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On pentaorganylstiborane

III *. Regio- and diastereoselective additions of acetylenic and allenic organoantimony compounds to aldehydes

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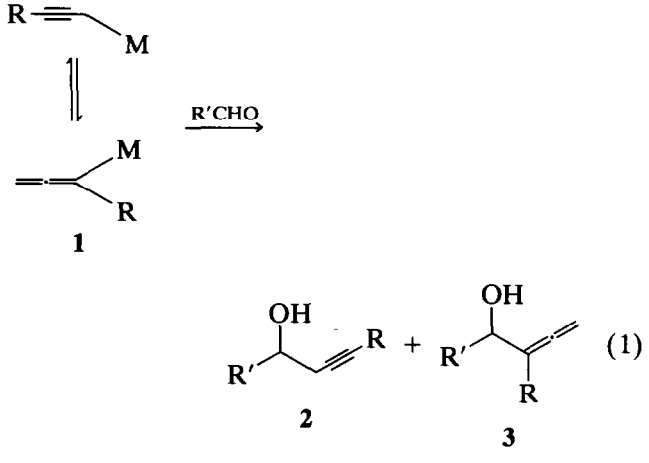
Abstract

The reaction of propargyl bromide (**4a**) with tributylstibine gave allenyltributylstibonium bromide (**5**), and its corresponding pentaorganylstiborane reacted with aldehyde to give homopropargylic alcohol (**10a**) exclusively in good yield. However, the reaction of 1-bromo-2-butyne (**4b**) with tributylstibine gave acetylenic stibonium bromide (**6b**), and its corresponding stiborane reacted with aldehyde to give allenic alcohol (**9b**) as major product. The reaction of 3-bromo-1-trimethylsilyl-1-propyne (**4d**) with tributylstibine also gave acetylenic stibonium bromide (**6d**), but the major product of the reaction of its corresponding stiborane with aldehyde was acetylenic alcohol (**10d**), and the regioselectivity was very high in the presence of LiBr. Further, it was found that the allenic stibonium bromide (**12**) was obtained by the reaction of 3-bromo-1-butyne (**11**) with tributylstibine. The corresponding stiborane (**13**) reacted with aldehyde to give acetylenic alcohol (**14**) exclusively in good yield, and the diastereoselectivity was moderately in favour of the threo isomer in the presence of $MgBr_2$. All of the reactions had good chemoselectivity for aldehyde.

Key words: Antimony; Silicon; Magnesium; Acetylene; Allene; Aldehyde

1. Introduction

The regioselectivity of reaction of an allenic or propargylic organometallic compound with a carbonyl compound is highly dependent on the substituent R [1]. The unsubstituted organometallic compound **1a** shows acetylenic selectivity (**2** being the major product), and alkylated **1b** exhibits allenic selectivity (**3** being the major product). As for silylated **1c**, the regioselectivity is dependent on the kind of metal, *e.g.*, zinc reagent shows acetylenic selectivity [2], while aluminium [2] and titanium [3] reagents show allenic selectivity.



a: R = H; **b**: R = alkyl; **c**: R = Me_3Si

M = Li, Mg, Zn, Ti, Al, Cr, Sn, *etc.*

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* For Part II, see ref. 6.

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We have previously reported some reactions of pentaorganylstiboranes [4]. Homobenzylic alcohols, homoallylic alcohols, ethyl 5-aryl-5-hydroxypent-2-enoates, and β-hydroxypropionic acid derivatives can be synthesized via pentaorganylstiboranes [4,5]. Many pentaorganylstiboranes can react readily with acyl chlorides to give ketones in good yields in the absence of any additional catalyst [4,6]. In the present paper, we report a new aspect of pentaorganylstiboranes [7]: regio- and diastereoselective additions of acetylenic and allenic organoantimony compounds to aldehydes. It was found that the selectivity of the reactions was not only dependent on the substituent R, but was also influenced by the Lewis acid LiBr or $MgBr_2$.

2. Results and discussion

Propargyl bromide (**4a**) reacted with tributylstibine to give allenic stibonium bromide (**5**), instead of acetylenic stibonium bromide. **5** is markedly stable unlike allylic stibonium bromide [8], and it does not react with aldehydes even under heating to 120°C. However, it can be readily converted into pentaorganylstiborane by reaction with BuMgBr in THF at low temperature, and it then reacts smoothly with aldehydes to give exclusively acetylenic alcohols **10a**, in good yields. The reaction also took place well in Et_2O. However, when BuLi was used instead of BuMgBr, the yield was fairly low (50%) and the product was a mixture of allenic alcohols **9a** and acetylenic alcohols **10a** (**9a**:**10a** = 1:1). These results were not influenced by the addition of LiBr or $MgBr_2$. The reason why this reaction has a different result when BuLi is used instead of BuMgBr is not yet clear. It may be due to the feeble ionic property of stibonium bromide **5** and the very high nucleophilicity of BuLi, because, in further studies, we found that the yield (77%) and the selectivity (**9a**:**10a** = 98:2) were good when the corresponding strong ionic stibonium tetraphenylborate (resulted from the anion exchange of **5** with $NaBPh_4$) were used.

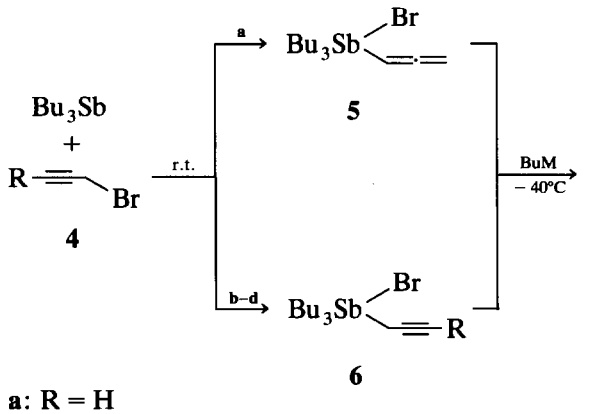
In contrast, the reaction of bromobutyne-2 (**4b**) with tributylstibine gave acetylenic stibonium bromide (**6b**), instead of allenic stibonium bromide. The reaction of **6b** with aldehyde gave only a very low yield of products on heating to 120°C for 24 h. Similarly, **6b** can be

TABLE 1. Regioselective additions of organoantimony to aldehydes

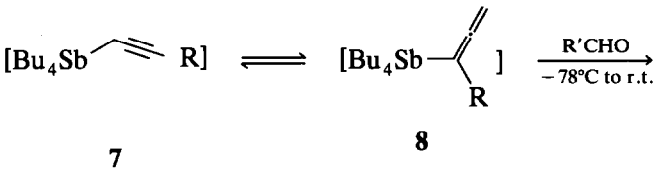
	R'CHO	R	Nucleophilic reagent	Major product	Ratio [a] (**9**/**10**)	Total yield (%) [b]
1	C_6H_5CHO	H	BuMgBr/THF	**10a-a**	–	92
2	C_6H_5CHO	H	BuMgBr/Et_2O	**10a-a**	–	82 [c]
3	p-$CH_3C_6H_4CHO$	H	BuMgBr/THF	**10a-b**	–	94
4	p-$CH_3OC_6H_4CHO$	H	BuMgBr/THF	**10a-c**	–	40 [d]
5	p-ClC_6H_4CHO	H	BuMgBr/THF	**10a-d**	–	92
6	C_6H_5CH=$CHCHO$	H	BuMgBr/THF	**10a-e**	–	85
7	$CH_3(CH_2)_8CHO$	H	BuMgBr/THF	**10a-f**	–	89
8	C_6H_5CHO	CH_3	BuMgBr/THF	**9b-g**	97:3	89
9	C_6H_5CHO	CH_3	BuLi/Hexane/THF [e]	**9b-g**	75:25	75
10	C_6H_5CHO	CH_3	BuMgBr/Et_2O	**9b-g**	95:5	85
11	p-$CH_3C_6H_4CHO$	CH_3	BuMgBr/THF	**9b-h**	97:3	86
12	p-ClC_6H_4CHO	CH_3	BuMgBr/THF	**9b-i**	97:3	86
13	c-$C_6H_{11}CHO$	CH_3	BuMgBr/THF	**9b-j**	65:35	87
14	$CH_3(CH_2)_7CHO$	CH_3	BuMgBr/THF	**9b-k**	77:23	83
15	C_6H_5CHO	n-C_5H_{11}	BuMgBr/THF	**9c-l**	83:17	90
16	$CH_3(CH_2)_6CHO$	n-C_5H_{11}	BuMgBr/THF	**9c-m**	70:30	86
17	C_6H_5CHO	Me_3Si	BuLi/Hexane/THF	**10d-n**	6:94	80
18	C_6H_5CHO	Me_3Si	BuMgBr/THF	**10d-n**	40:60	88
19	C_6H_5CHO	Me_3Si	BuMgBr/THF/LiBr	**10d-n**	10:90	85
20	C_6H_5CHO	Me_3Si	BuLi/Et_2O	**10d-n**	4:96	60 [c]
21	C_6H_5CHO	Me_3Si	BuMgBr/Et_2O	**10d-n**	28:72	64 [c]
22	p-ClC_6H_4CHO	Me_3Si	BuLi/Hexane/THF	**10d-o**	5:95	82
23	p-$CH_3C_6H_4CHO$	Me_3Si	BuLi/Hexane/THF	**10d-p**	5:95	80
24	c-$C_6H_{11}CHO$	Me_3Si	BuLi/Hexane/THF	**10d-q**	8:92	70
25	c-$C_6H_{11}CHO$	Me_3Si	BuMgBr/THF	**10d-q**	35:65	76
26	c-$C_6H_{11}CHO$	Me_3Si	BuMgBr/THF/LiBr	**10d-q**	8:92	86
27	$CH_3(CH_2)_5CHO$	Me_3Si	BuMgBr/THF/LiBr	**10d-r**	15:85	84

[a] Determined by 200 MHz ^1H NMR analysis. [b] Isolated yield based on aldehyde. [c] The nucleophilic reagent was added at −5°C. After 20 min, PhCHO was added at r.t., and stirred for 10 min. [d] 44% of aldehyde was recovered. [e] Hexane:THF = 1:5.

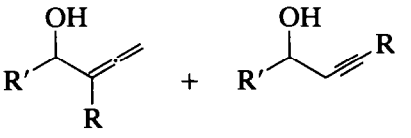
readily converted into the pentaorganylstiborane (**7b**, **8b**) which reacted with aldehydes to yield allenic alcohols (**9b**) and acetylenic alcohols (**10b**). The reaction selectivity for allenic alcohols was good in the case of aromatic aldehydes, and also influenced by the nucleophilic reagent. The selectivity was better in the case of BuMgBr than in the case of BuLi, and the additional Lewis acid LiBr and $MgBr_2$ had no obvious influence on the selectivity.



a: R = H
b: R = CH_3
c: R = n-C_5H_{11}
d: R = Me_3Si



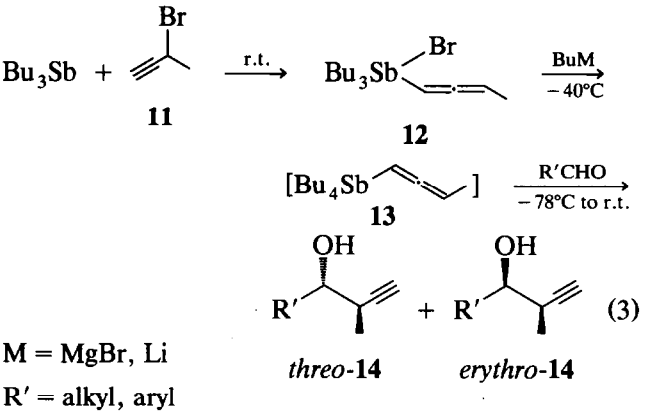
7 **8**



9 **10**

a: R = H		(major)
b, **c**: R = alkyl:	major	
d: R = Me_3Si:		major

(2)



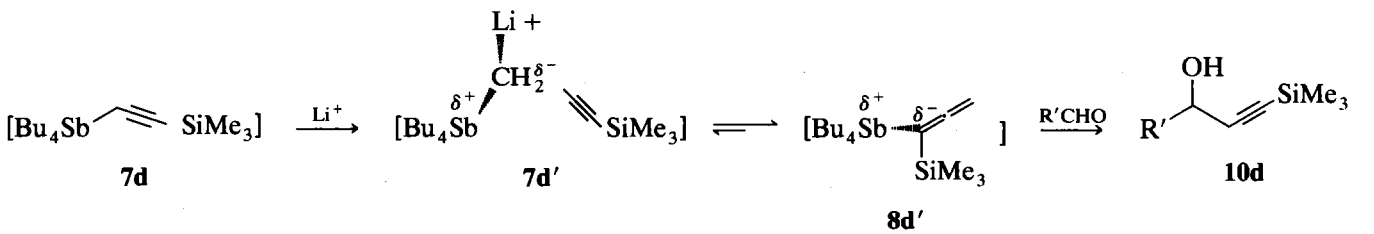
(3)

M = MgBr, Li
R' = alkyl, aryl

1-Bromo-2-octyne (**4c**) underwent the same reaction with similar selectivity (see Table 1).

Furthermore, as in the case of 1-bromo-2-butyne, 3-bromo-1-(trimethylsilyl)-1-propyne (**4d**) when reacted with tributylstibine also gave acetylenic stibonium bromide (**6d**), but the major adducts of its corresponding pentaorganylstiborane to aldehydes were acetylenic alcohols (**10d**). It was also found that the selectivity of the reaction was influenced by the nucleophilicity of the reagent. The regioselectivity was very high in the case of BuLi and moderate in the case of BuMgBr. Unlike the above two reactions, however, selectivity was influenced by the Lewis acid LiBr. High acetylenic selectivity can be achieved by the addition of LiBr when BuMgBr is used. The reason may be the pentaorganylstiborane **7d** having been polarized by Li + to form **7d'** [5], and then undergoing isomerization to give allenic **8d'**, which, owing to the stabilization of trimethylsilyl on α-carbanion ($p\pi$–$d\pi$ conjugation [9]), was more favoured in the equilibrium, and which then reacted with aldehydes to afford acetylenic alcohols **10d** as major products (Scheme 1).

Further, we found that the product of the reaction of 3-bromo-1-butyne (**11**) with tributylstibine was allenic stibonium bromide **12**, and, whether BuMgBr or BuLi was used, the corresponding pentaorganylstiborane **13** reacted with aldehydes to give acetylenic alcohols (ν-adducts) (**14**) exclusively, but with variable diastereoselectivity. When BuMgBr was used in the conversion of **12** to **13**, the reaction exhibited moderate



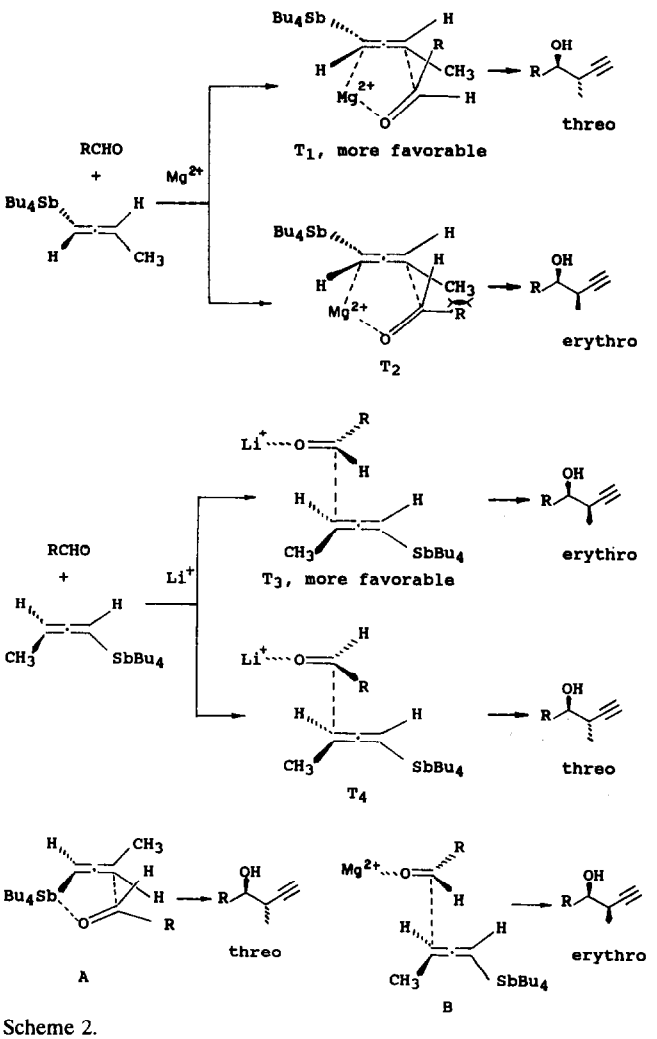
7d **7d'** **8d'** **10d**

Scheme 1.

threo selectivity, and this result was not influenced by the addition of LiBr. When BuLi was used, the reaction showed slight erythro selectivity, and this result was influenced by the addition of $MgBr_2$, exhibiting the same selectivity as when BuMgBr was used. LiBr or $MgBr_2$ was added five minutes after the nucleophilic reagent had been added. These results indicated that $MgBr_2$, added or formed, played a decisive role in the diastereoselectivity of this reaction. As long as in the presence of $MgBr_2$, the reaction exhibited moderate *threo* selectivity. The results are summarized in Table 2.

Our results differed from those of the reactions of allenylmagnesium halide with aldehydes, which resulted in threo selectivity in the case of aliphatic aldehydes, with no selectivity in the case of aromatic aldehydes [10]. While allenyl tin reagent reacts with aldehydes to exhibit *erythro* selectivity in the presence of Lewis acids [11], our results have shown the exact opposite.

A speculative mechanism is given in Scheme 2. In the presence of Mg^{2+}, the reaction takes place through a cyclic transition state [12]. It is obvious that the T1 transition state is more favourable than the T2 transition state because of the steric hindrance effect between the methyl and R group. The reaction therefore exhibits *threo* selectivity. On the other hand, in the presence of Li^+, the reaction takes place through the acyclic transition state. Obviously, if the T3 transition state is more favourable than T4, the reaction should exhibit *erythro* selectivity. However, the reaction only showed slight *erythro* selectivity. This may be due to the reactivity of pentaorganylstiborane being very high, or the coordinating ability of Li^+ being weak, the reaction proceeding partially through the cyclic transition state in favour of the *threo* isomer (Scheme 2, **A**). Similarly, the reason why the selectivity of the reaction was not very high in the presence of magnesium bromide may be due to the reactivity of pentaorganylstiborane being very high or the reaction proceeding partially through the acyclic transition state in favour of the *erythro* isomer (Scheme 2, **B**).



Scheme 2.

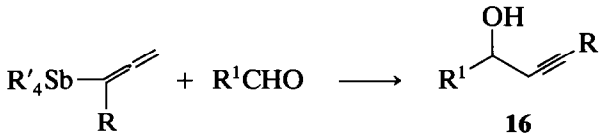
All reactions were chemoselective for aldehydes, and good yields for aldehydes were obtained even in

TABLE 2. Diastereoselective addition of organoantimony to aldehydes

	R'CHO	Condition	Product	*threo*/*erythro* [a]	Yield (%) [b]
1	C_6H_5CHO	BuLi/hexane/THF	**14a**	45:55	92
2	C_6H_5CHO	BuMgBr/THF	**14a**	75:25	91
3	C_6H_5CHO	BuMgBr/THF/LiBr	**14a**	75:25	94
4	C_6H_5CHO	BuLi/hexane/$MgBr_2$/THF	**14a**	75:25	88
5	C_6H_5CHO	BuMgBr/$BF_3 \cdot Et_2O$/THF	**14a**	50:50	91
6	*p*-$CH_3C_6H_4CHO$	BuMgBr/THF	**14b**	75:25	89
7	*p*-$CH_3C_6H_4CHO$	BuLi/hexane/$MgBr_2$/THF	**14b**	75:25	85
8	*p*-ClC_6H_4CHO	BuMgBr/THF	**14c**	75:25	90
9	*p*-BrC_6H_4CHO	BuMgBr/THF	**14d**	70:30	88
10	*c*-$C_6H_{11}CHO$	BuMgBr/THF	**14e**	85:15	72

[a] Determined by 200 MHz ^1H NMR analysis. [b] Isolated yield based on aldehyde.

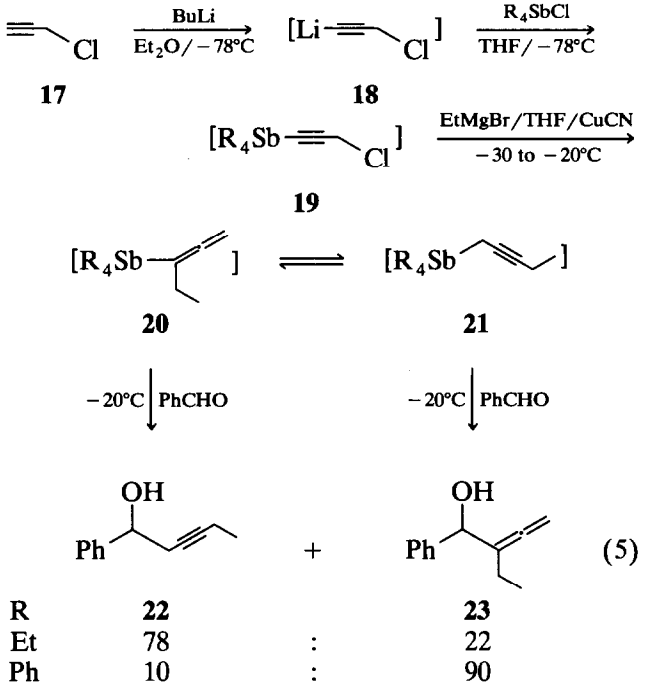
the presence of ketones. In addition, under the same conditions, ethyl benzoate and benzyl cyanide were unreactive towards the pentaorganylstiboranes. The reaction is therefore a new method for the selective synthesis of allenic or acetylenic derivatives, and especially useful in that other functional groups such as ketone, ester, nitrile and halogen can be present in the aldehydes.



15 **16** (4)

(R = alkyl)

The regiocontrolled synthesis of acetylenic alcohols of type **20** from the corresponding organometallics was not easy [13].



R	22		23
Et	78	:	22
Ph	10	:	90

We attempted to synthesize the allenic stiborane of type **15**, which reacted with aldehyde to give acetylenic alcohol of type **16**. At low temperature, propargyl chloride reacted with BuLi to give the lithium reagent **18**, which reacted with tetralkylstibonium chloride to give pentaorganylstiborane (**19**). Allenic stiborane **20** was obtained by the reaction of **19** with EtMgBr in the presence of a catalytic amount of CuCN. Allenic stiborane **20** was not very stable, and fairly easy to isomerize to acetylenic stiborane **21**, thus the adduct with benzaldehyde was a mixture of acetylenic alcohol **22** and allenic alcohol **23**. In the case of R = Et, acetylenic alcohol **22** was the major product, while in the case of R = Ph, it was allenic alcohol **23**.

3. Experimental details

Proton magnetic resonance (^{1}H NMR) spectra were recorded with an XL-200 instrument in $CDCl_3$ solution. Infrared spectra were recorded in neat liquid films unless indicated otherwise. All reactions were carried out under nitrogen. All solvents were dried by standard methods and redistilled before use. Tributylstibine [14], tetraethylstibonium chloride [15], tetraphenylstibonium chloride [15], propargyl bromide [16], bromobutyne-2 [16], 3-bromo-1-(trimethylsilyl)-1-propyne [16] and 3-bromo-1-butyne [16] were prepared according to literature methods.

3.1. Preparation of stibonium compounds

3.1.1. General procedure. Allenyltributylstibonium bromide (5)

Tributylstibine (735 mg, 2.5 mmol) and propargyl bromide (310 mg, 2.6 mmol) were mixed and stirred at room temperature for 12 h under nitrogen. The unreacted propargyl bromide was removed by water pump, giving the pale yellow oily product **5** (1000 mg, 97%). ^{1}H NMR: 0.96 (t, $J_1 = 7.5$ Hz, 9H), 1.37–1.50 (m, 6H), 1.70–1.85 (m, 6H), 2.50–2.60 (m, 6H), 4.25 (d, $J_2 = 7.2$ Hz, 2H), 5.05 (t, $J_2 = 7.2$ Hz, 1H). IR: 1925vs cm^{-1}. MS *m/e* (rel. intensity): 332 ($M^+ -$ Br, 100). Allenyltributylstibonium tetraphenylborate was obtained by the anion exchange reaction of **5** with sodium tetraphenylborate ($NaBPh_4$) in THF, and recrystallized from ethanol (1335 mg, 82%). ^{1}H NMR: 0.95 (t, $J_1 = 7.5$ Hz, 9H), 1.20–1.35 (m, 6H), 1.35–1.50 (m, 6H), 1.60–1.75 (m, 6H), 4.80 (s, 3H), 6.90–7.10 (m, 12H), 7.38–7.50 (m, 8H). IR (KBr): 1940vs cm^{-1}. Anal. Calcd. for $C_{39}H_{50}BSb$: C, 71.91; H, 7.74. Found: C, 71.57; H, 7.58%.

3.1.2. (2-Butynyl)tributylstibonium bromide (6b)

^{1}H NMR: 0.98 (t, $J_1 = 5.5$ Hz, 9H), 1.39–1.50 (m, 6H), 1.76–1.88 (m, 6H), 1.82 (t, $J_2 = 2.8$ Hz, 3H), 2.43 (m, 2H), 2.60–2.70 (m, 6H). IR: 2200vw cm^{-1}. MS *m/e* (rel. intensity): 346 ($M^+ -$ Br, 100). Its corresponding (2-butynyl)tributylstibonium tetraphenylborate: ^{1}H NMR: 0.95 (t, $J_1 = 7.5$ Hz, 9H), 1.20–1.35 (m, 6H), 1.35–1.75 (m, 12H), 1.80 (t, $J_2 = 2.8$ Hz, 3H), 2.10 (m, 2H), 6.90–7.10 (m, 12H), 7.40–7.50 (m, 8H), IR: 2200vw cm^{-1}. Anal. Calcd. for $C_{40}H_{52}BSb$: C, 72.20; H, 7.88. Found: C, 72.25; H, 7.83%.

3.1.3. (2-Octynyl)tributylstibonium bromide (6c)

^{1}H NMR: 0.9–1.0 (m, 12H), 1.40–1.55 (m, 12H), 1.76–1.88 (m, 8H), 2.10 (t, $J = 2.8$ Hz, 2H), 2.60–2.70

(m, 6H). IR: 2200vw cm^{-1}. MS *m/e* (rel. intensity): 402 (M^+ − Br, 100).

*3.1.4. [3-(Trimethylsilyl)-2-propynyl]tributylstibonium bromide (**6d**)*

^1H NMR: 0.10 (s, 9H), 0.95 (t, $J = 7.5$ Hz, 9H), 1.40–1.50 (m, 6H), 1.75–1.88 (m, 6H), 2.05 (s, 2H), 2.60–2.70 (m, 6H). IR: 2200vw cm^{-1}. MS *m/e* (rel. intensity): 404 (M^+ − Br, 100).

*3.1.5. 1,2-Butadienyltributylstibonium bromide (**12**)*

^1H NMR: 0.96 (t, $J = 7.5$ Hz, 9H), 1.35–1.50 (m, 6H), 1.70–1.85 (m, 9H), 2.55–2.65 (m, 6H), 5.08–5.25 (m, 1H), 5.30–5.38 (m, 1H). IR: 1950vs cm^{-1}. MS *m/e* (rel. intensity): 346 (M^+ − Br, 100).

3.2. Regio- and diastereoselective additions of organoantimony compounds to aldehydes

*3.2.1. General procedure. 1-Phenyl-3-butyn-1-ol (**10a–a**)*

See ref. 17. Allenic stibonium salt **5** (1000 mg, 2.43 mmol) in THF (4 ml) was treated with BuMgBr (2.4 mmol, 1 N, THF) at −40°C with vigorous stirring. After 5–10 min, the solution was cooled to −78°C, and benzaldehyde (210 mg, 2.0 mmol) was added. The temperature was kept at −78°C for 2 h, then allowed to rise to room temperature. After aqueous workup and chromatography on a silica gel column, 270 mg (92%) of product was obtained ^1H NMR: 2.08 (t, $J_1 = 2.8$ Hz, 1H), 2.40 (s br, 1H), 2.60 (dd, $J_1 = 2.8$ Hz, $J_2 = 6.5$ Hz, 2H), 4.78 (t, $J_2 = 6.5$ Hz, 1H), 7.32 (s, 5H). IR: 2200w cm^{-1}. MS *m/e* (rel. intensity): 146 (M^+, 1), 128 ($M^+ - H_2O$, 11).

*3.2.2. 1-(4-Methylphenyl)-3-butyl-1-ol (**10a–b**)*

300 mg, 94%. ^1H NMR: 2.06 (t, $J_1 = 2.8$ Hz, 1H), 2.36 (s, 3H), 2.45 (s br, 1H), 2.58 (dd, $J_1 = 2.8$ Hz, $J_2 = 6.5$ Hz, 2H), 4.80 (t, $J_2 = 6.5$ Hz, 1H), 7.16 (d, $J_3 = 7.5$ Hz, 2H), 7.26 (d, $J_3 = 7.5$ Hz, 2H). IR: 2200w cm^{-1}. HRMS *m/z* Calcd. for $C_{11}H_{12}O$, 160.0888; Found, 160.0853.

*3.2.3. 1-(4-Methoxyphenyl)-3-butyn-1-ol (**10a–c**)*

See ref. 18. 140 mg, 40% (120 mg, 44% of 4-methoxylbenzaldehyde was recovered). ^1H NMR: 2.02 (t, $J_1 = 2.5$ Hz, 1H), 2.60 (dd, $J_1 = 2.5$ Hz, $J_2 = 6.0$ Hz, 2H), 3.0 (s br, 1H), 3.85 (s, 3H), 4.75 (t, $J_2 = 6.0$ Hz, 1H), 6.90 (d, $J_3 = 8.5$ Hz, 2H), 7.30 (d, $J_3 = 8.5$ Hz, 2H). IR: 2120w cm^{-1}. MS *m/e* (rel. intensity): 176 (M^+, 4), 159 (M^+ − OH, 12).

*3.2.4. 1-(4-Chlorophenyl)-3-butyl-1-ol (**10a–d**)*

See ref. 18. 335 mg, 92%. ^1H NMR: 2.08 (t, $J_1 = 2.8$ Hz, 1H), 2.42 (s br, 1H), 2.62 (dd, $J_1 = 2.8$ Hz, $J_2 = 6.0$ Hz, 2H), 4.82 (t, $J_2 = 6.0$ Hz, 1H), 7.36 (s, 4H). IR: 2200w cm^{-1}. MS *m/e* (rel. intensity): 182, 180 (M^+, 0.1, 0.3), 165, 163 (M^+ − OH, 13, 41).

*3.2.5. 1-Phenyl-1-hexen-5-yn-3-ol (**10a–e**)*

See ref. 19. 290 mg, 85%. ^1H NMR: 2.08 (t, $J_1 = 2.5$ Hz, 1H), 2.60 (dd, $J_1 = 2.5$ Hz, $J_2 = 6.0$ Hz, 2H), 3.20 (s br, 1H), 4.65 (m, 1H), 6.32 (dd, $J_3 = 6.5$ Hz, $J_4 = 16.0$ Hz, 1H), 6.76 (d, $J_4 = 16.0$ Hz, 1H), 7.40 (s, 5H). IR: 2200w cm^{-1}. MS *m/e* (rel. intensity): 172 (M^+, 4), 155 (M^+ − OH, 46).

*3.2.6. 1-Tridecyl-4-ol (**10a–f**)*

See ref. 18. 345 mg, 89%. ^1H NMR: 0.96 (t, $J_1 = 7.0$ Hz, 3H), 1.30 (s br, 16H), 1.98 (t, $J_2 = 2.5$ Hz, 1H), 2.40 (dd, $J_2 = 2.5$ Hz, $J_3 = 6.0$ Hz, 2H), 3.10 (s br, 1H), 3.68 (m, 1H). IR: 2200w cm^{-1}. MS *m/e* (rel. intensity): 197 ($M^+ + 1$, 3), 179 (M^+ − OH, 1).

*3.2.7. 2-Methyl-1-phenyl-2,3-butadien-1-ol (**9b–g**)*

See ref. 20. 285 mg, 89% (mixture of **9b–g** and **10b–g**). ^1H NMR: 1.55 (t, $J = 3.0$ Hz, 3H), 3.35 (s br, 1H), 4.85 (m, 2H), 5.10 (s br, 1H), 7.30 (s, 5H). IR: 1950s cm^{-1}. MS *m/e* (rel. intensity): 160 (M^+, 4), 143 (M^+ − OH, 9). 1-Phenyl-3-pentyn-1-ol (**10b–g**) (see ref. 20) ^1H NMR: 1.78 (t, $J_1 = 2.5$ Hz, 3H), 2.48 (dq, $J_1 = 2.5$ Hz, $J_2 = 6.0$ Hz, 2H), 3.35 (s br, 1H), 4.60 (t, $J_2 = 6.0$ Hz, 1H), 7.30 (s, 5H).

*3.2.8. 2-Methyl-1-(4-methylphenyl)-2,3-butadien-1-ol (**9b–h**)*

300 mg, 86% (mixture of **9b–h** and **10b–h**). ^1H NMR: 1.59 (t, $J_1 = 3.2$ Hz, 3H), 2.37 (s, 3H), 2.55 (s br, 1H), 4.90 (m, 2H), 5.07 (s br, 1H), 7.16 (d, $J_2 = 8.2$ Hz, 2H), 7.27 (d, $J_2 = 8.2$ Hz, 2H). IR: 1950s cm^{-1}. 1-(4-Methyl-phenyl-3-pentyl-1-ol (**10b–h**): ^1H NMR: 1.82 (t, $J_1 = 2.5$ Hz, 3H), 2.37 (s, 3H), 2.45 (m, 2H), 2.55 (s br, 1H), 4.62 (t, $J_2 = 6.5$ Hz, 1H), 7.16 (d, $J_3 = 8.2$ Hz, 2H), 7.27 (d, $J_3 = 8.2$ Hz, 2H). HRMS (mixture) *m/z* Calcd. for $C_{12}H_{14}O$: 174.1044; Found: 174.1059.

*3.2.9. 2-Methyl-1-(4-chlorophenyl)-2,3-butadien-1-ol (**9b–i**)*

335 mg, 86% (mixture of **9b–i** and **10b–i**). ^1H NMR: 1.55 (t, $J = 3.0$ Hz), 3.48 (s br, 1H), 4.80 (m, 2H), 5.10 (s br, 1H), 7.30 (s, 4H). IR: 1960s cm^{-1}. 1-(4-chlorophenyl)-3-pentyn-1-ol (**10b–i**): ^1H NMR: 1.80 (t, $J_1 = 2.5$ Hz, 3H), 2.48 (m, 2H), 3.48 (s br, 1H), 4.60 (t, $J_2 = 6.5$ Hz, 1H), 7.30 (s, 4H). HRMS (mixture) *m/z* Calcd. for $C_{11}H_{11}ClO$: 194.0498; Found: 194.0531.

*3.2.10. 1-Cyclohexyl-2-methyl-2,3-butadien-1-ol (**9b–j**)*

See ref. 20. 295 mg, 87% (mixture of **9b–j** and **10b–j**). ^1H NMR: 0.9–2.20 (m, 11H), 1.68 (t, $J_1 = 3.2$

Hz, 3H), 2.64 (s br, 1H), 3.80 (dt, $J_1 = 3.2$ Hz, $J_2 = 7.2$ Hz, 1H), 4.72 (m, 2H). IR: 1960s cm^{-1}. 1-Cycohexyl-3-pentyl-1-ol (**10b–j**) see ref. 20: ^1H NMR: 0.90–2.20 (m, 11H), 1.80 (t, $J = 2.5$ Hz, 3H), 2.38 (m, 2H), 2.64 (s br, 1H), 3.45 (m, 1H). IR: 2240vw cm^{-1}.

3.2.11. 3-Methyl-1,2-dodecadien-4-ol (9b–k)

See ref. 20. 325 mg, 83% (mixture of **9b–k** and **10b–k**) ^1H NMR: 0.88 (t, $J_1 = 7.0$ Hz, 3H), 1.28 (s br, 14H), 1.70 (t, $J_2 = 3.2$ Hz, 3H), 1.92 (s br, 1H), 4.02 (m, 1H), 4.74 (m, 2H). IR: 1960s cm^{-1}. 2-tridecyn-5-ol (**10b–k**) see ref. 21: ^1H NMR: 0.88 (t, $J_1 = 7.0$ Hz, 3H), 1.28 (s br, 14H), 1.80 (t, $J_2 = 3.2$ Hz, 3H), 1.92 (s br, 1H), 2.30 (m, 2H), 3.68 (m, 1H). IR: 2240vw cm^{-1}.

3.2.12. 2-Pentyl-1-phenyl-2,3-butadien-1-ol (9c–l)

See ref. 22. 390 mg, 90% (mixture of **9c–l** and **10c–l**). ^1H NMR: 0.84 (t, $J_1 = 7.0$ Hz, 3H), 1.10–1.50 (m, 6H), 1.80 (m, 2H), 2.40 (s br, 1H), 4.98 (m, 2H), 5.08 (s br, 1H), 7.32 (s, 5H). IR: 1960s cm^{-1}. 1-Phenyl-3-nonyn-1-ol (**10c–l**) see ref. 22: ^1H NMR: 0.84 (t, $J_1 = 7.0$ Hz, 3H), 1.10–1.50 (m, 6H), 2.15 (m, 2H), 2.40 (s br, 1H), 2.60 (m, 2H), 4.78 (t, $J_2 = 6.5$ Hz, 1H), 7.32 (s, 5H). IR: 2240vw cm^{-1}.

3.2.13. 3-Pentyl-1,2-undecadien-4-ol (9c–m)

See ref. 23. 410 mg, 86% (mixture of **9c–m** and **10c–m**) ^1H NMR: 0.80–1.50 (m, 24H), 2.10 (m, 2H), 2.50 (s br, 1H), 4.00 (m, 1H), 4.72 (m, 2H). IR: 1960s cm^{-1}. 10-Hexadecyn-8-ol (**10c–m**) see ref. 23: ^1H NMR: 0.80–1.50 (m, 24), 2.15 (m, 2H), 2.35 (m, 2H), 2.50 (s br, 1H), 3.70 (m, 1H). IR: 2240vw cm^{-1}.

3.2.14. 1-Phenyl-4-(trimethylsilyl)-3-butyn-1-ol (10d–n)

See ref. 20. 260 mg (3.0 mmol) of LiBr was used in the reaction. 370 mg, 85% (mixture of **9d–n** and **10d–n**). ^1H NMR: 0.18 (s, 9H), 2.60 (d, $J = 7.0$ Hz, 2H), 3.15 (s br, 1H), 4.78 (t, $J = 7.0$ Hz, 1H), 7.35 (s, 5H). IR: 2180m cm^{-1}. MS *m/e* (rel. intensity): 218 (M^+, 0.5), 201 ($M^+ - OH$, 5). 1-Phenyl-2-(trimethylsilyl)-2,3-butadien-1-ol (**9d–n**) see ref. 20: ^1H NMR: 0.05 (s, 9H), 3.15 (s br, 1H), 4.50 (d, $J = 3.0$ Hz, 2H), 5.25 (t, $J = 3.0$ Hz, 1H), 7.35 (s, 5). IR: 1930m cm^{-1}.

3.2.15. 1-(4-Chlorophenyl)-4-(trimethylsilyl)-3-butyn-1-ol (10d–o)

See ref. 24. 415 mg, 82% (mixture of **9d–o** and **10d–o**). ^1H NMR: 0.20 (s, 9H), 2.62 (d, $J = 7.0$ Hz, 2H), 3.08 (s br, 1H), 4.80 (t, $J = 7.0$ Hz, 1H), 7.36 (s, 4H). IR: 2180m cm^{-1}. MS *m/e* (rel. intensity): 254, 252 (M^+, 0.2, 0.8), 237, 235 ($M^+ - OH$, 4, 11). 1-(4-Chlorophenyl)-2-(trimethylsilyl)-2,3-butadien-1-ol (**9d–o**): ^1H NMR: 0.05 (s, 9H), 3.08 (s br, 1H), 4.50 (d, $J = 3.0$ Hz, 2H), 5.32 (t, $J = 3.0$ Hz, 1H), 7.36 (s, 4H). IR: 1940m cm^{-1}.

3.2.16. 1-(4-Methylphenyl)-4-(trimethylsilyl)-3-butyn-1-ol (10d–p)

See ref. 24. 370 mg, 80% (mixture of **9d–p** and **10d–p**). ^1H NMR: 0.16 (s, 9H), 2.36 (s, 3H), 2.62 (d, $J_1 = 7.0$ Hz, 2H), 2.70 (s br, 1H), 4.80 (t, $J_1 = 7.0$ Hz, 1H), 7.16 (d, $J_2 = 7.2$ Hz, 2H), 7.25 (d, $J_2 = 7.2$ Hz, 2H). IR: 2180m cm^{-1}. 1-(4-Methylphenyl)-2-(trimethylsilyl)-2,3-butadien-1-ol (**9d–p**): ^1H NMR: 0.05 (s, 9H), 2.36 (s, 3H), 2.70 (s br, 1H), 4.52 (d, $J_1 = 3.0$ Hz, 2H), 5.34 (t, $J_1 = 3.0$ Hz, 1H), 7.16 (d, $J_2 = 7.2$ Hz, 2H), 7.25 (d, $J_2 = 7.2$ Hz, 2H). IR: 1940m cm^{-1}.

3.2.17. 1-Cyclohexyl-4-(trimethylsilyl)-3-butyn-1-ol (10d–q)

See ref. 20. 260 mg of LiBr was used. 385 mg, 86% (mixture of **9d–q** and **10d–q**). ^1H NMR: 0.14 (s, 9H), 0.90–1.96 (m, 11H), 2.24 (s br, 1H), 2.42 (2Xdd, $J_1 = 4.2$ Hz, $J_2 = 7.8$ Hz, $J_3 = 16.0$ Hz, 2H), 3,48 (m, 1H). IR: 2180m cm^{-1}. 1-Cyclohexyl-2-(trimethylsilyl)-2,3-butadien-1-ol (**9d–q**) see ref. 20: ^1H NMR: 0.12 (s, 9H), 0.90–1.96 (m, 11H), 2.24 (s br, 1H), 3.88 (m, 1H), 4.52 (t, $J = 2.0$ Hz, 2H). IR: 1940m cm^{-1}.

3.2.18. 1-(Trimethylsilyl)-1-decyn-4-ol (10d–r)

See ref. 25. (260 mg of LiBr was used) 380 mg, 84% (mixture of **9d–r** and **10d–r**). ^1H NMR: 0.14 (s, 9H), 0.88 (t, $J_1 = 7.0$ Hz, 3H), 1.28 (s br, 10H), 2.10 (s br, 1H), 2.40 (2Xdd, $J_2 = 4.2$ Hz, $J_3 = 7.5$ Hz, $J_4 = 16.0$ Hz, 2H), 3.74 (m, 1H). IR: 2180m cm^{-1}. 3-(Trimethylsilyl)-1,2-decadien-4-ol (**9d–r**) see ref. 25: ^1H NMR: 0.12 (s, 9H), 0.88 (t, $J = 7.0$ Hz, 3H), 1.28 (s br, 10 H), 2.10 (s br, 1H), 4.16 (m, 1H), 4.54 (m, 2H). IR: 1940m cm^{-1}.

3.2.19. 2-Methyl-1-phenyl-3-butyn-1-ol (14a)

See ref. 10 (370 mg (2.0 mmol) of $MgBr_2$ was used). 280 mg, 88% (mixture of *threo* and *erythro* isomers). ^1H NMR: *threo*, 1.08 (d, $J_1 = 7.5$ Hz, 3H), 2.20 (d, $J_2 = 2.0$ Hz, 1H), 2.50 (s br, 1H), 2.80 (m, 1H), 4.50 (d, $J_3 = 8.0$ Hz, 1H), 7.14 (s, 5H); *erythro*, 1.14 (d, $J_1 = 7.5$ Hz, 3H), 2.10 (d, $J_2 = 2.0$ Hz, 1H), 2.50 (s br, 1H), 2.80 (m, 1H), 4.70 (d, $J_3 = 6.0$ Hz, 1H), 7.14 (s, 5H). IR: 2100w cm^{-1}. MS *m/e* (rel. intensity): 160 (M^+, 1), 143 ($M^+ - OH$, 100).

3.2.20. 2-Methyl-1-(4-methylphenyl)-3-butyn-1-ol (14b)

See ref. 10. 310 mg, 89% (mixture of *threo* and *erythro* isomers). ^1H NMR: *threo*, 1.08 (d, $J_1 = 7.5$ Hz, 3H), 2.15 (d, $J_2 = 2.0$ Hz, 1H), 2.32 (s, 3H), 2.60–2.90 (m, 2H), 4.42 (d, $J_3 = 8.0$ Hz, 1H), 7.22 (s br, 4H); *erythro*, 1.08 (d, $J_1 = 7.5$ Hz, 3H), 2.05 (d, $J_2 = 2.0$ Hz,

1H), 2.32 (s, 3H), 2.60–2.90 (m, 2H), 4.60 (d, $J_3 = 6.0$ Hz, 1H), 7.22 (s br, 4H). IR: 2100w cm^{-1}. MS *m/e* (rel. intensity): 157 ($M^+ - OH$, 43).

3.2.21. 1-(4-Chlorophenyl)-2-methyl-3-butyn-1-ol (14c)

350 mg, 90% (mixture of *threo* and *erythro* isomers). ^1H NMR: *threo*, 1.10 (d, $J_1 = 7.5$ Hz, 3H), 2.20 (d, $J_2 = 2.0$ Hz, 1H), 2.60 (s br, 1H), 2.80 (m, 1H), 4.50 (d, $J_3 = 8.0$ Hz, 1H), 7.32 (s br, 4H); *erythro*, 1.12 (d, $J_1 = 7.5$ Hz, 3H), 2.12 (d, $J_2 = 2.0$ Hz, 1H), 2.60 (s br, 1H), 2.80 (m, 1H), 4.70 (d, $J_3 = 6.0$ Hz, 1H), 7.32 (s br, 4H). IR: 2100w cm^{-1}. HRMS *m/z* Calcd. for $C_{11}H_{11}ClO$, 194.0499; Found, 194.0521.

3.2.22. 1-(4-Bromophenyl)-2-methyl-3-butyn-1-ol (14d)

420 mg, 88% (mixture of *threo* and *erythro* isomers). ^1H NMR: *threo*, 1.12 (d, $J_1 = 7.5$ Hz, 3H), 2.22 (d, $J_2 = 2.0$ Hz, 1H), 2.60 (s br, 1H), 2.80 (m, 1H), 4.50 (d, $J_3 = 8.0$ Hz, 1H), 7.25 (d, $J_4 = 8.0$ Hz, 2H), 7.50 (d, $J_4 = 8.0$ Hz, 2H); *erythro*, 1.12 (d, $J_1 = 7.5$ Hz, 3H), 2.14 (d, $J_2 = 2.0$ Hz, 1H), 2.60 (s br, 1H), 2.80 (m, 1H), 4.70 (d, $J_3 = 6.0$ Hz, 1H), 7.25 (d, $J_4 = 8.0$ Hz, 2H), 7.50 (d, $J_4 = 8.0$ Hz, 2H). IR: 2150w cm^{-1}. HRMS *m/z* Calcd. for $C_{11}H_{11}BrO$, 239.9973; Found, 239.9957.

3.2.23. 1-Cyclohexyl-2-methyl-3-butyn-1-ol (14e)

See ref. 10. 240 mg, 72% (mixture of *threo* and *erythro* isomers). ^1H NMR: *threo*, 1.20 (d, $J_1 = 7.5$ Hz, 3H), 1.10–1.84 (m, 11H), 2.0 (s br, 1H), 2.12 (d, $J_2 = 2.0$ Hz, 1H), 2.76 (m, 1H), 3.08 (dd, $J_3 = 5.0$ Hz, $J_4 = 7.5$ Hz, 1H); *erythro*, 1.20 (d, $J_1 = 7.5$ Hz, 3H), 1.10–1.84 (m, 11H), 2.0 (s br, 1H), 2.06 (d, $J_2 = 2.0$ Hz, 1H), 2.76 (m, 1H), 3.36 (dd, $J_3 = J_4 = 6.0$ Hz, 1H). IR: 2200w cm^{-1}.

3.2.24. 1-Phenyl-3-hexyn-1-ol (22)

Butyllithium (3.0 mmol, 2 N in hexane) was added dropwise to the solution of propargyl chloride (225 mg, 3.0 mmol) in Et_2O (4 ml) at −78°C with vigorous stirring. After 10 min, tetraethylstibonium chloride (685 mg, 2.5 mmol, in 3 ml THF) was added, and the temperature kept at −78 to −70°C for 30 min. The solution was kept at −30 to −20°C for the next step using solution A. EtMgBr (2.0 mmol, 1.5 N in THF) was added dropwise to the solution of CuCN (10 mg, 0.1 mmol) in THF (2 ml) at −40°C with stirring. After 20 min, the temperature had risen to −20°C, and solution A was added dropwise to this solution with vigorous stirring, and kept at −20°C for 20 min. Benzaldehyde (160 mg, 1.5 mmol) was added. After 30 min, the reaction temperature was allowed to rise to room temperature. Work-up was as usual, 144 mg of a mixture of products **22** and **23** was obtained (55%) (along with *ca.* 5% of 1-phenyl-1-propanol). ^1H NMR: 1.10 (t, $J_1 = 7.5$ Hz, 3H), 2.18 (m, 2H), 2.58 (m, 2H), 2.85 (s br, 1H), 4.76 (t, $J_2 = 7.0$ Hz, 1H), 7.30 (s, 5H). IR: 2200w cm^{-1}. MS *m/e* (rel. intensity): 174 (M^+, 0.2), 157 ($M^+ - OH$, 13). 2-Ethyl-1-phenyl-2,3-butadien-1-ol (**23**): ^1H NMR: 0.98 (t, $J = 7.5$ Hz, 3H), 1.80 (m, 2H), 2.85 (s br, 1H), 4.95 (m, 2H), 5.08 (s br, 1H), 7.30 (s, 5H). IR: 1960m cm^{-1}.

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