Chlorinated Alcohols: II. The Chlorination of Oleyl Alcohol

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Abstract

Chlorination of oleyl alcohol gives mainly 9,10-dichlorostearic acid, but a variety of other products are also formed. By-products include 9(10)-(9,10-dichlorostearoxy)-10(9)-chlorostearic acid (14%) and 9,10-dichlorostearic acid (3-4%), in addition to three or four less clearly defined products (12%). One group of products is apparently derived from participation of the hydroxyl group in the chlorine addition step while the other products formed by the reaction of the hydroxyl group with chlorine or chlorine and hydrogen chloride.

Introduction

CHLORINATED FATTY ALCOHOLS have been of interest because they can be converted to the sodium dichloroalkyl sulfate detergents. Earlier work showed the additive chlorination of oleyl alcohol, sulfation, and detergency (9). The product, considered to be a purification.

Experimental Procedures

The oleyl alcohol used in this work was prepared by distillation of two commercial oleyl alcohols, Novol (Kroda) and Adol 90 (Ashland), on a 40-plate spinning band column. The alcohols obtained were from 95-98% oleyl alcohols containing from 1-3% stearyl alcohol and from 0.2-0.5% acidic material considered as oleic acid.

Reference compounds were collected and used to help identify components of the chlorination mixture. Methyl 9,10-dichlorostearate was prepared by chlorination of methyl oleate (5). Methyl 9(10)-methoxy-10(9)-chlorostearate was prepared by chlorination of oleic acid in methanol (6). A commercial sample of stearoyl alcohol (98%) was used without further purification.

9,10,12,13-Tetrachlorostearoyl Alcohol

Linoleic acid (90%) was chlorinated according to a procedure described by Lyness and Quackenbush (5) to produce a yellow paste. This crude material was reduced with diborane (2), producing tetra-chlorostearoyl alcohol as a paste, and then recrystallized from Skelly B several times to obtain a low yield of white solid, mp 105.5-106.5°C, homogeneous by TLC (benzene-ether, 75:25).

Analysis. Calculated for C_{18}H_{31}Cl_4O: C, 52.95; H, 8.40; Cl, 34.73. Found: C, 53.16; H, 8.41; Cl, 35.03.

A strong infrared absorption at 3300 cm⁻¹ indicated the presence of the hydroxyl group.

The mother liquor from the above room temperature recrystallization was cooled to −25°C and the resulting small amount of precipitate was removed. Deacetylation with calcium and concentration under vacuum resulted in a pale yellow oil. After purification by preparative TLC the material was still an oil.

9,10-Dichlorostearoyl 9,10-Dichlorostearate

9,10-Dichlorostearic acid was prepared by −15°C chlorination of oleic acid in methylene chloride. The crude product was recrystallized from Skelly B to obtain a material at mp 36.5-38°C (5). This acid (3 g, 0.0137 mole) was dissolved in Skelly B (20 ml) and mixed with thionyl chloride (1.71 g, 0.0144 mole). The mixture was heated to reflux for 24 hrs. It was then concentrated under vacuum, producing 9,10-dichlorostearoyl chloride, and used without further purification. The acyl chloride was dissolved in Skelly B (30 ml), mixed with 9,10-dichlorostearoyl alcohol (4.65 g, 0.014 mole) and pyridine (1.08 g, 0.014 mole), and the mixture was heated under reflux for 1.5 hr. The product was washed with water, dried (MgSO₄) and concentrated under vacuum to a pale yellow oil with a strong absorption, at 1735 cm⁻¹ (R–C–O–R), in the infrared spectrum.

Chlorination Procedures

The chlorination procedure was essentially that described in an earlier report (9). The details of our experiments are described in Table I.

Isolation and Identification

By comparing the infrared spectra of the reference compounds we were able to assign certain absorptions to certain structural features in these compounds. The following list describes these correlations.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Reaction temp.</th>
<th>Exotherm</th>
<th>% Cl</th>
<th>I.V.</th>
<th>Stearyl alcohol</th>
<th>Dichlorostearoyl alcohol</th>
<th>Residue</th>
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<tbody>
<tr>
<td>1</td>
<td>−13C</td>
<td>30</td>
<td>21.0</td>
<td>0.0</td>
<td>1</td>
<td>70</td>
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</tr>
<tr>
<td>2</td>
<td>−3</td>
<td>5</td>
<td>19.9</td>
<td>0.3</td>
<td>1.4</td>
<td>70</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>+6</td>
<td>7</td>
<td>20.0</td>
<td>0.5</td>
<td>1.8</td>
<td>72*</td>
<td>26*</td>
</tr>
<tr>
<td>4</td>
<td>+17</td>
<td>7</td>
<td>19.8</td>
<td>0.6</td>
<td>2.5</td>
<td>58</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>+26</td>
<td>6</td>
<td>19.8</td>
<td>0.6</td>
<td>2.5</td>
<td>58</td>
<td>28</td>
</tr>
</tbody>
</table>

* Oleyl alcohol (50 g) in methylene chloride (175 ml).
* Yields were consistent from 98-100% of theory.
* TLC of the various fractions indicates that only very small amounts of new products form during distillation.
* Dichlorostearoyl alcohol distills from 160-175°C/0.01 mm; the residue is material not distilling at 205°C/0.35 mm. The fraction collected between these ranges appears to be mainly 9,10-dichlorostearoyl alcohol.
* Yields based on column chromatography of the sample (silica gel, benzene-ether, 75:25). Residue is considered TLC spots 2, 3 and 4.
Thin-layer chromatography of the chlorinated alcohols was run on silica gel plates with benzene-ether (75:25) as an eluant. In this solvent system, four components were observed and arbitrarily numbered 1 through 4. The \( R_f \) values and numbers are: TLC 1, \( R_f = 0.27 \); TLC 2, \( R_f = 0.39 \); TLC 3, \( R_f = 0.47 \), and TLC 4, \( R_f = 0.8 \). The components were separated and purified mainly by preparative TLC, although component 4, because of its fast migration rate, was purified by a combination of column chromatography (benzene-ether, 75:25) and preparative TLC. Infrared spectra were run on a Perkin-Elmer 237-B; NMR were run on a Varian A-60 spectrometer.

Relative amounts of each component were obtained by distillation (see Table I); however, to double check these numbers we subjected a typical sample to column chromatography. All fractions were analyzed by TLC and amounts of each component were estimated and combined. On this sample (Table I, Experiment 3) the relative amounts were TLC 1, 74%; TLC 2, 14%; TLC 3, 3%; and TLC 4, 9%. In the solvent system (mainly benzene-ether, 75:25) we used stearyl alcohol; 9,10-dichlorostearyl alcohol and 9,10,12,13-tetrachlorostearyl alcohol were indistinguishable, i.e., they had similar \( R_f \) values. Presumably polychloroalcohols from substitution reactions would also escape detection by TLC. However, the agreement in the yield of 9,10-dichlorostearyl alcohol by distillation and chromatography and also the per cent chlorine in the crude reaction mixtures suggest that the polychloro alcohol content of the samples is quite low. Listed below is the information accumulated on each component.

**TLC Spot 1**

This component was easily separable by preparative TLC but was more conveniently purified by simple vacuum distillation. When carefully distilled, the product was a colorless oil containing only a trace of stearyl alcohol (VPC, 1/4 in. by 4 ft, OV-1 column) and only one major component. The NMR spectrum with absorptions at \( \delta 0.86-2.1 \) ppm (several absorptions, 31.3, \( \text{CH}_3(\text{CH}_2)_7\text{CC}(\text{CH}_2)_7\text{C}-\)), 2.74 ppm (singlet, 1.00, \(-\text{O}-\)), 3.51 ppm (triplet, 1.95, \(-\text{CH}_2\text{O}\), 3.92 ppm (complex, 1.95, \(-\text{CH}_2\text{ClCHCl}-\)) and the infrared spectrum with absorptions at 3340 and 1060 cm\(^{-1}\) (OH), 725 cm\(^{-1}\) (\(-\text{CH}_2\text{Cl}-\)) and 650 cm\(^{-1}\) (\(-\text{CH}_2\text{ClCHCl}-\)) show that this material is 9,10-dichloro-stearyl alcohol.

**Analysis.** Calculated for \( \text{C}_{35}\text{H}_{68}\text{OCl}_2 \): Cl, 20.89. Found: Cl, 21.04.

**TLC Spot 2**

Distillation of chlorinated oleyl alcohol results in the accumulation of components 2, 3 and 4 in the pot residue. Pure identical samples were obtained by preparative TLC of both the chlorinated alcohol and the pot residue. The infrared spectrum has absorptions at 3350 and 1060 cm\(^{-1}\) (\(\text{CH}_2\text{OH}\)), 1100 cm\(^{-1}\) (R–O–(CH\(_2\))\(_n\)), 725 cm\(^{-1}\) (–(CH\(_2\))\(_n\)), 685 cm\(^{-1}\) (–CH\(_2\text{ClCHOR–}\)) and 650 cm\(^{-1}\) (–CH\(_2\text{ClCHCl–}\)). The NMR spectrum showed many superimposed absorptions so the trichloroacetylurethane derivative was prepared. The spectrum of the derivative had absorptions at \( \delta 0.85-2.1 \) ppm (several absorptions, 62.2) 3.1-3.6 ppm (multiplet, 3.0), 3.6-4.35 ppm (multiplet, 4.8) and 8.2 ppm (singlet, 0.8, \(-\text{O-CNItCCC}1\)). The structure that best fits the data is that of \( \text{9}(10)-(9,10\text{-dichlorostearoxy})-10(9)\text{-chlorostearyl alcohol.} \)

**TLC Spot 3**

The component of TLC spot 3 was not entirely purified. The sample was mainly spot 3 but another compound moving slightly faster than spot 3 was observed. This compound was called 3a. In addition, the sample was also contaminated with a small amount of TLC spot 2. The infrared spectrum of this material has absorptions at 3400 and 1060 cm\(^{-1}\) (shoulder) (\(\text{CH}_2\text{OH}\)), a very intense band at 1100 cm\(^{-1}\) (\(\text{R}_6\text{C}–\text{OCH}_2\text{R}\)), 725 cm\(^{-1}\) (–(CH\(_2\))\(_n\)), 685 cm\(^{-1}\) (–CH\(_2\text{ClCHOR–}\)) and 650 cm\(^{-1}\) (–CH\(_2\text{ClCHCl–}\)). The spectrum is superimposable on that of TLC spot 2 except that the band at 1100 cm\(^{-1}\) is relatively more intense than the band at 1060 cm\(^{-1}\). Also, the absorption at 685 cm\(^{-1}\) is relatively more intense than the absorption at 650 cm\(^{-1}\). The yield of this material (ca. 3%) and the infrared data as well as its position on the TLC plate lead us to speculate that this material is the trimeric chloroether, the next higher homolog of TLC component 2.