adduct of olefinic group of MMA to SiH bonds of the poly (phenylsilane) and small amount of poly(MMA) and (2) no photoreaction of poly(MMA) with $PhSiH_3$ took place.

In conclusion, this work describes the photopolymerization of MMA with phenylsilane. The molecular weights of the poly(MMA) containing Si-H moieties are increased as the molar ratio of $PhSiH_3$ over MMA increased by cross-linking *via* hydrosilation of Si-H bond to C=O group of the polymer, but the isolated yield is in turn decreased. This is supported by the spectroscopic and solubility data and some reaction chemistry. AIBN accelerates the polymerization reaction rate and increases molecular weights. Phenylsilane seems to function as a chain transfer agent and solvent.

Acknowledgment. This research was supported in part by Non Directed Research Fund, Korea Research Foundation (1994), in part by Korea Science and Engineering Foundation (1994), and in part by CNU Research Foundation (1994).

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Hydroiminoacylation of Allyl and Homoallyl Alcohol Derivatives with Benzaldimine and Solvolysis of Hydroacylated Products

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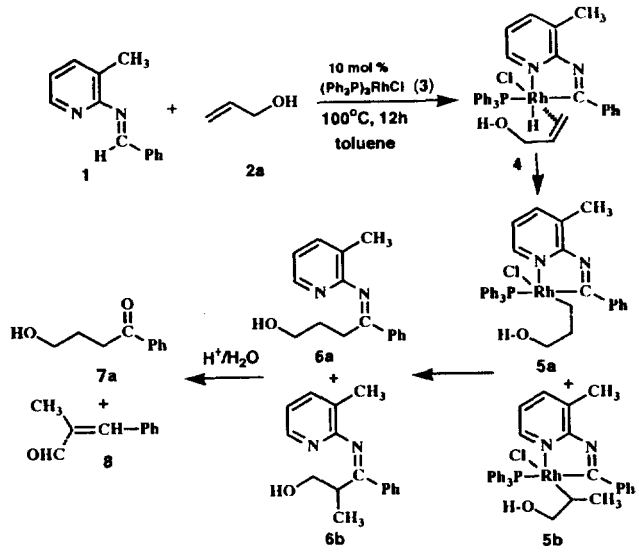
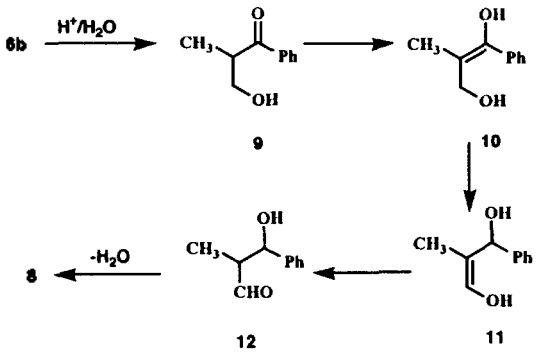
Hydroiminoacylations of allyl and homoallyl alcohol and their derivatives with benzaldimine by Wilkinson's complex have been studied. All these terminal alkene derivatives except allyl alcohol were hydroacylated according to anti-Markownikoff's rule to give the corresponding linear alkyl compounds without showing oxygen directing effect, even though hydroiminoacylation of 3-acetoxy-1,5-hexadiene showed strong allyloxy directing effect over homoallyloxy directing effect in a 92 : 8 ratio. Solvolysis of 4-acetoxy-1-phenylbutan-1-one, previously prepared by hydroiminoacylation, in ethanol led to etherification giving 4-ethoxy-1-phenylbutan-1-one through neighbouring group participation, while that of 5-acetoxy-1-phenylpentan-1-one led to common transesterification giving 5-hydroxy-1-phenylpentan-1-one. Application of branched alkanols such as isopropanol and *t*-butanol in solvolysis of 4-acetoxy-1-phenylbutan-1-one underwent competition between etherification and transesterification.

Introduction

Hydroacylation is one of interesting reactions in organometallic chemistry since ketone can be directly synthesized from olefin and aldehyde by organotransition metal catalyst.[1] However, decarbonylation of aldehyde is one of major side



Scheme 1.



Scheme 2.

reactions to produce alkanes.[2] When aldimine, prepared from aldehyde and 2-amino-3-picoline, was used instead of aldehyde to suppress this decarbonylation, ketimine was formed by hydroiminoacylation through C-H bond cleavage of aldimine.[3] The resulting ketimine could be easily hydrolyzed by aqueous acid solution to produce ketones. Hydroiminoacylation of 1,5-hexadien-3-ol and its derivatives having both allyl group and homoallyl group, with organometallic compound, ferrocenecarboxaldimine, showed strong allyloxy directing effect to give the corresponding alkanoylferrocene after hydrolysis.[4] Benzaldimine instead of ferrocenecarboxaldimine has been applied for hydroiminoacylation. This report explains hydroiminoacylation of various 1-alkene derivatives with benzaldimine to see the directing effect and the solvolysis reaction of the hydroacylated benzoylalkyl acetate.

Result and Discussion

Benzaldimine **1** (0.33 mmol), prepared from benzaldehyde and 2-amino-3-picoline, reacted with allyl alcohol (**2a**) (0.66 mmol) in toluene at 100 ℃ for 12 h under 10 mol % of Wilkinson's complex (**3**) (0.033 mmol) as a catalyst based upon **1**. Without isolation of the resulting ketimines **6a** and **6b**, their hydrolysis with 1 N aq. HCl solution for 2 h gave 4-hydroxy-1-phenylbutan-1-one (**7a**) and α-methylcinnamaldehyde (**8**) in a 73 : 27 ratio in 45% yield after isolation by silica-gel chromatography (Scheme 1).

Table 1. Hydroiminoacylation of olefins (**2**) with benzaldimine (**1**) under 10 mol% Wilkinson's complex (**3**) at 100 ℃ for 12 h, and hydrolysis of the resulting ketimine (**6**)

Entry	Olefin substrate	Product	Ratio	Isolated Yield
1	(**2a**)	(**7a**) / (**8**)	73 … 27	45%[a]
2	(**2b**)	(**7b**)		77%
3	(**2c**)	(**7c**)		92%
4	(**2d**)	(**7d**)	70 …	
		7a	7 …	70%
		(**7j**)	23	
5	(**2e**)	(**7e**)		78%[b]
6	(**2f**)			0%
7	(**2g**)	(**7g**)		73%[c]
8	(**2h**)	(**7h**)		57%

[a] A trace amount of unknown compound was detected. [b] A trace of hydrolysis product (**7a**) was obtained. [c] A trace of hydrolysis product (**7h**) was obtained.

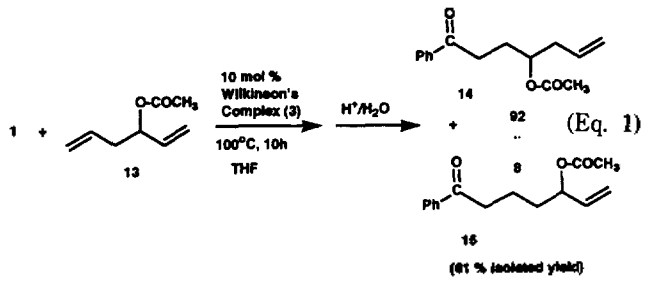
The first step of hydroiminoacylation must be C-H bond cleavage of aldimine **1** by Rh(I) in **3** and coordination of allyl alcohol (**2a**) to generate a transient intermediate **4**. The hydride insertion into allyl alcohol gives two hydrometallated complexes as intermediates, **5a** and **5b**, according to anti-Markownikoff's rule and Markownikoff's rule. Reductive eliminations of **5a** and **5b** produce two ketimines, **6a** and **6b**, respectively. The reason for formation of **5b** is not clear. Maybe the oxygen atom in **4** might coordinate to Rh with dissociation of the remaining triphenylphosphine, which makes close enough to deliver a hydride to terminal olefinic carbon. This result is very similar to that of ferrocenecarboxaldimine.[5]

For compound **8**, hydrolysis of branched alkyl ketimine **6b** might give **12** through enolization of the initial hydrolyzed branched alkanol **9** and subsequent isomerization of **10** to **12** (Scheme 2). Dehydration of **12** supposes to give **8** as a final product. This kind of dehydration has been shown in dehydration of α-hydroxyalkylferrocene since this type of compound is very susceptible for dehydration giving alkenylferrocenes.[6] Driving force for dehydration must be the for-

mation of the stable conjugate olefin connected with the cyclopentadienyl group in α-hydroxyalkylferrocene. Above result shows that even phenyl group as well as cyclopentadienyl group of ferrocene drives the dehydration process under mild conditions.

However, hydroiminoacylation of the hydroxy-group protected allyl alcohol derivatives afforded linear alkyl hydroacylated products after hydrolysis.

When allyl ethyl ether (**2b**) and allyl phenyl ether (**2c**), in which the hydroxy groups of allyl alcohols were protected by ethyl group and phenyl group, were applied for hydroiminoacylation under the identical conditions, only the linear alkyl hydroacylated products, 4-ethoxy-1-phenylbutan-1-one (**7b**) and 4-phenoxy-1-phenylbutan-1-one (**7c**), were obtained in 77% and 92% yield, respectively (Table 1). Any branched alkyl hydroacylated product has not been observed. Hydroiminoacylation of diallyl ether and the subsequent acid hydrolysis of the resulting ketimine produced three kinds of hydroacylated compounds, 4-allyloxy-1-phenylbutan-1-one (**7d**), **7a** and bis(benzoylpropyl)ether (**7j**) in a 70 : 7 : 23 ratio in 70% overall yield. Compound **7a** supposes to be formed during acid hydrolysis of **7d**. When alcohol group in allyl alcohol was protected with acetyl group, 4-acetoxy-1-phenylbutan-1-one (**7e**), linear alkyl hydroacylated product, was also obtained in 78% yield as expected. However, when vinyl acetate (**2f**), a shorter substrate than **2e**, was applied for hydroiminoacylation under the identical reaction conditions, any hydroacylated product was not detected. The reason might be favorable polymerization of vinyl acetate under this reaction conditions. Already we have seen the strong directing effect for allyloxy group compared with homoallyloxy group in hydroiminoacylation of 3-acetoxy-1,5-hexadiene with ferrocenecarboxaldimine.[4] To test the directing effect of 3-acetoxy-1,5-hexadiene (**13**), **1** reacted with **13** at 100 ℃ for 10 h under 10 mol % Wilkinson's complex (**3**) to give 4-acetoxy-1-phenyl-6-hepten-1-one (**14**) and 5-acetoxy-1-phenyl-6-hepten-1-one (**15**) in a 92 : 8 ratio in 61% yield after hydrolysis of the resulting ketimine (eq. 1).



(Eq. 1)

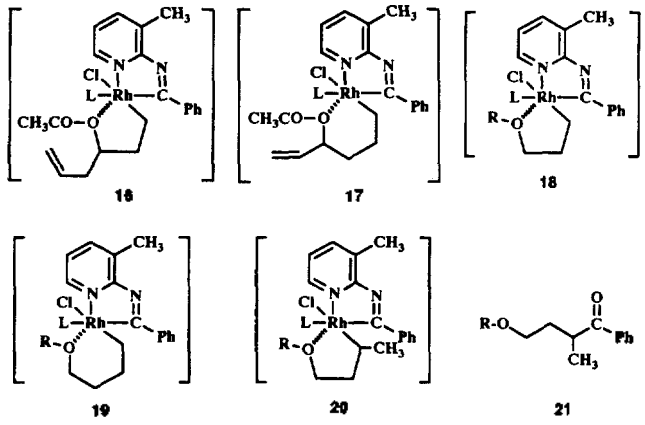
This strong directing effect of allyloxy group over homoallyloxy group in **13** can be explained by that a stable 5-membered metallacycle intermediate **16**, generated from hydrometallation of allyloxy group of **13**, would be the most plausible intermediate. The minor product **15** must be formed from an intermediate **17** with a 6-membered metallacyclic system which is less stable than a 5-membered one, **16**. This kind of oxygen directing effect has been observed in homogeneous hydrogenation with several transition metal complexes.[7]

Other candidates for hydroiminoacylation are 3-butenyl acetate (**2g**) and 3-butenol (**2h**). If strong oxygen-directing effect is operating in hydrometallation of 4-butenoxy group

Table 2. Solvolysis of **7e** in alcohol under *p*-toluenesulfonic acid as a catalyst[a]

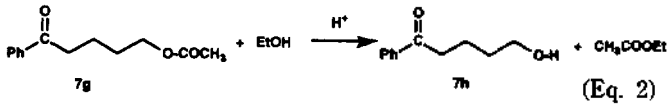
Entry	Alcohol	Product	Ratio[b]	Isolated overall yield[c]
1	ethanol	(**7b**)		57%
2	*n*-butanol	(**7k**)		53%
3	*iso*-propanol	(**7l**)	71	73%
		7a	29	
4	*t*-butanol	(**7m**)	35	89%
		7a	65	

[a]The reaction mixture was heated at 90 ℃ for 6 h. [b]The ratio was determined by GC-MSD. [c]Starting material **7e** could not be detected by GC-MSD before isolation.

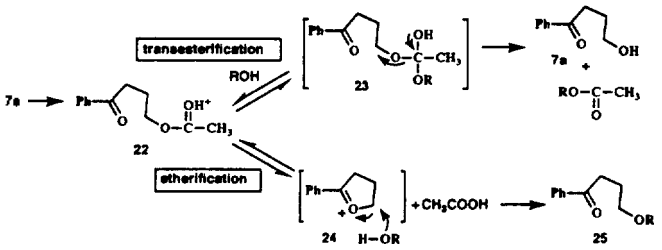


of **2g** or **2h**, it should have given **21** through a stable 5-membered metallacyclic intermediate **20**. On the contrary, hydroiminoacylation of **2g** and **2h** under the identical reaction conditions produced 5-acetoxy-1-phenylpentan-1-one (**7g**) and 5-hydroxy-1-phenylpentan-1-one (**7h**) in 73% and 57% yield, respectively, after hydrolysis of the resulting ketimine. Any branched alkyl product such as **21** has not been obtained, nor dehydrated product similar to **8**, generated from **21** (R=H). This result can be explained as follows. When the stability of complex **19** is compared with that of **20**, steric congestion at α-carbon to Rh seems to make **20** less stable than **19**, which may not show allyloxy-directing effect for **2g** and **2h**.

Solvolysis of **7g** in ethanol produced **7h** under catalytic amount of *p*-toluenesulfonic acid by transesterification as shown in eq. 2.[8] However, solvolysis of **7e** in ethanol gave **7h** exclusively in 57% isolated yield (Table 2).



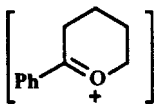
(Eq. 2)



Scheme 3.

This etherification can be explained by the effect of carbonyl-neighboring group participation to generate a 5-membered ring cyclic oxonium intermediate **24** (Scheme 3).[9]

The intermediate **24** has been proposed in many neighboring group participation solvolysis.[10] Solvolysis of several 4-haloalkyl ketones has shown to proceed faster than that of n-alkylhalides by neighboring group participation. Especially, when the solvolysis rate of 4-halo-1-phenylbutan-1-one was compared with that of 5-halo-1-phenylpentan-1-one, the solvolysis rate of 4-halo-1-phenylbutan-1-one was much faster than that of 5-halo-1-phenylpentan-1-one. This result could be explained by that 5-membered ring intermediate **24** is much more easily formed than 6-membered ring intermediate **26**.[9a]



26

That must be a reason why solvolysis of **7e** in ethanol afforded **7b** while that of **7g** gave **7h**. Solvolysis of **7e** in primary alcohols, ethanol and butanol, produced the corresponding ethers (Table 2, entry 1 and 2). However, when branched alcohols were used, this selectivity is lowered. As alcohol was changed to ethanol, isopropanol and *t*-butanol, the product ratio of ether/alcohol was decreased 100/0, 71/29, 35/65. The reason is not clear whether steric factor or nucleophilicity of alcohol is major role. Maybe nucleophilicities of alcohols seem to be an important role for this competition between etherification and transesterification. The intermediate **22** might be more susceptible to alcohol basicity, in which basicity is lowered as *t*-butanol, *iso*-propanol, ethanol, than the intermediate **24**.

Conclusion

We have seen hydroiminoacylations of various 1-alkene derivatives with benzaldimine. In case of hydroxy-group protected allyl alcohol derivatives (**2b-2e**), anti-Markownikoff's hydroacylated products were obtained by hydroiminoacylation and subsequent hydrolysis, while allyl alcohol (**2a**) afforded a mixture of anti-Markownikoff's product (**7a**) and dehydrated Markownikoff's product (**8**). Hydroiminoacylation of vinyl acetate (**2f**), one of shortest 1-alkene derivatives, did not show any hydroacylated product, maybe due to facile polymerization of vinyl acetate. Even though hydroiminoacylation of 3-acetoxy-1,5-hexadiene (**13**) showed much higher allyloxy group preference over homoallyloxy group in a 92 : 8 ratio due to oxygen directing effect, that of 3-butenyl acetate (**2g**) or 3-butenol (**2h**) did not produce any branched hydroacylated product **21** through a branched alkyl 5-membered metallacycle intermediate **20**. The steric congestion at the branched α-alkyl carbon to Rh in **20** might not tolerate the formation of the 5-membered metallacycle intermediate. Solvolysis of 4-acetoxy-1-phenylbutan-1-one (**7e**) in primary alcohol such as ethanol or butanol afforded etherification product, 4-alkoxy-1-phenylbutan-1-one, through a cyclic oxonium intermediate **24**, while that of 5-acetoxy-1-phenylpentan-1-one (**7g**) gave transesterification product, 5-hydroxy-1-phenylpentan-1-one (**7h**). By changing primary alcohols like ethanol and butanol to *sec*-alcohol and *tert*-alcohol such as isopropanol and *t*-butanol, the ratio of etherification product/transesterification product was decreased, maybe due to the difference of alcohol nucleophilicity strength.

Experimental

Compound **1** was prepared by the published procedure.[11] Wilkinson's complex (**3**), allyl alcohol (**2a**), allyl alcohol derivatives (**2b-2e**), vinyl acetate (**2f**), 3-butenol (**2h**) and 2-amino-3-picoline were purchased (Aldrich) and used without further purification. 3-Butenyl acetate (**2g**) and 3-acetoxy-1,5-hexadiene (**13**) were prepared by acetylation of 3-butenol and 1,5-hexadien-3-ol.[12] All solvents were distilled from sodium-benzophenone ketyl prior to use. The solvent system for column-chromatography was a mixture of hexane and ethylacetate in a 5 : 2 ratio in volume. NMR spectra were recorded with a Bruker AC-300 (300 MHz) spectrometer. The chemical shift values (δ) of the ^{1}H NMR and ^{13}C NMR resonances were expressed in ppm relative to internal Me_4Si. Infrared spectra were recorded with Nicolet Instrument Corp. Impact 400 FT-IR spectrometer. Mass spectra were obtained with a Shimadzu GCMS-QP2000A. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh).

Hydroiminoacylation of allyl alcohol (2a) with 1 and hydrolysis of the resulting ketimine. A screw capped pressure vial was charged with 15 mg (0.016 mmol) of Wilkinson's complex (**3**) dissolved in 3 mL of toluene, the solution was flushed with nitrogen, and 32 mg (0.16 mmol) of **1** was added. To the mixture was added 30 mg (0.49 mmol) of **2a**, followed by heating at 100 ℃ for 12 h. The reaction mixture was hydrolyzed with 10 mL of 1 N aq. HCl solution for 5 h. The products were extracted with 20 mL of ether and purified by column chromatography to give a mixture of 4-hydroxy-1-phenylbutan-1-one (**7a**) and α-methylcinnamaldehyde (**8**) in a 73 : 27 ratio in 45% yield. **7a**[13]: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (dd, J=7.6 and 1.6 Hz, 2H, 2, 6-Hs in phenyl group), 7.6-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.75 (t, J=6.1 Hz, 2H, γ-CH_2 to CO), 3.14 (t, J=6.9 Hz, 2H, α-CH_2 to CO), 2.03 (m, 2H, β-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.6 (CO), 133.1, 128.6, 128.1 (carbons in phenyl group), 62.3 (γ-carbon to CO), 35.3 (α-carbon to CO), 26.9 (β-carbon to CO); IR spectrum (neat) 3409 (br), 3062, 2929, 1683 (CO), 1599, 1449, 1240, 1060 (s) cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 147 (M-OH^-, 5), 146 (M^+-H_2O, 46), 145 (14), 117, (15), 115 (37), 105 ($PhCO^+$, 100), 91 (8), 77 ($C_6H_5^+$,

62). 8: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) 9.60 (s, 1H, CHO), 7.3-7.6 (m, 7H, PhCH=), 2.09 (s, 3H, CH_3); IR spectrum (neat) 2957, 2928, 2851, 1689 (CO), 1600, 1494, 1470, 1186, 1014 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 146 (M, 60), 145 (M-H, 100), 131 (M-CH_3, 9), 118 (M-CO, 10), 117 (M-CHO, 76), 116 (20), 115 (73), 103 (PhCH$=C^+$, 12), 91 ($PhCH_2^+$, 41), 89 (PhC^+, 20), 78 (C_6H_6, 44), 77 ($C_6H_5^+$, 17).

Hydroiminoacylation of allyl ethyl ether (2b) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 42 mg (0.49 mmol) of allyl ethyl ether (**2b**) gave 24 mg (77% isolated yield) of 4-ethoxy-1-phenylbutan-1-one (**7b**). **7b**[14]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (dd, 2H, 2, 6-Hs in phenyl group), 7.6-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.50 (t, J=6.5 Hz, 2H, γ-CH_2 to CO), 3.48 (q, J=7.1 Hz, 2H, CH_2 in ethyl group), 3.10 (t, J=7.2 Hz, 2H, α-CH_2 to CO), 2.03 (m, 2H, β-CH_2 to CO), 1.19 (t, J=7.0 Hz, 3H, CH_3); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.1 (CO), 132.9, 128.5, 128.0 (carbons in phenyl group), 69.5 (γ-carbon to CO), 66.1 (CH_2 in ethyl group), 35.2 (α-carbon to CO), 24.3 (β-carbon to CO), 15.2 (CH_3); IR spectrum (neat) 3065, 2969, 2861, 1692 (CO), 1597, 1453, 1381, 1267, 1117, 1021. 805 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 163 (M^+-CH_2CH_3, 2), 147 (M^+-CH_3CH_2O, 3), 146 (M^+-CH_3CH_2OH, 2), 120 ($PhC(OH)=CH_2^+$, 65), 105 ($PhCO^+$, 100), 91 (5), 77 ($C_6H_5^+$, 75).

Hydroiminoacylation of allyl phenyl ether (2c) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 66 mg (0.49 mmol) of allyl phenyl ether (**2c**) gave 36 mg (92% isolated yield) of 4-phenoxy-1-phenylbutan-1-one (**7c**) **7c**[12]; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (dd, 2H, 2, 6-Hs in phenyl group), 7.6-6.8 (m, 8H, two phenyl groups), 4.07 (t, J=6.0 Hz, 2H, γ-CH_2 to CO), 3.21 (t, J=7.1 Hz, 2H, α-CH_2 to CO), 2.24 (m, 2H, β-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 132.1, 129.4, 128.0, 120.7, 114.4 (carbons in two phenyl groups), 66.7 (γ-carbon to CO), 34.9 (α-carbon to CO), 23.8 (β-carbon to CO); IR spectrum (neat) 3068, 2966, 2906, 1687 (CO), 1603, 1501, 1470, 1374, 1248, 1211. 1037 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 148 (M^+-PhO+1, 8), 147 (M^+-PhO, 69), 120 ($PhC(OH)=CH_2^+$, 9), 106 (9), 105 ($PhCO^+$, 100), 91 (5), 77 ($C_6H_5^+$, 83).

Hydroiminoacylation of diallyl ether (2d) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 47 mg (0.49 mmol) of diallyl ether (**2b**) gave a mixture of 18 mg of 4-allyloxy-1-phenylbutan-1-one (**7d**), 2 mg of 4-hydroxy-1-phenylbutan-1-one (**7a**) and 9 mg of bis(benzoylpropyl)ether (**7j**) in 70% isolated yield. **7d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.97 (dd, 2H, 2, 6-Hs in phenyl group), 7.6-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 5.90 (m, 1H, -CH=), 5.23 (ABX system, 2H, $=CH_2$), 3.98 (d, 2H, O-CH_2-C=), 3.53 (t, J=6.1 Hz, 2H, -CH_2 to CO), 3.10 (t, J=7.2 Hz, 2H, α-CH_2 to CO), 2.06 (m, 2H, β-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.0 (CO), 134.8 (-CH=), 132.9, 128.5, 128.0 (carbons in phenyl group), 116.8 ($=CH_2$), 71.1 (O-CH_2-C=), 69.3 (γ-carbon to CO), 35.1 (α-carbon to CO), 24.2 (β-carbon to CO); IR spectrum (neat) 3062, 3027, 2935, 2854, 1690 (CO), 1598, 1454, 1362, 1206, 1109, 1005, 936, 757, 694 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 164 (M^+-C_3H_4, 2), 163 (M^+-C_3H_5, 20), 147 (M^+-C_3H_5O, 14), 120 ($PhC(OH)=CH_2^+$, 40.5), 117 (5), 105 ($PhCO^+$, 100), 91 (4), 85 (10), 77 ($C_6H_5^+$, 72). 7j: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 (d, 4H, 2, 6-Hs in two phenyl group), 7.7-7.3 (m, 6H, 3, 4, 5-Hs in two phenyl group), 3.51 (t, J=6.4 Hz, 4H, γ-CH_2 to CO), 3.05 (t, J=6.9 Hz, 4H, α-CH_2 to CO), 2.01 (m, 4H, β-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.0 (CO), 133.9-126.9 (carbons in two phenyl groups), 69.8 (γ-carbon to CO), 35.1 (α-carbon to CO), 24.2 (β-carbon to CO); IR spectrum (neat) 3066, 2931, 2853, 1691 (CO), 1595, 1455, 1370, 1208, 1124 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 148 ($PhCOCH_2CH_2CH_3^+$, 6), 147 ($PhCOCH_2CH_2CH_2^+$, 53), 146 ($PhCOCH_2CH=CH_2^+$, 42), 120 ($PhC(OH)=CH_2^+$, 25), 105 ($PhCO^+$, 100), 91 (4), 77 ($C_6H_5^+$, 69).

Hydroiminoacylation of allyl acetate (2e) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 50 mg (0.49 mmol) of allyl acetate (**2e**) gave 26 mg (78% isolated yield) of 4-acetoxy-1-phenylbutan-1-one (**7e**). **7e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.96 (dd, 2H, 2, 6-Hs in phenyl group), 7.6-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 4.17 (t, J=6.3 Hz, 2H, γ-CH_2 to CO), 3.08 (t, J=7.2 Hz, 2H, α-CH_2 to CO), 2.12 (m, 2H, β-CH_2 to CO), 2.03 (s, 3H, CH_3); ^{13}C NMR (72.5 MHz, $CDCl_3$) (ppm) 199.0 (PhCO), 133.1, 128.6, 127.9 (carbons in phenyl group), 63.7 (γ-carbon to CO), 34.8 (α-carbon to CO), 23.1 (β-carbon to CO), 20.9 (CH_3); IR spectrum (neat) 3064, 2970, 2929, 1741 (MeCO), 1688 (PhCO), 1600, 1453, 1371, 1241, 1041 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 163 (M^+-$COCH_3$, 2), 147 (M^+-CH_3COO, 3), 146 (M^+-CH_3COOH, 14), 120 ($PhC(OH)=CH_2^+$, 30), 105 ($PhCO^+$, 100), 91 (2), 77 ($C_6H_5^+$, 64).

Hydroiminoacylation of 3-acetoxy-1,5-hexadiene (13) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 68 mg (0.49 mmol) of 3-acetoxy-1,5-hexadiene (**13**) gave a mixture of 26 mg (61% isolated yield) of 4-acetoxy-1-phenyl-6-hepten-1-one (**14**) and 5-acetoxy-1-phenyl-6-hepten-1-one (**15**) in a 92 : 8 ratiodetermined by GC-MSD. **14**: ^{1}H NMR (100 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J=7.2 Hz, 2H, 2, 6-Hs in phenyl group), 7.6-7.3 (m, 3H, 3, 4, 5-Hs in phenyl group), 5.8-5.5 (m, 1H, -CH=), 5.14 (m, 2H, $=CH_2$), 3.01 (t, J=7.3 Hz, 2H, α-CH_2 to CO), 2.38 (t, J=6.5 Hz, 2H, α-CH_2 to -CH=CH_2), 2.01 (s, 3H, CH_3CO); ^{13}C NMR (25 MHz, $CDCl_3$) δ (ppm) 199.1 (CO), 170.7 (CH_3CO), 136.8 (-CH=), 133.3-128.0 (carbons in phenyl group) 118.0 (=CH2), 72.7 (CH-OAc) 38.8 (CH_2-CH=), 34.4 (β-carbon to CO), 28.0 (α-carbon to CO), 21.1 (CH_3 CO); IR spectrum (neat) 3073, 3021, 2930, 2850, 1741 (CH_3 CO), 1690 (PhCO), 1449, 1381, 1249, 1032, 992, 923 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 203 (M^+-$COCH_3$, 10), 186 (M^+-CH_3COOH, 7), 163 ($PhCOCH_2CH_2CHOH^+$, 24), 145 (17), 120 ($PhC(OH)=CH_2^-$, 10), 105 ($PhCO^+$, 100), 91 (4), 77 ($C_6H_5^+$, 56). **15**: mass spectrum, m/e (assignment, relative intensity) 203 (M^+-$COCH_3$, 8), 186 (M^+-CH_3COOH, 4), 133 ($PhCOCH_2CH_2^+$, 11), 120 ($PhC(OH)=CH_2^+$, 15), 105 ($PhCO^+$, 100), 91 (6), 77 ($C_6H_5^-$, 63).[15]

Hydroiminoacylation of 3-butenyl acetate (2g) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 56 mg (0.49 mmol) of 3-butenyl acetate (**2g**) gave 26 mg (73% isolated yield) of 5-acetoxy-1-phenylpentan-1-one (**7g**). **7g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J=7.0 Hz, 2H, 2, 6-Hs in phenyl group), 7.5-7.3 (m, 3H, 3, 4, 5-Hs in phenyl group), 6.11 (t, J=6.23

Hz, 2H, δ-CH_2 to CO), 3.02 (t, J=7.03 Hz, 2H, α-CH_2 to CO), 2.04 (s, 3H, CH_3), 1.83-1.70 (m, 4H, β,γ-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 199.9 (PhCO), 136.8, 133.5, 128.6 (carbons in phenyl group), 64.1 (δ-carbon to CO), 37.9 (α-carbon to CO), 28.2 (γ-carbon to CO), 20.9 (β-carbon to CO), 20.6 (CH_3); IR spectrum (neat) 3062, 2964, 1745 (MeCO), 1684 (PhCO), 1598, 1457, 1371, 1261, 1046 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 177 (M^+-$COCH_3$, 1), 161 (M^+-CH_3COO, 2), 160 (M^+-CH_3COOH, 11), 133 (2), 120 (PhC(OH)=CH_2, 7), 105 ($PhCO^+$, 100), 91 (2), 77 ($C_6H_5^+$, 54).

Hydroiminoacylation of 3-butenol (2h) with 1 and hydrolysis of the resulting ketimine. In the same way described for **2a**, 35 mg (0.49 mmol) of 3-butenol (**2h**) gave 16 mg (57% isolated yield) of 5-hydroxy-1-phenylpentan-1-one (**7h**). **7h**[16]: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J=7.23 Hz, 2H, 2, 6-Hs in phenyl group), 7.5-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.68 (t, J=6.23 Hz, 2H, δ-CH2 to CO), 3.49 (s, 1H, H in OH), 3.03 (t, J=7.05 Hz, 2H, α-CH_2 to CO), 1.7-1.6 (m, 4H, β,γ-CH_2 to CO); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.3 (PhCO), 136.9, 133.0, 128.6, 128.0 (carbons in phenyl group), 62.4 (δ-carbon to CO), 38.1 (α-carbon to CO), 32.2 (γ-carbon to CO), 20.1 (β-carbon to CO); IR spectrum (neat) 3392 (OH), 2929, 2870, 1679 (CO), 1602, 1454, 1228, 1068, 1003 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 161 (M^+-OH, 6), 160 (M^+-H_2O, 47), 159 (23), 131 (13), 117 (3), 115 (7), 105 ($PhCO^+$, 100), 91 (6), 77 ($C_6H_5^+$, 62).

Solvolysis (etherification) of 7e in ethanol. A screw capped pressure vial was charged with 15 mg (0.073 mmol) of **7e** dissolved in 2 mL of absolute ethanol, and 5 mg (0.0024 mmol) of *p*-toluenesulfonic acid was added. The reaction mixture was heated at 90 ℃ for 6 h. The resulting solution was concentrated and purified by column-chromatography to give 8 mg (57% isolated yield) of **7b**.

Solvolysis (transesterification) of 7g in ethanol. In the same way described for **7e**, reaction of 17 mg of **7g** in 2 mL of ethanol under 3 mg of *p*-toluenesulfonic acid catalyst gave 10 mg (73% isolated yield) of 5-hydroxy-1-phenylpentan-1-one (**7h**).

Solvolysis of 7e in 1-butanol. In the same way described for **7e** in ethanol, reaction in 2 mL of 1-butanol gave 9 mg (53% isolated yield) of 4-butoxy-1-phenylbutan-1-one (**7k**). **7k**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J=7.24 Hz, 2H, 2, 6-Hs in phenyl group), 7.6-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.50 (t, J=6.08 Hz, 2H, γ-CH_2 to CO), 3.41 (t, J=6.59 Hz, 2H, α-CH_2 in *n*-Butyl group), 3.08 (t, J=7.15 Hz, 2H, α-CH_2 to CO), 2.02 (m, 2H, β-CH_2 to CO), 1.5-1.3 (m, 4H, β,γ-CH_2 in *n*-Butyl group), 0.91 (t, J=7.34 Hz, 3H, CH_3 in *n*-Butyl group); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 132.9, 128.5, 128.0 (carbons in phenyl group), 70.7 (α-carbon in *n*-butyl group), 69.7 (γ-carbon to CO), 35.2 (α-carbon to CO), 31.8 (β-carbon in *n*-butyl group), 24.3 (β-carbon to CO), 19.4 (γ-carbon in *n*-butyl group), 13.9 (CH_3); IR spectrum (neat) 1966, 2931, 2873, 1729, 1689 (CO), 1596, 1452, 1261, 1106, 1036 cm^{-1}; mass spectrum, m/e (assigmnent, relative intensity) 163 (M^+-C_4H_9, 2), 147 (M^+-OC_4H_9, 8), 146 (M^+-BuOH, 2), 120 (PhC(OH)=CH_2, 81), 105 ($PhCO^+$, 100), 101 (33), 91 (5), 77 ($C_6H_5^+$, 80).

Solvolysis of 7e in 2-propanol. In the same way described for **7e** in ethanol, reaction in 2 mL of 2-propanol gave 10 mg (73% isolated yield) of a mixture of 4-(2-propoxy)-1-phenylbutan-1-one (**7l**) and **7a** in a 71 : 29 ratio determined by GC-MSD. **7l**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J=7.04 Hz, 2H, 2, 6-Hs in phenyl group), 7.5-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.57 (m, 1H, CH), 3.53 (t, J=6.13, 2H, γ-CH_2 to CO), 3.08 (t, J=7.11, 2H, α-CH_2 to CO), 2.03-1.98 (m, 2H, β-CH_2 to CO), 1.15 (d, J=5.99, 6H, $2CH_3$); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 200.2 (PhCO), 137.1, 132.9, 128.5, 128.0 (carbons in phenyl group), 69.5 (CH), 66.1 (γ-carbon to CO), 35.2 (α-carbon to CO), 24.3 (β-carbon to CO), 15.2 ($2CH_3$); IR spectrum (neat) 2972, 2932, 2856, 1736, 1695 (CO), 1602, 1451, 1369, 1265, 1085 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 164 (M^+-C_3H_6, 3), 163 (M^+-CH(CH_3)$_2$, 25), 147 (M^+-$OCH(CH_3)_2$, 20), 133 (8), 120 (PhC(OH)=CH_2, 60), 115 (3), 105 ($PhCO^+$, 100), 91 (6), 87 (36), 77 ($C_6H_5^+$, 88).

Solvolysis of 7e in 2-methyl-2-propanol. In the same way described for **7e** in ethanol, reaction in 2 mL of 2-methyl-2-propanol gave 12 mg (89% isolated yield) of a mixture of 4-(2-methyl-2-propoxy)-1-phenylbutan-1-one (**7m**) and **7a** in a 35 : 65 ratio determined by GC-MSD. **7m**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J=7.0 Hz, 2H, 2, 6-Hs in phenyl group), 7.5-7.4 (m, 3H, 3, 4, 5-Hs in phenyl group), 3.43 (t, J=6.08, 2H, γ-CH_2 to CO), 3.07 (t, J=7.1, 2H, α-CH_2 to CO), 2.0-1.9 (m, 2H, β-CH_2 to CO), 1.17 (s, 9H, $3CH_3$); ^{13}C NMR (72.5 MHz, $CDCl_3$) δ (ppm) 137.1, 132.8, 128.5, 128.0 (carbons in phenyl group), 72.6 (carbon in *t*-butyl group), 60.5 (γ-carbon to CO), 35.2 (α-carbon to CO), 27.5 ($3CH_3$), 25.2 (β-carbon to CO); IR spectrum (neat) 2976, 2925, 2856, 1735, 1690 (CO), 1598, 1449, 1369, 1204, 1078 cm^{-1}; mass spectrum, m/e (assignment, relative intensity) 164 (M^+-C_4H_8, 7), 163 (M^1-$C(CH_3)_3$, 55), 147 (M^+-$OC(CH_3)_3$, 45), 145 (7), 133 (8), 120 (PhC(OH)=CH_2, 12), 117 (31), 105 ($PhCO^+$, 100), 85 (10), 77 ($C_6H_5^+$, 72).

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