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Rhodium-catalyzed reaction of aroyl chlorides with alkynes or alkenes in the presence of disilanes

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

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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Abstract

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 reducing agent to produce the corresponding 1,3-diaryl-2-propen-1-one derivatives in good yields. The reaction can also proceed using relatively reactive alkenes such as norbornenes in place of the alkynes. Similar treatment of a terminal alkyne, phenylacetylene, with aroyl chlorides brings about aroylsilylation to give 1-aryl-2-phenyl-3-trimethylsilyl-2-propene-1-ones. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium catalyst; Aroyl chrolides; Alkynes; Alkenes; Disilanes

1. Introduction

Aroyl chlorides are known to smoothly react with low-valent transition-metal species, including rhodium and palladium complexes, to produce aroylmetal complexes which may be further transformed into arylmetal complexes by decarbonylation [1]. Thus, palladium-catalyzed aroylation of alkenes [2] and alkynes [3] and arylation of alkenes [4] and dienes [5] with aroyl chlorides, which involve the complexes as the key intermediates, have been successfully developed. While such reactions using rhodium species have been so far unexplored, they may be expected to be realized. Indeed, we found that aroyl chlorides smoothly react with terminal alkynes accompanied by decarbonylation in the presence of catalytic amounts of $[RhCl(cod)]_2$ and PPh_3 to give the corresponding chloroarylation products regio- and stereo-selectively in good yields, and with internal alkynes 2,3-disubstituted-1-indenones can also be obtained (Scheme 1) [6].

On the other hand, hydrosilanes [7] or disilanes [8] 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]. We herein report our new findings that by addition of hexamethyldisilane to the reaction using internal alkynes in Scheme 1 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 (Scheme 2), and with a terminal alkyne phenylacetylene, aroylsilylation also occurs [9].

2. Results and discussion

The reaction of benzoyl chloride (**1a**) (4 mmol) with 4-octyne (**2a**) (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 xylene at 120°C for 20 h under nitrogen

* Corresponding author. Tel.: +81 6 8797361; fax: +81 6 8797362.

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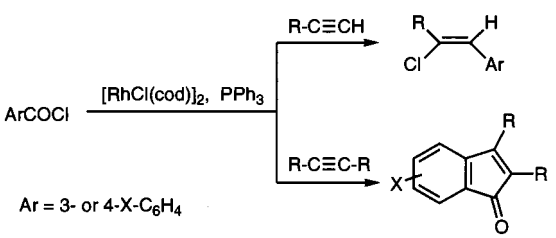
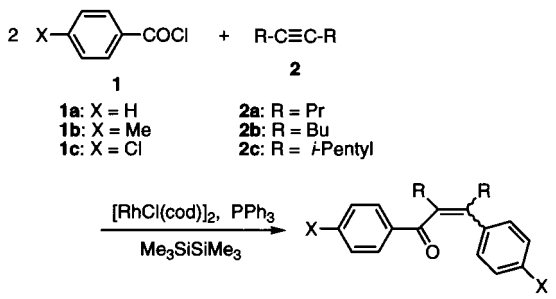
(Table 1). Without using the ligand 1,3-diphenyl-2-propyl-2-hexen-1-one (**3**) was obtained as the cross-coupling product in a yield of 16% (based on the amount of **2a** used) together with a trace amount of benzophenone (**4**) and biphenyl (**5**) (30%) (entry 1). Addition of PPh_3 up to 2 equivalent of Rh increased the yield of **3** 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** and the disilane to 6 mmol afforded 64% yield of **3**. 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 **3** was considerably decreased. It is noted that in each entry, (a) the product **3** was a mixture of two possible stereoisomers, forming 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, was $< 5\%$.

The results of the reaction of **1a** and **2a** using a number of reducing agents are recorded in Table 2. When dichlorotetramethyldisilane was employed in place of hexamethyldisilane, **3** was still produced in a yield of 53%, whereas hexaphenyldisilane, 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.

Table 3 summarizes the results for a number of reactions of aroyl chlorides with internal alkynes as well as alkenes. The reactions of 4-methyl- (**1b**) and 4-chlorobenzoyl chlorides (**1c**) with **2a** gave the corresponding compounds **6** and **7**, as did that of **1a**. Qualitative analysis of the reactions of **1a–c** with **2a** by GLC indicated that the rate of consumption of **1a–c** decreased in the order of **1c** > **1a** > **1b**. 5-Decyne (**2b**) and 2,9-dimethyl-5-decyne (**2c**) reacted with **1a** to give the corresponding unsaturated ketones **8** and **9**, respectively. All these products **3** and **6–9** were produced as mixtures of the corresponding (*Z*) and (*E*) isomers, and the (*Z*) isomers were the major ones. Note that the configuration of the products was determined by their ^{1}H-NMR spectra with the aid of NOE measurements. The following data for (*Z*)- and (*E*)-**6** are the representatives.

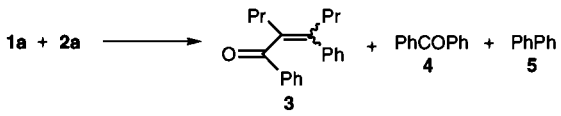


Scheme 1.



Scheme 2.

Table 1
Reaction of **1a** with **2a** in the presence of hecamethyldisilane[a]



Entry	Ligand/mmol	Solvent	Yield (%)[b]		
			3 (*Z*)/(*E*)	**4**	**5**
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**]:[**2a**]:[$Me_3SiSiMe_3$] = 4:2:4 (in mmol).
[b] [(mmol of product/2) × 100]. Determined by GLC.
[c] [**1a**]:[**2a**]:[$Me_3SiSiMe_3$] = 6:2:6 (in mmol).
[d] 1,1,2,2-Tetracholorethane.

Table 2
Aroylarylation of **1a** with **2a** in the presence of various reducing agents[a]

Entry	Reducing agent	% Yield of **3** (*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**]:[**2a**]:[Reducing agent] = 0.01:0.04:6:2:6 (in mmol).

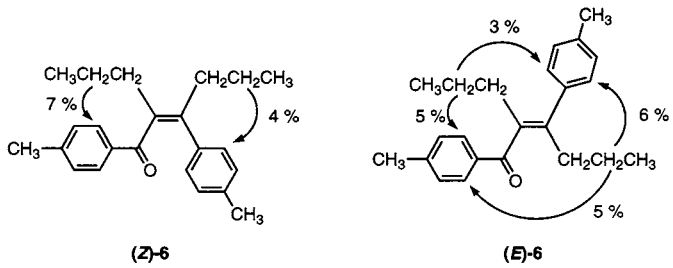
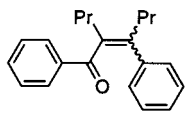
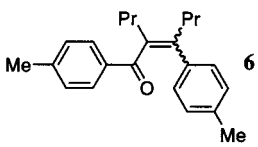
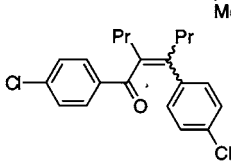
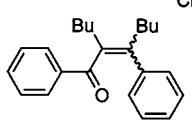
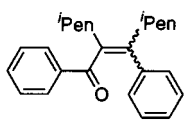
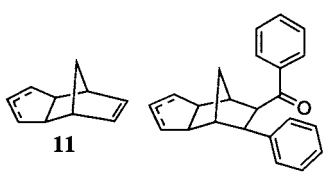
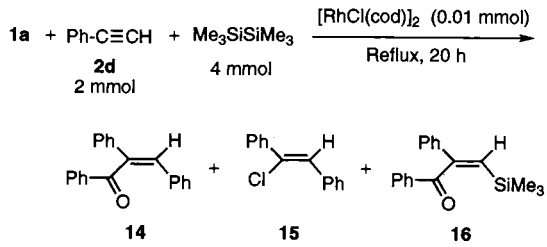


Table 3
Aroylarylation of **1** with **2**, **10** and **11** in the presence of hexamethyldisilane[a]

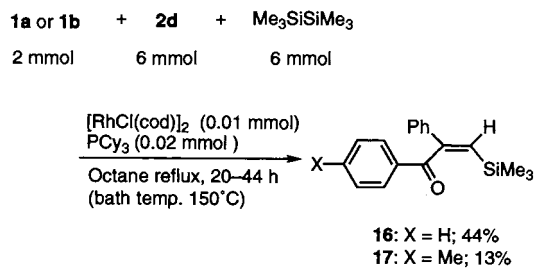
Substrates		Product, % yield[b]		(*Z*)/(*E*)
1	**2**			
1a	**2a**		**3** 83(73)	89/11
1b	**2a**		**6** 46[c]	79/21
1c	**2a**		**7** 86(76)[d]	68/32
1a	**2b**		**8** 70(50)[c]	86/14
1a	**2c**		**9** 54(51)	78/22
1a	**10**		**12** 64(61)[e]	
1a	**11**		**13** 60(58)[e,f]	

[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.



1a (mmol)	Ligand / mmol	Solvent / bath temp.	Yield (%) **14**	**15**	**16**
2	PPh_3 / 0.02	TCE / 140°C	0	11	5
4	PCy_3 / 0.04	Octane / 150°C	16	6	19

Scheme 3.



Scheme 4.

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 (**10**) and dicyclopentadiene (**11**) also gave aroylarylation products **12** and **13**, respectively. ^{1}H-NMR spectra of them suggested that both benzoyl and phenyl groups were introduced in the *exo*-positions (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), while the product **13** 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 **2a** did not give any cross-coupling products, only giving **4** (32%) and **5** (21%).

In the reaction of **1a** with 1-octyne as a terminal alkyne in the presence of hexamethyldisilane under the present conditions, (*Z*)-2-chloro-1-phenyl-1-octene 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 (**2d**) using PPh_3 as ligand in TCE at 140°C gave also no benzoylphenylation product, but (*Z*)-1,2-diphenyl-3-trimethylsilyl-2-propenone (**16**) (5%), which may be regarded as a benzoylsilylation product, was obtained along with (*Z*)-1-chloro-1,2-diphenylethene

(**15**) (11%) (Scheme 3). Treatment of **1a** with **2d** using tricyclohexylphosphine as ligand in refluxing octane was found to induce benzoylphenylation to produce compound **14** (16%) together with **15** (6%) and **16** (19%). In the reactions of **1a** and **1b** (2 mmol) with an excess amount of **2d** (6 mmol), **16** and **17** were obtained as the major products (Scheme 4).

Based on the observed results, a possible reaction mechanism for the present aroylarylation reaction with aroyl chloride **1** is illustrated in Scheme 5 using internal alkyne **2** as substrate. For the addition of both aroyl and aryl groups to **2**, it would involve two-fold oxidative additions of **1** to the metal center. Although the transformation of Rh(I) to Rh(III) by oxidative addition is very common, Rh(III) species does not seem to undergo further oxidative addition 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 ([1]b) [10]. However, the second CO seems to be capable of being replaced by alkyne **2** [6]. 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 [7]. 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 aroylrhodation to the coordinated alkyne in **C** is unlikely involved [6].

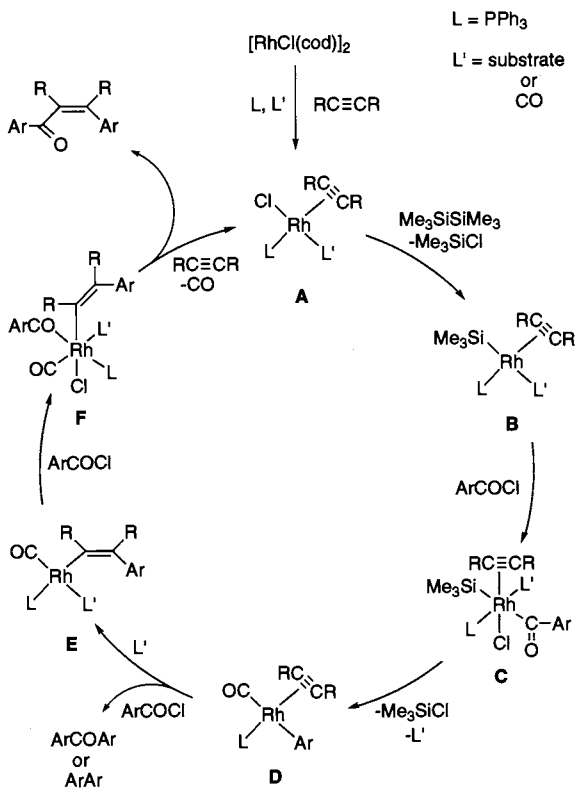
Formation of the benzoylsilylation products **16** and **17** may be explained by considering the mechanism involving silylrhodation in the intermediate **B** followed by oxidative addition of **1**. It is noted that the regioselectivity in the aroylsilylation is consistent with that observed in the rhodium-catalyzed silylformylation reactions of terminal alkynes [11]. The results shown in Schemes 3 and 4 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.

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. GLC analysis was carried out using a silicone OV-17 glass column (ϕ 2.6 mm × 1.5 m) or a CBP-1 capillary column (ϕ 0.5 mm × 25 m). The following experimental details given below may be regarded as typical in methodology and scale.

*3.1. Reaction of benzoyl chloride (**1a**) with 4-octyne (**2a**)*

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), **2a** (220 mg, 2 mmol), hexamethyldisilane (876 mg, 6 mmol), and 1-methylnaphthalene (ca. 100 mg) as internal standard in 1,1,2,2-tetrachloroethane (5 ml) and the resulting mixture was stirred at 120°C for 20 h. GLC and GLC-MS analyses of the mixture confirmed formation of 1,3-diphenyl-2-propyl-2-hexen-1-one (**3**) (485 mg, 83%, $(Z)/(E) = 89:11$), benzophenone (**4**) (69



Scheme 5.

mg, 19%), and biphenyl (**5**) (77 mg, 25%). Product **3** (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 3 afforded its (*Z*)- and (*E*)-isomers having $>90\%$ content.

3.2. Products

Compounds **14** [12], **15** [6], and **16** [13] are known and were compared with those authentic specimens. The analytical data of other products **3**, **6–9**, **12**, **13**, and **17** are as follows. The purity of these compounds was judged to be $>95\%$ by GC and/or ^{1}H- and ^{13}C-NMR analyses.

1,3-Diphenyl-2-propyl-2-hexen-1-one (**3**): (*Z*)-isomer; oil; ^{1}H-NMR (400 MHz) δ 0.92 (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, ^{1}H, $J=7.3$ 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; ^{1}H-NMR (400 MHz) δ 0.66 (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 (**6**): (*Z*)-isomer; oil; ^{1}H-NMR (400 MHz) δ 0.91 (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 (**7**): 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 (**8**): 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 (**9**): 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 (**12**): white solid; m.p. 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[5.2.1.02, 6]dec-3-enes (**13**): white solid; m.p. 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 (**17**): 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.

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