Chlorinated Alcohols: I. Preparation From Chlorinated Acids

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Abstract

Rhenium, ruthenium and rhodium oxides, hydrogenolysis catalysts for stearic acid at 150 C, were tried for the conversion of 9,10-dichlorostearic acid to the dichloro alcohol but only ReO_3 was effective in some degree (yield 14%). Dehydrochlorination or hydrogenolysis at the carbon-chlorine bond was the principal reaction. Reductions with diborane or with lithium aluminum hydride, however, were found to be excellent methods for preparing 9,10-dichlorostearyl alcohol.

Introduction

DICHLOROOCTADECANOL IS AN INTERMEDIATE for the detergent sodium 9,10-dichlorooctadecyl sulfate and has been obtained by the additive chlorination of oleyl alcohol (6,18,19). This paper deals with another possible route, the reduction of 9,10-dichlorostearic acid under conditions to avoid dehydrochlorination or hydrogenolysis at the carbon-chlorine bond. Some evidence is available to show that the 9,10-dichlorostearate system is stable to 200 C (16). Thermal gravimetric analysis (17) has shown that weight loss, presumably with dehydrochlorination occurs soon after this temperature. It would seem therefore that methods would be needed capable of carboxyl reduction at or below 200 C.

Commercial hydrogenolysis catalysts such as copper chromite require temperatures of 250–300 C (11) and were found to be unsuitable. Rhenium and ruthenium oxides are known to catalyze hydrogeneolysis at 150 C (1,5) and were investigated for this reason. Rhodium oxide, known as a hydrogenation (13) but not as a hydrogenolysis catalyst was included.

Other methods of reduction were explored. The diborane reduction of carboxylic acids (2,3) is known to be a rapid and quantitative reaction. Since reduction and hydrolysis of the labile borate ester may occur under mild conditions it is unlikely that the carbon-chlorine bond would be affected.

$$6RCO_2H + B_2H_6 \rightarrow 2(RCO_2)_3B + 6H_2$$
$$2(RCO_2)_3B + 2B_2H_6 \rightarrow 2(RCH_2OBO)_3$$
$$2(RCH_2OBO)_3 + 12H_2O \rightarrow 6RCH_2OH + 6H_3BO_3$$

Lithium aluminum hydride was also considered as a route to 9,10-dichlorostearyl alcohol. It is known to attack the chlorine in 6-chlorocaproic acid (7) but the greater stability of the chlorine atoms in 9,10-dichlorostearic acid made the method worth investigating.

Experimental Procedures

Oleic acid (Arizona Chemical Co., 97% 18 C monounsaturated, 1% *trans*) was chlorinated in methylene chloride at −15 C (10,19). 9,10-Dichlorostearic acid was isolated by crystallization from Skellysolve B, treatment with silver nitrate to remove labile chlorine (20), and recrystallization. Thin-layer chromatography from a benzene-ether-acetic acid (74:25:1) mixture showed only one species.

Catalytic Hydrogenolysis

Ruthenium dioxide and rhodium dioxide hydrate were purchased from Alfa Inorganics, Inc., and used as received. Rhenium (VI) oxide, ReO_3, was prepared from rhenium (VII) oxide, Re_2O_7 (1).

A magnetically stirred 300 ml autoclave made of Hastelloy C was charged with the catalyst, 15 g of dichlorostearic acid and 80 ml of water. The autoclave was sealed, charged with hydrogen at 2600 psig, and the stirrer (1000 rpm) was started. If no pressure drop occurred in 30 min the system was considered tight. The autoclave was heated to 155 C in 40 min and reaction was monitored by hourly analyses, by thin-layer and vapor-phase chromatography. At the end of the reaction the product was extracted with ethyl ether, and the ether extracts were washed, dried over Na_2SO_4, filtered and evaporated.

The analyses reported in Table I were by gas chromatography of the methyl esters (14). Complete conversion of acids and 36 C esters to methyl esters was checked by TLC. Good resolution was accomplished using a silicone gum rubber column at 230 C.

Alternate experiments with stearic acid in place of 9,10-dichlorostearic acid verified the choice of reaction conditions and minimized the possibility of accidental catalyst poisoning.

Reduction by Diborane

Diborane was generated in a 500 ml 3-neck flask equipped with a nitrogen inlet, pressure-equalizing addition funnel and gas-outlet tube. A solution of boron trifluoride etherate, 30 ml in 80 ml of diglyme, was flushed with nitrogen, the nitrogen flow was stopped and a solution of 6 g of sodium borohydride in 50 ml of diglyme was added dropwise.

The diborane (2.9 g, 0.053 moles) was bubbled into a solution of 20 g (0.057 moles) of dichlorostearic acid in 80 ml of tetrahydrofuran at a controlled rate to prevent excessive foaming. The reaction was slightly exothermic. The mixture was stirred 30 min and flushed with nitrogen. A sample at this point showed the presence of a borate ester with characteristic strong absorption at 1340 cm^{-1}.

The borate ester solution was hydrolyzed by stirring 30 min with 50 ml of water and 50 ml of ether. The aqueous layer was salted and re-extracted with ether. The ether extracts were dried and filtered and solvent was removed at 0.25 mm to give 9,10-dichlorostearyl alcohol as a pale yellow oil in a nearly quantitative yield. Gas chromatography showed a purity of greater than 98% but TLC showed the presence of two minor unknown components.

Analysis. Calculated for $C_{18}H_{36}Cl_2O$, hydroxyl value 165.3. Found 151.2, 151.0.

Reduction by Lithium Aluminum Hydride

A solution of 10 g (0.028 moles) of 9,10-dichloro-

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TABLE I

Catalytic Hydrogenolysis
Charge: Catalyst, 15 g 9,10-dichlorostearic acid, 80 ml water

Experiment	Catalyst[a]	Temperature, C	Pressure, psig	Time, hr	Products, Weight %	
1	None	170	3100	6	Dichlorostearic acid	89
					Stearic acid	11
2	1.3% ReO_3	155	3200	4	Dichlorostearic acid	17
					Dichlorostearyl alcohol	14
					Stearic acid	49
					Stearyl alcohol	19
3	1.3% RuO_2	155	3200	4.5	Dichlorostearic acid	42
					Stearic acid	58
4	0.8% Rh_2O_3	155	3150	5	Dichlorostearic acid	55
					Dichlorostearyl alcohol	Trace
					Stearic acid	45
					Stearyl alcohol	Trace

[a] Weight % of dichlorostearic acid.

stearic acid in 20 ml of anhydrous ether was placed in a 100 ml 3-neck flask equipped with stirrer, condenser and addition funnel. A solution of $LiAlH_4$ (1.55 g, 0.041 moles) in 20 ml of anhydrous ether was stirred into the acid solution at such a rate that gentle reflux occurred. Stirring was continued 1 hr, excess $LiAlH_4$ was destroyed with ethyl acetate and the mixture was poured slowly into a slurry of ice and dilute H_2SO_4. The product was extracted with ether and the ether extract was washed, dried, filtered and evaporated to give 74% yield of 9,10-dichlorostearyl alcohol as a pale yellow oil. Gas chromatography showed a purity greater than 98% with only traces of stearyl alcohol, stearic acid and 9,10-dichlorostearic acid. Thin-layer chromatography again showed the presence of minor amounts of two unknown components.

Analysis. Calculated for $C_{18}H_{36}Cl_2O$, hydroxyl value 165.3, acid value 0.0. Found 167.2, 0.1, resp.

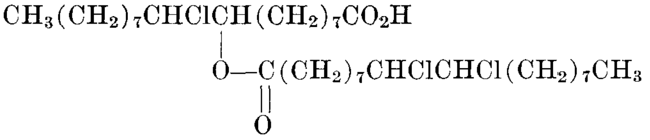
Discussion

The main reaction in attempts to reduce the dichloro acid to the dichloro alcohol by catalytic hydrogenolysis, as shown in Table I, was the undesired reaction at the carbon-chlorine bond. This took place even in the absence of catalyst and with RuO_2 was the only reaction. Although hardly successful with dichlorostearic acid Rh_2O_3 was found to be a good catalyst for the hydrogenolysis of pelargonic or stearic acid to the corresponding alcohol. Reduction was more successful with ReO_3 which gave a 14% yield of the dichloro alcohol in the form of the 36 C ester.

Reaction at the carbon-chlorine bond seemed to take place only with the loss of two chlorine atoms and there was no evidence for the formation of monochlorostearic acid.

The metal oxide catalysts were destroyed in the dichlorostearic acid experiments of Table I and gave bright green aqueous solutions of the metal chloride.

Reduction with diborane was found to be a very smooth method of converting 9,10-dichlorostearic acid to 9,10-dichlorostearyl alcohol. Carboxyl reduction was complete without loss of chlorine. The byproducts observed probably arose from impurities in the dichlorostearic acid. Leopold and Mutton (9) have reported that β-chloroester acids



$$\begin{array}{l} CH_3(CH_2)_7CHClCH(CH_2)_7CO_2H \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O{-}\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_7CHClCHCl(CH_2)_7CH_3 \end{array}$$

are by-products in the additive chlorination of oleic acid. Diborane would give products resulting from reduction of both the acid and ester groups and the unknown components shown by TLC are probably these.

Diborane is too expensive a reducing agent for commercial use at the present time but because of interest in diborane as a rocket fuel it may become quite inexpensive (4,8,12,15). Since only 80 lb are required to reduce a ton of 9,10-dichlorostearic acid under quite mild conditions, diborane reduction is an interesting possibility.

The lithium aluminum hydride reduction is likewise a suitable method for the laboratory preparation of 9,10-dichlorostearyl alcohol.

ACKNOWLEDGMENT

Work done under contract with the U.S. Department of Agriculture.

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[Received May 20, 1968]