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Highly efficient water promoted allylation and propargylation of arylepoxides via rearrangement-carbonyl addition

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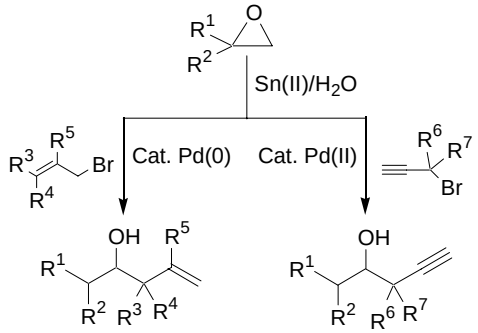
Abstract—A simple and highly efficient one-pot procedure for allylation and propargylation of arylepoxides has been developed. A combination of $SnCl_2$ and catalytic Pd(0) or Pd(II) promotes the reaction of organic halides and epoxides in DMSO with controlled water addition, leading to the regioselective formation of the corresponding homoallyl and homopropargyl alcohols in good yields.

1. Introduction

The addition of allyl, propargyl or allenylstannanes to organic electrophiles like aldehydes, imines, and epoxides is a well-known tool for carbon–carbon bond formation in organic chemistry.[1] Epoxides are one of the most useful and versatile substrates in organic synthesis due to their high reactivity. A number of methods have been reported for the cleavage of epoxides with various nucleophiles. On the other hand, only a few methods are known for the allylation and propargylation of epoxides.[2–4] Except for a few, the methods suffer from a lack of efficiency and simplicity. Therefore, the development of simple and novel reagents, which are more efficient and provide convenient procedures with improved yields still remains a challenge for synthetic organic chemists.

Along with others, we have been exploring a bimetallic strategy to generate allyl and propargyl organometallic reagents.[5] The strategy involves oxidative addition of an organic halide (RX) across catalytic d^8/d^{10} metal [M], followed by redox-transmetallation of R-[M]-X to tin(II) to generate R-Sn(IV) in situ. Successful delineation of the strategy for carbonyl allylation and propargylation prompted us to investigate the nucleophilic addition of organotin(IV) to an epoxide. Previously we reported that under strictly anhydrous condition, lithium hydroxide could promote such reactivity. However, a major synthetic limitation was the use of stoichiometric excess (3 equiv with respect to Sn^{II}) of lithium hydroxide, along with $Sn(OTf)_2$ as the second additive.[6] Remarkably, we now find that the reactivity of organotin towards epoxides can be tuned simply by the controlled addition of water in DMSO leading to homoallyl and homopropargyl alcohols via epoxide rearrangement-carbonyl addition reaction, and present our findings in this report (Scheme 1).



Scheme 1. Tandem epoxide rearrangement and allylation/propargylation.

2. Results and discussion

2.1. Effect of water and catalyst

Reaction of styrene oxide **2a** and 3-bromopropene **1a** in the presence of anhydrous stannous chloride and catalytic $Pd_2(dba)_3 \cdot CHCl_3$ in DMSO at 60 °C led to the formation of 1-phenyl-pent-4-en-2-ol **3a** in 39% yield (Table 1, entry 4). The yield of **3a** was negligible for reactions in DCM, and THF, while in DMF it was 33%. On the other hand, reaction in the absence of catalyst afforded majorly 1-phenyl-ethane-1,2-diol **6**, along with unreacted epoxide **2a** and epoxide rearrangement product, phenylacetaldehyde **7** (entry 5).

Keywords: Allylation; Propargylation; Organotin; Palladium; Aqueous promotion.
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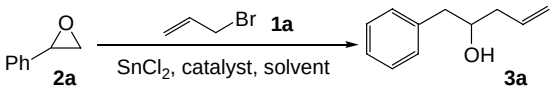
Table 1. Reaction of styrene epoxide with allyl bromide: effect of water[a]



#	Solvent	Water (μl)	Temperature (°C)	Yield (%)
1	DCM	—	40	Trace
2	THF	—	60	Trace
3	DMF	—	60	33
4	DMSO	—	60	39
5[b]	DMSO	—	60	Trace[c]
6	DMSO	70	60	73
7	DCM	70	40	Trace
8	THF	70	60	Trace
9	DMF	70	60	55

[a] Condition: styrene oxide 0.5 mmol, $SnCl_2$ 1 mmol, allyl bromide 1.5 mmol, $Pd_2dba_3\cdot CHCl_3$ 0.01 mmol, solvent 3 ml, 11 h.
[b] Without catalyst.
[c] Major products $PhCH(OH)CH_2OH$ **6** and $PhCH_2CHO$ **7**.

Remarkably, the addition of a controlled amount of water (~3 equiv) in DMSO dramatically increased the yield of **3a** to 73% (entry 6). Note that such dramatic enhancement is not observed for other organic-aqueous combinations (entries 7–9).

The effect of water on the yield of homoallyl alcohol **3a** and diol **6** was further scrutinised carefully for reactions conducted with 2 mmol of $SnCl_2$. As shown in Figure 1, upon slow addition of water the yield of **3a** slowly increases and reaches a maximum near 6–8 mmol, after which it decreases sharply. On the other hand, the yield of diol **6** remains below 20% until 6–8 mmol of water is added; beyond which it rises very rapidly. From data points for any two successive addition of water, one finds that the yield difference in case of **3a** does not correlate linearly with that of **6**. The above observations highlight the critical role of water in enhancing the nucleophilic addition reaction rate.

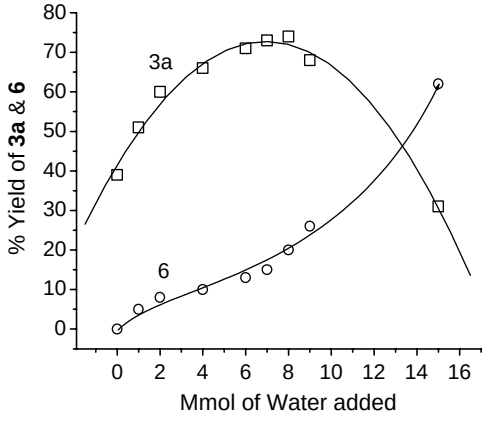
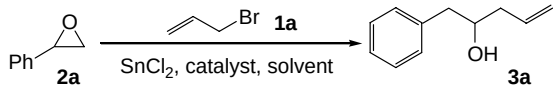


Figure 1. Effect of water on epoxide allylation. Homoallyl alcohol **3a** (□), diol **6** (○). Condition: styrene oxide **2a** 1 mmol, $SnCl_2$ 2 mmol, allyl bromide 3 mmol, Pd_2dba_3 2 mol%, DMSO 3 ml, 60 °C, 11 h.

Our findings on the role of water corroborates many recent reports on the increased reactivity of in situ or ex situ generated organometallic nucleophiles in aqueous or aqueous-organic medium.[7,8] It is now well established that the reagent combination of Pd(0/II)/$SnCl_2$/allyl bromide generates allyltrihalostannane.[9] That a stoichiometric 3 equiv of water with respect to tin is needed in our case suggests that a likely active species is $RSn(OH)_3$.[7c] This suggestion is close in line with the one proposed by Li et al. for the arylation of aldehydes.[8] It is presumed that by virtue of its coordinating ability DMSO could further stabilize the hydroxytin(IV) intermediate.[10]

Screening of catalysts at 2% loading (Table 2) indicates that among the metal complexes, $Pd_2dba_3\cdot CHCl_3$ and $NiCl_2(PPh_3)_2$ cause >60% product formation, while among the metal salts $Pd(OAc)_2$ and $Ni(OAc)_2\cdot 4H_2O$ are superior to others. The best condition is shown as in entry 15.

Table 2. Reaction of styrene epoxide with allyl bromide: effect of catalyst[a]

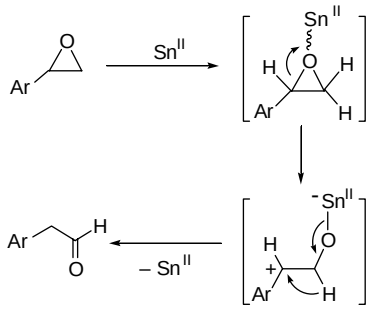


#	Catalyst	mol (%)	Time (h)	Yield (%)
1	None	—	24	Trace
2	CuCl	30	24	27
3	$CuCl_2,2H_2O$	30	24	33
4	$Cu(OAc)_2\cdot H_2O$	2	11	47
5	$Ni(OAc)_2\cdot 4H_2O$	2	11	55
6	$NiCl_2(PPh_3)_2$	2	11	64
7	$PtCl_2(PPh_3)_2$	2	11	50
8	$Pd(dba)_2$	2	11	43
9	$Pd(PPh_3)_4$	2	11	49
10	$PdCl_2(PPh_3)_2$	2	11	54
11	$PdCl_2(MeCN)_2$	2	11	55
12	$PdCl_2(Phen)$	2	11	59
13	$Pd(OAc)_2$	2	11	60
15	$Pd_2dba_3\cdot CHCl_3$	2	11	73

[a] Condition: styrene oxide 0.5 mmol, anhydrous $SnCl_2$ 1 mmol, allyl bromide 1.5 mmol, DMSO 3 ml, H_2O 70 μl, 60 °C.

2.2. Epoxide rearrangement-carbonyl allylation

The formation of homoallyl alcohol **3a** suggests that the reaction pathway does not involve direct allylation of the epoxide, instead is a case of allylation of a benzylic aldehyde. Lewis acid catalyzed rearrangement of epoxides to benzylic aldehydes is well documented.[11] Control experiments with styrene oxide confirmed that under our reaction conditions, such rearrangement is promoted by tin(II) in DMSO, but not the transition metal partner. Thus, reaction of **2a** (0.5 mmol) with $SnCl_2$ (0.3 mmol) in DMSO resulted in rapid rearrangement within 30 min leading to the formation of phenylacetaldehyde **7** (84%). Under similar conditions, but with $Pd_2dba_3\cdot CHCl_3$ the yield of phenylacetaldehyde **7** was negligible even after 6 h. Therefore, the epoxide rearrangement is viewed as a typical Lewis acid catalyzed pathway involving Sn^{II} (Scheme 2).[12]

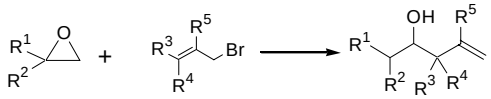


Scheme 2. Sn^{II} assisted rearrangement of arylepoxide.

2.3. Generality of the method: allylation of arylepoxide

The generality of the reaction was further tested for the allylation of epoxides (Table 3). Reaction of styrene epoxide **2a** with allyl bromides **1a**–**1e** afforded exclusively the γ-regioselective products **3a**, **3c**, **3e**, **3g**, and **3i** in 65–75% yields (entries 1, 3, 5, 7, 9). To test if steric crowding is tolerated, α-methylstyrene epoxide **2b** was reacted with allyl bromides **1a**, **1b**, and **1c** to afford the corresponding homoallyl alcohols **3b**, **3d**, and **3f** in 70–82% yield (entries 2, 4, 6). Furthermore, 1-(9-anthryl)-ethylene oxide **2c** reacted smoothly with allyl bromide **1a** giving rise to the allylation product **3h** in 83% yield (entry 8). For reactions with 3-substituted allyl bromides, the *syn*/*anti* diastereoselectivity in the product varied from case to case (entries 2–6). In comparison to the very good allylation reactivity of arylepoxides, attempted reactions with aliphatic epoxides provided complicated mixtures. Thus, reactions of cyclohexene oxide and **1a** even at lower temperature gave rise to a number of intractable products.

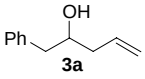
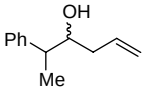
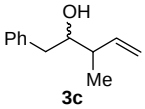
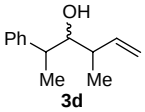
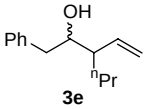
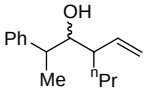
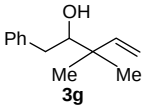
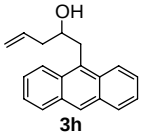
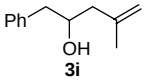
Table 3. Epoxide rearrangement-allylation[a]



2 **1** **3a - 3i**

2a: R^1=Ph, R^2=H
2b: R^1=Ph, R^2=Me
2c: R^1=Anthryl, R^2=H

1a: R^3=H, R^4=H, R^5=H
1b: R^3=Me, R^4=H, R^5=H
1c: R^3=^{n}Pr, R^4=H, R^5=H
1d: R^3=Me, R^4=Me, R^5=H
1e: R^3=H, R^4=H, R^5=Me

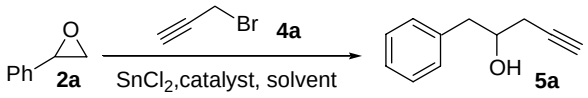
#	Bromide	Epoxide	Product	Time (h)	Yield (%)	*syn*/*anti*[b]
1	**1a**	**2a**	 **3a**	11	73	—
2	**1a**	**2b**	 **3b**	13	80	63/37
3	**1b**	**2a**	 **3c**	13	71	40/60
4	**1b**	**2b**	 **3d**	13	82	80/20
5	**1c**	**2a**	 **3e**	14	67	66/34
6	**1c**	**2b**	 **3f**	13	70	70/30
7	**1d**	**2a**	 **3g**	12	75	—
8	**1a**	**2c**	 **3h**	14	83	—
9	**1e**	**2a**	 **3i**	13	35	—

[a] Condition: epoxide 0.5 mmol, $SnCl_2$ 1 mmol, allyl bromide 1.5 mmol, $Pd_2dba_3 \cdot CHCl_3$ 0.01 mmol, DMSO–H_2O (3 ml–70 μl), 60 °C.
[b] Based on NMR.

2.4. Generality of the method: propargylation of arylepoxide

The scope of the reaction was successfully extended to the propargylation of epoxides. In the presence of catalytic $Pd(OAc)_2$, the model reaction of 3-bromo-prop-1-yne **4a** and styrene oxide **2a** yielded 68% of 1-phenyl-pent-4-yn-2-ol **5a** (Table 4, entry 4). In comparison, other catalysts showed poor efficiency. Complete absence of isomeric allenyl alcohol suggests that under the reaction conditions, metallotropic rearrangement between the propargyltin and allenyltin is completely arrested.[5f] The generality of the method was further tested for the reaction of styrene oxide **2a**, α-methyl styrene oxide **2b** and 1-(9-anthryl)-ethylene oxide **2c** with propargyl bromides **2a**–**2c** affording moderate to good yields of the corresponding homopropargyl alcohols **5a**–**5e** (Table 5).

Table 4. Reaction of styrene epoxide with propargyl bromide: effect of catalyst[a]



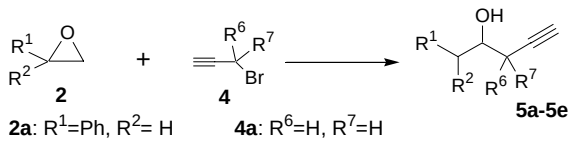
#	Catalyst	mol%	Yield (%)
1	None	—	Trace
2	$NiCl_2(PPh_3)_2$	2	31
3	$Ni(OAc)_2 \cdot 4H_2O$	4	26
4	$Pd(OAc)_2$	2	68
5	$PtCl_2(PPh_3)_2$	2	59
6	$PdCl_2$(Phen)	2	52
7	$Pd(PPh_3)_4$	2	31
8	$Pd(dba)_2$	2	28
9	$Pd_2dba_3 \cdot CHCl_3$	2	2

[a] Condition: styrene oxide 0.5 mmol, $SnCl_2$ 1 mmol, propargyl bromide 1.5 mmol, catalyst 0.01 mmol, DMSO–H_2O (3 ml–70 μl), rt, 20 h.

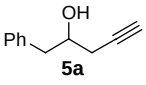
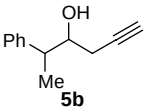
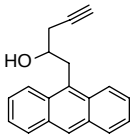
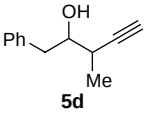
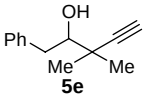
2.5. Comments on plausible mechanism

Whilst a detailed mechanism of the present reaction must await further studies, some of the plausible bond forming steps are enumerated below (Scheme 3, where R = allyl or propargyl). The suggestions are based on previous studies[7–11] and observations described in previous sections. In early stages of the reaction formation of organotrihalostannane R-$SnXCl_2$ **I** is postulated by a well-known redox transmetallation pathway involving oxidative addition of organic halide RX across palladium, insertion of tin(II) halide, followed by reductive elimination.[9] The profound involvement of water enables us to suggest the formation of a

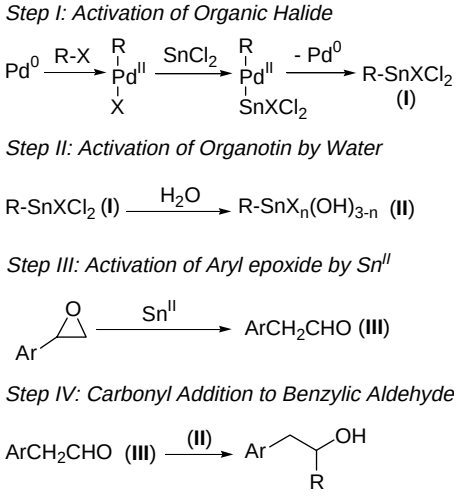
Table 5. Epoxide rearrangement-propargylation[a]



2a: R^1=Ph, R^2= H **4a**: R^6=H, R^7=H
2b: R^1=Ph, R^2=Me **4b**: R^6=Me, R^7=H
2c: R^1=Anthryl, R^2=H **4c**: R^7=Me, R^7=Me

#	Bromide	Epoxide	Product	Time (h)	Yield (%)	*syn*/*anti*[b]
1	**4a**	**2a**	 **5a**	18	61	—
2	**4a**	**2b**	 **5b**	22	43	65/35
3	**4a**	**2c**	 **5c**	15	92	—
4	**4b**	**2a**	 **5d**	14	71	40/60
5	**4c**	**2a**	 **5e**	16	48	—

[a] Condition: epoxide 0.5 mmol, $SnCl_2$ 1 mmol, propargyl bromide 1.5 mmol, $Pd(OAc)_2$ 0.01 mmol, solvent DMSO–H_2O (3 ml–70 μl), rt.
[b] Based on NMR.



Scheme 3. Plausible mechanism for epoxide rearrangement and carbonyl addition of reactive organotin.

more reactive organotin intermediate $RSnX_n(OH)_{3-n}$ **II** in solution.[7,8] Under the reaction conditions, simultaneous rearrangement of the arylepoxide to the benzylic aldehyde **III** occurs (vide Scheme 2).[12] The final step of the reaction would involve a carbonyl addition via S_E2' attack of organotin intermediate **II** to aldehyde **III** to furnish the end-organic product.

3. Conclusion

In summary, we have demonstrated a facile allylation and propargylation of arylepoxides to afford the corresponding homoallyl and homopropargyl alcohols with a two carbon extension. The reaction is promoted simply by the addition of a limited amount of water to generate a reactive organotin species. The end-organic product arises from simultaneous epoxide rearrangement and carbonyl addition, the latter being 100% γ-regioselective, and devoid of allenyl-isomers (in case of propargylation). All of the above features are expected to add to the synthetic utility of the present reaction. Further work is warranted to understand the mechanistic details of the reaction.

4. Experimental

4.1. General comments

^1H (200 MHz) NMR spectra were recorded on a BRUKER-AC 200 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet), coupling constant (Hz). ^{13}C (54.6 MHz) NMR spectra were recorded on a BRUKER-AC 200 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 77.0 ppm). ESI mass spectra were recorded on a Waters LCT mass spectrometer. Elemental analyses were carried out using a CHNS/O Analyzer Perkin Elmer 2400 Series II instrument. IR spectra were taken on a Thermo Nicolet FTIR Spectrometer (NEXUS-870). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

4.2. General procedure

The procedure given below was followed in all cases. All products showed satisfactory spectral and analytical data.

4.3. Allylation of epoxides

$Pd_2dba_3 \cdot CHCl_3$ (10 mg, 0.01 mmol) was added to a solution of allyl bromide (1.5 mmol) in a DMSO–H_2O solvent mixture (3 ml–70 μl) and was allowed to stir for 5 min at a bath temperature of 60 °C. Anhydrous $SnCl_2$ (190 mg, 1 mmol) was added and the reaction stirred for 6 h. Finally, epoxide (0.5 mmol) was added and the reaction was monitored by TLC. After completion, the reaction was quenched by adding water and ammonium fluoride. The mixture was extracted into ethylacetate. The combined organic layer was washed with water (4×50 ml), brine and dried over anhydrous $MgSO_4$. Solvent removal under reduced pressure followed by column chromatography

over silica gel 60–120 (eluent, 2% EtOAc in hexane) afforded the desired allylated product.

4.3.1. 1-Phenylpent-4-en-2-ol (3a).[13,7k,3c] Using the general procedure (as in Section 4.3) but with 3-bromo-propene **1a** (181 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **3a** (59 mg, 73%) as a light yellow oily liquid.

4.3.2. 2-Phenylhex-5-en-3-ol (3b).[3c] Using the general procedure (as in Section 4.3) but with 3-bromo-propene **1a** (181 mg, 1.5 mmol) and α-methylstyrene epoxide **2b** (67 mg, 0.5 mmol) afforded the title compound **3b** (70 mg, 80%) as a light yellow oily liquid.

4.3.3. 3-Methyl-1-phenylpent-4-en-2-ol (3c).[14] Using the general procedure (as in Section 4.3) but with 1-bromo-but-2-ene **1b** (202 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **3c** (63 mg, 71%) as a light yellow oily liquid.

4.3.4. 4-Methyl-2-phenylhex-5-en-3-ol (3d).[14b,15] Using the general procedure (as in Section 4.3) but with 1-bromo-but-2-ene **1b** (202 mg, 1.5 mmol) and α-methylstyrene epoxide **2b** (67 mg, 0.5 mmol) afforded the title compound **3d** (78 mg, 82%) as a light yellow oily liquid.

4.3.5. 1-Phenyl-3-propylpent-4-en-2-ol (3e).[5c,5e] Using the general procedure (as in Section 4.3) but with 1-bromo-hex-2-ene **1c** (245 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **3c** (68 mg, 67%) as a light yellow oily liquid.

4.3.6. 2-Phenyl-4-propylhex-5-en-3-ol (3f). Using the general procedure (as in Section 4.3) but with 1-bromo-hex-2-ene **1c** (245 mg, 1.5 mmol) and α-methylstyrene epoxide **2b** (67 mg, 0.5 mmol) gave the title compound **3f** (76 mg, 70%) as a yellow viscous liquid, *syn*:*anti* 70:30; IR (neat) 3450, 3020, 2958, 2928, 2871, 1495, 1454, 1261, 1070, 1031, 914,743,700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.75–0.95 (3H, m, $CH_2CH_2CH_3$), 1.15–1.47 (7H, m, $CH_2CH_2CH_3$+PhCH*Me*), 1.75 (1H, br s, O*H*), 1.96–2.06 (1H, m, CH_2=CH–C*H*), 2.81–2.88 (1H, m, Ph-C*H*), 3.58–3.71 (1H, m, C*H*–OH), 4.92–5.21 (2H, m, CH_2=CH), 5.61–5.71 (1H, m, CH_2=C*H*), 7.16–7.34 (5H, m, *Ph*). ^{13}C NMR ($CDCl_3$): δ [13.94, 14.01] (*anti*+*syn*), 17.19, [20.16, 20.32] (*anti*+*syn*), [33.6, 34.33] (*anti*+*syn*), 43.24, 47.31, 77.84, 117.63, 126.19, 127.72, [128.37, 128.45] (*anti*+*syn*), 138.05, 145.02. ESI-MS: for $C_{15}H_{22}O$ [M], $[M-OH]^+$=201.16. Anal. ($C_{15}H_{22}O$) Calcd, C: 82.52, H: 10.16; found, C: 82.58, H: 10.19.

4.3.7. 3,3-Dimethyl-1-phenylpent-4-en-2-ol (3g).[16] Using the general procedure (as in Section 4.3) but with 1-bromo-3-methyl-but-2-ene **1d** (224 mg, 1.5 mmol), and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **3g** (71 mg, 75%) as a light yellow oily liquid.

4.3.8. 1-Anthrylpent-4-en-2-ol (3h). Using the general procedure (Section 4.3) but with 3-bromo-propene **1a** (181 mg, 1.5 mmol) and 1-(9-anthryl)-ethylene oxide **2c** (110 g, 0.5 mmol) afforded the title compound **3h** (109 mg, 83%) as yellow solid, mp 90–92 °C; IR (KBr) 3396, 2963, 1262, 1098, 1019, 800 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.72 (1H, br s, O*H*), 2.42–2.48 (2H, m, CH_2=CH–CH_2), 3.79–3.83 (2H, m, anthryl-CH_2), 4.12–4.15 (1H, m, C*H*–OH), 5.16–5.26 (2H, m, CH_2=CH), 5.84–5.93 (1H, m, CH_2=C*H*), 7.42–7.56 (4H, m, aromatic), 7.97–8.02 (2H, m, aromatic), 8.28–8.36 (3H, m, aromatic). ^{13}C NMR ($CDCl_3$): δ 34.74, 41.93, 72.18, 118.40, 124.64, 124.89, 125.71, 126.57, 129.17, 130.53, 130.62, 131.52, 134.74. ESI-MS: for $C_{19}H_{18}O$ [M], $[M+H]^+$=263.14, $[M-OH]^+$=245.13. Anal. ($C_{19}H_{18}O$) Calcd, C: 86.99, H: 6.92; found, C: 86.92, H: 6.76.

4.3.9. 4-Methyl-1-phenylpent-4-en-2-ol (3i).[5a,16] Using the general procedure (as in Section 4.3) but with 3-bromo-2-methyl-propene **1e** (203 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **3i** (31 mg, 35%) as a light yellow oily liquid.

4.4. Propargylation of epoxide

$Pd(OAc)_2$ (3 mg, 0.01 mmol) was added to a solution of propargyl bromide (1.5 mmol) in a DMSO–H_2O solvent mixture (3 ml–70 μl) and was allowed to stir for 5 min at rt. Anhydrous $SnCl_2$ (190 mg, 1 mmol) was added and the reaction stirred for 6 h. Finally epoxide (0.5 mmol) was added and the reaction was monitored by TLC. After completion, the reaction was quenched by adding water and ammonium fluoride. The mixture was extracted into ethylacetate. The combined organic layer was washed with water (4×50 ml), brine and dried over anhydrous $MgSO_4$. Solvent removal under reduced pressure followed by column chromatography over silica gel 60–120 (eluent, 2% EtOAc in hexane) afforded the desired propargylated product.

4.4.1. 1-Phenyl-pent-4-yn-2-ol (5a).[16] Using the general procedure (as in Section 4.4) but with 3-bromo-propyne **4a** (179 mg, 1.5 mmol), and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **5a** (49 mg, 61%) as a light yellow oily liquid.

4.4.2. 2-Phenyl-hex-5-yn-3-ol (5b).[6] Using the general procedure (as in Section 4.4) but with 3-bromo-propyne **4a** (179 mg, 1.5 mmol) and α-methylstyrene epoxide **2b** (67 mg, 0.5 mmol) afforded the title compound **5b** (38 mg, 43%) as a light yellow oily liquid.

4.4.3. 1-Anthryl-pent-4-yn-2-ol (5c). Using the general procedure (as in Section 4.4) but with 3-bromo-propyne **4a** (179 mg, 1.5 mmol) and 1-(9-anthryl)-ethylene oxide **2c** (110 mg, 0.5 mmol) gave the title compound **5c** (120 mg, 92%) as a yellow solid, mp 84–87 °C (dec); IR (KBr) 3442, 3295, 2925, 1670, 1653, 1600, 1457, 1317, 1261, 1074, 1025, 734, 700, 668 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.85 (1H, br s, O*H*), 2.21–2.23 (1H, t, J=2.6 Hz, acetylenic), 2.54–2.58 (2H, m), 3.91–3.99 (2H, m), 4.28–4.31 (1H, m), 7.44–7.59 (4H, m, aromatic), 8.00–8.05 (2H, m, aromatic), 8.34–8.41 (3H, m, aromatic). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.06, 34.16, 71.25, 71.30, 80.81, 124.47, 124.96, 125.91, 127.28, 129.23, 129.86, 130.57, 131.54. ESI-MS: for $C_{19}H_{16}O$ [M], $[M+H]^+$=261.12, $[M-OH]^+$=243.12. Anal. ($C_{19}H_{16}O$) Calcd, C: 87.66, H: 6.19; found, C: 87.75, H: 6.21.

4.4.4. 3-Methyl-1-phenyl-pent-4-yn-2-ol(5d).[16] Using the general procedure (as in Section 4.4) but with 3-bromo-but-1-yne **4b** (200 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **5d** (62 mg, 71%) as a light yellow oily liquid.

4.4.5. 3,3-Dimethyl-1-phenyl-pent-4-yn-2-ol (5e).[5b,6] Using the general procedure (as in Section 4.4) but with 3-bromo-3-methyl-but-1-yne **4c** (220 mg, 1.5 mmol) and styrene epoxide **2a** (60 mg, 0.5 mmol) afforded the title compound **5e** (45 mg, 48%) as a light yellow oily liquid.

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Supplementary data

Supplementary data associated with this article can be found, in the online version at doi: 10.1016/j.tet.2005.10.005

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