

## Acyldemetallation of titanium(III) $\pi$ -allylic complexes

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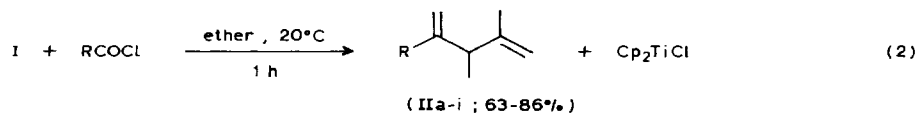
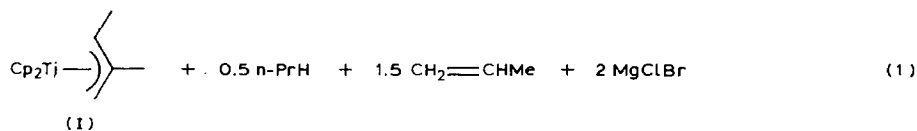
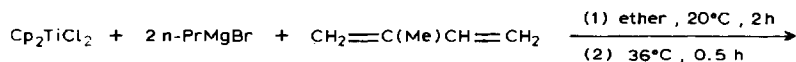
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### Abstract

Titanium(III)  $\pi$ -allylic complexes, prepared by the interaction of 1,3-dienes or trienes with  $\text{Cp}_2\text{TiCl}_2$  and  $n\text{-PrMgBr}$ , react with carboxylic acid chlorides  $\text{RCOCl}$  ( $\text{R}$  = alkyl, aryl, alkenyl) to give  $\beta$ ,  $\gamma$ -unsaturated ketones in high yields. The reaction takes place at the most substituted carbon atom of the  $\pi$ -allylic ligand.

Simple and effective routes to organometallic compounds are achieved by olefin, diene, and acetylene hydrometallations which are presently widely employed in organic synthesis (e.g. refs. 1, 2). The hydrotitanation of 1,3-dienes in particular, results in the  $\text{Ti}^{\text{III}}$   $\pi$ -allylic complexes, which can be usefully applied to regio- and stereoselective condensations with carbonyl compounds [3,4]. Here we report on our



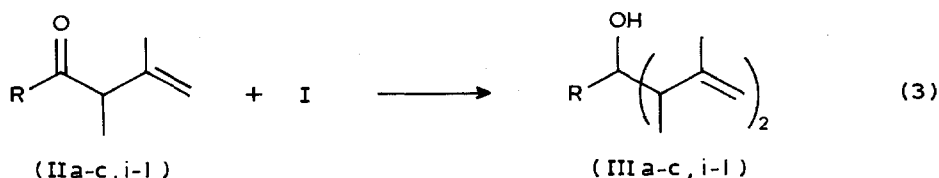
( $\text{R}$  = Ph (a),  $\text{PhCH}_2$  (b), 2-furyl (c),  
 3-pyridyl (d),  $i\text{-Pr}$  (e),  
 $\text{CH}_2=\text{C}(\text{Me})$  (f),  $\text{MeO}_2\text{C}(\text{CH}_2)_3$  (g),  
 $\text{Br}(\text{CH}_2)_4$  (h),  $i\text{-Bu}$  (i),  $\text{Me}(\text{CH}_2)_4$  (j))

studies of the reactions of  $Ti^{III}$   $\pi$ -allylic complexes with carboxylic acid chlorides with a view to developing some convenient methods for synthesizing asymmetrical ketones.

Complex I prepared in situ by the interaction of  $Cp_2TiCl_2$  and n-propylmagnesium bromide in the presence of isoprene [5], has been found to react with carboxylic acid chlorides under mild conditions and, as a result, gives high yields of related  $\beta$ ,  $\gamma$ -unsaturated ketones (II) (Table 1).

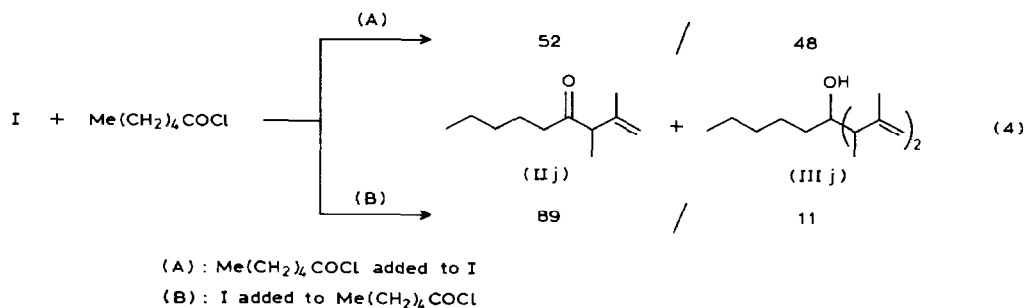
From the data obtained, it was seen that the reactions of I with chlorides of both the aromatic and the aliphatic series proceed with the exclusive involvement of the most-substituted end of the  $\pi$ -allylic system. The similarity in regioselectivities have been observed in reactions of  $Ti^{III}$   $\pi$ -allylic complexes with aldehydes and ketones [3,6,7].

The main side-reaction is the subsequent reaction of an acyldemetallation product with organotitanium reagent to give tertiary alcohol III after the usual work-up with water and ether.

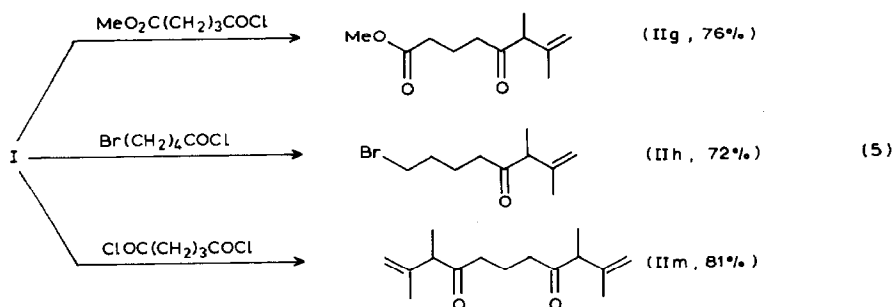


( R = Me (k) , *trans*-PhCH=CH (l) )

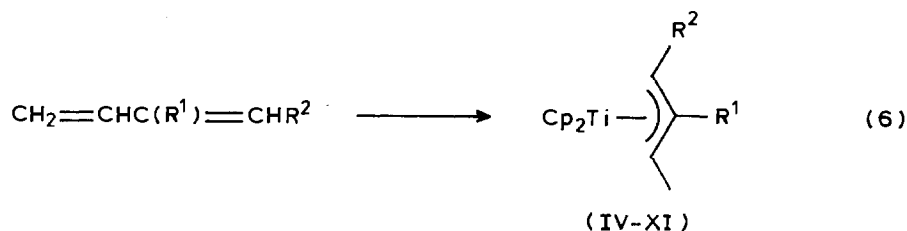
As a whole, the contribution by side-reaction 3 decreases with increase in the spatial hindrance by the initial chloride molecule. When RCOCl are added to solutions of complex I, the ratio of II/III was found to increase along this series of R: Me, *trans*-PhCH=CH < Me(CH<sub>2</sub>)<sub>4</sub> < 2-furyl < i-Bu, PhCH<sub>2</sub> < Ph < i-Pr, CH<sub>2</sub>=C(Me); the only tertiary alcohols (IIIk, l) were obtained from RCOCl in which R = Me, and *trans*-PhCH=CH, and the only asymmetrical ketones (IIe, f) were obtained from those with R = i-Pr, CH<sub>2</sub>=C(Me). In reactions involving the chlorides of acetic, capronic, pyromucic acids, the yields of acyldemetallation products are increased when the order in which the reagents are mixed is changed (solution of I added to that of RCOCl) in the presence of a 1.5-fold excess of chloride.



The reactions of complex I with MeO<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>COCl and Br(CH<sub>2</sub>)<sub>4</sub>COCl favour retention of ester and halide groups of the initial compounds. The reaction of



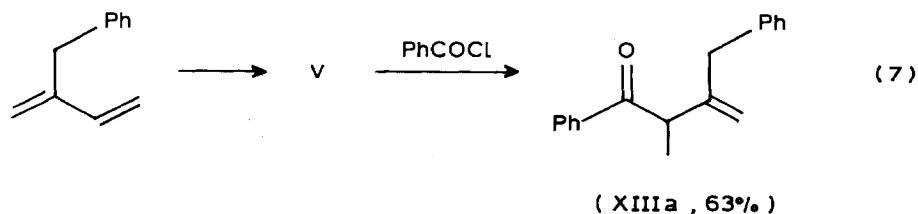
glutaric acid dichloride with two equivalents of I results in the related diketone (IIm).



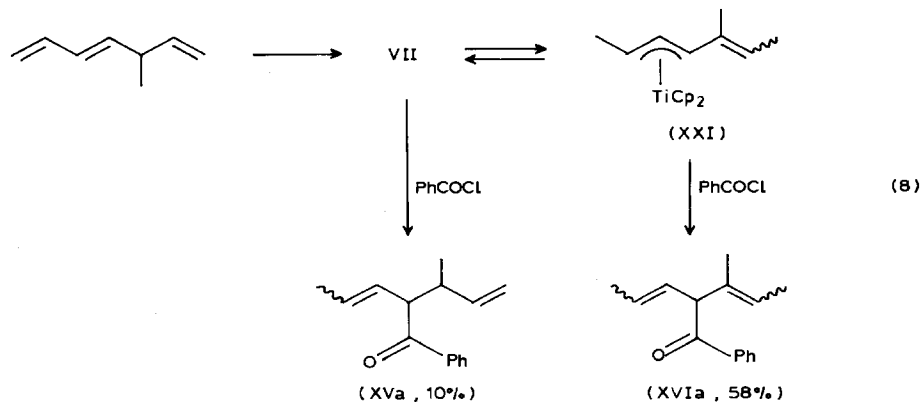
- (IV,  $\text{R}^1 = \text{R}^2 = \text{H}$  ;  
 V,  $\text{R}^1 = \text{CH}_2\text{Ph}$ ,  $\text{R}^2 = \text{H}$  ;  
 VI,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$  ;  
 VII,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{CH}(\text{Me})\text{CH}=\text{CH}_2$  ;  
 VIII,  $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2$ ,  $\text{R}^2 = \text{H}$  ;  
 IX,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{CH}=\text{CH}_2$  ;  
 X,  $\text{R}^1 = \text{SiEt}_2\text{Me}$ ,  $\text{R}^2 = \text{H}$  ;  
 XI,  $\text{R}^1 = \text{CH}_2\text{SiMe}_3$ ,  $\text{R}^2 = \text{H}$  )

In addition to complex I some other  $\pi$ -allylic complexes of  $\text{Ti}^{\text{III}}$ , prepared in situ by hydrotitanation of dienes [5] and trienes [8] under the same conditions as those of eq. 1, have been introduced into the reaction with carboxylic acid chlorides.

$\beta$ , $\gamma$ -Unsaturated ketones (XII-XX) were formed during the reaction of reagents IV-XI with  $\text{RCOCl}$  ( $\text{R} = \text{Ph}$ , i-Pr, i-Bu,  $\text{CH}_2=\text{C}(\text{Me})$ ) under mild conditions (ether,  $20^\circ\text{C}$ , 1 h) to give 50-80% yields and 100% regioselectivity (Table 2) \*.

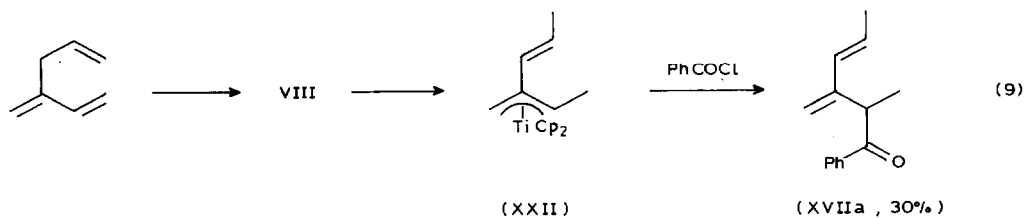


\* GLC analysis data indicate that the amount of tertiary alcohols formed as in eq. 3 does not exceed 5% in each case.

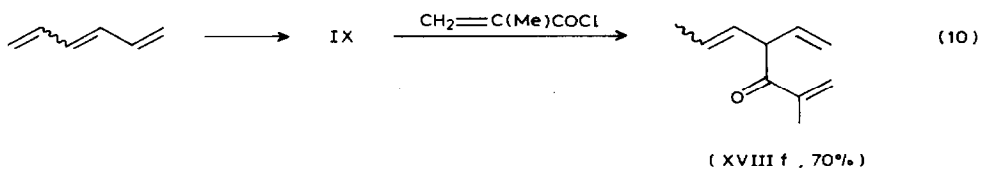


In addition to acyldemetallation products, the reactions of complex VI also gave the "dimerization" product of the initial organometallic compound, i.e. 4,5-dimethyl-2,6-octadiene in 11–34% yields (Table 2, nos. 3, 4).

Reagent VII, during its formation, is partially isomerized into XXI [8] and under the effect of PhCOCl, to give a mixture of two ketones (XVa, XVIa), XVIa without consequence, terminal double bonds being significantly prevalent in that mixture. In contrast to 5-methyl-1,3,6-heptatriene, 2-allyl butadiene is hydrotitanated so as to be transformed completely into the isomerized complex XXII, the reaction of which with PhCOCl gives ketone XVIIa containing a 1,3-diene system, along with the formation of small amount of resin.



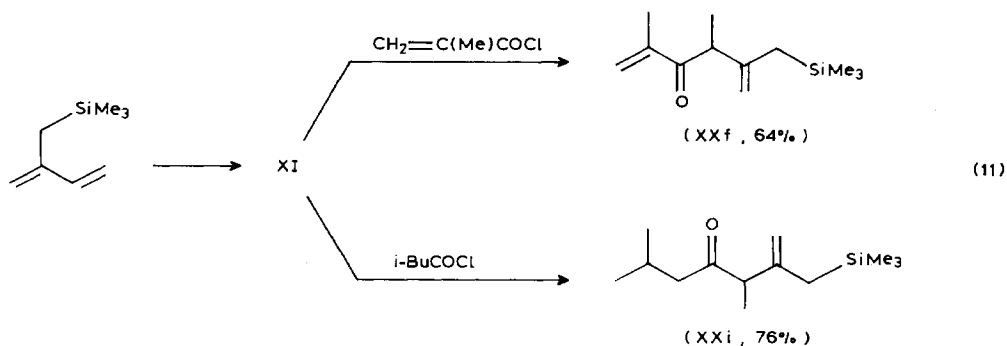
The reaction of organotitanium complex IX prepared from 1,3,5-hexatriene in each case gives only a single regioisomer, inasmuch as both reactive sites of the  $\pi$ -allyl fragments are represented by the secondary carbon atoms.



Analogous regular phenomena have been observed for the complexes VII and XXI (eq. 8).

$\pi$ -Allylic complexes X, XI containing trialkylsilylic substituents react with acid chlorides to form the related organosilicon  $\beta$ ,  $\gamma$ -unsaturated ketones.

It should be noted, that in each case (Tables 1, 2) after reaction was complete, the initial  $\text{Cp}_2\text{TiCl}_2$  was isolated in more than 90% yield after treatment of the reaction



mixture with 4*N* HCl in the presence of air \*.



Thus, acyldemetalation of  $\text{Ti}^{\text{III}}$   $\pi$ -allylic complexes is carried out under mild conditions to give high product yields and, therefore can serve as a convenient route to the various  $\beta$ ,  $\gamma$ -unsaturated ketones immediately from dienes (trienes) and carboxylic acid chlorides.

### Experimental

2-Benzyl- and 2-allyl butadienes were prepared by the reaction of  $\text{CH}_2=\text{C}(\text{MgCl})-\text{CH}=\text{CH}_2$  with  $\text{PhCH}_2\text{Cl}$  and  $\text{CH}_2=\text{CHCH}_2\text{Br}$  [9]. 2-(Methyldiethylsilyl)butadiene

(Continued on p. 30)

Table 1

Reactions of complex I with  $\text{RCOCl}$  (ether, 20 °C, 1 h)

R	Reaction conditions <sup>a</sup>	II/III <sup>b</sup>	Compound	Yield (%) <sup>c</sup>
Ph	A	95/5	IIa	86
PhCH <sub>2</sub>	A	90/10	IIb	84
2-furyl	A	73/27	IIIc	20 <sup>d</sup>
2-furyl	B	93/7	IIc	66
3-pyridyl	A	- <sup>e</sup>	IId	63
i-Pr	A	100/0	IIf	75
CH <sub>2</sub> =C(Me)	A	100/0	IIe	70
MeO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub>	B	100/0	IIg	76
Br(CH <sub>2</sub> ) <sub>4</sub>	B	100/0	IIh	72
i-Bu	A	90/10	IIi	79
i-Bu	B	100/0	IIj	30 <sup>d</sup>
Me(CH <sub>2</sub> ) <sub>4</sub>	A	52/48	IIk	80
Me(CH <sub>2</sub> ) <sub>4</sub>	B	89/11	IIl	48 <sup>d</sup>
Me	A	0/100	IIm	30 <sup>d</sup>
Me	B	50/50	IIn	42 <sup>d</sup>
<i>trans</i> -PhCH=CH	A	0/100	III	42 <sup>d</sup>

<sup>a</sup> A:  $\text{RCOCl}$  was added to I solution,  $\text{RCOCl}/\text{I}=1/1$ ; B: a solution of I was slowly added to one of  $\text{RCOCl}$  one,  $\text{RCOCl}/\text{I}=1.5/1$ . <sup>b</sup> II/III mole ratio was found with GLC method. <sup>c</sup> Yields of isolated products are given. <sup>d</sup> Yield calculated for the initial  $\text{RCOCl}$ . <sup>e</sup> II/III ratio was not determined.

\* With the exception of reactions as in eq. 11, in which the treatment with acid was impossible owing to likely desilylation.

Table 2

Reactions of titanium(III)  $\pi$ -allylic complexes with RCOCl (ether, 20 °C, 1 h, RCOCl/complex = 1/1) <sup>a</sup>

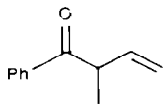
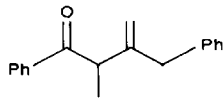
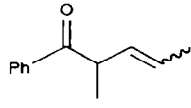
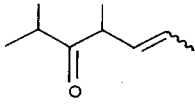
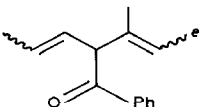
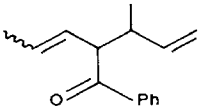
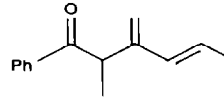
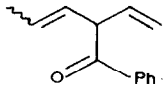
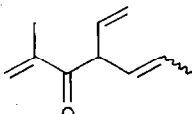
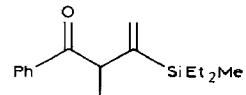
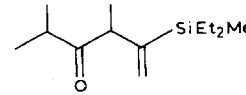
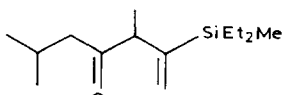
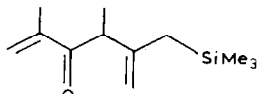
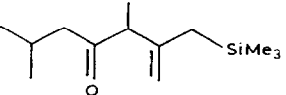
Initial diene (triene)	Complex	R	Reaction product	Yield (%) <sup>b</sup>
Butadiene	IV	Ph	 (XIIa)	81
2-Benzyl-butadiene	V	Ph	 (XIIIa)	63
Piperylene (E/Z = 93/7)	VI	Ph	 (XIVa) (E/Z ~ 1/1) <sup>c</sup>	51 34 <sup>d</sup>
Piperylene (E/Z = 93/7)	VI	i-Pr	 (XIVE) (E/Z ~ 1/1) <sup>c</sup>	77 11 <sup>d</sup>
<i>Trans</i> -5-methyl- 1,3,6-heptatriene	VII	Ph	 (XVIa)	58
			 (XVa)	10
2-Allylbutadiene	VIII	Ph	 (XVIIa)	30 <sup>f</sup>

Table 2 (continued)

Initial diene (triene)	Complex	R	Reaction product	Yield (%) <sup>b</sup>
1,3,5-Hexatriene ( <i>E/Z</i> = 65/35)	IX	Ph	 (XVIII a) ( <i>E/Z</i> ~ 3/2) <sup>c</sup>	80
1,3,5-Hexatriene ( <i>E/Z</i> = 65/35)	IX	CH <sub>2</sub> =C(Me)	 (XVIII f) ( <i>E/Z</i> ~ 3/2) <sup>c</sup>	70
CH <sub>2</sub> =C(SiEt <sub>2</sub> Me)CH=CH <sub>2</sub>	X	Ph	 (XIX a)	70
CH <sub>2</sub> =C(SiEt <sub>2</sub> Me)CH=CH <sub>2</sub>	X	i-Pr	 (XIX e)	68
CH <sub>2</sub> =C(SiEt <sub>2</sub> Me)CH=CH <sub>2</sub>	X	i-Bu	 (XIX i)	73
CH <sub>2</sub> =C(CH <sub>2</sub> SiMe <sub>3</sub> )CH=CH <sub>2</sub>	XI	CH <sub>2</sub> =C(Me)	 (XX f)	64
CH <sub>2</sub> =C(CH <sub>2</sub> SiMe <sub>3</sub> )CH=CH <sub>2</sub>	XI	i-Bu	 (XX i)	76

<sup>a</sup> RCOCl was added to the solution of a complex in each experiment. <sup>b</sup> Yields of isolated products.

<sup>c</sup> According to NMR spectral data. <sup>d</sup> Yield of [MeCH=CHCH(Me)]<sub>2</sub>. <sup>e</sup> Mixture of stereoisomers.

<sup>f</sup> Pronounced gumming.

was obtained from the reaction of 1,4-dichlorobut-2-yn and methyl-diethylsilane [10]. 2-(Trimethylsilylmethyl)butadiene was synthesized with chloroprene effected by  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  in the presence of  $\text{NiCl}_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$  [11]. *Trans*-5-methyl-1,3,6-heptatriene [12], 1,3,5-hexatriene (*E/Z* = 65/35) [13], bis(cyclopentadienyl)titanium dichloride [14], and carboxylic acid chlorides were prepared by standard procedures. All reactions were carried out under dry argon. Ether was dried over  $\text{LiAlH}_4$  immediately before use.

The samples were separated on a "Chrom-5" chromatograph with a flame-ionization detector, carrier gas He (50 ml/min); 1.2 m  $\times$  3 mm column, 5% SE-30 on Inerton-super. For the preparative separation of regioisomers, a Perkin-Elmer F-21 preparative chromatograph was used with He as carrier gas (300 ml/min) and 5 m  $\times$  8 mm column, 5% SE-30 on NAW chromaton. PMR spectra were recorded on a Tesla BS-567 (100 MHz) and Tesla BS-467 (60 MHz) spectrometers.  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FX-90Q spectrometer, with TMS as the internal standard. IR spectra were detected on UR-20 device with a thin layer of the sample. Mass spectra were recorded with an MX-1306 spectrometer with a lapping cylinder temperature of 100°C and ionization energies of 70 and 12 eV.

*Synthesis of  $\beta,\gamma$ -unsaturated ketones by the reaction of  $\pi$ -allylic complexes of  $\text{Ti}^{\text{III}}$  with carboxylic acid chlorides*

A solution of *n*-propylmagnesium bromide in 2.13 ml (3.2 mmol) of 1.5 *M* ether was added to 0.4 g (1.6 mmol) of a  $\text{Cp}_2\text{TiCl}_2$  suspension in 8 ml of ether with a 1.92–2.4 mmol content of freshly distilled diene (triene) under stirring and cooling to 0°C. The mixture was stirred for 2 h at 20°C, and then boiled for 0.5 h. Carboxylic acid chloride (1.6 mmol) was added to the prepared solution of  $\text{Ti}^{\text{III}}$   $\pi$ -allylic complex (or a solution of  $\pi$ -allylic complex was added dropwise to a solution of the chloride (2.4 mmol) in 5 ml of ether during 15 min. The reaction mixture was kept for 1 h at 20°C. After hydrolysis with 4*N* HCl (10 ml), the reaction mixture was stirred for 0.5 h in the presence of air, filtered to remove the precipitated  $\text{Cp}_2\text{TiCl}_2$ , and extracted with ether (3  $\times$  7 ml). The ether layer was washed with water (3  $\times$  7 ml), dried with  $\text{MgSO}_4$ , concentrated, and subjected to GLC. The reaction products were isolated by column chromatography on silica gel and were identified from their IR and NMR spectra.

The reactions of complexes I, IV–XI with  $\text{RCOCl}$  were carried out by the procedure described ( $\text{R} = \text{Ph}$ , 2-furyl-3-pyridyl,  $\text{PhCH}_2$ , *i*-Pr,  $\text{CH}_2=\text{CH}(\text{Me})$ , *i*-Bu,  $\text{Me}(\text{C}_2\text{H}_4)_4$  Me,  $\text{MeO}_2\text{C}(\text{CH}_2)_3$ ,  $\text{Br}(\text{CH}_2)_4$ ,  $\text{ClCO}(\text{CH}_2)_3$ , *trans*- $\text{PhCH}=\text{CH}$ ) (Tables 1, 2).

In the reaction of complex I with nicotiny chloride, the addition of 4*N* HCl and separation of  $\text{Cp}_2\text{TiCl}_2$  was followed by the neutralization of the aqueous layer with 10 ml of  $\text{NaHCO}_3$  saturated solution and subsequently extracted with ether (5  $\times$  7 ml); the ether layer was treated as described above.

*1-Phenyl-2,3-dimethyl-3-buten-1-one (IIa)*. 0.239 g (86%) isolated,  $R_f$  0.51 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.15 (d, 3H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.73 (s, 3H,  $\text{CH}_3\text{C}=\text{C}$ ), 4.1(q, 1H,  $J$  7 Hz), 4.87(m, 2H,  $\text{CH}_2=\text{C}$ ), 7.1–7.55 and 7.8–8.1(m, 5H arom.). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3085, 3045, 1695, 1650, 1610, 1510, 920, 760, 700. Mass spectrum ( $m/z$ ): 174 [ $M^+$ ].

*1-Phenyl-3,4-dimethyl-4-penten-2-one (IIb)*. 0.253 g (84%) isolated,  $R_f$  0.51 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.12 (d, 3H,  $\text{CH}_3$ ,  $J$  7 Hz),



1.61(s, 3H, CH<sub>3</sub>C=), 3.32(q, 1H, CH, *J* 7 Hz), 3.7(s, 2H, CH<sub>2</sub>Ph), 4.9(m, 2H, CH<sub>2</sub>=), 7.21 (m, 5H arom.). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3080, 3040, 1710, 1640, 1600, 1500, 910, 720, 690. Mass spectrum (*m/z*): 188 [*M*<sup>+</sup>].

*1-(2-Furyl)-2,3-dimethyl-3-buten-1-one (IIc)*. 0.173 g (66%) isolated, *R<sub>f</sub>* 0.48 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.23 (d, 3H, CH<sub>3</sub>, *J* 7 Hz), 1.71 (s, 3H, CH<sub>3</sub>C=), 3.91 (q, 1H, CH, *J* 7 Hz), 4.83 (m, 2H, CH<sub>2</sub>=), 6.35–6.6 and 7.0–7.7 (m, 3H of furane ring). IR spectrum ( $\nu$ (cm<sup>-1</sup>)): 3145, 3090, 1680, 1650, 1570, 1480, 900, 780. Mass spectrum (*m/z*): 164 [*M*<sup>+</sup>].

*1-(3-Pyridyl)-2,3-dimethyl-3-buten-1-one (II d)*. 0.176 g (63%) isolated, *R<sub>f</sub>* 0.32 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.35 (d, 3H, CH<sub>3</sub>, *J* 7 Hz), 1.73 (s, 3H, CH<sub>3</sub>C=), 4.1 (q, 1H, CH, *J* 7 Hz), 4.9 (m, 2H, CH<sub>2</sub>=), 7.2–7.5, 8.1–8.4, 8.5–8.9, 9.2 (m, 4H of pyridine ring). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3070, 3035, 1690, 1640, 1585, 1460, 900, 780, 735, 705. Mass spectrum (*m/z*): 175 [*M*<sup>+</sup>].

*2,4,5-Trimethyl-5-hexen-3-one (IIe)*. 0.168 g (75%) isolated, *R<sub>f</sub>* 0.45 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 0.95 and 1.0 (d, 6H, CH<sub>3</sub>, *J* 7 Hz), 1.08 (d, 3H, CH<sub>3</sub>CC=, *J* 7 Hz), 1.62 (s, 3H, CH<sub>3</sub>C=), 2.75 (qq, 1H, CH, *J*<sub>1</sub> = *J*<sub>2</sub> = 7 Hz), 3.3 (q, 1H, CH=, *J* 7 Hz), 4.8 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 1710, 1640, 910. Mass spectrum (*m/z*): 140 [*M*<sup>+</sup>].

*2,4,5-Trimethyl-1,5-hexadien-3-one (II f)*. 0.155 g (70%) isolated, *R<sub>f</sub>* 0.43 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.15 (d, 3H, CH<sub>3</sub>, *J* 6 Hz), 1.65 (s, 3H, CH<sub>3</sub>C=), 1.83 (s, 3H, =C(CH<sub>3</sub>)CO), 3.82 (q, 1H, CH, *J* 6 Hz), 4.75 (m, 2H, CH<sub>2</sub>=), 5.63 and 5.92 (m, 2H, CH<sub>2</sub>=CCO). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 1680, 1640, 900. Mass spectrum (*m/z*): 138 [*M*<sup>+</sup>].

*1-Carbomethoxy-5,6-dimethyl-6-hepten-4-one (II g)*. 0.241 g (76%) isolated, *R<sub>f</sub>* 0.23 (hexane/ether = 3/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.15 (d, 3H, CH<sub>3</sub>, *J* 7 Hz), 1.66 (s, 3H, CH<sub>3</sub>C=), 1.7–2.7 (m, 6H, CH<sub>2</sub>), 3.23 (q, 1H, CH, *J* 7 Hz), 3.68 (s, 3H, CH<sub>3</sub>O), 4.91 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3090, 1735, 1710, 1645, 910. Mass spectrum (*m/z*): 198 [*M*<sup>+</sup>].

*8-Bromo-2,3-dimethyl-1-octen-4-one (II h)*. 0.269 g (72%) isolated, *R<sub>f</sub>* 0.40 (hexane/ether = 3/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.15 (d, 3H, CH<sub>3</sub>, *J* 7 Hz), 1.66 (s, 3H, CH<sub>3</sub>C=), 1.65–2.0 (m, 4H, CH<sub>2</sub>), 2.47 (t, 2H, CH<sub>2</sub>CO, *J* 6 Hz), 3.23 (q, 1H, CH, *J* 7 Hz), 3.37 (t, 2H, CH<sub>2</sub>Br, *J* 6.5 Hz), 4.89 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3070, 1705, 1640, 900, 730. Mass-spectrum (*m/z*): 233 [*M*<sup>+</sup>].

*2,3,6-Trimethyl-1-hepten-4-one (II i)*. 0.194 g (79%) isolated, *R<sub>f</sub>* 0.45 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 0.8–1.5 (m, 7H, (CH<sub>3</sub>)<sub>2</sub>CH), 1.1 (d, 3H, CH<sub>3</sub>CC=, *J* 6.5 Hz), 1.63 (s, 3H, CH<sub>3</sub>C=), 2.23 (m, 2H, CH<sub>2</sub>), 3.1 (q, 1H, CHC=, *J* 6.5 Hz), 4.82 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 154 [*M*<sup>+</sup>].

*2,3-Dimethyl-1-nonen-4-one (II j)*. 0.214 g (80%) isolated, *R<sub>f</sub>* 0.41 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$  (ppm)): 1.1 (d, 3H, CH<sub>3</sub>, *J* 7 Hz), 0.85–1.55 (m, 9H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 1.63 (s, 3H, CH<sub>3</sub>C=), 2.33 (m, 2H, CH<sub>2</sub>CO), 3.15 (q, 1H, CH, *J* 7 Hz), 4.87 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 168 [*M*<sup>+</sup>].

*3,4-Dimethyl-4-penten-2-one (II k)*. 0.054 g (30%) isolated, *R<sub>f</sub>* 0.40 (hexane/ether = 7/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.12 (d, 3H, CH<sub>3</sub>, *J* 6.5 Hz), 1.63 (s, 3H, CH<sub>3</sub>C=), 2.06 (s, 3H, CH<sub>3</sub>CO), 3.1 (q, 1H, CH, *J* 6.5 Hz), 4.85 (m, 2H, CH<sub>2</sub>=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 1715, 1635, 900. Mass spectrum (*m/z*): 112 [*M*<sup>+</sup>].

*2,3,9,10-Tetramethyl-1,10-undecadien-4,8-dione (II m)*. 0.306 g (81%) isolated, *R<sub>f</sub>*

0.23 (hexane/ether = 3/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.07 (d, 6H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.57 (s, 6H,  $\text{CH}_3\text{C}=\text{C}$ ), 1.67 (tt, 2H,  $\text{CH}_2$ ,  $J_1 = J_2 = 7$  Hz), 2.38 (t, 4H,  $\text{CH}_2\text{CO}$ ,  $J$  7 Hz), 3.11 (q, 2H, CH,  $J$  7 Hz), 4.77 (m, 2H,  $\text{CH}_2=\text{C}$ ). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3065, 1710, 1640, 900. Mass spectrum ( $m/z$ ): 236 [ $M^+$ ].

*Bis(3-methyl-3-buten-2-yl)-2-furylcarbinol (IIIc)*. 0.075 g (20%) isolated,  $R_f$  0.55 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.13 and 1.23 (d, 6H,  $\text{CH}_3$ ,  $J$  6.5 Hz), 1.46 (s, 6H,  $\text{CH}_3\text{C}=\text{C}$ ), 2.63 and 2.82 (q, 2H, CH,  $J$  6.5 Hz), 2.37 (s, 1H, OH), 4.4–4.85 (m, 4H,  $\text{CH}_2=\text{C}$ ), 5.9–6.2 and 7.2 (m, 3H of furan ring). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3530, 3145, 3090, 1650, 1600, 1510, 900, 820, 750. Mass spectrum ( $m/z$ ): 234 [ $M^+$ ].

*Bis(3-methyl-3-buten-2-yl)amylcarbinol (IIIj)*. 0.114 g (30%) isolated,  $R_f$  0.49 (hexane/ether = 10/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 0.85–1.55 (m, 11H,  $\text{CH}_3(\text{CH}_2)_4$ ), 1.0 and 1.66 (d, 6H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.78 (m, 6H,  $\text{CH}_3\text{C}=\text{C}$ ), 2.1–2.6 (m, 2H, CH), 4.6–5.0 (m, 4H,  $\text{CH}_2=\text{C}$ ). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3500, 3085, 1635, 900. Mass spectrum ( $m/z$ ): 238 [ $M^+$ ].

*Bis(3-methyl-3-buten-2-yl)methylcarbinol (IIIk)*. 0.14 g (48%) isolated,  $R_f$  0.48 (hexane/ether = 7/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.0 and 1.05 (d, 6H,  $\text{CH}_3$ ,  $J$  7.5 Hz), 1.0 (s, 3H,  $\text{CH}_3\text{C}(\text{OH})$ ), 1.8 (m, 6H,  $\text{CH}_3\text{C}=\text{C}$ ), 2.1–2.6 (m, 2H, CH), 4.6–5.0 (m, 4H,  $\text{CH}_2=\text{C}$ ). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3450, 3080, 1640, 900. Mass spectrum ( $m/z$ ): 182 [ $M^+$ ].

*Trans-bis(3-methyl-3-buten-2-yl)- $\beta$ -styrylcarbinol (IIII)*. 0.181 g (42%) isolated,  $R_f$  0.34 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta$  (ppm)): 1.1 (d, 6H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.67 (s, 6H,  $\text{CH}_3\text{C}=\text{C}$ ), 2.55 and 2.62 (q, 2H, CH,  $J$  7 Hz), 4.5–4.95 (m, 4H,  $\text{CH}_2=\text{C}$ ), 6.2 and 6.38 (d, 2H,  $\text{CH}=\text{C}$ ,  $J_{\text{AB}}$  20 Hz), 7.18 (m, 5H arom.). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3450, 3070, 3030, 1640, 1600, 1500, 960, 900, 740, 690. Mass spectrum ( $m/z$ ): 270 [ $M^+$ ].

*1-Phenyl-2-methyl-3-buten-1-one (XIIa)*. 0.207 g (81%) isolated,  $R_f$  0.50 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.32 (d, 3H,  $\text{CH}_3$ ,  $J$  6.5 Hz), 4.15 (dq, 1H, CH,  $J_1 = J_2 = 6.5$  Hz), 4.9–5.35 (m, 2H,  $\text{CH}_2=\text{C}$ ), 5.6–6.3 (m, 1H,  $\text{CH}=\text{C}$ ), 7.2–7.6 and 7.85–8.1 (m, 5H arom.). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3070, 1680, 1640, 1600, 1580, 1010, 920, 730, 690. Mass spectrum ( $m/z$ ): 160 [ $M^+$ ].

*1-Phenyl-2-methyl-3-benzyl-3-buten-1-one (XIIIa)*. 0.252 g (63%) isolated,  $R_f$  0.38 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 1.3 (d, 3H,  $\text{CH}_3$ ,  $J$  7 Hz), 3.38 (s, 2H,  $\text{CH}_2$ ), 4.0 (q, 1H, CH,  $J$  7 Hz), 4.87 (m, 2H,  $\text{CH}_2=\text{C}$ ), 7.05–7.45 and 7.6–7.8 (m, 10H arom.). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3060, 3015, 1680, 1640, 1600, 1580, 1495, 905, 730, 700. Mass spectrum ( $m/z$ ): 250 [ $M^+$ ].

*1-Phenyl-2-methyl-3-penten-1-one (XIVa) ( $E/Z = 1/1$ )*. 0.142 g (51%) isolated,  $R_f$  0.51 (hexane/ether = 4/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta$  (ppm)): 1.26 (d, 3H,  $\text{CH}_3$ ,  $J$  6.5 Hz), 1.63 and 1.72 ( $d^{*,*}$ , 3H,  $\text{CH}_3\text{C}=\text{C}$ ,  $J$  6.5 Hz), 3.8–4.55 (m, 1H, CH), 5.35–6.0 (m, 2H,  $\text{CH}=\text{C}$ ), 7.15–7.6 and 7.85–8.15 (m, 5H arom.). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3070, 3030, 1680, 1640, 1595, 1480, 965, 740, 690. Mass spectrum ( $m/z$ ): 174 [ $M^+$ ].

*2,4-Dimethyl-5-hepten-3-one (XIVe) ( $E/Z = 1/1$ )*. 0.172 g (77%) isolated,  $R_f$  0.45 (hexane/ether = 10/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta(\text{ppm})$ ): 0.95–1.2 (m, 9H,  $\text{CH}_3$ ), 1.68 and 1.75 ( $d^*$ , 3H,  $\text{CH}_3\text{C}=\text{C}$ ,  $J$  6.5 Hz), 2.5–2.95 (m, 1H, CH), 3.15–3.7

\* Signals were assigned to various stereoisomers.

(m, 1H, CHC=), 5.35–6.0 (m, 2H, CH=). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3090, 1700, 1625, 960. Mass spectrum ( $m/z$ ): 140 [ $M^+$ ].

*1-Phenyl-2-propenyl-3-methyl-4-penten-1-one (XVa)*. 0.034 g (10%) isolated,  $R_f$  0.41 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$  (ppm)): 0.99 and 1.04 (d\*, 3H, CH<sub>3</sub>,  $J$  7 Hz), 1.65 and 1.68 (d\*, 3H, CH<sub>3</sub>C=,  $J$  5 Hz), 2.78 (ddq, 1H, CH,  $J_1 = J_2 = J_3 = 7$  Hz), 3.88 (dd, 1H, CHCO,  $J_1$  7,  $J_2$  8.5 Hz), 4.8–5.1 (m, 2H, CH<sub>2</sub>=), 5.45–6.0 (m, 3H, CH=), 7.3–7.6 and 7.9–8.05 (m, 5H arom.). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3090, 3045, 1675, 1600, 1450, 990, 960, 910, 720, 700. Mass spectrum ( $m/z$ ): 214 [ $M^+$ ].

*1-Phenyl-2-propenyl-3-methyl-3-penten-1-one (XVIa)*. 0.199 g (58%) isolated,  $R_f$  0.41 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$  (ppm)): 1.67 (m, 9H, CH<sub>3</sub>), 4.55 and 4.93 (d\*, 1H, CH,  $J$  5 Hz), 5.2–5.7 (m, 3H, CH=), 7.3–7.6 and 7.9–8.05 (m, 5H arom.). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3085, 3045, 1680, 1600, 1450, 960, 840, 730, 690. Mass spectrum ( $m/z$ ): 214 [ $M^+$ ].

*Trans-1-phenyl-2-methyl-3-methylen-4-hexen-1-one (XVIIa)*. 0.096 g (30%) isolated,  $R_f$  0.40 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.35 (d, 3H, CH<sub>3</sub>,  $J$  6 Hz), 1.83 (d, 3H, CH<sub>3</sub>C=,  $J$  5.5 Hz), 4.3 (q, 1H, CH,  $J$  6 Hz), 4.7–5.05 (m, 2H, CH<sub>2</sub>=), 5.5–6.4 (m, 2H, CH=), 7.25–7.6 and 7.8–8.1 (m, 5H arom.). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3060, 3025, 1680, 1635, 1600, 1450, 990, 975, 920, 700. Mass spectrum ( $m/z$ ): 200 [ $M^+$ ].

*1-Phenyl-2-vinyl-3-penten-1-one (XVIIIa) (E/Z = 3/2)*. 0.238 g (80%) isolated,  $R_f$  0.40 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.68 and 1.73 (d\*, 3H, CH<sub>3</sub>,  $J$  5 Hz), 4.4–5.25 (m, 3H, CH<sup>+</sup>=CH<sub>2</sub>), 5.9–6.3 (m, 3H, CH=), 7.2–7.5 and 7.75–8.0 (m, 5H arom.). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>,  $\delta$ (ppm)): 18.08(q), 55.03(d), 116.91(t), 128.50(d), 128.11(d), 128.66(d), 132.94(s), 136.23(d), 199.12(s) (*E*-isomer); 13.25(q), 50.33(d), 116.62(t), 126.83(d), 127.09(d), 128.50(d), 128.66(d), 132.94(s), 135.45(d), 199.12(s). (*Z*-isomer). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3080, 3030, 1680, 1640, 1600, 1460, 990, 970, 910, 730, 690. Mass spectrum ( $m/z$ ): 186 [ $M^+$ ].

*2-Methyl-4-vinyl-1,5-heptadien-3-one (XVIIIIf) (E/Z = 3/2)*. 0.168 g (70%) isolated,  $R_f$  0.39 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 1.67 and 1.72 (d\*, 3H, CH<sub>3</sub>,  $J$  5.5 Hz), 1.85 (s, 3H, CH<sub>3</sub>CCO), 4.28 and 4.63 (dd\*, 1H, CH,  $J_1 = J_2 = 6$  Hz), 4.75–5.15 (m, 2H, CH<sub>2</sub>=), 5.4–6.1 (m, 5H, CH= + CH<sub>2</sub>=CMe). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>,  $\delta$  (ppm)): 17.89(q), 54.05(d), 116.26(t), 125.00(t), 128.01(d), 128.34(d), 136.43(d), 143.48(s), 200.72(s) (*E*-isomer); 12.99(q), 17.89(q), 49.28(d), 116.00(t), 124.74(t), 126.12(d), 127.35(d), 135.78(d), 143.48(s), 200.72(s) (*Z*-isomer). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 1675, 1630, 995, 970, 915, 860. Mass spectrum ( $m/z$ ): 150 [ $M^+$ ].

*1-Phenyl-2-methyl-3-(methyldiethylsilyl)-3-buten-1-one (XIXa)*. 0.291 g (70%) isolated,  $R_f$  0.45 (hexane/ether = 4/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 0.03 (s, 3H, CH<sub>3</sub>Si), 0.5–1.2 (m, 10H, CH<sub>3</sub>CH<sub>2</sub>Si), 1.2 (d, 3H, CH<sub>3</sub>,  $J$  7 Hz), 4.07 (q, 1H, CH,  $J$  7 Hz), 5.37 and 5.53 (d, 2H, CH<sub>2</sub>=,  $J_{AB}$  2.5 Hz), 7.2–7.45 and 7.6–7.9 (m, 5H arom.). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3050, 1680, 1600, 1450, 1260, 920, 800, 730, 690. Mass spectrum ( $m/z$ ): 260 [ $M^+$ ].

*2,4-Dimethyl-5-(methyldiethylsilyl)-5-hexen-3-one (XIXe)*. 0.246 g (68%) isolated,  $R_f$  0.40 (hexane/ether = 10/1). PMR spectrum (CCl<sub>4</sub>,  $\delta$ (ppm)): 0.03 (s, 3H, CH<sub>3</sub>Si), 0.5–1.2 (m, 19H, CH<sub>3</sub> + CH<sub>2</sub>), 2.5 (qq, 1H, CH,  $J_1 = J_2 = 7$  Hz), 3.3 (q, 1H, CHC=,  $J$  7 Hz), 5.37 and 5.53 (d, 2H, CH<sub>2</sub>=,  $J_{AB}$  3 Hz). IR spectrum ( $\nu$  (cm<sup>-1</sup>)): 3065, 1710, 1260, 920, 800. Mass spectrum ( $m/z$ ): 226 [ $M^+$ ].

*2-(Methyldiethylsilyl)-3,6-dimethyl-1-hepten-4-one (XIXi)*. 0.28 g (73%) isolated,  $R_f$  0.40 (hexane/ether = 10/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta$  (ppm)): 0.03 (s, 3H,  $\text{CH}_3\text{Si}$ ), 0.5–1.2 (m, 20H,  $\text{CH}_3 + \text{CH}_2 + \text{CH}$ ), 2.23 (m, 2H,  $\text{CH}_2\text{CO}$ ), 3.3 (q, 1H,  $\text{CHC=}$ ,  $J$  7 Hz), 5.36 and 5.54 (d, 2H,  $\text{CH}_2=$ ,  $J_{\text{AB}}$  3 Hz). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3065, 1710, 1260, 910, 800. Mass spectrum ( $m/z$ ): 240 [ $M^+$ ].

*2,4-Dimethyl-5-methylene-6-trimethylsilyl-1-hexen-3-one (XXf)*. 0.215 g (64%) isolated,  $R_f$  0.38 hexane/ether = 10/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta$ (ppm)): 0.01 (s, 9H,  $\text{CH}_3\text{Si}$ ), 1.1 (d, 3H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.42 (s, 2H,  $\text{CH}_2$ ), 1.79 (s, 3H,  $\text{CH}_3\text{C=}$ ), 3.67 (q, 1H,  $\text{CH}$ ,  $J$  7 Hz), 4.61 (m, 2H,  $\text{CH}_2=$ ), 5.6 and 5.85 (m, 2H,  $\text{CH}_2=\text{CCO}$ ). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3060, 1675, 1625, 1260, 890, 850. Mass spectrum ( $m/z$ ): 210 [ $M^+$ ].

*1-Trimethylsilyl-2-methylene-3,6-dimethylheptan-4-one (XXi)*. 0.275 g (76%) isolated,  $R_f$  0.40 (hexane/ether = 10/1). PMR spectrum ( $\text{CCl}_4$ ,  $\delta$ (ppm)): 0.01 (s, 9H,  $\text{CH}_3\text{Si}$ ), 0.75–1.0 (m, 7H,  $(\text{CH}_3)_2\text{CH}$ ), 1.05 (d, 3H,  $\text{CH}_3$ ,  $J$  7 Hz), 1.4 (s, 2H,  $\text{CH}_2\text{Si}$ ), 2.15 (m, 2H,  $\text{CH}_2$ ), 2.88 (q, 1H,  $\text{CH}$ ,  $J$  7 Hz), 4.65 (m, 2H,  $\text{CH}_2=$ ). IR spectrum ( $\nu$  ( $\text{cm}^{-1}$ )): 3060, 1710, 1640, 1260, 890, 850. Mass spectrum ( $m/z$ ): 226 [ $M^+$ ].

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