2-(p-Nitrophenyl)-2,5-dihydrothiophene-1-dioxide.—A mixture of 12 g. (0.188 mole) of sulfur dioxide, 2 g. (0.114 mole) of 1-(p-nitrophenyl)-1,3-butadiene and 0.1 g. of phenyl-β-naphthylamine was heated for 2 hours at 75-80°. The residue (2.1 g.) after evaporation of sulfur dioxide was extracted three times with 20-ml. portions of Skellysolve B at 50° to give 1.2 g. of 1-(p-nitrophenyl)-1,3-butadiene. The dark insoluble material melted 107-111° with evolution of gas. Recrystallization from benzene raised the melting point of this sulfone to 119-121° with evolution of gas. A small portion was heated at 130° until gas evolution ceased. Extraction of the residue with 1 ml. of hot Skellysolve B and evaporating the supernatant liquid gave yellow crystals: m.p. 76-78°; a mixed melting point with 1-(p-nitrophenyl)-1,3-butadiene was 76-78°.

In a second experiment the mixture was placed in a pressure bottle and allowed to stand for 4 days at room temperature. Evaporation of the sulfur dioxide gave 2.5 g. of residue which was suspended in 15 ml. of benzene and filtered: 1.1 g. (41%), m.p. 110-115° with evolution of gas. This crude sulfone was further purified by dissolving in acetone and precipitating with water: m.p. 125-125.5°.

Anal. Calcd. for $C_{10}H_9NO_4S$: S, 13.40. Found: S, 13.49.

Two attempts to obtain the polysulfone were made. A mixture of 0.4 g. of 1-(p-nitrophenyl)-1,3-butadiene and 2.3 ml. of alcoholic silver nitrate (0.4%) was saturated with sulfur dioxide at 0° and allowed to stand 3 days. Evaporation gave 0.3 g., m.p. 70-75°, which on crystallization from Skellysolve B became 77-78°; this was not depressed in a mixed m.p. with the diene.

A greater concentration of sulfur dioxide was attained in the second experiment by allowing a mixture of 1 g. of hydrocarbon, 6 g. of sulfur dioxide and 1 ml. of alcoholic silver nitrate to stand in a pressure bottle for 8 days. About 0.2 g. of hydrocarbon was recovered; the remainder was polymer which did not give a positive qualitative test for sulfur.

1-(p-Anisyl)-1,3-butadiene.—1-(p-Anisyl)-3-buten-1-ol was made from 24 ml. (0.2 mole) of redistilled p-anisalde-hyde and the Grignard reagent from 34.5 ml. (0.39 mole) of allyl chloride and 8.5 g. (0.35 atom) of magnesium and the intermediate was hydrolyzed with 60 ml. of saturated ammonium chloride solution.[18] The yield was 30.2 g. (85.5%) boiling 117-118° (1.5 mm.), $n^{25}D$ 1.5353.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.24; H, 7.66.

A German patent refers to this alcohol but no constants are given.[31]

The alcohol was dehydrated in the presence of potassium acid sulfate.[14] From 4 g. of alcohol, 0.1 g. of catalyst and 0.1 g. of phenyl-β-naphthylamine there was obtained 2.5 g. (70%) of solid product distilling 93-95° (1.1 mm.). Crystallization from methanol and water gave m.p. 44-46°; lit. 46°.[14] The maleic anhydride adduct melted 142-145°; lit. 145°.[14] The quantitative reaction with maleic anhydride at room temperature for 4 days gave 89.7-90.5% reaction.

1-(p-Anisyl)-1,3-butadiene Plus Sulfur Dioxide.—The preparation of the cyclic sulfone was tried twice by the methods described above. Neither at 75-80° for 2 hours nor at room temperature for 3 days was there any indication of reaction with sulfur dioxide. Polysulfone formation was tried with silver nitrate as a catalyst (v.s.) in a reaction run for 2 days at 0°. The product contained no sulfur. In all of these experiments the diene polymerized considerably.

trans-1-Phenyl-1,3-butadiene Plus Sulfur Dioxide.—In view of the greater reactivity of the p-nitrophenylbutadiene to sulfur dioxide at room temperature than at 75-80°, phenylbutadiene[2] was tried at room temperature. No sulfone formed.

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(31) A. Knorr, German Patent 544,388 (Sept. 25, 1930).

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Steric Effects. II. Acid-catalyzed Esterification

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The rates of acid-catalyzed esterification of a number of highly branched aliphatic acids are reported. A discussion of the effect of structure on rate is made. It is shown that substitution of hydrogen atoms in the β-position by methyl groups decreases the rate to a greater degree than substitution in the α- or γ-positions.

In a previous publication[2] the acid-catalyzed esterification of aliphatic acids was discussed with the aid of an empirical rule, the rule of six, which stated "the greater the number of atoms in the six position the greater will be the steric effect." As applied to carboxylic acids, the six position is defined by numbering the carbonyl oxygen as one and then counting back into the chain. The six number was defined[2] as the number of atoms in the six position. This paper is concerned with the presentation of further data on the esterification of a number of branched aliphatic acids and a further analysis of the situation.

Experimental

Materials.—t-Butylacetic acid was prepared by the action of sodium hypobromite on methyl neopentyl ketone.[3] The samples used distilled at 95-96° at 26 mm.

Ethylisopropylacetic acid was prepared from ethyl ethylmalonate by a malonic ester synthesis carried out in the usual manner; b.p. 202.5-203.5°.[4]

t-Butylmethylacetic acid was synthesized by the action of alcohol-free sodium methylate on 4,4-dimethyl-3-bromo-2-pentanone.[5] After recrystallizing from a methanol-water solution the acid melted at 51-52°.

t-Butyldimethylacetic acid was prepared by reaction of 2,3,3-trimethyl-2-butyl chloride (108 g.) with magnesium and then treating with carbon dioxide in the usual way.[6] There was obtained 15.1 g. of crude acid which after two recrystallizations from petroleum ether yielded 8.3 g. (7.2%) of acid melting at 197-198°.[7]

Neopentylacetic acid was prepared by the Arndt-Eistert synthesis from t-butylacetic acid. As reagent for the rearrangement of the diazoketone silver benzoate in triethylamine[8] was employed. The purified acid distilled at 159° at 150 mm.[9]; the over-all yield was 57%.

(1) Taken from the Ph.D. thesis of Kurt L. Loening, O.S.U., 1951.

(2) M. S. Newman, THIS JOURNAL, 72, 4783 (1950).

(3) F. C. Whitmore, A. Homeyer and W. R. Trent, U. S. Patent 2,004,066; C. A., 29, P 4776 (1935).

(4) A. W. Crossley and H. R. LeSueur, J. Chem. Soc., 85 (1900).

(5) J. G. Aston, J. T. Clarke, K. A. Burgess and R. B. Greenburg, THIS JOURNAL, 64, 300 (1942).

(6) H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

(7) A. Byers and W. S. Hickinbottom, J. Chem. Soc., 1334 (1948).

(8) M. S. Newman and P. F. Beal, THIS JOURNAL, 72, 5163 (1950).

(9) F. C. Whitmore, et al., ibid., 63, 643 (1941).

t-Butylethylacetic and γ-ethyl-δ,δ-dimethylhexanoic acids were obtained through the courtesy of Dr. Earl Pelton of the Dow Chemical Company. The former was recrystallized twice from acetone, m.p. 76–77°; the latter was distilled at 10 mm. and a fraction boiling at 142° was collected. All other acids used were obtained years ago from the late Dr. F. C. Whitmore of Pennsylvania State College.

Methylneopentylacetic (b.p. 217° at 730 mm.) and triethylacetic (m.p. 39°) acids were used without purification.

Dimethylneopentylacetic acid was recrystallized twice from methanol–water solution, m.p. 44–45°.

Dineopentylacetic acid was recrystallized four times from methanol–water solution, m.p. 88–91°.

t-Butylmethylneopentylacetic acid was recrystallized four times from methanol–water solution, m.p. 123–127°.

All acids were tested for purity by titration with standard base and in all cases the purity as determined by this method was greater than 99%.

Methanol was obtained in a pure dry state by careful fractionation.[10]

Kinetic Data.—The rates of esterification of the acids were measured by the same procedure as that used by Smith and his co-workers.[10] Duplicate runs for each acid were carried out at 20, 30 and 40° unless the reaction was too slow to be measurable. The reaction temperature was controlled to ±0.02°. In all cases the initial concentration of organic acid was 0.5 mole per liter and that of hydrogen chloride 0.005 M.

Smith noted that a side reaction takes place between methanol and hydrogen chloride to give methyl chloride. Therefore blank runs were carried out with no organic acid present to determine the decrease in hydrogen chloride concentration with time and to enable one to make the proper corrections in the calculations of the rates of esterification. In agreement with Smith it was found that at 20° the side reaction did not interfere, but that at 30 and 40° it was appreciable and corrections had to be applied.

Rate constants were calculated by the following expression which was derived and tested by Goldschmidt and his co-workers[11] and used by Smith.[10]

$$k = \frac{(r + a)\ln\left[\dfrac{a}{a - x}\right] - x}{(HCl)\, rt}$$

where a = original concentration of organic acid; x = concentration of ester formed at time t; r = a constant depending on temperature and independent of the acid used.

The values of r, which were found to be 0.20 at 20°, 0.25 at 30° and 0.32 at 40°, are in excellent agreement with the ones reported by Smith.[10] For the faster reactions the values for k were calculated by averaging the individual figures obtained during 20–80% completion of the reaction, since in the early stages experimental errors are large and in the latter stages the values fall off due to the reverse hydrolysis reaction. For the slower acids all k values obtained were averaged; for the slowest acid (*t*-butyldimethylacetic) that we measured the reaction was only 10% complete after sixteen days.

Whenever it was possible to obtain rate constants for an acid at two or more temperatures the activation energy was computed by means of the Arrhenius equation.

(10) H. A. Smith, *ibid.*, **61**, 254 (1939).

(11) H. Goldschmidt and O. Udby, *Z. physik. Chem.*, **60**, 728 (1907); **61**, 30 (1912); **143**, 139 (1929).

Discussion

For the purpose of analysis of the rate studies on esterification reference will be made to column 13 in Table I which gives the ratio of the rate of esterification of acetic acid to that of substituted acid at 40°. This temperature was chosen because certain acids esterified too slowly for accurate measurement at low temperatures. Because of the slow rate of esterification of some acids and the competing reaction of methanol with hydrogen chloride which becomes serious at temperatures much above 40° some other reaction will have to be used to gain information about more highly hindered acids.

Perhaps the most important result of this study is found in a comparison of the rates for acids 1 and 6, 2 and 8, and 3 and 10. In going from acetic, 1, to trimethylacetic, 6 (replacing three α-hydrogens by methyl groups), the rate is decreased 26.8-fold. In going from propionic, 2, to *t*-butylacetic, 8 (replacing three β-hydrogens by methyl groups), the rate is decreased 36-fold.[12] However, in going from butyric acid, 3, to neopentylacetic acid, 10 (replacing three γ-hydrogens by methyl groups), the rate is almost unchanged. Thus, the greatest effect is found at the β-position (the only case where the six number is changed), next at the α- and least in the γ-position.

It should be stressed, however, that the slight change found on substituting three methyl groups for the γ-hydrogens of butyric acid does not mean that branching at the γ position is entirely unimportant (note acid 26). A comparison of the trend in acids 10 to 14 reveals that there is a thirty-fold decrease in rate whereas the decrease in acid 3 to 11 is only five-fold. Thus a similar structural change (replacing one α-hydrogen by a methyl group) has a much larger effect in an acid completely branched at the γ-carbon. In these four acids (3, 10, 11 and 14) the six number is constant at three. Acid 15 (six number of 3) is interesting in that it shows how complete branching on the α- and γ-carbons can produce a relatively hindered acid without much branching on the β-carbon. However, acid 13 (six number of 9) which is completely branched on α- and β-carbons is much more hindered.

The greater effect of an ethyl group on the α-carbon than a methyl group is well illustrated by comparing the decrease in going from 2 to 3, from 5 to 18, from 6 to 17, and from 12 to 24 and noting that as the rest of the chain becomes more branched the ethyl group is more and more effective in its hindering action. The balance between acids 12 and 16 is interesting. The effect of an ethyl group is strikingly illustrated by a comparison of acids 8, 13 and 24. Here, an ethyl group on the α-carbon (24) has a greater effect than two methyl groups (13), although how much greater is impossible to judge at present because of the extremely slow rate of 24.

In the previous publication[2] the prediction that

(12) The importance of β-substitution has been pointed out previously in a study of amide hydrolysis by J. Cason and H. Wolfhagen, *J. Org. Chem.*, **14**, 155 (1949).

TABLE I

DATA ON ACID-CATALYZED ESTERIFICATION OF ALIPHATIC ACIDS (0.005 MOLAR HCl)[a]

Acid	b	Atoms in position OH / C—C—C—C—C=O (6 5 4 3 2 1)						10^3 $k^c_{25°}$	10^4 $k^c_{35°}$	10^5 $k^c_{40°}$	$\dfrac{k^{40°}CH_3COOH}{k^{40°}RCOOH}$	E, kcal./mole	PZ (×10^5)	$S^{\ddagger} - S_0^{\ddagger}$
		C (6)	H (5)	tot (4)	C (3)	H (2)	tot (6, 1)							
1 CH₃COOH[d]	...	0	0	0	0	0	0	44.0	81.4	132	1	10.0	12	0
2 CH₃CH₂COOH[d]	Mono	0	0	3	0	0	0	40.0	67.0	111	1.19	10.0	10	-0.07
3 CH₃CH₂CH₂COOH[d]	Mono	1	2	3	0	3	3	21.1	37.2	65.2	2.02	10.0	6.2	-1.42
4 Higher alkanoic[d]	Mono	1	2	3	1	2	3				2.02 ave.			
5 (CH₃)₂CHCOOH[e]	Di	0	6	6	0	0	0	14.7	26.3	44.0	3.00	9.8	3.0	-2.88
6 (CH₃)₃CCOOH[f]	Tri	0	9	9	0	0	0	1.40	2.68	4.93	26.8	11.4	4.5	-2.10
7 (CH₃)₂CHCH₂COOH[e]	Mono	2	1	3	0	6	6	4.88	8.77	15.4	8.57	10.0	1.5	-4.44
8 (CH₃)₃CCH₂COOH[g]	Mono	3	0	3	0	9	9	0.814	1.59	3.09	42.7	12.2	10.0	-0.36
9 (CH₃)₂CHCH₂CH₂COOH[e]	Mono	1	2	3	2	1	3	22.4	38.3	63.4	2.08	9.6	3.2	-2.73
10 (CH₃)₃CCH₂CH₂COOH[g]	Mono	1	2	3	3	0	3	20.4	35.9	61.1	2.16	10.0	5.8	-1.44
11 CH₃CH₂CH(CH₃)COOH[e]	Di	1	5	6	0	3	3	4.05	7.20	13.1	10.1	10.4	2.4	-3.35
12 (CH₃)₃CCH(CH₃)COOH[g]	Di	3	3	6	0	9	9		0.0397	0.0817	1616	13.6	2.6	-3.05
13 (CH₃)₃CC(CH₃)₂COOH[g]	Tri	3	6	9	0	9	9			0.0170	7765			
14 (CH₃)₃CCH₂CH(CH₃)COOH[g]	Di	1	5	6	3	0	3	0.629	1.13	2.03	65.0	11.1	1.1	-4.85
15 (CH₃)₃CCH₂C(CH₃)₂COOH[g]	Tri	1	8	9	3	0	3	0.106	0.22	0.435	303	12.7	3.1	-2.68
16 (CH₃)₃CCHCH(C₂H₅)COOH[g]	Di	3	3	6	0	9	9		0.0380	0.0780	1692	13.6	2.3	-3.28
17 (CH₃CH₂)₃CCOOH[g]	Tri	3	6	9	0	9	9			0.0214	6170			
18 (CH₃CH₂)₂CHCOOH[f]	Di	2	4	6	0	6	6	0.351	0.711	1.32	100	12.4	6.0	-1.89
19 [(CH₃)₂CH]₂CHCOOH[h]	Di	4	2	6	0	12	12	Too slow						
20 (CH₃CH₂CH₂)₂CHCOOH[f]	Di	2	4	6	2	4	6	0.297	0.631	1.22	108	12.4	5.5	-1.76
21 (n-C₄H₉)₂CHCOOH[f]	Di	2	4	6	2	4	6	0.267	0.553	1.10	120	12.9	11	-0.27
22 [(CH₃)₂CHCH₂]₂CHCOOH[f]	Di	2	4	6	4	2	6	0.140	0.278	0.547	241	12.6	3.4	-2.58
23 [(CH₃)₃CCH₂]₂CHCOOH[g]	Di	2	4	6	6	0	6	0.0274	0.0562	0.115	1150	13.5	3.0	-2.76
24 (CH₃)₃CCH(C₂H₅)COOH[g]	Di	4	2	6	0	12	12	Too slow						
25 (CH₃)₃CCH₂C[C(CH₃)₃]COOH[g] / CH₃	Tri	4	5	9	3	9	12	Too slow						
26 (CH₃)₃CCH(C₂H₅)CH₂CH₂COOH[g]	Mono	1	2	3	3	1	3	4.34	7.70	13.4	9.85	10.5	2.6	-3.05

[a] Organic acid 0.5 mole/l. [b] Type of substituted acetic acid. [c] k expressed in liters per mole per second. [d] Data from H. A. Smith, THIS JOURNAL, 61, 254 (1939). [e] Data from H. A. Smith, ibid., 61, 1176 (1939). [f] Data from H. A. Smith, ibid., 62, 1136 (1940). [g] Data obtained in this work. [h] J. von Braun and F. Fischer, Ber., 66, 101 (1933), reported that they were unable to esterify this acid. We did not measure the rate.

of the three acids, 8, 16 and 17 (each having a six number of nine) the rates of esterification should be 8 > 16 > 17 has been verified. This points up the importance of branching in cases where the six number does not change.

Another noteworthy observation may be made by considering the following series of acids: 8, 12 and 13; 10, 14 and 15. It is noteworthy that a greater decrease in rate is made when the first α-hydrogen is substituted by methyl (8/12, 37.8-fold; 10/14, 30-fold) than when the second α-hydrogen is substituted (12/13, 4.7-fold; 14/15,

4.6-fold). This is not the case in the less highly branched series 2, 5 and 6.

An interesting series is provided by the di-substituted acetic acids. Of those which have a six number of six, the rate decreases as the atoms in the six position change from hydrogen to carbon (i.e., 18, 20, 21, 22 and 23 in order of decreasing rate). As the six number increases to nine (acid 16) the rate takes a marked drop, and when the six number reaches twelve (acids 19 and 24) the rate becomes too slow to measure.

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