

The Components of Wool Wax. Part II. Synthesis of the Acids
and Alcohols of the iso- and the (+)-anteiso-Series.*

By A. H. MILBURN and E. V. TRUTER.

[Reprint Order No. 5348.]

Acids of the *iso*-series (12 members up to C₂₈) and of the optically active (+)-*anteiso*-series (13 members up to C₃₁) have been prepared by anodic syntheses. These have been reduced to the corresponding alcohols, and derivatives of the acids and the alcohols have been prepared.

EXTENDED distillation of the methyl esters of the acidic fraction of wool wax has revealed the presence of no less than thirty-two acids, all containing more than 8 carbon atoms (Weitkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 447). These fall into four groups: normal, α -hydroxy-, *iso*- (terminal *iso*-propyl group) and *anteiso*-acids (terminal CHMeEt group). Identification of the branched-chain acids is based on a special mixed-melting-point analysis, by which it is possible to locate the position at which the carbon chain branches, and on physical measurements which indicate that the series are homologous. Several

* Part I, *J.*, 1952, 4628.

iso-acids have been synthesised but only in occasional instances is a synthetic *anteiso*-acid available for a direct comparison.

Four exactly parallel groups have been identified among the aliphatic alcohols of wool wax. Here, identification of the members of the two branched-chain series rest on oxidation to the corresponding acid and comparison with Weitkamp's data (Murray and Schoenfeld, *J. Amer. Oil Chem. Soc.*, 1952, **29**, 416). The syntheses recorded below provide material for a direct comparison of both the acids and the alcohols; in addition, several derivatives of each have been prepared in order to facilitate future reference.

In the *iso*-series the C₁₄, C₁₆, and C₁₈ acids were synthesised by Fordyce and Johnson (*J. Amer. Chem. Soc.*, 1933, **55**, 3368) by the action of Grignard reagents on the ester acid chlorides of dicarboxylic acids, and subsequent reduction of the resultant keto-esters. Stenhagen and his collaborators (*Arkiv Kemi Min., Geol.*, 1945, **19**, A, No. 8; 1949, **26**, A, No. 19) synthesised the C₁₄, C₁₆, C₁₈, C₂₄, and C₂₆ *iso*-acids by condensation of an ω -iodo-ester with the ester of a β -keto-*iso*-acid, followed by decarboxylation of the product and reduction of the resultant keto-acid to the *iso*-acid. Anodic coupling reactions have been used by Hougen, Ilse, Sutton, and Villiers (*J.*, 1953, 98) for the synthesis of the C₁₀, C₁₂, C₁₄, C₁₈, and C₂₀ *iso*-acids. The three lowest members were also synthesised by an alternative route. Buu-Hoï (*Rec. Trav. chim.*, 1953, **72**, 84) prepared 14-methylpentadecanoic acid by condensing *isovaleraldehyde* with ethyl undec-10-enoate.

In the *anteiso*-series only two of the optically active acids and one corresponding alcohol have been prepared. English and Velick (*J. Biol. Chem.*, 1945, **160**, 473) synthesised (+)-14-methylhexadecanoic acid from natural (–)-2-methylbutanol. First, the chain was lengthened by three carbon atoms by reaction with allylmagnesium bromide. Hydrogen bromide was added on to the olefin, and this was treated, as a Grignard reagent, with methyl 9-oxononanoate. The product, methyl 9-hydroxy-14-methylhexadecanoate, was dehydrated, hydrogenated, and hydrolysed to yield the desired acid. Crombie and Harper (*J.*, 1950, 2685) prepared (+)-6-methyloctanoic acid by oxidation of the corresponding alcohol. Natural (–)-2-methylbutanol was the starting material, and this, after conversion into the Grignard reagent, was treated with 2:3-dichlorodihydrofuran. Alkaline ring scission of the product, followed by hydrogenation, yielded (+)-6-methyloctanol.

Two racemic acids (C₉ and C₁₉) have been synthesised by Cason and Prout (*J. Amer. Chem. Soc.*, 1944, **66**, 49) and five (C₁₁, C₁₃, C₁₅, C₁₇, and C₂₁) by Nunn (*J.*, 1951, 1740). The melting points of the racemic acids are consistently higher than those of the corresponding optically active acids. Attempts by Nunn to resolve the (\pm)-acids failed.

The method of preparation used here is the elegant cross-coupling anodic synthesis of Linstead and Weedon (*J.*, 1950, 3326, and subsequent papers). It gives a fairly high yield (about 30%) for compounds containing less than 22 carbon atoms and has the advantage that, by suitable choice of starting materials, the products of side reactions are easily separated. Electrolysis of a branched-chain acid with the half-ester of a dicarboxylic acid affords the ester of a longer, branched-chain acid together with a hydrocarbon and the ester of a dicarboxylic acid as unwanted by-products. By using an excess of the half-ester, wastage of the more valuable branched-chain acid in the side reactions can be considerably diminished.

In the *anteiso*-series the starting material was (–)-2-methylbutanol isolated by distillation from commercial amyl alcohol. For use in the electrode synthesis it was first necessary to lengthen the carbon chain in order to remove the methyl substituent from the α -position. In effect, therefore, the starting material was (+)-4-methylhexanoic acid, obtained by condensation of the bromide with ethyl malonate. The starting material for the *iso*-acid electrode syntheses was 4-methylpentanoic acid derived from *iso*amyl bromide via the nitrile.

The results presented here for the synthetic branched-chain alcohols are in complete agreement with the findings of Murray and Schoenfeld (*loc. cit.*) for the alcohols isolated from wool wax. Those for the natural and the synthetic acids are also in accord except in the case of (+)-16-methyloctadecanoic acid, for which the melting point observed for the synthetic acid is 1.5° higher than that recorded by either Weitkamp or Murray and Schoenfeld. For the amides there are differences exceeding 1° in three cases: 10-methyl-

undecanamide (2.3°), 18-methylnonadecanamide (2.1°), and (+)-10-methyldodecanamide (2.7°). For two other acids the melting points obtained by different workers are not entirely self-consistent :

	12-Methyltridecanoic acid	amide	16-Methylheptadecanoic acid	amide
Fordyce and Johnson	50.0—50.3°	—	67.8—68.2°	—
Stenhagen <i>et al.</i>	53.3—53.6	107.8°	67.8—68.5	106.4—106.8°
Hougen <i>et al.</i>	53.3—53.6	108.1—108.3	69.5—69.7	107.8—107.9
Milburn and Truter	51.5—52.0	108.0—108.5	67.5—68.0	106.4—106.5
Natural acid (Weitkamp)	53.3	107.3	69.5	107.3

Notwithstanding these differences, the structural assignments made by Weitkamp for the branched-chain wool wax acids are undoubtedly correct.

EXPERIMENTAL

M. p.s are corrected.

Electrolytic Cell.—The cell consisted of a glass cylinder of 1 l. capacity, fitted with a cooling coil, a reflux condenser, and two platinum electrodes (4 × 2.5 cm.). The electrolytic solvent was methanol (sufficient to cover the electrodes, 200—300 ml.) containing a small amount of sodium methoxide (1—2% based on the free acid content). Electrolysis was carried out at 1—2.5 amp., and was discontinued when the solution had become slightly alkaline (pH 7.5 or more). During the reaction the current always fell owing to gradual deposition of insulating polymer on the electrodes.

Treatment of the Electrolysate.—The *iso*-acids up to 16-methylheptadecanoic and the *anteiso*-acids up to 12-methyltetradecanoic acid were worked up by method A. Acids containing a greater number of carbon atoms were worked up by method B.

Method A.—The reaction mixture was neutralised with acetic acid, and the methanol was distilled off. An ethereal solution of the residue was washed with water and with aqueous sodium carbonate, dried (MgSO₄), and distilled through a short column into its constituent fractions.

Method B.—After removal of the methanol from the reaction mixture, the lower-boiling hydrocarbons were separated, where possible, by vacuum-distillation. The residue was hydrolysed in a small volume of alcoholic potassium hydroxide (3.5*N* in 90% ethanol). On acidification with dilute hydrochloric acid the free acids were precipitated and were filtered off. Treatment of the solids with cold light petroleum (b. p. 60—80°) extracted the monobasic acid and any residual hydrocarbon, while the dicarboxylic acid remained insoluble. The former were separated by alternate crystallisation from ethyl formate and light petroleum.

Derivatives.—All derivatives were prepared by accepted methods. The alcohols were obtained by reduction with lithium aluminium hydride. Equivalent weights of the acids were determined by titration against alcoholic 0.1*N*-sodium hydroxide (phenolphthalein).

Half Esters.—Methyl hydrogen succinate was obtained by the addition of methanol to succinic anhydride. Methyl hydrogen adipate and methyl hydrogen sebacate were prepared by the half-esterification of the corresponding acids (Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2352). Partial saponification of the diester was used for the preparation of the half esters of azelaic and suberic acid (Walker, *J.*, 1892, **61**, 709) and hexadecane-1 : 16-dicarboxylic acid (Hunsdiecker and Hunsdiecker, *Ber.*, 1942, **75**, 291).

Syntheses in the *iso*-Series.

4-Methylpentanoic Acid.—Redistilled *iso*amyl bromide (b. p. 120—122°; 102 g.) was heated with an 80% alcoholic solution of potassium cyanide (45 g. in 250 ml.) under reflux for 16 hr. Potassium bromide was filtered off, and the nitrile in the filtrate was hydrolysed by heating it for 16 hr. with potassium hydroxide (45 g.). Subsequently most of the solvent was distilled off. Acidification of the residual solution resulted in the separation of the free acid as a separate phase which was removed; ethereal extraction of the aqueous layer gave a further small amount of acid. The extract and the acid were combined, washed with water, and dried (MgSO₄), and the ether distilled off, to give 4-methylpentanoic acid (56 g.), b. p. 102—104°/13 mm. Similar yields were obtained in preparations on a larger scale.

4-Methylpentanol.—Over a period of 45 min. sodium (207 g.) was slowly added to a boiling

solution of ethyl 4-methylpentanoate (144 g.) in absolute ethanol (1800 ml.). After all the sodium had dissolved the mixture was diluted with water (700 ml.), the bulk of the ethanol was distilled off, and the residue was extracted with ether. The extract was washed and dried and the ether distilled off, to give 4-methylpentanol (74.5 g.), b. p. 152°.

1-Bromo-4-methylpentane.—4-Methylpentanol was refluxed for 3 hr. with 48% hydrobromic acid (152 g.) and sulphuric acid (82 g.). The products were distilled off, and the lower layer of the distillate was washed successively with water, concentrated hydrochloric acid, water, aqueous sodium carbonate, and water, and then dried (MgSO_4) and again distilled, to give 1-bromo-4-methylpentane (104 g.), b. p. 144—146°.

6-Methylheptanoic Acid.—During 90 min. 1-bromo-4-methylpentane (220 g.) was added to a hot solution of ethyl sodiomalonate (246 g.) in ethanol (800 ml.), and the mixture was heated under reflux for a further 2 hr. The bulk of the ethanol was then distilled off, potassium hydroxide in water (200 g. in 300 ml.) was added, and the mixture heated for 2 hr. The ethanol formed in the hydrolysis was distilled off and the residue refluxed for 3.5 hr. with sulphuric acid diluted with water (174 + 450 ml.). The mixture separated into two layers; the upper was drawn off, and the aqueous layer was extracted with ether. The extract was combined with the upper layer, and the solution was washed with water, dried (MgSO_4), and distilled, to give 6-methylheptanoic acid (144 g.), b. p. 128—129°/15 mm. (Found: equiv., 145. Calc.: equiv., 144) [amide, m. p. 114.3—114.6°; p-bromophenacyl ester, m. p. 67.7° (Found: C, 56.4; H, 6.0. $\text{C}_{16}\text{H}_{21}\text{O}_3\text{Br}$ requires C, 56.3; H, 6.2%)].

6-Methylheptanol had b. p. 187°/760 mm., n_D^{20} 1.4268, and gave a 3 : 5-dinitrobenzoate, m. p. 57.2—57.4° (Found: C, 55.9; H, 6.5. $\text{C}_{15}\text{H}_{20}\text{O}_6\text{N}_2$ requires C, 55.55; H, 6.2%), and phenylurethane, m. p. 80.7—81.0° (Found: C, 72.3; H, 9.0. $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$ requires C, 72.3; H, 9.2%).

8-Methylnonanoic Acid.—4-Methylpentanoic acid (76.5 g.) and methyl hydrogen adipate (52.5 g., 0.5 mol.) were electrolysed and worked up in the manner outlined above, to give 8-methylnonanoic acid (28%), m. p. 19.0° (Found: equiv., 174. Calc.: equiv., 172). It gave a p-bromophenacyl ester, m. p. 67.4—68.0° (Found: Br, 22.0. $\text{C}_{18}\text{H}_{25}\text{O}_3\text{Br}$ requires Br, 21.6%), benzimidazole derivative, m. p. 155.8—156.3° (Found: N, 12.0. $\text{C}_{16}\text{H}_{24}\text{N}_2$ requires N, 11.5%), amide, m. p. 103.0° (Weitkamp reports 103.1°), and anilide, m. p. 88.9—90.3° (Found: C, 77.4; H, 10.05. $\text{C}_{16}\text{H}_{25}\text{ON}$ requires C, 77.7; H, 10.1%).

8-Methylnonanol, b. p. 110—111°/11.5 mm., n_D^{20} 1.4352, gave a phenylurethane, m. p. 51.9—52.1° (Found: N, 5.3. $\text{C}_{17}\text{H}_{27}\text{O}_2\text{N}$ requires N, 5.05%), and a 3 : 5-dinitrobenzoate, m. p. 59.6° (Found: C, 57.9; H, 6.7. $\text{C}_{17}\text{H}_{24}\text{O}_6\text{N}_2$ requires C, 57.95; H, 6.9%).

10-Methylundecanoic Acid.—3-Methylbutyric acid (115 g.) and methyl hydrogen azelate (122 g.) gave 10-methylundecanoic acid (26%), m. p. 41.0° (Found: equiv., 199. Calc.: equiv., 200); Hougén *et al.* give 41.4—41.5°; Weitkamp reports 41.2°. Its amide had m. p. 105.7° (Hougén *et al.* give 108.1—108.4°; Weitkamp reports 108.0°) (Found: N, 7.2. Calc. for $\text{C}_{12}\text{H}_{25}\text{ON}$: N, 7.0%), its anilide m. p. 64.5—64.8° (Found: C, 78.4; H, 10.3. $\text{C}_{18}\text{H}_{29}\text{ON}$ requires C, 78.5; H, 10.6%), and its p-bromophenacyl ester, m. p. 69.7—70.3° (Found: Br, 22.0. $\text{C}_{20}\text{H}_{29}\text{O}_3\text{Br}$ requires Br, 21.65%).

10-Methylundecanol, b. p. 147—149°/18 mm., n_D^{20} 1.4412 (Found: C, 77.3; H, 14.1. $\text{C}_{12}\text{H}_{26}\text{O}$ requires C, 77.35; H, 14.1%), gave a 3 : 5-dinitrobenzoate, m. p. 57.5—57.8° (Found: C, 60.3; H, 7.5. $\text{C}_{19}\text{H}_{25}\text{O}_6\text{N}_2$ requires C, 60.0; H, 7.4%), and phenylurethane, m. p. 71.2—72.0° (Found: N, 4.6. $\text{C}_{19}\text{H}_{31}\text{O}_2\text{N}$ requires N, 4.6%).

12-Methyltridecanoic Acid.—4-Methylpentanoic acid (98 g.) and methyl hydrogen sebacate (183 g.) were electrolysed to give 12-methyltridecanoic acid (28.5%), m. p. 51.5—52.0° (Found: C, 73.3; H, 12.1. Calc. for $\text{C}_{14}\text{H}_{28}\text{O}_2$: C, 73.6; H, 12.35%), giving an amide, m. p. 108.0—108.5° (Found: N, 5.9. Calc. for $\text{C}_{14}\text{H}_{29}\text{ON}$: N, 6.15%), anilide, m. p. 75.1° (Found: C, 79.3; H, 10.8. $\text{C}_{20}\text{H}_{33}\text{ON}$ requires C, 79.2; H, 10.95%), and p-bromophenacyl ester, m. p. 71.5—72.0° (Found: Br, 18.75. $\text{C}_{22}\text{H}_{33}\text{O}_3\text{Br}$ requires Br, 18.8%).

12-Methyltridecanol, b. p. 161—163°/11 mm., m. p. 16.0°, n_D^{20} 1.4464 (Found: C, 78.6; H, 13.9. $\text{C}_{14}\text{H}_{30}\text{O}$ requires C, 78.4; H, 14.1%), gave a 3 : 5-dinitrobenzoate, m. p. 62.2—63.0° (Found: N, 7.2. $\text{C}_{21}\text{H}_{32}\text{O}_6\text{N}_2$ requires N, 6.9%), and phenylurethane, m. p. 66.5—67.0° (Found: N, 4.35. $\text{C}_{21}\text{H}_{35}\text{O}_2\text{N}$ requires N, 4.2%).

14-Methylpentadecanoic Acid.—6-Methylheptanoic acid (86 g.) was electrolysed together with methyl hydrogen sebacate (129.6 g.) to give 14-methylpentadecanoic acid (29%), m. p. 61.4—62.0° (Found: C, 75.1; H, 12.3. Calc. for $\text{C}_{16}\text{H}_{32}\text{O}_2$: C, 74.95; H, 12.6%). Weitkamp reports 62.4°. For the synthetic acid Fordyce *et al.* report 61.8—62.4°, and Stenhagen *et al.* 61.6°. The acid gave a benzimidazole derivative, m. p. 101.0—101.5° (Found: N, 8.6. $\text{C}_{22}\text{H}_{36}\text{N}_2$ requires N, 8.5%), amide, m. p. 102.8° (Weitkamp reports 102.1°; Stenhagen *et al.*

report 101.4—101.7° (Found : N, 5.7. Calc. for $C_{16}H_{33}ON$: N, 5.5%), *anilide*, m. p. 82.0—82.2° (Found : C, 79.5; H, 11.05. $C_{22}H_{37}ON$ requires C, 79.7; H, 11.2%), and *p*-bromophenacyl ester, m. p. 76.6—77.1°.

14-Methylpentadecanol, m. p. 30.0° (Stenhagen *et al.* report 29.4—30.4°) (Found : C, 79.3; H, 14.05. Calc. for $C_{16}H_{34}O$: C, 79.25; H, 14.15%), gave a 3 : 5-dinitrobenzoate, m. p. 67.0—67.3° (Found : C, 63.3; H, 8.25. $C_{23}H_{36}O_6N_2$ requires C, 63.3; H, 8.3%), and a *phenylurethane*, m. p. 73.3—73.8° (Found : C, 76.8; H, 10.7. $C_{33}H_{39}O_2N$ requires C, 76.4; H, 10.9%).

16-Methylheptadecanoic Acid.—8-Methylnonanoic acid (52 g.) and methyl hydrogen sebacate (86 g.) were electrolysed and worked up, to give 16-methylheptadecanoic acid (22%), m. p. 67.5—68.0° (Found : equiv., 287. Calc. : equiv., 284). The benzimidazole derivative had m. p. 98.0—98.5°, the amide, m. p. 106.4—106.5°, the *anilide* m. p. 87.0—87.3° (Found : C, 80.2; H, 11.35. $C_{24}H_{41}ON$ requires C, 80.15; H, 11.5%), and the *p*-bromophenacyl ester, m. p. 79.7—80.0° (Found : Br, 16.9. $C_{26}H_{41}O_3Br$ requires Br, 16.6%).

16-Methylheptadecanol, m. p. 41.8—42.0° (Stenhagen *et al.* report 40.1—40.3°) (Found : C, 79.9; H, 14.3. Calc. for $C_{18}H_{38}O$: C, 79.9; H, 14.15%), gave a 3 : 5-dinitrobenzoate, m. p. 64.5—65.0° (Found : C, 65.0; H, 9.0. $C_{25}H_{40}O_6N_2$ requires C, 64.6; H, 8.7%), and a *phenylurethane*, m. p. 79.7° (Found : N, 3.4. $C_{25}H_{43}O_2N$ requires N, 3.6%).

18-Methylnonadecanoic Acid.—Electrolysis of 10-methylundecanoic acid (10 g.) and methyl hydrogen sebacate (10.8 g.) afforded 18-methylnonadecanoic acid (6.4%), m. p. 74.6—75.1° (Hougen *et al.* report 73.3—73.6°; Weitkamp gives 75.3°; Murray *et al.* give 75.0°) (Found : equiv., 314. Calc. : equiv., 312), which gave an amide, m. p. 103.0° (Hougen *et al.* give 105.9—106.1°; Weitkamp reports 105.1°) (Found : C, 77.0; H, 13.3. Calc. for $C_{20}H_{41}ON$: C, 77.2; H, 13.2%), *anilide*, m. p. 88.4—88.6° (Found : C, 80.7; H, 11.6. $C_{26}H_{45}ON$ requires C, 80.6; H, 11.7%), and *p*-bromophenacyl ester, m. p. 80.5—80.9° (Found : C, 66.0; H, 8.6. $C_{28}H_{45}O_3Br$ requires C, 66.0; H, 8.9%).

18-Methylnonadecanol, m. p. 49.8° (Murray *et al.* report 50.3° for the natural product) (Found : C, 80.3; H, 13.9. $C_{20}H_{42}O$ requires C, 80.45; H, 14.2%), gave a 3 : 5-dinitrobenzoate, m. p. 70.0—70.5°, and *phenylurethane*, m. p. 83.7—84.1° (Found : C, 78.0; H, 11.2. $C_{27}H_{47}O_2N$ requires C, 77.65; H, 11.35%).

20-Methylheneicosanoic Acid.—12-Methyltridecanoic acid (45 g.) was electrolysed with methyl hydrogen sebacate (86 g.) to give 20-methylheneicosanoic acid (28%), m. p. 79.1—79.5° (Weitkamp gives 79.4°; Murray *et al.* give 80.2°) (Found : equiv., 344. Calc. : equiv., 340). The benzimidazole derivative had m. p. 90.9—91.5° (Found : N, 6.8. $C_{28}H_{48}N_2$ requires N, 6.8%), the amide m. p. 108.0—108.5° (Weitkamp gives 108.4°) (Found : C, 77.9; H, 13.1. $C_{22}H_{45}ON$ requires C, 77.8; H, 13.4%), and the *p*-bromophenacyl ester m. p. 83.7—84.2° (Found : C, 67.2; H, 8.8. $C_{30}H_{49}O_3Br$ requires C, 67.0; H, 9.2%).

20-Methylheneicosanol, m. p. 56.8—57.2° (Murray and Schoenfeld give 57.1°) (Found : C, 80.7; H, 13.8. $C_{22}H_{46}O$ requires C, 80.9; H, 14.2%), gave a 3 : 5-dinitrobenzoate, m. p. 74.4—74.8° (Found : C, 67.0; H, 9.3. $C_{25}H_{48}O_6N_2$ requires C, 66.9; H, 9.3%), and a *phenylurethane*, m. p. 86.3—86.7° (Found : N, 3.3. $C_{29}H_{51}O_2N$ requires N, 3.15%).

22-Methyltricosanoic Acid.—14-Methylpentadecanoic acid (12.8 g.) and methyl hydrogen sebacate (12.2 g.) were electrolysed to give 22-methyltricosanoic acid, m. p. 82.7—83.2° (Found : equiv., 367. Calc. : equiv., 368). Weitkamp gives 83.1°; Murray *et al.* give 83.4°. For the synthetic acid Stenhagen *et al.* give 83.1—83.5°. It gave an amide, m. p. 110.5—110.8° (Weitkamp reports 110.5°), *anilide*, m. p. 90.9—91.4° (Found : C, 80.5; H, 12.0. $C_{30}H_{53}ON$ requires C, 81.2; H, 12.05%), and *p*-bromophenacyl ester, m. p. 84.5—85.2°.

22-Methyltricosanol, m. p. 62.0—62.4° (Murray and Schoenfeld give 62.4°), gave a 3 : 5-dinitrobenzoate, m. p. 76.2—76.5° (Found : C, 68.05; H, 9.6. $C_{31}H_{52}O_6N_2$ requires C, 67.85; H, 9.55%), and a *phenylurethane*, m. p. 88.9—89.2° (Found : C, 79.2; H, 11.5. $C_{31}H_{55}O_2N$ requires C, 78.6; H, 11.7%).

24-Methylpentacosanoic Acid.—Electrolysis of 16-methylheptadecanoic acid (8 g.) and methyl hydrogen sebacate (12.2 g.) afforded 24-methylpentacosanoic acid (10%), m. p. 86.8—87.2°; Weitkamp gives 86.9°; Murray *et al.* give 86.3°. For the synthetic acid Stenhagen *et al.* report 86.4—86.7°. It gave an amide, m. p. 112.3—112.5° (Weitkamp gives 112.1°), *anilide*, m. p. 89.4—89.6°, and *p*-bromophenacyl ester, m. p. 81.1—81.6°.

24-Methylpentacosanol, m. p. 67.0—67.2° (Murray and Schoenfeld give 67.2°), gave a *phenylurethane*, m. p. 89.7—90.2° (Found : C, 78.9; H, 11.9. $C_{33}H_{59}O_2N$ requires C, 79.1; H, 11.8%).

26-Methylheptacosanoic Acid.—10-Methylundecanoic acid (2 g.) and methyl hydrogen hexadecane-1 : 16-dicarboxylate (3.3 g.) were electrolysed in the usual way. The electrolysis was

stopped after 150 hr. although the solution was still acid. After removal of the methanol and the hydrocarbon by distillation, the residue was hydrolysed and the free acids were extracted. The acids were neutralised precisely, and 0.1N-hydrochloric acid was then added in an amount calculated to liberate only the monocarboxylic acid. After extraction with ether and recrystallisation from ethyl acetate it had m. p. 88.8—89.0° (Weitkamp gives 89.3°) (Found: equiv., 430. Calc.: equiv., 424) (yield: 50 mg.) (*p*-bromophenacyl ester, m. p. 83.3—83.6°).

26-Methylheptacosanol, m. p. 72.0—72.4°, gave a phenylurethane, m. p. 90.5—90.8°.

Syntheses in the (+)-anteiso-Series.

Isolation of (-)-2-Methylbutanol from Fusel Oil.—Fusel oil containing 15—20% of optically active amyl alcohol was distilled at atmospheric pressure, through a 22" electrically-jacketed column packed with wire-gauze rings. The take-off rate was 1.5 ml./hr. and the reflux ratio was 75:1. Four or five distillations through the column were required in order to obtain alcohol of the desired purity. The (-)-2-methylbutanol finally obtained had $\alpha_D -4.75^\circ$ ($l = 1$) and was 99% pure. Optically pure amyl alcohol has $\alpha_D -4.81^\circ$ ($l = 1$) (Couteur, Kenyon, and Rohan, *J. Appl. Chem.*, 1951, 1, 341).

(+)-1-Bromo-2-methylbutane.—Phosphorus tribromide (227 g.) was added slowly to an efficiently stirred solution of (-)-2-methylbutanol (184 g.) in pyridine (57 g.) at 0°. The crude product was distilled off at 100 mm., dissolved in light petroleum (b. p. 40—60°), and washed successively with 5% aqueous sodium hydroxide, 10% sulphuric acid, concentrated sulphuric acid, and water. The solution was dried and distilled, to give (+)-2-methylbutyl bromide (202 g.), b. p. 119—121°, n_D^{20} 1.4450, $\alpha_D +4.75^\circ$ ($l = 1$).

(+)-3-Methylpentanoic Acid.—1-Bromo-2-methylbutane (75.5 g.) was heated under reflux for 20 hr. with a solution of potassium cyanide (35 g.) in 80% ethanol (250 ml.). After the potassium bromide had been filtered off, the filtrate containing the nitrile was heated for a further 20 hr. with potassium hydroxide (40 g.). The solution was then worked up as described for 4-methylpentanoic acid, to give (+)-3-methylpentanoic acid (40.5 g.), b. p. 100—103°/12.5 mm.

(+)-4-Methylhexanoic Acid.—During 2 hr. optically active amyl bromide (202 g.) was added to an efficiently stirred, hot solution of ethyl sodiomalonate (251 g.) in absolute ethanol (900 ml.). After the mixture had been heated for a further 2 hr. some of the solvent (400 ml.) was distilled off, and the residue treated with aqueous potassium hydroxide (307 g. in 300 ml.) for 4 hr. under reflux. The alcohol was distilled off and the residue was heated under reflux for 4.5 hr. with a strong solution of sulphuric acid (272 ml. of H₂SO₄ in 600 ml. of H₂O). After cooling, the solution was extracted with ether, and the ethereal solution was washed, dried, and distilled, to give (+)-4-methylhexanoic acid (128 g.), b. p. 104—107°, n_D^{20} 1.4248, $[\alpha]_D^{20} +10.65^\circ$ (10% in CHCl₃) (Found: C, 65.0; H, 11.1%; equiv., 130. C₇H₁₄O₂ requires C, 64.7; H, 10.8%; equiv., 130). The acid gave a *p*-bromophenacyl ester, m. p. 49.6—49.8°.

(+)-4-Methylhexanol had b. p. 172°, n_D^{20} 1.4256 (Found: C, 72.1; H, 13.8. C₇H₁₆O requires C, 72.4; H, 13.8%).

(+)-6-Methyloctanoic Acid.—4-Methylhexanoic acid (117 g.) and methyl hydrogen succinate (231 g.) were electrolysed, to give 6-methyloctanoic acid (20%), b. p. 136—138°/10 mm., $[\alpha]_D^{20} +9.08^\circ$ (10% in CHCl₃) (Found: equiv., 157. Calc.: equiv., 158). The amide had m. p. 89.7—90.1° (Weitkamp gives 89.7°; Crombie and Harper give 90—91°), and the *p*-bromophenacyl ester m. p. 59.0—59.3° (Found: Br, 23.0. C₁₇H₂₃O₃Br requires Br, 22.5%).

6-Methyloctanol, b. p. 204—208°, $[\alpha]_D^{20} +9.80^\circ$ (10% in CHCl₃), n_D^{20} 1.4360 (Found: C, 75.0; H, 13.8. Calc. for C₉H₂₀O: C, 75.0; H, 14.0%), gave a phenylurethane, m. p. 52.5—53.0° (Found: C, 73.0; H, 9.5. C₁₅H₂₅O₂N requires C, 73.0; H, 9.6%).

(+)-8-Methyldecanoic Acid.—4-Methylhexanoic acid (117 g.) and methyl hydrogen adipate (192 g.) were electrolysed, to give 8-methyldecanoic acid (25%), b. p. 154—156°/10 mm., $[\alpha]_D^{20} +7.00^\circ$ (10% in CHCl₃) (Found: equiv., 185. Req'd.: equiv., 186), which yielded an amide, m. p. 86.9° (Weitkamp gives 87.1°), amide, m. p. 76.6—77.1° (Found: C, 78.1; H, 10.45. C₁₇H₂₇ON requires C, 78.1; H, 10.4%), and *p*-bromophenacyl ester, m. p. 49.6—50.1° (Found: C, 59.7; H, 7.0. C₁₉H₂₇O₃Br requires C, 59.5; H, 7.1%).

8-Methyldecanol, b. p. 234—238°/760 mm., $[\alpha]_D^{20} +8.64^\circ$ (10% in CHCl₃), n_D^{20} 1.4402 (Found: C, 76.5; H, 13.8. C₁₁H₂₄O requires C, 76.7; H, 14.05%), gave a phenylurethane, m. p. 46.5—46.8° (Found: C, 74.0; H, 9.9. C₁₈H₂₉O₂N requires C, 74.2; H, 10.05%).

(+)-10-Methyldodecanoic Acid.—Electrolysis of a mixture of 3-methylpentanoic acid (42.5 g.)

and methyl hydrogen azelate (145 g.) gave 10-methyldodecanoic acid (34%), b. p. 172—176°/10 mm., m. p. 5·8° (Weitkamp gives 6·2°), $[\alpha]_D^{20} + 5·88$ (10% in CHCl_3) (Found: equiv., 219. Calc.: equiv., 214) [benzimidazole derivative, m. p. 99·5—99·8°; amide, m. p. 89·5—90·0° (Weitkamp gives 92·5°) (Found: C, 73·0; H, 12·45. $\text{C}_{13}\text{H}_{22}\text{ON}$ requires C, 73·2; H, 12·7%); p-bromophenacyl ester, m. p. 55·5—56·0° (Found: C, 61·0; H, 7·3. $\text{C}_{21}\text{H}_{31}\text{O}_3\text{Br}$ requires C, 61·3; H, 7·6%)].

(+)-10-Methyldodecanol, b. p. 145—150/15 mm., n_D^{20} 1·4450, $[\alpha]_D^{20} + 7·29$ (Found: C, 77·6; H, 14·0. $\text{C}_{13}\text{H}_{28}\text{O}$ requires C, 77·9; H, 14·1%), gave a phenylurethane, m. p. 53·0—53·5° (Found: C, 75·0; H, 10·25. $\text{C}_{20}\text{H}_{35}\text{O}_2\text{N}$ requires C, 75·2; H, 10·4%).

(+)-12-Methyltetradecanoic Acid.—4-Methylhexanoic acid (130 g.) and methyl hydrogen sebacate (216 g.) were electrolysed and worked up in the usual manner, to give 12-methyltetradecanoic acid (24%), m. p. 22·8° (Weitkamp gives 23·0°), $[\alpha]_D^{20} + 5·04$ (10% in CHCl_3) (Found: equiv., 242. Calc.: equiv., 242). This gave a benzimidazole derivative, m. p. 119·5—120·0°, amide, m. p. 86·6° (Weitkamp gives 86·4°), anilide, m. p. 58·0—58·3° (Found: C, 79·5; H, 11·2. $\text{C}_{21}\text{H}_{35}\text{ON}$ requires C, 79·45; H, 11·1%), and p-bromophenacyl ester, m. p. 58·7—59·3° (Found: C, 63·0; H, 7·6. $\text{C}_{23}\text{H}_{35}\text{O}_3\text{Br}$ requires C, 62·9; H, 8·0%).

(+)-12-Methyltetradecanol, b. p. 170—175°/15 mm., $[\alpha]_D^{20} + 6·50$ (10% in CHCl_3), n_D^{20} 1·4493 (Found: C, 78·7; H, 14·15. $\text{C}_{15}\text{H}_{32}\text{O}$ requires C, 78·9; H, 14·1%), gave a 3:5-dinitrobenzoate, m. p. 43·3—43·7° (Found: C, 62·8; H, 8·1. $\text{C}_{22}\text{H}_{34}\text{O}_6\text{N}_2$ requires C, 62·55; H, 8·1%), and phenylurethane, m. p. 60·0—60·3° (Found: C, 76·05; H, 10·5. $\text{C}_{22}\text{H}_{37}\text{O}_2\text{N}$ requires C, 76·0; H, 10·7%).

(+)-14-Methylhexadecanoic Acid.—6-Methyloctanoic acid (20 g.) and methyl hydrogen sebacate (54 g.) were electrolysed, to give 14-methylhexadecanoic acid (45 g.), m. p. 36·0°, $[\alpha]_D^{20} + 4·38$ (10% in CHCl_3) (Found: equiv., 274. Calc.: equiv., 270). Weitkamp gives 36·8°; Murray *et al.* give 37·3°. For the optically active synthetic acid English and Velick give 36·0—36·8°. The benzimidazole derivative had m. p. 95·9—96·4°, the amide, m. p. 90·9—91·1° (Weitkamp reports 90·9°), the anilide, m. p. 61·3—61·6° (Found: C, 79·3; H, 11·2. $\text{C}_{23}\text{H}_{39}\text{ON}$ requires C, 79·95; H, 11·4%), and the p-bromophenacyl ester, m. p. 63·7—64·2° (Found: C, 64·4; H, 8·45. $\text{C}_{25}\text{H}_{39}\text{O}_3\text{Br}$ requires C, 64·4; H, 8·4%).

(+)-14-Methylhexadecanol had m. p. 18·5—19·0° (Murray and Schoenfeld give 18·4°), $[\alpha]_D^{20} + 5·25$ (10% in CHCl_3), n_D^{20} 1·4530 (Found: C, 79·7; H, 14·3. $\text{C}_{17}\text{H}_{36}\text{O}$ requires C, 79·6; H, 14·15%), its 3:5-dinitrobenzoate had m. p. 52·3—52·6° (Found: C, 64·0; H, 8·3. $\text{C}_{24}\text{H}_{38}\text{O}_6\text{N}_2$ requires C, 64·0; H, 8·5%), and its phenylurethane had m. p. 66·2—66·5° (Found: C, 77·0; H, 10·7. $\text{C}_{24}\text{H}_{41}\text{O}_2\text{N}$ requires 76·75; H, 11·0%).

(+)-16-Methyloctadecanoic Acid.—Electrolysis of 8-methyldecanoic acid (41 g.) and methyl hydrogen sebacate (47·5 g.) afforded 16-methyloctadecanoic acid (29%), m. p. 48·1—48·5° (Weitkamp gives 46·8°; Murray *et al.* give 46·0—46·3°), $[\alpha]_D^{20} + 3·90$ (10% in CHCl_3) (Found: C, 76·8; H, 12·7. $\text{C}_{19}\text{H}_{38}\text{O}_2$ requires C, 76·7; H, 12·7%). It gave an amide, m. p. 93·6° (Weitkamp reports 93·2°), anilide, m. p. 68·0—68·3° (Found: C, 80·1; H, 11·4. $\text{C}_{25}\text{H}_{43}\text{ON}$ requires C, 80·4; H, 11·6%), and p-bromophenacyl ester, m. p. 71·0—71·2° (Found: C, 65·3; H, 8·6. $\text{C}_{27}\text{H}_{43}\text{O}_3\text{Br}$ requires C, 65·45; H, 8·75%).

16-Methyloctadecanol had m. p. 30·4—30·7° (Murray and Schoenfeld give 27·5—31°), $[\alpha]_D^{20} + 4·70$ (10% in CHCl_3) (Found: C, 80·35; H, 14·05. $\text{C}_{19}\text{H}_{40}\text{O}$ requires C, 80·25; H, 14·15%), and gave a 3:5-dinitrobenzoate, m. p. 60·2—60·5° (Found: C, 65·6; H, 8·95. $\text{C}_{26}\text{H}_{42}\text{O}_6\text{N}_2$ requires C, 65·25; H, 8·85%), and phenylurethane, m. p. 73·4—73·7° (Found: C, 77·4; H, 11·3. $\text{C}_{26}\text{H}_{45}\text{O}_2\text{N}$ requires C, 77·4; H, 11·25%).

(+)-18-Methyleicosanoic Acid.—Electrolysis of a mixture of 10-methyldodecanoic acid (6 g.) and monomethyl sebacate (48·5 g.) gave 18-methyleicosanoic acid (200 mg.), m. p. 55·1—55·3° (Weitkamp gives 55·6°; Murray *et al.* give 55·8°), $[\alpha]_D^{20} + 3·50$ (10% in CHCl_3) (Found: equiv., 327. Req'd.: equiv., 326·5). It gave an amide, m. p. 94·4—94·6° (Weitkamp gives 94·1°), anilide, m. p. 73·8—74·1°, and p-bromophenacyl ester, m. p. 75·4—75·6° (Found: C, 66·3; H, 8·9. $\text{C}_{23}\text{H}_{47}\text{O}_3\text{Br}$ requires C, 66·5; H, 9·05%).

18-Methyleicosanol, m. p. 39·8—40·2° (Murray and Schoenfeld report 40·1°), $[\alpha]_D^{20} + 4·30$ (10% in CHCl_3), gave a 3:5-dinitrobenzoate, m. p. 64·1—64·3°, and a phenylurethane, m. p. 78·2—78·5° (Found: C, 77·8; H, 11·3. $\text{C}_{28}\text{H}_{46}\text{O}_2\text{N}$ requires C, 77·9; H, 11·45%).

(+)-20-Methyldocosanoic Acid.—A mixture of 12-methyltetradecanoic acid (29 g.) and methyl hydrogen sebacate (52 g.) was electrolysed, to give 20-methyldocosanoic acid (7 g.), m. p. 61·0—61·5° (both Weitkamp and Murray *et al.* give 62·1°), $[\alpha]_D^{20} + 3·47$ (Found: equiv., 357. Req'd.: equiv., 355), which afforded an amide, m. p. 99·0° (Weitkamp gives 99·9°), anilide, m. p. 79·2—79·4° (Found: C, 81·0; H, 12·0. $\text{C}_{23}\text{H}_{51}\text{ON}$ requires C, 81·05; H, 11·95%), and

p-bromophenacyl ester, m. p. 79.7—80.0° (Found: C, 67.5; H, 9.3. $C_{31}H_{51}O_3Br$ requires C, 67.5; H, 9.3%).

(+)-20-Methyldocosanol, m. p. 48.5—48.7° (Murray and Schoenfeld give 48.5°), $[\alpha]_D^{20} + 3.53^\circ$ (10% in $CHCl_3$) (Found: C, 81.2; H, 14.1. $C_{23}H_{48}O$ requires C, 81.1; H, 14.1%), gave a 3:5-dinitrobenzoate, m. p. 67.3—67.5°, and *phenylurethane*, m. p. 83.2—83.7° (Found: C, 78.4; H, 11.3. $C_{30}H_{53}O_2N$ requires C, 78.4; H, 11.6%).

(+)-22-Methyltetracosanoic Acid.—6-Methyloctanoic acid (1.2 g.) and monomethyl hexadecane-1:16-dicarboxylate (2.5 g.) were electrolysed and worked up as described for the C_{28} acid, to give 22-methyltetracosanoic acid (60 mg.), m. p. 67.5—67.8° (Weitkamp gives 67.8°; Murray *et al.* give 68.1°) (Found: C, 78.6; H, 13.0. $C_{25}H_{50}O_2$ requires C, 78.5; H, 13.1%) (*p*-bromophenacyl ester, m. p. 82.2—82.6°).

22-Methyltetracosanol had m. p. 54.0—54.5°; Murray and Schoenfeld give 54.6°.

(+)-24-Methylhexacosanoic Acid.—Electrolysis of 16-methyloctadecanoic acid (13 g.) and methyl hydrogen sebacate (28.3 g.) gave 24-methylhexacosanoic acid (150 mg.), m. p. 72.1° (Weitkamp gives 72.9°; Tiedt and Truter, *Chem. and Ind.*, 1952, 403, give 72.5°), $[\alpha]_D^{20} + 2.64^\circ$ (10% in $CHCl_3$) [amide, m. p. 104.7—104.9° (Weitkamp gives 104.5°)]; *p*-bromophenacyl ester, m. p. 86.4—86.7° (Found: C, 69.0; H, 10.0. $C_{35}H_{59}O_3Br$ requires C, 69.2; H, 9.7%).

24-Methylhexacosanol, m. p. 60.8° (Murray and Schoenfeld give 61.0°), $[\alpha]_D^{20} + 3.40^\circ$ (10% in $CHCl_3$), gave a *phenylurethane*, m. p. 87.0—87.4° (Found: C, 78.6; H, 11.6. $C_{34}H_{61}O_2N$ requires C, 79.15; H, 11.9%).

(+)-26-Methyltacosanoic Acid.—20-Methyldocosanoic acid (6.0 g.) and methyl hydrogen suberate (3.4 g.) were electrolysed, to give 26-methyltacosanoic acid (70 mg.), m. p. 76.2—76.5° (Tiedt and Truter give 76.1°) (Found: C, 79.8; H, 13.1. $C_{28}H_{58}O_2$ requires C, 79.5; H, 13.2%).

26-Methyltacosanol had m. p. 65.0—65.3°.

(+)-28-Methyltriacontanoic Acid.—Electrolysis of a mixture of 20-methyldocosanoic acid (3 g.) and monomethyl sebacate (7.4 g.) gave 28-methyltriacontanoic acid (10%), m. p. 79.8—80.3° (Weitkamp gives 80.7°; Tiedt and Truter give 78.8°), $[\alpha]_D^{20} + 2.43^\circ$ (10% in $CHCl_3$) [amide, m. p. 107.0—107.3° (Weitkamp gives 107.0°; Tiedt and Truter give 107.6°)]; anilide, m. p. 92.2—92.6°; *p*-bromophenacyl ester, m. p. 85.9—86.4°.

(+)-28-Methyltriacontanol had m. p. 69.0—69.3°, $[\alpha]_D^{20} + 3.06^\circ$ (10% in $CHCl_3$) (Found: C, 82.15; H, 14.1. $C_{31}H_{64}O$ requires C, 82.2; H, 14.25%), and gave a 3:5-dinitrobenzoate, m. p. 81.2—81.5°, and a *phenylurethane*, m. p. 90.9—91.4° (Found: C, 79.8; H, 11.9. $C_{38}H_{69}O_2N$ requires C, 79.8; H, 12.15%).

The authors are indebted to Prof. J. B. Speakman for his interest and encouragement, and to the International Wool Secretariat for financial assistance.

TEXTILE CHEMISTRY LABORATORY, DEPT. OF TEXTILE INDUSTRIES,
UNIVERSITY OF LEEDS.

[Received, May 3rd, 1954.]