Carbonylation of alkyltitanium compounds with allylic derivatives

Yasushi Tsuji * and Tetsuya Ishii

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11 (Japan)

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Abstract

Triisopropoxymethyltitanium (**1a**) or diisopropoxydimethyltitanium (**1b**) was treated with carbon monoxide (1 atm, balloon) at room temperature overnight (16–18 h), and then the reaction mixture was added to various allyl derivatives in the presence of palladium catalyst (5 mol% based on the allylic derivatives) at room temperature. From **1b** and cinnamyl acetate in the presence of tetrakis(triphenyl-phosphine)palladium, (*E*)-3,3-dimethyl-6-phenyl-5-hexen-2-one (**5a**) was afforded in 57% yield. A similar reaction with *trans*-2-hexenyl acetate also gave the corresponding γ,δ-unsaturated ketone in 57% yield. The formation of the products would be rationalized by titanium η^2-acyl and oxicarbenoid intermediates.

Introduction

Carbon monoxide can react with a wide variety of species including carbocations, radicals, and anions. In the Koch reaction [1], the mechanism [2] involves an attack of carbocation on carbon monoxide to give an acyl cation. The Gatterman–Koch reaction [3], formylation with carbon monoxide and HCl, utilizes formyl cations provided by protonations of carbon monoxide. Moreover, the reaction of carbon radicals with carbon monoxide affords acyl radicals, realizing free-radical promoted carbonylation [4].
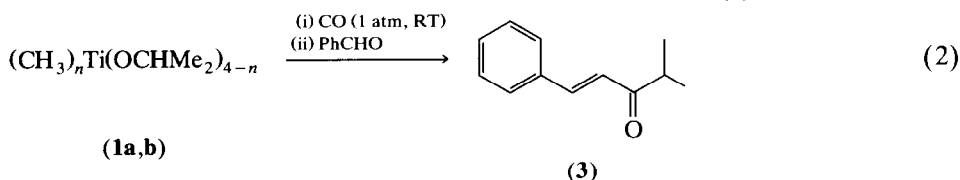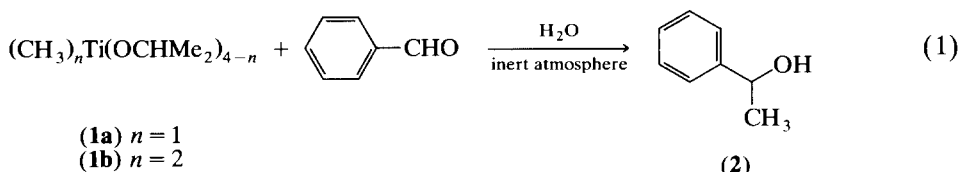
Another important class of the reaction is nucleophilic attack on carbon monoxide, since it affords a synthetically useful nucleophilic acyl anion [5]. Lithium reagents were widely used in this transformation [6]. These lithium reactions require carefully controlled reaction conditions (temperature below − 100°C) [6a–f] or introduction of a silyl substituent on the lithium reagents [6g,h].

On the other hand, recently a variety of alkyltitanium compounds have been devised and proved to be potent alkylating reagents [7]. We are interested in the reactivities of titanium compounds as nucleophiles towards carbon monoxide. The titanium metal center has vacant *d* orbitals and will have stronger interaction with carbon monoxide compared with alkyllithium and Grignard reagents. Thus, in this paper, alkyl titanium compounds are carbonylated, followed by reaction with electrophiles such as aldehyde or allyl derivatives/palladium catalyst system.

Results

Reaction of carbonylated methyl titanium compounds with aldehyde

Reetz *et al.* reported that aldehydes are alkylated with alkyl titanium compounds as shown by eq. 1 [7]. We carried out this reaction under a carbon monoxide atmosphere (eq. 2). First, triisopropoxymethyltitanium (**1a**) or diisopropoxydimethyltitanium (**1b**) was treated with carbon monoxide (1 atm, balloon) at room temperature overnight (16–18 h), and then benzaldehyde was added to the reaction mixture. As distinct from the reaction under an inert atmosphere (N_2 or Ar; eq. 1) [7], the simply alkylated product (**2**) was not detected at all. Furthermore, the acetylated product ($CH_3C(O)CH(OH)C_6H_5$) afforded by nucleophilic attack of the acetyl anion was not obtained either. Instead, α,β-unsaturated ketone (**3**) was isolated from the reaction mixture (eq. 2). Yield of **3** was low (8%) and all attempts to increase it have proved unsuccessful. However, careful GLC analysis (OV-17, 3 mm × 3 m, programmed from 120 to 270°C by 10°C/min, N_2 40 mL/min) revealed that **3** is the only major product among the volatile substances with high (> 90%) conversions of benzaldehyde. The product (**3**) was isolated in pure form and all the spectral data (see the Experimental section) are fully consistent with this structure, showing that the isopropyl unit which originates in the isopropoxyl functionality on titanium was incorporated into the product. Since this is an atypical and unprecedented (albeit in low yield) carbonylation, further elaborations with another electrophile were made.

$$(CH_3)_nTi(OCHMe_2)_{4-n} + \text{PhCHO} \xrightarrow[\text{inert atmosphere}]{H_2O} \text{Ph-CH(OH)-CH}_3 \qquad (1)$$

(**1a**) $n = 1$
(**1b**) $n = 2$

(**2**)

$$(CH_3)_nTi(OCHMe_2)_{4-n} \xrightarrow[\text{(ii) PhCHO}]{\text{(i) CO (1 atm, RT)}} \qquad (2)$$

(**1a,b**)

(**3**)

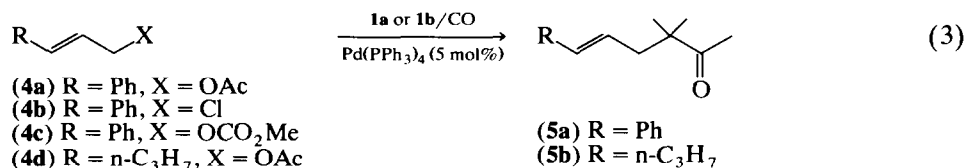*Reaction of carbonylated methyl titanium compounds with allylic derivatives in the presence of palladium catalyst*

Extensive studies have been made on the π-allyl transition metal complexes [9], since they are often key intermediates in various homogeneous catalytic reactions [10]. In particular, palladium catalyzed allylations with allylic derivatives, typically allylic acetates, have been successfully applied to synthetic organic chemistry [11]. We employed the allylic derivatives/palladium catalyst system as electrophile in the reaction of the carbonylated titanium compounds (eq. 3). First **1a** or **1b** was treated with carbon monoxide (1 atm, balloon) at room temperature overnight (16–18 h), and then the reaction mixture was added to the allylic derivative in the presence of Pd(PPh$_3$)$_4$. The palladium complex was used in a catalytic amount (5 mol% based on allylic acetate). The results are listed in Table 1. When cinnamyl acetate (**4a**) was employed, γ,δ-unsaturated ketone (**5a**) was obtained as the

Table 1
Reaction of carbonylated methyl titanium compounds with allylic derivatives [a]

Run	Titanium compound	Allylic derivatives	Solvent	Time (h) [b]	Converted (%)	Yield (%) [c]
1	**1a**	**4a**	THF	27	100	31
2	**1a**	**4a**	Toluene	24	100	39
3	**1a**	**4b**	THF	47	62	20
4	**1a**	**4b**	Toluene	95	35	14
5	**1a**	**4c**	THF	6	100	8
6	**1a**	**4d**	Toluene	2	–	16
7	**1b**	**4a**	THF	24	100	48
8	**1b**	**4a**	Toluene	48	100	57
9	**1b**	**4b**	THF	28	68	38
10	**1b**	**4b**	Toluene	25	100	47
11	**1b**	**4c**	THF	2	100	0
12 [d]	**1b**	**4d**	THF	48	100	41
13 [d]	**1b**	**4d**	Toluene	24	100	57

[a] **1** (2.0 mmol), **4** (1.0 mmol), Pd(PPh$_3$)$_4$ (0.05 mmol), CO (1 atm, balloon), solvent (3.8 ml for **1a** and 4.0 ml for **1b**). [b] Reaction time for the reaction with allylic derivatives (**4**). [c] By GLC. [d] **1b** (1.0 mmol).

product in 39% yield from **1a** (run 2) and in 57% yield from **1b** (run 8), respectively. *trans*-2-Hexenyl acetate (**4d**) also affords the corresponding unsaturated ketone (**5b**) in 41 and 57% yields (runs 12, 13). The structures of the product (**5**) were confirmed conclusively by spectral data (^{1}H, ^{13}C NMR, IR, MS (HR, CI), see Experimental section). The isopropylidene unit which originates in the isopropoxyl functionality on titanium is incorporated into the products. Thus, the present procedure realizes the direct introduction of the 1,1-dimethyl-2-oxopropyl moiety [12] via the carbonylation/isopropylidene transfer sequence.

$$ R\diagdown\diagup\diagdown X \xrightarrow[\text{Pd(PPh}_3)_4 \text{ (5 mol\%)}]{\text{1a or 1b/CO}} R\diagdown\diagup\diagdown\diagup\diagdown \overset{O}{\underset{}{}} \qquad (3) $$

(**4a**) R = Ph, X = OAc
(**4b**) R = Ph, X = Cl
(**4c**) R = Ph, X = OCO$_2$Me
(**4d**) R = n-C$_3$H$_7$, X = OAc

(**5a**) R = Ph
(**5b**) R = n-C$_3$H$_7$

The reaction can be carried out in toluene or THF (Table 1). However, other solvents such as dioxane, CH$_2$Cl$_2$, DMF were less favorable. The leaving groups (−X, eq. 3) of the allylic derivatives have a significant effect. Allylic chloride (**4b**) was less effective (runs 3, 4, 9, 10). Allylic carbonate (**4c**) [13] was mostly decarboxylated to the corresponding ether by the catalysis of the palladium complex prior to the reaction with the carbonylated titanium species.

The catalytic activities of several transition metal catalyst precursors were examined (Table 2). Palladium and platinum complexes showed some catalytic activities. However, other rhodium or ruthenium complexes showed almost no catalytic activities.

Carbonylation of other titanium compounds was attempted. Titanium(IV) compounds such as MeTiCl$_3$ [14], MeTi(NEt$_2$)$_3$ [15], PhTi(O^{i}Pr)$_3$ [16], ^{t}BuTi(O^{i}Pr)$_3$, MeTi(OEt)$_3$ provided almost no carbonylated products in the two reactions (eqs. 2 and 3), judging from FT–IR analysis. Titanium -ate complexes [17] such as

Table 2
Effect of catalyst precursor [a]

Run	Catalyst precursor	Time [b]	Yield (%) [c]
2	$Pd(PPh_3)_4$	24	39
14	$Pd(dppe)_2$	48	15
15	$PdCl_2(PPh_3)_4$	26	18
16	$Pd(CO)(PPh_3)_3$	26	19
17	$Pt(PPh_3)_4$	23	30
18	$PtCl_2(PPh_3)_2$	23	2
19	$PtHCl(PPh_3)_2$	7	7
20	$RhCl(PPh_3)_3$	74	0
21	$RhH(CO)(PPh_3)_3$	24	0
22	$RuCl_2(PPh_3)_3$	24	Trace
23	$RuH_2(PPh_3)_3$	27	0

[a] Under the same reaction conditions as in Table 1 with **1a** (2.0 mmol) and **4a** (1.0 mmol) in toluene.
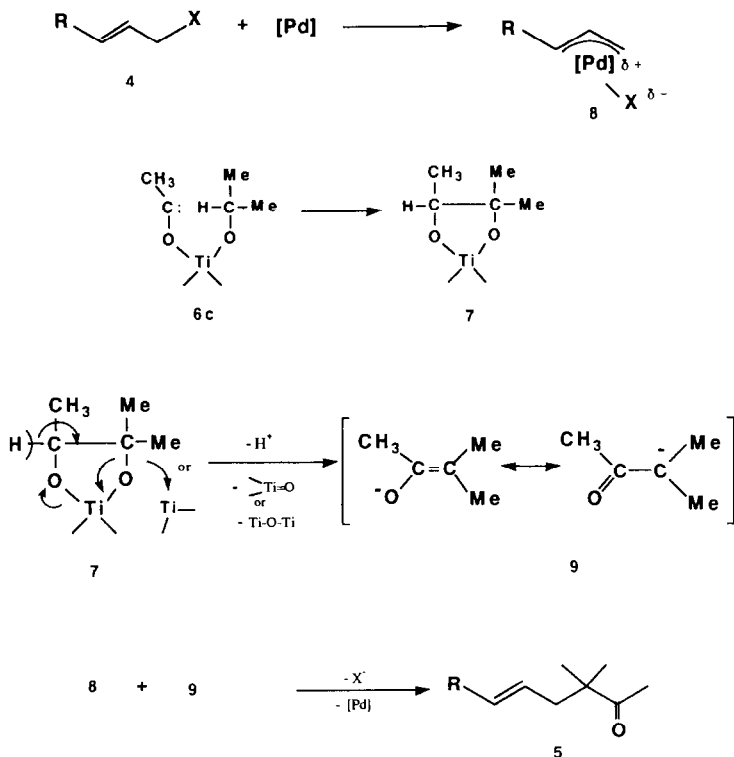[b] The reaction time for the reaction with **4a**. [c] Yield of **5a** determined by GLC.

$MeTi(O^iPr)_4Li$ and $MeTi(O^iPr)_4MgBr$ afforded some unidentified carbonylated products (including **3** or **5**), but in quite low yields.

Discussion

Carbonylation of the carbon–titanium bond has been extensively studied [18]. The resulting acyl complex can be formulated by three structures, i.e., η^1-acyl (**6a**), η^2-acyl (**6b**), and oxycarbenoid (**6c**) (eq. 4). Floriani et al. carried out carbonylation of the methyl–titanium bond using dicyclopentadienylmethylhalotitanium(IV), $(\pi$-$C_5H_5)_2Ti(X)$–CH_3, to give the corresponding acetyl complex, $(\pi$-$C_5H_5)_2Ti(X)$–$(COCH_3)$ [19]. X-Ray analysis of this product showed that the structure is regarded as the η^2-acyl (**6b**) [20].
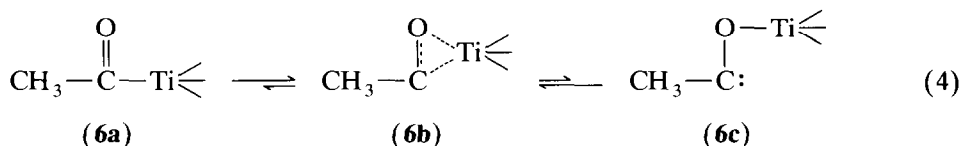
The reaction of **1a** with carbon monoxide was carried out in an NMR tube (5 mm in diameter, toluene-d_8) and characterized by ^{13}C NMR spectroscopy. The overnight reaction at room temperature under a carbon monoxide atmosphere (1 atm) gave a very clean spectrum. The Me–Ti resonance of **1a** (δ 41.19 ppm; lit. 42.9 ppm [21]) disappeared completely and a new resonance appeared at 26.47 ppm, while other resonances remained at almost the same field (O–CH; shifted from δ 76.88 ppm to 76.86 ppm, $-CHMe_2$ from δ 26.40 ppm to 27.17 ppm). No other new resonances appeared. However, as for the carbonyl carbon resonance, even by careful measurement at $-90°C$ to 40°C, no distinct resonances appeared in the carbonyl and carbenoid carbon region (δ 150–500 ppm). Meantime, FT-IR spectra of the same reaction mixture (in toluene, or also in THF) invariably show a distinct absorption at 1625 cm^{-1}. This absorption is close to those of η^2-acyl $Cp_2TiCl(COCH_3)$ at 1620 cm^{-1} [20], $[Cp_2Ti(COCH_3)(NCMe)]BPh_4$ at 1630 cm^{-1}, and $[Cp_2Ti(COCH_3)(PMe_2Ph)]BPh_4$ [18e] at 1610 cm^{-1}. Thus, taking account of

R⌒⌒X + [Pd] ⟶ R⌒⌒[Pd]δ+ ⟍X δ-

4　　　　　　　　　　　　8

CH₃ Me　　　　　　　CH₃ Me
C: H–C–Me ⟶ H–C——C–Me
O　O　　　　　　　O　O
 ⟍Ti/　　　　　　　 ⟍Ti/

6c　　　　　　　　　7

CH₃ Me　　　　　　　　　　　CH₃　　Me　　CH₃　　Me
H–C——C–Me　–H·　　　[C=C　　↔　　C–C·]
O　O　or　　　　　-O　　Me　　O　　Me
 Ti/ Ti——　- Ti=O
 　　　　　or
 　　　　- Ti-O-Ti

7　　　　　　　　　　　　　　　9

8 + 9 ——–X⁻→ R⌒⌒⨯⨯C(O)
　　　　　–[Pd]

5

Scheme 1.

the oxophilicity of titanium, the η^2-acyl species (6b) will be the product in the reaction of 1 with carbon monoxide, although full characterization has not been completed.

The reaction mechanism of the present carbonylations is not clear. However, formation of product 5 in the reaction with the allylic derivatives (eq. 3) might be rationalized by Scheme 1. The π-allyl palladium complex (8) is generated from the allylic derivatives (4) and the palladium catalyst [9]. It is well known that for some acyl complexes of early transition metals and actinides, the contribution of the oxycarbenoid (6c) has greater importance [22,23]. In the present reactions, a small amount of the oxycarbenoid species (6c) might be in equilibrium with the η^2-acyl species (6b). An intramolecular insertion of the carbenoid carbon [24] to the δ-CH bond might afford the five-membered titanacycle (7), and deprotonation of 7 followed by extrusion of titanium oxide could provide the enolate form of the α-acetyl anion (9). A similar titanacycle (2-titana-1,3-dioxolane derivative) containing two cyclopentadiene ligands has been isolated and fully characterized along with a preliminary X-ray analysis [25]. Nucleophilic attack of 9 onto cationic π-allyl species will finally afford the product 5. We could not detect any ^{13}C resonances assignable to 7 and 9. The lifetimes of 7 and 9 must be short. These intermediates might be generated within the coordination sphere of palladium. There might be some possibility that anion 9 is derived from 3-methyl-2-butanone (10). However, careful analysis (GC and FT-IR) indicated that no 10 was formed during the

course of the reactions. Furthermore, addition of **10** (0.5–2.0 equiv.) did not change the yields at all, indicating that intermediacy of **10** is not operative in the present reactions.

Experimental

Material

The reagents employed in this study were dried and purified before use by the usual procedures [26]. Carbon monoxide (> 99.9%) was used without further purification. ClTi(O^{i}Pr)$_3$ [16b], Cl$_2$Ti(O^{i}Pr)$_2$ [16b], ClTi(OEt)$_3$ [16b], MeTi(O^{i}Pr)$_3$ (**1a**) [16b], Me$_2$Ti(O^{i}Pr)$_2$ (**1b**) [16b] and ClTi(NEt$_2$)$_3$ [27] were obtained by the literature methods. MeTiCl$_3$, MeTi(NEt$_2$)$_3$, PhTi(O^{i}Pr)$_3$, ^{t}BuTi(O^{i}Pr)$_3$ and MeTi(OEt)$_3$ were prepared with the corresponding alkyl (or phenyl) lithiums and chlorotitanium derivatives *in situ*. MeTi(O^{i}Pr)$_4$Li and MeTi(O^{i}Pr)$_4$MgBr were obtained by the reaction between Ti(O^{i}Pr)$_4$ and the corresponding methyl reagents [17b]. Pd(PPh$_3$)$_4$ [28], PdCl$_2$(PPh$_3$)$_2$ [29], Pd(DBA)$_2$ (DBA = dibenzylideneacetone) [30], Pt(PPh$_3$)$_4$ [31], PtCl$_2$(PPh$_3$)$_2$ [32], RhCl(PPh$_3$)$_3$ [33], RhH(CO)(PPh$_3$)$_3$ [34], RuCl$_2$(PPh$_3$)$_3$ [35] and RuH$_2$(PPh$_3$)$_4$ [36] were prepared by the published methods. Pd(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) was purchased from Aldrich.

Analytical procedure

The products were isolated by Kugelrohr (Büchi) distillation and medium-pressure column chromatography (silica gel, Wako gel 300; hexane / ethyl acetate). The NMR spectra (in CDCl$_3$) were recorded with a JEOL GX-270 spectrometer with Me$_4$Si as an internal standard. FT-IR spectra were measured on a Perkin–Elmer 1640. The mass spectra were recorded with Shimadzu QP-1000 (EI, CI with isobutane) and Shimadzu 9020-DF (HR) equipped with a PAC 1100S computer system. The GLC analysis was made with a Shimadzu GC-8APF equipped with an integrator (C-R6A). The yields of the products were determined by the internal standard methods according to calibration curves.

Carbonylation of 1 with benzaldehyde

A mixture of **1** (6.0 mmol) and the solvent (12 ml) was stirred under a carbon monoxide atmosphere (1 atm, balloon) overnight (16–18 h) at room temperature. Successively into the resulting dark brown solution, benzaldehyde (5.0 mmol) was added dropwise over 2 min under an argon flow. The reaction was further carried out for 4 h under an argon atmosphere. After the reaction, ether (10 ml) and saturated aq. NH$_4$F solution (10 ml) were added to the reaction mixture. The ethereal layer was separated and dried over MgSO$_4$.

Carbonylation of 1 with allylic derivatives (4)

Triisopropoxymethyltitanium (**1a**) was purified by vacuum distillation (47°C, 0.01 mmHg; lit. [16b] 48–53°C, 0.01 mmHg). Diisopropoxydimethyltitanium (**1b**) was prepared *in situ* by the reaction of Cl$_2$Ti(O^{i}Pr)$_2$ with MeLi (1.4 M in ether, Aldrich) in ether at −40°C [16c]. After the reaction all the ether was evaporated off and **1b** was used without further purification. These methyl titanium compounds (**1**) (2.0 or 1.0 mmol; see Table 1) were dissolved in the solvent (1.8 ml for

1a and 2.0 ml for **1b**), and the solution was stirred under carbon monoxide (1 atm, balloon) overnight (16–18 h) at room temperature. Successively the resulting dark brown mixture was added to a mixture of **4** (1.0 mmol), Pd(PPh$_3$)$_4$ (0.05 mmol), and solvent (2.0 ml) over 2 min at room temperature under an argon flow. The reaction was further carried out under an argon atmosphere for 24 h. After the reaction, ether (10 ml) and saturated aq. NH$_4$F solution (10 ml) were added to the reaction mixture. The ethereal layer was separated and dried over MgSO$_4$.

(E)-2-Methyl-5-phenyl-4-penten-3-one (3)

Kugelrohr distillation: pot temperature 130°C, 15 mmHg. ^{13}C NMR (CDCl$_3$): δ 18.4 (q, CH(CH$_3$)$_2$), 39.2 (d, CH(CH$_3$)$_2$), 124.6 (d, Ph, 4), 128.2 (d, Ph, 2, 6), 128.8 (d, Ph, 3, 5), 130.1 (d, –CH=), 134.9 (s, Ph, 1), 142.2 (d, –CH=), 203.2 (s, C=O) ppm. ^{1}H NMR (CDCl$_3$): δ 1.18 (d, 6H, CH(CH$_3$)$_2$), 2.92 (hep, 1H, CH(CH$_3$)$_2$, 6.81 (d, $J = 16$ Hz, 1H, –CH=), 7.3–7.5 (m, 5H, Ph), 7.60 (d, $J = 16$ Hz, 1H, –CH=) ppm. IR (neat): ν(CO) 1680 cm^{-1}. MS: (EI) m/e 174 (M^+, CI, isobutane), 175 (MH$^+$).

(E)-3,3-Dimethyl-6-phenyl-5-hexen-2-one (5a)

Kugelrohr distillation: pot temperature 40°C, 1 mmHg. ^{13}C NMR (CDCl$_3$): δ 24.3 (q, C(CH$_3$)$_2$), 25.4 (q, COCH$_3$), 43.0 (t, =CHCH$_2$), 48.1 (s, C(CH$_3$)$_2$), 125.8 (d, –CH=), 126.1 (d, Ph, 2, 6), 127.2 (d, Ph, 4), 128.4 (d, Ph, 3, 5), 130.0 (d, =CH–), 137.3 (s, Ph, 1), 213.2 (s, C=O) ppm. ^{1}H NMR (CDCl$_3$): δ 1.17 (s, 6H, C(CH$_3$)$_2$), 2.15 (s, 3H, COCH$_3$), 2.40 (d, 2H, =CHCH$_2$), 6.09 (dt, $J = 16$ Hz, 7 Hz, 1H, =CHCH$_2$), 6.40 (d, $J = 16$ Hz, 1H, PhCH=), 7.2–7.35 (m, 5H, Ph) ppm. IR (neat): ν(CO) 1702 cm^{-1}. MS: (HR) m/e 202.13119 (M^+), 202.13568 calc. for C$_{14}$H$_{18}$O (CI, isobutane), 203 (MH$^+$).

(E)-3,3-Dimethyl-5-nonen-2-one (5b)

Kugelrohr distillation: pot temperature 90°C, 40 mmHg. ^{13}C NMR (CDCl$_3$): δ 13.6 (q, CH$_3$CH$_2$), 22.6 (t, CH$_3$CH$_2$), 24.1 (q, C(CH$_3$)$_2$), 25.3 (q, COCH$_3$), 34.7 (t, CH$_2$CH=), 42.9 (t, CH$_2$C(CH$_3$)$_2$), 48.0 (s, C(CH$_3$)$_2$), 125.3 (d, =CH–), 134.1 (d, =CH–), 213.5 (s, C=O) ppm. ^{1}H NMR (CDCl$_3$): δ 0.87 (t, 3H, CH$_3$CH$_2$), 1.10 (s, 6H, C(CH$_3$)$_2$), 1.36 (hex, 2H, CH$_3$CH$_2$), 1.96 (qua, 2H, CH$_2$CH$_2$CH=), 2.11 (s, 3H, COCH$_3$), 2.19 (d, 2H, =CHCH$_2$C(CH$_3$)$_2$), 5.27 (dt, $J = 15$ Hz, 6 Hz, –CH=), 5.44 (dt, $J = 15$ Hz, 6 Hz, –CH$_2$=) ppm. IR (neat): ν(CO) 1707 cm^{-1}. MS: (EI) m/e 153 ($M - 15$), (CI, isobutane) 169 (MH$^+$).

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