Journal of Organometallic Chemistry, 412 (1991) 47–52
Elsevier Sequoia S.A., Lausanne
JOM 21794

Stereoselective addition of allylstibonium bromide to aldehydes *

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(Received December 21st, 1990)

Abstract

Reaction of allylantimony with aldehydes provides homoallylic alcohols with high *threo* selectivity in the case of (*E*)-4-methyl-2-pentenylantimony (**2c**) and with preferential *erythro* selectivity in the case of crotylantimony (**2a**).

Introduction

Stereoselective synthesis of α-methylhomoallylic alcohols, of possible application to the synthesis of macrolide and polyether antibiotics and of some pheromones, is one of the most challenging problems for the synthetic chemist [1]. One successful strategy for this purpose involves stereoselective reaction of crotylmetals with aldehydes [2]. Of particular interest is the dependence of the stereoselectivity of crotylstannanes upon the reaction conditions [3]. However, the analogous reaction of allylantimony has hardly been studied [4]. Here we report a diastereoselective addition of allylantimony to aldehydes.

Results and discussion

Allylantimony **2** was readily obtained by mixing tributylstibine with bromides **1** at room temperature. Heating the salt **2** with a variety of aldehydes under nitrogen produced homoallylic alcohols **3** in high yield. This reaction was performed without any solvent. The reaction can also take place in 1,4-dioxane under reflux with moderate yield and similar diastereoselectivity. However, the reaction was slow in THF under reflux, because of the low boiling point of THF. The ratio of *threo* and *erythro* was determined by ^{1}H NMR and/or capillary GC analysis by comparison with authentic samples. The results are summarized in Table 1.

* This paper is the XCIII report on the studies of the application of elemento-organic compounds of the 15th and 16th groups in organic synthesis.

0022-328X/91/$03.50

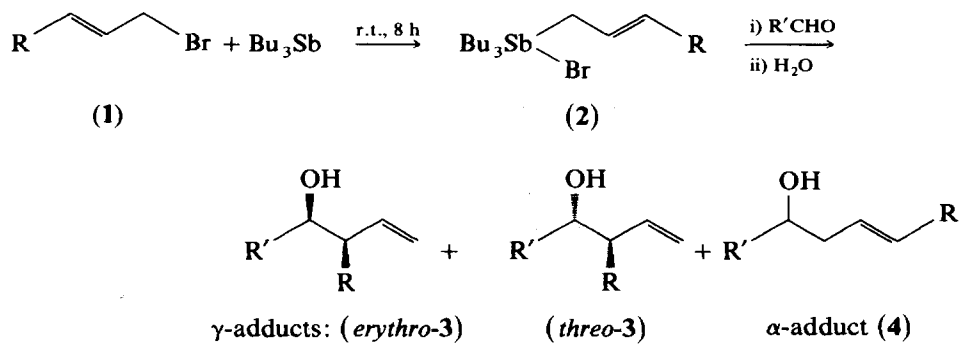
Table 1

Synthesis of homoallylic alcohols via allylantimony [a]

Allylantimony (*trans* and/or *cis*) [b]	Entry	Aldehyde	Total yields [c] (%)	Products ratio [d]	
				threo/*erythro*	3/4
$Bu_3Sb(Br)CH_2CH{=}CHCH_3$	a	C_6H_5CHO [e]	97	33:67	97:3
	b	*p*-BrC_6H_4CHO	93	35:65	98:2
	c	*p*-MeC_6H_4CHO	92	35:65	98:2
(*t* 86%, *c* 14%)	d	*p*-ClC_6H_4CHO [f]	92	35:65	98:2
	e	^{i}PrCHO	90	36:64	78:22
	f	$CH_3CH{=}CHCHO$	92	37:63	94:6
	g	n-$C_8H_{17}CHO$	95	35:65	95:5
$Bu_3Sb(Br)CH_2CH{=}CHC_3H_7$	h	*p*-ClC_6H_4CHO	95	44:56	93:7
	i	*p*-MeC_6H_4CHO	95	48:52	91:9
	j	^{i}PrCHO	91	65:35	80:20
(*t*)	k	$CH_3CH{=}CHCHO$	93	47:53	94:6
$Bu_3Sb(Br)CH_2CH{=}CHCH(CH_3)_2$	l	*p*-ClC_6H_4CHO	94	95:5	85:15
	m	*p*-MeC_6H_4CHO	95	95:5	82:18
	n	^{i}PrCHO	95	99:1	70:30
(*t*)	o	$CH_3CH{=}CHCHO$	93	85:15	90:10

[a] All reactions were performed as described in the text. [b] Determined by ^{1}H NMR and ^{13}C NMR. [c] Isolated yields. [d] Determined by ^{1}H NMR and/or capillary GC analysis by comparison with authentic materials. [e] If the reaction was carried out in refluxing 1,4-dioxane, the product was obtained in 60% yield with similar diastereoselectivity. [f] The same result was given by tributylstibine, crotylbromide and aldehyde in one pot.

The reaction of **2** with aldehydes results predominantly in γ-adduct as in the case of other crotylmetallic reagents, such as crotyltin [3]. Beside the γ-adduct, some α-adduct **4** is formed as a by-product. The production of α-adduct may be attributed to the more enhanced ionic nature of the allylic C–Sb bond, which is different from what applies in crotyltin [5*].



(**a**: R = CH_3; **b**: R = $CH_3CH_2CH_2$; **c**: R = $(CH_3)_2CH$)

* Reference number with an asterisk indicates a note in the list of references.

The diastereoselectivity of this reaction depends greatly upon the substituent R. In the case of **2a** ($R = CH_3$), a mixture of *erythro* and *threo* isomers was isolated in a ratio of about 2:1 (entries a–g). In the case of the highly hindered **2c** ($R = (CH_3)_2CH$), the *threo* isomer was obtained with 70–98% diastereoselectivity (entries (l–o).

As a result of the enhanced ionic nature of the Br–Sb bond, either the cyclic or acyclic transition state in this reaction could be favoured. In the case of **2a**, stibonium bromide may act as a lewis acid, and the propensity to an acyclic transition state seems to be greater than that to a cyclic transition state, consequently erythroselectivity was observed. Otherwise, in the case of **2c**, because of the steric properties of iso-propyl the propensity to a cyclic transition state was greater, so a high degree of *threo*-selectivity was observed as in the case of crotyltins [2]. As for **2b**, the result was intermediate. However, this mechanistic rationale is speculative. Confirmation of the mechanism of this reaction awaits more detailed understanding of the reaction course.

Experimental

IR spectra were obtained on a Schimadzu IR-440 spectrophotometer and are reported in cm^{-1} units (neat). Mass spectra were measured on a Finnigan GC-MC 4021 spectrometer. ^1H NMR spectra were recorded on a Varian EM-360 or AM-500 spectrometer in CCl_4 solution unless noted otherwise, with TMS as an internal standard and are reported in δ units (ppm).

*2-Methyl-1-phenyl-3-buten-1-ol (**3a** entry a) [3b]*

Typical procedure: Tributylstibine (675 mg, 2.3 mmol) and crotyl bromide (350 mg, 2.6 mmol) were mixed and stirred at ambient temperature for 8 h under nitrogen. The resulting oily product was heated with benzaldehyde (210 mg, 2.0 mmol) at 100 °C for 15–18 h. After protonolysis with wet alcohol, the mixture was chromatographed on an alumina–silica gel (1:1) column, eluting with 95:5 petroleum ether/ethyl acetate to give a mixture of α- and γ-adduct products (310 mg, 97%), b.p. 93–95 °C/1 mmHg. *threo*-Form. ^1H NMR: 0.88 (d, $J_1 = 7.0$ Hz, 3H); 1.70 (brs, 1H); 2.42 (m, 1H); 4.31 (d, $J_2 = 7.0$ Hz, 1H); 4.70–5.26 (m, 2H); 5.30–6.10 (m, 1H); 7.26 (s, 5H). IR: 3400, 1640, 1270, 1020, 980, 910, 760, 700 cm^{-1}. MS: 162 (M^+, 0.1), 145 (26), 108 (100), 107 (28), 105 (23), 80 (42), 79 (35), 77 (53). *erythro*-Form. ^1H NMR: 0.95 (d, $J_1 = 7.0$ Hz, 3H); 4.50 (d, $J_3 = 6$ Hz, 1H). The other data of ^1H NMR, IR and MS are the same as above.

*1-(4-Bromophenyl)-2-methyl-3-buten-1-ol (**3a** entry b)*

From 4-bromobenzaldehyde: 370 mg. Mixture products: 450 mg, 93%. B.p. 138–140 °C/1 mmHg. *threo*-Form. ^1H NMR: 0.83 (d, $J_1 = 7.0$ Hz, 3H); 2.20 (brs, 1H); 2.35 (m, 1H); 4.20 (d, $J_2 = 7.0$ Hz, 1H); 4.70–5.20 (m, 2H); 5.60 (m, 1H); 7.06 (d, $J_3 = 10.0$ Hz, 2H); 7.39 (d, $J_3 = 10.0$ Hz, 2H). IR: 3400, 1640, 1010, 920 cm^{-1}. MS: 242, 240 (M^+, 0.1), 225, 223 (14), 187 (84), 157 (19), 77 (100). *erythro*-Form. ^1H NMR: 0.92 (d, $J_1 = 7.0$ Hz, 3H); 4.37 (d, $J_4 = 5.5$ Hz, 1H). The other data of ^1H NMR, IR and MS are the same as above. Anal. Found: C, 54.57; H, 5.57. $C_{11}H_{13}BrO$ (mixture products) calcd.: C, 54.79; H, 5.43%.

*2-Methyl-1-*p*-tolyl-3-buten-1-ol (**3a** entry c) [3b]*

From *p*-tolualdehyde: 240 mg. Mixture products: 325 mg, 92%. B.p. 114–117 °C/1 mmHg. *threo*-form. ^{1}H NMR: 0.85 (d, $J_1 = 6.5$ Hz, 3H); 1.25–2.25 (m, 2H); 2.32 (s, 3H); 4.22 (d, $J_2 = 7.0$ Hz, 1H); 4.95–5.15 (m, 2H); 5.48–5.80 (m, 1H); 7.08 (bs, 4H). IR: 3610, 1620, 1050, 990, 910 cm^{-1}. MS: 176 (M^+, 0.2), 175 (0.4), 159 (14), 122 (100), 93 (59), 91 (40), 77 (30). *erythro*-Form. ^{1}H NMR: 0.95 (d, $J_1 = 6.5$ Hz, 3H); 4.40 (d, $J_3 = 6.0$ Hz, 1H). The other data of ^{1}H NMR, IR and MS are the same as above.

*1-(4-Chlorophenyl)-2-methyl-3-buten-1-ol (**3a** entry d) [3a]*

From 4-chlorobenzaldehyde: 281 mg. Mixture products: 360 mg, 92%. *threo*-Form. ^{1}H NMR ($CDCl_3$): 0.87 (d, $J_1 = 7.0$ Hz, 3H); 2.30 (m, 1H); 2.35 (brs, 1H); 4.35 (d, $J_2 = 6.8$ Hz, 1H); 4.80–5.25 (m, 2H); 5.40–6.10 (m, 1H); 7.20 (s, 4H). IR: 3400, 1640, 1095, 1010, 990, 920 cm^{-1}. MS: 196 (M^+, 0.2), 181 (6), 179 (18), 143 (41), 142 (55), 141 (100), 113 (27), 77 (88). *erythro*-Form. ^{1}H NMR: 0.98 (d, $J_1 = 7.0$ Hz, 3H); 4.60 (d, $J_3 = 5.6$ Hz, 1H). The other data of ^{1}H NMR, IR and MS are the same as above.

*2,4-Dimethyl-5-hexen-3-ol (**3a** entry e) [3b]*

From isobutyraldehyde: 144 mg. Mixture products: 230 mg, 90%. *threo*-Form. ^{1}H NMR: 0.8–1.1 (m, 9H); 1.4 (m, 1H); 1.64 (brs, 1H); 2.06 (m, 1H); 3.00 (dd, $J_1 = 5.0$, $J_2 = 10.5$ Hz, 1H); 4.75–5.16 (m, 2H); 5.68 (m, 1H). IR: 3400, 1630, 1000, 910 cm^{-1}. MS: 128 (M^+, 0.3), 111 (9), 73 (57), 56 (100). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*3-Methyl-1,5-heptadien-4-ol (**3a** entry f) [3b]*

From crotonaldehyde: 140 mg. Mixture products: 230 mg, 92%. *threo*-Form. ^{1}H NMR: 0.97 (d, $J_1 = 6.6$ Hz, 3H); 1.70 (d, $J_2 = 5.0$ Hz, 3H); 2.25 (m, 1H); 2.7 (bs, 1H); 3.8 (dd, $J_3 = 5.5$, $J_4 = 10.0$ Hz, 1H); 4.85–5.05 (m, 2H); 5.40–5.90 (m, 3H). IR: 3600, 1640, 990, 960, 910 cm^{-1}. MS: 126 (M^+, 0.2), 125 (1), 109 (46), 72 (100), 69 (23), 43 (58). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*3-Methyl-1-dodecen-4-ol (**3a** entry g) [6]*

From nonyl aldehyde: 284 mg. Mixture products: 375 mg, 95%. *threo*-Form. ^{1}H NMR: 0.85 (m, 6H); 1.15 (brs, 12H); 1.33 (brs, 1H); 1.53 (m, 2H); 2.0 (m, 1H); 3.20 (m, 1H); 4.65–5.05 (m, 2H); 5.55 (m, 1H). IR: 3400, 1640, 990, 910 cm^{-1}. MS: 198 (M^+, 0.4), 181 (0.5), 143 (11), 141 (14), 83 (48), 71 (23), 69 (79), 56 (100). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*1-(4-Chlorophenyl)-2-propyl-3-buten-1-ol (**3b** entry h)*

From 4-chlorobenzaldehyde: 281 mg. Mixture products: 425 mg, 95%. B.p. 140–145 °C/1 mmHg. *threo*-Form. ^{1}H NMR ($CDCl_3$): 0.78 (t, $J_1 = 7.0$ Hz, 3H); 1.13–1.48 (m, 4H); 2.10 (brs, 1H); 2.23 (m, 1H); 4.40 (d, $J_2 = 6.8$ Hz, 1H); 5.15–5.26 (m, 2H); 5.58–6.68 (m, 1H); 7.25 (m, 4H). IR: 3400, 1640, 1090, 1020, 920, 830 cm^{-1}. MS: 224 (M^+, 0.14), 207 (4), 143 (53), 141 (100), 113 (12), 77 (51). *erythro*-Form. ^{1}H NMR: 0.86 (t, $J_1 = 7.0$ Hz, 3H); 2.38 (m, 1H); 4.60 (d, $J_3 = 5.8$ Hz, 1H); 4.98–5.08 (m, 2H); 5.43–5.50 (m, 1H). The other data of ^{1}H NMR, IR and MS are the same as above.

*2-Propyl-1-p-tolyl-3-buten-1-ol (**3b** entry i)*

From *p*-tolualdehyde: 240 mg. Mixture products: 385 mg, 95%. B.p. 130–133°C/1 mmHg. *threo*-Form. ^{1}H NMR: 0.9 (t, $J_1 = 7.0$ Hz, 3H); 1.0–1.5 (m, 4H); 2.0 (brs, 1H); 2.20 (m, 1H); 2.30 (s, 3H); 4.25 (d, $J_2 = 7.8$, 1H); 4.8–5.2 (m, 2H); 5.3–5.9 (m, 1H); 7.05 (s, 4H). IR: 3400, 1640, 1030, 1000, 915, 820 cm^{-1}. MS: 204 (M^+, 3.7), 187 (9), 162 (56), 121 (7), 91 (100). *erythro*-Form. ^{1}H NMR: 4.36 (d, $J_3 = 6.0$ Hz, 1H). The other data of ^{1}H NMR, IR and MS are the same as above. Anal. Found: C, 82.47; H, 10.06. $C_{14}H_{20}O$ (mixture products) calcd.: C, 82.30; H, 9.87%.

*2-Methyl-4-propyl-5-hexen-3-ol (**3b** entry j)*

From isobutyraldehyde: 144 mg. Mixture products: 285 mg, 91%. B.p. 80–83°C/12 mmHg. *threo*-Form. ^{1}H NMR: 0.9–1.2 (m, 9H); 1.2–1.8 (m, 5H); 1.8–2.5 (m, 2H); 3.05–3.55 (m, 1H); 4.90–5.40 (m, 2H); 5.5–6.0 (m, 1H). IR: 3400, 1640, 1000, 910 cm^{-1}. MS: 156 (M^+, 0.5), 139 (7), 84 (77), 73 (44), 69 (30), 56 (100). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*3-Propyl-1,5-heptadien-4-ol (**3b** entry k)*

From crotonaldehyde: 140 mg. Mixture products: 285 mg, 93%. B.p. 96–100°C/15 mmHg. *threo*-Form. ^{1}H NMR: 0.9 (t, $J = 7.0$ Hz, 3H); 1.0–1.5 (m, 4H); 1.5–2.5 (m, 5H); 3.7–4.0 (m, 1H); 4.7–5.9 (m, 5H). IR: 3400, 1640, 1020, 970, 910 cm^{-1}. MS: 154 (M^+, 0.14), 138 (100), 136 (5), 95 (30), 81 (47), 71 (85). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*1-(4-Chlorophenyl)-2-iso-propyl-3-buten-1-ol (**3c** entry l)*

From 4-chlorobenzaldehyde: 281 mg. Mixture products: 420 mg, 94%. B.p. 138–142°C/1 mmHg. *threo*-Form. ^{1}H NMR: 0.85–1.15 (m, 6H); 1.60 (m, 1H); 2.05 (brs, 1H); 2.40 (m, 1H); 4.65 (d, $J_1 = 7.5$ Hz, 1H); 5.1–6.1 (m, 3H); 7.3 (s, 4H). IR: 3450, 1640, 1090, 1020, 920, 820 cm^{-1}. MS: 224 (M^+, 0.5), 207 (13), 182 (35), 121 (89), 91 (100). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above.

*1-(4-Methylphenyl)-2-isopropyl-3-buten-1-ol (**3c** entry m)*

From *p*-tolualdehyde: 240 mg. Mixture products: 385 mg, 95%. B.p. 127–130°C/1 mmHg. *threo*-Form. ^{1}H NMR ($CDCl_3$): 0.827 (d, $J_1 = 6.8$ Hz, 6H); 1.46 (m, 1H); 1.95 (brs, 1H); 2.15 (m, 1H); 2.35 (s, 3H); 4.56 (d, $J_2 = 8.6$ Hz, 1H); 5.15–5.29 (m, 2H); 5.80 (m, 1H); 7.23 (m, 4H). IR: 3400, 1640, 1040, 1000, 910, 810 cm^{-1}. MS: 204 (M^+, 0.1), 203 (0.5), 187 (42), 131 (19), 122 (100), 105 (20). *erythro*-Form. ^{1}H NMR: 0.90 (d, $J_1 = 6.8$ Hz, 6H); 2.22 (m, 1H); 4.68 (d, $J_3 = 8.0$ Hz, 1H); 4.85–4.98 (m, 2H); 5.36 (m, 1H). The other data of ^{1}H NMR, IR and MS are the same as above.

*2-Methyl-4-isopropyl-5-hexen-3-ol (**3c** entry n)*

From isobutyraldehyde: 144 mg. Mixture products: 295 mg, 95%. B.p. 78–82°C/12 mmHg. *threo*-Form. ^{1}H NMR: 0.80–1.0 (m, 12H); 1.2–1.5 (m, 2H); 1.9–2.4 (m, 2H); 3.0–3.3 (m, 1H); 4.9–6.0 (m, 3H). IR: 3400, 1640, 1010, 910 cm^{-1}. MS: 156 (M^+, 0.1), 113 (2), 84 (69), 73 (52), 69 (100), 55 (56), 43 (73), 41 (53). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above. Anal. Found: C, 76.82; H, 13.34. $C_{10}H_{20}O$ (mixture products) calcd.: C, 76.80; H, 12.90%.

3-Isopropyl-1,5-heptadien-4-ol (3c entry o)

From crotonaldehyde: 140 mg. Mixture products: 285 mg, 93%. B.p. 95–98 °C/15 mmHg. *threo*-Form. ^{1}H NMR: 0.9–1.6 (m, 7H); 1.7–2.4 (m, 5H); 4.0–4.4 (m, 1H); 5.10–6.20 (m, 3H). IR: 3400, 1640, 1020, 910 cm^{-1}. MS: 154 (M^+, 0.2), 153 (2), 138 (100), 136 (5), 95 (18), 81 (44), 71 (41). *erythro*-Form. The same ^{1}H NMR, IR and MS spectra as above. Anal. Found: C, 77.71; H, 11.73. $C_{10}H_{18}O$ (mixture products) calcd.: C, 77.87; H, 11.76%.

Acknowledgements

Thanks are due to the National Natural Science Foundation of China and Academia Sinica for financial support. Thanks are also due to Professor Xiao-Tian Liang for his valuable discussion.

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