Controlling factors determining the regiochemistry of intramolecular alkoxymercuration

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The intramolecular alkoxymercuration of (*E*)-5-arylpent-4-en-1-ols indicated that the regioselectivity is closely related to the Hammett constants of the *para*-substituents on the benzene ring. Large solvent effects on the regioselectivity were also observed. These results were compared with those of the methoxymercuration of β-methylstyrene analogues. The regioselectivity is discussed in terms of steric effects as well as the electronic effects which are suggested by the MO calculation for the mercurinium ion intermediates.

Introduction

The oxymercuration–demercuration procedure provides a convenient synthetic method for effecting the Markovnikoff hydration of a carbon–carbon double bond. The reaction of (*E*)-pent-2-ene, which has a symmetrically substituted carbon–carbon double bond, preferably yielded pentan-2-ol, but there is no clear explanation of this regiochemistry.[1] In a cyclic system, 3-methylcyclohexene exclusively gave 3-methylcyclohexanol, the regiochemistry of which was explained in terms of the relative stabilities of the two possible regiochemical transition states during the attack of the nucleophiles on their mercurinium ion intermediates.[2] In contrast to the cyclohexene series, the results for the flexible cyclopentenes are not attributable to any reasonable explanation.

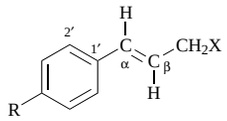
In order to examine the factors determining the regiochemistry of symmetrically substituted carbon–carbon double bonds in the formation of oxacyclic compounds by intramolecular alkoxymercuration, the reaction of (*E*)-5-phenylpent-4-en-1-ol (**1**), the *p*-methyl analogue, (*E*)-5-(*p*-methylphenyl)pent-4-en-1-ol (**2**) and the *p*-methoxy analogue, (*E*)-5-(*p*-methoxyphenyl)pent-4-en-1-ol (**3**), were carried out with mercuric acetate and their regioselectivity was compared with that obtained from the methoxymercuration of (*E*)-β-methylstyrene (**4**) and (*E*)-anethole (**5**). The products were characterized by demercuration with $NaBH_4$.

Results and discussion

Although the introduction of solvent into the product was also expected in the reaction of the unsaturated alcohols employed here, no such product was detected.

Since the resulting mixture included unidentified polymer-like substances as well as the intramolecular reaction products, the yields of the latter were relatively low (Tables 1 and 2).

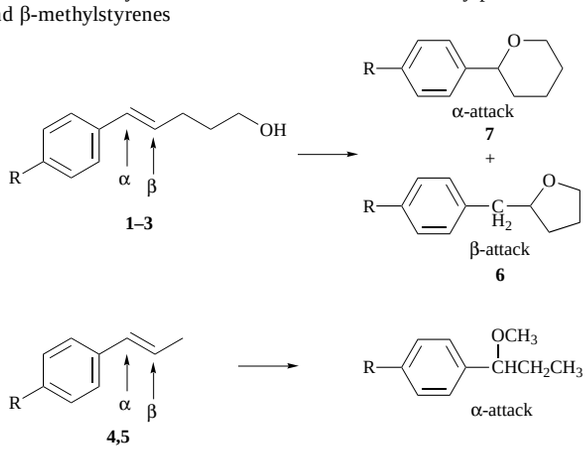
For comparison, the benzylic carbon is denoted C^{α} and the atom at the other end of the double bond is C^{β} for the mercurinium ion moiety in the series of substrates here. The nucleophile



	R	X
1:	H	CH_2CH_2OH
2:	CH_3	CH_2CH_2OH
3:	OCH_3	CH_2CH_2OH
4:	H	H
5:	OCH_3	H

was exclusively introduced to C^{α} irrespective of the *para*-substituent on the benzene ring during the reaction of β-methylstyrenes in methanol. The intramolecular alkoxymercuration of **1** in *tert*-butyl alcohol (under intramolecular reaction conditions), however, predominantly proceeded to give 2-benzyltetrahydrofuran (**6**). The minor product was 2-phenyltetrahydropyran (**7**). The reaction of **2** also gave a mixture of both five- and six-membered oxacyclic products, but the former

Table 1 Alkoxymercuration–demercuration of 5-arylpent-4-en-1-ols and β-methylstyrenes



Compound	R	Hammett constant (σ_p)	Regioselectivity α-attack (%) In MeOH	In Bu^{t}OH
1	H	0.00	52	19
2	CH_3	−0.17	82	53
3	OCH_3	−0.27	100	100
4	H	0.00	100	100
5	OCH_3	−0.27	100	100

Table 2 Solvent effect on regioselectivity of intramolecular alkoxymercuration of **1**

Solvent	Regioselectivity α-attack (%) and (yield)[a]	Swain's solvent polarity
H_2O–THF (1:1)	65 (39)	—
MeOH	52 (34)	1.25
EtOH	56 (33)	1.11
PrOH	46 (46)	1.08
BuOH	33 (54)	1.04
Pr^{i}OH	22 (48)	1.04
Bu^{t}OH	19 (40)	0.95

[a] The values in parentheses are the isolated yields of the intramolecular reaction products. THF = tetrahydrofuran.

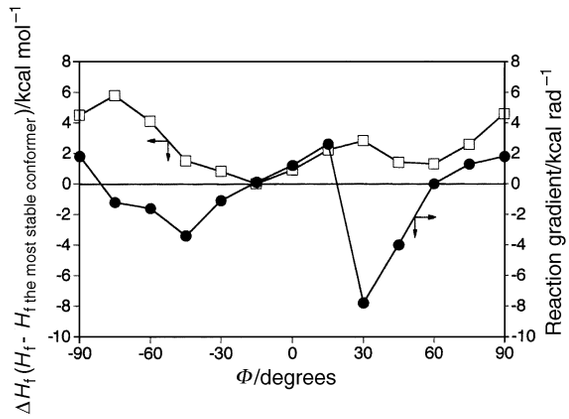


Fig. 1 Correlation between the dihedral angle and the heat of formation for (*E*)-β-methylstyrene mercurinium ion intermediate in methanol

no longer predominated. The amount of the six-membered product was slightly larger than that of the five-membered product (53 : 47). When a methoxy group was introduced at the *para*-position of the benzene ring, the reaction of **3** exclusively proceeded to give 2-(*p*-methoxyphenyl)tetrahydropyran. No product of the methoxymercuration was found but an appreciable amount of intramolecular reaction products was isolated for these three substrates in methanol. The substrate, **1**, provided the opposite regioselectivity in the case of *tert*-butyl alcohol. The major product was then **7**. The intramolecular nucleophilic attack on the benzylic position appreciably increased from 19 to 52% for **1** and 53 to 82% for **2** by replacing the solvent *tert*-butyl alcohol with methanol. The *p*-methoxy compound again exclusively gave the tetrahydropyran derivative as in *tert*-butyl alcohol. These results are shown in Table 1.

In order to investigate the solvent effects on the regioselectivity, the reaction of **1** was examined in various kinds of hydroxylic solvents. The regioselectivity of the reaction is shown in Table 2. The product distribution depended on Swain's solvent polarity.[3] Increasing the solvent polarity tends to decrease the amount of β-attack (Table 2). Such variation in regioselectivity depending on the solvent implies that the interaction of the mercurinium ion intermediate with the solvent affects the electron density of the reaction site. We accept the premise that the oxymercuration of olefins involves the rapid pre-equilibrium formation of a mercurinium ion as an unstable intermediate, followed by rate- and product-determining attack of the nucleophile.[4] The regioselectivity of the hydration of unsymmetrical carbon–carbon double bonds by oxymercuration obeys Markovnikoff's rule. The position of the nucleophilic attack on the mercurinium ion derived from a symmetrically substituted olefinic bond is considered to be controlled by the following two factors. First, an electronic factor; the relative electron densities on the two carbon atoms in the mercurinium ion moiety. Secondly, steric factors; the steric environment of the two carbon atoms in the mercurinium ion moiety and the ring size formed.

Because the steric factor which controls the regioselectivity is considered to be negligible during the methoxymercuration of simple hydrocarbons such as **4** and **5**, the attacking position of the nucleophile on the mercurinium ion moiety is practically determined by the electronic factor. In order to examine the factors determining the regiochemistry of these inter- and intra-molecular alkoxymercuriations, the optimised structures and the formal electronic charges of the mercurinium ion intermediates of **4**, **5** and the *para*-methyl analogue were obtained using semiempirical MO (MNDO/PM3) calculations.[5] The COSMO method[6] was used for the calculation because the relative permittivities of *tert*-butyl alcohol, isopropyl alcohol, ethanol and methanol, which are

Table 3 The formal electronic charges for the structure-optimized mercurinium ion intermediates of *para*-substituted β-methylstyrenes in some alcohols by PM3-COSMO calculation[a]

Substituent (Hammett constant, σ_p)	Solvent	Formal electronic charge C^α	C^β	ΔCharge ($C^\alpha - C^\beta$)
H	MeOH	−0.0654	−0.0816	0.0162
(0.00)	EtOH	−0.0662	−0.0811	0.0149
	Pr^iOH	−0.0669	−0.0805	0.0136
	Bu^tOH	−0.0685	−0.0794	0.0109
Me	Bu^tOH	−0.0598	−0.1015	0.0417
(−0.17)				
MeO	MeOH	−0.0419	−0.1161	0.0742
(−0.27)	Bu^tOH	−0.0499	−0.1078	0.0579

[a] MOPAC93 was used. Main parameters adopted are as follows: PM3, EF PRECISE (or GNORM = 0.2), RSOLV (1.0), NSPA (60), VDW (HG; 1.55 × 1.1 = 1.70), EPS (for MeOH, EtOH, Pr^iOH and Bu^tOH, 32.70, 24.55, 19.92 and 12.47, respectively).

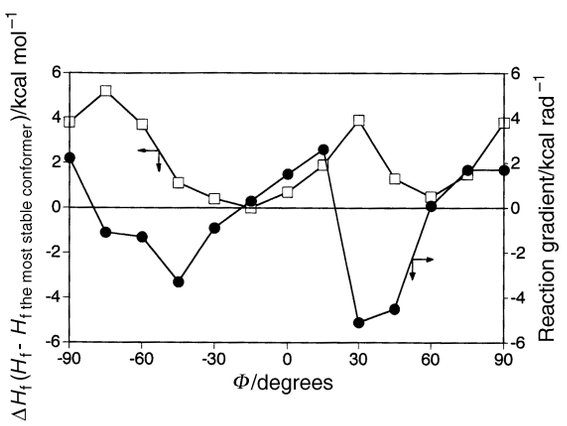


Fig. 2 Correlation between the dihedral angle and the heat of formation for (*E*)-anethole mercurinium ion intermediate in *tert*-butyl alcohol

employed in the reaction, are 12.47, 19.92, 24.55 and 32.70, respectively.[7]

The heats of formation for the conformers were monitored by changing the dihedral angles (C^β–C^α–$C^{1'}$–$C^{2'}$) every 15°; $C^{1'}$ is the phenyl carbon connected to C^α and $C^{2'}$ is one of the *ortho* carbon atoms of the phenyl ring. The correlation between the dihedral angle and the heat of formation for each conformer is shown in Figs. 1 and 2. Further detailed analysis of the correlation between the heats of formation and the dihedral angles in the vicinity of the roughly energy-minimized conformation indicated that, in the obtained optimized conformation, the C^α–$C^{1'}$ bond rotated counterclockwise with respect to the C^α–C^β bond by approximately 20°. No apparent effect of the methoxy substituent was found on examining the optimized conformer of **5**, which also showed that the dihedral angle of counterclockwise rotation was *ca.* 20° closer to that of **4**. The formal electronic charges on C^α and C^β in the structure-optimized mercurinium ion intermediates of **4** and **5**, together with the Hammett constants[8] of the *para*-substituents, are summarized in Table 3.

The regioselectivity of the reaction may be discussed on the basis of the energy-minimized structure of the mercurinium ion intermediates. The electron density of C^α for **4** was lower than those of C^β in all solvents used here and the differences between them are large in methanol which has a higher solvent polarity. Decreasing the solvent polarity decreases the differences in the electron density on C^α and C^β. Finally, the difference becomes smallest and the electron density on C^α is highest in *tert*-butyl alcohol. When a methoxy group is introduced to the *para*-position of the benzene ring, decreasing the solvent polarity

decreases the difference in the electron density on C^{α} and C^{β} similar to what happens with **4**. The difference is, however, larger than that in **4**. This indicates that the electrons lie more on C^{β} by replacement of the hydrogen at the *para*-position of the benzene ring with the electron donative methoxy group.

It is not necessary to take into account the participation of the steric factor on the reaction of β-methylstyrenes; therefore, the electronic factor plays a role in determining the regioselectivity of the reaction. As a consequence, it is reasonable for the methoxylation to take place at C^{α} which has a lower electron density.

The intramolecular attack of the nucleophile occurred on C^{β} as well as C^{α} in the reaction of 5-arylpent-4-en-1-ols, different from the case of **4** and **5**. Because the electronic situation of 5-arylpent-4-en-1-ols is considered to be not very different from that of β-methylstyrenes, the MO parameters of **4**, **5** and the *p*-methyl analogue were applied to the examination of 5-arylpent-4-en-1-ols. In the reaction of **1**, the intramolecular nucleophilic attack preferably occurred on C^{α} with a lower electron density in methanol and ethanol, while the attack apparently occurred more on C^{β} with a higher electron density than C^{α} in less polar solvents. The experimental evidence suggests that the regioselectivity is controlled by another factor as well as electronic factors in the intramolecular nucleophilic reaction.

There is no appreciable difference in the steric environment of the two carbon atoms in the mercurinium ion intermediate for the 5-arylpent-4-en-1-ols employed here. It is generally accepted that the formation of a five-membered ring is kinetically preferable to that of a six-membered ring.[9] Baldwin proposed that the opening of three-membered rings to form cyclic structures generally follows the *exo*-mode.[10] From a stereochemical point of view, the five-membered ring should be formed rather than the six-membered one in this reaction. The experimental evidence for **1** showed that electronic and steric factors operate competitively and that the latter becomes predominant when the difference in the electron density is small at the carbon atoms in the mercurinium ion moiety. The intramolecular nucleophile predominantly attacks at C^{β} with a higher electron density to give the five-membered ring compounds. The attack of an intramolecular nucleophile exclusively occurred on C^{α} in the reaction of the *para*-methoxy compounds irrespective of the nature of the solvent. Because the electron-donating ability of the methoxy group is large, an appreciable difference in the electron density between C^{α} and C^{β} is maintained in the solvents used and the regioselectivity of the intramolecular nucleophilic attack is preferably controlled by the electronic factor.

The *para*-methyl analogue showed regioselectivity between that of **1** and **3** due to the order of the electron donating ability of the substituents.

In summary, the electronic factor operates mainly to determine the regioselectivity of the intermolecular alkoxymercuration, whereas the regioselectivity is controlled by a delicate balance of both steric and electronic factors in the intramolecular reaction.

Experimental

Materials

(*E*)-1-Phenyl- and (*E*)-1-(*p*-methoxyphenyl)-pent-1-ene are commercially available. 5-(*p*-Methoxyphenyl)pent-4-en-1-ol was prepared by the method in the literature.[11] 5-Phenyl[12] and 5-(*p*-methylphenyl) analogues were prepared in a similar manner.

(*E*)-5-(*p*-Methoxyphenyl)pent-4-en-1-ol. Ethyl-4-chloroformylbutanoate (42.70 g, 0.24 mol) was slowly added to a stirred mixture of anisole (25.84 g, 0.24 mol) and $AlCl_3$ (63.48 g, 0.49 mol) in dichloromethane (100 cm^3) at 0 °C. The mixture was stirred at 0–5 °C for 3 h and quenched with cold dil. HCl. The solvent was evaporated and the residue was distillated *in vacuo* to give ethyl 4-(*p*-methoxybenzoyl)butanoate (23.17 g, 0.090 mol, 24%); mp 56–58°C.

The keto ester (9.97 g, 0.040 mol) was hydrogenated over Raney Ni prepared from Ni–Al alloy (6 g) in methanol for 12 h. The catalyst and solvent were removed and distillation gave ethyl 5-hydroxy-5-(*p*-methoxyphenyl)pentanoate (9.10 g, 96%).

The hydroxy ester (9.10 g, 0.037 mol) was heated in refluxing benzene with toluene-*p*-sulfonic acid (1.01 g, 0.005 mol) by using Dean–Stark trap for 10 min. The solution was washed with 5% sodium carbonate solution and dried over sodium sulfate. Distillation gave ethyl (*E*)-5-(*p*-methoxyphenyl)pent-4-enoate (6.8 g, 0.030 mol, 81%); mp 59–61 °C.

Treatment of the pentenoate with $LiAlH_4$ in diethyl ether gave (*E*)-5-(*p*-methoxyphenyl)pent-4-en-1-ol (2.79 g, 70%), mp 72–74 °C; δ_H(400 MHz; $CDCl_3$; *J* values in Hz), 1.72 (2 H, m, 2-H), 1.98 (1 H, s, OH), 2.26 (2 H, m, 3-H), 3.67 (2 H, t, *J* 6.4, 1-H), 3.79 (3 H, s, aromatic-OCH_3), 6.07 (1 H, dt, *J* 15.8, 6.8, 4-H) and 6.35 (1 H, d, *J* 5.6, 5-H), 6.81 (2 H, d, *J* 12.8, aromatic) and 7.26 (2 H, d, *J* 12.8, aromatic).

(*E*)-5-Phenylpent-4-en-1-ol: bp 115–122 °C (0.6 mmHg); δ_H(400 MHz; $CDCl_3$), 1.73 (2 H, m, 2-H), 1.93 (1 H, s, OH), 2.29 (2 H, m, 3-H), 3.67 (2 H, t, *J* 6.8, 1-H), 6.22 (1 H, dt, *J* 16.0, 6.8, 4-H), 6.41 (1 H, d, *J* 16.0, 5-H), 7.15–7.34 (5 H, m, aromatic); δ_C(100 MHz; $CDCl_3$), 29.2 (C2), 32.1 (C3), 62.2 (C1), 130.3 (C5), 130.0 (C4), 125.6, 125.9, 126.9, 128.3, 128.4, 137.6 (aromatic).

(*E*)-5-(*p*-Methylphenyl)pent-4-en-1-ol: bp 140–141 °C (0.5 mmHg) (Found: C, 81.50; H, 8.95. $C_{12}H_{16}O$ requires C, 81.77; H, 9.15); δ_H(400 MHz; $CDCl_3$), 1.73 (2 H, m, 2-H), 1.79 (1 H, s, OH), 2.31 (3 H, s, aromatic-CH_3), 2.48 (2 H, m, 3-H), 3.68 (2 H, t, *J* 6.6, 1-H), 6.16 (1 H, dt, *J* 15.6, 6.8, 4-H), 6.38 (1 H, d, *J* 15.6, 5-H), 7.06–7.24 (4 H, m, aromatic); δ_C(100 MHz; $CDCl_3$), 21.1 (CH_3), 29.2 (C2), 32.2 (C3), 62.3 (C1), 129.1 (C4), 130.1 (C5), 125.8, 126.4, 128.2, 128.9, 134.8, 136.6 (aromatic).

Methoxymercuration

Methoxymercuration of (*E*)-1-arylprop-1-ene. (*E*)-1-Phenylprop-1-ene (1.53 g, 0.013 mol) in methanol (30 cm^3) was added to a mixture of $Hg(OAc)_2$ (5.30 g, 0.016 mol) in methanol (100 cm^3) at room temp. and stirred for 24 h. Sodium hydroxide (3.0 M, 16 cm^3) was added, followed by $NaBH_4$ (0.32 g, 0.008 mol) in NaOH (3.0 M, 16 cm^3) at 0 °C. The precipitated Hg was removed by filtration. The product was isolated by diethyl ether extraction. After drying over Na_2SO_4, solvent was removed and distillation gave the product, which was subjected to analytical GLC.

The product from (*E*)-1-phenylprop-1-ene, 1-methoxy-1-phenylpropane, had bp 71–72 °C (25 mmHg); an authentic sample was prepared from commercially available 1-phenylpropan-1-ol by the Williamson synthesis; δ_H(400 MHz; $CDCl_3$), 0.87 (3 H, t, *J* 7.0, 3-H), 1.67–1.83 (2 H, m, 2-H), 3.21 (3 H, s, OCH_3), 4.01 (1 H, t, *J* 6.4, 1-H), 7.18–7.45 (5 H, m, aromatic); δ_C(100 MHz; $CDCl_3$), 10.2 (C3), 30.8 (C2), 56.6 (OCH_3), 85.5 (aromatic-OCH_3), 126.7, 127.4, 128.2, 142.1 (aromatic).

That from the *para*-methoxy compound, 1-methoxy-1-(*p*-methoxyphenyl)propane had bp 71–72 °C (25 mmHg); an authentic sample was prepared from 1-(*p*-methoxyphenyl)-propan-1-ol[13] by the Williamson synthesis; δ_H(400 MHz; $CDCl_3$), 0.85 (3 H, t, *J* 7.1, 3-H), 1.63–1.82 (2 H, m, 2-H), 3.15 (3 H, s, OCH_3), 3.80 (3 H, s, aromatic-OCH_3), 3.96 (1 H, t, *J* 6.4, 1-H), 7.18–7.45 (4 H, m, aromatic); δ_C(100 MHz; $CDCl_3$), 10.2 (C1), 30.8 (C2), 55.2 (OCH_3), 56.3 (aromatic-OCH_3), 85.0 (C1), 113.6, 127.9, 134.1, 159.0 (aromatic).

Intramolecular alkoxymercuration of (*E*)-5-arylpent-4-en-1-ol

The (*E*)-5-arylpent-4-en-1-ol (0.06 mol) in the appropriate solvent (10 cm^3) was added to a $Hg(OAc)_2$ (23.5 g, 0.07 mol) in the same solvent (50 cm^3) at room temp. and stirred for 24 h. Sodium hydroxide (3.0 M, 10 cm^3) was added, followed by $NaBH_4$ (0.2 g, 0.005 mol) in NaOH (3.0 M, 10 cm^3) at 0 °C. The

precipitated Hg was removed by filtration. The product was isolated by diethyl ether extraction. After drying over Na_2SO_4, solvent was removed and the residual oil was subjected to analytical GLC. The residual oil was also column chromatographed (SiO_2, 95:1 hexane–ethyl acetate) to give the pure compound.

The products from (*E*)-5-phenylpent-4-en-1-ol were: 2-benzyltetrahydrofuran,[14] bp 110–112 °C (10 mmHg); δ_H(400 MHz; $CDCl_3$), 1.56 (1 H, dd, *J* 10.5, 7.5), 1.88 (3 H, m), 2.74 (1 H, dd, *J* 13.4, 6.4, benzyl), 2.92 (1 H, dd, *J* 13.4, 6.4, benzyl), 3.48 (1 H, q, *J* 7.1, 5-H), 3.73 (1 H, dt, *J* 8.3, 7.1, 5-H), 3.89 (1 H, m, 2-H), 7.19–7.30 (5 H, m, aromatic); 2-phenyltetrahydropyran,[15] bp 105–108 °C (10 mmHg); δ_H(400 MHz; $CDCl_3$), 1.63 (4 H, m), 1.83 (1 H, br d, *J* 10.2), 1.93 (1 H, m), 3.61 (1 H, dt, *J* 10.2, 2.7, 6-H), 4.13 (1 H, dt, *J* 8.1, 2.0, 6-H), 4.31 (1 H, dd, *J* 10.2, 2.0, 2-H), 7.22–7.37 (5 H, m, aromatic).

The products from (*E*)-5-(*p*-methylphenyl)pent-4-en-1-ol were: 2-(*p*-methylbenzyl)tetrahydrofuran, bp 108–111 °C (10 mmHg) (Found: C, 82.01; H, 8.98. $C_{12}H_{16}O$ requires C, 81.77; H, 9.15%); δ_H(400 MHz; $CDCl_3$), 1.56 (1 H, m), 1.87 (2 H, m), 2.31 (3 H, s, aromatic-CH_3), 2.33 (1 H, t, *J* 3.4), 2.70 (1 H, dd, *J* 13.8, 6.2, benzyl), 2.88 (1 H, dd, *J* 13.8, 6.0, benzyl), 3.73 (1 H, m, 5-H), 3.89 (1 H, m, 5-H), 4.04 (1 H, m, 2-H), 7.07–7.26 (4 H, m); δ_C(100 MHz; $CDCl_3$), 21.1 (CH_3), 25.7, 26.0, 38.7 (benzyl), 66.9 (C5), 80.9 (C2), 125.6, 129.4, 137.5, 142.1 (aromatic); 2-(*p*-methylphenyl)tetrahydropyran, bp 108–111 °C (10 mmHg) (Found: C, 81.94; H, 8.81. $C_{12}H_{16}O$ requires C, 81.77; H, 9.15%); δ_H(400 MHz; $CDCl_3$), 1.67 (4 H, m, 3-H, 4-H), 1.80 (1 H, br d, *J* 9.6, 3-H), 1.93 (1 H, dd, *J* 6.4, 3.2, 3-H), 2.32 (3 H, s, aromatic-CH_3), 3.60 (1 H, dt, *J* 15.6, 2.4, 6-H), 4.12 (1 H, dd, *J* 11.2, 4.0, 6-H), 4.28 (1 H, br d, *J* 9.6, 2-H), 7.13 (2 H, d, *J* 8.0, aromatic), 7.23 (2 H, d, *J* 8.0, aromatic); δ_C(100 MHz; $CDCl_3$), 21.1 (CH_3), 24.0, 25.9, 30.0, 69.0 (C6), 80.0 (C2), 125.9, 128.9, 136.8, 140.4 (aromatic).

The product from (*E*)-5-(*p*-methoxyphenyl)pent-4-en-1-ol was 2-(*p*-methoxyphenyl)tetrahydropyran,[16] bp 138 °C (10 mmHg); δ_H(400 MHz; $CDCl_3$), 1.55–1.70 (4 H, m), 1.74 (1 H, br d, *J* 9.6), 1.92 (1 H, br s), 3.60 (1 H, t, *J* 11.6), 3.78 (3 H, s, aromatic-OCH_3), 4.11 (1 H, br t, *J* 10.0), 4.26 (1 H, dd, *J* 10.0, 2.0), 6.86 (2 H, d, *J* 8.8, aromatic), 7.27 (2 H, d, *J* 8.8, aromatic); δ_C(100 MHz; $CDCl_3$), 24.0, 25.9, 33.8 (C3), 55.2 (OCH_3), 69.0 (O–C), 79.7 (O–C), 113.6, 127.1, 135.6, 158.8 (aromatic).

NMR and GC analyses

^{1}H NMR and ^{13}C NMR spectra were obtained with a JEOL JNM α-400 instrument operating at 400 MHz and 100.13 MHz, respectively, in the pulse Fourier mode. Gas chromatographic analyses were performed on a Shimadzu model GC-8AIF with a Carbowax 20M chemical bonded silica capillary column (0.25 mm × 25 m or 11 m) at 120 and 140 °C.

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