cyanocyclopropane-substituted acrylate and methacrylate compounds were polymerized radically to obtain the polymers with multicyano functions. Monomer **3b** was more reactive than **3a** toward free radical initiators and monomer **3b** polymerized readily in high conversion. The resulting substituted polyacrylate **4a** was soluble in acetone but was not soluble in chloroform or diethyl ether. However, tetracyao-substituted polymethacrylate **4b** was not soluble in common solvents. The T_g value of the polymer was around 120℃. Films cast from polymer **4a** solution were brittle, which could be due to the rather low molecular weights, as indicated by the inherent viscosities, and/or to the presence of strong dipoles in the side chain.

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Hydroiminoacylation of α,ω-diene with Aldimine by Rh(I) and Isomerization of the Terminal Olefin to the Internal Olefin

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Catalytic iminohydroacylation has been achieved by the reaction of aldimine **1** and 1,5-hexadiene (**2a**) with Wilkinson's complex as catalyst. Compounds **7a**, **8a** and **9a** were obtained as final product after hydrolysis of the resulting iminohydroacylation products **4a**, **5a** and **6a**. Depending on the reactant ratio (**2/1**), the ratio of products were changed dramatically : As the **2/1** ratio was increased, **7a** is the major product after hydrolysis while **8a** is the major with an 1/1 ratio of **2/1**. The mechanism of the formation of **5a** is determined by the reaction of **1** and **2b** under the identical reaction conditions. Considering that **5a** may not be formed from the hydroiminoacylation of **14a** since **5b** cannot be formed from that of conjugate diene **14b** generated from isomerization of **2b**, **5a** must be formed from the reaction of **4a** and **10** by addition-elimination mechanism.

Introduction

The activation of the C-H bond by transition metal complexes has received much interest in organometallic chemistry[1]. The C-H bond of aldehyde can be easily cleaved by transition metals such as Wilkinson's complex[2]. Subsequent decarbonylation of the acylmetal hydride and reductive elimination of the resulting alkyl metal hydride gives alkane[3]. This decarbonylation can be prevented by cyclometallation using specially modified substrate such as 8-quinolinecarboxaldehyde, since a five-membered ring is the right size for a stable metallacycle complex[4]. The terminal olefins undergo hydroacylation with 8-quinolinecarboxaldehyde to give alkyl 8-quinolinyl ketone under Rh(I) catalyst. However 8-quinolinyl group used for a hydroacylation tool is hard to be discarded in order to apply for the general ketone synthesis from aldehyde. For this purpose 2-aminopicolinyl group of aldimine **1** has been used for the hydroacylation tool which can be easily discarded by hydrolysis after the reaction[5]. It has been reported that the terminal olefin can be hydroiminoacylated catalytically or stoichiometrically with aldimine **1** on the rhodium(I) complex to give ketimine, which can be hydrolyzed to give corresponding ketone[5a]. Aldimine **1** also had been reacted with conjugate diene stoichiometrically

Table 1. Results in The Catalytic Reaction of 1 and **2a** in a Different Ratio with 10 mol% Wilkinson's Complex (3) at 130℃ 4 h in Benzene and Hydrolysis

Entry	Reactant Ratio		Amount of solv.	Product Ratio			Yield(%)[a]
	1	2		7a	8a	9a	
1	1	1	3.5 ml	0	48	52	29[b]
2	1	2	3.0 ml	31	69[c]	0	43
3	1	4	3.0 ml	67	33	0	39
4	1	8	3.0 ml	75	25	0	55
5	1	24	2.0 ml	85	15	0	60
6	1	73	0 ml	96	4	0	64

[a] Isolated yield after column-chromatography. [b] The ratio of **8a/7a** is 100/0. [c] The ratio of *cis-/trans-isomer* is 15/85, determined by GC-MS[12].

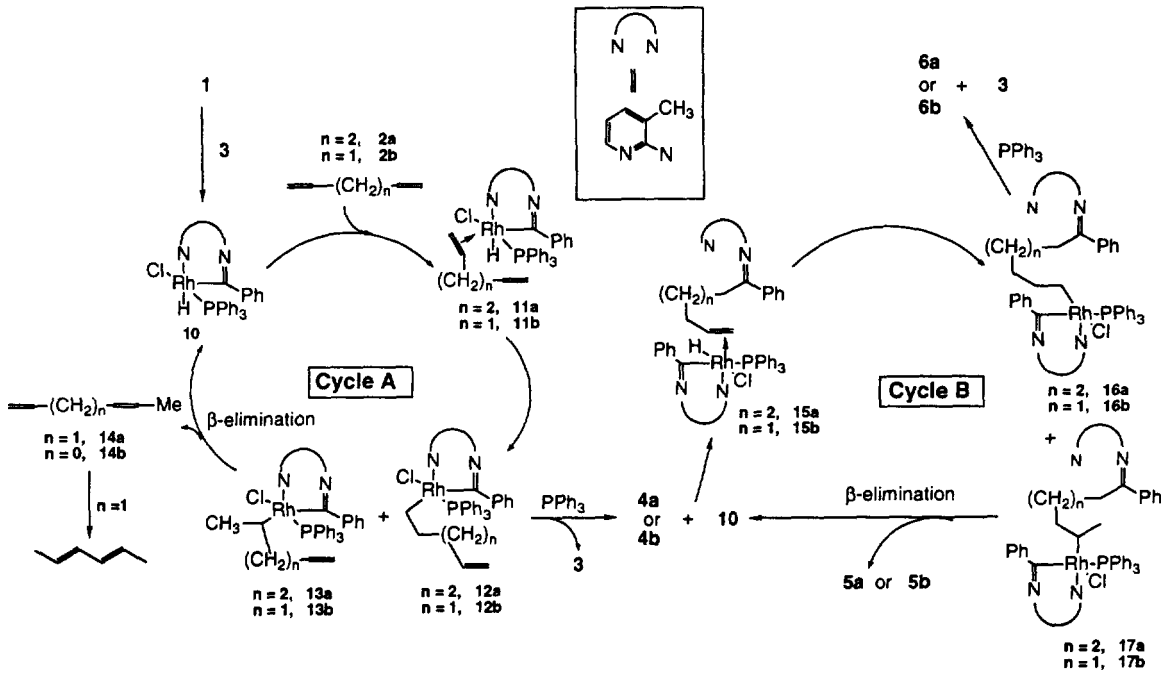
to give the π-allyl rhodium(III) complexes, which was reductive-eliminated to give β,γ-unsaturated ketimine, precursor for β,γ-unsaturated ketone[6]. We already reported that ferrocenecarboxaldehyde could be converted to alkyl acylferrocene by hydroiminoacylation catalytically[7]. This report explains the iminohydroacylation of diene with **1** on Wilkinson's complex as catalyst and the isomerization mechanism of the unreacted terminal olefin to the internal olefin in the resulting ketimine.

Results and Discussion

Aldimine **1** was allowed to react with 1,5-hexadiene (**2a**) in benzene at 130℃ for 4 h under 10 mol% Wilkinson's complex (**3**) as catalyst (the mole ratio of **2a/1** is 1/1). The resulting reaction mixture was treated with 1 N HCl aquous solution and ethyl ether (Eq. (1)). The organic layer was extracted and purified by column-chromatography to give phenyl hex-4-enyl ketone (**8a**) and 1,5-hexadiyl diphenylketone (**9a**) in 29% yield in a 48/52 ratio (Table 1, entry No. 1).

The precursors for **8a** and **9a** must be ketimine **5a** and 1,5-hexadiyl diketimine **6a**, because ketimine is easily hydrolyzed to ketone under the aqueous acidic solution. However large excess use of **2a** did not give any appreciable amount of double hydroacylated compound **9a** but the terminal olefinic ketone **7a** as well as **8a**, the hydrolysis products of **4a** and **5a** (Table 1, entry 2-6). When the ratio of reactants, **2a/1**, was increased, that of the reaction products was changed dramatically. As the ratio of **2a/1** was increased like 2/1, 4/1, 8/1, 24/1, 73/1, the product ratio of the **7a/8a** was also increased as 31/69, 67/33, 75/25, 85/15, 96/4. Large amount use of **2a** compared with that of **1**, make **7a** the major product with high yield in this catalytic reaction.

From the above result the mechanism can be inferred as shown in Scheme 1. The first step must be C-H bond cleavage of the aldimine **1** by the rhodium(I) complex **3** to form the iminoacylrhodium(III) complex **10**, already reported[5a]. One of double bonds in 1,5-hexadiene might coordinate to **10**, to form the complex **11a** as transient intermediate (cycle A). From the intermediate **11a**, two different hydride migrations are possible to form the intermediates **13a** and **12a** according to the Markownikoff's and the anti-Markownikoff's rule, respectively. The secondary alkenyl rhodium(III) complex **13a** undergoes β-elimination to produce the olefin-isomerized product **14a**, 1,4-hexadiene rather than the reductive-elimination product, while the primary alkenyl rhodium (III) complex **12a** does reductive-elimination to give the ketimine **4a**. The secondary alkenyl group in **13a** has better geometry for the β-elimination than the primary alkenyl group in **12a**, since the 2° carbon in **13a** is sterically more conges-

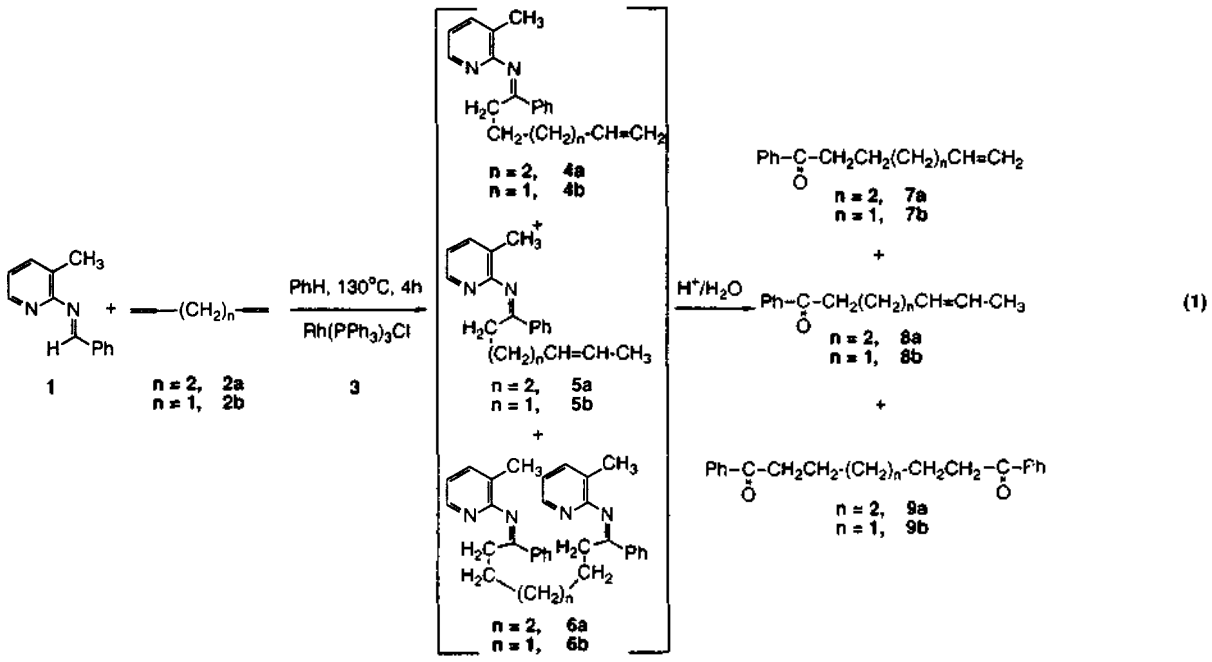


Scheme 1.

Table 2. Results in Catalytic Reaction of Pentadiene and **1** with 10 mol% Wilkinson's Complex and Hydrolysis

Entry	Diene	Diene/**1**	Reaction time	Temp.	Product Ratio				Yield[a]
					7b	**8b**	**9b**	**18**	
1	1,4-pentadiene	1/1	18 h	115℃		87[b]	10	3	20%
2	1,4-pentadiene	29/1	11 h	105℃	96	4			51%
3	1,3-pentadiene[c]	29/1	20 h	100℃		50		50	16%
4	1,3-pentadiene[d]	1/1	22 h	105℃					0%[e]

[a]Isolated yield after column-chromatography. [b]The ratio of *cis-/trans*-isomer is 13/87, determined by GC-MS[12]. [c]a mixture of *cis*- and *trans*-isomers was used[12]. [d]Both *cis*- and *trans*-isomers were used, separately. [e]Trace amount (<1%) of PhCO-CH(CH_3)CH=CH-CH_3 (**19**) was obtained.



(1)

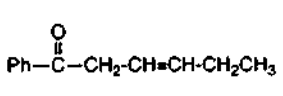
ted and the metal is supposed to be better access to β-hydrogen than that of the 1° carbon in **12a**. Compound **14a** and the further isomerized diene, 2,4-hexadiene, have been determined by ^{1}H-NMR spectra in the reaction mixture after the reaction.

The ketimine **4a** can undergo further reaction with the iminoacyl-rhodium(III) hydride complex **10** (cycle B). The hydrometallation of **4a** with **10** generates the alkyl complexes **16a** and **17a** through an intermediate **15a**. The primary alkyl rhodium(III) complex **16a** undergoes reductive-elimination to give the double iminoacylated product **6a** while the secondary alkyl rhodium(III) complex **17a** does β-elimination to give the olefin-isomerized ketimine **5a** with regeneration of **10**.

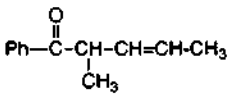
To test the cycle B, the ketimine **4a** was allowed to react with the catalytic amount (5 mol%) of **10** and aldimine **1** (Eq. (1) based on **4a**) at 110℃ for 4 h to give a mixture of **6a** and **5a** in a 9/91 in 61% to confirm that **5a** and **6a** can be produced from the reaction of **4a** and **10**. However still there seems to be two other possible mechanisms to produce **5a**.

One of them is that from the isomerization of **4a** by Rh(I) of **3** *via* π-allyl-hydrido mechansim[9]. With the rhdium(I) complex **3** as catalyst instead of **10**, **4a** did not isomerize to **5a** in an appreciable amount. Only the rhodium(III) hydride **10**, prepared from **1** and **3**, showed the isomerization of **4a** to **5a** efficiently as shown above, that is by addition-elimination mechanism[9]. Therefore the π-allyl hydrido mechanism can be eliminated in the isomerization mechanism.

Another possible way of **5a** formation is through the reaction of **10** and **14a**, already isomerized from **2a**, because the formation of **14a** has been previously measured during the catalytic reaction. To determine this reaction mechanism, 1,4-pentadiene (**2b**) instead of 1,5-hexadiene (**2a**) was applied in this catalytic reaction under identical condition. With an 1/1 ratio of **2b/1** reactants, **8b**, **9b** and phenyl 2-pentenyl ketone **18**, were produced in a 87/10/3 ratio in 20% yield after hydrolysis during which time **2b** has been coverted to 1,3-pentadiene (**14b**) exclusively (Table 2, entry 1). When **1** was reacted with **2b** in a 29/1 ratio (**2b/1**) at 115℃ for 18 h, **7b** and **8b** were obtained in a 96/4 ratio in 51% yield (Table 2, entry 2). The result except the formation of a little amount (3%) of β,γ-unsaturated ketone, phenyl pent-2-enyl ketone (**18**), is very similar to that of the iminohydroacylation of 1,5-hexadiene, which means that both mechanisms must be identical[10].



18



19

To determine whether **5a** is produced from **14a** and **10**, conjugate diene **14b** was applied to the iminohydroacylation. If **5a** is formed from **14** and **10**, **5b** should be also produced by the reaction of **14b** and **10** under the same reaction conditions. The catalytic reaction of **1** and **14b** in an 1/1 ratio with 3 as catalyst (10 mol% based on **1**) did not give appreciable amount of product (Table 2, entry 4), different result from that of the reaction from **1** and **2b**. Instead, a trace amount (<1%) of another kind of β,γ-unsaturated ketone, phenyl pent-3-en-2-yl ketone (**19**) was detected after hydrolysis (note e in Table 2). We can infer that the Rh(I) catalyst turns into the 1,3-dimethyl η^3-allyl rhodium(III) complex during the reaction since it has been reported that **19** can be formed by the ligand-promoted reductive elimination of the 1,3-dimethyl η^3-allyl rhodium(III) complex, prepared from 1,3-pentadiene rhodium(I) chloride and aldimine **1**[6]. This type of β,γ-unsaturated ketone has been synthesized by ligand-promoted reductive elimination of 1,3-dimethyl-η^3-allayl rhodium(III) complex in quinoline system, too[11]. The η^3-allyl rhodium(III) complexes must be too stable to work as catalyst. However when the reaction mixture of **1** and large excess of **14b** (29 eq.) based on **1**) in toluene was heated at 100℃ for 20 h with **3** (10 mol% based on **1**) as catalyst, **18** and **8b** were obtained in an about an 1/1 ratio in 16% yield after hydrolysis (Table 2, entry 3). This result is also different from that of the reaction from **1** and **2b**, indicating that **5b** is not formed from the reaction of **10** and **14b**. From the above result, the reaction mechanism through the reaction of **4a** and **14a** or **4b** and **14b** can be eliminated in producing **5a** and **5b**.

Now we can conclude the mechanism for this catalytic reaction. At the catalytic cycle A in Scheme 1, the rhodium (III) hydride **10** is formed first and the subsequent reaction of **10** with **2a** produces **12a** and **13a**. Whit an 1/1 ratio of **2a/1** as reactants, some of **2a** must be used to produce **14a** with regeneration of **10** and the other part of **2a** must produce **3** and **4a**. Even though there is sufficient **1** that **3** can react, resulting in **10**, there is not enough substrate **2a** that **10** can react, due to transformation of **2a** into **14a**. Therefore **10** can react further with **4a** to produce **6a** and **5a**. With large excess use of **2a** compared with that of **1**, major product is **4a** (Table 1, entry 6). Although the reaction of **10** and **2a** produces a mixture of **14a** and **4a**, the regenerated catalyst **10** does not need to react further with **4a** because of sufficient amount of **2a** to be reacted. So **10** reacts with **2a** to give **4a** until all of **1** is used up. This mechanism also explains the trend of product yields. As a **2a/1** ratio was increased, the yields were also increased (Table 1). The concentration of 2,4-hexadiene is higher in an 1/1 ratio than in a bigger ratio of **2a/1**, since **14a** can be easily converted to 2,4-hexadiene by catalytic isomerization with **10**. Conjugate diene, 2,4-hexadiene, must react with **10** to give the stable η^3-allyl rhodium(III) complex acting as a catalyst poisoning. However since the concentration of 2,4-hexadiene is very small with a bigger **2a/1** ratio, there is not enough chance to form the η^3-allyl rhodium(III) complex, which is hard to work as catalyst.

Other applications of the olefin isomerization are under study.

Experimental

Compound **1** was prepared by published procedure[5a]. Wilkinson's complex, 1,5-hexadiene, piperylene (*cis*- and *trans*-1,3-pentadiene) and 1,4-pentadiene were purchased from Aldrich Chemical Co. and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with either a Bruker AC-200 (200 MHz) or a Varian FT-80A (80 MHz) spectrometer. The chemical shifts (δ) of the ^1H and ^{13}C resonances are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Perkin-Elmer 683 spectrometer. Mass spectra were obtained on Hewlett-Packard HP 5971 A mass spectrometer equipped with a HP 5890 series II Gas Chromatograph. Column-Chromatography was performed on Merck Silica Gel 60.

General Procedure

Iminohydroacylation of diene with aldimine 1 and subsequent hydrolysis of the resulting ketimine. A scew-capped pressure vial is charge with Wilkinson's complex (5.1×10^{-5} M) dissolved in benzene or toluene (3 m*l*) and the solution flushed with nitrogen, and aldimine **1** (5.1×10^{-4} M) added. To the mixture is added the required amount of diene. The reaction vial is kept at the required reaction time and temperature by immersion in a hot oil bath. After reaction is complete, the reaction mixture was put into 5 m*l* of 1 N HCl aq. solution and the hydrolysis product was extracted with 20 m*l* of ethyl ether. The organic layer was dried in Na_2SO_4 and reduced in volume by solvent evaporation. The resulting residue was purified by column chromatography (hexane/ethyl acetate=10/1) to yield the final ketone products. The product ratio was determined by GC-MS.

Indentification of Products

Phenyl hex-5-enyl ketone (7a). ^1H-NMR (200 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J=7.9 Hz, 2H, *o*-protons in phenyl), 7.54-7.32 (m, 3H, *m*- & *p*-protons in phenyl), 5.80 (m, 1H, -CH=), 5.07-4.90 (ABX system, 2H, $=CH_2$), 2.96 (t, J=7.3 Hz, 2H, α-CH_2 to CO), 2.12 (q, J=7.2 Hz, 2H, CH_2-C=), 1.74 (m, 2H, β-CH_2 to CO), 1.50 (m, 2H, γ-CH_2 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 200.1 (CO), 138.4 (-CH=), 136.9-127.9 (phenyl), 114.5 ($=CH_2$), 38.3 (CO-CH_2), 33.5 (C-4 in hex-4-enyl) 28.5 (C-2 in hex-4-enyl) 23.7 (C-3 in hex-4-enyl); IR (neat) 3060 (m), 2920 (s), 2850 (m), 1680 (*vs.*, C=O) 1635 (m), 1594 (m), 1578 (m), 1445 (s), 1405 (w), 1350 (w), 1280 (w), 1220 (m), 1198 (m), 1180 (m), 1115 (w), 990 (m), 910 (m), 750 (m), 730 (w), 690 (s) cm^{-1}; mass spectra, m/z (assignment, relative intensity) 188 (M^+, 3), 417 ($PhCOCH_2CH_2CH_2^+$, 2), 133 ($PhCOCH_2CH_2^+$, 12), 120 ($PhC(OH)=CH_2^+$, 54), 105 ($PhCO^+$, 100), 77 (Ph^+, 32), 55 ($CH_2=CHCH_2CH_2^+$, 2).

Phenyl hex-4-enyl ketone (8a). ^1H-NMR (200 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J=7.9 Hz, 2H, *o*-protons in phenyl), 7.5-7.3 (m, 3H, *m*- & *p*-protons in phenyl), 5.4 (m, 2H, -CH=CH-), 2.9 (t, J=7.2 Hz, 2H, α-CH_2 to CO), 2.1 (m, 2H, CH_2-C=), 1.8 (m, 2H, β-CH_2 to CO), 1.6 (d, =3.5 Hz, 3H,

CH_3-C=); ^{13}C-NMR (50.5 MHz, $CDCl_3$)[12] δ (ppm) 133.9-128.0 (phenyl), 130.5 (C-4 in hex-3-enyl), 125.8 (C-5 in hex-3-enyl), 37.8 (CO-CH_2), 32.0 (C-3 in hex-3-enyl) 2.4.0 (C-2 in hex-3-enyl) 17.9 (CH_3-C=); IR (neat) 3050 (w), 3005 (w), 2925 (m), 2850 (w), 1680 (*vs.*, C=O), 1595 (m), 1575 (m), 1445 (s), 1435 (m), 1360 (w), 1225 (m), 1195 (m), 1175 (w), 1115 (w), 965 (m), 740 (m), 717 (w), 687 (s) cm^{-1}; mass spectra, m/z (assignment, relative intensity) 188 (M^+, 11), 133 ($PhCOCH_2CH_2^+$, 3), 120 ($PhC(OH)=CH_2^+$, 100), 105 ($PhCO^+$, 80), 91 (3), 77 ($C_6H_5^+$, 42), 55 (CH_3-CH=CH-CH_2^+, 6).

1,6-hexadiyl diphenylketone (9a). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.0-7.3 (m, 10H, Phenyl), 2.97 (t, J=7.2 Hz, 6H, α-CH_2 to CO), 1.76 (m, 4H, β-CH_2 to CO), 1.44 (m, γ-CH_2 to CO); Anal Calcd for $C_{20}H_{22}O_2$: C, 81.6; H, 7.53. Found: C, 81.8; H, 7.72. IR (neat) 2925 (m), 2850 (w), 1680 (s, CO), 1575 (w), 1460 (w), 1442 (m), 1405 (w), 1370 (w), 1335 (w), 1330 (w), 1072 (w), 1055 (w), 920 (w), 740 (s), 725 (m), 682 (s).

Phenyl pent-4-enyl ketone (7b). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.1-7.4 (m, 5H, Phenyl), 6.1-5.5 (m, 1H, -CH=), 5.2-4.9 (ABX system, 2H, $=CH_2$), 2.96 (t, J=7.2 Hz, 2H, $COCH_2$), 2.3-1.7 (m, 4H, β,γ-CH_2's in pent-4-enyl group); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 200.0 (CO), 137.9 (-CH=), 137-127 (Phenyl), 115.1 ($=CH_2$), 37.5 (α-CH_2 to CO, 33.0 (γ-CH_2 to CO), 23.1 (β-CH_2 to CO); IR (neat) 3050 (w), 2910 (m), 1680 (*vs.*, C=O) 1635 (w), 1590 (m), 1575 (w), 1442 (s), 1408 (w), 1360 (w), 1315 (w), 1228 (m), 1200 (m), 1175 (w), 990 (m), 970 (w), 910 (m), 750 (m), 740 (m), 678 (s) cm^{-1}; mass spectra, m/z (assignment, relative intensity) 174 (M^+, 8), 133 ($PhCOCH_2CH_2^+$, 1), 120 ($PhC(OH)=CH_2^+$, 57), 105 ($PhCO^+$, 100), 77 (Ph^+, 46), 55 ($CH_2=CHCH_2CH_2^+$, 2).

Phenyl pent-3-enyl ketone (8b). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.0-7.4 (m, 5H, phenyl), 5.6-5.4 (m, 2H, -CH=CH-), 3.03 (t, J=7.2 Hz, 2H, α-CO to CO), 2.6-2.25 (m, 2H, β-CH_2 to CO), 1.64 (d, J=3.5 Hz, 3H, -CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$)[12] δ (ppm) 200.0 (CO), 137-128 (Phenyl), 133.0 (C-3 in pent-3-enyl), 125.9 (C-4 in pent-3-enyl), 38.5 (CO-CH_2), 27.1 (C-2 in pent-3-enyl), 17.9 (-CH_3); IR (neat) 3050 (w), 3010 (w), 2950 (m), 2910 (m), 1680 (*vs.*, C=O) 1590 (m), 1575 (m), 1475 (w), 1442 (s), 1430 (s), 1408 (w), 1355 (w), 1318 (w), 1262 (w), 1230 (w), 1200 (s), 1175 (w), 1023 (w), 965 (s), 740 (s), 687(s) cm^{-1}; mass spectra, m/z (assignment, relative intensity) 174 (M^+, 5), 159 ($PhCOCH_2CH_2CH=CH^+$), 120 ($PHC(OH)=CH_2^+$, 8), 105 ($PhCO^+$, 100), 77 (Ph^+, 24), 55 (CH_3-CH=$CHCH_2^+$, 2).

1,5-Pentadiyl diphenylketone (9b). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.0-7.4 (m, 10H, Ph), 3.0 (t, J=7.1 Hz, 4H, α-CH_2 to CO), 2.1-1.1 (m, 6H, β- and γ-CH_2-); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 200.3 (CO), 137-128 (Phenyl), 38.3 (α-CH_2 to CO), 29 (γ-CH_2 to CO), 24 (β-CH_2 to CO); IR (neat) 2940 (s), 2890 (m), 1675 (*vs.*, C=O) 1590 (m), 1580 (w), 1465 (m), 1445 (s), 1410 (w), 1370 (w), 1340 (s), 1245 (s), 1185 (s), 1175 (m), 960 (s), 750 (s), 720 (s), 685 (s), 660 (m) cm^{-1}; mass spectra, m/z (assignment, relative intensity) 280 (M^+, 0.5), 175 ($PhCOCH_2CH_2CH_2CH_2CH_2^+$, 3), 161 ($PhCOCH_2CH_2CH_2CH_2^+$, 17) 120 ($PhC(OH)=CH_2^+$, 33), 105 ($PhCO^+$, 100), 77 ($Ph^+$, 40).

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