Allylation of Carbonyl Compounds by Allylic Acetates Using a Cobalt Halide as Catalyst

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Abstract: In acetonitrile as solvent and in the presence of a simple cobalt halide as catalyst, the reduction by zinc dust of a mixture of aldehydes or ketones and allylic acetates affords the corresponding homoallylic alcohols in good yields.

Key words: allylation, homo-allylic alcohols, carbonyl copmounds, cobalt halide, catalyst

Allylation of carbonyl compounds is one of the most interesting processes for the preparation of homoallylic alcohols. Over the past few decades, many reagents have been developed for such reactions.¹ Generally, allylation of carbonyl compounds from allylic acetates, which are easily derived from available allylic alcohols, requires catalysis by a palladium complex associated with a reducing reagent which are metals or salts such as Zn,² SnCl₂,³ SmI₂,⁴ and InI⁵ in a stoichiometric amount.

In most cases, only aldehydes are reactive except with SmI_2 , which also allows the allylation of ketones. Nevertheless, allylation is restricted since aromatic and α , β -unsaturated aldehydes or ketones lead to pinacol formation with this samarium salt. Another route to allylic anions from allylic acetate is their electrochemical generation. Indeed, a Pd(II)–Zn(II) system allows the reaction of allylic acetates with carbonyl compounds via electrochemical reduction.⁶ However, this process is carried out in a divided cell fitted with Pt electrodes and requires a stoichiometric amount of zinc chloride. To our knowledge, the only catalyst, which can replace palladium, is a ruthenium complex⁷ in the presence of carbon monoxide to ensure the catalytic activity of the ruthenium complex. Nevertheless, the reaction is limited to aldehydes.

Recently, we have discovered that cobalt halides are efficient catalysts for some reactions usually catalysed by palladium complexes.⁸ This cobalt catalyst associated with pyridine has also been used for the electroreductive allylation of aromatic halides by allylic acetates.⁹

In this paper, we report our investigations of the cobaltcatalysed coupling reaction of allyl acetates with carbonyl compounds using zinc dust as a reducing agent, leading to homoallylic alcohols (Scheme 1).



Scheme 1

Allylic alcohols were formed from the ketone (Scheme 1, Table 1) by reaction of cobalt bromide and zinc dust. This is a mild reaction that is carried out at room temperature and the pure allylic alcohol is isolated by column chromatography.

The use of DMF and THF as solvent inhibits the reaction and neither substrate is consumed. Besides acetonitrile, benzonitrile or adiponitrile can be used but the purification of the homoallylic alcohol is therefore difficult. The use of 2 equivalents of Zn powder and 0.3 equivalents of catalyst increased the rate of the reaction but smaller amounts (1 equiv of zinc, 0.2 equiv of CoBr₂) also result in the consumption of all the starting products. With only 0.1 equivalents of cobalt salt, only small amounts of homoallylic alcohol are obtained. The yield is similar even when the reaction is carried out at 50 °C, but the reaction time decreases (5 h instead of 7 h). Trifluoroacetic acid is necessary to activate the zinc dust. Iodine or acetic acid could also play this part. Undoubtedly, the zinc dust reduces CoBr₂ to a Co(I) species, which is the reactive species towards the allylic acetate. Further mechanistic studies, including the electrochemical characterisation of active catalyst species are now in progress. The results of the allylation of various ketones by allyl acetate are reported in Table 1.

Good yields are obtained with several aliphatic, aromatic, and even heteroaromatic ketones. Reaction times range from 5 to 7 hours. In the case of benzophenone (Table 1, entry 5), the ketone is not totally consumed, resulting in a moderate yield, this could result from steric hindrance due to the phenyl groups. In this case, an excess of allylic acetate is necessary (with 2 equiv of allylic acetate) to increase the the yield to 75%. With a more reactive ketone such as ethyl pyruvate, no traces of coupling with allyl acetate are detected, only the resulting pinacol is formed.

In order to study the regiochemistry of this carbonyl allylation, the reaction with cyclohexanone was extended to various allylic substrates (Table 2).

Substituted acetates are convenient as reagents for the carbonyl allylation catalysed by the Co–Zn system. These al-

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lylic derivatives react more slowly with cyclohexanone than simple allyl acetate (Table 2, entries 1–4). The ketone regioselectively attacks the more substituted allylic position to give a single regioisomer. This process exhibits the reverse regioselectivity in comparison with the Pd(0)–SmI₂ system.

Allylic alcohol can also be used, avoiding the preparation of the corresponding allylic acetate (Table 2, entry 4). This last reaction has been poorly developed except for Pd(0)– $SnCl_2^3$ and Pd(0)– InI^5 systems. In our case, the coupling reaction takes place for the cinnamyl alcohol but the starting products are consumed more slowly (4 days) than the corresponding acetate (Table 2, entry 4).

As shown in Scheme 2, the allylation of an α -chloroketone by cinnamyl acetate was also performed but the reactive ketone first undergoes a reduction reaction of the carbon–chlorine bond affording the corresponding ho-moallylic alcohol **10** in 72% yield.

The reaction of allyl acetate catalysed by Co–Zn system has also been extended to aldehydes, which are reactive in most allylation processes. The results are reported in Table 3.

Several aldehydes such as aromatic (Table 3, entries 1–3), aliphatic (Table 3, entries 4–6) and heteroaromatic (Table 3, entries 8,9) reacted with allyl acetate. With an α , β -unsaturated aldehyde (Table 3, entry 7), the 1,2-addition product is selectively obtained.

Our mechanistic interpretation is based on the mechanism described recently concerning the activation of allylic ac-

Biographical Sketches



Paulo Gomes was born in France in 1975. He received his PhD degree from the University of Paris XII-val de Marne, France, at the Laboratoire d'Electrochimie, Catalyse et Synthèse Organique in Thiais in 2002 under the supervision of Prof. Jacques Périchon and Corinne Gosmini. His thesis work concerned the synthesis and electrosynthesis of C–C bonds catalyzed by cobalt complexes. In October 2002, he moved to the group of Prof. Olivia Reinaud at the University René Descartes, France, where he is currently engaged in postdoctoral research, studying the synthesis of water soluble calix[6]arenes.





Corinne Gosmini was born in France and received her PhD degree from the University Pierre et Marie Curie, Paris, in 1992 under the supervision of Prof. Jean F. Normant and Raymond Sauvêtre. She obtained a research position at the CNRS in 1993 in the group of Prof. Jacques Périchon at the Laboratoire d'Electrochimie,

Jacques Périchon is Professor at the Université Paris Val de Marne, France. In 1985, he created the Laboratoire d'Electrochimie, Catalyse et Synthèse Organique at the CNRS of Thiais, which he directed for 12 years. In 1994, he received an award from the French Academy of Sciences. His research interests, originally devoted to analytical electrochemistry, moved to orCatalyse et Synthèse Organique in Thiais. She completed her habilitation at the University of Paris XII-Val de Marne in 2001. She was primarily interested in the electrosynthesis of arylzinc compounds and in the development of new electrochemical methods devoted to C–C bond formation. Since 1998, she has devel-

ganic electrosynthesis (in particular nickel catalysts) in the mid 1980's. Since 1983, he applied the sacrificial anode process to the development of a variety of reactions (preparation of aryl carboxylates, crosscoupling of aromatic halides, synthesis of arylzinc compounds, etc...), some of these electrochemical processes having no chemical analogues. For the last 5 oped new electrochemical reactions catalyzed by simple cobalt complexes. Recently, she has pioneered laboratory research devoted to the conversion of electrochemical synthetic processes to industry-adaptable pure chemical processes, notably in the preparation of arylzinc compounds.

years, his research has focused on the development of electrosynthetic reactions catalysed by cobalt or iron halides and on their transposition to 'all chemical' processes, to make organic chemists more familiar with electrosynthesis and easier to scale up in industry. He is still working on these topics with his group. Table 1 Ketones Allylation by Allyl Acetate with Co–Zn

OAc 10 mmol	+ $\begin{array}{c} R^1 \\ 0 \\ R^2 \\ 0 \\ 10 \\ 0 \\ 10 \\ 0 \\ 10 \\ 0 \\ 0 \\ 0 $	CoBr ₂ (3 mmol) Zn (20 mmol) MeCN, RT CF ₃ COOH (0.05 mL)	OH R ¹ R ²		
En-try	Ketone		Product	Yield (%) ^a	Time (h)
1	 0			84	7
2	 0		OH2	70	5
3			HO 3	65	5
4				84	7
5			HO 5	40	5
6	→=0 √S		HO S 6	55	3

^a Yields of isolated pure products.

 Table 2
 Cyclohexanone Allylation by Allylic Substrates with Co–Zn



^a Yields of isolated pure products.



Scheme 2

Table 3 Allylation of Aldehydes by Allyl Acetate with Co-Zn



^a Yields of isolated pure products.

etate by $CoBr_2$.¹⁰ In a preliminary step, cobalt(II) bromide is reduced to Co(I) by zinc dust previously activated by acid (trace amounts). That latter Co(I) complex undergoes oxidative addition with the allylic acetate which results in a η^3 -allyl Co(III) species, which is readily reduced by zinc dust into η^3 -allyl Co(II) species. That latter η^3 -allyl Co(II) complex is most likely the active species toward the carbonyl compound, as suggested in Scheme 3. This reaction using the new system Co–Zn provides a novel method for forming C–C bonds by coupling carbonyl compounds and allylic acetates or alcohols. This process is interesting since the starting allylating reagents, acetates, and alcohols, are easily prepared and relatively stable. The advantage of this method is its applicability to both ketones and aldehydes. Further studies are in progress to extend that reaction to other electrophilic reagents.



Scheme 3

All reactions were conducted under an atmosphere of argon. Reactions were monitored by GC analyses on a Varian 3300 by using a column CPSiL5CB (l = 25 m) coupled with a Chromjet Spectra-Physics. NMR spectra were obtained in CDCl₃ at r.t. on a Brucker AC-200 instrument [¹H NMR (200MHz), ¹³C NMR (50MHz)]. Mass spectra (MS) were determined on a Thermofinnigan GCQ recorded with a spectrometer coupled with a gas chromatograph (25m). All reagents and solvents were obtained from commercial suppliers and were used without further purification. All reactions involved the use of anhydrous CoBr₂ (Acros). Chromatograph was carried out using Merck 60 230–400 mesh silica gel. The starting substituted allylic acetates were prepared from the commercially available corresponding alcohols as described in the literature.¹¹

1-(Prop-2-enyl)cyclohexan-1-ol (1); Typical Procedure

In a solution of MeCN (20 mL) containing zinc dust (1.3 g, 20 mmol) and CoBr₂ (0.66 g, 3 mmol), allylic acetate (1.1 mL,10 mmol) and a stoichiometric amount of cyclohexanone (0.98 g,10 mmol) were added. The reaction medium is then activated by adding trifluoroacetic acid (0.05 mL) at r.t. The mixture was stirred at r.t. for 7 h, one of the two starting compounds was consumed. The mixture was quenched with HCl (2 N) and extracted with Et₂O (2×25 mL). The combined organic layers were washed with brine, dried (MgSO₄), and the solvent evaporated under vacuum to afford **1**. The residue was purified by column chromatography on silica gel with pentane–Et₂O (90:10) as eluent to give **1** in 84% (1.18 g) yield.

IR(film): 3440, 2940, 1720 cm⁻¹.

¹H NMR: δ = 5.69–5.48 (m, 1 H), 4.82–4.73 (m, 2 H), 1.91 (d, 2 H, J = 7.3 Hz), 1.72 (s, 1 H), 1.42–1.15 (m, 10 H).

¹³C NMR: δ = 133.8, 117.9, 71.3, 46.6, 37.0, 25.6, 22.0.

MS: *m*/*z* (%) = 123 (M – OH, 11), 99 (39), 81(100), 79 (72), 77 (15), 55 (15).

1-(Prop-2-enyl)cyclohex-2-en-1-ol (2)

By a similar procedure to that described for the synthesis of **1**, stirring cyclohexenone (0.96 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 5 h afforded **2**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **2** in 70% (0.98 g) yield.

IR(film): 3440, 3060, 2980, 2940, 1640, 1600 cm⁻¹.

¹H NMR: δ = 5.98–5.77 (m, 2 H), 5.64–5.59 (m, 1 H), 5.15–5.00 (m, 2 H), 2.29 (d, 2 H, *J* = 7.2 Hz), 2.02 (s, 1 H), 2.16–1.59 (m, 6 H).

¹³C NMR: δ = 133.5, 132.0, 129.7, 118.1, 68.9, 46.5, 35.2, 24.9, 18.7.

MS: *m*/*z* (%) = 121 (M – OH, 25), 97 (100), 79(44), 77 (30), 67 (14), 55 (20).

4-Methylnon-1-en-4-ol (3)

By a similar procedure to that described for the synthesis of $\mathbf{1}$, the stirring of heptan-2-one (1.14 g,10 mmol) with allylic acetate (1.1 ml, 10 mmol) for 5 h afforded $\mathbf{3}$. The residue was purified by col-

umn chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **3** in 65% (1.02 g) yield.

IR(film): 3420, 2940 cm⁻¹.

¹H NMR: δ = 5.97–5.76 (m, 1 H), 5.16–5.05 (m, 2 H), 2.22 (d, 2 H, J = 7.4 Hz), 1.68 (s, 1 H), 1.50–1.21 (m, 8 H), 1.16 (s, 3 H), 0.89 (t, 3 H, J = 6.6 Hz).

¹³C NMR: δ = 134.1, 118.4, 72.1, 46.2, 41.7, 32.3, 26.6, 23.4, 22.5, 13.9.

MS: m/z (%) = 139 (M – OH, 12), 115 (53), 97 (43), 69 (26), 55 (100).

2-Phenylpent-4-en-2-ol (4)

By a similar procedure to that described for the synthesis of **1**, stirring acetophenone (1.2 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 7 h afforded **4**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **4** in 84% (1.36 g) yield.

IR(film): 3440, 2980, 2940, 1640, 1600 cm⁻¹.

¹H NMR: δ = 7.36–7.08 (m, 5 H), 5.62–5.41 (m, 1 H), 5.06–4.97 (m, 2 H), 2.42 (d, 2 H, *J* = 8.0 Hz), 2.17 (s, 1 H),1.43 (s, 3 H).

¹³C NMR: δ = 147.4, 133.5, 127.9, 126.4, 124.6, 119.1, 73.4, 48.2, 29.6.

MS: *m/z*(%) = 145 (M – OH, 57), 129 (10), 122 (11), 121 (100), 105 (26), 77 (32), 51 (20).

1,1-Diphenylbut-3-en-1-ol (5)

By a similar procedure to that described for the synthesis of 1, stirring benzophenone (1.82 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 5 h afforded 5. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give 5 in 40% (0.9 g) yield.

IR(film): 3500, 3060, 3040, 1640, 1600 cm⁻¹.

¹H NMR: δ = 7.75–7.02 (m, 10 H), 5.72–5.51 (m, 1 H), 5.08–5.02 (m, 2 H), 3.00 (d, 2 H, *J* = 7.1 Hz), 2.70 (s, 1 H).

 ^{13}C NMR: $\delta = 146.9,\ 137.7,\ 135.1,\ 130.2,\ 128.3,\ 127.0,\ 126.2,\ 118.8,\ 78.1,\ 46.9.$

MS: *m*/*z* (%) = 206 (10), 184 (160), 183 (100), 105 (93), 77 (27).

2-(2-Thienyl)pent-4-en-2-ol (6)12

By a similar procedure to that described for the synthesis of **1**, stirring 2-acetylthiophene (0.94 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 3 h afforded **6**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (90:10) as eluent to give **6** in 55% (0.75 g) yield.

IR(film): 3450, 3060 cm⁻¹.

¹H NMR: δ = 7.02 (dd, 1 H, *J* = 1.5, 4.7 Hz), 6.81–6.75 (m, 2 H), 5.72–5.51 (m, 1 H), 5.02–4.93 (m, 2 H), 2.92 (s, 1 H), 2.59–2.40 (m, 2 H), 1.47 (s, 3 H).

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¹³C NMR: δ = 153.2, 133.6, 126.7, 123.9, 122.4, 119.2, 73.0, 46.3, 30.1.

MS: *m*/*z* (%) = 151 (M – OH, 10), 127 (160), 111 (13).

1-(1-Methylprop-2-en-1-yl)cyclohexan-1-ol (7)

By a similar procedure to that described for the synthesis of 1, stirring cyclohexanone (0.98 g, 10 mmol) with crotyl acetate (1.14 g, 10 mmol) for 24 h afforded 7. The residue was purified by column chromatography on silica gel with pentane– Et_2O (90:10) as eluent to give 7 in 94% (1.45 g) yield.

IR(film): 3460, 2940, 1640, cm⁻¹.

¹H NMR: δ = 5.92–5.74 (m, 1 H), 5.09–5.00 (m, 2 H), 2.24–2.09 (m, 1 H), 1.61 (s, 1 H), 1.56–1.08 (m, 10 H), 1.02 (d, 3 H, *J* = 6.9 Hz).

¹³C NMR: δ = 140.4, 115.6, 72.3, 48.3, 34.8, 34.3, 25.8, 21.7, 14.0.

MS: *m*/*z* (%) = 137 (M – OH, 5), 99 (47), 81(100), 81 (100), 79 (71), 77 (15).

1-(1-Phenylpropen-2-yl)cyclohexan-1-ol (8)

By a similar procedure to that described for the synthesis of **1**, stirring cyclohexanone (0.98 g, 10 mmol) with cinnamyl acetate (1.76 g, 10 mmol) for 16 h afforded **8**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (90:10) as eluent to give **8** in 69% (1.49 g) yield.

IR(film): 3450, 3030, 2920, 2860, 1640, 1600 cm⁻¹.

¹H NMR: δ = 7.26–7.08 (m, 5 H), 6.34–6.15 (m, 1 H), 5.11–4.98 (m, 2 H), 3.16 (d, 1 H, *J* = 9.8Hz), 1.62–1.05 (m, 11 H).

¹³C NMR: δ = 140.9, 137.7, 129.2, 128.1, 126.4, 117.1, 72.5, 61.0, 35.7, 35.4, 25.6, 21.8.

MS: m/z(%) = 199 (M-OH, 5), 118 (89), 117(100), 115 (33), 99 (17), 81 (52), 79 (37).

1-(1,1-Dimethylprop-2-en-1-yl)cyclohexan-1-ol (9)

By a similar procedure to that described for the synthesis of **1**, the stirring of cyclohexanone (0.98 g, 10 mmol) with 1,1-dimethyl prop-2-enyl acetate **21** (1.28 g, 10 mmol) for 7 d afforded **9**. The residue was purified by column chromatography on silica gel with pentane–Et₂O (90:10) as eluent to give **9** in 24% (0.4 g) yield.

IR(film): 3450 cm⁻¹.

¹H NMR: δ = 5.93 (dd, 1 H, *J* = 11, 17.4 Hz), 5.04–4.91 (m, 2 H), 1.61–1.31 (m, 11 H), 0.93 (s, 6 H).

¹³C NMR: δ = 145.5, 113.3, 74.4, 44.2, 31.3, 25.8, 21.9, 21.8, 21.7.

MS: *m/z* (%) = 151 (M – OH, 5), 99 (38), 81 (100), 77 (14), 70 (10), 55 (27).

3-Methyl-4-phenylhex-5-en-3-ol (10)¹³

By a similar procedure to that described for the synthesis of **1**, stirring 3-chloro 2-butanone (1.07 g, 10 mmol) with cinnamyl acetate (1.76 g, 10 mmol) for 7 h afforded **10**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (98:2) as eluent to give **10** in 72% (1.37 g) yield.

IR(film): 3450, 3030, 2920, 1640, 1600 cm⁻¹.

¹H NMR: δ = 7.23–7.05 (m, 5 H,), 6.31–6.09 (m, 1 H), 5.09–4.97 (m, 2 H), 3.20 (2 d, 1 H, *J* = 4.8 Hz), 1.88 (s, 1 H), 1.37 (2 q, 2 H, *J* = 7.4 Hz), 0.99 (2 s, 3 H), 0.81 (2 t, 3 H, *J* = 7.4 Hz).

 ^{13}C NMR: δ = 141.2, 141.0, 137.9, 137.8, 129.1, 128.1, 126.4, 117.2, 117.1, 74.1, 74.0, 59.9, 32.6, 32.4, 24.1, 24.0, 7.9.

MS: *m*/*z* (%) = 173 (M – OH, 5), 118 (69), 117 (100), 115 (38), 91 (12), 73 (12), 55 (26).

1-(4-Methoxyphenyl)but-3-en-1-ol (11)

By a similar procedure to that described for the synthesis of **1**, stirring 4-methoxybenzaldehyde (1.36 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 5 h afforded **11**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **11** in 83% (1.48 g).

IR(film): 3420, 3000, 2920, 2840, 1620 cm⁻¹.

¹H NMR: δ = 7.41 (d, 2 H, *J* = 8.7 Hz), 7.02 (d, 2 H, *J* = 8.7 Hz), 6.00–5.83 (m, 1 H), 5.32–5.23 (m, 2 H), 4.80 (t, 1 H, *J* = 6.6 Hz), 3.94 (s, 3 H), 2.68–2.61 (m, 2 H), 2.19 (s, 1 H).

¹³C NMR: δ = 159.0, 136.1, 134.7, 127.2, 118.0, 113.8, 73.1, 55.2, 43.6.

MS: *m*/*z* (%) = 161 (M – OH, 19), 160 (100), 159 (86), 145 (27), 144 (27), 129 (41), 128 (22), 115 (36), 151 (M – OH,10), 127 (160), 111 (13).

1-(2-Methoxyphenyl)but-3-en-1-ol (12)

By a similar procedure to that described for the synthesis of **1**, stirring 2-methoxybenzaldehyde (1.36 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 6 h afforded **12**. The residue was purified by column chromatography on silica gel with pentane/e–Et₂Other (95:5) as eluent to give **12** in 96% (1.71 g) yield.

IR (film): 3440, 2940, 1740, 1600 cm⁻¹.

¹H NMR: δ = 7.26–7.10 (m, 2 H,), 6.90–6.71 (m, 2 H,), 5.81–5.64 (m, 1 H,), 5.08–4.80 (m, 3 H,), 3.72 (s, 3 H,), 2.50–2.37 (m, 2 H,), 1.98 (s, 1 H,).

 ^{13}C NMR: δ = 156.2, 135.1, 131.5, 128.2, 126.7, 120.5, 117.3, 110.3, 69.5, 55.1, 41.7.

MS: m/z (%) = 161 (M – OH, 5), 138 (11), 137 (100), 107 (61), 77 (11).

1-Naphthylbut-3-en-1-ol (13)

By a similar procedure to that described for the synthesis of **1**, stirring 1-naphtaldehyde (1.59 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 96 h afforded **13**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **13** in 63% (1.25 g) yield.

IR (film): 3400, 3060, 2940, 1680 cm⁻¹.

¹H NMR: δ = 8.12–7.47 (m, 7 H), 6.07–5.86 (m, 1 H), 5.57–5.30 (m, 1 H), 5.29–5.19 (m, 2 H), 4.99 (s, 1 H), 2.86–2.59 (m, 2 H).

 ^{13}C NMR: δ = 139.3, 134.6, 133.7, 130.2, 128.1, 127.8, 125.9, 125.4, 122.9, 117.9, 70.0, 42.6.

MS: *m*/*z* (%) = 199 (M + 1, 23), 158 (12), 157 (100), 129 (64), 128 (25), 127 (11).

Dodec-1-en-4-ol (14)

By a similar procedure to that described for the synthesis of **1**, stirring nonyl aldehyde (1.42 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 4 h afforded **14**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **14** in 92% (1.69 g) yield.

IR (film): 3460, 2920, 1730 cm⁻¹.

¹H NMR: δ = 5.75–5.54 (m, 1 H), 4.96–4.88 (m, 2 H), 3.51–3.46 (m, 1 H), 2.16–1.91 (m, 2 H), 1.86 (s, 1 H), 1.44–1.10 (m, 14 H), 0.70 (t, 3 H, *J* = 6.3 Hz).

¹³C NMR: δ = 134.6, 117.4, 70.9, 41.5, 36.4, 31.7, 29.4, 29.1, 25.4, 22.4, 20.3, 13.8.

MS: *m*/*z* (%) = 167 (M – OH, 69), 153 (64), 149 (60), 135 (76), 121 (60), 109 (60), 107 (55), 98 (100), 97 (48), 95 (57), 93 (84), 84 (47), 83 (69), 81 (82), 79 (73), 67 (79), 55 (41).

6,10-Dimethylundeca-1,9-dien-4-ol (15)

By a similar procedure to that described for the synthesis of 1, stirring of 3,7-dimethyl-6-octenal (1.54 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 6 h afforded **15**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **15** in 73% (1.43 g) yield.

IR (film): 3400, 2920 cm⁻¹.

¹H NMR: δ = 5.94–5.73 (m, 1 H), 5.15–5.08 (m, 3 H), 3.80–3.68 (m, 1 H), 2.33–2.01 (m, 3 H), 1.97 (s 1 H), 1.68 (s, 3 H) 1.60 (s, 3 H), 1.55–1.11 (m, 6 H), 0.92 (2 d, 3 H, *J* = 6.5 Hz).

 ^{13}C NMR: δ = 134.8, 130.9, 124.6, 117.8, 68.6, 68.3, 44.2, 42.7, 42.0, 37.8, 36.6, 29.2, 28.8, 20.1, 19.0, 17.5.

MS: *m*/*z* (%) = 155 (46), 137 (47), 121 (22), 107 (32), 95 (71), 93 (28), 81 (100), 79 (50), 69 (29), 67 (79).

1-Phenylpent-4-en-2-ol (16)

By a similar procedure to that described for the synthesis of **1**, stirring phenylacetaldehyde (1.2 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 4 h afforded **16**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **16** in 94% (1.52 g) yield.

IR (film): 3420, 2980, 2920, 1620 cm⁻¹.

 $^1\mathrm{H}$ NMR: δ = 7.22–7.04 (m, 5 H), 5.86–5.65 (m, 1 H), 5.06–4.99 (m, 2 H), 3.81–3.68 (m, 1 H), 2.74–2.54 (m, 2 H), 2.24–2.05 (m, 3 H)

¹³C NMR: δ = 138.6, 134.1, 129.5, 128.5, 126.4, 117.9, 71.8, 43.3, 41.2.

MS: *m*/*z* (%) = 145 (M – OH, 19), 144 (16), 121 (37), 103 (33), 92 (70), 91 (100), 79 (16), 77 (13), 65 (13).

1-Phenylhexa-1,5-dien-3-ol (17)

By a similar procedure to that described for the synthesis of **1**, stirring *trans*-cinnamaldehyde (1.32 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 72 h afforded **17**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **17** in 57% (0.99 g) yield.

IR (film): 3420, 2940 cm⁻¹.

¹H NMR: δ = 7.48–7.11 (m, 5 H), 6.58–6.40 (m, 1 H), 6.13–5.61 (m, 2 H), 5.09–4.95 (m, 2 H), 4.09–3.95 (m, 2 H), 2.44–2.24 (m, 1 H), 1.98 (s, 1 H).

 ^{13}C NMR: $\delta = 136.7,\ 134.6,\ 132.7,\ 130.4,\ 128.5,\ 126.5,\ 125.6,\ 116.9,\ 96.5,\ 40.7.$

MS: *m*/*z* (%) = 156 (100), 155 (51), 153 (39), 141 (63), 128 (47), 115 (39), 91 (26).

1-(2-Furyl)but-3-en-1-ol (18)

By a similar procedure to that described for the synthesis of **1**, the stirring of 2-furaldehyde (0.96 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 20 h afforded **18**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **18** in 75% (1.04 g) yield.

IR (film): 3400, 3080, 2920, 1740, 1700, 1600 cm⁻¹.

¹H NMR: δ = 7.26 (dd, 1 H, *J* = 0.9 Hz, 1.9 Hz), 6.22 (dd, 1 H, *J* = 1.9, 3.1 Hz), 6.13 (d, 1 H, *J* = 3.1 Hz), 5.79–5.59 (m, 1 H), 5.10–4.98 (m 2 H), 4.61 (t, 1 H, J = 6.6 Hz) 2.68 (s, 1 H) 2.54–2.46 (m, 2 H).

¹³C NMR: δ = 156.2, 141.9, 133.9, 118.3, 110.1, 106.1, 67.0, 40.1.

MS: *m*/*z* (%) = 138 (5), 121 (M – OH, 5), 97 (100), 69 (20).

1-(3-Thienyl)but-3-en-1-ol (19)

By a similar procedure to that described for the synthesis of 1, stirring 3-thiophenecarboxaldehyde (1.12 g, 10 mmol) with allylic acetate (1.1 mL, 10 mmol) for 20 h afforded **19**. The residue was purified by column chromatography on silica gel with pentane– Et_2O (95:5) as eluent to give **19** in 89% (1.37 g) yield.

IR (film): 3400, 3080, 2920, 1640 cm⁻¹.

¹H NMR: δ = 7.11 (dd, 1 H, *J* = 3.0, 4.9 Hz), 6.99 (dd, 1 H, *J* = 1.2, 3.0 Hz), 6.91 (dd, 1 H, *J* = 1.2, 4.9 Hz), 5.74–5.53 (m, 1 H), 5.02–4.92 (m, 2 H), 4.60 (t, 1 H, J = 7.1 Hz), 4.06 (s, 1 H), 2.40–2.33 (m, 2 H).

¹³C NMR: δ = 145.3, 134.3, 125.7, 120.6, 117.7, 65.6, 42.7.

MS: *m*/*z* (%) = 154 (5), 137 (M – OH, 26), 113 (78), 85 (100).

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