JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2 93–102 (1989)

SELECTIVE 1,2-ADDITION OF ORGANOCERIUM(III) REAGENTS TO α,β-UNSATURATED CARBONYL COMPOUNDS

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ABSTRACT

Organocerium(III) reagents reacted with α,β-unsaturated carbonyl compounds to give 1,2-addition products (allylic alcohols) in good to high yields. The reaction was studied from a mechanistic point of view by the use of (*E*)- and (*Z*)-1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-ones and 4,4-ethylenedioxy-2,6-dimethyl-2,5-cyclohexadienone as the probe compounds. A polar pathway was suggested for the reaction with the former enones. On the other hand, the operability of single electron transfer processes was demonstrated in the reaction with the latter probe compound.

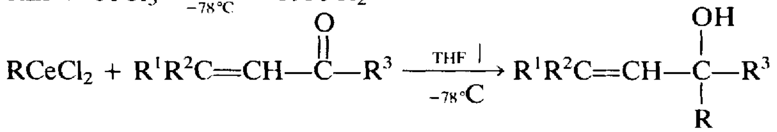
In previous papers we have described the generation and reactivities of organocerium(III) reagents.[1] The reagents are generated by the reaction of organolithium reagents with anhydrous cerium(III) chloride or cerium(III) iodide in tetrahydrofuran (THF) at − 78 °C. The reagents react with various carbonyl compounds to afford the corresponding addition products in high yields, even though the substrates are susceptible to enolization or metal–halogen exchange with simple alkyl lithiums or the Grignard reagents. The results revealing the strong nucleophilicity of the reagents toward carbonyl groups prompted us to study the reaction of the reagents with α-enones. In this paper we report the scope and mechanistic aspect of the reaction of organocerium reagents with α,β-unsaturated carbonyl compounds.[2]

RESULTS AND DISCUSSION

General scope

Our initial experiments were conducted with the reactions of several organocerium reagents with simple α,β-unsaturated carbonyl compounds. The results are summarized in Table 1.[3]

$$RLi + CeCl_3 \xrightarrow[-78\,^{\circ}C]{THF} RCeCl_2{}^{\dagger} + LiCl$$



$$RCeCl_2 + R^1R^2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R^3 \xrightarrow[-78\,^{\circ}C]{THF} R^1R^2C{=}CH{-}\underset{\displaystyle R}{\overset{\displaystyle OH}{C}}{-}R^3$$

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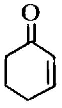
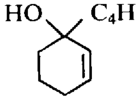
[†] This formulation merely expresses the basic stoichiometry, and some other species such as an ate complexe ($[R\text{-}CeCl_3]^-$ Li^+) may exist in equilibrium.

0894–3230/89/020093–10$05.00

Received 25 February 1988
Revised 16 April 1988

Table 1. Reaction of organocerium reagents with α,β-unsaturated carbonyl compounds[a]

Entry	Carbonyl compound	Reagent	Reaction time (min)	Product(s)	Yield (%)[b]
1	PhCH=CHCHO	$C_4H_9CeCl_2$	180	PhCH=CHCHOHC_4H_9	96
2	PhCH=CHCOCH_3	CH_3CeCl_2	180	PhCH=CHC (OH) $(CH_3)_2$	97
3	"	$C_4H_9CeCl_2$	180	PhCH=CHC (OH) (CH_3) C_4H_9	95
4	"	i-$C_3H_7CeCl_2$	20	PhCH=CHC (OH) (CH_3) (i-C_3H_7)	49
				PhCH (i-C_3H_7) CH_2 COCH_3	29
5	"	$PhCeCl_2$	180	PhCH=CHC (OH) (CH_3) Ph	95
6	PhCH=CHCOPh	$C_4H_9CeCl_2$	180	PhCH=CHC (OH) (Ph) C_4H_9	42
				PhCH (C_4H_9) CH_2 COPh	40
7		$C_4H_9CeCl_2$	180		98

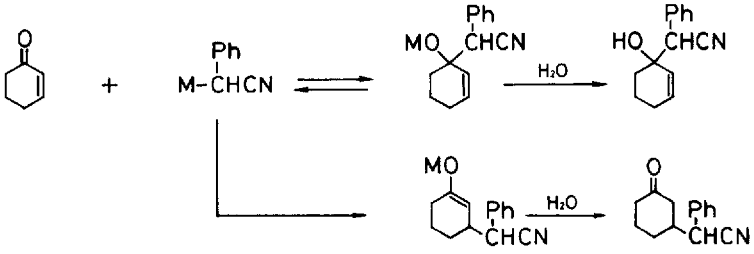
[a] All reactions were carried out at −78 °C.
[b] Isolated yield.

It is noted that all the reactions except entries 4 and 6 afforded 1,2-addition products (allylic alcohols) in excellent yields. The present method is in contrast to the Grignard reactions which are often accompanied by conjugate addition.[4] Our results are favorably compared with those obtained by the use of other lanthanide reagents such as organoytterbium(II) σ-complexes[5–7] and homoleptic organolanthanide complexes.[8,9]

Another area of interest to us is the reaction of stable carbanions with α-enones. Seyden-Penne *et al.* have extensively investigated the reaction of α-cyanobenzyllithium with α-enones.[10–12] The reaction is undoubtedly an equilibrium one. The carbanion, stabilized by the conjugation with α-cyano and phenyl groups, acts not only as a nucleophile but also as a leaving group. Thus, the initially formed 1,2-adduct dissociates to the starting carbanion and α-enone, which in turn are gradually converted to the thermodynamically stable 1,4-adduct. It is one of the authors' interests to know the chemical behavior of organocerium(III) reagents in this type of reaction.

α-Cyanobenzyllithium was treated with anhydrous cerium chloride at −78 °C and was allowed to react with 2-cyclohexeneone. It is noted that the 1,2-addition product is formed in 60–62% yield, regardless of reaction time. (A similar result was also obtained in the reaction of benzalacetone with α-cyanobenzylcerium. The reaction at −78 °C for 5 h afforded 1,2-addition product (1-cyano-1,4-diphenyl-2-methyl-3-buten-2-ol) in 89% yield.) These results are remarkably different from those of the reaction of the corresponding lithium reagent. Our results are reasonably explained in terms of kinetic control rather than thermodynamic control. Thus, trivalent cerium possesses strong oxaphilicity and intercepts the intermediate 1,2-adduct by virtue of the strong bonding with the alkoxide oxygen so that the reverse reaction is suppressed.

The regiocontrol of [1,2] vs. [1,4] addition of organometallic nucleophiles to α-enones is an important problem in synthetic organic chemistry.[13,14] The present method using cerium reagents may be useful for the synthesis of allylic alcohols from α,β-unsaturated carbonyl compounds.[15]



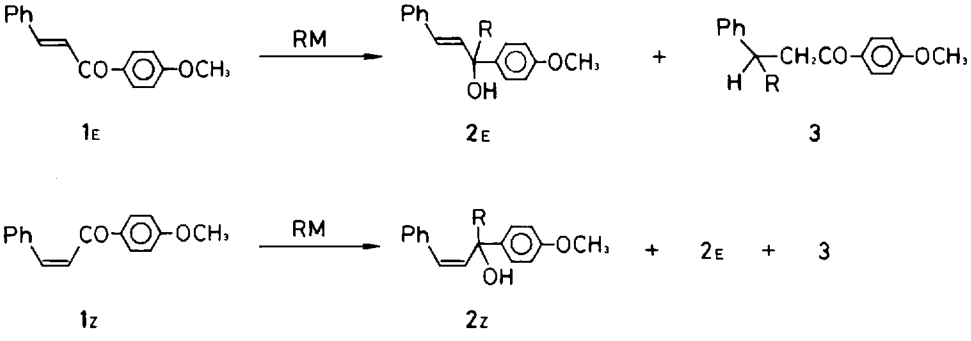
Scheme 1

Table 2.

M	Conditions		Yield (%) 1,2-addn	Yield (%) 1,4-addn	
Li	THF, −70 °C,	1 min	29	36	(Ref. 10)
	〃	15 min	21	49	(〃)
	〃	180 min	0	90	(〃)
$CeCl_2$	THF, −78 °C,	4 min	61	0	
	〃	15 min	60	0	
	〃	240 min	62	0	

Reactions of organocerium(III) reagents with (*E*)- and (*Z*)-1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-one

Next we were interested in the mechanistic aspect of the reactions. Our attention has been focused on the question of whether the reaction of organocerium reagents with carbonyl compounds proceeds via a single-electron-transfer (SET) pathway or a polar pathway. For the last two decades many internal probe compounds have been devised to determine the mechanism of the reactions of organometallic nucleophiles with carbonyl compounds.[16,17] In this study we have employed the methodology utilizing the *cis-trans* isomerization of α-enones.[17c,g,h,i,j]



R = CH_3, C_4H_9, C_6H_5, i-C_3H_7 ; M = $CeCl_2$, Li, MgBr

Scheme 2

Table 3. Reaction to organocerium, organolithium, or the grignard reagent with (*E*)- or (*Z*)-$C_6H_5CH{=}CHCOC_6H_4OCH_3$-*p*

Entry	Substrate	Reagent	Conditions[a]		Yield of products (%)[b]		
			Solvent	Time (min)	$\mathbf{2}_E$	$\mathbf{2}_Z$	**3**
1	$\mathbf{1}_E$	CH_3CeCl_2	THF–ether(12:1)	30	98	0	trace
2	″	CH_3Li	THF–ether(5:1)	30	65	0	17
3	″	CH_3MgBr	THF	30	38	0	65
4	″	$C_4H_9CeCl_2$	THF–hexane(8:1)	30	50	0	43
5	″	C_4H_9Li	THF–hexane(2:1)	30	36	0	50
6	″	C_4H_9MgBr	THF	30	10	0	76
7	″	$C_6H_5CeCl_2$	THF–ether(8:1)	30	90	0	4
8	″	C_6H_5Li	THF–ether(3:1)	30	85	0	10
9	″	C_6H_5MgBr	THF	30	14	0	78
10	″	i-$C_3H_7CeCl_2$	THF–hexane(4:1)	30	42	0	35
11	″	i-C_3H_7Li	THF–hexane(3:1)	30	39	0	57
12	″	i-C_3H_7MgCl	THF	30	44	0	51
13	$\mathbf{1}_Z$	CH_3CeCl_2	THF–ether(12:1)	60	trace	97	trace
14	″	CH_3Li	THF–ether(5:1)	60	trace	96	trace
15	″	CH_3MgBr	THF	60	26	20	38
16	″	$C_4H_9CeCl_2$	THF–hexane(8:1)	60	trace	97	trace
17	″	C_4H_9Li	THF–hexane(2:1)	60	trace	70	20
18	″	C_4H_9MgBr	THF	60	20	25	50
19	″	$C_6H_5CeCl_2$	THF–ether(8:1)	90	trace	93	4
20	″	C_6H_5Li	THF–ether(3:1)	90	trace	90	4
21	″	C_6H_5MgBr	THF	90	25	20	45

[a] All reactions were carried out at −78°C.
[b] Isolated yield.

As the probe compounds, (*E*)- and (*Z*)-1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-ones ($\mathbf{1}_E$ and $\mathbf{1}_Z$) were chosen, since α,β-enones conjugating with an aryl group are known to be susceptible to 1,4-addition with organometallic reagents.[4] At first, the (*E*)-enone ($\mathbf{1}_E$) was allowed to react with organocerium reagents in THF or THF/ether at −78 °C. Furthermore, the corresponding organolithium and the Grignard reagents were treated with $\mathbf{1}_E$ under the same conditions for comparison. The results are summarized in Table 3.

The reaction of methylcerium reagent with $\mathbf{1}_E$ provided 1,2-adduct (*E*)-2-(4′-methoxyphenyl)-4-phenyl-3-buten-2-ol in 98% yield. The yield of 1,4-adduct 1-(4′-methoxyphenyl)-3-phenyl-1-butanone was very poor. The results are remarkably different from those of the reactions of methyllithium and methylmagnesium bromide which afforded the 1,4-adducts in 17% and 60% yields, respectively. On the other hand, the reaction of the butylcerium reagent resulted in almost no selectivity (entry 4). But it may be worthy to mention that the yield (50%) of the 1,2-adduct is higher than those of the reactions of the corresponding lithium reagent (36%) and the Grignard reagent (10%). The similar tendency was also observed in the phenyl series (entries 7–9).

Next we examined the reactions of $\mathbf{1}_Z$ in order to obtain the mechanistic aspect. Figure 1 illustrates anticipated reaction pathways. If the reaction proceeds through a polar pathway, (*Z*)-1,2-adduct ($\mathbf{2}_Z$) and 1,4-adduct (**3**) should be formed; no trace of isomeric allylic alcohols ($\mathbf{2}_E$) should be detected. On the contrary, if the reaction proceeds via a SET pathway, $\mathbf{2}_E$ should be formed via a radical anion intermediate.

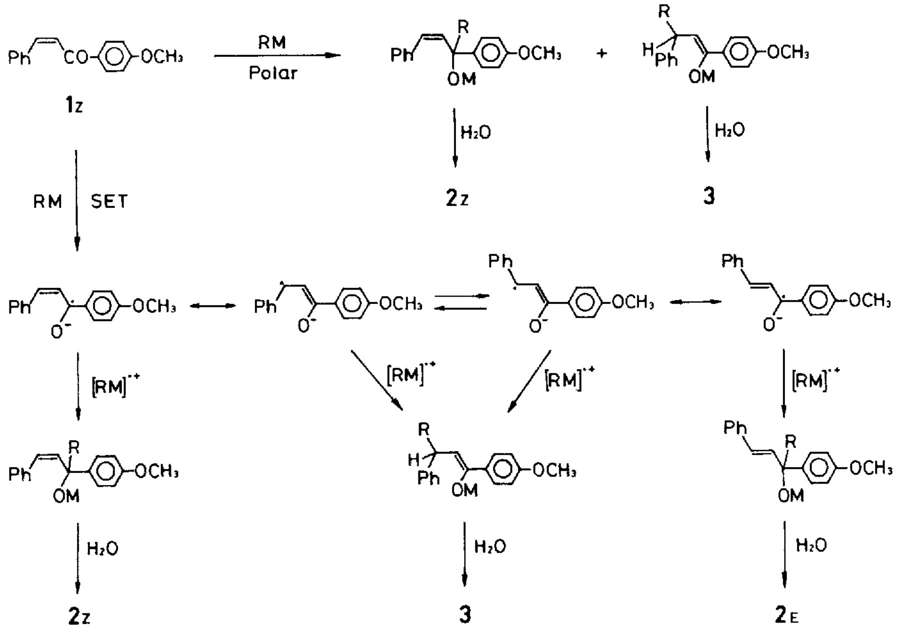


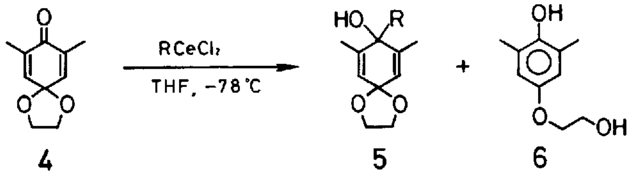
Figure 1.

Based on these considerations, methyl-, butyl-, and phenyl-cerium reagents were allowed to react with 1_Z. At the same time, the corresponding organolithiums and the Grignard reagents were treated with the same (*Z*)-enone. The results are added in Table 3. Methyl- and butylcerium reagents provided (*Z*)-allylic alcohols in excellent yields. Phenylcerium reagent also provided the corresponding adduct in 93%. It is noted that the yields of (*E*)-allylic alcohols 2_E and 1,4-adducts **3** were extremely poor in all cases examined. Lithium reagents afforded similar results except entry 17 in that the 1,4-adduct was formed in 20% yield. In the cases of the Grignard reagents, 2_E and **3** were produced in moderate yields together with 2_Z.

The formation of 2_Z in excellent yields (entries 13, 16, and 19) suggests that the reaction of the organocerium reagents with 1_Z proceeds almost exclusively through a polar pathway. On the contrary, the reaction of the Grignard reagents involves a SET pathway as is well described in the literature.[17]

Reactions with 4,4-ethylenedioxy-2,6-dimethyl-2,5-cyclohexadienone

In order to obtain further information on the mechanism, we examined the reaction of cerium reagents with 4,4-ethylenedioxy-2,6-dimethyl-2,5-cyclohexadienone (**4**) which was proposed by Liotta as a useful probe for detecting SET processes.[18] Methyl-, butyl-, and i-propylcerium reagents were treated with **4** at −78 °C and the reaction mixtures were analyzed by 270 Mz ^{1}H-NMR. The results are shown in the following scheme. In all cases compound **6** was detected together with addition products (**5**); significant amounts of **6** were produced in the reactions of butyl- and i-propylcerium reagents. (The ^{1}H-NMR spectra of the reaction mixtures showed that the combined yields of **5** and **6** were more than 90% in all cases examined.) These results apparently demonstrate the operability of a SET mechanism.



R	5		6
R = CH_3	97	:	3
C_4H_9	45	:	55†
i-C_3H_7	57	:	43

Scheme 3

In summary, organocerium(III) reagents react with α,β-unsaturated carbonyl compounds to give 1,2-addition products in high regioselectivity. A polar pathway is suggested for the reaction with 1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-one and an operability of a SET process is demonstrated in the reaction of 4,4-ethylenedioxy-2,6-dimethyl-2,5-cyclohexadienone.

EXPERIMENTAL

General

All experiments were carried out under an argon atmosphere in well dried glassware. The products were isolated by preparative thin layer chromatography on silica gel (Wakogel B-5F) or by column chromatography on silica gel (Wakogel C-200).

High resolution ^{1}H-NMR spectra were determined on a JEOL FX-270. IR spectra were recorded on Hitachi 275 IR Spectrometer. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer at the Chemical Analysis Center of Chiba University.

Materials

Anhydrous diethyl ether and *n*-hexane were obtained according to the literature procedures, and were stored with sodium wires. Anhydrous THF was distilled from sodium benzophenone prior to use. Cerium(III) chloride seven hydrate was purchased from Wako Pure Chemical Co. Ltd. Methyl-, *n*-butyl-, and phenyllithiums were purchased from Kanto Chemical Co., Ltd. Isopropyllithium was prepared by a literature procedure,[19] and the concentration was determined by titration with 2,2′-dipyridyl as an indicator. (*E*)-1-(4′-Methoxyphenyl)-3-phenyl-2-propen-1-one was prepared by a standard method. 4,4-Ethylene-dioxy-2,6-dimethyl-2,5-cyclohexadienone was synthesized according to Liotta's method.[20] Other simple organic materials were purchased and purified by distillation under reduced pressure before use.

(Z)-1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-one

This compound was prepared according to the procedure described in the literature.[21] A solution of (*E*)-1-(4′-methoxyphenyl)-3-phenyl-2-propen-1-one in 100 ml of chloroform or benzene in a Pyrex flask was exposed to sunlight for 2 days. The solvent was evaporated under

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† The ratio of 5/6 was largely varied; another run of the experiment under almost the same conditions provided a ratio of 30:70.

reduced pressure. The brown residue was seeded with (*E*)-isomer and triturated in ether at 0 °C. The crystalline solid, which consisted largely of (*E*)-isomer, was removed by decanting. The solution was subjected to column chromatography (silica gel, 3:1 hexane/diethyl ether) in the dark. Lemon yellow fractions were collected. This operation of chromatography was repeated for 3–5 times. The yield of pure product was ordinally 30–40%. Yellow pasty oil; ^{1}H-NMR (CCl_4) δ 3·75 (s, 3 H), 6·45 (d, *J* = 12 Hz, 1 H), 6·78 (d, *J* = 9 Hz, 2 H), 6·88 (d, *J* = 12 Hz, 1 H), 7·0–7·5 (m, 5 H), 7·85 (d, *J* = 9 Hz, 2 H); UV (CCl_4) λ_{max} = 286 nm (log ε 3·8).

4,4-Ethylenedioxy-2,6-dimethyl-2,5-cyclohexadienone

This compound was prepared from 2,6-dimethylbenzoquinone[22] according to Liotta's procedure.[20] Mp 47–50 °C (hexane); ^{1}H-NMR (CCl_4) δ 1·80 (s, 6 H), 3·91 (s, 4 H), 6·12 (s, 2 H); IR (KBr) 1680, 1640 cm^{-1}; Analysis calculated for $C_{10}H_{12}O_3$: C, 66·65; H, 6·71. Found: C, 66·59; H, 6·72.

General procedure for the reaction of organocerium(III) reagents with α,β-unsaturated carbonyl compounds

Cerium chloride ($CeCl_3 \cdot 7H_2O$) (1·5 mmol) was quickly and finely powdered in a mortar and was placed in a 30-ml two-necked flask. The flask was immersed in an oil bath and heated gradually to 135–140 °C, with evacuation (*ca.* 0·1 Torr). After maintaining the temperature for 1 h, a magnetic stirrer bar was inserted and the cerium chloride was completely dried in vacuum with stirring at the same temperature for an additional 1 h. While the flask was still hot, argon gas was introduced and the flask was cooled in an ice bath. THF (5 ml) freshly distilled from sodium/benzophenone was added with stirring and the suspension was well stirred for 2–4 h at room temperature. The resulted milky suspension was then cooled to − 78 °C and an organolithium reagent (1·5 mmol) was added dropwise with stirring, whereupon the color of the suspension turned to yellow or orange immediately. After stirring for 30 min, a carbonyl compound (1 mmol) was added with 2 ml of THF and the mixture was stirred until the reaction was completed (usually for 30 min). The reaction mixture was treated with water (10 ml) containing 0·3 ml of acetic acid. The mixture was extracted with ether, and the combined extracts were washed with brine, $NaHCO_3$ solution, and brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to preparative TLC on silica gel to give the addition product.

(*E*)-2-(4′-Methoxyphenyl)-4-phenyl-3-buten-2-ol

Colorless oil; ^{1}H-NMR (CCl_4) δ 1·60 (s, 3 H), 2·72 (s, 1 H), 3·65 (s, 3 H), 6·35 (d, *J* = 16 Hz, 1 H), 6·40 (d, *J* = 16 Hz, 1 H), 6·68 (d, *J* = 9 Hz, 2 H), 6·9–7·4 (m, 5 H), 7·25 (d, *J* = 9 Hz); IR (neat) 3420 cm^{-1}. Analysis calculated for $C_{17}H_{18}O_2$: C, 80·28; H, 7·13. Found: C, 80·52; H, 7·18.

1-(4′-Methoxyphenyl)-3-phenyl-1-butanone

Mp 85–87 °C (hexane–ethanol); ^{1}H-NMR (CCl_4) δ 1·31 (d, *J* = 6 Hz, 3 H), 3·0–3·7 (m, 3 H), 3·81 (s, 3 H), 6·90 (d, *J* = 9 Hz, 2 H), 7·28 (s, 5 H), 7·93 (d, *J* = 9 Hz, 2 H); IR (KBr) 1635 cm^{-1}. Analysis calculated for $C_{17}H_{18}O_2$: C, 80·28; H, 7·13. Found: C, 80·12; H, 7·06.

(*E*)-3-(4′-Methoxyphenyl)-1-phenyl-1-hepten-3-ol

Colorless oil; ^{1}H-NMR (CCl_4) δ 0·6–2·2 (m, 9 H), 2·53 (br s, 1 H), 3·67 (s, 3 H), 6·43 (d, *J* = 16 H, 1 H), 6·53 (d, *J* = 16 Hz, 1 H), 6·77 (d, *J* = 9 Hz, 2 H), 6·9–7·4 (m, 5 H), 7·30 (d, *J* = 9 Hz, 2 H); IR (neat) 3430 cm^{-1}. Analysis calculated for $C_{20}H_{24}O_2$: C, 81·04; H, 8·16. Found: C, 81·19; H, 8·11.

1-(4′-Methoxyphenyl)-3-phenyl-1-heptanone

Mp 72–74 °C (hexane–ethanol); ^{1}H-NMR (CCl_4) δ 0·5–2·0 (m, 9 H), 3·0–3·6 (m, 3 H), 3·75 (s, 3 H), 6·83 (d, *J* = 9 Hz, 2 H), 7·20 (m, 5 H), 7·85 (d, *J* = 9 Hz, 2 H); IR (KBr) 1665 cm^{-1}. Analysis calculated for $C_{20}H_{24}O_2$: C, 81·04; H, 8·16. Found: C, 81·01; H, 8·05.

(*E*)-3-(4′-Methoxyphenyl)-4-methyl-1-phenyl-1-penten-3-ol

Mp 92–93 °C; ^{1}H-NMR (CCl_4) δ 0·82 (d, *J* = 7 Hz, 3 H), 0·93 (d, *J* = 7 Hz, 3 H), 1·77 (s, 1 H), 1·95–2·35 (m, 1 H), 3·68 (s, 3 H), 6·47 (s, 2 H), 6·66 (d, *J* = 8 Hz, 2 H), 6·9–7·4 (m, 7 H); IR (KBr) 3470 cm^{-1}. Analysis calculated for $C_{19}H_{22}O_2$: C, 80·82; H, 7·85. Found: C, 80·95; H, 7·88.

1-(4′-Methoxyphenyl)-4-methyl-3-phenyl-l-pentanone

Mp 73–74 °C; ^{1}H-NMR (CCl_4) δ 0·75 (d, *J* = 6 Hz, 3 H), 0·92 (d, *J* = 6 Hz, 3 H), 1·6–2·1 (m, 1 H), 3·08 (br s, 3 H), 3·65 (s, 3 H), 6·60 (d, *J* = 9 Hz, 2 H), 6·95 (br s, 5 H), 7·57 (d, *J* = 9 Hz, 2 H); IR (KBr) 1670 cm^{-1}. Analysis calculated for $C_{19}H_{22}O_2$: C, 80·82; H, 7·85. Found: C, 80·96; H, 7.88.

(*E*)-1-(4′-Methoxyphenyl)-1,3-diphenyl-2-propen-1-ol

(This compound was unstable and did not give a satisfactory elemental analysis.) Pale yellow oil; ^{1}H-NMR (CCl_4) δ 2·70 (s, 1 H), 3·60 (s, 3 H), 6·43 (d, *J* = 15 Hz, 1 H), 6·60 (d, *J* = 15 Hz, 1 H), 6·65 (d, *J* = 9 Hz, 2 H), 6·9–7·5 (m, 12 H); IR (neat) 3430 cm^{-1}.

(*Z*)-2-(4′-Methoxyphenyl)-4-phenyl-3-buten-2-ol

Colorless oil; ^{1}H-NMR (CCl_4) δ 1·48 (s, 3 H), 2·41 (s, 1 H), 3·62 (s, 1 H), 3·62 (s, 1 H), 5·97 (d, *J* = 13 Hz, 1 H), 6·70 (d, *J* = 9 Hz, 2 H), 7·08 (s, 5 H), 7·32 (d, *J* = 9 Hz, 2 H); IR (neat) 3540, 3430 cm^{-1}. Analysis calculated for $C_{17}H_{18}O_2$: C, 80·28; H, 7·13. Found: C, 80·13; H, 7·09.

(*Z*)-2-(4′-Methoxyphenyl)-4-phenyl-1-hepten-3-ol

Colorless oil; ^{1}H-NMR (CCl_4) δ 0·6–2·0 (m, 9 H), 2·05 (s, 1 H), 3·60 (s, 3 H), 5·97 (d, *J* = 13 Hz, 1 H), 6·40 (d, *J* = 13 Hz, 1 H), 6·67 (d, *J* = 9 Hz, 2 H), 7·03 (s, 5 H), 7·22 (d, *J* = 9 Hz, 2 H); IR (neat) 3540, 3450 cm^{-1}. Analysis calculated for $C_{20}H_{24}O_2$: C, 81·04; H, 8·16. Found: C, 81·16; H. 8·17.

(Z)-1-(4′-Methoxyphenyl)-1,3-diphenyl-2-propen-1-ol

Pale oil; ^{1}H-NMR (CCl_4) δ 2·43 (s, 1 H), 3·53 (s, 3 H), 6·13 (d, J = 12 Hz, 1 H), 6·43 (d, J = 12 Hz, 1 H), 6·57 (d, J = 9 Hz, 2 H), 6·8–7·4 (m, 12 H); IR (neat) 3530, 3440 cm^{-1}. Analysis calculated for $C_{22}H_{20}O_2$: C, 83·52; H, 6·37. Found: C, 83·40; H, 6·38.

ACKNOWLEDGEMENT

This work was supported by grants from the Ministry of Education, Japanese Government, and the Saneyoshi Scholarship Foundation.

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