# Improved Preparation of 9-Octadecenes

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## Abstract

*cis-* and *trans*-9-Octadecenes have been obtained in about 55–60% yield on a preparative scale by an improved procedure from commercially pure oleyl alcohol (90–95%) and elaidyl alcohol, respectively, by conversion to the tosylates followed by reduction with lithium aluminum hydride (LAH). The improvement consists in using saturated sodium chloride solution to coagulate the slimy, intractable, insoluble salts obtained after the LAH reduction and destruction of excess LAH with water, prior to ether extraction of the crude hydrocarbons. Total time required for the preparation is about three days.

C IS- AND TRANS-9-OCTADECENE are valuable model compounds for use in the development and study of new reactions of fats and their derivatives. The introduction of functional groups into these relatively simple, uncomplicated molecules can be readily followed by a variety of physical and chemical methods. Since the solubility and volatility characteristics of these long-chain unsaturated hydrocarbons are similar to those of fatty acid derivatives, it is preferable to use them as model compounds rather than analogous shorter chain olefins, such as *trans*-3-hexene and 2-octene.

The preparation of *cis-* and *trans*-9-octadecene from methyl oleate and elaidate (or oleyl and elaidyl alcohol), respectively, is described in the literature (1), but the procedures are inadequately described or the scale of the preparation is too small to be generally useful. Most important, however, is that the literature procedures, at least in our hands, are not readily duplicated and leave much to be desired in the way of yield and purity of final products.

The usual procedure for obtaining the 9-octadecenes is: a) reduction of methyl oleate or elaidate with lithium aluminum hydride (LAH) to the corresponding alcohols, b) conversion of the alcohols to the toluenesulfonate esters (tosylates), c) reduction of the tosylates with LAH to the unsaturated hydrocarbons, and d) fractional distillation of the crude hydrocarbons.

Although the yields in each step are high, the major problem is the separation of the crude unsaturated hydrocarbons from the tosylate reduction mixture. This mixture, after destruction of excess LAH with water, also contains slimy, intractable inorganic salts and salts of toluenethiol, the other reduction product of the tosylate. Acidification of this reduction mixture dissolves the insoluble salts and permits facile extraction of the hydrocarbons but toluenethiol is also formed and this compounds is a good *cis-trans* isomerization catalyst, besides having an objectionable odor. The presence of toluenethiol in the hydrocarbons during the final work-up and especially during the fractional distillation should be scrupulously avoided. Alternatively, the slimy salts can be separated by filtration but the experience is very discouraging, especially on a preparative scale (100–200 g).

We have found that the final reaction mixture can be maintained on the alkaline side and the hydrocarbons readily extracted from the lithium and/or alumi-
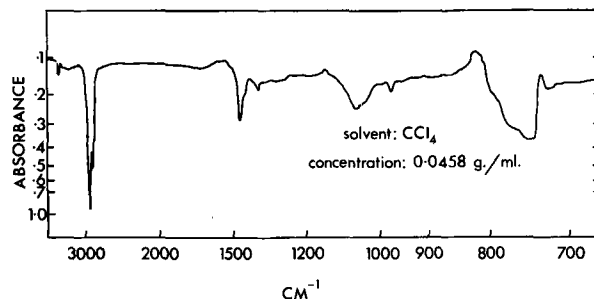


FIG. 1. Infrared absorption spectrum of commercial oleyl alcohol starting material.

num salts by adding saturated sodium chloride solution. This coagulates the inorganics and permits the extraction with ether to proceed readily. The ether solution is dried and, after evaporation of the ether, the crude hydrocarbons are distilled.

In this work we started with a good commercial grade of oleyl alcohol containing about 90–95% octadecenols, of which about one-fourth had the *trans*-configuration (Fig. 1). This starting material was selected because of its low price and availability and also because we wished to test and check the procedure an a fairly large scale with both undergra- and graduate students. We did not wish to commit ourselves to too large an expenditure of time and money to obtain 100% *cis*-9-octadecenol.

The most important question to be answered was whether the *cis/trans* ratio is altered by the procedure. The octadecenes we obtained from commercial alcohol contained about 15–20% of *trans*-isomers (Fig. 2), showing apparently that no alteration in the double bond system had occurred. Overall yield of distilled 9-octadecenes, bp 133C/0.5 mm, was based on the oleyl alcohol starting material. GLC analysis on a 10 ft × ¼ in. 10% butanediol succinate column on Anakron ABS showed that the hydrocarbon product contained >98% of C-18. Portions of three consecutive working days were sufficient for the preparation.

The procedure was repeated on a larger scale with the more readily accessible pure *trans*-9-octadecenol (elaidyl alcohol) (Fig. 3) as the starting material. *trans*-9-Octadecene, bp 138–141C/0.3 mm and mp 12–13C, was obtained (Fig. 4) in about 60% yield from alcohol. The melting point of the *trans*-9-octadecene we obtained was significantly higher than the literature value of 5C (1).
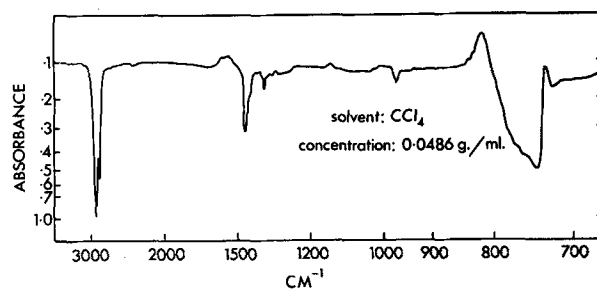


FIG. 2. Infrared absorption spectrum of 9-octadecenes obtained from commercial oleyl alcohol.
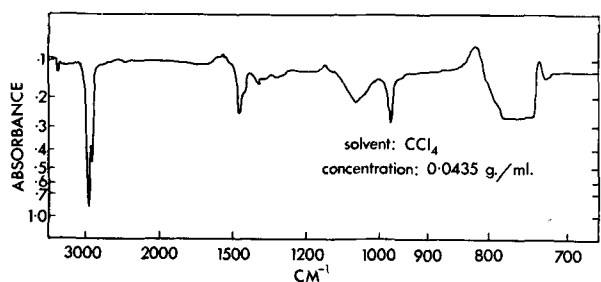
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FIG. 3. Infrared absorption spectrum of *trans*-9-octadecenol (elaidyl alcohol).

## Experimental

### Starting Materials

Adol 90, obtained from the Archer-Daniels-Midland Co., was used for the preparation of 9-octadecenes. It contained about 20% of *trans*-isomers (Fig. 1). Elaidyl alcohol (Fig. 3), mp 35.3–36.0C, was prepared from pure oleyl alcohol by short-time selenium isomerization at 225C (2). LAH was obtained from Metal Hydrides, Inc. All solvents were of highest quality; they were dried and distilled before use. p-Toluenesulfonyl chloride, mp 63–5C, was Eastman White Label Grade.

### Infrared Spectra

A Perkin-Elmer Infracord Spectrophotometer Model 137 B with 0.103 mm matched cells was used. Approximately 4% solutions in carbon tetrachloride were examined. Infrared spectra areshown in Figures 1–4.

### Procedure

*9-Octadecenes.* In a one-liter, three-neck flask equipped with a stirrer and thermometer, commercial oleyl alcohol (100 g; 0.37 mole) was dissolved in 200 ml of dry pyridine. The stirred solution was cooled to 10–15C in an ice bath and p-toluenesulfonyl chloride (96 g; 0.5 mole) was added in 3–5 equal portions over a 30–45 min period. The solution was stirred for 2–3 hr and then placed in a refrigerator overnight.

The solid-liquid slush from the refrigerator was poured into a separatory funnel and extracted with 4 × 200 ml of petroleum ether using a minimum volume of water (10–20 ml) or, if necessary, saturated sodium chloride solutions to separate the layers. The
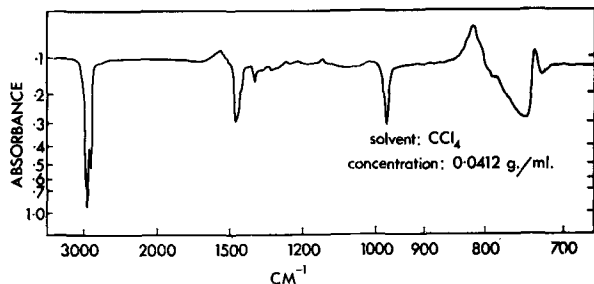
combined petroleum ether extracts were washed with 10 × 250 ml of water, dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent under vacuum in a rotary evaporator yielded 137 g (87% yield) of tosylates as a pale yellow oil.

The tosylates, dissolved in 300–500 ml of anhydrous tetrahydrofuran (THF), were added dropwise over a 30–45 min period to a stirred refluxing mixture of 500 ml of THF and LAH (15 g; 0.4 mole) in a three-neck flask equipped with an efficient condenser to which a calcium chloride drying tube was attached. When addition was complete, stirring and refluxing were continued for an additional 30–45 min.

The heater was then replaced by an ice bath and the reaction mixture was cooled to room temperature. With *caution*, 10 ml of a 10% aqueous solution of sodium hydroxide was added *dropwise* to destroy the excess LAH. In this step, considerable heat is evolved and an efficient ice bath should be used. To coagulate the insoluble salts, 100–200 ml of a saturated sodium chloride solution was added and the mixture was stored overnight in a refrigerator.

The solid-liquid mixture was extracted in portions with 3 × 100 ml volumes of ether and the lower aqueous phase containing salts was discarded. (Occasionally saturated sodium chloride solution had to be added to effect a clean separation of layers). The ether extracts were washed with water until free of salt, dried over anhydrous magnesium sulfate and filtered. Evaporation of the ether in a rotary evaporator gave 68 g (84% yield based on tosylate) of crude hydrocarbons as a yellow oil. Distillation through a 3 ft × 1 in. heated Vigreux column yielded 55 g (59% yield based on oleyl alcohol) of colorless 9-octadecenes, bp 133C/0.5 mm. The heart cut had $n_D^{26}$ 1.4464 [lit. $n_D^{25}$ 1.4450 (1)] and contained about 17% of *trans* isomers (Fig. 2) (3). GLC analysis through a 10 ft. × 1/4 in. 10% butanediol succinate column of Anakron ABS indicated >98% C-18.

*trans-9-Octadecene.* In similar fashion, elaidyl alcohol (200 g; 0.75 mole) and p-toluenesulfonyl chloride (160 g; 0.83 mole) in 500 ml of dry pyridine yielded 235 g (75%) of elaidyl tosylate which on LAH reduction in a total of 1700 ml of refluxing THF for 12 hr followed by fractional distillation yielded 105 g (55% yield based on elaidyl alcolhol) of *trans*-9-octadecene, bp 138–141C/0.3 mm and mp 12–13C [lit. 5C (1)]. It was a colorless liquid the infrared spectrum of which is shown in Figure 4.

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FIG. 4. Infrared absorption spectrum of *trans*-9-octadecene.