Esterification and Transesterification of 9(10)-Carboxystearic Acid and Its Methyl Esters. Kinetic Studies[1]

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ABSTRACT

9(10)-Carboxystearic acid and its mono- and dimethyl esters were esterified and transesterified with 1-butanol, 2-methoxyethanol, 2-chloroethanol, 2,2-dimethylpentanol, 2-ethylhexanol and 1-octanol. Rate studies for the sulfuric acid-catalyzed esterification of 9(10)-carboxystearic acid to alkyl 9(10)-carboxystearate and alkyl 9(10)-carboalkoxystearate indicate than on an average the terminal carboxyl is approximately 26-27 times more reactive than the branched carboxyl group. Esterification is highly dependent on catalyst concentration. Steric hindrance in 2,2-dimethylpentanol and the electrophilic character of 2-methoxyethanol and 2-chloroethanol markedly retard the rate. In addition to the expected diesters, 2-chloroethanol yields esters containing extra $-O-CH_2CH_2-$ groups. The rate of transesterification of the terminal ester group of mono- and dimethyl esters of 9(10)-carboxystearic acid is about two times faster than the rate of esterification of the branched carboxyl group. Transesterification of the branched 9(10)-ester group is extremely slow.

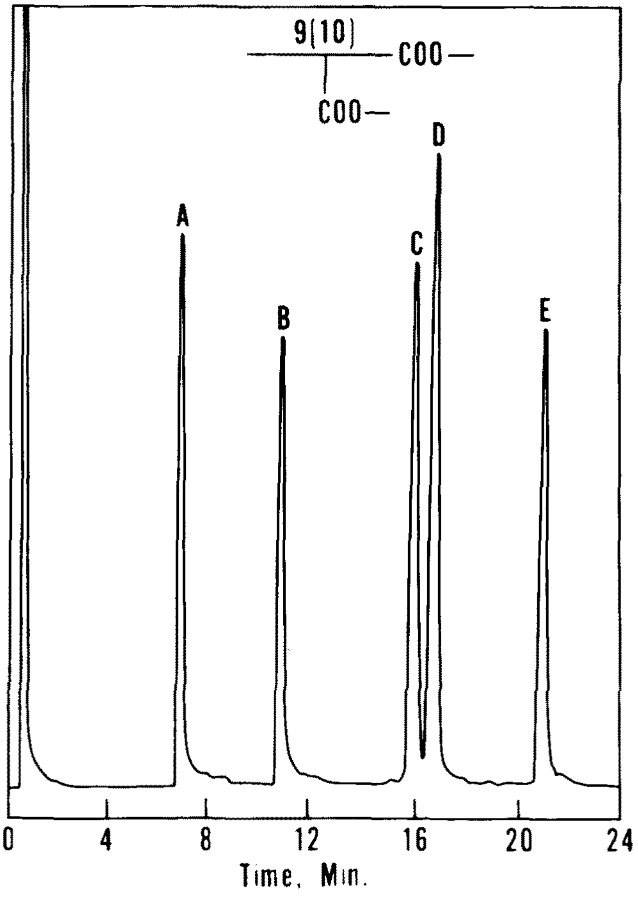

FIG. 1. Gas chromatogram of (A) methyl stearate (reference compound); (B) methyl 9(10)-carbomethoxystearate; (C) methyl 9(10)-carbo(dimethylpentoxy)stearate; (D) dimethylpentyl 9(10)-carbomethoxystearate; (E) dimethylpentyl 9(10)-carbo(dimethylpentoxy)stearate.

INTRODUCTION

In the past decade, several papers have reported the preparation and properties of carboxystearic acid and its esters for use in formulations of polyesters, polyamides, alkyds, plasticizers and lubricants. Carboxystearic acid is prepared either by the oxo process or by the Koch reaction. In the oxo process catalyzed with cobalt carbonyl, carbon monoxide and hydrogen are added to unsaturated esters and to such oils as soybean, safflower or tall oil. The formyl ester or oil is then oxidized and saponified. In the Koch reaction, studied in detail by Roe and Swern (1), carbon monoxide and water are added directly to oleic acid in the presence of sulfuric acid. The diacid products obtained by the oxo and Koch reactions have been generally referred to as 9(10)-carboxystearic acid (CSA), but as shown by Lai et al. (2) and by Frankel et al. (3,4), the oxo products are mixtures of C_{19} diacids with positional isomers distributed from carbon-6 to carbon-17. These products are formed by isomerization of oleate unsaturation during the reaction.

At the Northern Laboratory, a new selective hydroformylation of methyl oleate with a rhodium-triphenylphosphine catalyst was found (4) to yield exclusively 9- and 10-formylstearate in about equal amounts. The corresponding 9- and 10-carboxy acids were obtained by catalytic air oxidation of the formyl esters followed by saponification (5).

Roe et al. (6) reported that the branched carboxyl group was much less reactive to esterification than the terminal carboxyl group and that special methods were needed to prepare diesters. Since CSA and methyl 9(10)-carboxystearate (Me-CS) are now readily available, this paper compares the reactivity of the more homogeneous mixture of 9(10)-diacids with the isomeric mixture obtained conventionally. Further, kinetic studies of esterification and transesterification of CSA and its methyl esters have now determined the relative reactivity of the two carboxyl groups. The results reported here are the basis of future studies on the preparation and evaluation of some mixed alkyl and bis-alkyl diesters.

RESULTS AND DISCUSSION

In abbreviating the complex diesters, the terminal alkyl ester will always be named first, followed by the branched alkyl ester. Thus Dmp-Me diester and Me-Dmp diester represent 2,2-dimethylpentyl 9(10)-carbomethoxystearate and methyl 9(10)-carbo(2,2-dimethylpentoxy)stearate, respectively. For the six alcohols the following notations will be used: Bu-OH for 1-butanol; ClEt-OH for 2-chloroethanol; MeOEt-OH for 2-methoxyethanol, Dmp-OH for 2,2-dimethylpentanol; EtHex-OH for 2-ethylhexanol; and Oct-OH for 1-octanol.

The progress of esterification was followed by gas liquid chromatography (GLC) analysis. Unreacted carboxyl groups were methylated with diazomethane. Analysis of a

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TABLE I

Alkyl 9(10)-Carboalkoxystearates

Alkyl	9(10)-Alkoxy	Boiling point		Carbon, %		Hydrogen, %	
		C	mm Hg	Calculated	Found	Calculated	Found
Methyl	Methyl	158-161	0.060	70.73	70.81	11.30	11.51
Methyl	*n*-Butyl	163-164	0.050	72.31	71.92	11.63	11.62
Methyl	Methoxyethyl	166-170	0.060	68.95	68.67	11.07	11.11
Methyl	Chloroethyl	173-177	0.075	65.23	65.54	10.20	10.26
Methyl	Dimethylpentyl	178-181	0.050	73.58	73.56	11.89	11.95
Methyl	Ethylhexyl	185-188	0.050	73.96	73.78	11.96	12.36
n-Butyl	*n*-Butyl	177-180	0.075	73.58	73.44	11.89	11.80
Methoxyethyl	Methoxyethyl	180-184	0.050	67.52	67.48	10.88	11.12
Chloroethyl	Chloroethyl	205-208	0.075	60.91	60.72	9.33	9.29
Dimethylpentyl	Dimethylpentyl	212-214	0.050	75.51	75.16	12.29	12.20
Ethylhexyl	Ethylhexyl	219-221	0.075	76.02	75.77	12.39	12.49
n-Octyl	*n*-Octyl	226-231	0.020	76.02	75.74	12.39	12.46

sulfuric acid-catalyzed esterification mixture of methyl carboxystearate and Dmp-OH indicated the presence of Me-Dmp, Dmp-Me and Dmp-Dmp diesters. A gas chromatogram (Fig. 1) shows the retention times and degree of separation of the various methyl and dimethylpentyl diesters compared to methyl stearate as internal standard. The peaks in Figure 1 were identified by comparison with authentic diesters. Addition of the mono- and diacyl chlorides of Me-CS and CSA to Dmp-OH in pyridine gave Me-Dmp and Dmp-Dmp diesters, respectively. The Dmp-Me diester was prepared from methyl 9(10)-hydroxymethylstearate (4) in four steps: saponification, esterification with Dmp-OH, oxidation to Dmp-CS and esterification with diazomethane. The various diesters prepared and their analyses are given in Table I.

Rates of esterification and transesterification of CSA and its esters were followed by GLC analysis of the reaction mixture. The weight per cent obtained by GLC was converted to mole per cent and then to moles per liter. In this study the initial molar concentration of acid [CSA] to be esterified was 0.14 molar and the ratio of alcohol to acid was kept constant at either 15:1 or 30:1. The final volume of solution was also kept constant by dilution with benzene and assumed constant even though there was a volume change after the solution temperature changed from 25 C to reflux temperature. Water was removed azeotropically in a Dean-Stark trap. No correction was made for the small change in volume upon removal of each 0.1 ml sample.

The rate constants (k values) for pseudo-first-order esterification and transesterification reactions with excess alcohol ([ROH] is constant) are in reciprocal hour units and were determined by a digital computer program (DRATE) outlined by Butterfield (7). Esterification of CSA with excess ROH was programed according to the scheme in Figure 2, which also shows a computer plot of the reaction with Dmp-OH.

For the transesterification-esterification of Me-CS the scheme in Figure 3 was used, and a computer plot for this reaction with Dmp-OH is also shown. The reaction constants, k_5, refer to the same reaction in both schemes, and for any given alcohol were in good agreement. An assumption was made that $k_2 = 0$ since a simultaneous collision of three molecules in solution (CSA + 2 ROH) is unlikely.

Effects of acid concentration are shown in Table II (experiments 1-3 and 12-14). The k_5 values doubled for each additional 20 mg of sulfuric acid catalyst. Linear plots of [CSA] against time at a given catalyst concentration [cat] were obtained up to ca. 90% conversion consistent with first-order kinetics. As shown by van de Zeeuw (8) for a given active [cat] with various normal alkyl alcohols, a first-order relationship exists. The [cat] at a given level was therefore eliminated in calculating k values.

The reaction mixtures were diluted with benzene to constant volume to obtain a constant pot temperature of 83-85 C. At an alcohol-CSA molar ratio of 30:1, the increase in molecular weight of Dmp-OH and EtHex-OH correspondingly increased the volume of alcohol and decreased the volume of benzene required to maintain constant volume. Consequently the pot temperature increased (Table II, experiments 3, 7, 9, 14, 18 and 20). When the alcohol-CSA ratio was reduced to 15:1, the volume of benzene was correspondingly increased to maintain constant volume, and the resulting pot temperature was reduced considerably. With Bu-OH the rates at ratios of 15:1 and 30:1 were similar. It was therefore assumed that dilution with benzene would not significantly affect the reaction rate for the higher molecular weight alcohols. Decreasing the temperature by 20 C for the esterification with EtHex-OH halved k_5 values (experiments 9, 10, 20 and 21).

The k_5 values for the reactions with Bu-OH, Dmp-OH, EtHex-OH and Oct-OH (experiments 15, 19, 21 and 22) were in the order of 0.105, 0.035, 0.088 and 0.146 units, respectively. Therefore steric hindrance in 2,2-Dmp-OH significantly decreases the rate of esterification of the branched carboxyl group. A similar effect of steric hindrance on k_3 for esterification of the terminal carboxyl was observed in experiments 4, 8, 10 and 11. The single-branched alkyl group in 2-EtHex-OH has some effect on steric hindrance, and this alcohol reacts more like Bu-OH. The k value for esterification of CSA with Oct-OH is about one and one-half times that with Bu-OH. As reported by van der Zeeuw (8), the rate of esterification with Oct-OH is

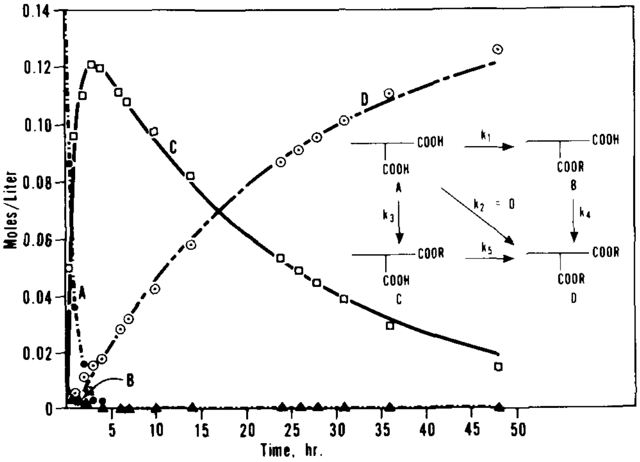


FIG. 2. Scheme and computer plot of esterification of 0.14 molar 9(10)-carboxystearic acid with 4.2 molar dimethylpentanol in benzene at 99 C using 85 mg sulfuric acid. Samples for the computer plot were methylated. (A) 9(10)-Carboxystearic acid; (B) 9(10)-carbo(dimethylpentoxy)stearic acid; (C) dimethylpentyl 9(10)-carboxystearic acid; (D) dimethylpentyl 9(10)-carbo(dimethylpentoxy)stearate.

TABLE II

Rates of Esterification and Transesterification

Experiment	Alcohol	Moles/ liter	Catalyst, mg H_2SO_4	Pot temperature, C	Rates,[a] hr^{-1}				
					k_1	k_3	k_4	k_5	k_3/k_5
9(10)-Carboxystearic Acid (0.1398 molar)									
1	*n*-Butyl	4.2	42.4	85	0.031	0.582	0.776	0.019	31
2	*n*-Butyl	4.2	63.1	85	0.067	1.16	1.15	0.039	30
3	*n*-Butyl	4.2	83.8	85		2.32		0.088	26
4	*n*-Butyl	2.1	85.8	83		2.60		0.104	25
5	2-Methoxyethyl	4.2	83.8	84		1.01		0.029	35
6	2-Chloroethyl	4.2	81.0	84		1.48		0.054	27
7	2,2-Dimethylpentyl	4.2	85.0	99		1.09		0.042	26
8	2,2-Dimethylpentyl	2.1	82.5	86		0.84		0.031	27
9	2-Ethylhexyl	4.2	84.5	106		2.44		0.155	16
10	2-Ethylhexyl	2.1	83.6	86		2.44		0.095	25
11	*n*-Octyl	2.1	80.2	87		3.83		0.155	25
Methyl 9(10)-Carboxystearate (0.1398 molar)									
12	*n*-Butyl	4.2	40.3	85	0.029	0.049	0.042	0.025	
13	*n*-Butyl	4.2	66.6	85	0.056	0.099	0.082	0.052	
14	*n*-Butyl	4.2	84.3	85	0.080	0.163	0.117	0.090	
15	*n*-Butyl	2.1	85.1	83	0.102	0.144	0.114	0.105	
16	2-Methoxyethyl	4.2	86.2	84	0.039	0.083	0.093	0.032	
17	2-Chloroethyl	4.2	82.8	85	0.052	0.138	0.161	0.053	
18	2,2-Dimethylpentyl	4.2	81.6	101	0.047	0.111	0.096	0.045	
19	2,2-Dimethylpentyl	2.1	82.1	88	0.031	0.073	0.052	0.035	
20	2-Ethylhexyl	4.2	83.8	109	0.215	0.330	0.336	0.177	
21	2-Ethylhexyl	2.1	85.6	88	0.091	0.145	0.112	0.088	
22	*n*-Octyl	2.1	82.1	87	0.153	0.207	0.145	0.146	

[a] In Figures 2 and 3, assume $k_2 = 0$.

about double the rate with Bu-OH.

With Bu-OH, MeOEt-OH and ClEt-OH, which have similar molecular weights and boiling points, rates of esterification of the branched carboxyl are 0.090, 0.032 and 0.053 (experiments 14, 16 and 17), respectively. The electrophilic and inductive character of the alkyl, chloro- and methoxy- groups are well known (9-11) and ClEt-OH was expected to have the lowest rate of reaction. Experimentally, however, MeOEt-OH had the lowest rate. The ionization constants reported by Ballinger and Long (12) and by Hine and Hine (13) show a slight difference in acidity between ClEt-OH and MeOEt-OH but a larger difference when compared with Bu-OH. The order of acidity is ClEt-OH≫MeOEtOH>Bu-OH. The increase in esterification rate with ClEt-OH over MeOEt-OH could be attributed to the formation of HCl, which would increase the total effective [cat] for esterification. The presence of HCl (litmus and $AgNO_3$ test of the water collected) in the reaction of CSA and Me-CS (experiments 6 and 17) with ClEt-OH and H_2SO_4 catalyst was observed after 8 hr of reaction when a GLC peak for a new product appeared. After 27 hr a second product was noticed. After 72 hr the composition of the reaction mixture by GLC was: ClEt-Me (2.3%) and ClEt-ClEt (58.4%) diesters, unknown A (34.8%) and unknown B (4.4%).

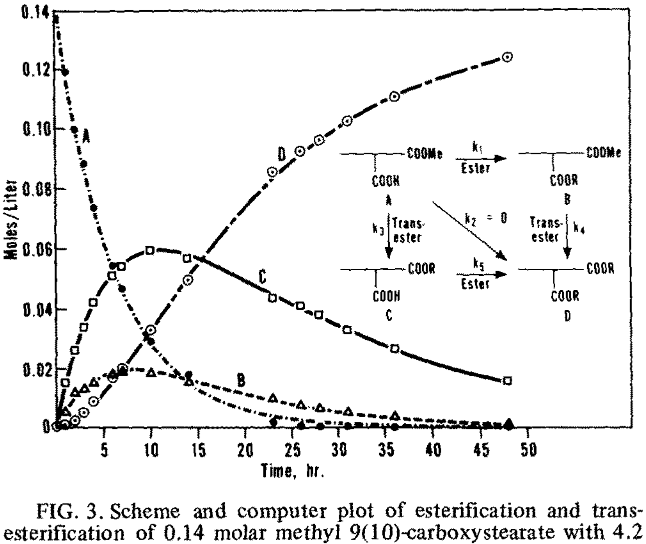
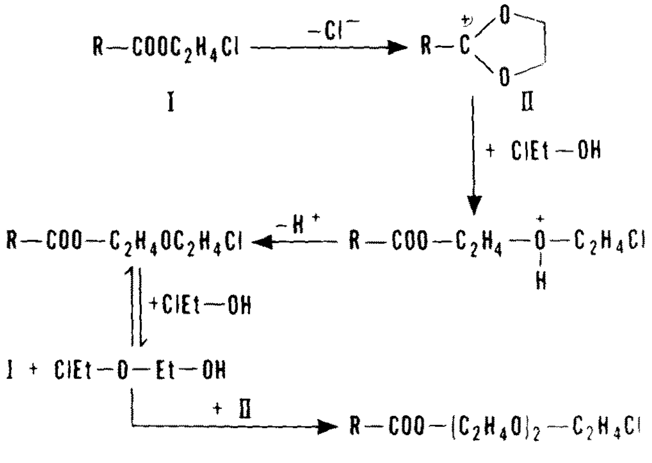


FIG. 3. Scheme and computer plot of esterification and transesterification of 0.14 molar methyl 9(10)-carboxystearate with 4.2 molar dimethylpentanol in benzene at 101 C using 81.6 mg sulfuric acid. Samples for the computer plot were methylated. (A) Methyl 9(10)-carboxystearate; (B) methyl 9(10)-carbo(dimethylpentoxy)-stearate; (C) dimethylpentyl 9(10)-carboxystearate; (D) dimethylpentyl 9(10)-carbo(dimethylpentoxy)stearate.

The two unidentified products are believed to be esters containing additional $-O-CH_2CH_2-$ groups and are the ClEtOEt-ClEt (k_6 = 0.009) and the ClEtOEt-ClEtOEt diesters (k_7 = 0.003) of CSA. Similar products were formed in the transesterification of methyl stearate with ClEt-OH and H_2SO_4 catalyst. 2-Chloroethyl stearate, 2-(2-chloroethoxy)ethyl stearate and 2-[2-(2-chloroethoxy)-ethoxy]ethyl stearate were isolated. A possible mechanism for the formation of these esters involves the formation of five-membered carbonium ions from chloroethyl stearate as follows:



Alternatively either an etherification reaction of 2-ClEt-

OH $\xrightarrow{-HCl}$ ClEtOEt-OH or the formation of ethylene oxide may be involved. No attempt was made to isolate the 2-(2-chloroethoxy)ethanol formed, even though a peak for a low boiling product appeared on GLC. No reference in the literature was found for the formation of chloroethoxyethyl esters from ClEt-OH.

Analysis of the scheme in Figure 2 and the results in Table II (experiments 1-11) for the esterification of CSA indicate that k_3/k_1 and k_4/k_5 should give the reactivity of the terminal carboxyl compared to the brahcned carboxyl. From these ratios the terminal carboxyl is about 17-40 times more reactive than the branched carboxyl (experiments 1 and 2), but low values and insufficient data for the formation of Me-alkyl diesters (Fig. 2, product B after methylation) make k_1, k_2 and the reactivity ratios questionable.

Although comparison of k_3 and k_5 (scheme in Fig. 2) for the conversion of CSA to alkyl-CS to alkyl-alkyl diester can be made, the validity is also questioned since the reactivity of a diacid is compared to the reactivity of a methyl acid ester. Nevertheless the k_3/k_5 ratio varies from 16-35 and indicates that the terminal carboxyl group of 9(10)-CSA is on an average about 26-27 times more reactive than the branched carboxyl group.

Complete esterification of CSA (N.E. 173.5) prepared by the Koch reaction was extremely difficult, as Roe et al. had found earlier (6). The terminal group of the Koch CSA was readily esterified to Dmp-CS, but after 10 days of reaction at 100 C less than 10% of the branched carboxyl was esterified. Under identical conditions 90-95% of the branched carboxyl in 9(10)-CSA was esterified in 4 days. Conversion of Koch CSA to the diacyl chloride was also more difficult. Only 88% was converted while the 9(10)-CSA gave complete conversion to the diacyl chloride. This difference in reactivity between Koch diacid and 9(10)-diacid may be attributed to a certain degree of α-methyl branching due to skeletal rearrangement (14).

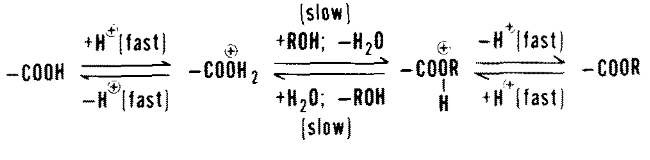
Rates of transesterification of Me-CS (scheme in Fig. 3) to alkyl-CS (k_3) and Me-alkyl diester to alkyl-alkyl diester (k_4) are about equal (Table II, experiments 12-22). Comparison of the transesterification rates (k_3 and k_4) with esterification rates of the branched carboxyl (k_1 and k_5) indicates that transesterification of the primary ester is about twice as fast as esterification of the branched carboxyl.

For the transesterification Me-Me diester $\xrightarrow{k_3}$ Dmp-Me diester $\rightarrow$ Dmp-Dmp diester, the k_3 value of 0.064 agrees favorably with the k_3 value of 0.073 for the transesterification of Me-CS to Dmp-CS (Table II, experiment 19). Transesterification of the 9(10)-Me ester group with Dmp-OH was extremely slow ($k = 0.0009$).

Transesterification of Dmp-Dmp diester with methanol for 96 hr gave only the Me-Dmp diester with a k value of 0.022. This value, however, is low because the presence of methanol lowered the pot temperature to 67 C and cannot be compared with those from the other reactions run at 83-86 C.

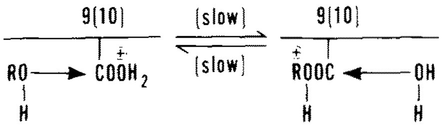
These rate studies of esterification and transesterification of branched C_{19} diacids and esters show a pronounced effect of steric hindrance on the branched 9(10)-carboxyl group. The mechanism for esterification (8,15) can be outlined briefly as:

Terminal Carboxyl



$$-COOH \underset{-H^{\oplus}(fast)}{\overset{+H^{\oplus}(fast)}{\rightleftharpoons}} -\overset{\oplus}{C}OOH_2 \underset{+H_2O;\ -ROH\ (slow)}{\overset{(slow)\ +ROH;\ -H_2O}{\rightleftharpoons}} -\overset{\oplus}{C}O\underset{H}{O}R \underset{+H^{+}(fast)}{\overset{-H^{+}(fast)}{\rightleftharpoons}} -COOR$$

Branched Carboxyl



The branched substituent at either C_9 or C_{10} positions hinders nucleophilic attack of the alcohol on the protonated complex. Similar results would be expected for alkaline transesterification reactions, and some data already collected show that branching definitely does hinder attack by alkoxide ion.

EXPERIMENTAL PROCEDURES

All melting points were taken on a Kofler hot stage and are uncorrected. Samples (ca. 1 mg) for GLC analysis were treated with diazomethane and programmed from 180-300 C at 4 deg/min, 30 cc/min on an F&M Model 5750 equipped with a 6 ft x 1/4 in., 3% JXR column. Alumina (chromatography grade F20, 80-200 mesh, Alumina Company of America) and silicic acid (chromatography grade, 100 mesh, Mallinckrodt Chemical Co.) were heated overnight at 110 C before use. Bu-OH, ClEt-OH, MeOEt-OH, Dmp-OH, EtHex-OH and Oct-OH obtained from Eastman Kodak were distilled before use. Methyl stearate was 99% pure based on GLC analysis.

Methyl 9(10)-Carboxystearate (Me-CS)

This compound was prepared by oxidation of methyl 9(10)-formylstearate (125 g) dissolved in acetone (300 ml) with a solution of potassium permanganate (43 g) in water (600 ml) (5). For purification the product was dissolved in hexane (250 ml) and extracted portionwise with the theoretical amount (based on GLC) of NaOH solution (5 g NaOH, 200 ml methanol and 50 ml water). The methanolic solution was extracted once with hexane and acidified. After ether extraction and water washing, the product (119.8 g, 99% pure) was distilled, bp 201-205 at 0.07 mm.

9(10)-Carboxystearic Acid (CSA)

This compound was prepared from Me-CS by saponification followed by acidification. The product was recrystallized from hexane.

Methyl 9(10)-Chlorocarbonylstearate and 9(10)-Chlorocarbonylstearoyl Chloride

The procedure (16) for linseed acyl chloride was used to prepare these compounds from Me-CS and 9(10)-CSA. The methyl monoacyl chloride prepared from 25 g of methyl ester was distilled through a falling film still. The yield was 22.6 g, 83.6% of theory, bp 190 C at 0.06 mm. The methyl monoacyl chloride was 101% pure as determined by hydrolysis and titration (16).

The diacyl chloride was decanted from the viscous phosphorus residues, stripped to dryness at 100 C in vacuo and used without further purification. The yield was 100%. Analysis by hydrolysis and titration for HCl and for CSA indicated the product to be 103 and 102% pure, respectively.

Methyl 9(10)-Carboalkoxystearates

Methyl 9(10)-chlorocarbonylstearate (5 g) was added dropwise in 15 min to a stirred solution of the appropriate alcohol (10 ml) and pyridine (3 ml) maintained at <10 C. The solution was stirred for 2 hr and poured into water. The product was extracted with ether, acidified with HCl and washed with water. After removal of the ether and drying at 100 C in vacuo, the methyl carboalkoxystearates were distilled (Table I).

Alkyl 9(10)-Carboalkoxystearates

Six alkyl-alkyl diesters were prepared from 9(10)-chlorocarbonylstearoyl chloride and the appropriate alcohol in pyridine as described above. These esters except ClEt-ClEt diester were also obtained from the kinetic studies (96 hr of reaction) by combining the reaction mixtures containing the same product. The products were dissolved in ether, washed with water and stripped to dryness. Distillation gave the desired alkyl-alkyl diesters (Table I).

KINETIC STUDIES

A 250 ml, three-necked, round-bottomed flask was equipped with a septum, thermometer, Dean-Stark trap and condenser. The Dean-Stark trap was filled carefully to overflow level with benzene. The solutions to be studied were prepared from 9(10)-CSA (3.444 g) or Me-CS (3.591 g) and the appropriate amount of alcohol (15 or 30 molar excess) diluted to 75 ml with benzene and then transferred quantitatively to the reaction flask. The solution was stirred magnetically and a weighed amount of sulfuric acid was added. A preheated oil bath (100-115 C) was raised into place, and the pot temperature was measured at reflux. Samples (ca. 0.1 ml) were withdrawn periodically through the septum with a syringe, treated immediately with diazomethane and analyzed by GLC. The weight per cent obtained by GLC was converted to mole per cent and then to moles per liter. The rates of reaction were determined by a digital computer program (7).

Transesterification of Methyl Stearate with Chloroethanol

Methyl stearate (3.12 g) and ClEt-OH (25.35 g) were diluted to 75 ml with benzene. Sulfuric acid (80 mg) was added, and the reaction was studied kinetically as described. After 14 days the mixture was poured into water and extracted with ether. The ether solution was washed with water and stripped to dryness. The product was recrystallized from a small amount of acetone. Yield was 3.4 g, and GLC analysis indicated the presence of three products.

The product (1.5 g) was dissolved in hexane, passed through a silicic acid column (10 g, 7.5 x 1.8 cm) and eluted with 10-50 ml portions of hexane. After distillation of the hexane the residue was recrystallized from methanol. The yield of chloroethyl stearate, mp 49-49.5 C, was o.71 g (17). Mass spectrometry showed prominent peaks at m/e = 346; m/e = 267 for $C_{17}H_{35}CO$; m/e = 191 for $ClC_2H_4CO_2(CH_2)_6$; m/e = 135 for $ClC_2H_4CO_2CH_2CH_2$ and m/e = 122 for $ClC_2H_4CO_2CH_3$.

The silicic acid column was eluted with 5-50 ml portions of 1% ethyl acetate in hexane. The ethyl acetate-hexane was distilled. The residue was recrystallized three times from hexane to yield 0.16 g of 2-(2-chloroethoxy)ethyl stearate, mp 37-37.5 C. Analytic calculations for $C_{22}H_{43}O_3Cl$: C, 67.57; H, 11.08; Cl, 9.06. Found: C, 67.60; H, 11.40: Cl, 8.93. Mass spectrometry showed prominent peaks at m/e = 390; m/e = 311 for M - ClC_2H_4O; m/e = 267 for $C_{17}H_{35}CO$; m/e = 166 for $ClC_2H_4OC_2H_4O$-$COCH_3$; and m/e = 107 for $ClC_2H_4OC_2H_4$.

The silicic acid column was eluted with methanol (200 ml). After removal of methanol the third component 2-(2-[2-chloroethoxy]ethoxy)ethyl stearate was isolated by preparative GLC and identified by mass spectrometry. Prominent peaks were present at m/e = 434; m/e = 311 for M - $ClC_2H_4OC_2H_4O$; m/e = 267 for $C_{17}H_{35}CO$; m/e = 210 for $Cl(\text{-}C_2H_4O\text{-})_3COCH_3$; m/e = 151 for $ClC_2H_4OC_2H_4OC_2H_4$; m/e 107 for $ClC_2H_4OC_2H_4$.

Transesterification of Me-Me Diester of CSA with Dimethylpentanol

A solution of Me-Me diester (3.728 g), Dmp-OH (18.27 g) and sulfuric acid (84.8 mg) was diluted to 75 ml with benzene, and the rate of reaction was studied. The pot temperature was 86 C. The composition of the mixture after 96 hr was Dmp-Me diester (92.3%) (k_3 = 0.063) and Dmp-Dmp diester (7.7%) (k_5 = 0.0009).

Transesterification of Dmp-Dmp Diester of CSA with Methanol

A solution of Dmp-Dmp diester (5.502 g), methanol (5.04 g) and sulfuric acid (82.1 mg) was diluted to 75 ml with benzene and the rate of reaction studied as described. Pot temperature was 67 C. The composition after 96 hr was Me-Dmp diester (82.9%) (k= 0.022) and Dmp-Dmp diester (17.0%).

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