Very Long Hydrocarbon Chains

I. The Synthesis of *n*-Dooctacontane and *n*-Hectane

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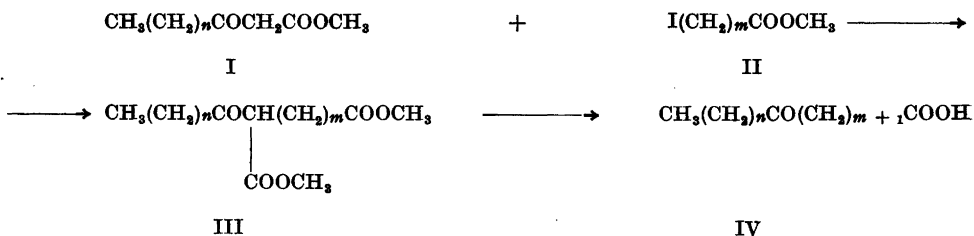*Institute of Medical Chemistry, University of Uppsala, Sweden*

The normal hydrocarbon chain is one of the simplest types of chain polymers possible, and the properties of very long chain hydrocarbons are therefore of considerable theoretical interest. Bunn [1] has attempted to determine the shape of the $-CH_2-$ group from the powder diffraction patterns given by polythene obtained by thermal polymerization of ethylene under high pressure. He found serious discrepancies between the calculated and observed values of the intensities of the diffractions which were explained as partly due to anisotropic thermal motions of the atoms in the crystal, and partly due to a distortion of the electron clouds of the $-CH_2-$ groups. However, it has since been shown by infra-red spectroscopy that polythene contains a certain number of methyl side chains [2-5]. Polythene shows a band at 1 378 cm^{-1} which lies at the position characteristic of the symmetrical deformation vibration of the methyl group, and from a comparison of the intensity of this band in polythene and in branched chain hydrocarbons of known structure, Thompson and Torkington [3] estimate that approximately one methyl group is present per fifty methylene groups. They further found a weak absorption at about 1 720 cm^{-1}, indicating the presence of carbonyl groups. Ethylenic bonds and hydroxyl groups may also be present [5]. As the crystal behaviour of long chain hydrocarbons is markedly affected by the presence of methyl side chains [6], it seems possible that at least some of the discrepancies encountered by Bunn are due to the methyl side chains present.

It thus appears desirable to repeat the X-ray and spectroscopic studies using very long chain hydrocarbons of exactly known structure and chain length. One of the aims of the present work was to develop methods for the synthesis of such compounds.

The chain-lengthening method involving the use of long chain β-keto esters. has been used in this laboratory for the synthesis of a large number of long chain compounds of different types. The method has yielded satisfactory results in the synthesis of ketones [6] and keto-acids [7,8] of fairly high molecular weight, and the yields in the case of keto-compounds with 30—36 carbon atoms have been at least as good as in the case of compounds with shorter chains. It was of interest to investigate the possibilities of the method for the preparation of very long carbon chains. The longest normal chain carboxylic acid so far described in the literature is n-hexatetracontanoic acid ($C_{46}H_{92}O_2$) prepared by Francis, King and Willis [9]. This acid was prepared by Clemmensen reduction of the corresponding 13-keto-acid, which was prepared by the modified Robinson — Robinson method [10]. The yield of the keto-acid was only 7 % of the theoretical, however.

The separation of very long chain compounds in which the chain lengths differ only by a few. Carbon atoms is usually very difficult. It is essential, therefore, to use homologue-free starting material, and to employ chain-lengthening methods that do not give rise to by-products of chain-lengths comparable to that of the desired product.

The long chain β-keto ester method can be used in two different ways in the synthesis of long chain keto-acids. A long chain ω-iodo ester (II) may be used to alkylate a long chain β-keto ester (I) and the resulting mono-alkylation product (III), after hydrolysis and decarboxylation, gives the keto-acid (IV).

$$CH_3(CH_2)_nCOCH_2COOCH_3 \quad + \quad I(CH_2)_mCOOCH_3 \longrightarrow$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

$$\longrightarrow CH_3(CH_2)_nCOCH(CH_2)_mCOOCH_3 \longrightarrow CH_3(CH_2)_nCO(CH_2)_m + {}_1COOH$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad COOCH_3$$

$$\text{III} \qquad\qquad\qquad\qquad\qquad \text{IV}$$

The second route uses 1-iodoalkanes (V) and β-keto esters (VI) derived from a monoester of a dibasic acid, and gives in an analogous manner the alkylation product (VII) and the keto-acid (VIII).

Both routes have been used in the work to be described. It has been found possible to prepare β-keto esters of the type (I) with $n = 28$ but the difficulty of separating the methyl ester of the acid used as initial material in the preparation of the β-keto ester increases as n gets larger. The preparation of pure ω-iodoesters of the type (II) with m larger than 16 is also laborious. For these reasons it was found advantageous to employ the second route for the syn-

$$CH_3(CH_2)_nI \qquad + \qquad CH_3OOCCH_2CO(CH_2)_mCOOCH_3 \longrightarrow$$

$$\text{V} \qquad\qquad\qquad\qquad \text{VI}$$

$$\longrightarrow CH_3(CH_2)_nCHCO(CH_2)_mCOOCH_3 \qquad \longrightarrow \qquad CH_3(CH_2)_{n+1}CO(CH_2)_mCOOH$$

$$\underset{\displaystyle COOCH_3}{|}$$

$$\text{VII} \qquad\qquad\qquad\qquad\qquad\qquad \text{VIII}$$

$$\underset{CH_3CH_2CH_2OH}{\overset{ZnHg_x;HCl}{\xrightarrow{\hspace{2cm}}}} CH_3(CH_2)_pCOOCH_2CH_2CH_3 \qquad \longrightarrow$$

$$(p = n + m + 2)$$

$$\text{IX}$$

$$\overset{H_2(250 \text{ atms})}{\xrightarrow{\hspace{2cm}}} CH_3(CH_2)_pCH_2OH \overset{I_2, P}{\xrightarrow{\hspace{1.5cm}}} CH_3(CH_2)_pCH_2I$$

$$\text{X} \qquad\qquad\qquad\qquad \text{XI}$$

$$2\ CH_3(CH_2)_pCH_2I \overset{Na}{\xrightarrow{\hspace{1.5cm}}} CH_3(CH_2)_{2p+2}CH_3$$

$$\text{XI} \qquad\qquad\qquad\qquad \text{XII}$$

thesis of the long chain keto-acids described in this communication, using the comparatively easily accessible methyl 2-ketooctadecane-1,18-dicarboxylate (VI, $m = 16$) (8) as "chain extender". Alkylation of (VI) with 1-iodododecane (V, $n = 11$) and 1-iododocosane (V, $n = 21$) respectively gave, after hydrolysis and ketonic cleavage of the alkylation product (VII), 18-ketohentriacontanoic acid (VIII, $n = 11$, $m = 16$), m.p. 103.6—104.1°, and 18-ketohentetracosanoic acid (VII, $n = 21$, $m = 16$), m.p. 112.4—112.8°, in yields of 69 and 64 %. 1-Iodononacosane (V, $n = 28$) and 1-iodohentriacontane gave in an analogous manner 18-ketooctatetracontanoic acid (VIII, $n = 28$, $m = 16$), m.p. 116.0—116.3°, and 18-ketopentacontanoic acid (VIII, $n = 30$, $m = 16$), m.p. 116.5—117.3°, respectively, in yields of 75—80 % of the theoretical.

The keto-acids crystallize with vertical double molecules. They may be obtained from solvents such as glacial acetic acid in the form of small, well-developed rhombic plates [Cf. 12] with an obtuse angle of 113°. They give excellent X-ray diffraction patterns showing many 00l reflexions. No polymorphism has been observed.

In order to prepare long chain primary alcohols (X) the keto-acids of the type (VIII) had first to be reduced to the corresponding n-acids and the latter further reduced to the alcohols. Considerable work had to be performed in

order to get a satisfactory procedure for the reduction of the carbonyl group of the keto-acids. Various modifications of both the Wolff-Kishner [13] and Clemmensen method [14] were tried. The convenient modification of the former method due to Huang-Minlon [15] could not be used as the potassium salts of the long chain keto-acids were too insoluble in the reaction mixture. It was found that the Clemmensen method using concentrated hydrochloric acid and glacial acetic acid (or propionic acid) did not give satisfactory results, and that an improvement could be effected by carrying out the reduction in n-propanol saturated with dry hydrogen chloride. The Clemmensen reduction performed in this manner gives the n-propyl esters (IX) of the reduced acids. The two highest propyl esters were purified by molecular distillation and the yields of the pure distilled esters of n-hentetracontanoic acid and n-pentacontanoic acid were 70 and 73 % of the theoretical respectively.

The n-propyl esters are comparatively soft. Two crystalline modifications have been observed in each case but only a single melting point. In the case of the two highest esters, *viz.* n-propyl n-hentetracontanoate (IX, $p = 39$), m.p. 84.1—84.3°, and n-propyl n-pentacontanoate (IX, $p = 48$), m.p. 93.4—93.6°, crystallization from solvents gives a crystal form with long spacings of 60 and 70 Å respectively. It was found, however, that in both cases a very gradual transition took place on heating to a crystalline form with a shorter long spacing. The transition occurs over a large temperature interval (30° or more) and is complete just before the m.p. n-Propyl n-hentriacontanoate showed a different behaviour in that the melting point at 68.6—68.8° is that of the crystal form with the longer spacing.

The long chain n-propyl esters were converted into alcohols by high pressure hydrogenation over copper chromite catalyst. It was found that the best results were obtained when the hydrogenation was performed without solvent. The yield of n-pentacontanol-1 (X, $p = 48$) from n-propyl n-pentacontanoate was 87 % of the theoretical.

It is stated in the literature [16] that the melting points of the odd- and even-numbered higher n-alcohols lie on one curve, and that this indicates that the chains are vertical (A form) at the melting point. The odd-numbered alcohols crystallize in the A form at room temperature but the even-numbered alcohols crystallize with tilted chains (B form) and it is assumed that they adopt the A form near the m.p. Although this may be true for alcohols with less than 29 carbon atoms, we have found that it is not true for higher alcohols. Investigations with the recording high temperature camera [17] showed that the C_{29} and C_{31} alcohols prepared in the course of the present work, which were present in the A form at room temperature, changed to a tilted form, which we have called B′, just before the melting point. Furthermore, a specimen of the C_{32}

alcohol * was found to retain the B form up to the melting point. It seems likely, therefore, that the higher alcohols show alternation in the melting points, with those of the odd-alcohols falling on a curve lying very slightly below that of the even numbered ones. The behaviour of the n-alcohols near the m.p. should to be further studied.

n-Hentetracontanol-1 (X, $p = 39$) showed a transition at a temperature of 87° to a form with a shorter long spacing, which melted at 97.3—97.6°. The alcohol was found to melt at 96.3—96.5° on immediate reheating after solidification. n-Pentacontanol-1 (X, $p = 48$) showed a similar thermal behaviour with melting points at 104.5—104.7° and 103.4° respectively.

The iodides (XI) with 29, 31, 41 and 50 carbon atoms were synthesized from the corresponding alcohols by means of iodine and phosphorus in the usual manner. The yields were satisfactory, even in the case of the longest chain iodide so far prepared, viz. 1-iodopentacontane (XI, $p = 48$), for which the figure for the yield was 88 % of the theoretical.

1-Iodononacosane and 1-iodohentriacontane show a crystal behaviour similar to that of the lower homologues. They crystallize from solvents with tilted double molecules and the melting points of this form are 61.6—61.8° and 71.4—72.2° respectively. In both cases a lower melting modification has been observed, but, as has previously been found for the lower homologues (11), this form is only obtained after previous heating of the molten iodide to a temperature considerably above the m.p. of the higher melting modification.

1-Iodohentetracontane is also dimorphous with melting points at 84.0—84.3° and 81.8—82.0° respectively, the lower m.p. being observed for previously melted material. This iodide crystallizes in a manner quite different from that of the lower homologues, in that the higher-melting form crystallizes with tilted single molecules. The intensity distribution among the various 00l reflexions resembles that of a n-hydrocarbon. 1-Iodopentacontane also crystallizes with single molecules. Only one melting point, viz. 92.2—92.4°, has been observed in this case.

In 1889 Hell and Hägele [18] described the synthesis of dimyricyl from myricyl iodide. The iodide was prepared from myricylalcohol derived from carnauba wax. They considered their hydrocarbon to be n-hexacontane. The exact constitution of myricyl alcohol has been the subject of discussion. Gascard [19] was of the opinion that this alcohol contains 31 carbon atoms, and this is probably the reason why the dimyricyl of Hell and Hägele in a recent monograph dealing with hydrocarbons [20] is described as n-dohexacontane. However, the extensive studies of Chibnall, Piper et al. [21] indicate that

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* We are indebted to Professor A. C. Chibnall, Cambridge, England, for this specimen.

the higher alcohols found in natural waxes are in most cases mixtures of closely related even-numbered homologues. Koonce and Brown [22] have recently shown that carnauba wax contains a mixture of the C_{28}, C_{30} and C_{32} alcohols, with the last mentioned predominating. Owing to the nature of the starting material the hydrocarbon of Hell and Hägele was thus not a pure compound, but their work showed that the Wurtz reaction could be used for the synthesis of hydrocarbons of very high molecular weight. The Wurtz reaction has since been used for the preparation of a large number of long chain hydro-carbons [Cf. e.g. 19] and long chain ethers [23]. The longest n-hydrocarbon pre-viously reported in the literature, viz. n-heptacontane, was prepared by the Wurtz reaction from decamethylene dibromide by Carothers, Hill, Kirby and Jacobson [24]. In this case the reaction products contains a series of n-hydro-carbons differing in chain length by 10 carbon atoms, but the isolation of hydrocarbons with more than 70 carbon atoms was not accomplished.

Ziegler, Weber and Gellert [23] have made a detailed study of the Wurtz reaction in order to find the conditions for optimum yield. Their work refers to the coupling of halogenalkyl-aryl ethers. They found that 1) iodides give better results than bromides, 2) potassium gives lower yields than sodium 3) up to a certain point an increase in the concentration of the halide improves the yield, and finally 4) when ethers are used as solvents an increase in the reac-tion temperature lowers the yield.

Our results are in general agreement with those of Ziegler et al. The presence of very long hydrocarbon chains is equivalent to dilution of the halide groups, with the result that the best yields were obtained when no solvent was used. Under these conditions, a fairly high reaction temperature (about 150°) together with vigorous shaking of the reaction vessel were necessary. The yields of practically pure hydrocarbons were 60—70 % of the theoretical.

n-Dooctacontane (XII, $p = 39$) and n-hectane (n-decacontane) (XII, $p = 48$) were thus obtained from 1-iodohentetracontane and 1-iodopenta-contane respectively. Final purification of the hydrocarbons was carried out by treatment with hot sulphuric acid [21]. Although this treatment leads to considerable losses [Cf. 25], it appeared the best way of purification available as the molecular weight was too large for molecular distillation. n-Doocta-contane melted at 110.3—110.4° and n-hectane at 115.1—115.4°.

A large number of empirical relations expressing the melting point as a function of the number of carbon atoms or the molecular weight of n-alkanes have been put forward [26,27]. The most satisfactory equation to date appears to be that due to Etessam and Sawyer [28]

$$T = \frac{414.5 \cdot M}{M + 94.4}$$

where T is the melting point in degrees Kelvin and M the molecular weight. The melting points of n-dooctacontane and n-hectane calculated with the aid of the above equation are 109.9° and 115.2° C respectively. These values agree well with those found experimentally.

The crystal behaviour of the hydrocarbons and some of the intermediates will be the subject of further study.

EXPERIMENTAL *

n-*Nonacosanol-1*. n-Nonacosanoic acid was prepared by Clemmensen reduction of 13-ketononacosanoic acid. The keto-acid of m.p. 102.8—103.0° was synthesized in 73 % yield from methyl 3-ketononadecanoate [29] and ethyl 11-iodohendecanoate in the manner described previously for the synthesis of 13-ketotetratriacontanoic acid [7]. The reduction of the keto-acid was carried out in the manner described for the C_{34} acid [7]. After crystallization from benzene, extraction of the crystalline material with hot acetone, and recrystallization from benzene, a 55 % yield of n-nonacosanoic acid of m.p. 90.1—90.4° was obtained. Francis and Piper [30] give m.p. 90.3°.

The acid was converted into the methyl ester by means of diazomethane, and the ester, after recrystallization from light petroleum (b. p. 40—60°), converted into alcohol by high pressure hydrogenation over copper chromite catalyst in the manner described below for the higher alcohols. After crystallization from ethanol, from chloroform, and from light petroleum (b.p. 40—60°), the alcohol formed lustrous plates melting at 84.5—84.7°. Piper, Chibnall and Williams [16] give m.p. 84.6—85.0°. At room temperature the alcohol gave a long spacing of 77.8 Å. Piper *et al.* give a value of 78.0 Å for the A form (with vertical chains) at room temperature. The diffraction pattern-temperature diagram (DPT-diagram[*Cf.* 17]) showed that a transition from the A form to a form with tilted chains (B'), having a long spacing of 72 Å, occurred at 83°.

1-Iodononacosane. n-Nonacosanol-1 (2.42 g), iodine (0.80 g), and red phosphorus (0.06 g) were kept at a temperature of 145° for 5.5 hours. The iodide was extracted with benzene, and the benzene solution washed with water followed by 2 N sodium hydroxide solution. After washing with water again part of the benzene was distilled off. On cooling the benzene solution 1-iodononacosane (2.80 g or 92 % of the theoretical) crystallized out. The iodide had m.p. 67.5—68.0°. After recrystallization from benzene the iodide formed colourless lustrous plates of m.p. 67.5—67.8°. The long X-ray spacing at room temperature, calculated from a very good photograph, was 72.0 Å. The DPT-diagram showed that this crystal form persisted up to the m.p. just recorded. After heating the melt to about 85°, solidification occurred at 61.5°. On immediate reheating melting took place at 61.6—61.8°, indicating the existence of a low melting modification.

Calcd. for $C_{29}H_{59}I$ (534.7) I 23.73 %,
Found   » 23.76 »

18-Ketooctatetracontanoic acid. 1-Iodononacosane (2.63 g), methyl 2-ketooctadecane-1,18-dicarboxylate (1.90 g [*Cf.* 8]), dry potassium carbonate (2 g), and methyl-n-propyl ketone (7 ml, the ketone was distilled from dry potassium carbonate immediately before use)

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* Melting points and crystal spacings were determined in the manner previously described [*Cf. e.g.* 6]. The molecular still used was one made by Schott und Gen., Jena [*Cf.* 6].

were refluxed (calcium chloride tube) for 24 hours. The mixture was acidified with dilute sulphuric acid and extracted with hot benzene. The hot benzene solution was washed with several portions of hot water. The benzene was distilled off, and the residue subjected to hydrolysis and ketonic cleavage by dissolving it in benzene (25 ml), and adding a solution of potassium hydroxide (8 g) in water (8 ml) and methanol (120 ml). The mixture was kept at a temperature of 55° for 60 hours with occasional shaking. Excess dilute hydrochloric acid and benzene were added, and the mixture heated to the boiling point for a few minutes. The lower clear water-methanol layer was removed. The upper (benzene) layer still contained undissolved material, and further portions of dilute hydrochloric acid and benzene (until the benzene layer had a volume of about 1 500 ml) were therefore added, and the mixture refluxed for 45 minutes. After this time both layers were clear. The benzene layer was separated and washed with hot water. Water and part of the benzene were distilled off from the benzene solution. On cooling, the benzene solution deposited crystals (2.87 g or 81.2 % of the theoretical) of 18-ketooctatetracontanoic acid, m.p. 115.5−116.2°. Crystallization from glacial acetic acid gave 2.80 g of m.p. 115.7−116.2°. Further crystallization of a portion of this material from chloroform gave the keto-acid in the form of lustrous, easily electrified crystals of m.p. 116.0−116.3°. Long X-ray spacing (pressed specimen) 126 Å.

Calcd. for $C_{48}H_{94}O_3$ (719.2)   C   80.15,   13.17 %
Found   »   80.13,   13.13 »

18-Ketohentriacontanoic acid was prepared in an analogous manner from 1-iodododecane (b.p. 118°, 2 mm) and methyl 2-ketooctadecane-1,18-dicarboxylate. The iodide was prepared from *n*-dodecanol-1 that had been distilled through a one metre electrically heated and packed column, the b.p. of the alcohol being 102°, 0.9 mm. The keto-acid was crystallized from light petroleum (b.p. 95−100°) and from glacial acetic acid. From the latter solvent the keto-acid was obtained in the form of lustrous plates melting at 103.6−104.1°. The yield of pure keto-acid was 69 % of the theoretical. Long X-ray spacing (pressed specimen) 82.4 Å.

Calcd. for $C_{31}H_{60}O_3$ (480.8)   C   77.44,   H   12.58 %
Found   »   77.31,   »   12.71 »

n-Propyl n-hentriacontanoate. The keto-acid just described was reduced by Clemmensen's method in *n*-propanol solution in a manner similar to that described below for the C_{50} homologue, the only difference being that benzene was used instead of xylene in the extractions. After crystallization from light petroleum (b.p. 40−60°), the ester formed small colourless, soft, lustrous plates melting at 68.6−69.0°. Solidification occurred at 68.4°, and remelting took place at 68.6−68.8°. Yield 82 % of the theoretical.

The X-ray diffraction pattern of a crystallized specimen at room temperature showed that two crystalline forms with long spacings of 45 and 40.5 Å respectively were present. The DPT-diagram showed that the form with the shorter spacing disappeared on heating at about 54°. A previously melted specimen showed the 45 Å spacing only.

Calcd. for $C_{34}H_{68}O_2$ (508.9)   C   80.24,   H   13.47 %
Found   »   80.44,   »   13.48 »

n-Hentriacontanol-1 was prepared by high pressure hydrogenation of the ester just described, the procedure being similar to that described for the C_{50} alcohol. After crystallization from a mixture of chloroform and light petroleum (b.p. 95−100°), the alcohol formed colourless lustrous plates melting at 87.1−87.2°. Solidification occurred at 86.5°, and the alcohol remelted at 87.0−87.2°. The melting and solidification points were unchanged after further crystallization from a mixture of ether and benzene (1 : 1) and from

light petroleum (b.p. 95—100°). Long X-ray spacing (crystallized specimen at room temperature) 83.0 Å. The DPT-diagram showed that a transition occurred at 85.5° to a form with a long spacing of 76 Å. The m.p. of this form as read from the DPT-diagram was 87.4°, which agrees, within the experimental error, with that recorded above.

Calcd. for $C_{31}H_{64}O$ (452.8)   C   82.22,   H   14.25 %
Found   »   82.24,   »   14.23 »

1-*Iodohentriacontane* was prepared from the alcohol in the manner described for the C_{50} homologue. After crystallization from ethanol-light petroleum (b.p. 100—120°) (5:1) the iodide formed colourless lustrous plates of m.p. 71.4—72.2°. The yield was 89 % of the theoretical. The melting point was unchanged after crystallization from acetone. Solidification occurred at about 68° and the iodide remelted at the temperature just mentioned. After the melt had been heated to 95°, however, solidification occurred at 65.9° and remelting took place at 66.0—66.2°, showing the existence of a lower melting modification. Long X-ray spacing (pressed specimen) 75.8 Å.

Calcd. for $C_{31}H_{63}I$ (562.7)   I   22.56 %
Found   »   22.25 »

18-*Ketohentetracontanoic* acid was prepared in a manner analogous to that just described for the C_{48} acid, using n-docosyl iodide instead of n-nonacosyl iodide. The n-docosyl iodide used had m.p. 48.2—48.4° and s.p. 41.4° (Francis et al. [11] give m.p. 48.2°, s.p. 40.6°). After crystallization from propionic acid, the keto-acid (64 % of the theoretical) melted at 111.5—112.0°, but a small part of the material did not melt until at about 125°. On further crystallization from methyl-n-hexyl ketone and from light petroleum (b.p. 95°) the amount of higher melting material increased, and after three recrystallizations the m.p. of the high-melting material was 130—131°. On cooling, solidification in the form of fine needles began at 129.5°. The compound contained nitrogen (found: N, 1.25 %), and evidently consisted of the acid ammonium salt of the keto-acid (calcd: N, 1.11 %), ammonia having been taken up from the laboratory air. The long X-ray spacing was the same as that of the free keto-acid reported below.

After crystallization from glacial acetic acid, the keto-acid was obtained in the form of small rhombic plates melting at 112.2—112.6°. Solidification with the formation of well-developed plates in the melt began at 111.5°, and remelting occurred at 111.8—112.6°.

A pressed specimen of the keto-acid gave a good X-ray diffraction pattern with a long spacing of 108 Å.

Calcd. for $C_{41}H_{80}O_3$ (621.1)   C   79.29,   H   12.98 %
Found   »   78.75,   »   12.95 »

n-*Propyl* n-*hentetracontanoate* was prepared from 4.54 g of 18-ketohentetracontanoic acid in a manner exactly analogous to that described for n-propyl n-pentacontanoate. After crystallization from ethyl acetate the ester (4.4 g) melted at 84.0—84.5°, solidified at 83.5°, and remelted at 83.9—84.0°. After molecular distillation the m.p. of the main fraction (3.2 g) as obtained in the still was 84.2—84.3°. The ester solified without nucleus at 83.9° and remelted at 84.1—84.3°. After crystallization from n-propanol the ester was obtained in the form of very small lustrous plates melting at 83.9—84.4°. Solidification occurred at 83.9° and the ester remelted at 84.1—84.3°. The long X-ray spacing of a crystallized specimen at room temperature was 60 Å, and a melted specimen showed a spacing of 53 Å. The DPT-diagram showed that on heating a crystallized specimen with a long crystal spacing of 60 Å at room temperature, a gradual transition to the form with the shorter spacing occurred. The diagram showed no discontinuity in the lines.

The decrease of the long spacing took place continously from 60° upwards, and the transition to the form with the shorter spacing was complete just before the m.p.

Calcd. for $C_{44}H_{88}O_2$ (649.1)   C   81.41,   H   13.66 %

Found   »   81.52,   »   13.68 »

n-*Hentetracontanol-1* was obtained by high pressure hydrogenation of the above ester (14.43 g) in the manner described for the C_{50} alcohol. The yield of n-hentetracontanol-1 of m.p. 97.2—97.4° was 10.45 g or 79 % of the theoretical. After recrystallization from light petroleum (b.p. 96—100°) the alcohol was obtained in the form of lustrous plates of m.p. 97.3—97.6°. Solidification (without nucleus) occurred at 95.6° and on rapid reheating melting took place at 96.3—96.5°. The DPT-diagram for a specimen crystallized from light petroleum showed that the alcohol at room temperature possessed the A form with a long spacing of 108.2 Å. On heating a transition occurred at 87° to a form with a long spacing of 93 Å. The m.p. of this form as read from the diagram was 98.0°.

Calcd. for $C_{41}H_{84}O$ (593.1)   C   83.03,   H   14.28 %

Found   »   83.04,   »   14.28 »

1-Iodohentetracontane. The iodide was prepared from the alcohol in the manner described for the C_{50} homologue. The reaction mixture was extracted with hot xylene. After part of the xylene had been distilled off the solution was allowed to cool to room temperature. The iodide separated in the form of slightly brownish, lustrous plates. The crystals were dissolved in ethyl acetate and the solution filtered. On cooling, the iodide separated in the form of colourless lustrous plates of m.p. 84.0—84.3°. Solidification occurred at 81.6° and the iodide remelted at 81.8—82.0°. The mode of solidification of the low-melting modification was similar to that of the lower homologues just described, but in this case it was not necessary to heat the melt much above the m.p. in order to obtain the low-melting form on solidification. The iodide (crystallized from ethyl acetate) gave a beautiful diffraction pattern with a long spacing of 49.0 Å. The DPT-diagram showed that this crystal form persisted up to the higher of the two melting points recorded above. A previously melted specimen showed two sets of lines, corresponding to long spacings of 49.0 and 46.8 Å respectively.

Calcd. for $C_{41}H_{83}I$ (703.0)   I   18.06 %

Found   »   17.71 »

18-Ketopentacontanoic acid was prepared in the manner described for the lower homologues, starting from 1-iodohentriacontane and methyl 2-ketooctadecane-1,18-dicarboxylate. After crystallization from xylene the keto-acid (75 % of the theoretical) melted at 116.5—117.3°. The keto-acid is very insoluble in most organic solvents at room temperature. It is best crystallized from hot xylene, methyl-n-hexyl ketone, or propionic acid, and separates on cooling in the form of small rhombic plates. The keto-acid dissolves in concentrated sulphuric acid on slight warming to give colourless solutions, but on cooling the solution to temperatures below room temperature gelation takes place.

Long X-ray spacing (pressed specimen) 131 Å. No polymorphism has been observed.

Calcd. for $C_{50}H_{98}O_3$ (747.3)   C   80.36,   H   13.22

Found   »   80.04,   »   13.20

n-*Propyl* n-*pentacontanoate.* 18-Ketopentacontanoic acid (3.68 g), mossy amalgamated zinc (100 g, Baker's Analyzed) and n-propanol (150 ml) were placed in a round bottomed flask of 500 ml capacity, fitted with gas inlet tube and reflux condenser. The mixture was heated in order to dissolve the keto-acid, and the solution saturated with dry hydrogen chloride from a commercial cylinder. After refluxing on the sand bath for three hours, the solution was again saturated with hydrogen chloride, and this was repeated at three

hours intervals. After nine hours the solution was no longer homogeneous. In order to remove water and zinc chloride formed, the reduction was interrupted. Water was added and the organic material extracted with hot xylene. The xylene solution and the zinc used were washed with hot water, the xylene solution added to the zinc, and water and xylene removed by distillation under reduced pressure. Fresh amalgamated zinc was added to replace the metal used up, n-propanol added, the mixture saturated with dry hydrogen chloride and the reduction continued in the manner described above for nine hours, after which time water and zinc chloride were again removed in the manner just described. The reduction was then continued for a third period of 9 hours, the solution being saturated with hydrogen chloride at three hours intervals.

The organic material was extracted with hot xylene and the solution washed with hot water. The solvent was removed under reduced pressure, and the colourless residue dissolved in ethyl acetate. The solution was filtered hot in order to remove a small amount of undissolved material. On cooling, the filtrate gave 3.48 g of white, crystalline n-propyl ester of n-pentacontanoic acid. The m.p. of the ester obtained was 92.8 — 93.2°. The ester was distilled in the molecular still, the following fractions being taken:

I	0.50 g	93.4 — 93.6°
II	2.30 g	93.4 — 93.6°
III	0.07 g	93.2 — 93.4°

The yield of pure n-propyl n-pentacontanoate (fractions I + II) was 2.80 g or 73 % of the theoretical, calculated on the keto-acid used. After crystallization from light petroleum (b.p. 95 — 100°) the ester formed small lustrous plates melting at 93.4 — 93.6°. Solidification took place at 93.35° with the formation of small needles within the melt.

The long X-ray spacing of a crystallized specimen at room temperature was 70 Å. A melted specimen gave a spacing of 61.5 Å. The DPT-diagram of a crystallized specimen showed a gradual transition to the form with the shorter spacing, the transition being of the same type as in the case of the lower homologue.

Calcd. for $C_{53}H_{106}O_2$ (775.4)   C   82.09,   H   13.78 %
Found   »   82.17,   »   13.73 »

n-*Pentacontanol-1.* n-Propyl n-pentacontanoate (3.48 g) and copper chromite catalyst (2.5 g) were placed in a high pressure reaction vessel of 40 ml capacity. The vessel was filled with hydrogen at a pressure (at room temperature) of 150 kgs/sq. cm, and the hydrogenation carried out at a temperature of 250°. After 2.5 hours at 250° there was no further drop in the pressure. The reaction products were taken up in 500 ml of hot light petroleum (b.p. 96 — 100°). The solution was filtered to remove suspended catalyst, and on cooling 2.80 g (87 % of the theoretical) of n-pentacontanol-1 were obtained. The m.p. of the alcohol was 104.5 — 104.7°. Solidification occurred at 102.1°. On immediate reheating melting occurred at 103.4°, but after cooling down a few degrees followed by slow reheating the m.p. was 104.3 — 104.6°. The X-ray diffraction pattern of a crystallized specimen showed a long spacing of 131 Å (A form). A few weak lines corresponding to a second crystalline form were seen in the diffraction patterns of some specimens. The DPT-diagram showed that the latter form disappeared on heating and that the form with the 131 Å spacing persisted up to the melting point.

Calcd. for $C_{50}H_{102}O$ (719.3)   C   83.48,   14.29 %
Found   »   83.83,   14.40 »

1-Iodopentacontane. n-Pentacontanol-1 (2.0 g), iodine (0.4 g) and red phosphorus (0.03 g) were kept at a temperature of 148° for 9 hours. The iodide was extracted from the reaction mixture by warm xylene. The xylene solution was washed with water, fol-

lowed by 2 N sodium hydroxide solution and water again. Part of the xylene was distilled off *in vacuo* and, on cooling to room temperature, the remaining solution deposited yellow-greyish crystals of iodide. The material was dissolved in 400 ml of diisopropyl ether, and the hot solution treated with charcoal, filtered, and allowed to cool to room temperature. 2.0 Grams (88 % of the theoretical) of 1-iodopentacontane, m.p. 92.1 — 92.3°, s.p. 91.5°, were obtained in the form of small colourless lustrous plates. Remelting took place at 92.2 — 92.4°. After heating the melt to 113° the same solidification and remelting points were obtained. A crystallized specimen of the iodide gave a long spacing of 54 Å.

Calcd. for $C_{50}H_{101}I$ (829.2)   I   15.31 %
Found   »   15.11 »

n-*Dooctacontane.* 1-Iodohentetracontane (1.0 g) and sodium (0.5 g) were placed in a thick-walled glass tube of 25 ml volume. The tube was sealed off, placed in a shaking oven and shaken at a temperature of 155° for 34 hours. The temperature of the oven was kept constant within very close limits by a thermocouple and a temperature controller.

After cooling, the tube was opened and the solid cake dissolved in a mixture of xylene and ethanol. The mixture was heated and boiled until all sodium had disappeared. The solution was then washed twice with hot water, and the xylene layer, which now contained a suspended precipitate of hydrocarbon, separated and allowed to cool slightly. The precipitated material was filtered off and crystallized from light petroleum (B.D.H., b.p. above 120°), giving 0.48 g (58 % of the theoretical) of colourless n-dooctacontane melting at 109.6 — 110.0°. In order to remove unsaturated impurities, the hydrocarbon was treated with concentrated sulphuric acid at 110° for one hour. Water was added, and the dark-coloured hydrocarbon taken up in hot xylene. The xylene was distilled off and the residue dissolved in butyl acetate and treated with charcoal. After crystallization from butyl acetate the product was slightly yellow, and the charcoal treatment was therefore repeated. After a final crystallization from butyl acetate 0.20 g of n-dooctacontane was obtained in the form of small colourless lustrous plates. The m.p. was 110.3 — 110.4°. Solidification took place at 110.0° with the formation of long needles within the melt, and the hydrocarbon remelted at 110.3—110.4°.

Long X-ray spacing (pressed specimen) 106 Å.

Calcd. for $C_{82}H_{166}$ (1.152.1)   C   85.48,   H   14.52 %
Found   »   85.50,   »   14.52 »

n-*Hectane* (n-*Decacontane*). 1-Iodopentacontane (1.09 g) and sodium (0.5 g) were placed inside a thick-walled tube, which was sealed off and heated for 38 hours to a temperature of 154° in the shaking oven. After cooling, the tube was opened and the solid cake dissolved in a mixture of xylene and ethanol. The mixture was boiled gently until all sodium had disappeared. Owing to the low solubility of the hydrocarbon, it became necessary to add light petroleum (b.p. above 120°) to the xylene-ethanol mixture in order to get a clear solution. The solution was washed with hot water and allowed to cool, giving 0.78 g of crude hydrocarbon. Crystallization from butyl acetate gave 0.76 g of white microcrystalline material of m.p. (after previous melting) 111.7 — 112.5°. After two crystallizations from high-boiling (b.p. above 120°) light petroleum and one from butyl acetate, in each case using a solvent volume of about 200 ml and filtering off the crystals formed at a temperature of 50°, 0.50 g (61 % of the theoretical) of hydrocarbon was obtained. M.p. 113.8 — 114.2°. The hydrocarbon solidified at 113.6°. 0.3 Gram of this product was treated with concentrated sulphuric acid for one hour at 110°. After cooling, water was cautiously added, and the hydrocarbon extracted with hot light petroleum (b.p. 96 — 100°). The solution was washed twice with hot water. The light-

petroleum layer was separated and allowed to cool. The hydrocarbon separated on cooling in microcrystalline form and was filtered off with some difficulty. The greyish mass obtained was dissolved in 100 ml of butyl acetate, and the still slightly greyish crystals obtained on cooling this solution treated with charcoal in hot butyl acetate solution and again crystallized from this solvent, giving 0.06 g of n-hectane in the form of small, colourless, lustrous plates. M.p. 115.1—115.4°. The hydrocarbon solidified at 114.9° and remelted at 115.1—115.4°. Long X-ray spacing (pressed specimen) 130 Å.

Calcd. for $C_{100}H_{202}$ (1.404.6)   C   85.50,   H   14.50 %
Found   »   85.45,   »   14.47 »

SUMMARY

The long chain β-keto ester method has been applied to the synthesis of a series of long chain keto-acids, up to and including 18-ketopentacontanoic acid. Alkylation of methyl 2-ketooctadecane-1,18-dicarboxylate with the appropriate long normal chain iodides gives, after hydrolysis and ketonic cleavage, 18-keto-acids in 63 to 81 % yield. The keto-acids are reduced by Clemmensen's method using n-propanol and dry hydrogen chloride. The propyl esters obtained in the reduction have been converted into the corresponding alcohols by high pressure hydrogenation over copper chromite. The alcohols have finally been converted into the iodides. The overall yield keto-acid → iodide is of the order of 50 % of the theoretical. The long chain compounds have been carefully purified, in many cases by molecular distillation, and their purity checked by means of thermal and X-ray investigations. It has been found that the crystal behaviour of n-alcohols and iodides with more than 40 carbon atoms is considerably different from that of the lower homologues.

1-Iodohentetracontane and 1-iodopentacontane give in the Wurtz reaction n-dooctacontane and n-hectane (n-decacontane) respectively. The latter hydrocarbon with a molecular weight of 1 404.6 and m.p. 115.1—115.4° is the longest chain n-hydrocarbon so far synthesized.

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