along with its 1,2-fused isomer **4e'**. Alkynes **2g–k** could react

Table 2-4. Reaction of Aroyl Chlorides 1 with Internal Alkynes 2f-k[a]

substrates 1	substrates 2	product 4, % yield[b]		
1a	**2f**		**4a**	76 (73)
1b	**2f**		**4b**	61 (57)
1c	**2f**		**4c**	67 (47)
1h[c]	**2f**		**4d**	88 (81)
1i[d]	**2f**	 (92:8)  **4e** **4e'**		69 (59)
1a	**2g**[e]		**4f**	49
1a	**2h**		**4g**	13
1a	**2i**	 (1:1)  **4h** **4h'**		27
1a	**2j**	 (1:1)  **4i** **4i'**		36
1a	**2k**	 (3:1)  **4j** **4j'**		23

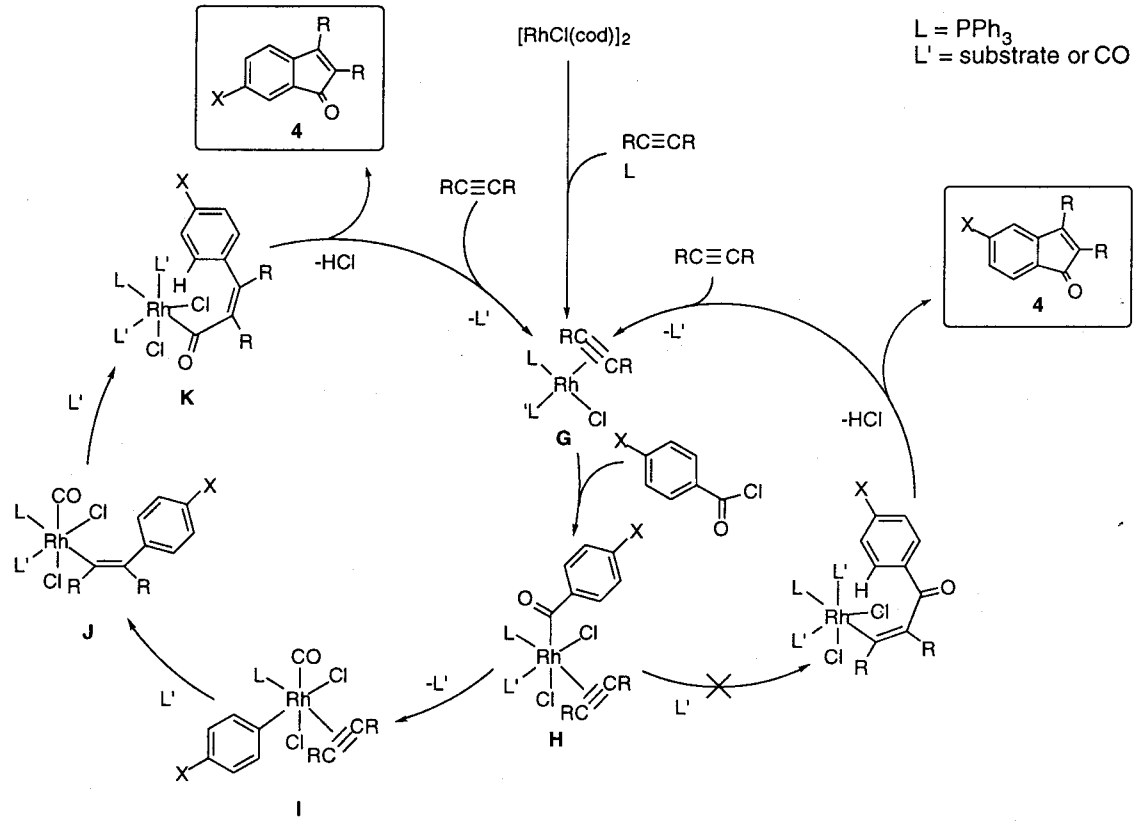
[a]The reaction was carried out in *o*-xylene at 145 °C for 24 h under N_2. $[[RhCl(cod)]_2]:[PPh_3]:[\mathbf{1}]:[\mathbf{2}]:[Na_2CO_3]$ = 0.02:0.04: 3 : 2 : 2 (in mmol). [b]GC yield based on **2** used. Value in parentheses indicates yield after isolation. [c]3-Methylbenzoyl chloride. [d]2-Naphthoyl chloride. [e]Reaction was carried out in a sealed tube.

with **1a** to give the corresponding indenones, while the product yields were moderate to low. In the reactions using the unsymmetrical alkynes **2i–k**, two possible regio-isomers were formed in each case. In contrast to the reactions with **2i–k**, treatment of **1a** with ethyl 2-heptynoate (**2l**) gave ethyl (*E*)-3-chloro-2-phenylheptenoate (**3k**) in a yield of 41 % (eq 2-7), no indenone product being detected. Reaction of cinnamoyl chloride (**1d**) with **2f** afforded a mixture of chlorodienes **3l** and **3l'** in a ratio of 77:23, the combined yield being 36 % (eq 2-8). These results suggest that the precedence of the reaction courses leading to vinyl chlorides and indenones depends on the structure of acid chlorides as well as that of alkynes.



Reaction Scheme for the Formation of 4. A most plausible mechanism to account for the formation of indenones **4** based on the observed results is illustrated in Scheme 2-3. The key intermediate leading to **4** may be arylchlororhodium(III) species **I**, which is the equivalent to **C** in Scheme I, formed *via* complexes **G** and **H**. Arylrhodation in **I** followed by re-insertion of carbon monoxide coordinated to the metal center affords complex **K**. The subsequent cyclization reaction accompanied by regeneration of **G** and evolution of HCl gives product **4**. While aroylrhodation in **H** would lead to **4**, the route may be ruled out, since the structure of **4b–d** and **4e'** is not consistent with it. The structures of **4d** and **4e** may suggest that each final cyclization step of **K** to **4** is sterically controlled; steric hindrance by the methyl group and the

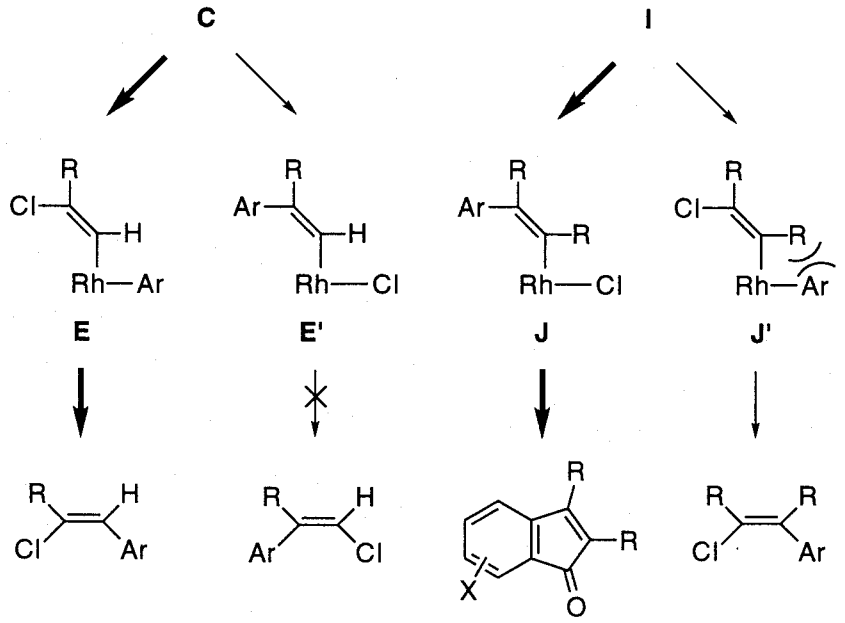
Scheme 2-3



peri-hydrogen on the benzene and the naphthalene rings, respectively, may be the major reason for the selective formation of these products. The byproduct **5** may be formed *via* insertion of another alkyne molecule in complex **J** (L' = **2**).

Thus, it may be reasonable to consider that the present rhodium-catalyzed reaction of **1** with **2** involve arylchlororhodium(III)-alkyne complexes such as **C** and **I** as the common intermediates; chlororhodation and arylrhodation in them lead to vinyl chlorides **3** and indenones **4**, respectively. One of the major factors determining the reaction routes and the product structures may be steric repulsion in the vinylrhodium intermediates from **C** and **I** (Scheme 2-4). Of the two possible intermediates **J** and **J'** from **I**, there seems to be considerable steric repulsion between the R group and the rhodium moiety in **J'** and hence, arylrhodation to give **J** predominates. The steric interaction in **E** from **C** appears to be small and therefore, in

Scheme 2-4

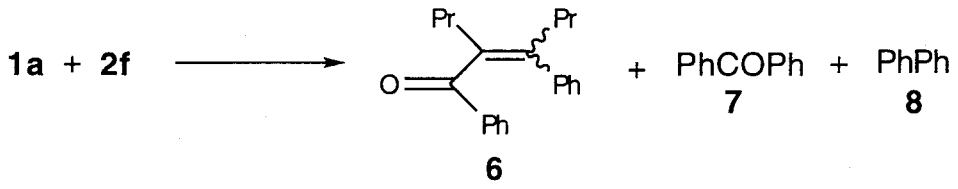


the case of terminal alkynes, chlororhodation may be the favorable path. The repulsion in **J'** in the reactions of **1a** with **2l** (Ar = Ph, R = COOEt) and of **1d** with **2f** (Ar = PhCH=CH-, R = Pr) may be relatively small to produce vinyl chlorides **3k** and **3l**. Consequently, chlororhodation may be considered to be the energetically favorable route relative to arylrhodation, when steric hindrance dose not intervene.

2-2-3. Aroylarylation Reaction of Internal Alkynes or Reactive Alkenes with Aroyl Chlorides in the Presence of Disilanes

Reaction of Benzoyl Chloride (1a) with 4-Octyne (2f) in the Presence of Hexamethyldisilane. The reaction of benzoyl chloride (**1a**, 4 mmol) with 4-octyne (**2f**, 2 mmol) was first examined using hexamethyldisilane (4 mmol) in the presence of $[RhCl(cod)]_2$ (0.01 mmol) with or without addition of a phosphorous ligand in

Table 2-5. Reaction of 1a with 2f in the Presence of Hexamethyldisilane[a]



6 **7** **8**

entry	ligand / mmol	solvent	%yield[b]		
			6 (*Z*)/(*E*)	**7**	**8**
1	PPh_3 / 0	xylene	16 (94/6)	tr	30
2	PPh_3 / 0.02	xylene	42 (90/10)	tr	20
3	PPh_3 / 0.04	xylene	51 (96/4)	tr	19
4	PPh_3 / 0.06	xylene	45 (89/11)	8	16
5	dppp / 0.02	xylene	47 (92/8)	23	18
6	$P(OPh)_3$ / 0.04	xylene	30 (37/63)	16	14
7	PBu_3 / 0.04	xylene	28 (86/14)	7	14
8[c]	PPh_3 / 0.04	xylene	64 (94/6)	21	46
9[c]	PPh_3 / 0.04	octane	58 (81/19)	26	46
10[c]	PPh_3 / 0.04	TCE[d]	83 (89/11)	19	25

[a]The reaction was carried out in the presence of $[RhCl(cod)]_2$ (0.01 mmol) at 120 °C for 20 h under N_2. [**1a**]:[**2f**]:[$Me_3SiSiMe_3$] = 4 : 2 : 4 (in mmol). [b][(mmol of product / 2) x 100]. Determined by GLC. [c][**1a**]:[**2f**]:[$Me_3SiSiMe_3$] = 6 : 2 : 6 (in mmol). [d]1,1,2,2-Tetrachloroethane.

xylene at 120 °C for 20 h under nitrogen (Table 2-5). Without using the ligand 1,3-diphenyl-2-propyl-2-hexen-1-one (**6**) was obtained as the cross-coupling product in a yield of 16% (based on amount of **2f** used) together with a trace amount of benzophenone (**7**) and biphenyl (**8**, 30%) (entry 1). Addition of PPh_3 up to 2 equivalent of Rh increased the yield of **6** to 51% (entries 2–4). Although a bidentate ligand, dppp (1,3-bis(diphenylphosphino)propane), could be used as well as PPh_3, $P(OPh)_3$ and PBu_3 were less effective (entries 5–7). An increase in the amount of **1a**

Table 2-6. Aroylarylation Reaction of 2f with 1a in the Presence of Various Reducing Agents[a]

entry	reducing agent	%yield of **6** (*Z*)/(*E*)	
1	$Me_3SiSiMe_3$	83	(89/11)
2	$ClMe_2SiSiMe_2Cl$	53	(87/13)
3	$Ph_3SiSiPh_3$	0	
4	$HSiEt_3$	10	(90/10)
5	$Me_3SnSnMe_3$	3	(84/16)
6	H_2	0	

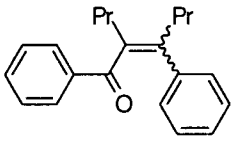
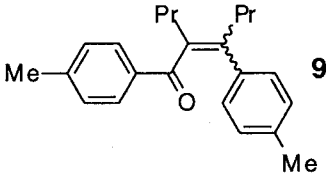
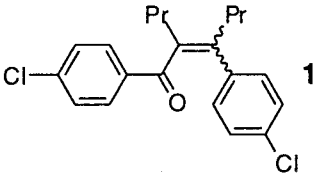
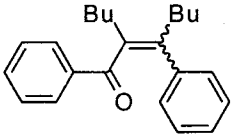
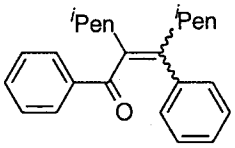
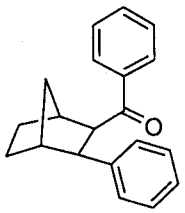
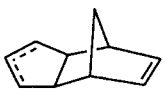
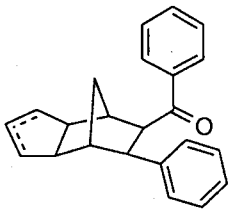
[a]The reaction was carried out in 1,1,2,2-tetrachloroethane at 120 °C for 20 h under N_2. $[[RhCl(cod)]_2]$:$[PPh_3]$:[**1a**]:[**2f**]:[reducing agent] = 0.01:0.04: 6 : 2 : 6 (in mmol).

and the disilane to 6 mmol afforded 64% yield of **6**. A further enhancement of the product yield to 83% was attained by using 1,1,2,2-tetrachloroethane (TCE) as solvent in place of xylene, while octane was less effective. At a lower or higher reaction temperature of 100 or 140 °C the yield of **6** was considerably decreased. It is noted that in each entry, (a) the product **6** was obtained as a mixture of two possible stereoisomers, giving the (*Z*) isomer preferentially and (b) the yield of 2,3-dipropyl-1-indenone, which is the predominant product in the reaction in the absence of the disilane (chapter 2-2-2), was less than 5%.

The results of the reaction of **1a** and **2f** using a number of reducing reagents are recorded in Table 2-6. When dichlorotetramethyldisilane was employed in place of hexamethyldisilane, **6** was still produced in a yield of 53 %, whereas hexaphenyl-disilane, triethylsilane, hexamethylditin, and hydrogen were far less effective or ineffective, suggesting that the identity of reducing agents is also one of the significant factors determining the reaction efficiency.

Reaction of Various Aroyl Chlorides with Internal Alkynes and Alkenes in the Presence of Hexamethyldisilane. Table 2-7 summarizes the results for a number

Table 2-7. Aroylarylation Reaction of 1 with 2, 13 or 14 in the Presence of Hexamethyldisilane[a]

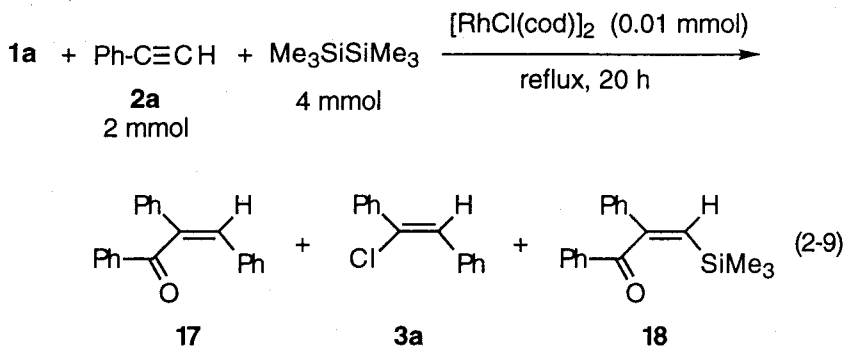
substrates 1	substrates 2	product , % yield[b]			(*Z*)/(*E*)
1a	**2a**		**6**	83(73)	89/11
1b	**2a**		**9**	46[c]	79/21
1c	**2a**		**10**	86(76)[d]	68/32
1a	**2b**		**11**	70(50)[c]	86/14
1a	**2c**		**12**	54(51)	78/22
1a	 **13**		**15**	64(61)[e]	
1a	 **14**		**16**	60(58)[e,f]	

[a]The reaction was carried out in 1,1,2,2-tetrachloroethane at 120 °C for 20 h under N_2 unless otherwise noted. $[[RhCl(cod)]_2]$:$[PPh_3]$:[**1**]:[**2**]:$[Me_3SiSiMe_3]$ = 0.01:0.04: 6 : 2 : 6 (in mmol). [b]GLC yield based on **2** used. Value in parentheses indicates yield after isolation. [c]Reaction for 30 h. [d]Reaction for 14 h. [e]$[[RhCl(cod)]_2]$:$[PPh_3]$ = 0.01:0.02 (in mmol). [f]Mixture of double-bond isomers.

of reactions of aroyl chlorides with internal alkynes as well as alkenes. The reactions of 4-chloro- and 4-methylbenzoyl chlorides (**1b** and **1c**) with **2f** gave the corresponding compounds **9** and **10**, as did that of **1a**. Qualitative analysis of the reactions of **1a–c** with **2f** by GLC indicated that the rate of consumption of **1a–c** decreased in the order of **1b** > **1a** > **1c**. 5-Decyne (**2m**) and 2,9-dimethyl-5-decyne (**2n**) reacted with **1a** to give the corresponding unsaturated ketones **11** and **12**, respectively. All these products **6** and **9–12** were produced as mixtures of the corresponding (*Z*) and (*E*) isomers, and the (*Z*) isomers were the favorable ones. Note that the configuration of the products was determined by their ^{1}H NMR spectra with the aid of NOE measurements.[18] It is conceivable that each (*E*) isomer may be, at least in part, formed by isomerization of the corresponding (*Z*) isomer during the reaction. Indeed, it was confirmed that treatment of **3** with a (*Z*)/(*E*) ratio of 85:15 under the reaction conditions for 24 h gave the compound with a ratio of 68:32. The reactions of **1a** with norbornene (**13**) and dicyclopentadiene (**14**) also gave aroylarylation products **15** and **16**, respectively. ^{1}H NMR spectra of them suggested that both benzoyl and phenyl groups were introduced in the *exo*-positions,[19] while the product **16** was obtained as a mixture of two possible double-bond isomers. This is in harmony with the selective *cis*-addition of aroyl and aryl groups to internal alkynes. The reaction of benzoyl bromide in place of **1a** with **2f** did not give any cross-coupling products, only giving **7** (32%) and **8** (21%).

Reaction of Benzoyl Chloride with Terminal Alkynes in the Presence of Hexamethyl disilane. In the reaction of **1a** with 1-octyne (**2b**) as a terminal alkyne in the presence of hexamethyldisilane under the present conditions, (*Z*)-2-chloro-1-phenyl-1-octene (**3f**) was formed as a sole characterizable cross-coupling product in 14% yield, no benzoylphenylation product being detected. It was of interest that the reaction of **1a** with phenylacetylene (**2a**) using PPh_3 as ligand in TCE at 140 °C gave also no benzoylphenylation product, but (*Z*)-1,2-diphenyl-3-trimethylsilyl-2-propenone (**18**, 5%), which may be regarded as a benzoylsilylation product, was

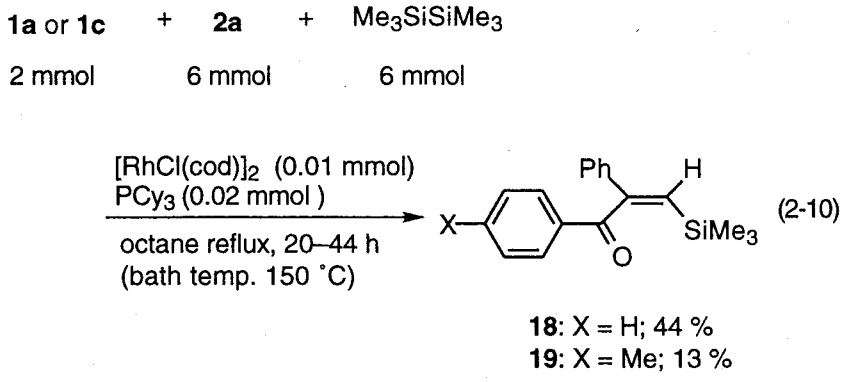
obtained along with (*Z*)-1-chloro-1,2-diphenylethene (**3a**, 11%) (eq 2-9).



(2-9)

1a (mmol)	ligand / mmol	solvent / bath temp.	yield (%) **17**	**3a**	**18**
2	PPh_3 / 0.02	TCE / 140 °C	0	11	5
4	PCy_3 / 0.04	octane / 150 °C	16	6	19

Treatment of **1a** with **2a** using tricyclohexylphosphine as ligand in refluxing octane was found to induce benzoylphenylation to produce compound **17** (16 %) together with **3a** (6%) and **18** (19%). In the reactions of **1a** and **1c** (2 mmol) with an excess amount of **2a** (6 mmol), **18** and **19** were obtained as the major products (eq 2-10).

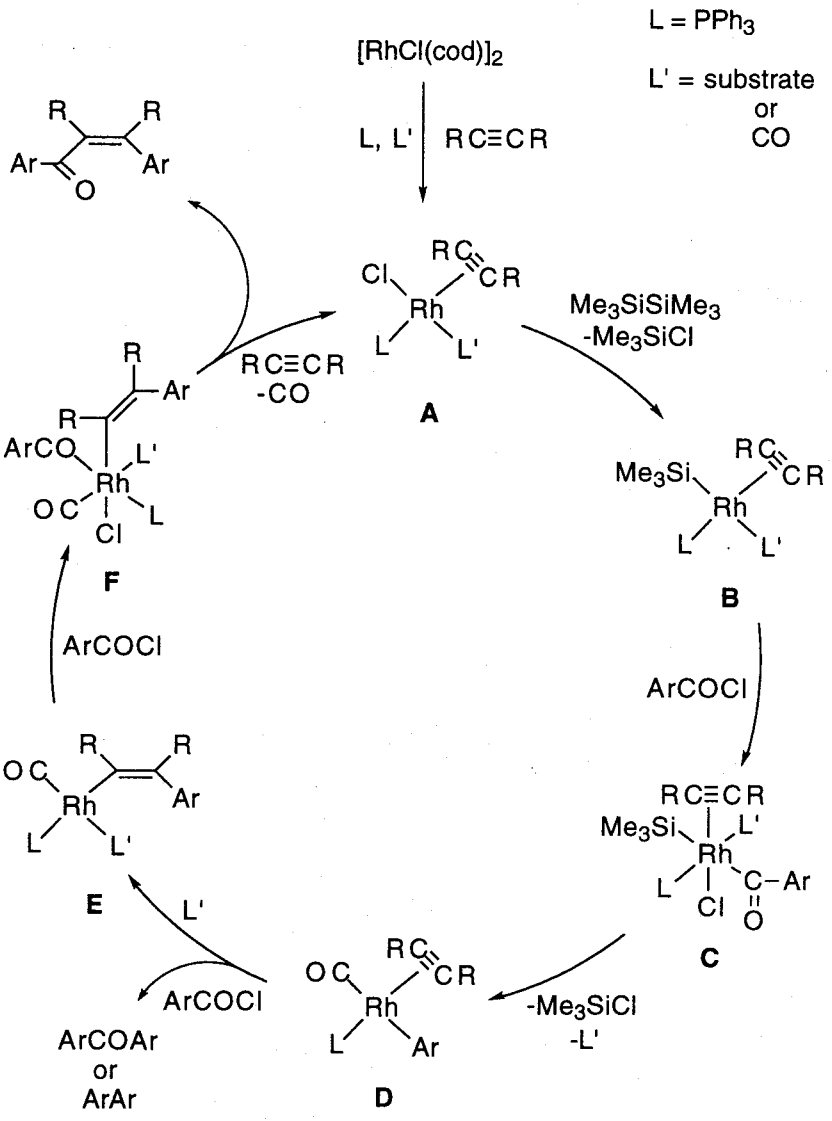


(2-10)

18: X = H; 44 %
19: X = Me; 13 %

Reaction Scheme for the Formation of 6. Based on the observed results, a possible reaction mechanism for the present aroylarylation reaction with aroyl chloride **1** is illustrated in Scheme 2-5 using internal alkyne **2** as the substrate. For the addition of both aroyl and aryl groups to **2**, it would contain two-fold oxidative additions of **1** to the metal center. Although the transformation of Rh(I) to Rh(III) by

Scheme 2-5



oxidative addition is very common, Rh(III) species does not seem to undergo further oxidative addition, since it is unlikely to form Rh(V) species. Therefore, it is reasonable to consider that the second oxidative addition may occur via aroyl- and aryl-rhodium(I) intermediates. This leads us to deduce initial formation of trimethylsilylrhodium(I) species **B** by the reaction of the disilane with chlororhodium(I) species **A**, which is generated in the reaction medium from $[RhCl(cod)]_2$ in the presence of

PPh_3 and **2**, accompanied elimination of trimethylsilyl chloride. The subsequent oxidative addition of **1** gives intermediate **C**, followed by the second elimination of trimethylsilyl chloride to afford arylrhodium species **D**. Oxidative addition of another aroyl chloride molecule, after arylrhodation to the coordinated alkyne molecule in the complex **D** to form **E**, gives aroylvinyl species **F**. Then, reductive elimination of aroylarylation product regenerates complex **A**. While the catalytic cycle proceeds, ligand L' is possibly CO, since it is known that complete removal of CO from rhodium(I) species is rather difficult.[1b,20] However, the second CO seems to be capable of being replaced by alkyne **2**.[21] On the other hand, oxidative addition of **2** to **D**, before formation of **E**, may also occur to lead to formation of diarylketone and biaryl as byproducts. It is noted that aroyl chlorides are known to be reduced by a hydrosilane in the presence of a rhodium catalyst to give the corresponding diarylketones.[9] Since no diarylation product could not be detected in each reaction, the reductive elimination in **F** appears to be a rather fast step. Another possible path via aroyl-rhodation to the coordinated alkyne in **C** is unlikely involved.[21]

Formation of the benzoylsilylation products **18** and **19** may be explained by considering the mechanism involving silylrhodation in the intermediate **B** followed by oxidative addition of **1**. It is noted that the regioselectivity in the aroylsilylation is consistent with that observed in the rhodium-catalyzed silylformylation reactions of terminal alkynes.[22] The results shown in eqs 2-9 and 2-10 suggest that the precedence of the steps **B** to **C** and silylrhodation depends on the relative amount of **1** to **2** as well as the structure of alkynes.

2-3. Experimental Section

^1H and ^{13}C NMR spectra were recorded at 400 or 270 MHz and 100 or 68 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis

was carried out using a silicone OV-17 glass column (ϕ 2.6 mm x 1.5 m) or a CBP-1 capillary column (ϕ 0.5 mm x 25 m). (E)-1,2-Diphenyl-2-propenoyl chloride[23] (**1f**), 3-butoxy-1-propyne[24] (**2e**), and ethyl 2-heptynoate[25] (**2l**) were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of Benzoyl Chloride (1a) with Phenylacetylene (2a). To a flask containing $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) and PPh_3 (5.2 mg, 0.02 mmol) under nitrogen (with a balloon) was added a solution of **1a** (281 mg, 2 mmol), **2a** (306 mg, 3 mmol), and 1-methylnaphthalene (ca. 100 mg) as an internal standard in octane (5 mL) and the resulting mixture was stirred at 140 °C for 20 h. GC and GC-MS analyses of the mixture confirmed formation of **3a** (439 mg, 92 %). Product **3a** (434 mg, 91 %) was also isolated by column chromatography on silica gel using hexane as eluent.

Reaction of Benzoyl Chloride (1a) with 4-Octyne (2f). To a flask containing $[RhCl(cod)]_2$ (9.8 mg, 0.02 mmol), PPh_3 (10.4 mg, 0.04 mmol), Na_2CO_3 (212 mg, 2 mmol) under nitrogen (with a balloon) was added a solution of **1a** (422 mg, 3 mmol), **2f** (220 mg, 2 mmol), and 1-methylnaphthalene (ca. 100 mg) as an internal standard in *o*-xylene (5 mL) and the resulting mixture was stirred at 145 °C for 24 h. GC and GC-MS analyses of the mixture confirmed formation of **4a** (325 mg, 76 %). Product **4a** (312 mg, 73 %) was also isolated by column chromatography on silica gel using hexane-dichloromethane (9:1, v/v) as eluent.

Reaction of Benzoyl Chloride (1a) with 4-Octyne (2f) in the Presence of Hexamethyldisilane. To a flask containing $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) and PPh_3 (10.4 mg, 0.04 mmol) under nitrogen (with a balloon) was added a solution of **1a** (843 mg, 6 mmol), **2f** (220 mg, 2 mmol), hexamethyldisilane (876 mg, 6 mmol), and 1-methylnaphthalene (ca. 100 mg) as an internal standard in 1,1,2,2-tetrachloroethane (5 mL) and the resulting mixture was stirred at 120 °C for 20 h. GC and GC-MS

analyses of the mixture confirmed formation of 1,3-diphenyl-2-propyl-2-hexen-1-one (**6**) (485 mg, 83 %, (*Z*)/(*E*) = 89:11), benzophenone (**7**) (69 mg, 19 %), and biphenyl (**8**) (77 mg, 25 %). Product **6** (426 mg, 73 %) was also isolated by column chromatography on silica gel using hexane-ethyl acetate (99.5:0.5, v/v) as eluent. Elaborated column chromatography of **6** afforded its (*Z*)- and (*E*)-isomers having >90 % content.

Products. Compounds **3a**,[23] **3a'**,[27] **3e**,[28] **3j**,[29] **3j'**,[29] **4a**,[8b] **4f**,[8a] **4g**,[8a] **4h**,[8a] **4h'**,[8a] **4j'**,[8b] **17**,[30] and **18**[31] are known and were compared with those authentic specimens. The analytical data of other products **3**, **4–6**, **9–12**, **15**, **16**, and **20** are as follows.

(*Z*)-1-Chloro-2-(4-chlorophenyl)-1-phenylethene (3b): mp 60.0–60.5 °C; ^{1}H NMR (400 MHz) δ 7.00 (s, 1H), 7.35–7.43 (m, 5H), 7.67–7.70 (m, 4H); MS *m/z* 248, 250, 252 (M^+). Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.69; H, 4.05; Cl, 28.36.

(*Z*)-1-Chloro-2-(4-methylphenyl)-1-phenylethene (3c): mp 45.5–46.0 °C; ^{1}H NMR (400 MHz) δ 2.38 (s, 3H), 7.04 (s, 1H), 7.21 (d, 2H, *J* = 8.1 Hz), 7.33–7.42 (m, 3H), 7.64–7.71 (m, 4H); MS *m/z* 228, 230 (M^+). Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.81; H, 5.92; Cl, 15.45.

(*Z, E*)-2-Chloro-1,4-diphenyl-1,3-butadiene (3d): mp 111–112 °C; ^{1}H NMR (400 MHz) δ 6.80 (d, 1H, *J* = 7.9 Hz), 6.94 (d, 1H, *J* = 5.3 Hz), 7.25–7.40 (m, 7H), 7.49–7.52 (m, 2H), 7.67–7.69 (m, 2H); MS *m/z* 240, 242 (M^+). Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44; Cl, 14.73. Found: C, 79.52; H, 5.70; Cl, 14.38.

(*Z*)-2-Chloro-1-phenyl-1-octene (3f): oil; ^{1}H NMR (400 MHz) δ 0.90 (t, 3H, *J* = 6.8 Hz), 1.30–1.37 (m, 6H), 1.65 (quintet, 2H, *J* = 7.3 Hz), 2.48 (t, 2H, *J* = 7.3 Hz), 6.46 (s, 1H), 7.23–7.27 (m, 1H), 7.32–7.36 (m, 2H), 7.58–7.59 (m, 2H); MS *m/z* 222, 224 (M^+). Anal. Calcd for $C_{14}H_{19}Cl$: C, 75.49; H, 8.60; Cl, 15.92. Found: C, 75.69; H, 8.73; Cl, 15.84.

(*Z*)-1-Chloro-1-(1-cyclohexenyl)-2-phenylethene (3g): oil; ^{1}H NMR (400

MHz) δ 1.60–1.68 (m, 2H), 1.72–1.78 (m, 2H), 2.22–2.27 (m, 2H), 2.34-2.39 (m, 2H), 6.50–6.52 (m, 1H), 6.69 (s, 3H), 7.32–7.37 (m, 2H), 7.63 (d, 2H, J = 7.3 Hz); MS *m/z* 218, 220 (M^+). Anal. Calcd for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91; Cl, 16.21. Found: C, 76.63; H, 6.96; Cl, 16.09.

(*Z*)- and (*E*)-3-Butoxy-2-chloro-1-phenyl-1-propene (3h and 3h'; 85:15): oil; ^1H NMR (400 MHz) δ 0.93 (t, 3H, J = 7.6 Hz), 1.38–1.44 (m, 2H), 1.57–1.65 (m, 2H), 3.45 (t, 2H, J = 6.6 Hz; **3h'**), 3.52 (t, 2H, J = 6.6 Hz; **3h**), 4.17 (s, 2H; **3h**), 4.21 (s, 2H; **3h'**), 6.74 (s, 1H; **3h**), 6.94 (s, 1H; **3h'**), 7.24-7.29 (m, 1H), 7.32–7.37 (m, 2H), 7.63 (d, 2H, J = 7.3 Hz); MS *m/z* 224, 226 (M^+). HRMS *m/z* (M^+) Calcd for $C_{13}H_{17}OCl$: 224.0968. Found: 224.0960.

(*Z, Z*)-2,7-Dichloro-1,8-diphenyl-1,7-octadiene (3i): mp 58.5–59.5 °C; ^1H NMR (400 MHz) δ 1.71–1.75 (m, 4H), 2.51–2.55 (m, 4H), 6.49 (s, 2H), 7.23–7.27 (m, 2H), 7.32–7.36 (m, 4H), 7.58–7.60 (m, 4H); MS *m/z* 330, 332, 334 (M^+). Anal. Calcd for $C_{20}H_{20}Cl_2$: C, 72.51; H, 6.09; Cl, 21.40. Found: C, 72.47; H, 6.11; Cl, 21.32.

Ethyl (*Z*)-3-chloro-2-phenyl-2-heptenoate (3k): oil; ^1H NMR (400 MHz) δ 0.96 (t, 3H, J = 7.3 Hz), 1.23 (t, 3H, J = 7.1 Hz), 1.42 (sextet, 2H, J = 7.3 Hz), 1.67–1.75 (m, 2H), 2.79 (t, 2H, J = 7.7 Hz), 4.19 (q, 2H, J = 7.1 Hz), 7.25-7.38 (m, 5H); MS *m/z* 266, 268 (M^+). HRMS *m/z* (M^+) Calcd for $C_{15}H_{19}O_2Cl$: 266.1073. Found: 266.1077.

(*E, Z*)- and (*E, E*)-4-Chloro-1-phenyl-3-propyl-1,3-heptadiene (3l and 3l'; 3:1): oil; ^1H NMR (400 MHz) δ0.93–1.01 (m, 6H), 1.49–1.69 (m, 4H), 2.38–2.63 (m, 4H), 6.59 (d, 1H, J = 15.8 Hz; **3l'**), 6.60 (d, 1H, J = 15.8 Hz; **3l**), 7.00 (d, 2H, J = 15.8 Hz), 7.21–7.48 (m, 10H); MS *m/z* 248, 250 (M^+). HRMS *m/z* (M^+) Calcd for $C_{15}H_{19}O_2Cl$: 248.1332. Found: **3l**; 248.1332, **3l'**; 248.1329.

6-Chloro-2,3-dipropyl-1-indenone (4b): yellow solid, mp 50.5–50.7 °C; ^1H NMR (400 MHz) δ0.93 (t, 3H, J = 7.3 Hz), 1.03 (t, 3H, J = 7.3 Hz), 1.49 (sextet, 2H, J = 7.5 Hz), 1.63 (sextet, 2H, J = 7.7 Hz), 2.23 (t, 2H, J = 7.6 Hz), 2.51 (t, 2H, J = 7.8 Hz), 6.96 (d, 1H, J = 7.7 Hz), 7.28 (dd, 1H, J = 7.7, 2.0 Hz), 7.32 (d, 1H, J = 2.0 Hz);

MS *m/z* 248, 250 (M^+); IR (KBr): 1707.2 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89; Cl, 14.25. Found: C, 72.26; H, 6.93; Cl, 14.10.

2,3-Dipropyl-6-methyl-1-indenone (4c): yellow oil; ^1H NMR (400 MHz) δ 0.92 (t, 3H, J = 7.3 Hz), 1.01 (t, 3H, J = 7.3 Hz), 1.47 (sextet, 2H, J = 7.4 Hz), 1.63 (sextet, 2H, J = 7.5 Hz), 2.21 (t, 2H, J = 7.6 Hz), 2.30 (s, 3H), 2.49 (t, 2H, J = 7.8 Hz), 6.90 (d, 1H, J = 7.3 Hz), 7.08 (dt, 1H, J = 7.3, 1.0 Hz), 7.18 (d, 1H, J = 1.0 Hz); MS *m/z* 228 (M^+); IR (neat): 1707.2 (C=O) cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1512.

2,3-Dipropyl-5-methyl-1-indenone (4d): yellow oil; ^1H NMR (400 MHz) δ 0.93 (t, 3H, J = 7.3 Hz), 1.03 (t, 3H, J = 7.3 Hz), 1.48 (sextet, 2H, J = 7.3 Hz), 1.63 (sextet, 2H, J = 7.3 Hz), 2.22 (t, 2H, J = 7.8 Hz), 2.38 (s, 3H), 2.50 (t, 2H, J = 7.8 Hz), 6.83 (s, 1H), 6.93 (d, 1H, J = 7.3 Hz), 7.26 (d, 1H, J = 7.3 Hz); MS *m/z* 228 (M^+); IR (neat): 1705.3 (C=O) cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1529.

2,3-Dipropylbenz(*d*)-1-indenone (4e): yellow solid, mp 46.0–46.5 °C; ^1H NMR (400 MHz) δ0.97 (t, 3H, J = 7.3 Hz), 1.08 (t, 3H, J = 7.3 Hz), 1.54 (sextet, 2H, J = 7.3 Hz), 1.73 (sextet, 2H, J = 7.3 Hz), 2.32 (t, 2H, J = 7.8 Hz), 2.63 (t, 2H, J = 7.8 Hz), 7.32 (s, 1H), 7.41 (t, 1H, J = 7.8 Hz), 7.48 (t, 1H, J = 7.8 Hz), 7.73 (d, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 7.8 Hz), 7.81 (s, 1H); MS *m/z* 264 (M^+); IR (KBr): 1699.5 (C=O) cm^{-1}. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.23; H, 7.62.

2,3-Dipropylbenz(*e*)-1-indenone (4e'): red solid, mp 43.5–44.5 °C; ^1H NMR (400 MHz) δ0.96 (t, 3H, J = 7.3 Hz), 1.06 (t, 3H, J = 7.3 Hz), 1.54 (sextet, 2H, J = 7.6 Hz), 1.69 (sextet, 2H, J = 7.3 Hz), 2.25 (t, 2H, J = 7.6 Hz), 2.56 (t, 2H, J = 7.6 Hz), 7.26 (d, 1H, J = 8.3 Hz), 7.31 (t, 1H, J = 8.3 Hz), 7.47 (t, 1H, J = 8.3 Hz), 7.69 (d, 1H, J = 8.3 Hz), 7.85 (d, 1H, J = 8.3 Hz), 8.69 (d, 1H, J = 8.3 Hz); MS *m/z* 264 (M^+); IR (KBr): 1693.7 (C=O) cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{19}H_{20}O$: 264.1514. Found: 264.1516.

3 (or 2)-Butyl-2 (or 3)-methyl-1-indenone (4i and 4i'; 1:1): yellow oil; ^1H

NMR (400 MHz) δ0.89–0.98 (m, 6H), 1.30–1.46 (m, 6H), 1.56–1.60 (m, 2H; **4i**), 1.80 (s, 3H; **4i'**), 2.11 (s, 3H; **4i**), 2.27 (t, 2H, J = 7.5 Hz; **4i'**), 2.53 (t, 2H, J = 7.5 Hz), 7.00-7.02 (m, 2H), 7.13–7.17 (m, 2H), 7.26–7.37 (m, 4H); MS *m/z* 200 (M^+); IR (neat): 1709.1 (C=O) cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1203.

2-Phenyl-3-trimethylsilyl-1-indenone (4j): yellow solid, mp 111.5–112.0 °C; ^1H NMR (400 MHz) δ0.08 (s, 9H), 7.10–7.42 (m, 9H); MS *m/z* 278 (M^+); IR (KBr): 1705.3 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{18}OSi$: C, 77.65; H, 6.52. Found: C, 77.75; H, 6.56.

1,2,3,4-Tetrapropylnaphthalene (5): oil; ^1H NMR (400 MHz) δ 1.08–1.13 (m, 12H), 1.56–1.71 (m, 8H), 2.71–2.75 (m, 4H), 2.98–3.03 (m, 4H), 7.38–7.41 (m, 2H), 7.97–8.00 (m, 2H); MS *m/z* 296 (M^+); HRMS *m/z* (M^+) Calcd for $C_{22}H_{32}$: 296.2504. Found: 296.2501.

1,3-Diphenyl-2-propyl-2-hexen-1-one (6): (*Z*)-isomer; oil; ^1H NMR (400 MHz) δ0.92 (t, 3H, J = 7.3 Hz), 0.98 (t, 3H, J = 7.3 Hz), 1.32–1.40 (m, 2H), 1.45–1.54 (m, 2H), 2.53–2.60 (m, 4H), 6.94–7.01 (m, 5H), 7.18 (t, 2H, J = 7.8 Hz), 7.29 (t, 1H, J = 7.3 Hz), 7.62 (d, 2H, J = 7.3 Hz); ^{13}C NMR (100 MHz) δ 13.97, 14.33, 21.49, 22.14, 33.59, 35.62, 126.96, 127.70, 127.15, 128.80, 129.10, 132.03, 137.86, 138.17, 141.42, 142.95, 201.55; HRMS *m/z* (M^+) Calcd for $C_{21}H_{24}O$: 292.1827. Found: 292.1837. (*E*)-isomer; oil; ^1H NMR (400 MHz) δ0.66 (t, 3H, J = 7.3 Hz), 0.73 (t, 3H, J = 7.3 Hz), 1.15–1.34 (m, 4H), 2.11–2.18 (m, 4H), 7.25 (dd, 2H, J = 7.3, 1.5 Hz), 7.31 (td, 1H, J = 7.3, 1.5 Hz), 7.40 (t, 2H, J = 7.3 Hz), 7.51 (t, 2H, J = 7.3 Hz), 7.60 (t, 1H, J = 7.3 Hz), 8.04 (dd, 2H, J = 7.3, 1.5 Hz); ^{13}C NMR (100 MHz) δ 13.81, 13.97, 21.03, 21.95, 33.95, 38.13, 126.87, 128.19, 128.30, 128.34, 128.65, 129.32, 133.24, 137.17, 140.73, 141.29, 200.98; HRMS *m/z* (M^+) Calcd for $C_{21}H_{24}O$: 292.1827. Found: 292.1823.

1,3-Di(4-methylphenyl)-2-propyl-2-hexen-1-one (9): (*Z*)-isomer; oil; ^1H NMR (400 MHz) δ0.91 (t, 3H, J = 7.3 Hz), 0.94 (t, 3H, J = 7.3 Hz), 1.33–1.48 (m, 4H), 2.14 (s, 3H), 2.28 (s, 3H), 2.48–2.56 (m, 4H), 6.83 (d, 2H, J = 8.1 Hz), 6.93 (d, 2H, J = 8.1

Hz), 7.01 (d, 2H, J = 8.1 Hz), 7.58 (d, 2H, J = 8.1 Hz); ^{13}C NMR (68 MHz) δ 13.99, 14.28, 20.99, 21.51, 22.10, 33.67, 35.53, 128.41, 128.57, 129.39, 135.06, 136.42, 137.83, 138.50, 141.89, 142.76, 201.16; HRMS *m/z* (M^+) Calcd for $C_{23}H_{28}O$: 320.2140. Found: 320.2139. (*E*)-isomer; oil; ^{1}H NMR (400 MHz) δ 0.65 (t, 3H, J = 7.3 Hz), 0.72 (t, 3H, J = 7.3 Hz), 1.14–1.31 (m, 4H), 2.11–2.16 (m, 4H), 2.38 (s, 3H), 2.44 (s, 3H), 7.13 (d, 2H, J = 8.1 Hz), 7.20 (d, 2H, J = 8.1 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.93 (d, 2H, J = 8.1 Hz); ^{13}C NMR (68 MHz) δ 13.84, 13.99, 21.08, 21.19, 21.72, 21.96, 34.05, 38.15, 128.20, 128.84, 129.33, 129.48, 134.76, 136.37, 137.14, 137.75, 140.73, 144.04, 200.78; HRMS *m/z* (M^+) Calcd for $C_{23}H_{28}O$: 320.2140. Found: 320.2148.

1,3-Di(4-chlorophenyl)-2-propyl-2-hexen-1-one (10): oil; ^{1}H NMR (270 MHz) ((*Z*)/(*E*) = 85:15) δ 0.67 (t, 3H, J = 7.3 Hz; *E*), 0.78 (t, 3H, J = 7.3 Hz; *E*), 0.91 (t, 3H, J = 7.3 Hz; *Z*), 0.96 (t, 3H, J = 7.3 Hz; *Z*), 1.14–1.50 (m, 4H), 2.07–2.14 (m, 4H; *E*), 2.49–2.56 (m, 4H; *Z*), 6.94 (dt, 2H, J = 8.3, 2.2 Hz; *Z*), 7.02 (dt, 2H, J = 8.3, 2.2 Hz; *Z*), 7.20 (d, 2H, J = 8.3 Hz; *Z*), 7.31–7.50 (m, 4H; *E*), 7.57 (d, 2H, J = 8.3 Hz; *Z*), 7.63–7.69 (m, 2H; *E*), 7.95 (d, 2H, J = 8.3 Hz; *E*); MS *m/z* 360, 362, 364 (M^+). Anal. Calcd for $C_{21}H_{22}Cl_2O$: C, 69.81; H, 6.14; Cl, 19.62. Found: C, 69.61; H, 6.17; Cl, 19.59.

2-Butyl-1,3-diphenyl-2-hepten-1-one (11): oil; ^{1}H NMR (400 MHz) ((*Z*)/(*E*) = 97:3) δ 0.64 (t, 3H, J = 7.3; *E*), 0.70 (t, 3H, J = 7.3 Hz; *E*), 0.85–0.92 (m, 6H; *Z*), 1.30–1.47 (m, 8H), 2.13–2.19 (m, 4H; *E*), 2.55–2.61 (m, 4H; *Z*), 6.94–7.00 (m, 5H; *Z*), 7.17 (t, 2H, J = 7.3 Hz; *Z*), 7.25–7.29 (m, 1H; *Z*), 7.60–7.62 (m, 2H; *Z*), 8.03 (d, 2H, J = 8.3 Hz; *E*); HRMS *m/z* (M^+) Calcd for $C_{23}H_{28}O$: 320.2140. Found: 320.2140.

1,3-Diphenyl-6-methyl-2-(3-methylbutyl)-2-hepten-1-one (12): oil; ^{1}H NMR (400 MHz) ((*Z*)/(*E*) = 78:22) δ 0.58 (d, 6H, J = 6.4 Hz; *E*), 0.66 (d, 6H, J = 6.4 Hz; *E*), 0.88 (d, 6H, J = 6.4 Hz; *Z*), 0.91 (d, 6H, J = 6.4 Hz; *Z*), 1.18–1.40 (m, 4H), 1.53–1.63 (m, 2H), 2.13–2.17 (m, 4H; *E*), 2.53–2.59 (m, 4H; *Z*), 6.94–8.04 (m, 10H); MS *m/z* 348 (M^+). Anal. Calcd for $C_{25}H_{32}O$: C, 86.16; H, 9.25. Found: C, 85.89; H, 9.26.

***exo*-2-Benzoyl-*exo*-3-phenylbicyclo[2.2.1]heptane (15):** white solid, mp

87.0–88.0 °C; ^{1}H NMR (270 MHz) δ 1.40–1.52 (m, 2H), 1.69–1.73 (m, 2H), 2.43–2.49 (m, 2H), 2.69 (s, 1H), 3.29 (d, 1H, J = 10.3 Hz), 3.84 (d, 1H, J = 10.3 Hz), 6.88–6.96 (m, 5H), 7.21 (t, 2H, J = 7.3 Hz), 7.34 (t, 1H, J = 7.3 Hz), 7.54 (d, 2H, J = 7.3 Hz); ^{13}C NMR (68 MHz) δ 28.95, 31.15, 37.38, 39.17, 43.52, 53.90, 56.19, 125.80, 127.60, 127.85, 127.97, 128.38, 131.94, 138.50, 141.78, 201.66; MS *m/z* 276 (M^+). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.75; H, 7.33.

***exo*-8-Benzoyl-*exo*-9-phenyl- and *exo*-9-Benzoyl-*exo*-8-phenyl-tricyclo [5.2.1.0^{2,6}]dec-3-enes (16):** white solid, mp 118.5–119.0 °C; ^{1}H NMR (400 MHz) (mixture of double bond isomers in a ratio of 2:1) δ 1.73 (t, 1H, J = 10.3 Hz), 2.32–2.77 (m, 6H), 3.25–3.45 (m, 1.33H), 3.44 (d, 0.67H, J = 10.3 Hz), 3.84 (d, 0.67H, J = 10.3 Hz), 3.91 (d, 0.33H, J = 10.3 Hz), 5.70–5.72 (m, 1H), 5.92–5.94 (m, 1H), 6.87–6.97 (m, 5H), 7.16–7.25 (m, 2H), 7.29–7.37 (m, 1H), 7.48 (d, 0.67H, J = 8.3 Hz), 7.57 (d, 1.33H, J = 8.3 Hz); ^{13}C NMR (100 MHz) δ 32.41, 32.54, 40.19, 40.37, 41.92, 42.12, 43.35, 43.41, 45.30, 46.27, 48.06, 48.14, 48.63, 51.26, 52.79, 54.22, 125.72, 125.76, 127.58, 127.61, 127.77, 127.94, 127.98, 128.03, 128.52, 128.72, 131.76, 131.84, 132.06, 132.08, 132.24, 132.41, 138.46, 141.82, 142.05, 201.85; HRMS *m/z* (M^+) Calcd for $C_{23}H_{22}O$: 314.1670. Found: 314.1676.

(*Z*)-1-(4-Methylphenyl)-2-phenyl-3-trimethylsilyl-2-propen-1-one (20): oil, ^{1}H NMR (400 MHz) δ 0.01 (s, 9H), 2.37 (s, 3H), 6.45 (s, 1H), 7.19 (d, 2H, J = 8.1 Hz), 7.24–7.30 (m, 3H), 7.36–7.39 (m, 2H), 7.82 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ –0.53, 21.71, 125.97, 128.22, 128.61, 129.26, 130.10, 132.04, 134.33, 138.66, 144.31, 155.25, 198.78; MS *m/z* 294 (M^+). Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.54; H, 7.61.

2-4. References and Notes

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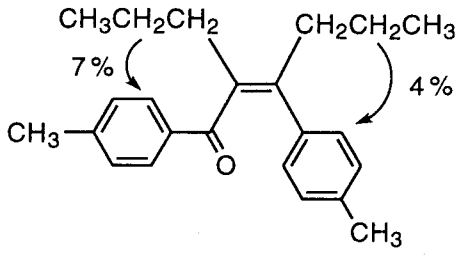
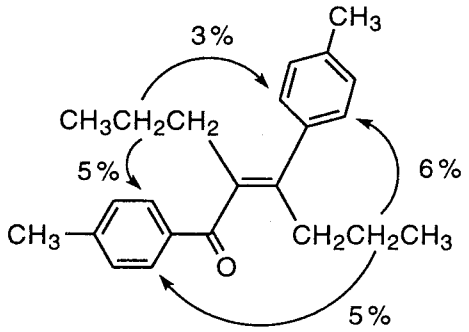
18) For example, selective NOE peak enhancements were observed for the (*Z*)-

isomer of compound **6**, while they were non-selective for its (*E*)-isomer as follows.



(*Z*)-6



(*E*)-6

19) Coupling constant between *vicinal* protons at the carbons attached benzoyl and phenyl groups in both compounds **12** and **13** was observed to be uniformly 10.3 Hz.

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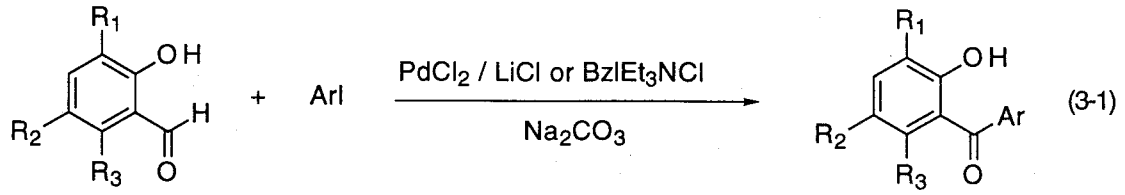
Chapter 3. Rhodium-Catalyzed Hydroacylation of Alkynes with Salicylaldehydes via Cleavage of Aldehyde C–H Bond

3-1. Introduction

The activation of C–H bonds in organic compounds by transition metal complexes is currently one of the most significant subjects in both organic and organometallic chemistry. An effective strategy to regioselectively activate a C–H bond in a given molecule has been known to introduce a functional group having ligating ability at an appropriate position of it.[1] Recently, a number of *catalytic* coupling reactions of aromatic or vinylic compounds bearing carbonyl or nitrogen-containing groups with alkenes and/or alkynes involving such a C–H bond activation mode as the key step have been developed, especially by using ruthenium and rhodium complexes.[2,3] The reaction of acylarenes has also been minutely described by Murai et al.[2b,c]

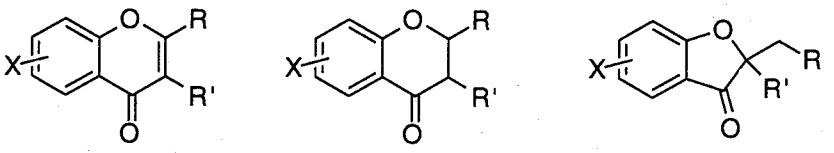
Meanwhile, we have recently reported that salicylaldehydes smoothly react with aryl iodides in the presence of a palladium catalyst and a base to give 2-aroylphenols, demonstrating that the phenolic function can act as a good anchor for the catalytic intermolecular C–C coupling via cleavage of the aldehyde C–H bond (eq 3-1).[4]



(3-1)

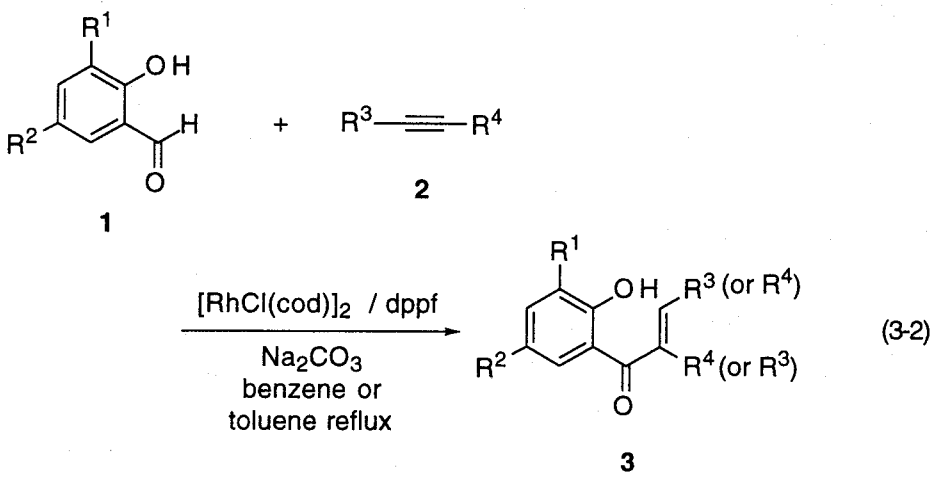
It was expected that, if vinyl halides could be used in place of aryl iodides, 2-alkenoylphenols could also be obtained in one step: The phenolic compounds are

valuable precursors of chromones, chromanones, and 3-benzofuranones,[5,6] whose skeletons are widely found in naturally occurring compounds, and a number of them exhibit interesting biological activities.[5]



Chromones Chromanones 3-Benzofuranones

However, the reaction using vinyl halides was less efficient. One of other possible routes to prepare 2-alkenoylphenols using salicylaldehydes via the C–H cleavage is their coupling with alkynes, which may be regarded as a hydroacylation reaction.[7,8] Indeed, in the present study the latter route have been able to be realized with high efficiency by using a rhodium-based catalyst system to produce the corresponding 2-alkenoylphenols in good yields (eq 3-2).



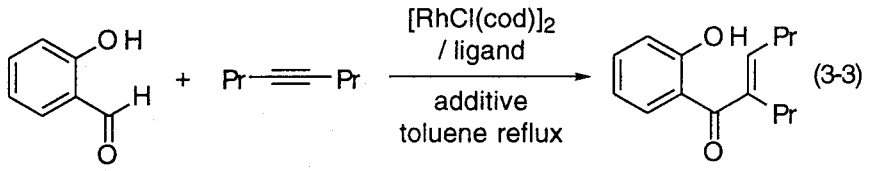
1 2 3 (3-2)

1a: R^1=R^2=H
1b: R^1=OMe, R^2=H
1c: R^1=H, R^2=OH
1d: R^1=H, R^2=Cl

2a: R^3=R^4=Pr
2b: R^3=R^4=Ph
2c: R^3=Hex, R^4=H
2d: R^3=Ph, R^4=H
2e: R^3=Me_2(OH)C-, R^4=H
2f: R^3=$(CH_2)_5$C(OH)-, R^4=H
2g: R^3=Pen(AcO)C-, R^4=H

3-2. Results and Discussion

The reaction of salicylaldehyde (**1a**) with 4-octyne (**2a**) was first examined in the presence of $[RhCl(cod)]_2$ and a variety of ligands in toluene (5 mL) under nitrogen (monitored by GLC), the relative amount of **1a**, **2a**, $[RhCl(cod)]_2$ being 2:2:0.01 (in mmol) (eq 3-3).



(3-3)

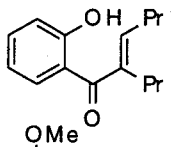
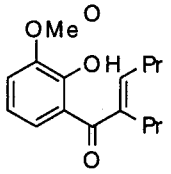
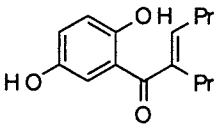
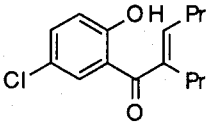
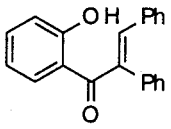
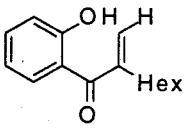
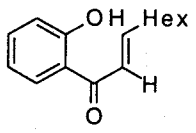
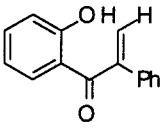
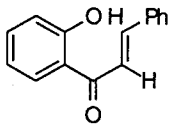
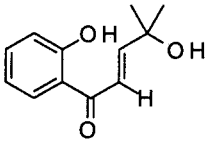
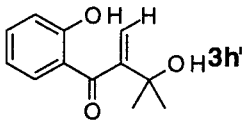
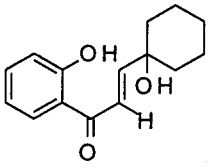
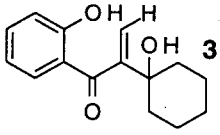
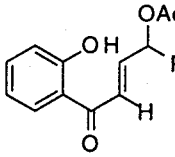
1a **2a** **3**

ligand	additive	time / h	% yield
dppf	none	0.5	5
dppf	none	24	99
dppf	Na_2CO_3	0.5	100
dppp	Na_2CO_3	21	52
PPh_3	Na_2CO_3	20	33

It was found that, by using dppf (0.02 mmol) as ligand and refluxing the solvent for 24 h, the expected product, (*E*)-1-(2-hydroxyphenyl)-2-propyl-2-hexen-1-one (**3**), was produced in an almost quantitative yield, no isomer being accompanied.[9] Addition of an inorganic carbonate, Na_2CO_3 (0.1 mmol), was also found to significantly enhance the rate of the reaction, so that it was completed within 0.5 h, while a tertiary amine, $NEt(i\text{-}Pr)_2$, which is effective for the rhodium-catalyzed hydroacylation of alkenes with acid anhydrides and molecular hydrogen,[10] showed no meaningful effect. Although other bidentate phosphine ligands, dppe, dppp, and dppb as well as monodentate ones, PPh_3 and tricyclohexylphosphine, could be used in place of dppf, they were much less effective.[9]

The reaction of **1a** with **2a** using the catalyst system of $[RhCl(cod)]_2$/ dppf/Na_2CO_3 could also be completed in refluxing benzene in a period of 2.5 h

Table 3-1. Hydroacylation Reaction of Salicylaldehydes 1 with Alkynes 2[a]

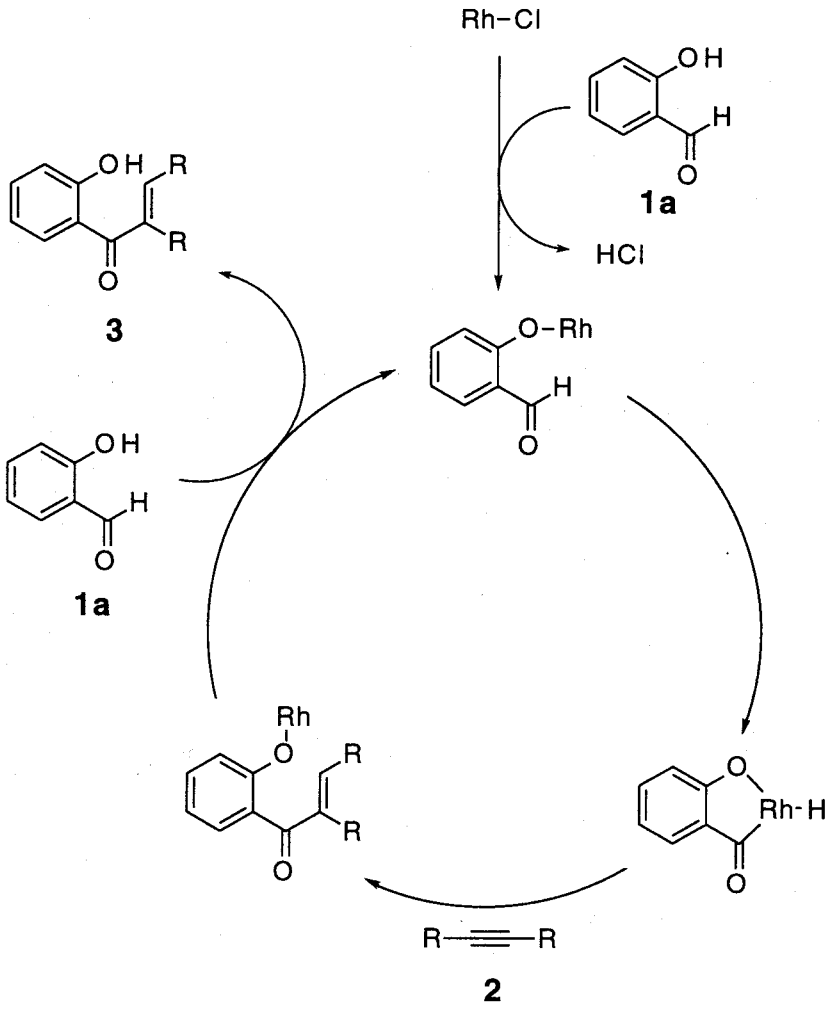
substrates 1	substrates 2	time /h	product 3, % yield[b]		
1a	**2a**	4		**3a**	> 99 (99)
1b	**2a**	0.5		**3b**	> 99 (99)
1c	**2a**	1		**3c**	> 99 (98)
1d	**2a**	4		**3d**	> 99 (98)
1a	**2b**	7		**3e**	94 (86)
1a	**2c**	2		**3f** (55:45) 	**3f'** > 99 (99)
1a	**2d**	4		**3g** (66:34) 	**3g'** 93 (75)
1a	**2e**	5.5[c]		**3h** (83:17) 	**3h'** 75 (72)
1a	**2f**	4[c]		**3i** (85:15) 	**3i'** 86 (83)
1a	**2g**	2[c]		**3j**	70 (68)

[a]The reaction was carried out in refluxing benzene under N_2. [[RhCl(cod)]$_2$]:[dppf]:[Na_2CO_3]:[**1**]:[**2**] = 0.01:0.02: 0.1 : 2 : 2 (in mmol). [b]Determined by GLC. Yield in parentheses indicates that after isolation. [c]Reaction in refluxing toluene.

(Table 3-1, eq 3-2); product **3a** (99%) also was cleanly isolated by means of flash chromatography on silica gel. Similarly, 3-methoxy-, 5-hydroxy-, and 5-chlorosalicylaldehydes, (**1b**), (**1c**), and (**1d**), quantitatively reacted with **2a** to give the corresponding alkenoylphenols **3b**, **3c**, and **3d**, respectively. Note that the reaction using 20 mmol of each of **1b** and **2a** in refluxing toluene was quantitatively proceeded within 2 h, the turnover rate being approximately estimated to be as high as 500 h^{-1}. The reaction of **1a** with 1,2-diphenylacetylene (**2b**) also gave product **3e**. In contrast to other catalytic C–H/alkyne coupling reactions,[2e,2g,3c] terminal alkynes, 1-octyne (**2c**) and 1-phenylacetylene (**2d**), could smoothly react with **1a**, giving pairs of regioisomers **3f/3f'** and **3g/3g'** in comparable amounts. Styrene, however, did not react with **1a**. Good regioselectivities were observed in the reactions with propargyl alcohols **2e** and **2f**. The regioisomers of **3f–i** and **3f'–i'** could be also separated by column chromatography on silica gel. The reaction of **1a** with 3-acetoxy-1-octyne (**2g**) predominantly afforded compound **3j** along with minor amounts of some unidentified products.

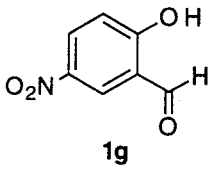
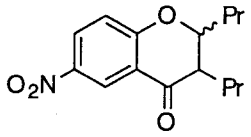
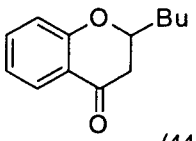
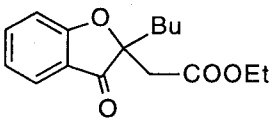
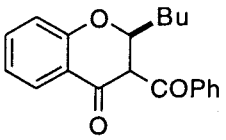
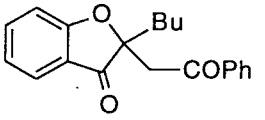
The present reaction may involve initial coordination of **1** to a chlororhodium(I) species complexed by dppf to form a 2-formylphenolate complex accompanied by liberation of HCl, and then, oxidative addition of the aldehyde C-H bond to the metal center occurs to give a aroylhydridorhodium(III) as the key steps (scheme 3-1).[4, 11, 12] It should be noted that 4-hydroxybenzaldehyde and 2-methoxybenzaldehyde as well as benzaldehyde itself could not be used in place of **1a**, supporting the above consideration that coordination of the phenolic oxygen to the metal center plays an significant role. It was confirmed that addition of AgOTf or $AgClO_4$ in place of Na_2CO_3 to the reaction of **1a** with **2a**, which may generate a cationic rhodium(I) species, could not enhance the reaction. Thus, the insoluble solid base seems to effectively remove initially formed HCl which could be a poison for the catalysis. The origin of high efficiency of dppf as ligand, however, is not definitive at the present stage.

Scheme 3-1



The reaction of 5-nitrosalicylaldehyde (**1g**) with **2a** was found to give a cyclized product, 5-nitro-2,3-dipropyl-4-chromanone (**4a**). The strong electron withdrawing substituent, nitro group, is considered to increase the acidity of the phenolic hydrogen, so that the oxygen may attack the double bond in the corresponding 2-alkenoylphenol **3** once formed. Its ^{1}H NMR showed that **4a** is a mixture of *trans*- and *cis*-isomers in a ratio of 64:36.

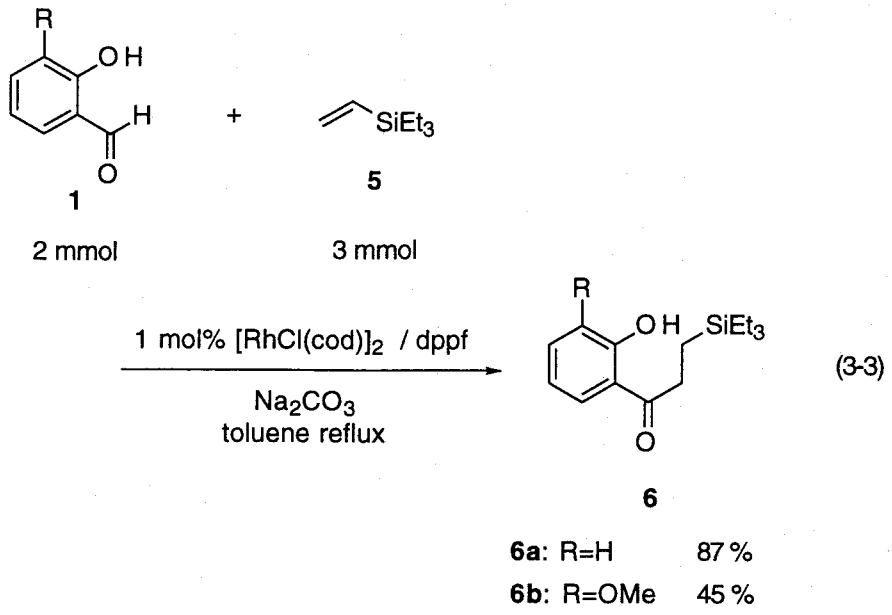
Table 3-2. Cyclization Coupling Reaction of Salicylaldehydes 1 with Alkynes 2[a]

substrates 1	substrates 2	time / h	product 3, % yield[b]
 **1g**	**2a**	2	 **4a** 68
1a	Bu—≡—COOEt **2h**	30	 **4b** (44 : 56)  **4b'** 70 (63)
1a	Bu—≡—COPh **2i**	5	 **4c** (43 : 57)  **4c'** 99 (94)

[a]The reaction was carried out in refluxing toluene under N_2. [[RhCl(cod)]$_2$]:[dppf]:[Na_2CO_3]:[**1**]:[**2**] = 0.01:0.02: 0.1 : 2 : 2 (in mmol). [b]Determined by GLC. Yield in parentheses indicates that after isolation.

From the reaction of **1a** with internal alkynes **2h** and **2i**, each of which has an electron withdrawing group, also gave the corresponding chromanone derivatives **4b** and **4c**, together with 3-benzofuranone derivatives **4b'** and **4c'**, respectively. Note that the ethoxy carbonyl group in **2h** was eliminated in the reaction of **1a** with **2h**, giving **4b**.

It was also attempted to use alkenes in place of alkynes. While styrene, 1-octene, butyl vinyl ether did not afford no expected products, triethylvinyl-silane **5** was observed to react with **1a** and **1b** regioselectively to give the corresponding ketones **6a** and **6b**, respectively (eq 3-3).

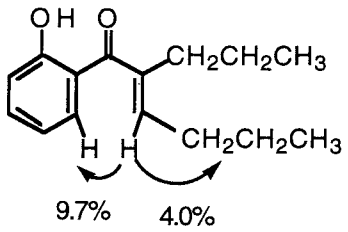


In summary, it was described in this chapter that salicylaldehydes can readily react with alkynes accompanied by cleavage of the aldehyde C–H bond in the presence of a catalytic amount of a rhodium(I) complex to produce synthetically useful 2-alkenoylphenols.

3-3. Experimental Section

Typical procedure for the reaction of 1 with 2: A mixture of **1a** (244mg, 2 mmol), **2a** (220mg, 2 mmol), $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol,), dppf (11.1 mg, 0.02 mmol), and Na_2CO_3 (10.6 mg, 0.1 mmol) in refluxing benzene (5 mL) was stirred under nitrogen for 2 h. After evaporation of the solvent, product **3a** (460 mg, 99%) was isolated by flash chromatography on silica gel using hexane-ethyl acetate (98:2, v/v) as eluent. The enone **3** was an yellow oil: ^{1}H NMR (400 MHz) δ0.94 (t, 3H, J = 7.3 Hz), 0.98 (t, 3H, J = 7.3 Hz), 1.43–1.53 (m, 4H), 2.27 (q, 2H, J = 7.3 Hz), 2.47 (t, 2H, J = 7.3 Hz), 5.97 (t, 1H, J = 7.3 Hz), 6.86 (t, 1H, J = 7.8 Hz), 7.00 (d, 1H, J = 7.8 Hz), 7.45 (t, 1H, J = 7.8 Hz), 7.67 (d, 1H, J = 7.8 Hz), 11.95 (s, 1H); ^{13}C NMR δ13.96,

14.10, 22.04, 22.32, 29.71, 30.49, 118.22, 118.27, 119.54, 132.77, 135.70, 139.66, 141.25, 162.93, 204.21; MS *m/z* 232 (M^+). IR ν 1624 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.44; H, 8.72. The observed NOE peak enhancements in the measurement of ^1H NMR were as follows:



Products. Compounds **3e**[13] and **3f'**[14] are known and were compared with those authentic specimens. Characterization data of other new compounds, **3b–d**, **3f–j**, **3f'**, **3g'–i'**, **4a–c**, **4b'–c'**, and **6a–b** are as follows. ^1H and ^{13}C NMR spectra were recorded at 400 or 270 MHz and 100 or 68 MHz, respectively, in $CDCl_3$.

(*E*)-1-(2-Hydroxy-3-methoxyphenyl)-2-propyl-2-hexen-1-one (3b): yellow oil; ^1H NMR (400 MHz) δ0.93 (t, 3H, J = 7.3 Hz), 0.97 (t, 3H, J = 7.3 Hz), 1.43–1.53 (m, 4H), 2.27 (q, 2H, J = 7.3 Hz), 2.46 (t, 2H, J = 7.3 Hz), 3.92 (s, 3H), 5.99 (t, 1H, J = 7.3 Hz), 6.80 (t, 1H, J = 7.8 Hz), 7.05 (d, 1H, J = 7.8 Hz), 7.26 (d, 1H, J = 7.8 Hz), 12.10 (s, 1H); ^{13}C NMR δ 13.95, 14.08, 22.05, 22.28, 29.63, 30.50, 56.23, 116.55, 117.55, 119.82, 124.10, 139.79, 141.67, 148.88, 152.98, 204.26; MS *m/z* 262 (M^+). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.13; H, 8.53.

(*E*)-1-(2,5-Dihydroxyphenyl)-2-propyl-2-hexen-1-one (3c): yellow oil; ^1H NMR (400 MHz) δ 0.92 (t, 3H, J = 7.3 Hz), 0.96 (t, 3H, J = 7.3 Hz), 1.41–1.51 (m, 4H), 2.25 (q, 2H, J = 7.3 Hz), 2.45 (t, 2H, J = 7.3 Hz), 5.22 (s, 1H), 5.99 (t, 1H, J = 7.3 Hz), 6.89 (d, 1H, J = 8.8 Hz), 7.02 (dd, 1H, J = 8.8, 2.9 Hz), 7.15 (d, 1H, J = 3.4 Hz), 11.49 (s, 1H); ^{13}C NMR δ 13.96, 14.09, 22.04, 22.27, 29.69, 30.48, 117.91, 118.96, 119.35, 124.00, 139.64, 141.32, 147.08, 156.77, 203.73; MS *m/z* 248 (M^+). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.30; H, 8.11.

(*E*)-1-(5-Chloro-2-hydroxyphenyl)-2-propyl-2-hexen-1-one (3d): yellow oil;

^{1}H NMR (400 MHz) δ 0.94 (t, 3H, J = 7.3 Hz), 1.00 (t, 3H, J = 7.3 Hz), 1.41–1.57 (m, 4H), 2.29 (q, 2H, J = 7.3 Hz), 2.45 (t, 2H, J = 7.3 Hz), 6.00 (t, 1H, J = 7.3 Hz), 6.96 (d, 1H, J = 8.8 Hz), 7.40 (dd, 1H, J = 8.8, 2.4 Hz), 7.61 (d, 1H, J = 2.4 Hz), 11.79 (s, 1H); ^{13}C NMR δ 13.92, 14.14, 22.08, 22.26, 29.63, 30.56, 119.87, 120.17, 123.01, 131.80, 135.47, 139.50, 142.41, 161.33, 202.97; MS *m/z* 266, 268 (M^+). Anal. Calcd for $C_{15}H_{19}ClO_2$: C, 67.54; H, 7.18; Cl, 13.29. Found: C, 67.30; H, 7.22; Cl, 13.21.

1-(2-Hydroxyphenyl)-2-methyleneoctan-1-one (3f): yellow oil; ^{1}H NMR (270 MHz) δ 0.87 (t, 3H, J = 6.8 Hz), 1.28–1.51 (m, 8H), 2.46 (t, 2H, J = 6.8 Hz), 5.38 (s, 1H), 5.65 (s, 1H), 6.87 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.48 (t, 1H, J = 7.8 Hz), 7.75 (d, 1H, J = 7.8 Hz), 12.00 (s, 1H); ^{13}C NMR δ 14.01, 22.52, 27.88, 28.92, 31.54, 33.40, 118.30, 118.51, 118.96, 121.16, 132.85, 136.34, 147.41, 163.14, 204.00; MS *m/z* 232 (M^+). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.19; H, 8.74.

(*E*)-1-(2-Hydroxyphenyl)-2-nonen-1-one (3f'): yellow oil; ^{1}H NMR (270 MHz) δ 0.90 (t, 3H, J = 6.8 Hz), 1.28–1.59 (m, 8H), 2.35 (q, 2H, J = 6.8 Hz), 6.90 (t, 1H, J = 7.8 Hz), 6.98–7.05 (m, 2H), 7.21 (dt, 1H, J = 15.6, 6.8 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 7.8 Hz), 12.75 (s, 1H); ^{13}C NMR δ 14.04, 22.53, 28.09, 28.91, 31.59, 32.97, 118.49, 118.71, 119.59, 123.82, 129.81, 136.18, 151.01, 163.55, 194.17; HRMS *m/z* (M^+) Calcd for $C_{15}H_{20}O_2$: 232.1463. Found: 232.1456.

1-(2-Hydroxyphenyl)-2-phenyl-2-propen-1-one (3g): yellow oil; ^{1}H NMR (270 MHz) δ 5.54 (s, 1H), 6.03 (s, 1H), 6.82 (t, 1H, J = 7.8 Hz), 7.04 (d, 1H, J = 7.8 Hz), 7.27–7.52 (m, 6H), 7.66 (d, 1H, J = 7.8 Hz), 12.11 (s, 1H); ^{13}C NMR δ 118.33, 118.36, 118.86, 119.20, 126.47, 128.72, 128.83, 133.30, 136.41, 136.88, 147.07, 163.36, 203.33; HRMS *m/z* (M^+) Calcd for $C_{15}H_{12}O_2$: 224.0837. Found: 224.0849.

(*E*)-4-Hydroxy-1-(2-hydroxyphenyl)-4-methyl-2-penten-1-one (3h): yellow oil; ^{1}H NMR (270 MHz) δ 1.45 (s, 6H), 1.71 (s, 1H), 6.91 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.19 (d, 1H, J = 15.6 Hz), 7.30 (d, 1H, J = 15.6 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 12.65 (s, 1H); ^{13}C NMR δ 29.54, 71.47, 118.50, 118.85,

119.72, 120.06, 130.02, 136.50, 155.34, 163.50, 194.53; HRMS *m/z* (M^+) Calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0942.

3-Hydroxy-1-(2-hydroxyphenyl)-3-methyl-2-methylenebutan-1-one (3h'): oil; ^1H NMR (270 MHz) δ 1.26 (s, 1H), 1.52 (s, 6H), 5.36 (s, 1H), 5.93 (s, 6H), 6.89 (t, 1H, J = 7.8 Hz), 7.02 (d, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.70 (d, 1H, J = 7.8 Hz), 11.91 (s, 1H); ^{13}C NMR δ 29.37, 72.37, 118.48, 118.76, 119.34, 119.48, 133.38, 136.99, 151.79, 163.43, 205.12; HRMS *m/z* (M^+) Calcd for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0941.

(*E*)-3-(1-Hydroxycyclohexyl)-1-(2-hydroxyphenyl)-2-propen-1-one (3i): yellow oil; ^1H NMR (270 MHz) δ 1.61–1.71 (m, 11H), 6.91 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.23 (d, 1H, J = 15.6 Hz), 7.34 (d, 1H, J = 15.6 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 12.68 (s, 1H); ^{13}C NMR δ 21.49, 25.14, 37.18, 72.46, 118.50, 118.82, 119.78, 120.52, 130.03, 136.45, 155.50, 163.53, 194.62; MS *m/z* 246 (M^+). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.88; H, 7.40.

2-(1-Hydroxycyclohexyl)-1-(2-hydroxyphenyl)-2-propen-1-one (3i'): oil; ^1H NMR (270 MHz) δ 1.25–1.82 (m, 10H), 2.99 (s, 1H), 5.37 (s, 1H), 5.90 (s, 1H), 6.88 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.71 (d, 1H, J = 7.8 Hz), 11.96 (s, 1H); ^{13}C NMR δ 21.83, 25.43, 36.66, 73.26, 118.47, 118.73, 119.43, 119.60, 133.55, 136.99, 152.10, 163.48, 205.59; MS *m/z* 246 (M^+). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.43; H, 7.15.

(*E*)-4-Acetoxy-1-(2-hydroxyphenyl)-2-nonen-1-one (3j): yellow oil; ^1H NMR (270 MHz) δ 0.89 (t, 3H, J = 6.8 Hz), 1.25–1.40 (m, 6H), 1.70–1.78 (m, 2H), 2.15 (s, 3H), 5.52 (q, 1H, J = 5.9 Hz), 6.93 (t, 1H, J = 7.8 Hz), 6.98–7.06 (m, 2H), 7.15 (d, 1H, J = 15.6 Hz), 7.50 (t, 1H, J = 7.8 Hz), 7.79 (d, 1H, J = 7.8 Hz), 12.54 (s, 1H); ^{13}C NMR δ 13.94, 21.09, 22.44, 24.65, 31.47, 33.91, 73.11, 118.59, 118.91, 119.54, 123.75, 129.93, 136.66, 146.12, 163.56, 170.16, 193.69; MS *m/z* 290 (M^+). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.21; H, 7.63

6-Nitro-2,3-dipropyl-4-chromanone (4a): (*trans/cis* = 64:36); oil; ^1H NMR

(270 MHz) δ 0.90–1.03 (m, 12H), 1.26–1.90 (m, 16H), 2.58 (dd, 1H, J = 12.7, 5.9, Hz; *trans*), 2.68–2.74 (m, 1H; *cis*), 4.53–4.63 (m, 2H), 7.07 (d, 1H, J = 8.8 Hz), 7.08 (d, 1H, J = 8.8 Hz), 8.32, (d, 1H, J = 8.8 Hz), 8.33 (d, 1H, J = 8.8, Hz), 8.75 (s, 1H), 8.76 (s, 1H); ^{13}C NMR δ 13.63, 13.72, 13.92, 14.00, 18.47, 18.76, 19.79, 20.05, 25.72, 30.02, 31.90, 34.23, 48.96, 49.78, 81.49, 81.75, 118.90, 119.14, 119.67, 119.80, 123.72, 123.91, 130.05, 130.23, 141.85, 141.96, 163.68, 164.61, 192.78, 193.39; MS *m/z* 277 (M^+). Anal. Calcd for $C_{15}H_{19}O_4N$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.20; H, 6.93; N, 5.04.

2-Butyl-4-chromanone (4b): oil; ^{1}H NMR (270 MHz) δ 0.98 (t, 3H, J = 6.8 Hz), 1.23–1.89 (m, 8H), 2.69 (d, 2H, J = 7.8 Hz), 4.45 (qd, 1H, J = 7.8, 4.9 Hz), 6.96–7.02 (m, 2H), 7.47 (td, 1H, J = 7.8, 2.0 Hz), 7.88 (dd, 1H, J = 7.8, 2.0 Hz); ^{13}C NMR δ 13.94, 22.47, 27.02, 34.63, 42.99, 77.92, 117.90, 121.02, 121.10, 126.92, 135.90, 161.69, 192.66: HRMS *m/z* (M^+) Calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1144.

Ethyl 2-(2-butyl-3-oxo-benzofuranyl)acetate (4b'): oil; ^{1}H NMR (270 MHz) δ 0.82 (t, 3H, J = 7.3 Hz), 0.96 (t, 3H, J = 7.3 Hz), 1.07–1.34 (m, 4H), 1.79–1.85 (m, 2H), 2.93 (d, 2H, J = 15.6 Hz), 3.03 (d, 2H, J = 15.6 Hz), 3.87–4.00 (m, 2H), 7.05–7.10 (m, 2H), 7.60 (t, 1H, J = 7.8 Hz), 7.69 (d, 1H, J = 7.8 Hz); ^{13}C NMR δ 13.65, 13.70, 22.68, 24.78, 36.49, 40.99, 60.76, 88.87, 112.92, 121.71, 121.89, 124.12, 137.63, 168.51, 171.59, 202.82; MS *m/z* 276 (M^+). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29. Found: C, 69.62; H, 7.22.

***trans*-3-Benzoyl-2-butyl-4-chromanone (4c):** (this **4c** accompanies a tautomer (2-butyl-4-chromanon)-3-ylidene(phenyl)methanol (**7**) in $CDCl_3$ in ca. 30 mol%) white solid, mp 71.5–72.5 °C; ^{1}H NMR (400 MHz) δ 0.73 (t, 3H, J = 7.3 Hz; **7**), 0.88 (t, 3H, J = 7.3 Hz; **4c**), 1.04–1.93 (m, 12H), 4.69 (d, 1H, J = 11.0, Hz; **4c**), 4.97 (ddd, 1H, J = 11.0, 8.3, 3.3 Hz; **4c**), 5.28 (dd, 1H, J = 9.6, 4.7 Hz; **7**), 6.92 (d, 1H, J = 8.2 Hz; **7**), 7.01–7.07 (m, 3H), 7.46–7.57 (m, 9H), 7.62, (td, 1H, J = 7.3, 1.1 Hz; **4c**), 7.87 (dd, 1H, J = 7.7, 1.7 Hz; **4c**), 7.93 (dd, 1H, J = 7.7, 1.7 Hz; **7**), 7.98 (d, 2H, J = 7.3 Hz; **4c**), 16.24

(s, 1H; **7**); ^{13}C NMR δ 13.79, 13.87, 21.83, 22.33, 27.11, 27.51, 33.20, 35.34, 58.44, 75.77, 79.67, 117.97, 120.65, 121.39, 121.44, 126.40, 127.25, 128.63, 128.79, 128.89, 130.75, 133.72, 135.02, 135.48, 136.44, 137.61, 157.53, 161.18, 190.29, 196.63; MS *m/z* 308 (M^+). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.61; H, 6.54.

2-(2-Butyl-3-oxo-benzofuranyl)acetophenone (4c'): white solid, mp 119.5 °C; ^1H NMR (400 MHz) δ 0.85 (t, 3H, J = 7.3 Hz), 1.16–1.39 (m, 4H), 1.83–1.97 (m, 4H), 3.58 (d, 1H, J = 17.3 Hz), 3.84 (d, 1H, J = 17.3 Hz), 7.03 (d, 1H, J = 8.3 Hz), 7.10 (t, 1H, J = 7.8 Hz), 7.42 (t, 2H, J = 7.8, 1.5 Hz), 7.53–7.61 (m, 2H), 7.74 (dd, 1H, J = 7.8, 1.5 Hz), 7.86 (dt, 2H, J = 8.3, 1.5 Hz); ^{13}C NMR δ 13.75, 22.78, 24.84, 36.81, 44.90, 88.80, 112.79, 121.62, 122.33, 124.02, 128.20, 128.56, 133.38, 136.32, 137.33, 171.33, 194.78, 203.45; MS *m/z* 296 (M^+). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.60; H, 6.57.

3-(Triethylsilyl)-1-(2-hydroxyphenyl)propanone (6a): oil; ^1H NMR (400 MHz) δ0.59 (t, 6H, J = 7.8 Hz), 0.92–0.99 (m, 11H), 2.93–2.97 (m, 2H), 6.90 (td, 1H, J = 7.8, 1.0 Hz), 6.99 (d, 1H, J = 7.8 Hz), 7.46 (td, 1H, J = 7.8, 1.5 Hz), 7.74 (dd, 1H, J = 7.8, 1.5 Hz); ^{13}C NMR δ 3.18, 6.22, 7.39, 32.87, 118.59, 118.81, 118.91, 129.79, 136.12, 162.56, 207.78; MS *m/z* 264 (M^+). Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 68.41; H, 8.97.

3-(Triethylsilyl)-1-(2-hydroxy-3-methoxyphenyl)propanone (6b): yellow oil; ^1H NMR (400 MHz) δ0.59 (t, 6H, J = 7.8 Hz), 0.92–0.99 (m, 11H), 2.93–2.97 (m, 2H), 3.90, (s, 3H), 6.84 (t, 1H, J = 7.8 Hz), 7.05 (d, 1H, J = 7.8 Hz), 7.35 (dd, 1H, J = 8.3, 1.5 Hz), 12.72 (s, 1H); ^{13}C NMR δ3.09, 6.07, 7.29, 33.16, 56.05, 116.60, 118.06, 118.86, 120.90, 148.99, 152.94, 208.07; MS *m/z* 294 (M^+). Anal. Calcd for $C_{16}H_{26}O_3Si$: C, 65.26; H, 8.90. Found: C, 65.54; H, 8.80.

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Conclusion

This thesis deals with the development of novel synthetic methods for coupling reaction of aromatic carbonyl compounds with unsaturated compounds by means of rhodium catalysis, forming carbon–carbon bonds. The results obtained through this work are summarized as follows.

In chapter 1, it was found that styrenes undergo intermolecular hydro-benzoylation by aromatic acid anhydrides under a normal pressure of molecular hydrogen in the presence of a tertiary amine and a catalytic amount of $[RhCl(cod)]_2$ and a phosphorous ligand to give a mixture of 1,2- and 1,3-diaryl-1-propanones. The catalyst efficiency was observed to be a marked function of the ligand employed; triphenylphosphite appeared to be one of the favorable ones. The results of the reaction using deuterium in place of hydrogen gave suggestive information about the reaction mechanism.

In chapter 2, aroyl chlorides were found to react with terminal alkynes accompanied by decarbonylation in the presence of a catalytic amount of $[RhCl(cod)]_2$ and PPh_3 to give the corresponding vinyl chloride derivatives regio- and stereo-selectively in good yields. The catalyst efficiency was a marked function of the ratio of PPh_3 to the rhodium species; satisfactory results were obtained by employing a PPh_3/Rh ratio of 1.0. The reaction may involve chlororhodation to the alkynes by intermediary arylchlororhodium(III) species generated *in situ* followed by reductive elimination of the products, which are suggested by the results of some control experiments. In contrast to the reaction with terminal alkynes, that with some internal ones proceeded without decarbonylation to produce 2,3-disubstituted-1-indenones as the predominant products. The product structures suggested that, while the arylchlororhodium intermediate is also involved, arylrhodation to the alkynes, reinsertion of CO (coordinated to the metal), and intramolecular cyclization sequentially take place to give the indenones. Moreover, internal alkynes was

observed to effectively undergo aroylarylation, that is 1,2-addition of aroyl and aryl groups, on treatment with aroyl chlorides in the presence of a catalytic amount of $[RhCl(cod)]_2$ and PPh_3 using hexamethyldisilane as a reducing agent to produce the corresponding 1,3-diaryl-2-propen-1-one derivatives in good yields. The reaction could also proceed using relatively reactive alkenes such as norbornenes in place of the alkynes. Similar treatment of a terminal alkyne, phenylacetylene, with aroyl chlorides brought about aroylsilylation to give 1-aryl-2-phenyl-3-trimethylsilyl-2-propene-1-ones.

In chapter 3, salicylaldehydes were found to smoothly and efficiently react with both internal and terminal alkynes accompanied by cleavage of the aldehyde C-H bond by using a rhodium-based catalyst system of $[RhCl(cod)]_2$ / dppf / Na_2CO_3 to give the corresponding 2-alkenoylphenols in good to excellent yields. The regioselectivity in the reaction appeared to depend on the structure of alkynes.

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