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# Regioselective Propargylation of Aldehydes and Ketones by Electrochemical Reaction using Zinc and Aluminum Anodes

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**Abstract**—Electrochemical propargylation of aldehydes and ketones with unsubstituted or α-substituted propargylic bromides using platinum cathode and zinc anode proceeded efficiently under mild conditions to give the corresponding homopropargyl alcohols exclusively in high yields. Similar electrochemical propargylation with γ-substituted propargyl bromides gave the corresponding homoallenyl alcohols as major products. Regioselectivity in the introduction of a propargyl or an allenyl group was controlled simply by a change of the anode material, zinc or aluminum. 

## Introduction

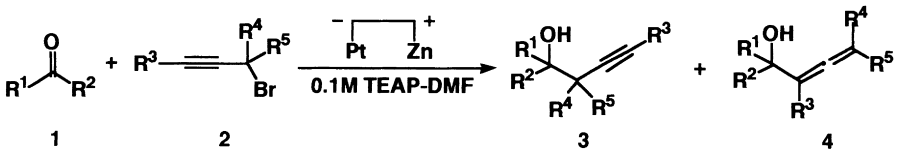
Introduction of propargyl or allenyl groups into carbonyl compounds is one of the important reactions in organic synthesis. These propargylations or allenylations are usually carried out by using organometallic reagents[1] such as organolithium,[2] -magnesium,[3] -zinc,[3,4] -aluminum,[4–6] and -titanium.[7] Similar propargylation can also be carried out without the use of organometallic compounds when a mixture of propargyl halide and carbonyl compound is electrolyzed by the use of a reactive-metal anode such as magnesium or zinc. For example, we previously reported electrochemical carboxylation of propargylic halides using a magnesium anode.[8] In propargylation using organometallic or electrochemical reaction, considerable attention has been paid to regioselectivity in the introduction of propargyl or allenyl function.[1,8] We previously reported that regioselectivity in the electrochemical allylation of carbonyl compounds is greatly affected by the kind of electrode material used.[9,10]

As one of our continuing studies on the electrochemical formation of carbon–carbon bonds using a reactive-metal anode, we recently carried out an electrochemical propargylation of aldehydes and ketones using various anode materials. In this article, we report the results of an efficient electrochemical propargylation of aldehydes and ketones using a zinc or an aluminum anode and their regioselectivities.

## Results and Discussion

Propargylation of aldehydes or ketones was carried out by the electrolysis of a DMF solution (15 ml) containing 0.1 M $Et_4NClO_4$, carbonyl compound (5 mmol), and propargylic bromide (7.5 mmol) in a one-compartment cell fitted with a platinum plate cathode (2×3 $cm^2$) and a zinc plate anode (2×3 $cm^2$). Electrolysis was carried out at a constant current of 17 $mA/cm^2$ at room temperature under a nitrogen atmosphere. The electricity passed was 3 F/mol of the carbonyl compound. Usual work-up of the reaction mixture gave the corresponding homopropargyl or homoallenyl alcohols in good yields (Scheme 1).

Results of the reactions of unsubstituted propargyl bromide with various aldehydes and ketones are summarized in Table 1. Electrochemical propargylation of various aldehydes and ketones gave exclusively or preferentially the corresponding homopropargyl alcohols (**3a**–**3g**) in isolated




1 2 3 4

**Scheme 1.**

*Keywords*: electrochemical reactions; alkynyl halides; regiocontrol; zinc and compounds.
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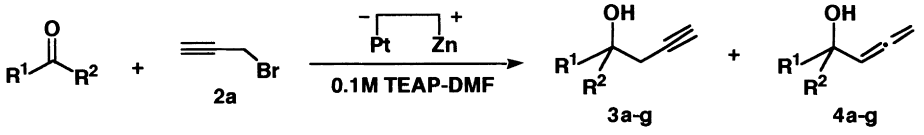
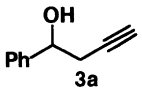
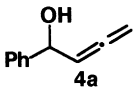
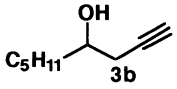
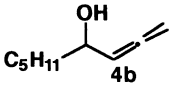
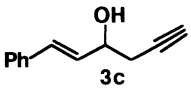
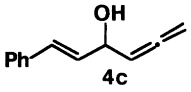
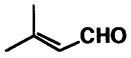
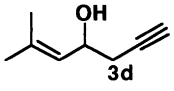
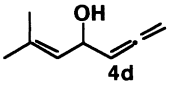
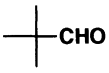
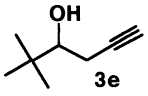
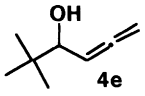
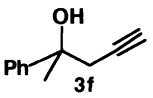
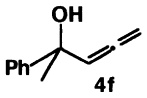
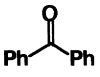
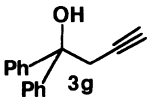
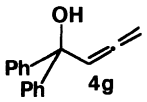
**Table 1.** Electrochemical propargylation of aldehydes and ketones using a Zn anode (a mixture of aldehyde (5 mmol) and propargyl bromide (7.5 mmol) in 0.1 M $Et_4NClO_4$–DMF (32 ml) was electrolyzed at 17 mA/cm$^2$ with a Pt cathode and Zn anode. Electricity passed was 3 F/mol)




| Entry | | Yield of 3+4 (%)[a] | Products | | Isomer ratio[b] 3 : 4 |
|---|---|---|---|---|---|
| 1 | PhCHO | 91 |  3a |  4a | 96 : 4 |
| 2 | $CH_3(CH_2)_4CHO$ | 98 |  3b |  4b | 92 : 8 |
| 3 |  | 95 |  3c |  4c | 96 : 4 |
| 4 |  | 68 |  3d |  4d | 100 : 0 |
| 5 |  | 66 |  3e |  4e | 81 : 19 |
| 6 |  | 84 |  3f |  4f | 84 : 16 |
| 7 |  | 58 |  3g |  4g | 69 : 31 |

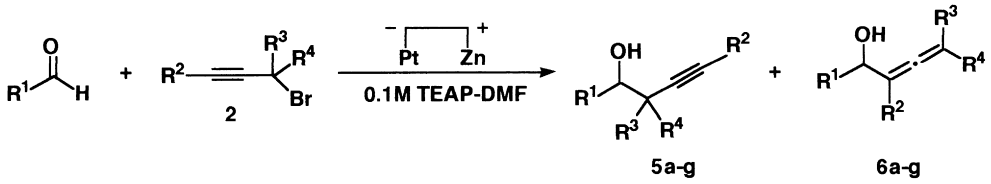
[a] Isolated yields.
[b] Isomer ratios were determined by $^1$H NMR analysis.

yields of 58–98%. Even in the propargylation of bulky aldehyde, the corresponding homopropargyl alcohol **3e** was obtained in a 66% yield (entry 5). On the other hand, electrochemical propargylation of aldehydes with α- and γ-substituted propargyl bromides also took place to give the corresponding homopropargyl (**5a**–**5g**) and/or homoallenyl alcohols (**6a**–**6g**) in moderate to good yields (Table 2). Propargylation using α,α-disubstituted propargyl halides gave the corresponding homopropargyl alcohols **5b** and **5c** as major products although their yields were lowered due to a steric hindrance (Table 2, entries 2 and 3). The yields and regioselectivities in the present electrochemical propargylations are, generally, higher than those of the published propargylations using propargylzinc compounds.[1,3,5]

Considerable attention has been given to regioselectivity and its control in propargylation when organometallic compounds are used in the reactions.[1,4,7] Similar problems of regioselectivity appear in the introduction of substituted allylic groups. We previously reported that these regioselectivities are affected by the kind of cathode or anode material used in the electrochemical allylation of carbonyl compounds.[9–11] Therefore, in the present study we examined the effects of various anode materials on the regioselectivity of the electrochemical propargylation of benzaldehyde. The results are summarized in Table 3. Electrochemical propargylation by the use of In, Al, Sn, or Pb metal as an anode gave the products in 42–67% yields (entries 8–11), although propargylation using a Pt, Ti, Cu, Co, Fe, Mg, or Ni anode proceeded with much lower efficiencies (entries 1–7).

Zinc metal was found to be the best anode for propargylation, and the product was obtained in a 91% yield with an exclusive formation of the homopropargyl alcohol **3a** (entry 12). It is worth noting that a dramatic change in the isomer ratios of **3a** and **4a** were observed when aluminum, instead of zinc, was used for the anode (entry 9). Therefore, we examined the regioselectivity of several other propargylations using an aluminum anode. The results are summarized in Table 4. The isomer ratios of **5** and **6** in the propargylation of benzaldehyde with 1-bromo-2-butyne (**2e**) and that of hexanal with 1-phenyl-3-bromo-1-propyne (**2f**) were opposite to those using a zinc anode (entries 1 and 4 in Table 4 vs entries 4 and 7 in Table 2), although the isomer ratios shown in the entries 2 and 3 in Table 4 were almost the same as those using a zinc anode, as shown in entries 5

**Table 2.** Electrochemical propargylation of aldehydes with substituted propargyl bromide using a zinc anode (a mixture of aldehyde (5 mmol) and propargyl bromide (7.5 mmol) in 0.1 M $Et_4NClO_4$–DMF (32 ml) was electrolyzed at 17 mA/cm$^2$ with a Pt cathode and Zn anode. Electricity passed was 3 F/mol)



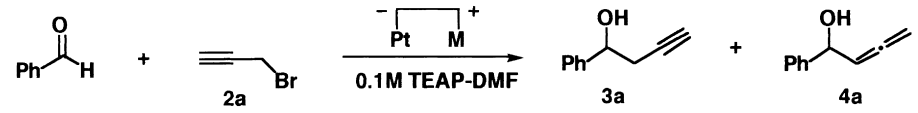

| Entry | $R^1CHO$ | | Yield of 5+6 (%) [a] | Products | | Isomer ratio [b] 5 : 6 |
|---|---|---|---|---|---|---|
| 1 | PhCHO | 2b | 90 | 5a | 6a | 100: 0 |
| 2 | PhCHO | 2c | 44 | 5b | 6b | 79 : 21 |
| 3 | PhCHO | 2d | 27 | 5c | 6c | 77 : 23 |
| 4 | PhCHO | 2e | 93 | 5d | 6d | 25 : 75 |
| 5 | PhCHO | 2f | 66 | 5e | 6e | 60 : 40 |
| 6 | $CH_3(CH_2)_4CHO$ | 2e | 98 | 5f | 6f | 26 : 74 |
| 7 | $CH_3(CH_2)_4CHO$ | 2f | 67 | 5g | 6g | 75 : 25 |

[a] Isolated yields.
[b] Isomer ratios were determined by $^1$H NMR analysis.

and 6 in Table 2. These results show that the control of the regioselectivity of propargylic or allenylic introduction can be achieved simply by employing an appropriate anode metal in the electrolysis when carbonyl compound and propargylic bromide are adequately employed (Table 4, entries 1 and 4).

The present electrochemical propargylation using a zinc anode probably proceeds via formation of an organozinc compound as an intermediate. This is supported by the fact that the reaction of benzaldehyde with propargyl bromide in the presence of electrochemically generated reactive zinc (EGZn)[12–14] in DMF solution resulted in the formation of propargylzinc bromide and, finally, gave homopropargyl (**3a**) and allenyl alcohol (**4a**) in 72% yield with an isomer ratio of 99:1 (Scheme 2). Probable reaction pathways are shown in Schemes 3 and 4. These can rationalize the regioselectivity of electrochemical propargylations with substituted propargyl bromide (**2**) using a zinc anode. Electrolysis of α-unsubstituted (**2a**), α-substituted (**2b**), and α,α-disubstituted propargylic bromide (**2c**, **2d**) with a platinum cathode and a zinc anode would give propargylzinc bromide (**7**), which might be in equilibrium with allenylzinc bromide (**8**). Preferred organozinc **8**[1] reacts with benzaldehyde through a six-membered transition state (**A**) to give the homopropargyl alcohol **5** as a major product (Scheme 3). In the case of α,α-disubstituted propargylic bromide (**2c**, **2d**), the yields and the regioselectivities were lowered due to a steric congestion in the transition state **A** (Table 2, entries 2 and 3). On the other hand, reaction pathways of the electrochemical propargylation using γ-substituted propargylic bromide are shown in

**Table 3.** Effects of anode metals on the regioselectivity of electrochemical propargylation of benzaldehyde (a mixture of benzaldehyde (5 mmol) and propargyl bromide (7.5 mmol) in 0.1 M $Et_4NClO_4$–DMF (32 ml) was electrolyzed at 17 mA/cm$^2$ with a Pt cathode. Electricity passed was 3 F/mol)



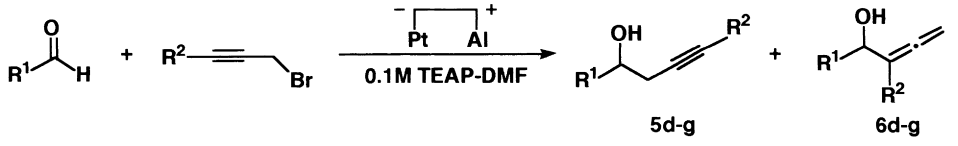

| Entry | Anode M | Yield of **3a**+**4a**[a] (%) | Isomer Ratio[b] **3a**:**4a** |
|---|---|---|---|
| 1 | Pt | 18 | 78:22 |
| 2 | Tl | 8 | 66:34 |
| 3 | Cu | 10 | 82:18 |
| 4 | Co | 10 | 90:10 |
| 5 | Fe | 10 | 96:4 |
| 6 | Mg | 11 | 51:49 |
| 7 | Mi | 12 | 84:16 |
| 8 | In | 42 | 87:13 |
| 9 | Al | 55 | 38:62 |
| 10 | Sn | 64 | 89:11 |
| 11 | Pb | 67 | 80:20 |
| 12 | Zn | 91 | 96:4 |

[a] Yields were determined by GC.
[b] Isomer ratios were determined by GC.

Scheme 4. In this case, a more stable propargylzinc bromide **9**[1] would react with benzaldehyde through a cyclic transition state (**B**) to give homoallenyl alcohol **6**. Propargylation with 1-phenyl-3-bromo-1-propyne (**2f**) is rather complicated. In this case, an allenylzinc bromide (**10**; $R^1$=Ph) would be slightly more stabilized due to an electron-withdrawing nature of a phenyl group and, hence, give the homopropargyl alcohols **5e** and **5g** as major products through the transition state **A**.

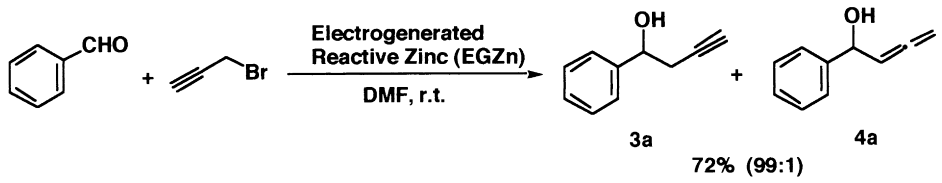
Regioselectivity of the electrochemical propargylation using an aluminum anode was completely different from that using a zinc anode. These behaviors of regioselectivity using an aluminum anode are very similar to those of

**Table 4.** Electrochemical propargylation of aldehydes with substituted propargyl bromide using an aluminum anode (a mixture of aldehyde (5 mmol) and propargyl bromide (7.5 mmol) in 0.1 M $Et_4NClO_4$–DMF (32 ml) was electrolyzed at 17 mA/cm$^2$ with a Pt cathode and Zn anode. Electricity passed was 3 F/mol)

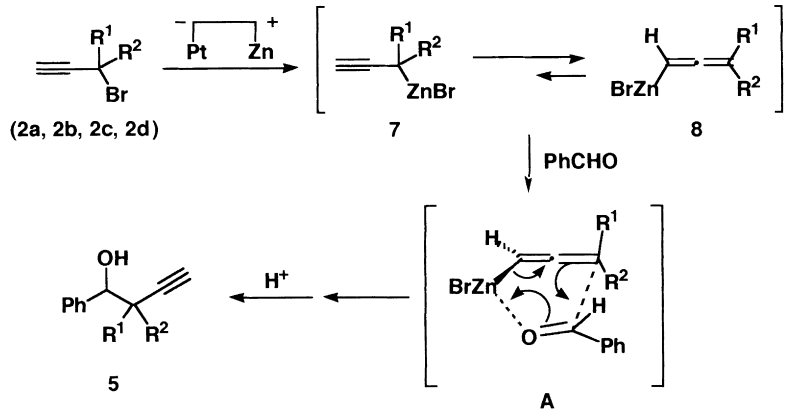



| Entry | | | Yield of 5+6 (%) | Products | | Isomer ratio[a] 5 : 6 |
|---|---|---|---|---|---|---|
| 1 | PhCHO | 2e | 89 | 5d | 6d | 65 : 35 |
| 2 | PhCHO | 2f | 54 | 5e | 6e | 65 : 35 |
| 3 | $CH_3(CH_2)_4CHO$ | 2e | 76 | 5f | 6f | 37 : 63 |
| 4 | $CH_3(CH_2)_4CHO$ | 2f | 58 | 5g | 6g | 36 : 64 |

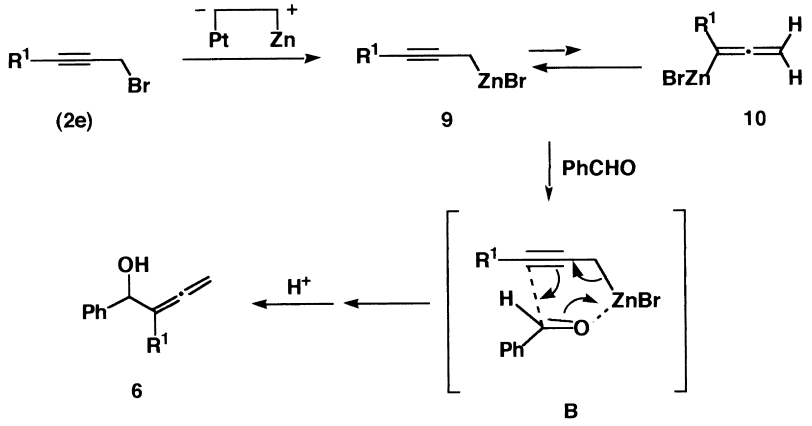
[a] Isomer ratios were determined by $^1$H NMR.



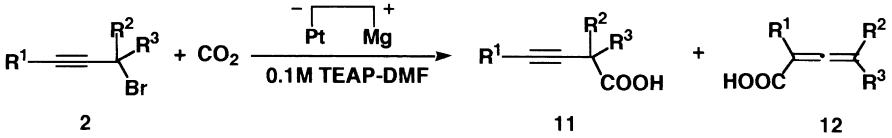

**Scheme 2.**




**Scheme 3.**




**Scheme 4.**




**Scheme 5.**

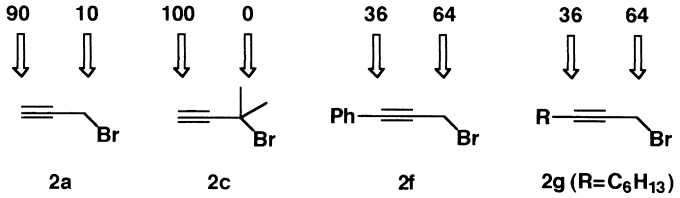



**Figure 1.** Regioselectivity in electrochemical carboxylation using a magnesium anode.[8]

electrochemical carboxylation using a magnesium anode. We previously reported that an electrochemical carboxylation of propargylic halides with a platinum cathode and a magnesium anode gave the corresponding 3-alkynoic acid (**11**) and 2,3-alkadienoic acid (**12**) (Scheme 5).[8] Regioselectivities of these carboxylations are summarized in Fig. 1. We assumed that the active species of these carboxylations were not the corresponding Grignard-type reagents but, rather, the carbanions having a tetraethylammonium ion as a counter cation. The present electrochemical propargylation using an aluminum anode probably proceeds via propargylic or allenylic carbanion generated by a two-electron reduction, or via different propargylaluminum species from those of Paquette[4], although divergent behaviors of zinc and aluminum reagents have been reported by Paquette et al.[4] Therefore, the electrochemical reduction of propargyl bromide (**2a**) using an aluminum anode would preferentially generate an allenyl carbanion, which would directly attack a carbonyl carbon to give homoallenyl alcohol **4a** as a major product.

## Experimental

IR spectra were recorded on a JASCO IR-810 infrared spectrometer (neat between NaCl plates). $^1$H NMR spectra were recorded on a JEOL JNM-EX270 FT NMR spectrometer operated at 270 MHz (solvent $CDCl_3$). Proton-decoupled $^{13}$C spectra were recorded at 67.8 MHz on a JEOL JNM-FX270 spectrometer. $^1$H and $^{13}$C chemical shifts are reported in ppm ($\delta$) using $SiMe_4$ as an internal standard. High and low resolution mass spectra were determined with a JEOL JMS-AX500 or JEOL JMS-SX102A spectrometer. Elemental analysis was performed at the Analytical Laboratory, Faculty of Pharmaceutical Science of Hokkaido University. Thin-layer chromatography and column chromatography were carried out on a Merck Kieselgel 60 $PF_{254}$ and Florisil (100∼200 mesh, nacalai tesque), respectively. Gas chromatographic analysis was performed on a Hitachi G-5000 or Hitachi 263-50 gas chromatograph using stainless steel columns packed with PEG, OV-17 with nitrogen as the carrier gas.

*N*,*N*-Dimethylformamide (DMF) was freshly distilled under nitrogen from $P_2O_5$ and stored over 4 Å molecular sieves. Tetraethylammonium perchlorate was prepared according to the previously reported method.[14] Metal plates (magnesium, aluminum, titanium, iron, cobalt, nickel, copper, zinc, indium, tin, and lead) are commercially available in more than 99.9% purities, and they were washed with 2N HCl. Methanol and acetone were dried before electrolysis. Most of the aldehydes, ketones, and propargylic bromides are commercially available, and they were used after distillation. 1-Phenyl-3-bromo-1-propyne was prepared according to the procedure reported in the literature.[15,16]

### General procedure for electrochemical propargylation

A mixture of carbonyl compound (5 mmol), propargyl bromide (7.5 mmol) and $Et_4NClO_4$ (3.2 mmol) in 32 ml of DMF was added into a one-compartment cell equipped with a platinum cathode and a metal plate anode (2×3 cm$^2$). The solution was electrolyzed at room temperature at 17 mA/cm$^2$, and electricity of 3 F/mol of propargyl bromide was passed. Usual work-up of the electrolyzed mixture gave homopropargyl alcohols and homoallenyl alcohols.

Spectral data of the products are shown below.

**1-Phenyl-3-butyn-1-ol (3a).** Bp 90°C/2 mmHg; IR (neat) 3384, 3290, 2118, 1605, 1496, 1455, 1052, 757, 701 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.07 (1H, t, $J$=2.6 Hz), 2.45 (1H, d, $J$=3.3 Hz), 2.63 (2H, dd, $J$=2.6 Hz, $J$=6.6 Hz), 4.86 (1H, m), 7.33 (5H, m); $^{13}$C NMR ($CDCl_3$): $\delta$ 29.40, 70.94, 72.29, 80.65, 125.71, 127.96, 128.45, 142.41; EIMS *m*/*z* (relative intensity) 146 (2), 128 (8), 107 (100), 79 (54), 77 (36), 51 (10), 39 (5); HRMS Calcd for $C_{10}H_{10}O$. *m*/*z* 146.0732. Found *m*/*z* 146.0719; Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.04; H, 7.03.

**1-Phenyl-2,3-butadien-1-ol (4a).** IR (neat) 3342, 1957, 1604, 1494, 1453, 1025, 851, 762, 700 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.16 (1H, s), 4.93 (2H, m), 5.27 (1H, m), 5.44 (1H, q, $J$=6.6 Hz), 7.39 (5H, m); EIMS *m*/*z* (relative intensity) 145 (14), 107 (100), 79 (79), 77 (53), 51 (24); HRMS Calcd for $C_{10}H_9O$ ($M^+-1$). *m*/*z* 145.0653. Found *m*/*z* 145.0681

**1-Nonyn-4-ol (3b).** Bp 40–50°C/15 mmHg; IR (neat) 3312, 3310, 2120, 1459, 1421, 1379, 1262, 1127, 1036, 948, 932, 847, 756, 724 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.90 (3H, t, $J$=6.6 Hz), 1.36 (6H, m), 1.55 (2H, m), 1.89 (1H, brs), 2.06 (1H, t, $J$=2.6 Hz), 2.38 (2H, m), 3.76 (1H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.03, 22.61, 25.30, 27.37, 31.73, 36.23, 69.94, 70.78, 80.99; EIMS *m*/*z* (relative intensity) 139 (2), 101 (39), 83 (62), 69(100), 55(52), 41(33); HRMS Calcd for $C_9H_{15}O$ ($M^+-1$). *m*/*z* 139.1123. Found *m*/*z* 139.1110

**1,2-Nonadien-4-ol (4b).** IR (neat) 3312, 3310, 1959, 1459, 1421, 1379, 1262, 1127, 1036, 948, 932, 847, 756, 724 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (3H, t,), 1.38 (6H, m), 1.58 (2H, m), 1.70 (1H, br), 4.17 (1H, m), 4.85 (2H, dd, $J$=2.3, 4.6 Hz), 5.24 (1H, q, $J$=6.6, 6.3 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.03, 22.61, 25.07, 31.73, 37.48, 69.77, 77.45, 94.93, 207.02; EIMS *m*/*z* (relative intensity) 139 (2), 101 (39), 83 (62), 69 (100), 55 (52), 41 (33); HRMS Calcd for $C_9H_{15}O$ ($M^+-1$). *m*/*z* 139.1123. Found *m*/*z* 139.1110; Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.91; H, 11.64.

**1-Phenyl-1-hexen-5-yn-3-ol (3c).** Bp 90°C/0.4 mmHg; IR (neat) 3366, 3294, 2118, 1600, 1579, 1496, 1450, 1101, 1072, 1035 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.09 (1H, t, $J$=2.6 Hz), 2.18 (1H, d, $J$=3.3 Hz), 2.55 (2H, m), 4.47 (1H, m), 6.28 (1H, dd, $J$=6.3, 15.8 Hz), 6.63 (1H, d, $J$=15.8 Hz), 7.31 (5H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 27.69, 70.68, 71.09, 80.18, 126.58, 127.87, 128.57, 129.94, 131.30, 136.30; EIMS *m*/*z* (relative intensity) 172 (9), 133 (100), 115 (44), 103 (22), 91 (17), 77 (28), 55 (47), 51 (11), 39 (9); HRMS Calcd for $C_{12}H_{12}O$. *m*/*z* 172.0888. Found *m*/*z* 172.0900; Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.67; H, 7.22.

**1-Phenyl-1,4,5-hexatrien-3-ol (4c).** IR (neat) 3366, 3294, 1957, 1657, 1600, 1579, 1496, 1450, 1101, 1072, 1035,

965 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.09 (1H, d, $J$=2.6 Hz), 4.94 (2H, dd, $J$=2.3, 6.3 Hz), 5.18 (1H, m), 5.37 (1H, m), 6.27 (1H, dd, $J$=6.3, 15.8 Hz), 6.65 (1H, d, $J$=15.8 Hz), 7.31 (5H, m).

**2-Methyl-2-hepten-6-yn-4-ol (3d).** IR (neat) 3298, 2118, 1678, 1631, 1584, 1442, 1377, 1270, 1217, 1168, 1112, 1035, 952, 836, 631 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.72 (3H, d, $J$=1.3 Hz), 1.75 (3H, d, $J$=1.3 Hz), 1.85 (1H, s), 2.05 (1H, t, $J$=2.6 Hz), 2.41 (2H, m, $J$=2.6 Hz), 4.53 (1H, m, $J$=8.6 Hz), 5.26 (1H, m, $J$=1.3, 8.6 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 18.28, 25.64, 27.60, 66.69, 70.33, 80.81, 125.84, 136.66.

**2,2-Dimethyl-5-hexyn-3-ol (3e).** IR (neat) 3446, 3306, 2118, 1482, 1426, 1399, 1366, 1291, 1243, 1208, 1178, 1073, 1011, 908, 849, 769, 628 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.92 (9H, s), 2.06 (1H, t, $J$=2.6 Hz,), 2.16 (1H, brs), 2.25 (1H, ddd, $J$=2.6, 9.9, 16.4 Hz), 2.40 (1H, dt, $J$=2.6, 3.45, 16.4 Hz), 3.45 (1H, dd, $J$=2.6, 9.9 Hz); EIMS $m/z$ (relative intensity) 126 (1), 87 (56), 69 (26), 57 (55), 41 (100), 39 (35); HRMS Calcd for $C_8H_{14}O$. $m/z$ 126.1045. Found $m/z$ 126.1058.

**2,2-Dimethyl-4,5-hexadien-3-ol (4e).** IR (neat) 3446, 1959, 1482, 1426, 1291, 1178, 1073, 1011, 908, 849 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.93 (9H, s), 2.16 (1H, brs), 3.83 (1H, m), 4.86 (2H, dd, $J$=2.6 Hz,), 5.28 (1H, q, $J$=6.6 Hz).

**2-Phenyl-4-pentyn-2-ol (3f).** IR (neat) 3426, 3294, 2118, 1603, 1495, 1447, 1425, 1376, 1274, 1183, 1102, 1070, 1029, 948, 912, 854, 765, 700 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.64 (3H, s), 2.05 (1H, t, $J$=2.6 Hz), 2.39 (1H, s), 2.73 (2H, m, $J$=2.6 Hz), 7.37 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 29.11, 34.50, 71.68, 73.14, 80.38, 124.64, 127.06, 128.18, 146.25; EIMS $m/z$ (relative intensity) 159 (0.6), 121 (100), 105 (13), 77 (15), 43 (83); HRMS Calcd for $C_{11}H_{11}O$ ($M^+-1$). $m/z$ 159.0809. Found $m/z$ 159.0829; Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.25; H, 7.72.

**2-Phenyl-3,4-pentadien-2-ol (4f).** IR (neat) 3426, 1959, 1603, 1495, 1447, 1425, 1376, 1274, 1183, 1102, 1070, 1029, 948, 912, 854, 765, 700 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.66 (3H, s), 2.14 (1H, s), 4.96 (2H, dd, $J$=6.6 Hz), 5.56 (1H, t, $J$=6.6 Hz), 7.35 (5H, m).

**1,1-Diphenyl-3-butyn-1-ol (3g).** IR (neat) 3540, 3288, 2118, 1600, 1494, 1449, 1427, 1349, 1278, 1254, 1168, 1054, 1033, 1014, 895, 860, 763, 699 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.04 (1H, t, $J$=2.6 Hz), 2.95 (1H, s), 3.16 (2H, d, $J$=2.6 Hz), 7.35 (10H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 33.37, 72.51, 77.20, 80.22, 126.07, 127.30, 128.19, 145.39; EIMS $m/z$ (relative intensity) 222 (1), 183 (100), 105 (74), 77 (39), 51 (8); HRMS Calcd for $C_{16}H_{14}O$. $m/z$ 222.1045. Found $m/z$ 222.1066; Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.21; H, 6.51.

**1,1-Diphenyl-2,3-butadien-1-ol (4g).** IR (neat) 3462, 1959, 1600, 1494, 1448, 1349, 1279, 1254, 1168, 1054, 1033, 1014, 895, 852, 757, 700 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.62 (1H, s), 4.98 (2H, d, $J$=6.6 Hz), 5.95 (1H, t, $J$=6.6 Hz), 7.35 (10H, m).

**2-Methyl-1-phenyl-3-butyn-1-ol (5a).** Mp 90–91°C; IR (neat) 3406, 3292, 2110, 1605, 1495, 1454, 1376, 1195, 1125, 1024, 988, 913, 760, 702, 632 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.10 (3H, d, $J$=9.9 Hz), 1.13 (3H, d, $J$=9.9 Hz), 2.11 (1H, d, $J$=2.6 Hz), 2.20 (1H, d, $J$=2.3 Hz), 2.28 (1H, d, $J$=3.6 Hz), 2.55 (1H, d, $J$=3.0 Hz), 2.83 (2H, m, $J$=5.3, 6.9, 9.9 Hz), 4.50 (1H, dd, $J$=6.9 Hz), 4.73 (1H, dd, $J$=5.28 Hz), 7.33 (10H, m); $^{13}C$ NMR ($CDCl_3$): $\delta$ 15.51, 17.33, 33.95, 35.01, 70.86, 71.29, 76.12, 77.36, 85.45, 85.79, 126.47, 126.60, 127.76, 128.03, 128.10, 128.30, 141.20, 141.26; EIMS $m/z$ (relative intensity):160 (2), 79(50), 107(100), 79(47), 77(28), 51(9); HRMS Calcd for $C_{11}H_{12}O$ 160.0888. Found $m/z$ 160.0898; Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.26; H, 7.74.

**2,2-Dimethyl-1-phenyl-3-butyn-1-ol (5b).** Bp 80–100°C/0.4 mmHg; IR (neat) 3450, 3296, 2110, 1605, 1494, 1455, 1385, 1363, 1292, 1190, 1084,1046, 1010, 967, 921, 887, 825, 777, 701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.11 (3H, s), 1.28 (3H, s), 2.26 (1H, s), 2.42 (1H, d, $J$=4.0 Hz), 4.51 (1H, d, $J$=4.0 Hz), 7.34 (5H, m); $^{13}C$ NMR ($CDCl_3$): $\delta$ 24.30, 26.33, 37.68, 70.77, 80.15, 89.27, 127.66, 127.69, 127.87, 139.78; EIMS $m/z$ (relative intensity): 174 (3), 107(100), 79(50), 68(47), 51(9); HRMS Calcd for $C_{12}H_{14}O$ 174.1044. Found $m/z$ 174.1073; Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C 82.66; H, 8.27.

**4-Methyl-1-phenyl-2,3-pentadien-1-ol (6b).** IR (neat) 3418, 1956, 1605, 1495, 1455, 1363, 1335, 1218, 1191, 1045, 1028 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$(1.39 (3H, s), 1.43 (3H, s), 2.42 (1H, s), 4.72 (1H, d, $J$=6.6 Hz) 4.93 (1H, d, $J$=6.6 Hz), 7.33 (5H, m).

**1-Phenyl-2,2-pentamethylene-3-butyn-1-ol (5c).** IR (neat) 3430, 2106, 1604, 1494, 1452, 1350, 1302, 1277, 1236, 1201, 1164, 1106, 1086, 1079, 1039, 1024, 908, 815, 706 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.16 (3H, m), 1.46 (1H, m), 1.62 (5H, m), 2.03 (1H, m), 2.31 (1H, s), 2.47 (1H, d, $J$=2.6 Hz), 4.41 (1H, d, $J$=4.6 Hz), 7.34 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.50, 22.66, 25.77, 32.83, 34.90, 43.70, 73.71, 80.76, 86.70, 127.58, 127.84, 140.04; EIMS $m/z$ (relative intensity) 214 (1), 107(29), 93(36), 79(100), 77(95). 51(24), 39(21); HRMS Calcd for $C_{15}H_{18}O$ $m/z$ 235.1361. Found $m/z$ 235.1363. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.11; H, 8.63.

**1-Phenyl-4,4-pentamethylene-2,3-butadien-1-ol (6c).** IR (neat) 3344, 1967, 1604, 1493, 1448, 1344, 1280, 1262, 1240, 1018, 851 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (6H, m), 2.11 (4H, m), 2.18 (1H, s), 5.20 (1H, d, $J$=5.6 Hz), 5.30 (1H, m, $J$=2.0, 5.6 Hz), 7.34 (5H, m); EIMS $m/z$ (relative intensity) 214 (100), 213 (11), 196 (13), 132 (13), 131 (97), 128 (15), 109 (13), 108 (58), 107 (65), 105 (12), 103 (29), 93 (54), 91 (17), 80 (15), 79 (68), 77(46), 51 (11), 41 (12); HRMS Calcd for $C_{15}H_{18}O$ $m/z$ 214.1358. Found $m/z$ 214.1355.

**1-Phenyl-3-pentyn-1-ol (5d).** IR (neat) 3386, 1604, 1496, 1455, 1432,1400, 1333, 1202, 1083, 1049, 915, 873, 841, 756, 700 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.81 (3H, t, $J$=2.6 Hz), 2.44 (1H, d, $J$=3.3 Hz), 2.57 (2H, m), 4.81 (1H, m), 7.34 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 3.52, 29.99, 72.60, 75.22, 78.67, 125.70, 127.75, 128.37, 142.80; EIMS $m/z$ (relative intensity) 159 (2), 107 (38), 77 (100), 51 (55), 39 (15); HRMS Calcd for $C_{11}H_{11}O$ ($M^+-1$). $m/z$ 159.0810. Found

*m*/*z* 159.0795; Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.28; H, 7.69.

**2-Methyl-1-phenyl-2,3-butadien-1-ol (6d).** IR (neat) 3362, 1961, 1604, 1494, 1452, 1372, 1193, 1172, 1080, 1039, 917, 850, 801, 734, 699, 648 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.57 (3H, t, *J*=3.0, 3.3 Hz), 2.22 (1H, s), 4.91 (2H, m, *J*=3.0, 3.3 Hz), 5.11 (1H, s), 7.32 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.48, 74.63, 77.70, 102.59, 126.54, 127.74, 128.32, 141.81, 204.76; EIMS *m*/*z* (relative intensity) 159 (30), 145 (9), 128 (7), 107 (74), 79 (100), 77 (76), 51 (29), 39 (9); HRMS Calcd for $C_{11}H_{11}O$ ($M^+-1$). *m*/*z* 159.0810. Found *m*/*z* 159.0819; Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.01; H, 7.56.

**1,4-Diphenyl-3-butyn-1-ol (5e).** IR (neat) 3376, 2230, 1599, 1572, 1491, 1454, 1420, 1331, 1201, 1049, 945, 914, 863, 757, 717, 693 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.47 (1H, s), 2.84 (2H, d, *J*=6.3 Hz), 4.95 (1H, t, *J*=6.3 Hz), 7.36 (10H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 30.53, 72.55, 83.16, 85.95, 123.20, 125.76, 127.86, 127.94, 128.19, 128.39, 131.61, 142.64; EIMS *m*/*z* (relative intensity) 222 (6), 204 (10), 116 (100), 107 (84), 79 (87), 77 (47), 51 (12), 39 (6); HRMS Calcd for $C_{16}H_{14}O$. *m*/*z* 222.1045. Found *m*/*z* 222.1067; Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.30; H, 6.56.

**1,2-Diphenyl-2,3-butadien-1-ol (6e).** IR (neat) 3376, 1942, 1599, 1572, 1491, 1454, 1420, 1331, 1201, 1049, 945, 914, 863, 757, 717, 693 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.32 (1H, s), 5.26 (2H, m), 5.71 (1H, s), 7.36 (10H, m).

**2-Decyn-5-ol (5f).** IR (neat) 3332, 1459, 1378, 1118 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (3H, m), 1.31 (6H, m), 1.56 (2H, m), 1.82 (3H, m, *J*=2.6 Hz), 2.30 (2H, m, *J*=2.6 Hz), 3.68 (1H, m).

**3-Methyl-1,2-nonadien-4-ol (6f).** IR (neat) 3332, 1961, 1459, 1378, 1118, 845 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (3H, m), 1.31 (6H, m), 1.56 (2H, m), 1.71 (3H, m, *J*=3.3 Hz), 4.04 (1H, m), 4.77 (2H, m, *J*=3.3 Hz).

**1-Phenyl-1-nonyn-4-ol (5g).** IR (neat) 3370, 1599, 1491, 1460, 1379, 1123, 1070, 1028, 914, 851, 756,692 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (3H, t, *J*=6.3 Hz), 1.53 (8H, m), 1.96 (1H, br), 2.59 (2H, m), 3.83 (1H, m), 7.33 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.00, 22.59, 25.30, 28.38, 36.34, 70.21, 80.59, 83.00, 86.20, 123.38, 126.76, 128.23, 131.66; EIMS *m*/*z* (relative intensity) 216 (3), 146 (9), 116 (100), 105 (8), 83 (12), 77 (5), 55 (19), 43 (6); HRMS Calcd for $C_{15}H_{20}O$. *m*/*z* 216.1514. Found *m*/*z* 216.1492; Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 82.62; H, 9.39.

**3-Phenyl-1,2-nonadien-4-ol (6g).** IR (neat) 3384, 1943, 1300, 1492, 1467, 1379, 1070, 1029, 914, 851, 756, 692 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.89 (3H, t, *J*=6.3 Hz), 1.53 (8H, m), 1.96 (1H, brs), 4.62 (1H, m), 5.22 (1H, d, *J*=2.3 Hz), 7.33 (5H, m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.00, 22.59, 25.45, 31.66, 36.25, 69.81, 77.20, 110.03, 127.06, 127.89, 128.54, 134.66, 207.03.

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