238. *Synthetic Long-chain Aliphatic Compounds. Part III. A Critical Examination of Two Methods of Synthesis of Olefinic Acids.*

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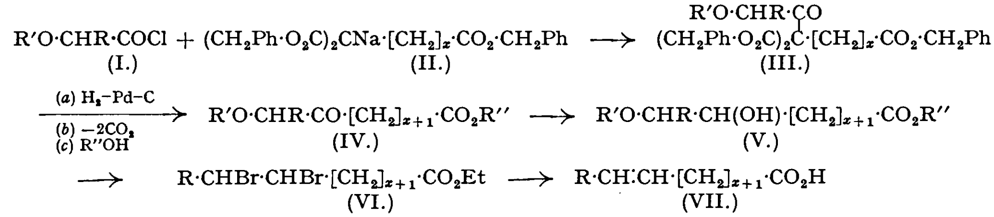
Syntheses of olefins, acyloins and alkoxy-ketones being used as intermediates, have been submitted to a careful scrutiny at each stage, whereby techniques have been developed for the preparation of unsaturated acids of a high degree of purity. The acyloin route is to be preferred for the straight-chain acids since it allows the separate preparation of *cis*- and *trans*-isomers *via* the two racemic crystalline dihydroxy-acids (V; R′ = R″ = H) which are readily separated by fractional crystallisation. Both *cis*- and *trans*-heptadec-9-enoic acids * have been thus prepared.

The alkoxy-ketone route has yielded oleic and elaidic acids.

An improved method of converting αβ-glycols into the corresponding dibromides by means of hydrogen bromide–acetic acid–sulphuric acid is reported.

As already outlined (*J.*, 1950, 177) our main interest in unsaturated long-chain compounds is to develop a method for their synthesis of the greatest flexibility capable of yielding, in the first instance, both the normal straight-chain mono-olefinic acids and their branched-chain analogues in a pure condition. Although the usual organic techniques, *e.g.*, low-temperature crystallisation, may be used to free the former from contaminants of a similar molecular weight, this is not likely to be possible in the case of the branched-chain materials, which will be obtained as oily mixtures of the possible geometric and stereo-isomers. It was therefore necessary to have available a synthetical route wherein, once the chain was brought into being, the subsequent steps could be carried out quantitatively or, at least, unchanged materials be destroyed before the last stage.

The new ketone synthesis recently described (Bowman, *J.*, 1950, 325) permits the preparation of olefinic acids by way of either alkoxy-ketones (IV; R′ = alkyl) or the corresponding acyloins (IV; R′ = H):



$$\underset{\text{(I.)}}{R'O{\cdot}CHR{\cdot}COCl} + \underset{\text{(II.)}}{(CH_2Ph{\cdot}O_2C)_2CNa{\cdot}[CH_2]_x{\cdot}CO_2{\cdot}CH_2Ph} \longrightarrow \underset{\text{(III.)}}{(CH_2Ph{\cdot}O_2C)_2\overset{R'O\cdot CHR\cdot CO}{C}{\cdot}[CH_2]_x{\cdot}CO_2{\cdot}CH_2Ph}$$

$$\xrightarrow[\substack{(b)\ -2CO_2 \\ (c)\ R''OH}]{(a)\ H_2-Pd-C} \underset{\text{(IV.)}}{R'O{\cdot}CHR{\cdot}CO{\cdot}[CH_2]_{x+1}{\cdot}CO_2R''} \longrightarrow \underset{\text{(V.)}}{R'O{\cdot}CHR{\cdot}CH(OH){\cdot}[CH_2]_{x+1}{\cdot}CO_2R''}$$

$$\longrightarrow \underset{\text{(VI.)}}{R{\cdot}CHBr{\cdot}CHBr{\cdot}[CH_2]_{x+1}{\cdot}CO_2Et} \longrightarrow \underset{\text{(VII.)}}{R{\cdot}CH{:}CH{\cdot}[CH_2]_{x+1}{\cdot}CO_2H}$$

The practicability of the first route has already been demonstrated (*ibid.*, p. 177) although it was evident that many experimental details required further investigation. A critical examination of both routes has now been carried out to compare their suitability for our purposes. This communication deals with the straight-chain acids, and the results on the branched materials are reported in Part IV (succeeding paper).

First, the preparation of oleic and elaidic acids, both of which have been obtained in a high state of purity by Smith (*J.*, 1939, 974), has been investigated by the alkoxy-ketone route starting from ethyl heptane-1 : 1 : 7-tricarboxylate and 2-methoxydecanoic acid.* The latter is conveniently prepared (Bowman, *loc. cit.*, p. 177) by hydrolysis of the product of interaction of sodium methoxide and methyl 2-bromodecanoate and we have now confirmed its homogeneity by independent synthesis. Carbethoxylation of ethyl methoxyacetate by means of ethyl carbonate in the presence of sodium ethoxide (Wallingford, Hofmeyer, and Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 2057) afforded ethyl methoxymalonate, which on alkylation with *n*-octyl bromide and subsequent hydrolysis and decarboxylation of the reaction product yielded 2-methoxydecanoic acid identical in every respect with the material obtained previously.

Condensation of 2-methoxydecanoyl chloride (I; R = C_8H_{17}, R′ = Me) with tribenzyl sodioheptane-1 : 1 : 7-tricarboxylate (II; $x = 6$) (Ames, Bowman, and Mason, *J.*, 1950, 174) proceeded normally and gave a keto-ester which on debenzylation, decarboxylation, and

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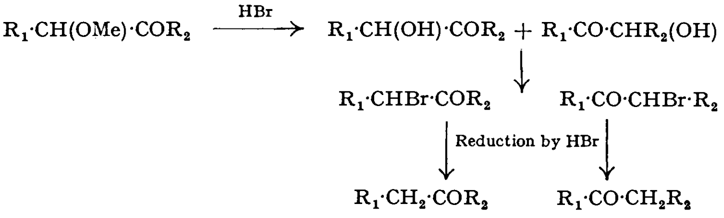
* Geneva convention, $CO_2H = 1$.

subsequent esterification furnished methyl 9-keto-10-methoxyoctadecanoate (IV; $R = C_8H_{17}$, $R' = R'' = Me$, $x = 6$) in 60% yield (almost quantitative when allowance was made for recovery of both starting materials). Ponndorf reduction of the latter with aluminium *iso*propoxide in *iso*propanolic solution in the usual manner furnished ethyl 9-hydroxy-10-methoxyoctadecanoate (V; $R = C_8H_{17}$, $R' = Me$, $R'' = Et$, $x = 6$), the product being saponified and then re-esterified with ethanol to avoid isolation of mixed esters arising from partial alcoholysis (cf. Owen, *J.*, 1949, 1583). However, this material was not homogeneous and presumably contained some unreduced keto-ester.

In the earlier experiments, the remaining steps (V $\longrightarrow$ VII) had proved difficult, but since then we became aware of the work of Baudart (*Bull. Soc. chim.*, 1946, **13**, 87) who following Ruzicka, Plattner, and Widmer (*Helv. Chim. Acta*, 1942, **25**, 604, 1086) converted αβ-glycols into the corresponding olefins by treatment with hydrogen bromide in acetic acid (15%) at 90° followed by dehalogenation of the resulting dibromides in acetone solution with zinc dust in the presence of sodium iodide. Application of these techniques to our hydroxy-methoxy-ester gave, first, an impure dibromo-ester, and then an unsaturated ester of iodine value 72 (Calc. : 82). Fractional crystallisation of the derived acids revealed the presence of approximately 10% of stearic acid in addition to oleic and elaidic acids. Similar results were obtained on using high-pressure catalytic hydrogenation in the presence of Raney nickel (Mozingo, *Org. Synth.*, 1941, **21**, 15) in place of the Ponndorf reduction.

Interpretation of these unexpected results was complicated by the uncertainty regarding the purity of the hydroxy-methoxy-ester. Many experiments were carried out to ascertain the source of the stearic acid, but without result. Noteworthy, however, is the reaction of the original 9-keto-10-methoxyoctadecanoic ester with the hydrogen bromide reagent to give a black tar from which, in small yield, a crystalline keto-octadecanoic acid thought to be a mixture of the 9- and the 10-isomer was isolated. A possible mechanism for the formation of these is as follows :



$$\begin{tikzcd}
R_1{\cdot}CH(OMe){\cdot}COR_2 \arrow[r, "HBr"] & R_1{\cdot}CH(OH){\cdot}COR_2 & + \arrow[d] & R_1{\cdot}CO{\cdot}CHR_2(OH) \\
& R_1{\cdot}CHBr{\cdot}COR_2 \arrow[d] \arrow[rr, phantom, "\text{Reduction by HBr}"] & & R_1{\cdot}CO{\cdot}CHBr{\cdot}R_2 \arrow[d] \\
& R_1{\cdot}CH_2{\cdot}COR_2 & & R_1{\cdot}CO{\cdot}CH_2R_2
\end{tikzcd}$$

(cf. the reduction of α-bromo-ketones by hydrogen bromide, Kröhnke and Timmler, *Ber.*, 1936, **69**, 614).

A similar product containing approximately the same amount of stearic acid was obtained by starting with the readily purified, higher-melting, *erythro*-9 : 10-dihydroxystearic acid, and applying Baudart's techniques (*loc. cit.*). A sample of the required final product, ethyl 9 : 10-dibromo-octadecanoate, was prepared for comparison by careful bromination of a purified sample of ethyl oleate followed by repeated fractionation of the product under reduced pressure to give material of constant refractive index.

An analogous result is that of Young, Jasaitis, and Levanas (*J. Amer. Chem. Soc.*, 1937, **59**, 403), who obtained *n*-oct-4-ene containing some *n*-octane by treatment of octane-4 : 5-diol with hydrobromic acid in the presence of zinc bromide, followed by debromination of the resulting dibromide with zinc. These workers attributed the presence of the saturated hydrocarbon to the formation of the 4 : 4-dibromo-compound during the first stage, and it may well be that the stearic acid, reported above, arose in a similar manner.

Many variations of the reaction conditions with hydrogen bromide, however, failed to yield a product with either the correct bromine content or the expected refractive index; the use of chromatography was unsuccessful.

The literature on the reaction of αβ-glycols with hydrogen bromide in acetic acid is confusing. Albitski (*J. pr. Chem.*, 1903, **67**, 295) describes the formation of acetoxy-bromo-compounds from dihydroxystearic acids, Baudart (*loc. cit.*) reports (without analyses) the isolation of dibromides, and Hunsdiecker (*Ber.*, 1943, **76**, 142) obtained the corresponding tribromide from aleuritic acid : Ruzicka *et al.* (*loc. cit.*), however, record the necessity for chomatographic purification of dibromides (low yields) prepared with the same reagent. In the macrocyclic field, Stoll, Hulstkamp, and Rouvé (*Helv. Chim. Acta*, 1948, **31**, 543) and Stoll and Commarmont (*ibid.*, p. 1077) obtained acetoxybromo-, or mixtures of this with the corresponding diacetoxycompounds, according to the conditions of reaction. Our experiences lead us to conclude that even the prolonged use of a large excess of hydrogen bromide does not bring about complete conversion of αβ-glycols into their dibromides.

Finally, in an attempt to surmount these difficulties, we examined the reaction in the presence of sulphuric acid and at once obtained the required dibromo-acid and thence its ethyl ester in a pure condition; attempts to replace the sulphuric acid by phosphoric acid were unsuccessful. It is noteworthy that, contrary to expectation, the crude dibromo-acid thus obtained was light-coloured, in contrast to that formed in the *absence* of sulphuric acid, which was frequently almost black owing to presence of tar.

Next, the final debromination stage was examined, authentic 9 : 10-dibromoctadecanoic ester being used. The method employing zinc dust in acetone containing sodium iodide (Ruzicka *et al.*, *loc. cit.*) did not give reproducible results, but treatment with activated zinc dust in ethanol (Rollett, *Z. physiol. Chem.*, 1909, **63**, 410; Bloomquist, Holley, and Spencer, *J. Amer. Chem. Soc.*, 1948, **70**, 36; Silberman and Silberman-Martyncewa, *J. Org. Chem.*, 1948, **13**, 707) proved highly satisfactory, furnishing almost quantitative yields of ethyl oleate of theoretical iodine value.

While these experiments were in progress, we also succeeded in effecting reduction of the keto-methoxy-ester (IV; $R = C_8H_{17}$, $R' = R'' = Me$, $x = 6$) catalytically by using Raney nickel W7 (Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 698), the theoretical volume of hydrogen being rapidly taken up to give a quantitative yield of the pure methyl 9-hydroxy-10-methoxyoctadecanoate (V; $R = C_8H_{17}$, $R' = R'' = Me$, $x = 6$). Treatment of the latter with hydrogen bromide–acetic acid–sulphuric acid followed by esterification and passage of the crude ester in light petroleum solution through a short column of activated alumina gave the pure dibromo-octadecanoic ester and thence, by reaction with zinc in ethanol, an unsaturated ester of the required iodine value. Hydrolysis and fractional crystallisation of the resulting acid yielded oleic and elaidic acids, again of the correct iodine value and identical with authentic material; there was no evidence of the presence of saturated contaminants. The oleic acid had a rather low melting point owing, doubtless, to the presence of a small amount of the *trans*-isomer which is difficult to eliminate on the scale employed.

With these methods now available, attention was next directed to the acyloin route as applied to the synthesis of the *cis*- and *trans*-heptadec-9-enoic acids. A somewhat similar route has been used by Ruzicka *et al.* and Baudart (*locc. cit.*), but a circuitous series of reactions was necessary owing to the absence of a direct synthesis of unsymmetrical acyloins. Successive treatment of 2-hydroxynonanoic acid with acetyl chloride and thionyl chloride gave 2-acetoxynonanoyl chloride (I; $R = C_7H_{15}$, $R' = Ac$) which was condensed with tribenzyl sodioheptane-1 : 1 : 7-tricarboxylate as before. Hydrogenolysis, decarboxylation, and deacetylation under *acid* conditions furnished 10-hydroxy-9-ketoheptadecanoic acid (IV; $R = C_7H_{15}$, $R' = R'' = H$, $x = 6$), more conveniently isolated as its ethyl ester (71%). Alkaline hydrolysis could not be used to remove the acetyl group, for King (*J.*, 1936, 1788) has shown that, in alkaline solution, substances of this type are partially isomerised to mixtures of the 10-hydroxy-9-keto- and the 9-hydroxy-10-keto-acids. We have confirmed this isomerisation in the case of 10-hydroxy-9-ketoheptadecanoic acid and isolated a mixture of the two isomers in addition to a small quantity of azelaic acid formed by oxidative fission of the acyloin linkage (cf. King, *loc. cit.*).

Reduction of the acyloin ester was effected catalytically by use of Raney nickel W7 as before, whereas by the Ponndorf method both the acid and its ester were reduced. The latter method is more suitable for acyloins than for alkoxy-ketones, since unreduced material may be readily removed by crystallisation or by oxidative fission in alkaline solution with air or hydrogen peroxide; the catalytic method is, however, more convenient. By either process a mixture of the two stereoisomeric dihydroxy-acids was obtained from which *erythro*-9 : 10-dihydroxyheptadecanoic acid, m. p. 129° (V; $R = C_7H_{15}$, $R' = R'' = H$, $x = 6$) was readily separated by virtue of its sparing solubility in cold ethanol. The more soluble *threo*-isomer, m. p. 86°, was obtained from the mother-liquors. [The assignment of *erythro*- and *threo*-configurations is based on the close analogy to the corresponding dihydroxyoctadecanoic acids, m. p. 129° and 93°, respectively (cf. Bader, *J. Amer. Chem. Soc.*, 1948, **70**, 3938).]

Both compounds were separately treated as before, *i.e.*, with hydrogen bromide–sulphuric acid–acetic acid, followed by zinc in ethanol, to give the pure dibromo-esters and thence the pure *cis*- and *trans*-heptadec-9-enoic acids, respectively.

Our confidence in the purity of the unsaturated acids obtained in the above manner is based on the following considerations. The mechanisms by which αβ-glycols are converted into olefins *via* the requisite dibromides with aid of hydrogen bromide and zinc have been elucidated by a number of workers, in particular Young, Lucas, Winstein, and their co-workers (*J. Amer. Chem. Soc.*, 1930 *et seq.*), who have shown that the first stage of the reaction is accompanied by a change of configuration at one carbon atom only (Lucas and Wilson, *ibid.*, 1936, **58**, 2396) and that subsequent debromination gives rise to a sterically homogeneous product (Young, Jasaitis, and Levanas, *loc. cit.*). Nevertheless, Campbell, and Eby (*ibid.*, 1941, **63**, 216) have since drawn attention to the work of van Risseghem (*Bull. Soc. chim. Belg.*, 1938, **47**, 194), who demonstrated by means of Raman spectra the presence of the alternative isomer in each *cis*- and *trans*-hex-3-ene obtained from the appropriate dibromide; but as she used a different reagent, *viz.*, phosphorus tribromide, for the preparation of her dibromides, this criticism is not relevant to our substances. In the long-chain field, the debromination of pure *threo*-9 : 10-dibromostearic acid to give oleic acid of the highest purity (m. p. 14°) (Holde and Gorgas, *Z. angew. Chem.*, 1926, **39**, 1443) is further evidence that the last stage occurs in a undirectional manner.

For the heptadec-9-enoic acids synthesised above, the evidence is no less convincing : the *cis*-acid obtained by direct distillation of the crude hydrolysis product of its ester, with no attempt at fractionation beyond rejection of the first drop of distillate, had m. p. 13—13·5° unchanged by further purification including repeated crystallisation of its lithium salt and regeneration therefrom with dilute acid; the crude *trans*-acid, obtained similarly from its ester but without distillation, had m. p. 37—38° raised only to 38° by crystallisation.

In conclusion, it is evident that, although both the alkoxy-ketone and the acyloin route are satisfactory for the synthesis of the straight-chain higher unsaturated acids, yet the latter is superior since it allows the separate preparation of the individual *cis*- and *trans*-isomers. In this connection, it is particularly fortunate that the readily purified, higher-melting *erythro*-dihydroxy-acid gives rise to the more difficultly purified *cis*-acid, which can be thus obtained in a pure state.

The way now appears to be open for the synthesis of many naturally occurring polyunsaturated acids *via* the appropriate polyhydroxy-acids, and experiments in this direction are in progress.

EXPERIMENTAL.

The methods used for the conversion of the malonic ester into the benzyl sodio-ester and the reaction of the latter with the acid chloride were as described by Bowman (*J.*, 1950, 325).

Substituted Keto-acids.—The following modification is a considerable improvement on the original method (*loc. cit.*). A solution of the crude benzyl keto-ester (0·2 mol.) in dry ethyl acetate (400 ml.) was stirred in an atmosphere of hydrogen at room temperature in the presence of anhydrous magnesium sulphate (20 g.) and palladised strontium carbonate (6 g., 10% of Pd) until hydrogenation was complete. The filtered solution (together with ethyl acetate washings) was diluted with dry toluene (250 ml.) and concentrated to about half its volume under reduced pressure to remove water and thus minimise hydrolytic degradation of the acylmalonic acid. The residue was then boiled under reflux for 1 hour to effect decarboxylation and the remaining solvent was then removed mainly at atmosphere pressure and finally *in vacuo*.

Ethyl Methoxymalonate.—Ethyl methoxyacetate (177 g., 1·5 mols.) was added to a suspension of sodium ethoxide (from 34 g. of sodium; 1·5 mols.) in dry, redistilled ethyl carbonate (1250 ml.), and the mixture slowly distilled through a Fenske column until no further distillation of ethanol occurred. The ethyl sodiomethoxymalonate, which separated from the reaction mixture on cooling, was removed by filtration, washed with dry benzene, and decomposed by shaking a suspension of it in benzene with dilute sulphuric acid. The organic layer was separated, washed with water, dried (Na_2SO_4), and distilled to give *ethyl methoxymalonate* as a colourless oil, b. p. 95°/3 mm., n_D^{20} 1·4229 (135 g., 50%) (Found : C, 50·7; H, 8·0. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4%). The diamide, obtained by keeping a portion of the ester for 60 hours with excess of concentrated aqueous ammonia, crystallised from methanol in needles, m. p. 205° (slight decomp.) (Pryde and Williams, *J.*, 1933, 1627, give m. p. 203—204° with slight decomp.).

Ethyl Methoxy-n-*octylmalonate.*—Ethyl methoxymalonate (0·1 mol.) was converted into its slightly soluble potassio-derivative by addition to a solution of potassium *tert.*-butoxide (0·1 mol.) in *tert.*-butanol (150 ml.) with stirring, and *n*-octyl bromide (0·1 mol.) added. The mixture was stirred under reflux (bath, 110°) for 8 hours, cooled, and poured into dilute sulphuric acid. The product was isolated in the usual manner and distilled to give, after rejection of a small fore-run, *ethyl methoxy*-n-*octylmalonate* as a colourless oil, b. p. 128°/0·4 mm., n_D^{20} 1·4363 (23 g., 77%) (Found : C, 64·1; H, 10·0. $C_{16}H_{30}O_5$ requires C, 63·6; H, 10·0%).

2-*Methoxydecanoic Acid.*—The foregoing ester (23 g.) was refluxed for 0·5 hour with sodium hydroxide (120 ml. of 4N.). After addition of water (80 ml.), most of the ethanol was distilled off, and the mixture was then cooled and acidified with sulphuric acid (50 ml. of 20N.); vigorous decarboxylation occurred and the product separated as an oil. The latter was isolated with ether and distilled to give 2-methoxydecanoic acid as a colourless oil, b. p. 130°/1 mm., which rapidly solidified, f. p. 42·5° (thermometer in liquid), identical with a specimen (f. p. 43°) obtained by a different route (Part II, *loc. cit.*).

Methyl 9-*Keto*-10-*Methoxyoctadecanoate* (IV; $R = C_8H_{17}$, $R' = R'' = Me$, $x = 6$).—Ethyl *n*-heptane-1 : 1 : 7-tricarboxylate (66 g., 0·21 mol.) was converted into the tribenzyl sodio-ester by means of sodium (4·8 g., 0·21 mol.) and benzyl alcohol (68 g., 0·63 mol.) in benzene (350 ml.), and the product treated with 2-methoxydecanoyl chloride (44 g., 0·20 mol.) according to the general procedure. Titration of a sample of the crude benzyl acylmalonate showed the presence of 0·01 equiv. of free acid, corresponding to only 5% of uncombined 2-methoxydecanoic acid. After debenzylation, decarboxylation, and removal of solvent, the residue was shaken with light petroleum (b. p. 40—60°; 350 ml.), the insoluble, viscous heptane-1 : 1 : 7-tricarboxylic acid being removed by washing with 50% aqueous ethanol (2 × 40 ml.) and then water (40 ml.). The dried (Na_2SO_4) petroleum layer was evaporated, and the crude residual acid was converted into the methyl ester by the method of Brown *et al.* (*J. Org. Chem.*, 1947, **12**, 160), chloroform (130 ml.), methanol (100 ml.), and concentrated sulphuric acid (1·5 ml.) being used. Isolation with chloroform in the usual manner, followed by distillation, yielded methyl 2-methoxydecanoate (b. p. 84°/0·5 mm.; 9 g.), an intermediate fraction, and the *ester* as a colourless oil, b. p. 188°/0·5 mm., n_D^{20} 1·4512 (41 g., 60% calculated on the acid chloride but almost quantitative when allowance is made for both the recovered starting materials) (Found : C, 70·1; H, 11·1. $C_{20}H_{38}O_4$ requires C, 70·1; H, 11·2%). In experiments otherwise similar, but omitting use of anhydrous magnesium sulphate and concentration of the solution in the cold before decarboxylation, yields of 50% were obtained.

Ponndorf Reduction of Methyl 9-*Keto*-10-*methoxyoctadecanoate.*—The ester (20 g.) in *iso*propanol (20 ml.) was added during 3 hours to a solution of pure aluminium *iso*propoxide in *iso*propanol (70 ml. of 1M.) being distilled through a Fenske column, and the reaction continued by slow, constant-volume distillations for a further 5 hours. Hydrolysis of the ester and decomposition of the aluminium complex were effected by addition of sodium hydroxide solution (150 ml. of 2N.), refluxing the mixture for 1 hour, and removing the *iso*propanol by distillation. After acidification, the products were isolated with benzene, the organic layer being concentrated to about 100 ml. and subjected to azeotropic esterification with ethanol (50 ml.) and concentrated sulphuric acid (0·5 ml.). Isolation of the ester in the usual manner, followed by distillation, furnished impure *ethyl* 9-*hydroxy*-10-*methoxyoctadecanoate* (17 g.), b. p. 185—190°/0·1 mm., n_D^{20} 1·4536 (Found : C, 70·6; H, 11·9. $C_{21}H_{42}O_4$ requires C, 70·3; H, 11·8%).

Reaction with Hydrogen Bromide in Acetic Acid.—Treatment of the foregoing ester (16 g.) with hydrogen bromide in acetic acid (300 ml.; *d* 1·2) at 90—100° for 40 hours, followed by removal of volatile acids *in vacuo*, furnished a tarry product which was triturated with light petroleum (b. p. 40—60°). The filtered extract was evaporated, the residue esterified azeotropically, and the resulting impure ethyl 9 : 10-dibromoctadecanoate distilled as a yellow oil, n_D^{20} 1·4771 (18 g.) (Found : C, 53·4; H, 8·7. Calc. for $C_{20}H_{38}O_2Br_2$: C, 51·1; H, 8·2%).

Ethyl threo-9 : 10-*Dibromoctadecanoate.*—Commercial oleic acid was crystallised from acetone at −30°, and stearic acid removed by crystallisation at −20° (Smith, *loc. cit.*). The resulting yellow oil was esterified azeotropically, and the crude, undistilled ester (14 g.) in dry ether (200 ml.) at −15° to −20° was treated with bromine (7·5 g.) with stirring. Addition was completed in 10 minutes, and the mixture was warmed to room temperature, washed with water, and dried (Na_2SO_4). Distillation yielded a small fore-run and then the bromo-ester (14 g.), b. p. 195—200°/0·1 mm., n_D^{20} 1·4861. After two redistillations, the product had n_D^{20} 1·4871, unchanged by further fractionation.

Debromination of the Impure Synthetic Dibromo-ester.—The dibromo-ester (17 g.; from hydrogen bromide treatment of the Ponndorf reduction product) was refluxed for 3 hours with zinc (25 g.), sodium iodide (34 g.), and acetone (400 ml.), the filtered solution being concentrated under reduced pressure and diluted with water. The unsaturated ester was isolated with light petroleum (b. p. 60—80°) and distilled as a colourless oil, b. p. 157—160°/0·1 mm. (I.V., 72·1. Calc. for $C_{20}H_{38}O_2$: I.V., 82·0). Saponification in the usual manner, followed by fractional crystallisation from acetone at progressively lower temperatures, yielded stearic acid (m. p. and mixed m. p. 69—70°), elaidic acid (m. p. and mixed m. p. 43·5°; *p*-phenylphenacyl ester, m. p. and mixed m. p. 73—74°), and oleic acid, isolated as the lithium salt, which was directly converted into *p*-phenylphenacyl oleate (m. p. and mixed m. p. 60°).

Reaction of 9-*Keto*-10-*methoxyoctadecanoic Acid with Hydrogen Bromide in Acetic Acid.*—The acid (from saponification of 5 g. of methyl ester) was heated with hydrogen bromide in acetic acid under the same conditions as used previously with the hydroxy-methoxy-compound. After removal of volatile acids as previously, the residual brown viscous material was repeatedly extracted with boiling light petroleum (b. p. 60—80°), leaving a residue which was still acidic since it readily dissolved in aqueous alkali. Attempts to purify it either by low-temperature crystallisation from ethyl acetate, in which it is readily soluble, or by distillation of the ethyl ester (not volatile at 300°/0·5 mm.) were unsuccessful. Evaporation of the light petroleum extracts furnished a crystalline residue, which separated from acetone (charcoal) at −70° in small plates, m. p. 72° (1·2 g.). Recrystallisation from light petroleum (b. p. 60—80°) yielded a material, m. p. 73—74° (Found : C, 72·5; H, 11·5. Calc. for keto-octadecanoic acids, $C_{18}H_{34}O_3$: C, 72·4; H, 11·5%), which was recovered unchanged, m. p. and mixed m. p. 73°, after being warmed with a solution of chromic acid in acetic acid, and after attempted catalytic hydrogenation in ethyl acetate solution in the presence of palladised strontium carbonate. Reduction by the modified Wolff–Kishner method, exactly as described by Huang-Minlon (*loc. cit.*), gave stearic acid, plates (from acetone), m. p. 68° undepressed by admixture with an authentic specimen.

Catalytic Hydrogenation of Methyl 9-*Keto*-10-*methoxyoctadecanoate.*—(a) *Using Raney nickel.* A solution of the ester (12 g.) in methanol (100 ml.) was stirred with Raney nickel (Mozingo, *loc. cit.*) in hydrogen (50 atm.; 100—110°) for 18 hours. The filtered solution was distilled to give crude methyl 9-hydroxy-10-methoxyoctadecanoate as a colourless oil, b. p. 190°/0·5 mm., n_D^{20} 1·4551 (9 g.). The analytical results (Found : C, 70·6; H, 12·0. Calc. for $C_{20}H_{40}O_4$: C, 69·7; H, 11·7%) suggest that side reactions involving loss of oxygen had occurred. This material was converted by the procedures already used for the ethyl ester into the crude dibromo-ester and thence into the corresponding unsaturated ester (I.V., 70·2). Saponification yielded a mixture of acids which were separated as before into stearic, elaidic, and oleic acids.

(b) *Using Raney nickel* W7. The ester (15·5 g.) was added to Raney nickel W7 catalyst (*ca.* 5 g.; Adkins and Billica, *loc. cit.*) previously stirred under hydrogen with ethanol (250 ml.). Absorption was rapid and ceased when 1000 ml. had been taken up (theory, 1010 ml.). After the catalyst had been filtered off and washed with ethanol, the combined filtrates were concentrated to small bulk under reduced pressure, and then light petroleum (b. p. 60—80°; 150 ml.) was added. The solution was washed with dilute sulphuric acid, potassium hydrogen carbonate solution, and water, then dried (Na_2SO_4) and distilled. The pure *methyl* 9-*hydroxy*-10-*methoxyoctadecanoate* was thus obtained as a colourless oil, b. p. 178°/0·5 mm. (14 g.), n_D^{20} 1·4553 (Found: C, 70·0; H, 11·9. $C_{20}H_{40}O_4$ requires C, 69·7; H, 11·7%).

Model Experiments with erythro-9 : 10-*Dihydroxyoctadecanoic Acid*.—(1) *With hydrogen bromide in acetic acid.* (i) The dihydroxy-acid (4 g.; m. p. 130°) was warmed with the reagent (40 ml.; *d* 1·2) to 90° during 3 hours and then kept at this temperature for a further 12 hours, whereafter the products were isolated and esterified as before. Distillation yielded the following fractions: (*a*) b. p. 180—192°/0·2 mm., n_D^{20} 1·4787 (0·5 g.), (*b*) b. p. 192—197°/0·2 mm., n_D^{20} 1·4823 (1·5 g.), and (*c*) b. p. 197—198°/0·2 mm., n_D^{20} 1·4853 (0·5 g.). Comparison of these refractive indices with that of the pure product (n_D^{20} 1·4871) obtained from ethyl oleate and bromine, shows that even the highest-boiling fraction (*c*) contains much impurity. A solution of the combined fractions in light petroleum (b. p. 40—60°; 150 ml.) was run on a 6″ column of activated alumina, and elution effected with the same solvent (200 ml.), but only slight separation was realised, the fractions having n_D^{20} 1·4818—1·4842.

(ii) A sample of the hydroxy-acid (7 g.) was treated with hydrogen bromide as above for 40 hours at 100°; a portion of the light petroleum-soluble dibromo-acid was dried to constant weight *in vacuo* and analysed (Found: Br, 34·1. Calc. for $C_{18}H_{34}O_2Br_2$: Br, 36·2%). The remainder was converted into ester (9 g.; n_D^{20} 1·4832), which was then debrominated by the zinc–sodium iodide–acetone method to give an unsaturated ester (I.V. 72). Saponification, followed by crystallisation of the resulting acid from light petroleum (b. p. 40—60°) at 0°, yielded stearic acid, m. p. 68—69° and mixed m. p. 69—70° (0·05 g. from 1·5 g. of the unsaturated ester).

(2) *With hydrogen bromide–acetic acid–sulphuric acid.* To the dihydroxy-acid (5 g.) was added hydrogen bromide–acetic acid (50 ml.; *d* 1·25), followed by concentrated sulphuric acid (5 ml.) in small portions with shaking and cooling. The solid had completely dissolved in a few hours, but after 16 hours a small layer of oil separated; the mixture was then heated at 100° for 8 hours (a further 5 ml. of the hydrogen bromide reagent were added after 4 hours). Water was then added, and the pale-red oil isolated with light petroleum (b. p. 60—80°). After being washed with water and dried ($MgSO_4$), the solvent was removed, and the residue esterified azeotropically. The crude ester was dissolved in light petroleum (b. p. 40—60°; 200 ml.), run on a 6″ column of activated alumina, and eluted with the same solvent (400 ml.). Distillation of the colourless total eluates yielded ethyl *threo*-9 : 10-dibromoctadecanoate as a pale yellow oil, b. p. 210°/0·3 mm., n_D^{20} 1·4866 (6·5 g.) (Found: C, 51·5; H, 8·3; Br, 34·1. Calc. for $C_{20}H_{38}O_2Br_2$: C, 51·1; H, 8·2; Br, 34·0%). If the purification using alumina was omitted, some decomposition occurred on distillation.

Zinc (15 g.) was activated by 5 minutes' boiling with ethanol (75 ml.) and aqueous hydrobromic acid (1 ml. of 60%), and after addition of the foregoing dibromo-ester (6·5 g.), the mixture was refluxed for 1 hour in an atmosphere of nitrogen. The zinc was removed by filtration and washed with light petroleum (b. p. 60—80°; 100 ml.), and the combined filtrates were washed with dilute sulphuric acid and then water. After drying ($MgSO_4$), the solution was distilled (nitrogen leak) to give ethyl oleate as a colourless oil, b. p. 148°/0·4 mm., n_D^{20} 1·4516 (3·4 g.) (I.V., 81·9. Calc.: I.V., 82·0). When the ester was saponified (in nitrogen) in the usual manner, the oleic acid (b. p. 160°/0·1 mm.) obtained had m. p. 12° (capillary) [α-form has m. p. 13·36° according to Smith (*loc. cit.*)], n_D^{20} 1·4608, I.V., 90·0 (Calc. for $C_{18}H_{34}O_2$: I.V., 89·9). The low m. p. is attributed to the presence of isomeric octadecenoic acids in the sample of oleic acid used as starting material.

Comparison of Debromination Methods.—(a) *Use of zinc–sodium iodide.* The substantially pure ethyl *threo*-dibromoctadecanoate (obtained from ethyl oleate, see p. 1083) was debrominated by the method described on p. 1083 to give ethyl oleate (b. p. 148—150°/0·1 mm.) having I.V. 78·2 (theory, 82·0) although no bromine was present.

(b) *Use of activated zinc in ethanol.* When the same sample of dibromo-ester was debrominated by use of activated zinc as above, the ethyl oleate produced (b. p. 150—152°/0·1 mm.) had I.V. 82·6.

Synthetic Ethyl 9 : 10-*Dibromoctadecanoate.*—Methyl 9-hydroxy-10-methoxyoctadecanoate (obtained by using Raney nickel W7; 9 g.) was treated with hydrogen bromide–acetic acid reagent (100 ml.) in the presence of sulphuric acid (25 ml.) as previously. Esterification of the crude product followed by passage through alumina furnished ethyl 9 : 10-dibromoctadecanoate (*erythro-* and *threo-*isomers) as an almost colourless oil, b. p. 200°/0·3 mm., n_D^{20} 1·4870 (9 g., 73%).

Oleic and Elaidic Acids.—Debromination of the latter ester (13 g.) by means of activated zinc yielded a mixture of ethyl oleate and elaidate as a colourless oil, b. p. 155°/0·2 mm., n_D^{20} 1·4513 (7·5 g.) (Found: I.V., 81·4. Calc. for $C_{20}H_{38}O_2$: I.V., 82·0). Saponification in the usual manner furnished a mixture of acids separated by low-temperature crystallisation from acetone into elaidic acid (1·9 g.; crude) and oleic acid (isolated as the lithium salt; 1·5 g.). The elaidic acid separated from light petroleum (b. p. 40—60°) in large rectangular plates, m. p. and mixed m. p. 44—44·5° (capillary) (Smith, *loc. cit.*, gives 43·5—44·5°, capillary) (Found: I.V., 88·3, 88·4. Calc.: 89·9). Lithium oleate separated from ethanol in plates, m. p. 196°. This salt (1·5 g.) was shaken with ethanol-free ether (100 ml.) and dilute hydrochloric acid (100 ml. of 2N.) until all solid had dissolved. Light petroleum (b. p. 60—80°; 100 ml.) was added, and after being washed with water and dried (Na_2SO_4), the oleic acid was distilled as a colourless oil, b. p. 165°/0·4 mm., n_D^{20} 1·4596, m. p. 11·5° (capillary) [α-form, 13·36° (thermometer in liquid); Smith, *loc. cit.*] undepressed by admixture with the natural product (Found: I.V., 89·3. Calc.: 89·9).

A portion of the elaidic acid (0·5 g.) in ethyl acetate (40 ml.) was shaken in hydrogen with palladised strontium carbonate (0·5 g. of 10%) and the stearic acid resulting from evaporation of the filtered solution was crystallised once from acetone, separating in plates, m. p. and mixed m. p. 70·5°.

Ethyl 2-Bromononanoate.—A sample of commercial pelargonic acid was converted into its ester azeotropically, and the product fractionated through a Fenske column (total-reflux head), the fraction, b. p. 105—107°/10 mm., being collected. Saponification and distillation yielded nonanoic acid, b. p. 126°/2 mm., f. p. 12° (thermometer in liquid). Thionyl chloride (240 ml.) was added to the foregoing acid (126 g.) and, after being kept at 30° for 1 hour, the mixture was heated at 100° for 1 hour and then at 110° for 3 hours while bromine (135 g.) was added. After refluxing for a further 3 hours the mass was set aside overnight, and, when excess of thionyl halides had been removed by distillation *in vacuo*, was poured into ethanol (400 ml.). The resulting clear yellow solution was kept at room temperature for 3 hours and then diluted with water (1 l.), the product being isolated with chloroform (cf. Schwenk and Papa, *J. Amer. Chem. Soc.*, 1948, **70**, 3627). Distillation through a Vigreux column afforded ethyl 2-bromononanoate as a colourless oil, b. p. 87—89°/1 mm., n_D^{20} 1·4530 (193 g., 91%).

2-Hydroxynonanoic Acid.—(*a*) The foregoing ester (193 g.) was added to a solution of potassium acetate (290 g.) in glacial acetic acid (400 ml.), and the mixture stirred under reflux for 7 hours (bath 180°) (cf. Mendel and Coops, *Rec. Trav. chim.*, 1939, **58**, 1133). After removal of acetic acid (200 ml.) by distillation, water (800 ml.) was added and the products were isolated with benzene (2 × 150 ml.). Evaporation yielded an oil, which was dissolved in ethanol (150 ml.) and refluxed for 0·5 hour with sodium hydroxide solution (200 ml.; 10N.) whereafter water (600 ml.) was added and most of the ethanol removed by distillation before the solution was acidified with sulphuric acid (600 ml.; 5N.). The crude product, which crystallised on cooling, was removed by filtration and washed with water (2 × 100 ml.), some oily material being removed with the filtrate. The damp solid was dissolved in benzene–ethyl acetate (1200 ml.; 3 : 1 by vol.) and, after being washed with water, the solution was dried (Na_2SO_4) and evaporated under reduced pressure. Crystallisation of the residue from light petroleum (b. p. 60—80°; 600 ml.) yielded 2 hydroxynonanoic acid (87 g.), m. p. 70°. A further crop (4 g.; m. p. 70°) was obtained by concentration of the mother-liquors (total yield 65% on the nonanoic acid). The acid was crystallised from light petroleum (b. p. 60—80°), giving lustrous plates, m. p. 70·5° unchanged by further crystallisation from light petroleum and chloroform (Found: C, 62·2; H, 10·3. Calc. for $C_9H_{18}O_3$: C, 62·1; H, 10·4%). The p-*bromophenacyl* ester separated from ethanol in colourless leaflets, m. p. 95·5° (Found: C, 55·5; H, 6·0. $C_{17}H_{23}O_4Br$ requires C, 55·0; H, 6·2%).

(*b*) In another experiment on the same scale, the crude α-bromo-acid chloride, obtained by removal of the thionyl halides as before, was mixed with acetic acid (250 ml.), and then formic acid (150 ml. of 98%) was added during 50 minutes with gentle warming. The mixture was kept at 100° for 1 hour and after removal of formic and acetic acids *in vacuo*, sodium hydroxide solution (1250 ml.; 2N.) and dioxan (100 ml.) were added. After 1 hours' refluxing, more sodium hydroxide solution (120 ml.) was added, and the solution refluxed for a further 7 hours. Dioxan (200 ml.) and sulphuric acid (500 ml., 10N.) were added with cooling but the hydroxy-acid did not crystallise and was therefore extracted with light petroleum (b. p. 40—60°)–ethyl acetate (750 ml.; 4 : 1). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated as previously. Crystallisation of the residue from light petroleum (b. p. 60—80°) yielded a total of 91 g. of 2-hydroxynonanoic acid, m. p. 70° (65% on the nonanoic acid).

2-Acetoxynonanoyl Chloride.—A mixture of acetyl chloride (75 ml.) and the foregoing acid (50 g.) was set aside at room temperature for 2 hours, excess of acetyl chloride removed *in vacuo*, and thionyl chloride (50 ml.) added. After being warmed at 40° for 1·5 hours and then at 60° for a similar period, the mixture was distilled to give the *acid chloride* as a colourless oil, b. p. 94°/0·5 mm. (53 g.) (Found: Cl, 15·3. $C_{11}H_{19}O_3Cl$ requires Cl, 15·1%).

10-Hydroxy-9-ketoheptadecanoic Acid (IV; $R = C_7H_{15}$, $R' = R'' = H$, $x = 6$).—The foregoing acid chloride (47 g., 0·2 mol.) was condensed with tribenzyl sodioheptane-1 : 1 : 7-tricarboxylate (0·21 mol.), and the product hydrogenated and decarboxylated, as in the previous example. The crude acetoxy-ketone was shaken with light petroleum (b. p. 40—60°; 350 ml.) and aqueous ethanol (3 × 40 ml. of 50%), forming a three-phase system from which the lowest, aqueous layer, containing heptane-1 : 1 : 7-tricarboxylic acid, was separated on each occasion. Removal of the solvent from the combined upper and middle layers furnished an oil, which was dissolved in ethanol (350 ml.) and refluxed for 3 hours with sulphuric acid (250 ml. of 2N.). Water was then added to the cooled mixture and the products were isolated with benzene. Crystallisation from light petroleum (b. p. 40—60°; 350 ml.) at 0° yielded the *acid* (8 g.), which separated from light petroleum (b. p. 60—80°) –ethyl acetate (200 : 80 ml.) in plates, m. p. 72·5° (Found: C, 68·0; H, 10·6. $C_{17}H_{32}O_4$ requires C, 68·0; H, 10·7%). By evaporation of the mother-liquors, refluxing of the residue with ethanol–sulphuric acid for 20 hours, and isolation as before, a further crop of the acid (10 g.) was obtained (total yield 18 g.; 30% on the acid chloride).

Ethyl 10-Hydroxy-9-ketoheptadecanoate.—The mother-liquors from the crystallisation of the foregoing acid were evaporated, and the residual mixed acids esterified azeotropically with ethanol (100 ml.), benzene (150 ml.), and sulphuric acid (0·5 ml.). Isolation with benzene followed by fractional distillation of the esters yielded crude ethyl 2-hydroxynonanoate and *ethyl 10-hydroxy-9-ketoheptadecanoate* (16 g., 25%) as a pale yellow oil, b. p. 184°/0·3 mm., which rapidly solidified and then separated from light petroleum (b. p. 40—60°) at −15° in plates, m. p. 32·5° (Found: C, 69·6; H, 10·9. $C_{19}H_{36}O_4$ requires C, 69·4; H, 11·0%). In a later series of experiments on the same scale, ethanol (200 ml.) and concentrated sulphuric acid (1 ml.) were added to the benzene solution obtained from the ethanol–sulphuric acid treatment, and this mixture was esterified azeotropically to give the hydroxy-keto-ester in improved yield (47 g., 71%).

Partial Isomerisation of 10-*Hydroxy*-9-*ketoheptadecanoic Acid.*—The acid (0·5 g.), dissolved in ethanol, (30 ml.), was refluxed in an atmosphere of commercial nitrogen with sodium hydroxide solution (10 ml. 2N.) for 0·5 hour. After addition of water (40 ml.), most of the ethanol was removed by distillation, and the residue acidified with sulphuric acid (15 ml.; 4N.), the resulting solid being collected by filtration. Crystallisation from light petroleum (b. p. 60—80°)–ethyl acetate furnished a small quantity of azelaic acid (m. p. 105°, undepressed on admixture with an authentic specimen), and evaporation of the mother-liquors, followed by crystallisation of the residue from light petroleum (b. p. 60—80°), yielded the equilibrium mixture of 10-hydroxy-9-keto- and 9-hydroxy-10-keto-heptadecanoic acids as plates, m. p. 61° (Found: C, 67·9; H, 10·7%).

The 9 : 10-*Dihydroxyheptadecanoic Acids.*—(*a*) When 10-hydroxy-9-ketoheptadecanoic acid (15 g.), dissolved in *iso*propanol (180 ml.), was added to a solution of aluminium *iso*propoxide in *iso*propanol (120 ml., 1M.) a large amount of solid separated, but gradual reduction was effected by slow distillation through a Fenske column fitted with a reflux head. After 1 hour, xylene (100 ml.) was added but the solid did not dissolve and the distillation was therefore resumed. When no further distillation of acetone occurred (10 hours), most of the remaining *iso*propanol was removed by distillation. Sulphuric acid (200 ml.; 5N.) was added to the residue, and the xylene removed by steam-distillation. The oily product solidified on cooling and was filtered off. Entrained inorganic materials were removed by boiling with water and, after cooling, the product was again filtered off. Crystallisation from ethanol (100 ml.), evaporation of the filtrate, and crystallisation of the residue from ethanol–ethyl acetate (80 ml.; 1 : 1) furnished erythro-9 : 10-*dihydroxyheptadecanoic acid* (6·4 g.), which separated from ethanol–ethyl acetate in plates, m. p. 128—129°, unchanged by further crystallisation (Found: C, 67·9; H, 10·9. $C_{17}H_{34}O_4$ requires C, 67·5; H, 11·3%). The *ethyl* ester, prepared by the azeotropic method, separated from light petroleum (b. p. 60—80°) in plates, m. p. 98·5° (Found: C, 69·3; H, 11·6. $C_{19}H_{38}O_4$ requires C, 69·1; H, 11·6%).

The ethyl acetate–ethanol mother-liquors from which the above acid had been crystallised were evaporated to dryness *in vacuo*. Crystallisation of the residue from ethyl acetate afforded a material, m. p. 80—90° (3·6 g.). Fractional crystallisation from ethyl acetate furnished threo-9 : 10-*dihydroxyheptadecanoic acid*, m. p. 85—86° (Found: C, 67·4; H, 10·8%). Alternatively, ethyl 10-hydroxy-9-ketoheptadecanoate (16 g.) was reduced in exactly the same manner as for methyl 9-keto-10-methoxyoctadecanoate, and the acids were separated as above to give the *erythro*- (6·6 g.) and *threo*-acids (3·6 g.).

(*b*) A solution of ethyl 10-hydroxy-9-ketoheptadecanoate (25 g.) in ethanol (200 ml.) was hydrogenated at normal pressure and temperature in the presence of Raney nickel W7 catalyst (*ca.* 5 g.), absorption being complete in 8 hours when 1670 ml. had been taken up (theory, 1710 ml.). Saponification and fractional crystallisation as in the previous case yielded the isomeric dihydroxy-acids in approximately the same proportions.

cis-*Heptadec*-9-*enoic Acid.*—*erythro*-9 : 10-Dihydroxyheptadecanoic acid (7 g.) was treated with hydrogen bromide and acetic–sulphuric acids, and the crude reaction product esterified exactly as for the corresponding stearic acid derivative. *Ethyl* threo-9 : 10-*dibromoheptadecanoate* was thus obtained as a pale yellow oil, b. p. 208°/0·5 mm., n_D^{20} 1·4871 (Found: C, 49·9; H, 7·9; Br, 34·9. $C_{19}H_{36}O_2Br_2$ requires C, 50·0; H, 8·0; Br, 35·0%). This ester (7 g.) was then treated with activated zinc in ethanol as before and furnished *ethyl* cis-*heptadec*-9-*enoate* (4·5 g.), a colourless oil, b. p. 139°/0·1 mm., n_D^{20} 1·4507 (Found: C, 77·2; H, 12·5%; I.V., 86·6. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·2%; I.V., 85·6).

Hydrolysis of the latter ester (4 g.) in an atmosphere of nitrogen furnished cis-*heptadec*-9-*enoic acid* as a colourless oil, b. p. 175°/0·5 mm., n_D^{20} 1·4598, m. p. 13—13·5° (capillary) (Found: C, 76·2; H, 12·2%; I.V., 95·3. $C_{17}H_{32}O_2$ requires C, 76·1; H, 12·0%; I.V., 94·6). The *lithium* salt separated from ethanol in rectangular plates, m. p. 198° (Found: C, 74·0; H, 11·5. $C_{17}H_{31}O_2Li$ requires C, 74·4; H, 11·4%). The p-*phenylphenacyl* ester, prepared directly from the lithium salt, crystallised from light petroleum (b. p. 60—80°) at −15° in plates, m. p. 61—62° (Found: C, 80·5; H, 9·2. $C_{31}H_{42}O_3$ requires C, 80·5; H, 9·2%).

A sample of the free acid (0·25 g.) in ethyl acetate (25 ml.) was shaken with palladised strontium carbonate (0·2 g. of 10%) in hydrogen for 4 hours. The filtered solution was evaporated to dryness, and the residual heptadecanoic acid crystallised from light petroleum (b. p. 60—80°), from which it separated in lustrous plates, m. p. 62—63° (lit., 61°).

trans-*Heptadec*-9-*enoic Acid.*—*threo*-9 : 10-Dihydroxyheptadecanoic acid (2·5 g.) was treated with hydrogen bromide–acetic acid–sulphuric acid as in the previous cases to give *ethyl* erythro-9 : 10-*dibromoheptadecanoate* as an almost colourless oil, b. p. 202°/0·4 mm., n_D^{20} 1·4876 (2·5 g.) (Found: C, 49·8; H, 8·4. $C_{19}H_{36}O_2Br_2$ requires C, 50·0; H, 8·0%). Debromination with activated zinc yielded *ethyl* trans-*heptadec*-9-*enoate* as a colourless oil, b. p. 150°/0·5 mm., n_D^{20} 1·4499 (1·5 g.) (Found: C, 77·2; H, 12·0%; I.V., 85·7. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·2%; I.V., 85·6). By saponification in the usual manner, trans-*heptadec*-9-*enoic acid* was obtained by isolation with light petroleum (b. p. 60—80°). A portion of the residue, dried *in vacuo*, had m. p. 37—38° (showing absence of any significant amount of the *cis*-isomer) raised to 38° by crystallisation from light petroleum (b. p. 40—60°) at −5° (Found: C, 76·1; H, 12·1%; I.V., 95·2. $C_{17}H_{32}O_2$ requires C, 76·1; H, 12·0%; I.V., 94·6). The p-*phenylphenacyl* ester separated from acetone at 0° in large rectangular plates, m. p. 74—75° (Found: C, 80·2; H, 9·4. $C_{31}H_{42}O_3$ requires C, 80·5; H, 9·2%).

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