

HYDROZIRCONATION/OXIDATION OF INTERNAL OLEFINS  
A SIMPLE SYNTHESIS OF TRIACONTANOL

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**Abstract:** Hydrozirconation of internal olefins followed by oxidation with anhydrous t-butyl hydroperoxide generates primary alcohols in good yields and high purity.

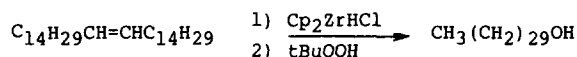
Recent interest in 1-triacontanol as a potential plant growth stimulant<sup>1</sup> has prompted numerous reports of synthesis of this compound.<sup>2,3,4</sup> Our recently reported method for the preparation of long chain iodides,<sup>5</sup> involving metathesis of 1-olefins followed by hydrozirconation/iodination seemed well suited for triacontanol. Maruyama et al<sup>2</sup> reported that the hydrozirconation method failed, and they resorted to hydroboration to prepare primary alcohol, contaminated with varying amounts of secondary triacontanol. Reported here are results for the successful application of the hydrozirconation method for olefins in the range of C<sub>8</sub> to C<sub>30</sub>.

Schwarz et al<sup>6</sup> reported the oxidation of alkylzirconium compounds, in good yields, by various peroxides and oxygen. In our hands, hydrozirconation<sup>7</sup> of 1-octene followed by oxidation with 70% tert-butyl hydroperoxide<sup>8</sup> gave 1-octanol in 47% yield, accompanied by substantial amounts of unidentified by-products. A similar result was obtained with 7-tetradecene, while 15-triacontene gave mainly olefin and saturated hydrocarbon and 5-10% yields of triacontanol. Reasoning that the water in 70% t-butyl hydroperoxide was interfering, we carried out the oxidation with anhydrous t-butyl hydroperoxide, prepared by the method recently described by Sharpless.<sup>9</sup> Good, reproducible yields of alcohols were obtained from a number of olefins, including cyclohexene. Results are assembled in the Table.

Comparison of the product derived from 1-octene with authentic samples of 2- and 3-octanol revealed the complete absence of these compounds. The purity of the 1-triacontanol is dependent only on the purity of the triacontene used. The metathesis of 1-hexadecene as described<sup>2,5</sup> generally gives a mixture of cis- and trans-15-triacontene contaminated with 2-3% of nonacosene and smaller amounts of octacosene. Gas chromatographic analysis of the triacontanol obtained revealed the presence of 0.4 and 2.1%, respectively, of octacosanol and nonacosanol. No evidence for the presence of secondary alcohols could be obtained using the TLC system which is claimed to separate these isomers as the acetates.<sup>2</sup> An experimental description follows.

Preparation of 1-triacontanol. To a solution of 2.92 g (10 mmole) of Cp<sub>2</sub>ZrCl<sub>2</sub> in 30 ml THF at 23°C was added 1.45 g (5 mmole) of a 70% solution of Vitride in toluene over about 10 minutes. After 2 hours, 2.10 g (5 mmole) of 15-triacontene<sup>5</sup> was added through a side arm under a strong flow of argon. The resulting suspension was heated in an oil bath at 40°C for 96 hours, cooled to room temperature, and treated with 2.75 ml of 3.66 M t-BuOOH in ClCH<sub>2</sub>CH<sub>2</sub>Cl.<sup>9</sup> After 1 hour at room temperature, about 3 ml of water was added and the mixture filtered hot to remove inorganic salts. Concentration in vacuo to about 50 ml followed by dilution with acetone (300 ml) gave 2.0 g of crude triacontanol on cooling. Recrystallization from ClCH<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub> gave 1.50 g of 97%

pure 1-triacontanol, m.p. 89-90°C, contaminated with nonacosanol and octacosanol as noted in the text. Identifications were made by gas chromatographic comparison with authentic samples, and by mass spectrometry. Chromatography of the mother liquor gave 0.23 g (11%) of triacontane, containing 10% triacontene. Recrystallization from hexane of the filtrate from acetone gave 80% recovery of a mixture of  $\text{Cp}_2\text{ZrCl}_2$  and  $(\text{Cp}_2\text{ZrCl})_2\text{O}$ .



Olefin	$\text{Cp}_2\text{ZrHCl}^b$	Table <sup>a</sup>		Product	Yield % <sup>d</sup>
			Time <sup>c</sup>		
1-Octene <sup>e</sup>	1.0		4 hr.	1-octanol	76
Trans-4-octene	1.5		24 hr.	1-octanol	73
Cyclohexene	1.5		24 hr.	Cyclohexanol	63
Cyclooctene	1.5		72 hr.		0 <sup>f</sup>
7-Tetradecene	1.5		72 hr.	1-tetradecanol	70 <sup>g</sup>
15-triacontene	2.0		96 hr.	1-triacontanol	68 <sup>h</sup>

a) Reactions in THF ( $\text{CaH}_2$ ) at 40°C. After the indicated time, the reaction was cooled, and one equivalent of *t* BuOOH was added (based on hydride). After one hour at room temperature, reactions were worked up. b) Mole equivalents to olefin, assuming quantitative yield in the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with Vitride. c) For hydrozirconation step. d) Distilled or crystallized, based on olefin. e) Reaction at 23°C. f) A similar result was reported by Schwartz (ref. 6). g) Also 10% tetradecane. h) Also 10% triacontane. Toluene solvent gave 30-35% yields.

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