Journal of Organometallic Chemistry, 359 (1989) 255–266
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Rhodium-catalyzed isomerization of 1,3-diene monoepoxides to α,β-unsaturated carbonyl compounds

Susumu Sato, Isamu Matsuda *, and Yusuke Izumi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464 (Japan)

(Received May 13th, 1988)

Abstract

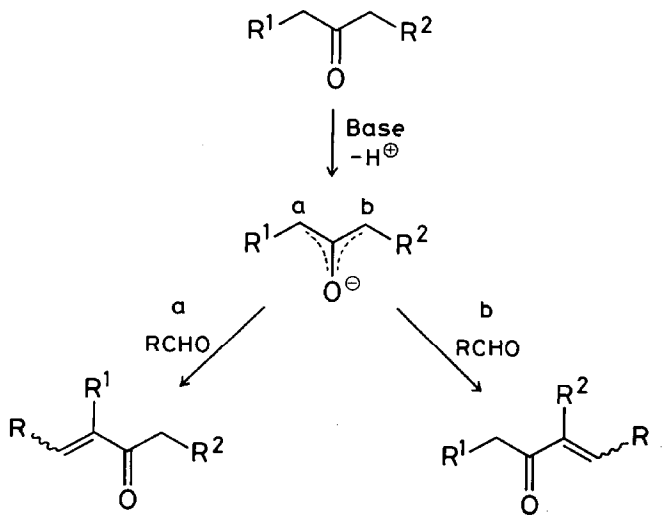
α,β-Unsaturated aldehydes and ketones are readily formed by the rhodium(I) catalyzed isomerization of 1,3-diene monoepoxides. When $RhH(PPh_3)_4$ is used as a catalyst, only (*E*)-α,β-unsaturated carbonyl compounds are obtained selectively. The initial 1,3-diene monoepoxides are prepared regiospecifically from α-trimethylsilyl ketones by a two step procedure, bromination and subsequent vinylative epoxidation of resulting α-bromo ketones. The overall transformation from α-trimethylsilyl ketones to α,β-enones is formally regarded as an equivalent of the regiospecific aldol condensation, and also enables the use of unsymmetrically substituted ketones as an enolate source. The significance of the isomerization as a key step in the synthesis of *ar*-turmerone is described.

Introduction

A regio- and stereoselective synthesis of α,β-unsaturated carbonyl compounds is attractive and desirable for some organic syntheses. Cross-aldol condensation of enolate anions with carbonyl compounds is one of the most useful tools for making these skeletons. However, the concurrent formation of the regio-isomers often presents a serious problem in unsymmetrically substituted ketones because the regiocontrol is not complete in the formation of enolate anions [1] (Scheme 1). Thus, a number of intriguing methods have been devised for the regio- and stereo-controlled synthesis of α,β-enones [2–8].

We reported recently several rhodium(I) catalyzed reactions, such as the isomerization of β-trimethylsilylallyl alcohols [9], the transfer-dehydrogenation of β-trimethylsilyl alcohols [9b,10], and the coupling reaction of vinyl ketones with aldehydes [11]. In these reactions, it is suggested that the starting step is a Michael-type addition of Rh–H to an α,β-enone to form a rhodium enolate. These observations prompted us to investigate the interaction of rhodium(I) hydride complexes with 1,3-diene monoepoxide (**3**) as an analogue of the α,β-enones.

0022-328X/89/$03.50



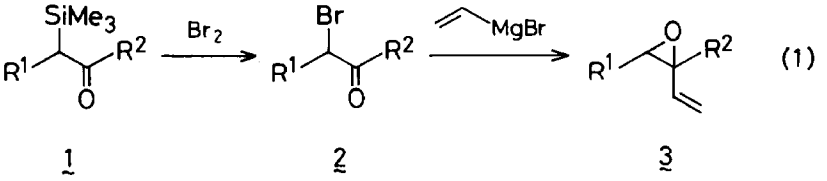
Scheme 1.

We report here a novel regio- and stereo-controlled synthesis of the α,β-enones. The process entails the regiodefined formation of 1,3-diene monoepoxides from α-bromo ketones and the subsequent rhodium catalyzed rearrangement of these compounds to α,β-enones under neutral conditions.

Results and discussion

Preparation of 1,3-diene monoepoxides (3) from α-bromo ketones (2)

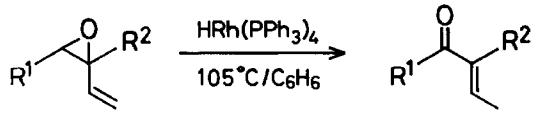
A general route to **3** is illustrated in eq. 1. Although easy access to α-trimethylsilyl ketones (**1**) is required fortunately we have found a unique and regiodefined route to **1** [9]. The regiospecific formation of **2** has been achieved by direct bromination of **1** [12]. Thus, subsequent reactions of a vinyl carbanion with **2** proceeded in a one-pot procedure to give **3** in moderate yields, which all could be purified by chromatography and distillation. The results are summarized in Table 1.



1 2 3

Catalytic rearrangement of 1,3-diene monoepoxide

Isomerization of 3,4-epoxy-1-dodecene (**3j**) was catalyzed by $RhH(PPh_3)_4$ at 105 °C to give 2-dodecen-4-one (**4j**) in 91% yield (eq. 2). The structure of **4j** was deduced from the presence of a ν(C=O) absorption band at 1670 cm^{-1} in the IR spectrum, and the presence of the allyl methyl group (δ 1.92, dd, C=CHCH_3) and two olefinic proton (δ 6.11, dq, =C*H*CO and 6.83, dq, C=C*H*CH_3) signals in the ^{1}H NMR spectrum. The *E*-geometry of **4j** was indicated by the coupling constant (16.2 Hz) between the two olefinic protons. The absence of *Z*-**4j** was confirmed by the GLC analysis of isolated **4j**.



3 4 (2)

Several other catalysts were effective for the isomerization of **3j**; however, the product was a mixture of *E*- and *Z*-isomers. The results are summarized in Table 2.

It has been reported that di-μ-chlorotetracarbonyldirhodium $[Rh(CO)_2Cl]_2$ catalyzed the isomerization of 3,4-epoxy-1-butene to 2-butenal. The driving force behind catalytic reaction suggested to be the Lewis acid character of the rhodium(I) center [19]. However, when $[Rh(CO)_2Cl]_2$ was used as a catalyst in the isomerization of **3j**, the product was a **4j** mixture of geometric isomers obtained in moderate yield (entries 6 and 7, Table 2). $RhH(CO)(PPh_3)_3$ also catalyzed the isomerization of **3j** to give **4j** in high yield but the geometrical purity of **4j** was low (entries 4 and 5, Table 2). $RuH_2(PPh_3)_4$, which has the surprising ability to couple a vinyl ketone with an aldehyde [14], was rather less effective in the isomerization of **3j** (entry 8, Table 2). Therefore, $RhH(PPh_3)_4$ is the most effective catalyst in the isomerization of **3** to **4**. Several results catalyzed by $RhH(PPh_3)_4$ listed in Table 3.

In all the cases shown in Table 3, the corresponding α,β-enones were obtained as the sole products after purification by simple distillation. It is well known that a rhodium(I) complex is a good catalyst in the decarbonylation of aldehydes [15]. In our case however, no decarbonylation was observed even in those cases in which α,β-enals were obtained (entries 1–3, Table 3). The stereochemistry of **4** was found to be in *E*-form in all cases except for **4h**, on the basis of the ^1H NMR data which were compared with those in the literature [16] and those of authentic compounds prepared by aldol condensations. In the case of **4h** (entry 7, Table 3), the vinyl proton signal appeared at much higher field (δ 5.46) than the corresponding vinyl proton signals (δ 6.38–6.86) of the other α,β-enones in their respective ^1H NMR spectra. A large high field shift implies that the vinyl proton of **4h** is located trans to the carbonyl group. The steric bulk of the isopropyl group may regulate the geometry of the alkene.

In contrast to the successful isomerization of the 1,3-alkadiene monoepoxide, cyclopentadiene monoepoxide (**3k**) did not isomerize under the same conditions (105 °C, 13 h) in the presence of $RhH(PPh_3)_4$. Starting **3k** was recovered intact. On the other hand, when a cationic complex $[Rh(COD)(DPPE)]ClO_4$ (COD = 1,5-cyclooctadiene, DPPE = 1,2-bis(diphenylphosphino)ethane) was used as a catalyst, 3-cyclopentenone was obtained in a low yield. It has already been reported that the isomerization of **3k** is catalyzed far more effectively by $Pd(PPh_3)_4$ to give 3-cyclopentenone and that quite different compounds, 1,3-dienols, were formed as the sole products in the isomerization of 1,3-alkadiene monoepoxides [17]. Both types of reactions are explained by the putative intermediacy of η^3-allylpalladium complexes.

These points suggest strongly that an interaction of $RhH(PPh_3)_4$ with **3** is quite different from that of $Pd(PPh_3)_4$ or $[Rh(COD)(DPPE)]ClO_4$. It is reported that a Michael type interaction of Rh–H with the vinyl ketones plays an important role in the isomerization of β-trimethylsilylallyl alcohols [9] and in the coupling of vinyl

Table 1

Preparation of **3** from **2**

Entry	3	R^1	R^2	Yield (%)	B.p. (°C/Torr)	^{1}H NMR (CCl_4) [a] $COCH_2$ or $COCH$	Analysis (Found(calc.)(%)) C	H	Formula
1	**3b**	H	$^nC_5H_{11}$	40	59/4	2.45 (d, *J* 6.0) 2.63 (d, *J* 6.0)	ref. 24		
2	**3c**	H	1-Methylethyl	36	62/6	2.48 (d, *J* 6.0) 2.67 (d, *J* 6.0)	74.88 (74.95)	10.79 (10.78)	$C_7H_{12}O$
3	**3d**	H	1-Ethylpropyl	72	60/6	2.39 (d, *J* 5.9) 2.53 (d, *J* 5.9)	77.21 (77.09)	11.41 (11.50)	$C_9H_{16}O$
4	**3e**	Et	$^nC_3H_7$	56	72/18	2.54 (t, *J* 5.6)	77.18 (77.09)	11.63 (11.50)	$C_9H_{16}O$
5	**3f**	$^nC_5H_{11}$	Et	60	73/2	2.56 (t, *J* 5.3)	78.62 (78.51)	11.92 (11.98)	$C_{11}H_{20}O$
6	**3g**	$^nC_5H_{11}$	$^nC_3H_7$	56	85/2	2.58 (t, *J* 4.8)	78.98 (79.06)	12.22 (12.16)	$C_{12}H_{22}O$
7	**3h**	$^nC_5H_{11}$	1-Methylethyl	80	135/4	2.50 (broad t, *J* 6.0)	79.01 (79.06)	12.10 (12.16)	$C_{12}H_{22}O$
8	**3i**	$^nC_7H_{15}$	H	41	78/5	2.5–3.0 (m)	ref. 25a		
9	**3j**	$^nC_8H_{17}$	H	50	95/1	2.4–3.0 (m)	ref. 25b		

[a] Shifts are in ppm, coupling constants in Hz, relative to $SiMe_4$ at 60 MHz and 25 °C.

Table 2

Effects of catalyst on the isomerization of **3j** [a]

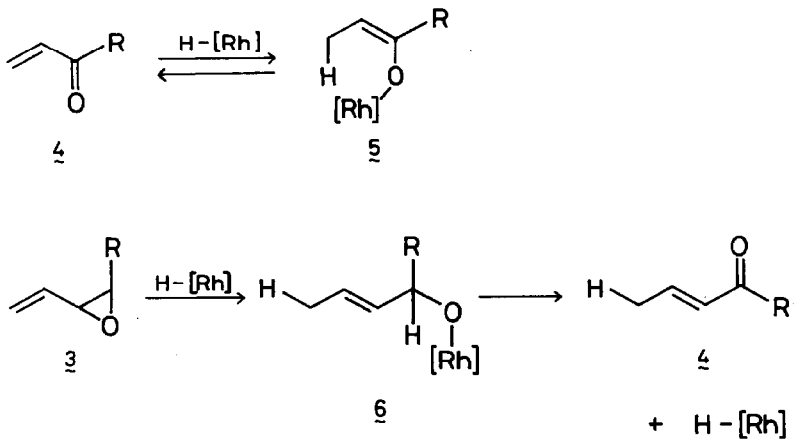
Entry	Catalyst	Amount (mol %)	Conditions (°C/h)	Yield of **4j** [b] (%)	*E*/*Z* [c]
1	$RhH(PPh_3)_4$	5.0	105/17	91	100/0
2	$RhH(PPh_3)_4$	4.6	105/6	81	100/0
3	$RhH(PPh_3)_4$	5.8	105/4	72	88/12
4	$RhH(CO)(PPh_3)_3$	6.9	110/17	86	79/21
5	$RhH(CO)(PPh_3)_3$	4.3	80/8 [d]	89	70/30
6	$[Rh(CO)_2Cl]_2$	7.3	108/4	55	81/19
7	$[Rh(CO)_2Cl]_2$	8.5	80/7 [d]	57	60/40
8	$RuH_2(PPh_3)_4$	9.2	110/17	61	80/20

[a] A benzene solution of **3j** (1 mmol) and catalyst was heated in a sealed tube. [b] Isolated yield. [c] Determined by GLC analysis. [d] Refluxed under nitrogen.

ketones with aldehydes [11]. The intermediacy of the rhodium enolate **5** is postulated on the basis of these reactions. Therefore, if an analogous interaction of Rh–H with **3** is possible, the formation of **4** could be rationalized by the putative intervention of **6** as shown in Scheme 2.

The following experiments were designed in order to clarify the origin of *E*-selectivity in the present reaction. First, a mixture of geometric isomers of **4j** (*E*/*Z* 70/30), which is prepared by the isomerization of **3j** with the aid of $RhH(CO)(PPh_3)_3$ (entry 5, Table 2), was heated in the presence of a catalytic amount of $RhH(PPh_3)_4$ at 105 °C in benzene. After 19 h, it was found that *Z*-**4j** had been consumed completely and only the *E*-isomer was present in the reaction mixture. Secondly, when isomerization of **3j** was stopped before conversion was complete (i.e. at 78%) in the presence of $RhH(PPh_3)_4$, the obtained **4j** was a mixture of *E*- and *Z*-isomer (*E*/*Z* 88/12), whereas only the *E*-isomer was isolated after complete conversion (8 h).

These results strongly suggest that the rhodium catalyzed isomerization of **3** gives a mixture of *Z*-**4** and *E*-**4** in early stages of the reaction, and later on *Z*-**4** isomerizes to *E*-**4** by action of the rhodium complex. In the case of **4h**, it is possible that



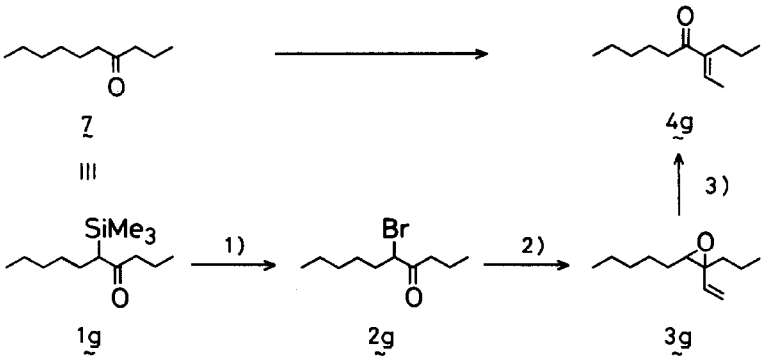
Scheme 2.

Table 3

Isomerization of **3** catalyzed by $RhH(PPh_3)_4$

Entry	3	R^1	R^2	4	Yield [a] (%)	B.p. (°C/Torr)	Product					Formula
							IR (CCl_4)		^1H NMR (CCl_4) [b]	Analysis (Found (calc.) (%))		
							ν(C=O) (cm^{-1})	ν(C=C)	CH=C(C=O)	C	H	
1	**3a**	H	Me	**4a**	35	52/145	1677	1638	6.43 (q, *J* 7.1)		ref. 26	
2	**3b**	H	$^nC_5H_{11}$	**4b**	75	60/4	1683	1637	6.38 (q, *J* 7.1)		ref. 27	
3	**3d**	H	1-Ethylpropyl	**4d**	70	58/2	1680	1625	6.40 (q, *J* 7.2)	77.30 (77.09)	11.61 (11.50)	$C_9H_{16}O$
4	**3e**	Et	$^nC_3H_7$	**4e**	83	84/20	1669	1632	6.67 (q, *J* 7.4)	77.21 (77.09)	11.53 (11.50)	$C_9H_{16}O$
5	**3f**	$^nC_5H_{11}$	Et	**4f**	78	72/2	1670	1630	6.43 (q, *J* 7.4)	78.62 (78.51)	11.89 (11.98)	$C_{11}H_{20}O$
6	**3g**	$^nC_5H_{11}$	$^nC_3H_7$	**4g**	83	80/2	1663	1628	6.66 (q, *J* 7.5)	79.11 (79.06)	12.06 (12.16)	$C_{12}H_{22}O$
7	**3h**	$^nC_5H_{11}$	1-Methylethyl	**4h**	80	61/0.4	1682	1620	5.46 (dq, *J* 7.4, 1.4)	79.24 (79.06)	12.11 (12.16)	$C_{12}H_{22}O$
8	**3i**	$^nC_7H_{15}$	H	**4i**	83	67/2	1670	1620	6.77 (q of d, *J* 16.2, 6.8)		ref. 28	
9	**3j**	$^nC_8H_{17}$	H	**4j**	91	85/0.2	1668	1622	6.83 (q of d, *J* 16.2, 6.5)		ref. 29	

[a] Isolated yield. [b] Shifts are in ppm, coupling constants in Hz, relative to $SiMe_4$ at 60 MHz and at 25 °C.



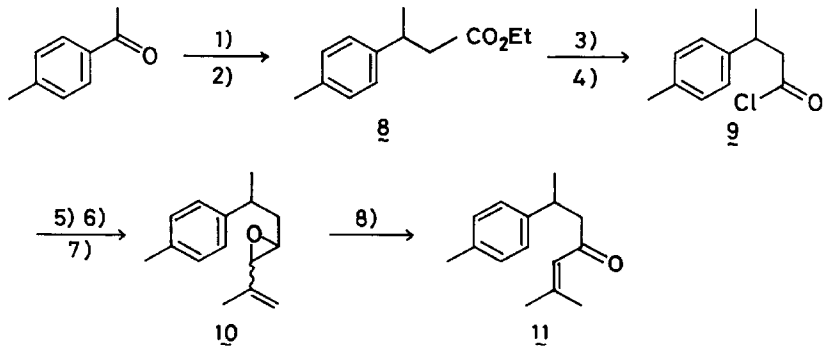
1) Br_2 / CH_2Cl_2, -78°C
2) CH_2=CHMgBr / THF
3) $RhH(PPh_3)_4$ / C_6H_6, 105°C, 20h

Scheme 3.

Z-geometry is favored above *E*-geometry because of the steric repulsion between the methyl group and the bulky isopropyl group.

In conclusion, the present approach promises an *E*-selective and regioselective route to α,β-unsaturated carbonyl compounds, which are accompanied by formation of regio-isomers along an aldol route. The regiospecificity can be readily attained by using the α-trimethylsilyl ketone **1**. The preparation of **4g** is outlined in Scheme 3. α-Trimethylsilyl ketone **1g** is readily prepared as the synthetic equivalent of **7** and led selectively to α-bromo ketone **2g**, which in turn is converted to the epoxide **3g** after reaction with vinylmagnesium bromide. The overall transformation can be envisaged as an alkenylative 1,2-carbonyl transposition of ketone **7** with concomitant introduction of an ethylidene group.

Finally, our isomerization of 1,3-diene monoepoxides could form the key step in the regiospecific synthesis of *ar*-turmerone (**11**) [7,18], an outline is given in Scheme 4. The overall yield of **11** was slightly in excess of 25% after 8 repeated operations.



1) LDA / $TMSCH_2CO_2Et$ / THF, -78°C, 73% 2) H_2 / Pd-C / EtOH, r.t., 96% 3) TMSI / CCl_4, reflux, 72% 4) $SOCl_2$, reflux, 85% 5) ClCH=C(Me)CH_2TMS / $TiCl_4$ / CH_2Cl_2, -78°C, 92% 6) $NaBH_4$ / MeOH, r.t., 85% 7) NaOH / aq. MeOH, r.t., 73% 8) $HRh(PPh_3)_4$ 5 mol% / C_6H_6, 105°C, 20h, 86%

Scheme 4.

Experimental

All reactions were carried out under argon or nitrogen. Boiling points are bath temperatures for bulb-to-bulb distillations. IR spectra were recorded on a JASCO IRA-1 spectrometer, and proton NMR spectra were obtained on a JEOL-C60HL instrument using tetramethylsilane as an internal standard. Benzene was distilled over sodium metal and degassed under vacuum just before use. Dichloromethane was dried over phosphorus pentoxide and distilled. Tetrahydrofuran (THF) was distilled from sodium metal in the presence of benzophenone just before use.

The preparation of α-bromo ketones (**2**) has been described previously [12]. 3,4-Epoxy-3-methyl-1-butene (**3a**) [19], cyclopentadiene monoepoxide (**3k**) [20], hydridotetrakis(triphenylphosphine)rhodium [21], hydridocarbonyltris(triphenylphosphine)rhodium [22], di-μ-chlorotetracarbonyldirhodium [23], and dihydridotetrakis (triphenylphosphine)ruthenium [21] were prepared by published procedures. Vinylmagnesium bromide (1.15 *M*, THF solution) was prepared from vinyl bromide and magnesium by a standard method.

Preparation of 1,3-diene monoepoxide 3

The procedures for **3b** and **3i** are described as typical examples. The data for **3** are listed in Table 1.

3,4-Epoxy-3-pentyl-1-butene (3b) [24]

To a solution of 2.83 g (14.7 mmol) of 1-bromo-2-heptanone (**2b**) in THF (80 ml) was added a solution of vinylmagnesium bromide (1.15 *M*, 17.3 mmol) in THF(15 ml) at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature and quenched with aqueous NH_4Cl (20 ml). The organic phase was separated and the aqueous phase was extracted with diethyl ether (2 × 20 ml). The combined organic portions were washed with brine (2 × 40 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate 98/2) as an eluent. Bulb-to-bulb distillation yielded 0.82 g (40%) of **3b** as a colorless oil. B.p.: 59 °C/4 Torr. ^1H NMR(CCl_4): δ 0.80 (t, *J* 4.5 Hz, 3H, CH_3), 1.0–2.3 (broad m, 8H, 4 × CH_2), 2.45 (d, *J* 6.4 Hz, 1H, C–O–C*H*), 2.63 (d, *J* 6.0 Hz, 1H, C–O–C*H*), 4.9–6.0 (m, 3H, C*H*=CH_2).

3,4-Epoxy-1-undecene (3i) [25a]

To a solution of 1.93 g (11.9 mmol) of octanoyl chloride in dichloromethane (30 ml) were added dropwise, 2.33 g (12.3 mmol) of titanium tetrachloride and 1.93 g (13.0 mmol) of 1-chloro-3-trimethylsilylpropene at −78 °C. The resulting mixture was stirred for 2 h at −78 °C and quenched with aqueous Na_2CO_3 (20 ml) at the same temperature. The organic phase was separated off by decantation and the frozen aqueous phase was extracted with Et_2O (2 × 20 ml). The combined organic portions were washed with brine (3 × 30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give crude 3-chloro-1-undecen-4-one (1.93 g, 80%) as a yellow oil. IR(CCl_4): 1720 (C=O), 1620 (C=C) cm^{-1}. ^1H NMR(CCl_4): δ 0.86 (t, *J* 5.4 Hz, 3H, CH_3), 1.2–1.8 (broad m, 12H, 6 × CH_2), 2.56 (t, *J* 6.8 Hz, 2H, CH_2C=O, 4.59 (d, *J* 6.9 Hz, 1H, C*H*Cl), 5.2–6.3 (m, 3H, C*H*=CH_2).

To a solution of 0.68 g (17.9 mmol) of $NaBH_4$ in methanol (50 ml) was added 1.93 g (9.5 mmol) of crude 3-chloro-1-undecen-4-one. The resulting solution was stirred for 13 h at room temperature and extracted with hexane (5 × 40 ml). The combined extracts were dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, 1.69 g (106%) of crude 3-chloro-1-undecen-3-ol was obtained as a yellow oil. IR(CCl_4): 3580 (OH), 1620 (C=C) cm^{-1}. This compound was immediately used in the next reaction.

To a solution of 0.4 g (10 mmol) of NaOH in a mixed solvent (50 ml of MeOH and 2 ml of water) was added 1.69 g (10.1 mmol) of the crude 3-chloro-1-ol and the mixture was stirred for 3 h at room temperature. The aqueous layer was extracted with hexane (5 × 40 ml). The combined extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate 98/2) as an eluent. Bulb-to-bulb distillation yielded 0.82 g (41% based on octanoyl chloride) of **3i** as a pale yellow oil. B.p.: 78°C/5 Torr. ^1H NMR(CCl_4): δ 0.91 (t, J 4.5 Hz, 3H, CH_3), 1.1–1.8 (braod m, 14H, 7 × CH_2), 2.5–3.0 (m, 2H, CH–O–CH), 5.0–5.6 (m, 3H, CH=CH_2).

Isomerization of 3 to 4 with the aid of $RhH(PPh_3)_4$

The procedure for **4a** is described as a typical example. The data for **4** are summarized in Tables 2 and 3.

(E)-2-Methyl-2-butenal (4a) [26]

A solution of 251 mg (3.0 mmol) of **3a** and 36 mg (0.031 mmol, 1.0 mol%) of $RhH(PPh_3)_4$ in benzene (1 ml) was placed in a 10-mm ϕ Pyrex tube under argon. The tube was sealed and heated at 105°C in an oil bath for 3 h. The resulting red solution was concentrated under reduced pressure and submitted to bulb-to-bulb distillation, which yielded 87 mg (35%) of **4a** as a colorless oil. B.p.: 52°C/145 Torr. IR(CCl_4): 1677 (C=O), 1638 (C=C) cm^{-1}. ^1H NMR(CCl_4): δ 1.75 (d, J 2.1 Hz, 3H, H_3CCHO), 1.84 (d, J 7.1 Hz, 3H, =CHCH_3), 6.43 (q, J 7.1 Hz, 1H, =CH), 9.33 (s, 1H, CHO).

Synthesis of ar-turmerone (11) [18]

Preparation of ethyl 3-p-tolylbutanoate (8). To a solution of lithium diisopropylamide (32.3 mmol) in THF (90 ml) was added a solution of 5.0 g (31.1 mmol) of ethyl trimethylsilylacetate in THF (100 ml) at −78°C and the solution was stirred for 2 h. Then a solution of 4.2 g (31.1 mmol) of 1-*p*-tolylethanone in THF (70 ml) was added to the reaction mixture at the same temperature. The mixture was stirred for another hour at −78°C and quenched with aqueous NH_4Cl (80 ml) at −10°C. The organic phase was separated off and the aqueous phase was extracted with Et_2O (3 × 40 ml). The combined organic portions were washed with brine (3 × 50 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate 97/3) as an eluent. Bulb-to-bulb distillation yielded 4.6 g (73%) of ethyl 3-*p*-tolyl-2-butenoate as a colorless oil. B.p.: 117°C/0.2 Torr. Anal. Found: C, 76.35; H, 7.92. $C_{13}H_{16}O_2$ calcd.: C, 76.44; H, 7.89%. IR (CCl_4): 1715 (C=O) cm^{-1}. ^1H NMR (CCl_4): δ 1.33 (t, J 7.1 Hz, 3H, OCH_2CH_3), 2.41 (s,

3H, ArCH_3), 2.58 (d, J 1.5 Hz, 3H, =CCH_3), 4.24 (q, J 7.1 Hz, 2H, OCH_2CH$_3$), 6.15 (q, J 1.5 Hz, 1H, =CH), 7.1–7.6 (m, 4H, Ar).

Into a suspension of 0.2 g of Pd–C (5%) and 4.6 g (22.1 mmol) of ethyl-3-*p*-tolyl-2-butenoate in ethanol (30 ml) was bubbled hydrogen for 1 h at room temperature. After filtration of the mixture, the filtrate was concentrated to give 4.4 g (96%) of **8** as a colorless oil. IR (CCl_4): 1740 (C=O) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.20 (t, J 7.5 Hz, 3H, OCH$_2$CH_3), 1.30 (d, J 7.0 Hz, 3H, ArCHCH_3), 2.35 (s, 3H, ArCH_3), 2.4–2.6 (m, 2H, CH_2CO), 2.9–3.4 (m, 1H, ArCH), 4.08 (q, J 7.5 Hz, 2H, OCH$_2$CH$_3$), 7.13 (s, 4H, Ar).

Preparation of 3-p-tolylbutanoyl chloride (9). To a carbon tetrachloride (30 ml) solution of iodotrimethylsilane (10.1 mmol, prepared from iodine and hexamethyldisilane [30]) was added 2.1 g (10.1 mmol) of **8** at room temperature. The resulting solution was refluxed for 29 h and quenched with water (50 ml). The mixture was diluted with Et_2O (50 ml) and washed with aqeuous $Na_2S_2O_3$ (10%, 5 × 40 ml) and brine (2 × 40 ml). The organic phase was separated, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give 1.3 g (72%) of 3-*p*-tolylbutanoic acid as a pale yellow solid. The product was immediately used in the next reaction.

A mixture of 1.3 g (7.2 mmol) of 3-*p*-tolylbutanoic acid and 5 ml (68.2 mmol) of thionyl chloride was refluxed for 4 h. The remaining $SOCl_2$ was evaporated under reduced pressure and the resulting oil was submitted to bulb-to-bulb distillation to give 1.2 g (85%) of **9** as a yellow oil. B.p. 127 °C/0.2 Torr. IR (CCl_4): 1800 (C=O) cm^{-1}. ^{1}H NMR(CCl_4): δ 1.36 (d, J 6.4 Hz, 3H, ArCHCH_3), 2.38 (s, 3H, ArCH_3), 2.9–3.7 (m, 3H, ArCHCH_2CO), 7,20 (s, 4H, Ar).

Preparation of 3,4-epoxy-2-methyl-6-p-tolyl-1-heptene (10). To a solution of 0.54 g (2.8 mmol) of **9** in CH_2Cl_2 (25 ml) were added 0.3 ml (2.8 mmol) of $TiCl_4$ and 0.47 g (2.9 mmol) of 1-chloro-3-trimethylsilyl-2-methylpropene at −78 °C. The resulting mixture was stirred for 2 h and quenched with aqueous Na_2CO_3 (20 ml) at the same temperature. The organic phase was separated by decantation and the frozen aqueous phase was extracted with Et_2O (4 × 30 ml). The combined organic portions were washed with brine (2 × 30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate 95/5) as an eluent to give 0.63 g (92%) of 3-chloro-2-methyl-6-p-tolyl-1-hepten-4-one as a colorless oil. IR (CCl_4): 1715 (C=O) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.27 (d, J 6.8 Hz, 3H, ArCHCH_3), 1.6–1.8 (m, 3H, =CCH_3), 2.36 (s, 3H, ArCH_3), 2.7–3.5 (m, 3H, ArCHCH_2CO), 4.61 (s, 1H, CHCl), 5.1–5.4 (m, 2H, =CH_2), 7.17 (s, 4H, Ar).

To a solution of 0.10 g (2.7 mmol) of $NaBH_4$ in methanol (20 ml) was added 0.63 g (2.5 mmol) of 3-chloro-2-methyl-6-p-tolyl-1-hepten-4-one. The resulting solution was stirred for 13 h at room temperature and extracted with hexane (5 × 20 ml). The combined extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give 0.54 g (85%) of crude 3-chloro-2-methyl-6-*p*-tolyl-1-hepten-4-ol as a colorless oil (a small amount of **10** was included). This product was immediately used in the next reaction.

To a solution of 84 mg (2.1 mmol) of NaOH in a mixed solvent (15 ml of MeOH and 0.5 ml of water) was added 0.54 g (2.2 mmol) of 3-chloro-2-methyl-6-*p*-tolyl-1-hepten-4-ol in MeOH (3 ml) solution. The mixture was stirred for 2 h at room temperature and then extracted with hexane (5 × 30 ml). The combined extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The

residual oil was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate 98/2) as an eluent. Bulb-to-bulb distillation yielded 0.34 g (73%) of **10** as a colorless oil. B.p. 109°C/0.2 Torr. Anal. Found: C, 83.38; H, 9.35. $C_{15}H_{20}O$ calcd.: C, 83.29; H, 9.32%. ^{1}H NMR (CCl_4): δ 1.36 (d, J 7.2 Hz, 3H, ArCHCH_3), 1.4–1.9 (m, 5H, =CCH_3, ArCHCH_2), 2.36 (s, 3H, ArCH_3), 2.5–3.3 (broad m, 3H, CH–O–CH, ArCH), 4.8–5.2 (broad m, 2H, =CH_2), 7,16 (s, 4H, *Ar*).

Catalytic isomerization of 10 to 11

A solution of 140 mg (0.6 mmol) of **10** and 40 mg (0.03 mmol, 5 mol%) of $RhH(PPh_3)_4$ in benzene (0.5 ml) was placed in a 10-mm ϕ Pyrex tube under argon. The tube was sealed and heated at 105°C in an oil bath for 20 h. The resulting solution was concentrated under reduced pressure and submitted to bulb-to-bulb distillation to give 120 mg (86%) of **11** as a colorless oil. B.p.: 109°C/0.2 Torr. IR (CCl_4): 1680 (C=O), 1615 (C=C) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.23 (d, J 6.8 Hz, 3H, ArCHCH_3), 1.85 (d, J 1.5 Hz, 3H, =CCH_3), 2.12 (d, J 1.5 Hz, 3H, =CCH_3), 2.33 (s, 3H, ArCH_3), 2.5–2.6 (m, 2H, CH_2C=O), 2.9–3.7 (m, 1H, ArCH), 5.92 (septet, J 1.5 Hz, 1H, =CH), 7,02 (s, 4H, *Ar*).

Acknowledgments

The author (I.M.) thanks The Kurata Foundation for the Kurata Research Grant and Shin-etsu Chemical Co. Ltd. for a gift of chlorotrimethylsilane.

References

1 (a) G. Stork, G.A. Kraus, and G.A. Garcia, J. Org. Chem., 39 (1974) 3459; (b) I. Kuwajima, T. Sato, M. Arai, and N. Minami, Tetrahedron Lett., (1976) 1817; (c) H.O. House, L.J. Czuba, M. Gall, and H.D. Olmstead, J. Org. Chem., 34 (1969) 2324; (d) T. Mukaiyama, K. Inomata, and M. Muraki, J. Am. Chem. Soc., 95 (1973) 967.
2 W.S. Wadsworth, J. Am. Chem. Soc., 83 (1961) 1733.
3 H.J. Bestmann, K. Roth, and M. Ettlinger, Angew. Chem. Int. Ed. Engl., 18 (1979) 687.
4 J.A. Miller and G. Zweifel, J. Am. Chem. Soc., 103 (1981) 2481.
5 A.A. Croteau and J. Termini, Tetrahedron Lett., 24 (1983) 2481.
6 I. Matsuda, H. Okada, S. Sato, and Y. Izumi, Tetrahedron Lett., 24 (1984) 3879.
7 J. Durman, J. Elliot, A.B. McElroy, and S. Warren, Tetrahedron Lett., 24 (1983) 3927.
8 N. Jabri, A. Alexakis, and J.F. Normant, Tetrahedron Lett., 24 (1983) 5081.
9 (a) S. Sato, I. Matsuda, and Y. Izumi, Tetrahedron Lett., 24 (1983) 3855; (b) S. Sato, I. Matsuda, and Y. Izumi, J. Organomet. Chem., 344 (1988) 71.
10 S. Sato, I. Matsuda, and Y. Izumi, Tetrahedron Lett., 26 (1985) 4229.
11 S. Sato, I. Matsuda, and Y. Izumi, Chem. Lett., (1985) 1875.
12 I. Matsuda and S. Sato, J. Organomet. Chem., 314 (1986) 47.
13 (a) R. Grigg, R. Hayes, and A. Sweeny, J. Chem. Soc. Chem. Comm., (1971) 1248; (b) G. Adames, C. Bibby, and R. Grigg, J. Chem. Soc. Chem. Comm., (1972) 491.
14 I. Matsuda, M. Shibata, and S. Sato, J. Organomet. Chem., 340 (1988) C5.
15 D.H. Doughty and L.H. Pignolet, J. Am. Chem. Soc., 100 (1978) 7083.
16 (a) D.D. Faulk and A. Fry, J. Org. Chem., 35 (1970)364; (b) J. Elguero and C. Marzin, Bull. Soc. Chim. France, (1973) 3401; (c) H.J. Bestmann, K. Roth, and M. Ettlinger, Chem. Ber., 115 (1982) 161.
17 M. Suzuki, Y. Oda, and R. Noyori, J. Am. Chem. Soc., 101 (1979) 1623.
18 (a) C.H. Heathcock, Total Synthesis of Natural Products, Vol. 5, ed. by J. Apsimon; Wiley, New York, 1983, p. 38; (b) P.A. Grieco and R.S. Finkelhor, J. Org. Chem., 38 (1973) 2909; (c) O.S. Park, Y. Grillasea, G.A. Garcia, and L.A. Maldonado, Synth. Comm., 7 (1977) 345; (d) P. Gosselin, S. Masson, and A. Thuillier, J. Org. Chem., 44 (1979) 2807.

19 R. Pummerer and W. Reindel, Ber., 66 (1933) 335.
20 M. Korach, D.R. Nielson, and W.H. Rideout, Org. Syn., Coll. Vol. 5, (1973) 414.
21 J.J. Levison and S.D. Robinson, J. Chem. Soc. A, (1970) 2947.
22 D. Evans, G. Yagupsky, and G. Wilkinson, J. Chem. Soc. A, (1968) 2660.
23 J.A. McCleverty and G. Wilkinson, Inorg. Chem., 8 (1966) 211.
24 A. Yasuda, M. Takahashi, and H. Takaya, Tetrahedron Lett., 22 (1981) 2413.
25 (a) J. Auge and S. David, Tetrahedron Lett., 24 (1983) 4009; (b) M. Ochiai and E. Fujita, ibid., 21 (1980) 4389.
26 R.E. Klink and J.B. Stothers, Can. J. Chem., 44 (1966) 45.
27 (a) E.E. Royals and E.R. Covington, J. Am. Chem. Soc., 77 (1955) 3155; (b) F. Barbot and P. Miginac, Synthesis, (1983) 651.
28 (a) M.T. Reetz and B. Wenderoth, and R. Urz, Chem. Ber., 118 (1985) 348; (b) J.P. Quintard, B. Ellisondo, T. Hattich, and M. Pereyre, J. Organomet. Chem., 285 (1985) 149.
29 Y. Masuyama, M. Takahashi, and Y. Kurusu, Tetrahedron Lett., 25 (1984) 4417.
30 (a) H. Sakurai, A. Shirahata, K. Sasaki, and A. Hosomi, Synthesis, (1979) 740; (b) G.A. Olah, S.C. Narang, B.G.B. Gupta, and R. Malhotra, Angew. Chem. Int. Ed. Engl., 18 (1979) 612; (c) G.A. Olah, S.C. Narang, B.G.B. Gupta, and R. Malhotra, J. Org. Chem., 44 (1979) 1247.