# Synthesis of Unsaturated Aldehydes[1]

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## Abstract

Olealdehyde, linolealdehyde and stearolalde-hyde were prepared from the corresponding acid chlorides by reduction with lithium tri-*tert*-butoxyhydroaluminate. Multiple bond location by means of ozonolysis techniques and determination of configuration of the double bond by spectral techniques indicate that this reaction proceeds without substantial bond migration or *cis,trans* isomerization.

## Introduction

In 1959, Mangold (7) synthesized unsaturated fatty aldehydes in yields of 20-30% by a modification of the Grundmann synthesis (4). This reaction involves preparing a 1,2-diol containing one carbon more than the desired aldehyde and cleaving this diol with lead tetraacetate. In 1966, Mahadevan et al. (6) described the synthesis of saturated and unsaturated aldehydes without bond migration or *cis,trans* isomerization by oxidation of the corresponding alcohol tosylates and mesylates with dimethyl sulfoxide and sodium bicarbonate at elevated temperatures.

In 1967, White et al. (13) applied the Rosenmund acid chloride reduction to the synthesis of fatty aldehydes. This method gave yields of 70-96% for saturated aldehydes. In the preparation of olealde-hyde, however, there was partial reduction to stearaldehyde, substantial (ca. 26%) *cis,trans* isomerization, and extensive migration of the double bond (from $C_6$ through $C_{14}$, with less than half remaining on $C_9$).

Since a reductive noncatalytic method that would not cause bond migration or *cis,trans* isomerization would be a useful synthetic tool which would supplement Mahadevan's oxidative technique, a study of the reaction described by Brown and Subba Rao (2) was undertaken. In this reaction, acid chlorides are converted to aldehydes in good yield by reduction with lithium tri-*tert*-butoxyhydroaluminate. After our study of the reaction was complete, an article by Venkata Rao et al. appeared (11) describing the use of the reagent for the preparation of palmitaldehyde and olealdehyde. By infrared analysis they determined that no *cis,trans* isomerization had occurred. They did not determine if bond migration occurred.

## Experimental Procedures

### Materials

Oleoyl chloride and linoleoyl chloride were obtained from the Hormel Institute. Stearoloyl chloride was prepared by the reaction of oxalyl chloride with stearolic acid (14). The stearolic acid was prepared by the procedure of Butterfield and Dutton (3) starting with olive oil which was brominated, dehydro-brominated, methylated, purified by countercurrent distribution and then saponified. Lithium tri-*tert*-butoxyhydroaluminate was purchased from Metal Hydrides Inc. Diglyme purchased from Aldrich Chemical Company was distilled from lithium aluminum hydride under reduced pressure (80 C/40 mm). Distillation of diglyme from LiAlH₄ at atmo-

spheric pressure reportedly results in a violent explosion (12).

### Equipment

Gas liquid chromatographic (GLC) analyses were conducted on a Varian Aerograph Model 1621 gas chromatograph equipped with a hydrogen flame and with a thermal conductivity detector. Analyses were conducted on an all-glass column 5 ft by ¼ in. packed with 25% DEGS (diethyleneglycol succinate) on 60/80 mesh Chromosorb W.

Infrared spectra of the unsaturated aldehydes were recorded on a Perkin-Elmer Model 621 infrared spectrophotometer. The ultraviolet spectrum of linoleal-dehyde was determined on a Cary Model 14 ultraviolet spectrophotometer.

The melting points of the unsaturated aldehydes were determined on a DuPont Model 900 differential thermal analyzer.

### Reduction of Acid Chlorides

Stearoloyl chloride (5.5 g, 0.0108 moles) was dissolved in 20 ml of diglyme in a 100 ml three-necked flask equipped with a Hershberg stirrer, a dropping funnel with a pressure equalizing tube and a low-temperature thermometer. Dry nitrogen was passed through the system, which had been flamed dry in a stream of nitrogen before use. The exit gases passed through a tube containing Drierite.
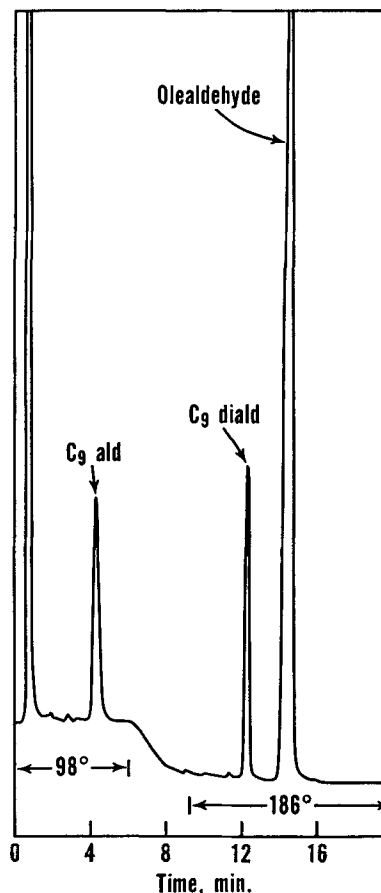
Lithium tri-*tert*-butoxyhydroaluminate (5.1 g;



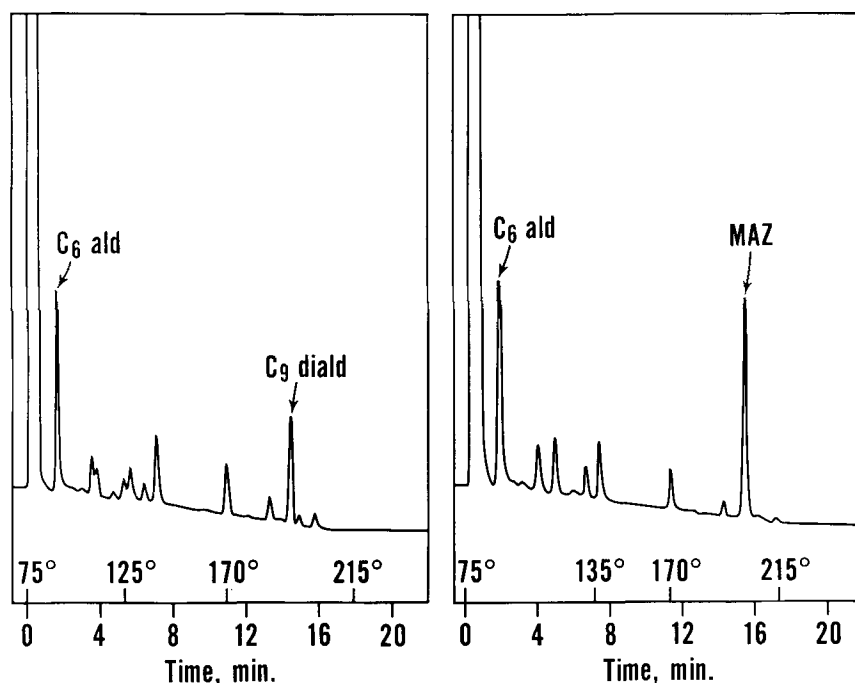FIG. 1. Gas liquid chromatogram of the ozonolysis products of olealdehyde.

FIG. 2. Gas liquid chromatogram of the ozonolysis products of linolealdehyde and methyl linoleate. MAZ, methyl azelaaldehydate.

0.0198 moles) was dissolved in 20 ml of diglyme in the dropping funnel. Contents of the reaction flask were cooled by a dry ice-acetone bath to −64 C and the hydride solution was added over a period of 37 min while the temperature varied from −64 to −58 C. Twenty minutes later the cooling bath was removed and about 1 hr later an aliquot of the reaction mixture was added to a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl in order to estimate the amount of aldehyde formed (5). A yield of 59% was indicated.

The rest of the flask contents was added to ice and water, acidified with 1:1 HCl, and extracted several times with ether. The ether solution was washed several times with water and dried first over $Na_2SO_4$ and then over Drierite. The ether was re-

moved by distillation and the residue was distilled under reduced pressure to give 1.665 g (33% yield) of a product boiling at 160–170 C/1.5 mm.

*Elemental Analysis.* Calculated for $C_{18}H_{32}O$: C, 81.82%; H, 12.12%. Found: C, 81.19%; 12.12%.

Stearolaldehyde oxidized readily in air as shown by the rapid formation of a white deposit of stearolic acid that melted without purification at 41–44 C (uncor.).

Olealdehyde and linolealdehyde were prepared in a similar manner in isolated yields of 45% and 50%, respectively.

### Purification of the Aldehydes

GLC analysis of each of the aldehydes after purification by means of vacuum distillation or passage through a column of Adsorbosil CAB showed an impurity as a small peak, which followed closely after the aldehyde peak. The aldehyde could be separated from this impurity by making and decomposing the bisulfite addition product (9). Consequently, the impurity is not a carbonyl compound; no further attempts were made to identify it.

### Ozonolysis

The positions of unsaturation in the unsaturated aldehydes were determined by ozonolysis and subsequent examination of the ozonolysis products by GLC. For olealdehyde and linolealdehyde, ozone was generated in an apparatus described by Bitner et al. (1), and bubbled through a sample of the aldehyde dissolved in dichloromethane. The ozonide was reduced by the addition of triphenylphosphine (10) and the cleavage products were examined by GLC.
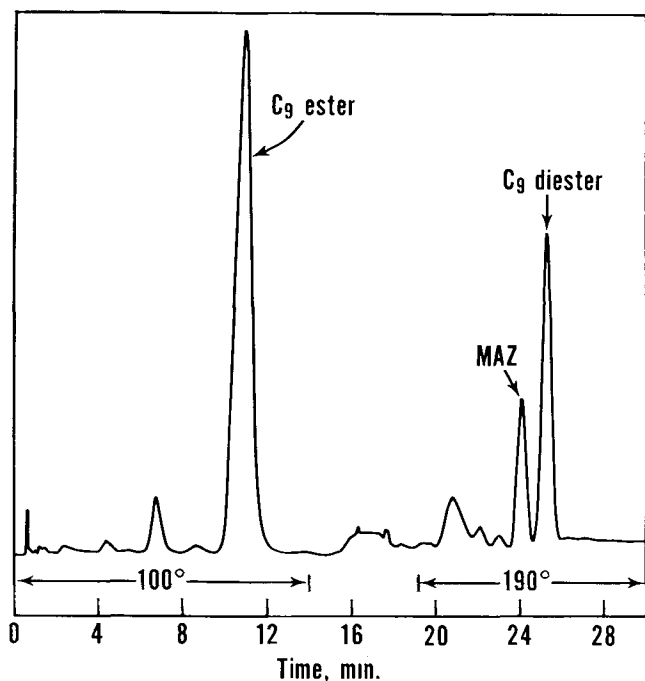
Ozonization of stearolaldehyde was carried out in



FIG. 3. Gas liquid chromatogram of the ozonolysis products of stearolaldehyde.

TABLE I

Physical Constants of Unsaturated Aldehydes

| Aldehyde | MP[a] °C | $n^{20}_D$ | MP, 2,4 DNPH,[b] °C |
|---|---|---|---|
| Olealdehyde | −12.4 | 1.4580[c] | 66–67 |
| Linolealdehyde | −32.3 | 1.4650 | 50–50.5 |
| Stearolaldehyde | 17.2 | 1.4584 | 70–71 |

[a] By differential thermal analysis.
[b] 2,4-Dinitrophenylhydrazone.
[c] At 23 C.

acetic acid solution. Water was added and the solution boiled for 20 min. After further dilution with water, the solution was extracted with ether and the ether extract dried over $Na_2SO_4$. The ether was removed on a rotary evaporator and the residue esterified with methanol catalyzed with $BF_3 \cdot CH_3OH$ (8). The mixed esters and aldehyde esters were examined by GLC.

## Results and Discussion

The physical constants of the unsaturated aldehydes prepared and of their 2,4-dinitrophenylhydrazones are presented in Table I.

Stearolaldehyde is a new compound. The melting points of the three aldehydes were determined by differential thermal analysis; there are no melting points recorded in the literature.

The refractive indices for olealdehyde and linolealdehyde are somewhat higher than literature values (7). The melting points of the 2,4-DNPH's of olealdehyde and linolealdehyde agree with those published by Mahadevan et al. (6) but do not completely agree with those of Mangold (7).

The infrared spectrum of stearolaldehyde resembles that of olealdehyde. None of the unsaturated aldehydes showed absorption at 965 cm$^{-1}$ in the infrared region of the spectrum. This indicates no *cis,trans* isomerization had occurred during the reduction. The ultraviolet spectrum of linolealdehyde was examined in the region of 240–300 m$\mu$ and no evidence of conjugation was visible. Consequently no bond migration occurred during preparation of linolealdehyde.

Ozonization of olealdehyde, followed by reduction of the ozonide, should yield a mixture of nonanal ($C_9$ aldehyde) and nonanedial ($C_9$ dialdehyde). The only significant peaks in Figure 1, the GLC curve of the ozonolysis products of olealdehyde, correspond to the $C_9$ aldehyde, the $C_9$ dialdehyde and olealdehyde. If the double bond had moved, peaks corresponding to the $C_8$ and the $C_{10}$ aldehydes, at least, would be present.

Ozonization of linolealdehyde, followed by reduction of the ozonide, would be expected to yield a mixture of hexanal, propanedial (malonaldehyde), and nonanedial. Figure 2 shows the $C_6$ aldehyde and the $C_9$ dialdehyde, in addition to a number of smaller peaks which may represent aldehydes other than hexanal. Almost all these peaks appear in the chromatogram of methyl linoleate, which was prepared from the same linoleoyl chloride used to make the aldehyde. Isomer distribution of the product aldehyde differs little from the parent acid chloride, and reduction of the latter to the aldehyde involves no bond migration.

Ozonization of stearolaldehyde followed by hydrolysis and esterification of the ozonide gave the expected methyl nonanoate ($C_9$ ester) and methyl azelaaldehydate (MAZ). These peaks are found in Figure 3. The large peak following MAZ has the same retention time as that of dimethyl azelaate obtained from ozonization of methyl stearolate. It could arise from stearolic acid contamination, as stearolaldehyde oxidizes readily in air to stearolic acid. The small peak at 7 min has a retention time corresponding to that of the $C_8$ ester. If bond migration occurs, it should proceed in both directions, so if this peak represents the $C_8$ ester, there should be a peak corresponding to the $C_{10}$ ester. Since such a peak does not appear, we conclude that the peak at 7 min does not represent $C_8$ ester. This sample was not purified through the bisulfite addition product,
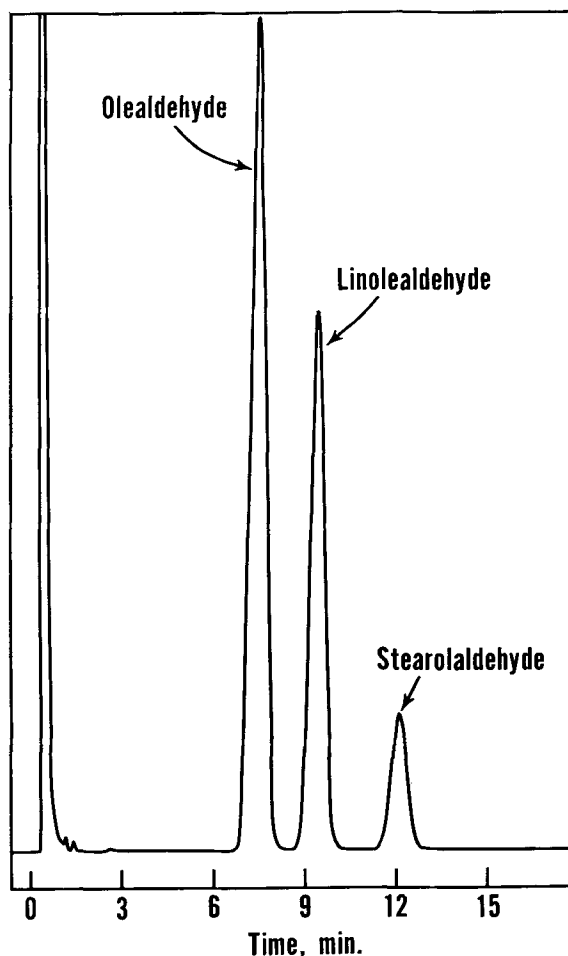


FIG. 4. Gas liquid chromatogram of a mixture of olealdehyde, linolealdehyde, and stearolaldehyde. 5 ft × ⅛ in. stainless column; 25% DEGS on 60/80 Chromosorb W; 190 C 20 ml/min.

and these other peaks may represent impurities.

Figure 4 shows the relative elution times of the three aldehydes. Methyl stearate would come out just a little later than olealdehyde and, under these conditions, would appear as a shoulder on the trailing edge of the olealdehyde peak.

Thus it has been shown that lithium tri-*tert*-butoxyhydroaluminate may be used to convert mono-ethylenic, diethylenic, and monoacetylenic acid chlorides to the corresponding aldehydes without any appreciable *cis,trans* isomerization or bond migration.

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