Insect Pheromones. Stereoselective Reduction of β- or ω-Alkynols to the Corresponding (*E*)-Alkenols by Lithium Tetrahydroaluminate

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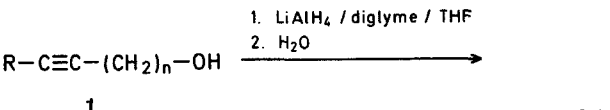
Several insect pheromone components are comprised of unsaturated alcohols or their derivatives having disubstituted double bonds with the *E* configuration[1-9].

While (*E*)-2-alkenols may be conveniently prepared by reduction of the corresponding 2-alkynols with lithium tetrahydroaluminate in diethyl ether[10,11], (*E*)-β- and, in general, (*E*)-ω-alkenols cannot be obtained in a similar manner. A classic method to prepare such pure compounds consists of reducing the *O*-tetrahydropyran-2-yl derivatives of the corresponding alkynols with metallic sodium in liquid ammonia[12,13]. Nevertheless, high molecular weight alkynic compounds, which are less soluble in liquid ammonia, are reduced in low yields. In this case, to increase significantly the yields it is necessary to use a very large excess of liquid ammonia[13]. It must be noted, however, that when we have employed this procedure[13] for the preparation of (*E*)-14-methyl-8-hexadecen-1-ol (**2a**), a component of the sex pheromone of female *Trogoderma glabrum*[5], we have only obtained a rather low yield (~50%).

In this paper we wish to report a general method for preparing in one-step, stereoselectively, and in high yield, low and high molecular weight (*E*)-β- or (*E*)-ω-alkenols from the corresponding alkynols. This method consists of reacting the alkynic alcohols at 140° for 48–55 h, under nitrogen, with a large excess of lithium tetrahydroaluminate in a mixture of diglyme and tetrahydrofuran. Careful hydrolysis of the reaction mixture affords the desired (*E*)-alkenols in high yield. G.L.C. analysis shows that the reduction of the alkynols having a C—chain shorter than C_{13} is quantitative and that the (*E*)-alkenols so obtained contain less than 1% of the corresponding (*Z*)-isomers[14]. On the other hand, reduction of high molecular weight alkynols affords (*E*)-alkenols which are contamined by 2–4% of the starting acetylenic compounds. Such (*E*)-alkenols may, however, be conveniently purified by column chromatography on silver nitrate—impregnated silica gel.



	R	n
a	sec-C_4H_9–$(CH_2)_4$–	7
b	n-C_6H_{13}	2
c	n-C_4H_9	6
d	n-C_8H_{17}	6

The (*E*)-alkenols prepared in the present work are (*E*)-14-methyl-8-hexadecen-1-ol (**2a**), (*E*)-3-decen-1-ol (**2b**), (*E*)-7-dodecen-1-ol (**2c**), and (*E*)-7-hexadecen-1-ol (**2d**). The acetate of **2c** is the sex pheromone of the false codling moth, *Argyroploce leucotreta*[15].

It may be concluded that the reduction of β- or ω-alkynols by lithium tetrahydroaluminate usefully complements the reduction with sodium in liquid ammonia. However, when high molecular weight (*E*)-alkenols must be prepared, the high yields of the reduction with lithium tetrahydroaluminate make this the procedure of choice.

Table 1. Physical Properties of the Alkynols **1**

Compound	b.p./torr	n_D^{25}	Molecular formula[a]	I.R. (film) ν [cm^{-1}]
1a	133–134°/0.15	1.4645	$C_{17}H_{32}O$ (252.4)	3300; 2940; 2860; 1465; 1380; 1300; 1200; 1060; 720
1c	99–100°/0.20	1.4614	$C_{12}H_{22}O$ (182.3)	3300; 2940; 2920; 2840; 1440; 1410; 1360; 1310; 1070; 1050; 1025; 720
1d	134–135°/0.45	1.4627	$C_{16}H_{30}O$ (238.4)	3300; 2940; 2915; 2840; 1440; 1410; 1360; 1320; 1070; 1025; 715

[a] All products gave satisfactory microanalyses (C ±0.25; H ±0.20%) and the expected mass and ^{1}H-N.M.R. spectra; microanalyses were carried out by Dr. V. Nuti, Istituto di Chimica Farmaceutica, Pisa.

General Procedure for Preparing ω-Alkynols (1):

3-Decyn-1-ol (**1b**) is a commercially available product. 14-Methyl-8-hexadecyn-1-ol (**1a**) is synthesized in 51% yield by reaction

Table 2. Physical Properties of the (*E*)-Alkenols (**2**)

Compound	Yield [%]	b.p./torr (Lit. b.p./torr)	n_D^{25}	Molecular formula[a]	^{1}H-N.M.R. (CCl_4, 60 MHz) δ [ppm]
2a	85	108–109°/0.03	1.4584	$C_{17}H_{34}O$ (254.5)	0.89 (t, 6H); 1.33 (br, 19H); 1.97 (br, 4H); 3.25 (s, 1H); 3.50 (t, 2H); 5.16 (m, 2H)
2b	89	113–114°/15 (56–57°/0.1)[18]	1.4473	$C_{10}H_{20}O$ (156.3)	0.87 (t, 3H); 1.30 (br, 8H); 1.7–2.2 (br, 4H); 3.33 (s, 1H); 3.50 (t, 2H); 5.40 (m, 2H)
2c[b]	93	99–100°/0.30 (78–81°/0.06)[19]	1.4521	$C_{12}H_{24}O$ (184.3)	0.88 (t, 3H); 1.33 (br, 12H); 1.7–2.2 (br, 4H); 3.50 (t, 2H); 4.11 (s, 1H); 5.33 (m, 2H)
2d	94	126–127°/0.30	—[c]	$C_{16}H_{32}O$ (240.4)	0.88 (t, 3H); 1.33 (br, 20H); 1.7–2.2 (br, 4H); 3.30 (s, 1H); 3.51 (t, 2H); 5.33 (m, 2H)

[a] All products gave satisfactory microanalysis (C ±0.25; H ±0.25%) and the expected I. R. and mass spectra.

[b] This alcohol was converted into the corresponding acetate having b.p. 86–88°/0.1 torr and n_D^{25} = 1.4410 (Lit. [19], b.p. 78–82°/0.05; n_D^{25} = 1.4420). (*E*)-7-Dodecen-1-yl acetate is the sex pheromone of false codling moth[16].

[c] m.p. 27–28°.

of 1-lithio-7-methyl-1-nonyne with 1-tetrahydropyranyloxy-7-iodoheptane in hexamethylphosphoric triamide solution and subsequent removal of the Thp-protective group[16]. Analogously, 7-dodecyn-1-ol (**1c**) and 7-hexadecyn-1-ol (**1d**) are obtained in 52% yield by reaction of 1-tetrahydropyranyloxy-6-iodohexane with 1-lithio-1-hexyne and 1-lithio-1-decyne, respectively, and subsequent removal of the Thp group. Table 1 summarizes some physical properties of **1a**, **1c**, and **1d**.

General Procedure for Reducing β- or ω-Alkynols to the Corresponding (*E*)-Alkenols (2):

A mixture of tetrahydrofuran (10 ml), diglyme (80 ml), and lithium tetrahydroaluminate (5 g, 0.131 mol) is heated under nitrogen and a low boiling fraction is distilled off (~ 7 ml). A solution of the alkynol **1** (0.038 mol) in diglyme (10 ml) is slowly added to the magnetically stirred mixture cooled at 10°. Then temperature is raised and kept at 140° for 48–55 h. The reaction mixture is cooled and slowly hydrolyzed under nitrogen with degassed ice-cold water. The aqueous slurry is neutralized with dilute hydrochloric acid and extracted with pentane (300 ml in 6 portions). The pentane extracts are washed with water and saturated sodium chloride solution. After drying, the (*E*)-alkenol is isolated by fractional distillation.

G.L.C. analysis (8% Carbowax 20 M on Chromosorb W 60–80 mesh; 15% BDS on Chromosorb W 80–100 mesh; UCON LB 550 X on Chromosorb W 80–100 mesh) shows that the (*E*)-alkenols having a C—chain longer than C_{12} are contamined by 2–4% of the corresponding alkynols. Their purification is performed by column chromatography over silver nitrate impregnated-silica gel[17]. Elution with hexane yields pure (*E*)-alkenols (**2**). Table 2 summarizes some physical properties of **2a**, **2b**, **2c**, and **2d**.

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