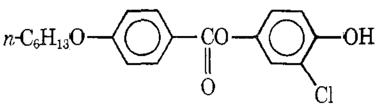
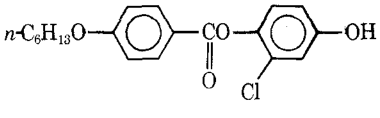
possibility of cis–trans isomerism. The ester molecules are dissymmetric because of the chloro substituent and the two different acyl groups.

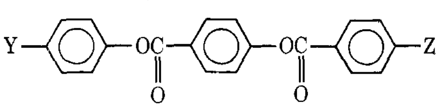
Three of the four materials are nematic. The exception is **6c**, demonstrating again the powerful deleterious effect of bulky lateral substituents on mesomorphism. The high melting and N–I points of **6d**, although it is obviously a mixture, suggest that the main components are the *trans*-4-methoxycinnamates of **7a** and **7b**. **6a** and **6b** are the lowest melting examples of type **1** esters to date. This is consistent with their being mixtures and with their structures. The combination of a chloro substituent on the central *p*-phenylene ring with terminal *n*-alkyl or *n*-alkoxy groups in a very closely related system (**9**) has been shown[16] to result in low-melting (39–70°) (nematic) compounds. The relatively low melting point of **3d** is also consistent with this.



7a



7b



9

Acknowledgment. We wish to thank Stephen A. Haut for suggesting the preparation of compound **2**.

Registry No.—**2**, 51933-64-3; **3a**, 51933-65-4; **3b**, 51933-66-5; **3c**, 51933-67-6; **3d**, 51933-68-7; **4**, 51933-69-8; **5a**, 51933-70-1; **5b**, 51933-71-2; **5c**, 51933-72-3; **6a**, 52003-48-2; **6b**, 52003-49-3; **6c**, 52003-50-6; **6d**, 52124-32-0; **7**, 52003-51-7.

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(15) Ester **3c** is also polymorphic. Two distinct fusions were seen in the melting point determination (Table I), and a DSC trace gave peaks at 163 and 172°. Cooling and reheating the sample in the DSC gave mainly a peak at 177.5°, which was also the result when the compound was recrystallized from ethanol rather than ethyl acetate.
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A Reexamination of the Effect of α- and β-Methyl Substitution on the Esterification Rates of Saturated Aliphatic Acids

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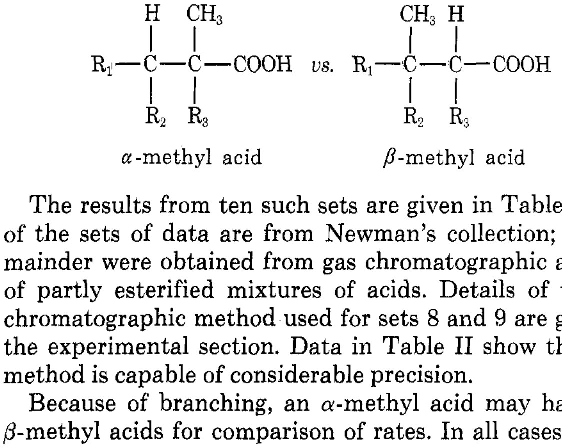
From an examination of his collection of data concerning the hydrogen chloride catalyzed esterification rates in methanol of various aliphatic acids, Newman concluded "... substitution of methyl groups for hydrogen causes a greater decrease in rate when at the beta-carbon than when at the alpha- or gamma-carbon."[1] Essentially the same conclusion was reached by Taft, "In each case methyl substitution is more effective in the beta than in the alpha position,"[2] and by Schulte and Kirschner, "... the influence of the methyl group in the beta position is somewhat greater than in the alpha position."[3] This general conclusion has been widely accepted.[4]

However, by looking at the effect of α- and β-methyl substitution in a much simpler scheme, one not generally carried out by the authors cited, the opposite effect is observed, namely that an α-methyl substitution decreases the rate *more* than a β-methyl substitution. This simple and direct scheme consists of the comparison of the rates of sets of two isomeric acids, differing only in the α or β placement of a methyl group.



$$R_1-\overset{H}{\underset{R_2}{C}}-\overset{CH_3}{\underset{R_3}{C}}-COOH \quad vs. \quad R_1-\overset{CH_3}{\underset{R_2}{C}}-\overset{H}{\underset{R_3}{C}}-COOH$$

α-methyl acid β-methyl acid

The results from ten such sets are given in Table I. Five of the sets of data are from Newman's collection; the remainder were obtained from gas chromatographic analysis of partly esterified mixtures of acids. Details of the gas chromatographic method used for sets 8 and 9 are given in the experimental section. Data in Table II show that this method is capable of considerable precision.

Because of branching, an α-methyl acid may have two β-methyl acids for comparison of rates. In all cases except example number 10 of Table I, the β-methyl acid of the set esterifies faster than the α-methyl isomer. The average for the k_β/k_α ratios in examples 1–9 is 1.8 ± 0.5. Example number 10 consists of a set of much more sterically hindered acids than the others and appears to be the only case where Newman made use of the comparison of such isomers to demonstrate his conclusion. No actual numerical ratio was established by Newman between the rates of these two acids since the rate for the β-methyl acid was considered to be too slow for measurement.

Yufit has apparently taken Newman's data (without crediting him) and developed an empirical method for calculating the esterification rates of the aliphatic acids from their structures.[7] Unfortunately, his calculations for the various acids do not always seem to follow his method as stated; however, for the simple case of placing a methyl group in the α or β position of a normal acid, it can be shown that the general prediction is that the β-methyl acid will esterify (presumably at 40°) ~1.4 times as fast as the α-methyl acid. Thus, from exactly the same body of data entirely different conclusions were reached by the methods of Yufit and Newman.

From an examination of the data in Table I, it seems rea-

Table I
Relative Esterification Rates in Methanol of α-Methyl- and β-Methyl-Substituted Aliphatic Acids

No.	α-Methyl acid, $(R_1)(R_2)CHC(R_3)(CH_3)COOH$	β-Methyl acid, $(R_1)(R_2)(CH_3)CCH(R_3)COOH$	k_β/k_α	Temp, °C	Ref
1	$(CH_3)_2CHCOOH$	$CH_3CH_2CH_2COOH$	1.5	40	1
2	$CH_3CH_2CH(CH_3)COOH$	$CH_3CH(CH_3)CH_2COOH$	1.2 (1.1)	40	1 (3)
3	$(CH_3)_3CCOOH$	$CH_3CH_2CH(CH_3)COOH$	2.7	40	1
4	$CH_3CH_2CH_2CH(CH_3)COOH$	$CH_3CH_2CH(CH_3)CH_2COOH$	1.2	65	5
5	$CH_3CH_2C(CH_3)_2COOH$	$CH_3CH(CH_3)CH(CH_3)COOH$	2.3	65	5
6	$CH_3CH_2C(CH_3)_2COOH$	$CH_3CH_2CH(C_2H_5)COOH$	2.3	65	5
7	$(CH_3)_2CHCH(CH_3)COOH$	$(CH_3)_3CCH_2COOH$	1.5 (1.6)	15–20 (65)	1 (5)
8	$CH_3CH_2CH_2CH_2C(CH_3)_2COOH$	$CH_3CH_2CH_2CH_2CH(C_2H_5)COOH$	1.6	50	This report
9	$(CH_3)_2CHCH_2C(CH_3)_2COOH$	$(CH_3)_2CHCH_2CH(C_2H_5)COOH$	2.2	50	This report
10	$(CH_3)_3CC(CH_3)_2COOH$	$(CH_3)_3CCH(C_2H_5)COOH$	<1[6]	40	1

Table II
Determination of Relative Esterification Rates in Methanol at 50° of α-Methyl- and β-Methyl-Substituted Aliphatic Acids

Fraction remaining after partial esterification		
α-Methyl acid (A) 2,2,4-Trimethylpentanoic acid[a]	β-Methyl acid (B) 2-Ethyl-4-methylpentanoic acid[b]	Log B/log A
0.6622	0.4150	2.13
0.6413	0.4014	2.05
0.5428	0.2589	2.21
0.5503	0.2621	2.24
0.4704	0.1775	2.29
0.4553	0.1731	2.23
2,2-Dimethylhexanoic acid[c]	2-Ethylhexanoic acid[d]	Log B/log A
0.8118	0.7208	1.57
0.6714	0.5319	1.58
0.5054	0.3298	1.63
0.3272	0.1750	1.56
0.1791	0.0731	1.52

[a] Registry number, 866-72-8. [b] Registry number, 108-81-6. [c] Registry number, 813-72-9. [d] Registry number, 149-57-5.

sonable to put forth the following generalization: a β-methyl-substituted saturated aliphatic acid esterifies with methanol at a greater rate (~1.8 times as fast at 40°) than the corresponding α-methyl acid.

Although the above statement deals only with certain isomeric pairs of acids, it certainly presents a multitude of "exceptions" to the generally accepted conclusion that a methyl substitution at the β carbon is more effective in reducing the esterification rate than a methyl substitution at the α carbon. How the conclusion developed in this present report can be employed to predict more satisfactorily the effect of structure on esterification rates will be the topic of a forthcoming paper.

Experimental Section

Materials. Purity of the acids was indicated by the neutralization equivalent (144.2 calcd) and the per cent area by glc under the conditions described in the next section.

2-Ethylhexanoic acid, neut equiv 144.6, glc per cent area 99.8, was obtained from Baker Chemical Co.

2-Ethyl-4-methylpentanoic acid, neut equiv 144.8, glc per cent area 99.1, was obtained from Pfaltz and Bauer.

2,2-Dimethylhexanoic acid, neut equiv 145.1, glc per cent area 95.7, was prepared by alkaline permanganate oxidation of 2,2-dimethyl-1-hexanol obtained from K & K Laboratories.

2,2,4-Trimethylpentanoic acid, neut equiv 146.5, glc per cent area 98.6, was prepared by alkaline permanganate oxidation of 2,2,4-trimethyl-1-pentanol obtained from Pfaltz and Bauer.

Methyl myristate, glc per cent area 99.8, was obtained from Lachat Chemicals Inc.

Gas–Liquid Chromatography. Chromatography was carried out with a Beckman GC 4 chromatograph equipped with a flame ionization detector which was interfaced with a Perkin-Elmer PEP-1 data processer. The column was 6 ft by ⅛ in. stainless steel packed with 20% diethylene glycol adipate polyester and 3% phosphoric acid on 60/80 mesh Gas-Chrom P. Column temperature was 150°, *inlet temperature was 200°*, and helium flow was 25 cc/min.

Determination of the Relative Esterification Rates. The reaction mixture was composed of 20 ml of methyl alcohol, 2 drops of each of the two acids whose esterification rates are to be determined, and 2 drops of methyl myristate, the internal standard. It is, of course, necessary that all three components are adequately resolved by the chromatographic method. Six drops of concentrated hydrochloric acid was added; the mixture was divided up into a number of small screw-cap tubes and heated in an aluminum block at 50 ± 0.5°. Samples were analyzed at various times over a 4-hr heating period. Readouts from the data processer were given as fraction remaining of each of the acids. The relative esterification *rate was calculated from the equation*

$$\frac{k_{\beta\text{-methyl acid}}}{k_{\alpha\text{-methyl acid}}} = \frac{\text{log fraction remaining of }\beta\text{-methyl acid}}{\text{log fraction remaining of }\alpha\text{-methyl acid}}$$

Readouts and the calculated relative esterification rates are given in Table II.

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Absence of Catalysis of Salicylate Ester Hydrolysis by Hexadecyltrimethylammonium Bromide Micelles

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Rate enhancements by cationic micelles have been observed in the base-catalyzed hydrolysis of several carboxylic esters having good leaving groups.[1] With simple alkyl esters rate retardations have been observed; they have been