58. *The Use of Thiophen as a Chain Extender. Part II.*[1] *Synthetic Branched-chain Alkanoic Acids.*

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The preparation of 10-methylundecanoic, 10-methyldodecanoic, 12-methyltridecanoic, 12-methyltetradecanoic, 16-methylheptadecanoic, and 16-methyloctadecanoic acid, and of some intermediates, by desulphurisation of suitably 2,5-disubstituted thiophens with Raney nickel is described. The preparation of undecanoic acid by the same method is also described.

The synthesis of branched-chain aliphatic acids is of considerable interest in view of their wide distribution in Nature. Although a number of such acids has been obtained from a variety of sources,[2, 3] including tubercle bacilli [4] and *Mycobacterium smegmatis*,[5] their widest distribution is probably to be found in wool wax.[6] The branched-chain acid constituents of degras belong to the *iso*- and *anteiso*-series, and several of these have been prepared by Milburn and Truter [7] by anodic syntheses. The interest in these acids has stimulated much research in this field,[7, 8] and the use of thiophen as a chain extender seemed a convenient way of synthesising such compounds. The preparation of 5-ethyloctanoic [9] and other branched-chain acids [10] by this method has already been described.

[1] Part I, *J.*, 1960, 1502.

[2] Hansen, Shorland, and Cooke, *Chem. and Ind.*, 1951, 839; 1953, 516; 1956, 1149; *Biochem. J.*, 1952, **50**, 207, 358; 1952, **52**, 203; 1953, **53**, 374; 1954, **58**, 358; 1955, **61**, 141, 547; 1956, **64**, 214; Shorland, Gerson, and Hansen, *ibid.*, 1955, **59**, 350; **61**, 702; Morice and Shorland, *ibid.*, 1956, **64**, 214; *Chem. and Ind.*, 1952, 1267; Weitzel and Lennert, *Z. physiol. Chem.*, 1951, **288**, 251.

[3] Hansen, Shorland, and Cooke, *Chem. and Ind.*, 1954, 1229.

[4] Anderson and Chargaff, *J. Biol. Chem.*, 1929, **85**, 77; Spielman, *ibid.*, 1934, **106**, 87; Cason, Sumrell, Allen, Gillies, and Elberg, *ibid.*, 1953, **205**, 435; Spielman and Anderson, *ibid.*, 1936, **112**, 759; Stenhagen and Ställberg, *ibid.*, 1941, **139**, 345; Polgar and Robinson, *J.*, 1945, 389; David, Polgar, and Robinson, *J.*, 1949, 1541; Polgar, Robinson, and Seijo, *ibid.*, p. 1545; Cason and Sumrell, *J. Biol. Chem.*, 1951, **192**, 405; Chanley and Polgar, *J.*, 1954, 1003; Polgar, *ibid.*, pp. 1008, 1011.

[5] Barbier and Lederer, *Angew. Chem.*, 1954, **66**, 155; *Biochim. Biophys. Acta*, 1954, **14**, 246.

[6] Weitkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 447.

[7] Milburn and Truter, *J.*, 1954, 3344.

[8] Hougen, Ilse, Sutton, and de Villiers, *J.*, 1953, 98.

[9] Badger, Rodda, and Sasse, *J.*, 1954, 4162.

[10] Sy, Buu-Hoï, and Xuong, *J.*, 1954, 1976; *Compt. rend.*, 1954, **239**, 1224, 1813; Sy, *Bull. Soc. chim. France*, 1955, **22**, 1175.

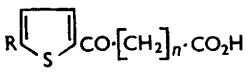
In the present work, eighteen 2,5-disubstituted thiophens of type I were prepared, where R = Me, Et, and Pr (n = 2 and 3), Bu, Bu^i, and 2-methylbutyl (n = 2, 3, 4, and 8). The alkylthiophens were prepared by acylation followed by reduction. The alkylthiophens were converted into acids of type (I) by reaction with succinic anhydride, glutaric anhydride, 5-methoxycarbonylpentanoyl chloride, and 9-ethoxycarbonylnonanoyl chloride. The melting points of these acids, and of some of their derivatives, are summarised in Table 1.

TABLE 1.

Substituted thiophen acids (I).

R	n	M. p.	2,4-Dinitrophenylhydrazone, m. p.	Me ester, m. p.
Me	2	112°	—	—
	3	118—120	231—232°	40—42°
Et	2	94—95[9]	—	—
	3	90—92	230—231	—
Pr	2	95—96	193—194	45—47
	3	87—88	209—210	45—47
Bu	2	94—95	158—159	44—46
	3	90	192—193	—
	4	66—68	159·5—160·5	—
	8	63—64[1]	109—110[1]	45—47
Bu^i	2	104—105	189—190	—
	3	113—114	190—191	—
	4	62—63	150—151	—
	8	56—58	—	—
CHMeEt·CH_2	2	92—94	189—190	—
	3	107—109	—	—
	4	59—60	—	—
	8	51—53	—	—

Of these acids, only the last eight yield branched-chain acids on desulphurisation and suitable reduction. Desulphurisation of the isobutyl and the 2-methylbutyl derivatives of type (I; n = 2, 4, and 8) and also of the acid (I; R = Et; n = 3) was carried out with Raney nickel (W7). The product, which was the crude hydroxy-acid, was either reduced by sodium borohydride or oxidised by Kiliani's chromic acid solution. The oxo-acids thus produced were then reduced to the alkanoic acids by the modified Wolff–Kishner procedure, the results being summarised in Table 2.



(I)

TABLE 2.

Desulphurisation products.

Acid (I) R	n	Lactone, b. p./mm.	Hydroxy-acid, m. p.	Oxo-acid, m. p.	Alkanoic acid	M. p.
Et	3	—	—	59—60°	Undecanoic	27—28°[11]
Bu^i	2	120—121°/0·4	—	70—72	10-Methylundecanoic	40—41[7]
	4	—	55—56°	61—62	12-Methyltridecanoic	53—54[7, 8]
	8	—	60—61	71—72[12]	16-Methylheptadecanoic	69—70[8]
CHMeEt·CH_2	2	119—121/0·3	—	67—68	10-Methyldodecanoic	Solid at 0°[3]
	4	—	—	45—46	12-Methyltetradecanoic	24—26[13]
	8	—	46—47	53—54[14]	16-Methyloctadecanoic	50—51[14]

EXPERIMENTAL

2-Methylthiophen.—Thiophen-2-aldehyde, prepared as described by Weston and Michaels[15] (78%), b. p. 90—93°/25 mm., was reduced by the modified Wolff–Kishner procedure according to King and Nord[16] to 2-methylthiophen (60%), b. p. 111—113°.

[11] Pickard and Kenyon, *J.*, 1913, **103**, 1947.
[12] Fordyce and Johnson, *J. Amer. Chem. Soc.*, 1933, **53**, 3368.
[13] Weitzel and Wojahn, *Z. physiol. Chem.*, 1951, **287**, 65.
[14] Cason and Prout, *J. Amer. Chem. Soc.*, 1944, **66**, 46.
[15] Weston and Michaels, *J. Amer. Chem. Soc.*, 1950, **72**, 1422.
[16] King and Nord, *J. Org. Chem.*, 1949, **14**, 641.

2-Ethylthiophen.—2-Acetylthiophen, prepared as described by Hartough and Kosack [17] (76%), b. p. 78—79°/25 mm., was similarly reduced to 2-ethylthiophen (86%), b. p. 132—134°.

2-Propylthiophen and 2-Butylthiophen.—Similar methods gave these two compounds (50% and 58% overall), b. p. 158—160° and 181—183°, respectively.

2-Isobutylthiophen.—(*a*) Freshly distilled anhydrous stannic chloride (131 g.) was added with stirring during 30 min. to thiophen (42 g.) and isobutyryl chloride (53·2 g.) in anhydrous benzene (500 c.c.) at 0°. After a further hr., 10% hydrochloric acid (360 c.c.) was added, and the benzene layer was separated and washed with sodium carbonate solution. Removal of the solvent and distillation gave *2-isobutyrylthiophen* (74%), b. p. 102°/20 mm. The *2,4-dinitrophenylhydrazone*, orange plates from ethanol, had m. p. 156—157° (Found: C, 50·1; H, 4·6. $C_{14}H_{14}N_4O_4S$ requires C, 50·3; H, 4·2%).

(*b*) Phosphorus pentoxide (71 g.) was added to thiophen (60 g.) and isobutyric acid (40 g.) in dry benzene (450 c.c.). After 3 hr. under reflux, the benzene solution was decanted, and the sludge was repeatedly extracted with benzene. Removal of the solvent and distillation gave 2-isobutyrylthiophen (64%). Reduction as above gave *2-isobutylthiophen* (71%), b. p. 172°, n_D^{20} 1·49871 (Found: C, 68·7; H, 8·5. $C_8H_{12}S$ requires C, 68·5; H, 8·6%).

2-2′-Methylbutylthiophen.—2-α-Methylbutyrylthiophen (73%), b. p. 114°/20 mm., was prepared by method (*b*) above. The *2,4-dinitrophenylhydrazone*, orange plates from ethanol, had m. p. 128—130° (Found: C, 51·7; H, 5·1. $C_{15}H_{16}N_4O_4S$ requires C, 51·7; H, 4·6%). Reduction gave *2-2′-methylbutylthiophen* (66%), b. p. 112—116°/25 mm., n_D^{20} 1·49721 (Found: C, 70·0; H, 8·9. $C_9H_{14}S$ requires C, 70·1; H, 9·1%).

β-(5-Alkyl-2-thenoyl)propionic Acids.—Crushed anhydrous aluminium chloride (30 g.) was added in 1 hr. to a solution of succinic anhydride (10 g.) and the alkylthiophen (0·12 mole) in nitrobenzene (100 c.c.) at 0°. After a further hr., the product was decomposed with dilute hydrochloric acid, and the nitrobenzene was removed in steam. The crude acid, which separated on cooling, crystallised from benzene–light petroleum (b. p. 60—80°). Thus were prepared:

β-(5-Methyl-2-thenoyl)propionic acid (76%), m. p. 112° (Found: C, 54·5; H, 4·9. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·1%).

β-(5-Ethyl-2-thenoyl)propionic acid [9] (82%), m. p. 94—95°.

β-(5-Propyl-2-thenoyl)propionic acid (71%), m. p. 95—96° (Found: C, 58·3; H, 6·0. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2%). The *2,4-dinitrophenylhydrazone*, red needles from ethanol, had m. p. 193—194° (Found: C, 49·8; H, 4·6. $C_{17}H_{18}N_4O_6S$ requires C, 50·2; H, 4·5%). Ethereal diazomethane yielded the *methyl ester*, needles [from light petroleum (b. p. 60—80°)], m. p. 45—47° (Found: C, 60·2; H, 6·9. $C_{12}H_{16}O_3S$ requires C, 60·0; H, 6·7%).

β-(5-Butyl-2-thenoyl)propionic acid (79%), m. p. 94—95° (Found: C, 60·3; H, 6·7. $C_{12}H_{16}O_3S$ requires C, 60·0; H, 6·7%). The *2,4-dinitrophenylhydrazone*, red needles from ethanol, had m. p. 158—159° (Found: C, 51·3; H, 5·2. $C_{18}H_{20}N_4O_6S$ requires C, 51·4; H, 4·8%). The *methyl ester*, needles from light petroleum (b. p. 40—60°), had m. p. 44—46° (Found: C, 61·0; H, 7·4. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1%).

β-(5-Isobutyl-2-thenoyl)propionic acid (84%), m. p. 104—105° (Found: C, 60·3; H, 6·2. $C_{12}H_{16}O_3S$ requires C, 60·0; H, 6·7%). The *2,4-dinitrophenylhydrazone*, red needles from ethanol, had m. p. 189—190° (Found: C, 51·6; H, 4·4. $C_{18}H_{20}N_4O_6S$ requires C, 51·4; H, 4·8%).

β-(5-2′-Methylbutyl-2-thenoyl)propionic acid (74%), m. p. 92—94° (Found: C, 61·3; H, 6·9. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1%). The *2,4-dinitrophenylhydrazone*, red needles from ethanol, had m. p. 189—190° (Found: C, 52·5; H, 4·8. $C_{19}H_{22}N_4O_6S$ requires C, 52·5; H, 5·1%).

γ-(5-Alkyl-2-thenoyl)butyric Acids.—Glutaric acid (60 g.) and acetic anhydride (100 c.c.) were heated for 1 hr. at 100°. Acetic acid and anhydride were distilled off, and the glutaric anhydride (70%), after distillation, b. p. 160°/20 mm., solidified and had m. p. 55—57°. With glutaric anhydride in place of succinic anhydride as above, the following substituted butyric acids were obtained:

γ-(5-Methyl-2-thenoyl)butyric acid (72%), m. p. 118—120° (Found: C, 56·8; H, 5·8. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·7%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 231—232° (Found: C, 49·2; H, 4·3. $C_{16}H_{16}N_4O_6S$ requires C, 49·0; H, 4·1%); *methyl*

[17] Hartough and Kosack, *J. Amer. Chem. Soc.*, 1948, **70**, 3093.

ester, needles, m. p. 40—42°, from light petroleum (b. p. 40—60°) (Found: C, 57·9; H, 6·2. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2%)].

γ-(5-Ethyl-2-thenoyl)butyric acid (71%), m. p. 90—92° (Found: C, 58·5; H, 6·1. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 230—231° (Found: C, 50·0; H, 4·6. $C_{17}H_{18}N_4O_6S$ requires C, 50·2; H, 4·5%)].

γ-(5-Propyl-2-thenoyl)butyric acid (67%), m. p. 87—88° (Found: C, 59·5; H, 6·4. $C_{12}H_{16}O_3S$ requires C, 60·0; H, 6·7%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 209—210° (Found: C, 51·9; H, 4·7. $C_{18}H_{20}N_4O_6S$ requires C, 51·4; H, 4·8%); *methyl ester*, needles, m. p. 45—47°, from light petroleum (b. p. 40—60°) (Found: C, 61·5; H, 7·0. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1%)].

γ-(5-Butyl-2-thenoyl)butyric acid (81%), m. p. 90° (Found: C, 61·1; H, 7·1. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 192—193° (Found: C, 52·8; H, 5·3. $C_{19}H_{22}N_4O_6S$ requires C, 52·5; H, 5·1%)].

γ-(5-Isobutyl-2-thenoyl)butyric acid (79%), m. p. 113—114° (Found: C, 61·2; H, 7·4. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 190—191° (Found: C, 53·0; H, 5·4. $C_{19}H_{22}N_4O_6S$ requires C, 52·5; H, 5·1%)].

γ-(5-2′-Methylbutyl-2-thenoyl)butyric acid (62%), m. p. 107—109° (Found: C, 63·2; H, 7·8. $C_{14}H_{20}O_3S$ requires C, 62·7; H, 7·5%).

δ-(5-Alkyl-2-thenoyl)valeric Acids.—(*a*) A mixture of dimethyl adipate (202 g.), adipic acid (292 g.), dibutyl ether (100 c.c.), and hydrochloric acid (50 c.c.) was heated under reflux until homogeneous. The solution was cooled to 60°, and methanol (80 c.c.) was added. After 2 hr. under reflux, more methanol (30 c.c.) was added, and heating was continued for a further 2 hr. The portion of b. p. 138—140°/2 mm. was redistilled, to give methyl hydrogen adipate (83 g.). This was heated under reflux with thionyl chloride (250 c.c.) for 2 hr. Removal of the excess of thionyl chloride and distillation (b. p. 141°/36 mm.) gave 5-methoxycarbonylpentanoyl chloride (90 g.).

Freshly distilled stannic chloride (120 g.) was added at 0° during 1 hr. to a stirred solution of 2-butylthiophen (64 g.) and 5-methoxycarbonylpentanoyl chloride (82 g.) in benzene (500 c.c.). After 2 hours' stirring, the product was treated with 10% hydrochloric acid (350 c.c.), and the benzene layer was separated, washed with sodium carbonate solution, and evaporated. The residual oil was heated under reflux for 3 hr. with potassium hydroxide (100 g.) in ethanol (500 c.c.). Acidification produced a yellow solid, which, on recrystallisation from benzene–light petroleum (b. p. 60—80°), yielded pale yellow needles of *δ-(5-butyl-2-thenoyl)valeric acid* (66%), m. p. 66—68° (Found: C, 62·4; H, 7·3. $C_{14}H_{20}O_3S$ requires C, 62·7; H, 7·5%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 159·5—160·5° (Found: C, 53·4; H, 5·8. $C_{20}H_{24}N_4O_6S$ requires C, 53·6; H, 5·4%)].

Similarly prepared were:

δ-(5-Isobutyl-2-thenoyl)valeric acid (63%), m. p. 62—63° (Found: C, 63·1; H, 7·6. $C_{14}H_{20}O_3S$ requires C, 62·7; H, 7·5%) [*2,4-dinitrophenylhydrazone*, red needles (from ethanol), m. p. 150—151° (Found: C, 53·1; H, 5·7. $C_{20}H_{24}N_4O_6S$ requires C, 53·6; H, 5·4%)].

δ-(5-2′-Methylbutyl-2-thenoyl)valeric acid (51%), m. p. 59—60° (Found: C, 63·5; H, 7·6. $C_{15}H_{22}O_3S$ requires C, 63·8; H, 7·8%).

9-(5-Alkyl-2-thenoyl)nonanoic Acids.—(*a*) 9-(5-Butyl-2-thenoyl)nonanoic acid and its 2,4-dinitrophenylhydrazone were prepared as described previously.[1] The *methyl ester* had m. p. 45—47°, after crystallisation from light petroleum (b. p. 40—60°) (Found: C, 67·6; H, 9·4. $C_{19}H_{30}O_3S$ requires C, 67·4; H, 8·9%).

Similarly prepared were:

9-(5-Isobutyl-2-thenoyl)nonanoic (80%), m. p. 56—58° (Found: C, 66·6; H, 8·3. $C_{18}H_{28}O_3S$ requires C, 66·7; H, 8·7%), and *9-(5-2′-methylbutyl-2-thenoyl)nonanoic acid* (80%), m. p. 51—53° (Found: C, 67·4; H, 8·4. $C_{19}H_{30}O_3S$ requires C, 67·4; H, 8·9%).

5-Oxoundecanoic Acid.—Raney nickel (25 g.) (W7) [18] was added to γ-(5-ethyl-2-thenoyl)-butyric acid (5 g.) in N-sodium carbonate (125 c.c.). The mixture was heated for 2 hr. on a water-bath with shaking. The product was filtered, and the nickel residue was washed repeatedly with sodium carbonate solution. The combined sodium carbonate solutions were poured into an excess of dilute hydrochloric acid at 0°. Kiliani's chromic acid solution (25 c.c.) was added with stirring in 10 min. at 0° to the precipitated acid dissolved in benzene (40 c.c.) and acetic acid (6 c.c.). Stirring was continued for 15 min. at room temperature, and the

[18] Billica and Adkins, *Org. Synth.*, 1949, **29**, 24.

excess of oxidant was then decomposed with sulphur dioxide. Evaporation of the separated benzene layer, followed by crystallisation from light petroleum (b. p. 60—80°), yielded *5-oxoundecanoic acid* (3·5 g.), m. p. 59—60° (Found: C, 66·1; H, 10·2. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%). Reduction of a sample by the modified Wolff–Kishner process gave an oil, which deposited undecanoic acid, m. p. 27—28° (Pickard and Kenyon [11] give m. p. 28°) from a solution in light petroleum (b. p. 40—60°) after 24 hr. at −10°.

10-*Methylundecanoic Acid*.—β-(5-Isobutyl-2-thenoyl)propionic acid (5·0 g.) in N-sodium carbonate solution (200 c.c.) was stirred under reflux for 3 hr. with freshly prepared Raney nickel (W7) [18] (35 g.). The product was filtered, and the residue was washed with sodium carbonate solution (2 × 75 c.c.). The combined sodium carbonate solutions were poured into an excess of dilute hydrochloric acid at 0°. The product was extracted with benzene (3 × 50 c.c.), and the combined extracts were washed with water until neutral, dried (Na_2SO_4), and evaporated. Distillation yielded *4-hydroxy-10-methylundecanoic acid lactone* (3·1 g.), b. p. 120—121°/0·4 mm., n_D^{21} 1·4490 (Found: C, 72·3; H, 11·4. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·2%) (band at 1770 cm.$^{-1}$).

The lactone (0·8 g.) in acetic acid (10 c.c.) was added to sodium dichromate dihydrate (0·7 g.) in water (0·7 c.c.), sulphuric acid (0·3 c.c.), and acetic acid (6 c.c.). After 3 hr. at room temperature, the product was heated at 100° for 1 hr. After cooling, the product was poured into water (75 c.c.), and the precipitated acid was filtered off, washed with water, and dried. Crystallisation from light petroleum (b. p. 60—80°) gave *10-methyl-4-oxoundecanoic acid* (0·6 g.), m. p. 70—72° (Found: C, 66·9; H, 10·7. $C_{12}H_{22}O_3$ requires C, 67·2; H, 10·4%). Reduction of a sample (2·5 g.) by the modified Wolff–Kishner method gave 10-methylundecanoic acid (1·2 g.), m. p. 40—41°, after crystallisation from light petroleum (b. p. 40—60°) (Milburn and Truter [7] give m. p. 41°).

12-*Methyltridecanoic Acid*.—δ-(5-Isobutyl-2-thenoyl)valeric acid (5·0 g.) was desulphurised with Raney nickel (W7) as described above. The usual method gave a colourless solid (3·3 g.), m. p. 46—48°. This product (2·5 g.) in methanol (30 c.c.) was treated with sodium borohydride (1·5 g.) at room temperature. Next day, the product was poured into water (100 c.c.) and acidified with 2N-hydrochloric acid. The product was filtered off, washed, and dried. Crystallisation from light petroleum (b. p. 60—80°) gave *6-hydroxy-12-methyltridecanoic acid* (2·3 g.), m. p. 55—56° (Found: C, 69·1; H, 11·8. $C_{14}H_{28}O_3$ requires C, 68·8; H, 11·6%).

The desulphurisation product (0·8 g.), on chromic acid oxidation by the method previously described and crystallisation from light petroleum (b. p. 60—80°), gave *12-methyl-6-oxotridecanoic acid* (0·6 g.), m. p. 61—62° (Found: C, 69·6; H, 11·1. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·8%). Reduction of this acid (2·5 g.) gave 12-methyltridecanoic acid (1·4 g.), m. p. 53—54° after crystallisation from light petroleum (b. p. 60—80°) (Hougen *et al.*[8] give m. p. 53·3—53·6°).

16-*Methylheptadecanoic Acid*.—9-(5-Isobutyl-2-thenoyl)nonanoic acid (5·5 g.) on desulphurisation with Raney nickel (W7) and working up in the usual way yielded a product (3·0 g.), m. p. 59—60°, after crystallisation from light petroleum (b. p. 60—80°). Sodium borohydride reduction of this material (1·2 g.) gave *10-hydroxy-16-methylheptadecanoic acid* (0·9 g.), m. p. 60—61° after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 72·3; H, 12·0; $C_{18}H_{36}O_3$ requires C, 72·0; H, 12·1%). The desulphurisation product (1·5 g.), on chromic acid oxidation by the method previously described and crystallisation from benzene–light petroleum (b. p. 60—80°), gave 16-methyl-10-oxoheptadecanoic acid (1·2 g.), m. p. 71—72° (Fordyce and Johnson [12] give m. p. 71·2—72°). Reduction of this acid (2·5 g.) gave 16-methylheptadecanoic acid (1·9 g.), m. p. 69—70°, after crystallisation from light petroleum (b. p. 60—80°) (Hougen *et al.*[8] give m. p. 69·5—69·7°).

10-*Methyldodecanoic Acid*.—β-(5-2′-Methylbutyl-2-thenoyl)propionic acid (5 g.) on desulphurisation with Raney nickel (W7) in the usual way gave an oil (2·0 g.). Sodium borohydride reduction of this material (2·0 g.) gave *4-hydroxy-10-methyldodecanoic acid lactone* (1·6 g.), b. p. 119—121°/0·3 mm., n_D^{21} 1·4528 (Found: C, 73·6; H, 11·6. $C_{13}H_{24}O_2$ requires C, 73·5; H, 11·4%) (band at 1783 cm.$^{-1}$). Oxidation of this lactone (1·4 g.) in the usual way yielded *10-methyl-4-oxododecanoic acid* (1·1 g.), m. p. 67—68°, after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 68·8; H, 10·8. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·6%). This oxo-acid (1·1 g.) on reduction yielded 10-methyldodecanoic acid (0·8 g.) as an oil, which solidified at 0° (Hansen, Shorland, and Cooke [3] give m. p. 4°).

12-*Methyltetradecanoic Acid*.—δ-(5-2′-Methylbutyl-2-thenoyl)valeric acid (3·7 g.) on

desulphurisation by Raney nickel (W7) gave a sticky solid (2·0 g.). Chromic acid oxidised this solid (2·0 g.) to **12-*methyl*-6-*oxotetradecanoic acid*** (1·7 g.), m. p. 45—46° [from light petroleum (b. p. 40—60°)] (Found: C, 69·9; H, 11·0. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%). This oxo-acid (1·1 g.) on reduction yielded a pale-yellow sticky solid (0·7 g.). From light petroleum (b. p. 60—80°) at 0°, 12-methyltetradecanoic acid, m. p. 24—26°, was obtained (Weitzel and Wojahn [13] give m. p. 26·5—27°).

16-*Methyloctadecanoic Acid*.—9-(5-2′-Methylbutyl-2-thenoyl)nonanoic acid (4·9 g.) on desulphurisation by Raney nickel (W7) gave a solid (3·2 g.). This product (3·2 g.) with sodium borohydride gave, after crystallisation from benzene–light petroleum (b. p. 60—80°), **10-*hydroxy*-16-*methyloctadecanoic acid*** (3·0 g.), m. p. 46—47° (Found: C, 72·9; H, 12·3. $C_{19}H_{38}O_3$ requires C, 72·6; H, 12·2%). 9-(5-2′-Methylbutyl-2-thenoyl)nonanoic acid (5·0 g.) on reduction by Raney nickel alloy, followed by chromic acid oxidation as previously described and crystallisation from light petroleum (b. p. 60—80°), gave 16-methyl-10-oxo-octadecanoic acid (4·1 g.), m. p. 53—54° (Cason and Prout [14] give m. p. 52·7—54·1°). This oxo-acid (3·0 g.) was reduced by the modified Wolff–Kishner method to 16-methyloctadecanoic acid (2·1 g.), m. p. 50—51° (Cason and Prout [14] give m. p. 49·9—50·6°).

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