# Convenient Synthesis of *cis*-3-Hexen-1-ol

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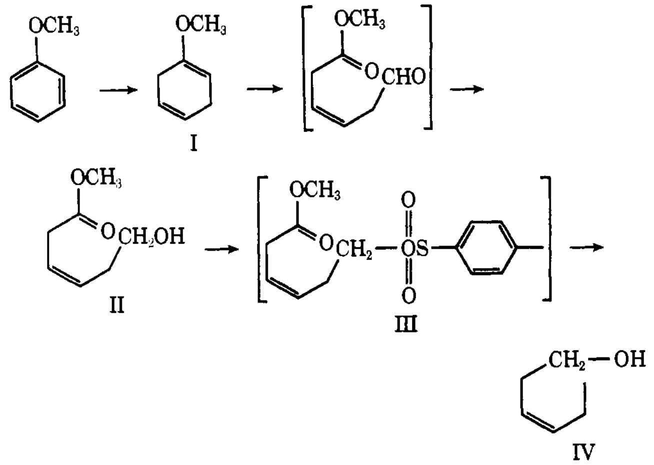
**A new synthesis of leaf alcohol, *cis*-3-hexen-1-ol, from anisole is reported.**

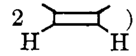
The *cis*-3-Hexen-1-ol, commonly known as leaf alcohol, is a naturally occurring substance with a delicate green odor. Many syntheses of this alcohol have been recorded (*1*) but only the route via 3-hexyn-1-ol led to the pure cis olefin. The increased importance of leaf alcohol in flavors and fragrances prompted us to develop an alternate synthesis to *cis*-3-hexen-1-ol. Corey and coworkers (*2*) have recently utilized the double bond in a cyclohexene system as a source of cis olefins. Here we report the conversion of anisole to *cis*-3-hexen-1-ol employing a similar scheme to produce the desired cisoid structure.

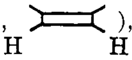


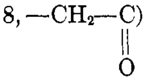
Birch reduction of anisole gave 1-methoxy-1,4-cyclohexadiene (I) (*3*). Ozonolysis of this compound in methanol, followed by sodium borohydride reduction, produced methyl *cis*-6-hydroxy-3-hexenoate (II) in 88% yield. Treatment of this alcohol with *p*-toluenesulfonyl chloride gave a crude tosylate (III) which was reduced without further purification to *cis*-3-hexen-1-ol with lithium aluminum hydride.

## EXPERIMENTAL SECTION

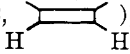
**1-Methoxy-1,4-cyclohexadiene (I).** This compound was prepared by Birch reduction of anisole with lithium in ether and liquid ammonia (*3*). The crude product was distilled through a 37-cm column packed with glass helices to give an 86.5% yield of product which was 92.5% 1-methoxy-1,4-cyclohexadiene and 7.5% 1-methoxy-1,3-cyclohexadiene. The physical constants agree with the published values for the 1,4 diene (*3*).

**Methyl *cis*-6-Hydroxy-3-hexenoate (II).** A mixture of 2.85 grams (22 mmol) of 1-methoxy-1,4-cyclohexadiene and 30 ml of absolute methanol was treated with ozone (1.25 grams, 26 mmol) at −78°C. The resulting mixture was flushed with nitrogen. The mixture was allowed to come to 0°C, 2.42 grams (39 mmol) of dimethylsulfide were added, and the mixture was stirred at this temperature for 80 min. After cooling to −78°C, a suspension of 1.47 grams (39 mmol) of sodium borohydride in 20 ml of absolute ethanol was added dropwise. The resulting mixture was allowed to come to room temperature and then stirred for 80 min. The methanol was removed under vacuum to produce 3.3 grams of product (88%). Boiling point 60°C (0.2-mm short path distillation), ir 2.90 and 5.74 μ; nmr ($CDCl_3$) ϒ 4.32 (m, 2 ), 6.30 (s, 3, —OC$\underline{H}_3$), 6.32 (t, 2, *J* = 7, —C$\underline{H}_2$—OH), 6.84 (d, 2, *J* = 8, —C$\underline{H}_2$—CO), 7.48 (6, 1, —$\underline{OH}$), and 7.66 (m, 2, $HOCH_2$—C$\underline{H}_2$—CH=). *Anal.* Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.47; H, 8.51.

**Methyl *cis*-6-hydroxy-3-hexenoate *p*-toluenesulfonate (III).** *p*-Toluenesulfonyl chloride (1.425 grams, 7.5 mm) was added at 0°C to a 1-gram solution (6.95 mmol) of methyl *cis*-6-hydroxy-3-hexenoate in 2.37 grams of dry pyridine. The resulting mixture was stirred at 0°C for 4 hr. The crude product was poured on ice and concentrated hydrochloric acid and extracted with benzene. The organic layer was washed with 2*N* hydrochloric acid, sodium carbonate (aq) until neutral and dried over potassium carbonate. Evaporation of the solvent produced 1.43 grams (68% of theory) of crude tosylate (III), ir 5.80, 6.25, and 6.98 μ; nmr ($CDCl_3$) ϒ 2.65 (m, 4, aromatic H), 4.40 (m, 2, ), 5.93 (t, 2, *J* = 7, —C$\underline{H}_2$—O), 6.31 (s, 3, —OC$\underline{H}_3$), 6.94 (d, 2, *J* = 8, —$CH_2$—C(=O)), 7.56 (5, 3, —$CH_3$), 7.62 (m, 2, —C$\underline{H}_2$—CH=).



$$-CH_2-\overset{\displaystyle C}{\underset{\displaystyle O}{\Vert}}$$

***cis*-3-Hexen-1-ol (IV).** Crude methyl *cis*-6-hydroxy-3-hexenoate *p*-toluenesulfonate (1.36 grams, 4.85 mmol) was dissolved in 20 ml of dry ether. To this solution was added 0.343 gram (9.00 mmol) of lithium aluminum hydride in 20 ml of dry ether at 25°C with stirring. After the addition was complete, the mixture was stirred at 25°C for 1 hr. The excess lithium aluminum hydride was decomposed by the addition of wet ether and followed by water. The product was extracted with ether and dried over sodium sulfate. After the ether was evaporated, the product was distilled through a short path distillation apparatus to give 0.36 gram (3.6 mmol, 74% of theory) of *cis*-3-hexen-1-ol, bp 70°C (27 mm) ir 3.00 and 13.80 μ; nmr ($CDCl_3$) ϒ 4.54 (m, 2, ), 6.37 (t, 2, *J* = 7, —C$\underline{H}_2$—O—) 7.68 (q, 4, *J* = 7 —C$\underline{H}_2$—CH=CH—C$\underline{H}_2$).

The infrared spectra were taken neat on a Perkin-Elmer Model 137 spectrophotometer. Proton nmr spectra were obtained or a Varian Associates A-60A spectrometer with $Si(CH_3)_4$ as an internal standard.

## LITERATURE CITED

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(2) Corey, E. J., Katzenellenbogen, J. A., Gilman, N. W., Roman, S. A., Erickson, B. W., *J. Amer. Chem. Soc.*, **90**, 5618 (1968).
(3) Wilds, A. L., Nelson, N. A., *ibid.*, **75**, 5360 (1953).

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