gave a faint Liebermann reaction and was therefore dissolved in 50 cc. of chloroform, 40 cc. of acetic anhydride, cooled and treated with 15 cc. of concentrated sulfuric acid. The acetate was then recrystallized from alcohol and melted at 130–131°, $[\alpha]^{24}D$ +17°. These are also the constants for stigmastyl acetate. The acetate was saponified and converted into the 3,5-dinitrobenzoate, m. p. 213–214°, $[\alpha]^{24}D$ +15°. This derivative yielded after saponification stigmastanol, m. p. 135–136°, $[\alpha]^{24}D$ +24°.

Ozonization.—Two grams of the acetate of stigmastatrienol suspended in 20 cc. of acetic acid was ozonized for one hour; 100 cc. of water was then added and the mixture distilled through a column. The receiver contained *p*-nitrophenylhydrazine in 50% acetic acid. The distillation was discontinued when about 20 cc. had come over. The yield of crude hydrazone was 341 mg. On digestion with benzene it left undissolved 81 mg. of an unknown orange-yellow compound, m. p. 204°. The benzene soluble fraction was chromatographed on aluminum oxide and developed with benzene. The lower, orange layer was eluted with ether, giving a crude hydrazone of m. p. 118–123°. This was recrystallized from hot water and also from benzene–petroleum ether and melted then at 128–129°. Its identity with acetaldehyde *p*-nitrophenylhydrazone was shown by a nitrogen determination and mixed melting point determination. *Anal.* Calcd. for $C_8H_9O_2N_3$: N, 23.47. Found: N, 23.65.

Summary

Stigmasteryl acetate 22,23-dibromide yields stigmasterol or its acetate when treated with alcoholic potassium hydroxide, pyridine or quinoline. With potassium acetate in a high boiling alcohol a new stigmastatrienol acetate is obtained. Observations are reported indicating that the new compound is Δ-5,23,24:28-stigmastatrienol.

NEW BRUNSWICK, N. J. RECEIVED MARCH 23, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Saponification of Ethyl Esters of Aliphatic Acids

BY H. S. LEVENSON AND HILTON A. SMITH

In a previous paper it was demonstrated that the effect of chain length on the velocity of acid catalyzed esterification of normal acids was quite similar to its effect on the velocity of saponification of the ethyl esters of the same acids.[1] The purpose of the present paper is to supplement the work on the saponification of aliphatic esters which is already available in the literature[2] so that a complete comparison of the effect of an aliphatic radical on the velocity of saponification of ethyl esters may be made with the recently published material on the catalyzed esterification of their corresponding acids.[3]

Experimental

Ethyl laurate was obtained from Eastman Kodak Co. The ester was fractionated under reduced pressure in a 5 ft. (1.5 meter) Vigreux column, and constant-distilling fractions were used.

Ethyl β-methylvalerate and ethyl isocaproate were prepared by esterification of the corresponding acids[4] with ethanol using sulfuric acid as a catalyst. The preparation of these acids has already been described.[3,5] The esters were purified by fractionation in a small 2-foot (0.6 meter) Vigreux column.

The ethyl esters of diethylacetic acid, dipropylacetic acid, dibutylacetic acid and di-isobutylacetic acid were prepared by esterification of the acids. Diethylacetic acid was obtained from Eastman Kodak Co. and the other acids were prepared by malonic ester syntheses.[3] The diethyl and di-isobutylacetic acid esters were purified by fractionation in a 5 foot (1.5 meter) Vigreux column, while the 2-foot column was used for purification of the other two.

Each ester was analyzed by complete saponification of weighed samples with excess alkali, and back titration with standard acid. All of the esters gave analyses between 99.5 and 100.5%, the precision of this method being about 0.5%.

The velocity determinations were carried out in 85% aqueous ethanol, this medium being prepared in the manner already described.[1] The method of making velocity determinations was similar to that previously employed.

Experimental Calculations and Results

In general, the rate constants were calculated using the second order reaction rate equation

$$k = x/t(a - x)a \qquad (1)$$

where a is the initial concentration of each reactant, and x represents the concentration of each reactant at the time t. The results of a typical run are given in Table I.

The runs with the esters of diethyl, dipropyl, and dibutyl acetic acids were so slow that, at higher temperatures, the action of alcoholic sodium hydroxide on the Pyrex glass reaction flasks was appreciable. This was indicated by an

---

[1] Smith and Levenson, THIS JOURNAL, **61**, 1172 (1939).

[2] Evans, Gordon and Watson, *J. Chem. Soc.*, 1439 (1938).

[3] Smith, THIS JOURNAL, **62**, 1136 (1940).

[4] The authors are greatly indebted to Mr. A. S. Raff for his aid in the preparation of these acids.

[5] Smith, THIS JOURNAL, **61**, 1176 (1939).

TABLE I

SAPONIFICATION OF ETHYL LAURATE AT 55°

a = (ester) = (NaOH) = 0.0500 mole/liter

t, min.	x	10^3k (liters mole^{-1} sec.$^{-1}$)
3.08	0.00713	18.4
6	.01279	19.1
9	.01633	18.0
15	.02281	18.6
25	.02917	18.7
42	.03513	18.7
80	.04079	18.5
115	.04334	18.9

increase in the values of the velocity constant toward the latter portion of each run. An approximate correction was applied as follows.

The relation between the total amount of sodium hydroxide (x) reacting with ester plus glass to that (y) reacting with the ester only is given by the equation

$$x = y + 2.303 \frac{k_g}{k_s} \log \frac{a}{a - y} \qquad (2)$$

where a is the initial concentration of ester and alkali, k_s is the reaction velocity constant for the saponification reaction and k_g is the unimolecular reaction rate constant representing the action of the alkali on the glass bottle. The values of k_g at 45 and 55° were 1.4×10^{-7} and 9.6×10^{-7} sec.$^{-1}$, respectively. The corrected k values were found by determining y for each experimental x, using for k_s the uncorrected figure, and substituting in equation I. These corrections were applied for runs at temperatures of 45 and 55°. Table II gives a sample of such calculations.

TABLE II

SAPONIFICATION OF ETHYL DIPROPYLACETATE AT 55°

a = (ester) = (NaOH) = 0.05 mole/liter

t, min.	x	y	10^3k (liters mole^{-1} sec.$^{-1}$) Uncor.	Cor.
460	0.01028	0.0096	0.188	0.172
1230	.02052	.0184	.189	.157
1860	.02610	.0232	.196	.155
2820	.03237	.0282	.217	.153
4290	.03859	.0331	.263	.152

The values of k for each ester are given in Table III. These were calculated by averaging the individual rate constants over 20 to 80% reaction except where corrections were made for glass reaction. For these only, figures for 20–60% reaction were averaged since the corrections are approximate, and become relatively large after 60% reaction.

TABLE III

REACTION RATE CONSTANTS FOR THE SAPONIFICATION OF ETHYL ESTERS OF ALIPHATIC ACIDS IN 85% ETHANOL

For all esters, (NaOH) = (ester) = 0.05 mole/liter

Ethyl ester	$k \times 10^3$ (liters mole^{-1} sec.$^{-1}$)			
	t = 25°	t = 35°	t = 45°	t = 55°
Butyrate[a]	1.83	4.25	9.18	19.0
Laurate	1.81	4.11	9.31	18.6
	1.86	4.10	9.23	18.8
Average	1.84	4.11	9.27	18.7
Isocaproate	1.85	4.34	9.01	18.9
	1.87	4.28	9.06	18.9
Average	1.86	4.31	9.04	18.9
β-Methylvalerate	0.414	0.968	2.20	4.67
	.407	.959	2.19	4.62
Average	.411	.963	2.20	4.65
Diethylacetate	.0151	.0385	0.0955	0.216
	.0152	.0387	.0966	.211
	.0159	.0381	.0981	.217
Average	.0154	.0384	.0968	.215
Dipropylacetate	.0105	.0283	.0644	.154
	.0107	.0280	.0669	.154
Average	.0106	.0282	.0656	.154
Dibutylacetate	.0101	.0254	.0629	.153
	.0099	.0256	.0640	
Average	.0100	.0255	.0635	.153

[a] The figures for the butyrate are given for comparison purposes, and are interpolated from the data of Smith and Levenson.[1]

The plot of log k against $1/T$ is shown in Fig. 1.

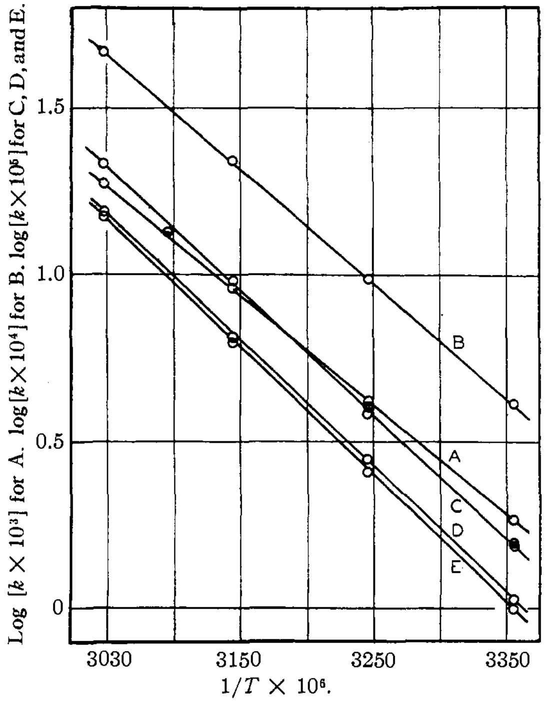

Fig. 1.—Temperature coefficients of saponification reactions: A, ethyl laurate and ethyl isocaproate; B, ethyl β-methylvalerate; C, ethyl diethylacetate; D, ethyl dipropylacetate; E, ethyl dibutylacetate; ○, points from data of Levenson and Smith; ◒, points for ethyl diethylacetate from data of Evans, Gordon and Watson.[2]

The saponification of ethyl diethylacetate in 85% ethanol was also studied by Evans, Gordon and Watson.[2] Figure 1 shows reasonable agreement with their data. The activation energies for these reactions are given in Table IV. They were calculated from the slopes of the lines in Fig. 1, and were checked by the method of least squares.

TABLE IV

ACTIVATION ENERGIES FOR THE SAPONIFICATION OF ALKYL SUBSTITUTED ALIPHATIC ETHYL ESTERS

Ethyl ester	E, cal./mole
Butyrate[a]	15,100
Laurate	15,100
Isocaproate	15,000
β-Methylvalerate	15,700
Diethylacetate	17,200 (17,400)[b]
Dipropylacetate	17,200
Dibutylacetate	17,700

[a] From the data of Smith and Levenson (ref. 1).

[b] The value obtained by Evans, Gordon, and Watson (ref. 2).

Discussion

The rate constants for ethyl laurate when compared with those for ethyl butyrate give additional confirmation to the fact that an increase of the chain length of an alkyl chain beyond four carbon atoms has no measurable effect on the velocity of saponification of esters under the conditions of the experiments here reported.

The results for β-methylvalerate and isocaproate combined with the earlier work of Smith and Levenson[1] and of Evans, Gordon and Watson[2] show the same effect for methyl substitution as was found for acid-catalyzed esterification in methanol.[5] The effect of substitution of a methyl group in the α, β, or γ position is the same in each process, as is shown in Table V.

TABLE V

EFFECT OF METHYL SUBSTITUTION ON REACTION VELOCITY

Position in which substitution takes place	Esterification	% Change saponification
α, (propionic ⟶ isobutyric)	62	78
β, (butyric ⟶ isovaleric)	76	77
γ, (valeric ⟶ isocaproic)	0	0

It is thus evident that in saponification as well as in esterification, only when substitution of a methyl group for a H atom in a normal alkyl chain takes place in the α or β position is the reaction velocity affected.

The effect of the simultaneous lengthening of two normal alkyl chains is shown in Table VI.

TABLE VI

EFFECT OF CHAIN LENGTH OF ETHYL ESTERS OF DISUBSTITUTED ACETIC ACIDS ON THEIR VELOCITY OF SAPONIFICATION

Ethyl ester	$10^3 \times k_{25°}$	E
Acetate[a]	6.92	14,700
Isobutyrate[b]	0.801	15,000
Diethylacetate	.0154	17,200
Dipropylacetate	.0106	17,200
Dibutylacetate	.0100	17,700

[a] $k_{25°}$ and E for ethyl acetate are from the data of Smith and Levenson.[1] [b] $k_{25°}$ for ethyl isobutyrate was taken from the data of Evans, Gordon, and Watson, and E is a value recalculated from their data.[6]

Just as in esterification, there is a much larger decrease in k when the chains are lengthened from the isobutyrate to the diethylacetate than was caused by the change from acetate to isobutyrate. Further lengthening of the carbon chain results in relatively smaller changes in saponification velocity. The changes in the activation energy also parallel those found for esterification.

The k values for the saponification of ethyl di-isobutylacetate are not included in Table III. This compound saponifies so slowly that the glass reaction correction becomes quite large. All that can be said with certainty is that this ester saponifies about one-third as fast as does dibutylacetic acid ester. ($k_{25°}$ for the di-isobutyl substituted ester is approximately 0.0031×10^{-3}.) A similar result was found in esterification studies.

The effect of increased methyl substitution in the α position also parallels that found for esterification, as is shown by the data of Evans and co-workers[2] for the saponification of esters of isobutyric and trimethylacetic acids.

In short, the processes of the acid catalyzed esterification of aliphatic acids and of the saponification of their ethyl esters are completely similar at least as far as the effect of the character of the alkyl chain upon reaction velocity is concerned.

Summary

The kinetics of the saponification in 85% ethanol of the following esters has been studied: ethyl laurate, ethyl isocaproate, ethyl β-methylvalerate, ethyl diethylacetate, ethyl dipropylacetate, ethyl dibutylacetate, and ethyl di-isobutyl acetate.

It is demonstrated that the effect of the character of the alkyl chain on reaction velocity is the same for the processes of acid-catalyzed esterification and saponification.

BETHLEHEM, PENNA. RECEIVED APRIL 23, 1940

---

(6) See Smith and McReynolds, THIS JOURNAL, **61**, 1963 (1939).