under petroleum ether. This material (1.8 g. yield) appeared to be completely amorphous under the polarizing microscope. A 100-mg. sample was heated to boiling for about five minutes with 1 cc. of 12 *N* sodium hydroxide solution, but the material remained unchanged. In a capillary tube the product softened and liquefied between 130 and 160°.

Anal. Calcd. for $C_7H_4F_2O$: C, 59.16; H, 2.82. Found: C, 59.28; H, 2.97.

A solution of 1.0 g. of *m*-trifluoromethylphenol[12] in 5 cc. of 50% aqueous sodium hydroxide was heated at 100° for fifteen minutes. There was no evidence of reaction. When the solution was diluted and acidified, it gave a negative test for fluoride ion.

Summary

Improved methods for the preparation of *o*- and *p*-nitrobenzotrifluorides have been described.

p-Aminobenzotrifluoride; *o*-fluorobenzotrifluoride, *o*- and *p*-bromobenzotrifluorides, *o*- and *p*-iodobenzotrifluorides and *o*- and *p*-trifluoromethylphenols have been prepared and characterized.

o-Bromo, *o*-iodo and *p*-bromobenzotrifluorides have been found to form Grignard reagents which have been carbonated to yield *o*- and *p*-trifluoromethylbenzoic acids.

o- and *p*-trifluoromethylphenols have been found to be decomposed readily by aqueous alkali.

INDIANAPOLIS, INDIANA RECEIVED APRIL 9, 1947

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

The Synthesis of Some Long-chain Primary Alcohols and Related Compounds[1]

BY REUBEN G. JONES

During an investigation of naturally-occurring waxy materials, it became necessary to have pure authentic samples of a number of long, straight-chain primary alcohols for purposes of comparison. This paper describes the synthesis of all of the straight-chain, primary alcohols and the ethyl esters of all of the straight-chain carboxylic acids containing twenty-eight to thirty-five carbon atoms. Greatly improved methods have been developed for the preparation of these compounds in comparatively large quantities from the readily available starting materials, octadecyl bromide, sebacic acid and undecylenic acid.

The synthesis of the long-chain aliphatic acids and their derivatives containing more than twenty-five carbon atoms has usually been accomplished by the conventional methods of lengthening the chain by successive increments of one[1a] or two[2] carbon atoms starting from stearic or behenic acid. These methods become exceedingly tedious when derivatives containing thirty or more carbon atoms are desired. Robinson has devised a method[3] for adding long chains in one operation. The intermediate ketonic acids [A] are obtained through acetoacetic ester condensations and can be readily reduced by the Clemmensen method to the unsubstituted long-chain acid.

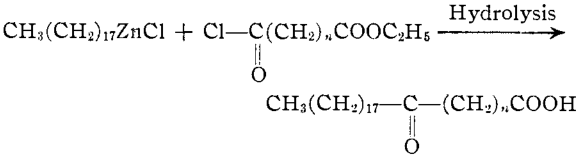
$$CH_3(CH_2)_nCO(CH_2)_{n_1}COOH$$

[A]

Over-all yields by the Robinson procedure, however, leave much to be desired.[3b]

It has now been found that the long-chain ketonic acids such as [A] can be prepared in excellent yields by the reaction of alkyl zinc or cadmium compounds with ω-carbalkoxyacyl halides. Indeed, reactions of this type have been used for the preparation of lower members of the ketonic acid series by a number of investigators.[4]

In the present work octadecylzinc chloride was treated with a series of ω-carbethoxyacyl chlorides to produce the ketonic acids (Table IV) in 75 to 90% yields.



$$CH_3(CH_2)_{17}ZnCl + Cl-\underset{\overset{\|}{O}}{C}(CH_2)_nCOOC_2H_5 \xrightarrow{\text{Hydrolysis}} CH_3(CH_2)_{17}-\underset{\overset{\|}{O}}{C}-(CH_2)_nCOOH$$

The ω-carbethoxyacyl chlorides, $C_2H_5OOC(CH_2)_nCOCl$, were made by the reaction of thionyl chloride with the acidic esters (Table III), which, in turn, were made from the straight-chain dicarboxylic acids by a modification of the "Organic Syntheses" method[5] for ethyl hydrogen sebacate (see experimental). Undecylenic acid served as the starting material for the preparation of 1,9-nonanedicarboxylic acid, 1,10-decanedicarboxylic acid, and brassylic acid according to the methods of Walker and Lumsden.[6] 1,12-Dodecanedicarboxylic acid, 1,13-tridecanedicarboxylic acid, 1,14-tetradecanedicarboxylic acid and 1,15-penta-

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[1] Presented at the 111th meeting of the American Chemical Society, Division of Organic Chemistry, April 14, 1947.

[1a] Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

[2] (a) Francis, Collins and Piper, *Proc. Roy. Soc.* (*London*), **A158**, 691 (1937); (b) Bleyberg and Ulrich, *Ber.*, **64**, 2504 (1931); Schuette and Vogel, *Oil & Soap*, **20**, 263 (1943).

[3] (a) Robinson, *J. Chem. Soc.*, 745 (1930); 1543 (1934); (b) Francis and King, *ibid.*, 999 (1937).

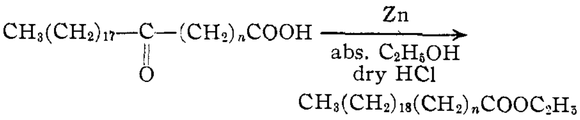
[4] (a) Blaise and Koehler, *Bull. soc. chim.*, **7**, 215(1910); (b) Ruzicka and Stoll, *Helv. Chim. Acta*, **10**, 691 (1927); (c) Späth and Darling, *Ber.*, **63**, 737 (1930); (d) Spielman, *J. Biol. Chem.*, **106**, 87 (1934); (e) Schneider and Spielman, *ibid.*, **142**, 345 (1942); (f) Cason, *Chem. Rev.*, **40**, 15 (1947); (g) the author's attention has been called to a recent publication by Schuette, Roth and Christenson, *Oil & Soap*, **22**, 107 (1945), which describes the preparation of 10-ketohentriacontanoic acid from docosylzinc chloride and ω-carbethoxynonoyl chloride.

[5] Swann, Oehler and Buswell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 276.

[6] Walker and Lumsden, *J. Chem. Soc.*, **79**, 1191 (1901).

decanedicarboxylic acid were prepared according to the methods of Chuit.[7]

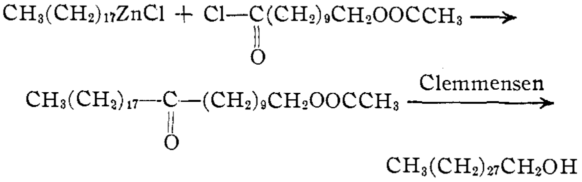
Clemmensen reduction of the ketonic acids in absolute alcohol as recommended by Schneider and Spielman[4e] gave 85 to 95% yields of the long-chain esters (Table II).



$$CH_3(CH_2)_{17}-\underset{\underset{O}{\|}}{C}-(CH_2)_nCOOH \xrightarrow[\text{abs. } C_2H_5OH \text{ dry HCl}]{Zn} CH_3(CH_2)_{18}(CH_2)_nCOOC_2H_5$$

Reduction of the ethyl esters with sodium and butyl alcohol as outlined by Francis, Collins and Piper[2a] led to the primary alcohols (Table I) which were purified by high-vacuum sublimation followed by crystallization from petroleum ether. With the exception of ethyl nonacosanoate,[2a] the members of both the ester and the alcohol series containing an odd number of carbon atoms appear not to have been previously described.

A modification of the general procedure described above allows the direct preparation of long-chain alcohols without the necessity of carrying out Bouveault–Blanc reductions on the corresponding long-chain esters. This is accomplished by causing an alkyl zinc compound to react with an ω-acetoxyacyl chloride and reducing the resulting long-chain ketonic acetoxy compound.



$$CH_3(CH_2)_{17}ZnCl + Cl-\underset{\underset{O}{\|}}{C}(CH_2)_9CH_2OOCCH_3 \longrightarrow$$

$$CH_3(CH_2)_{17}-\underset{\underset{O}{\|}}{C}-(CH_2)_9CH_2OOCCH_3 \xrightarrow{\text{Clemmensen}} CH_3(CH_2)_{27}CH_2OH$$

By this two-step process a large quantity of pure nonacosyl alcohol was synthesized from octadecylzinc chloride and ω-acetoxyundecanoyl chloride. This sequence of reactions should prove highly useful in the syntheses of other members of the long-chain alcohol series, especially since many of the intermediate ω-hydroxy aliphatic acids are available.[8]

In Table I are recorded the melting points of the alcohols and in Table II, the melting points of the esters. In the last columns (marked m. p., F. C. and P.) of Tables I and II, are listed the most recently published figures for the melting points of the alcohols and esters containing an even number of carbon atoms as reported by Francis, Collins and Piper.[2a] It will be seen that the melting points of the esters reported at this time lie from 0.2 to 1.0° below the values observed by the British workers. Also in the case of the thirty-two and thirty-four carbon alcohols, the present melting points are, respectively, 1.0 and 0.6° lower than the earlier published values. These discrepancies are more clearly illustrated in Fig. 1, where the melting points of the esters and of the alcohols are plotted against the carbon content of the compounds. The melting points of the esters fall on a smooth curve as is the case with the lower mem-

TABLE I

LONG-CHAIN ALCOHOLS, $CH_3(CH_2)_nOH$

Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	M. p., °C.	M. p., F. C. & P.
$C_{28}H_{58}O$					82.7	82.6
$C_{29}H_{60}O$	82.00	14.24	81.87	14.10	83.8	
$C_{30}H_{62}O$					86.5	86.5
$C_{31}H_{64}O$	82.22	14.25	82.20	14.00	87.0	
$C_{32}H_{66}O$					88.2	89.2
$C_{33}H_{68}O$	82.42	14.25	82.43	14.20	88.6	
$C_{34}H_{70}O$					91.1	91.7
$C_{35}H_{72}O$	82.58	14.26	82.38	13.90	91.5	

TABLE II

ETHYL ESTERS OF LONG-CHAIN ACIDS, $CH_3(CH_2)_n$-$COOC_2H_5$

Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	M. p., °C.	M. p., F. C. & P.
$C_{30}H_{60}O_2$					64.2	64.6
$C_{31}H_{62}O_2$	79.76	13.39	79.56	13.44	66.6	66.6
$C_{32}H_{64}O_2$					68.3	68.5
$C_{33}H_{66}O_2$	80.09	13.44	80.15	13.54	70.2	
$C_{34}H_{68}O_2$					71.8	72.5
$C_{35}H_{70}O_2$	80.39	13.49	80.18	13.52	73.2	
$C_{36}H_{72}O_2$					74.4	75.4
$C_{37}H_{74}O_2$	80.65	13.54	80.70	13.71	75.9	

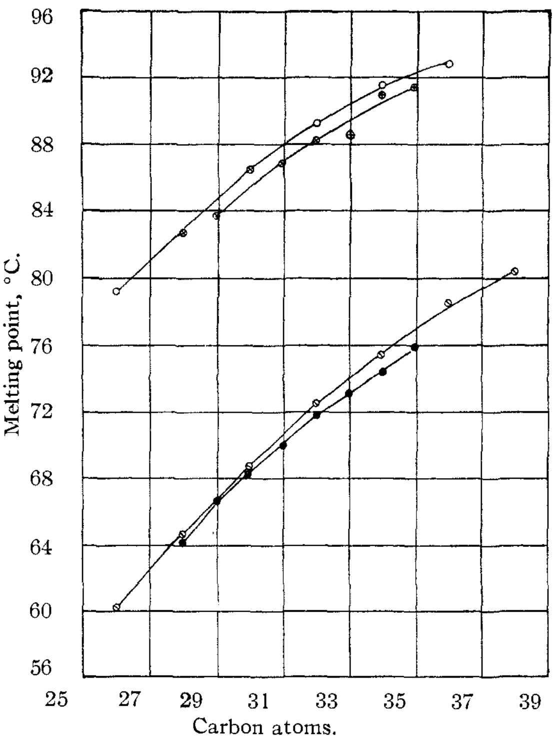


Fig. 1.—Melting point *versus* carbon content: ●, esters; ◐, esters (Francis, Collins and Piper)[2a]; ⊗, alcohols; ○, alcohols (Francis, Collins and Piper).[2a]

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(7) Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

(8) Chuit and Hausser, *ibid.*, **12**, 463 (1929); Lycan and Adams, THIS JOURNAL, **51**, 625 (1929).

bers of the series.[2a] No extensive purification was carried out on the esters (*i. e.*, they were not distilled or sublimed but merely recrystallized twice) and, therefore, the slightly low melting points might have been caused by the presence of small quantities of impurities. On the other hand these differences in melting points may arise from different crystalline modifications of the esters. It has been shown[2a] that the even members of the series containing less than twenty-eight carbon atoms possess at least two crystalline forms, the melting points of which may differ by 0.2 to 5.0°, although for the esters of the C_{28}, C_{30}, C_{32}, C_{34} and C_{36} acids, Francis, Collins and Piper[2a] obtained no evidence which would indicate more than one crystalline form.

The melting points of the alcohols lie on two smooth curves (Fig. 1), one for the even and the other for the odd members. Definitely out of line are the points for the C_{32} and C_{33} alcohols. On the basis of the curves and in comparison with the published value[2a] for C_{32}, these melting points appear to be 0.8 to 1.0° low. Also based on the curve for the even-carbon alcohols, the melting point reported by Francis, Collins and Piper[2a] for the C_{34} alcohol appears to be about 0.5 to 0.7° too high.

Experimental

α,ω-Dicarboxylic Acids.—ω-Bromoundecanoic acid, which served as the starting material for the synthesis of most of the dicarboxylic acids, was prepared by the addition of hydrogen bromide to undecylenic acid. After trying a number of procedures,[6,9] the following was found to give the best results. Dry hydrogen bromide[10] was passed into a solution of 370 g. (2 moles) of undecylenic acid (b. p. 174–176° at 20 mm.) in 3 liters of petroleum ether to which had been added 10 g. of benzoyl peroxide. The solution was kept at about 10 to 20° until thoroughly saturated, and then it was cooled to −10°. The crystalline precipitate of ω-bromoundecanoic acid was collected on a filter and the filtrate was concentrated, under vacuum, to about 500 ml. After chilling to −10°, this solution deposited an additional quantity of the desired compound. The product was recrystallized from petroleum ether, and the yield of material melting at 49–50° was usually 350–370 g. (66–70%).

1,9-Nonanedicarboxylic acid, 1,10-decanedicarboxylic acid and brassylic acid were prepared on a one-mole scale in yields of 65, 93 and 87%, respectively, according to the methods of Walker and Lumsden.[6]

1,12-Dodecanedicarboxylic Acid.[7]—Diethyl sebacate (1.0 mole) was quantitatively reduced over 30 g. of copper chromite catalyst at 260° with hydrogen at 350 atmospheres pressure[11] to 1,10-decanediol,[7] b. p. 148–150° (2 mm.); m. p. 72°. The glycol was converted to 1,10-dibromodecane,[7] b. p. 135–137° (2 mm.). The dibromodecane, 210 g. (0.7 mole), was added in portions to sodiomalonic ester made by dissolving 46 g. (2.0 g. atom) of sodium in 600 ml. of absolute alcohol and adding 350 g. (2.15 mole) of malonic ester. The mixture was boiled under reflux for eighteen hours, and then saponified with 500 ml. of 12 *N* sodium hydroxide solution. The resulting tetracarboxylic acid was decarboxylated by heating gradually up to 200°. The dicarboxylic acid obtained was taken into hot benzene, the solution was decolorized with carbon, and crystallization was effected by the addition of petroleum ether and cooling. The yield was 115 g. (64%); m. p. 122–123°. (lit. 123–124°).

1,14-Tetradecanedicarboxylic Acid.[7]—1,12-Dodecanediol,[7] m. p. 76–78° (lit. 79°), was obtained in quantitative yield by the catalytic reduction of the diethyl 1,10-decanedicarboxylate. The dibromide,[7] b. p. 165–167° (3 mm.) obtained from the glycol was converted by the use of malonic ester to 1,14-tetradecanedicarboxylic acid (83% yield), m. p. 121–123° (lit. 124°).

1,15-Pentadecanedicarboxylic Acid.[7]—Catalytic hydrogenation of diethyl brassylate gave 1,13-tridecanediol,[7] m. p. 75–76° (lit. 74°). This was converted to the dibromide,[7] b. p. 168–169° (2 mm.) and then to the dicarboxylic acid in 86% yield, m. p. 112–114° (lit. 118°).

1,13-Tridecanedicarboxylic Acid.[7]—A mixture of 175 g. (0.5 mole) of 1,13-tridecane dibromide and a solution of 130 g. (2.0 mole) of potassium cyanide in 200 ml. of water and 350 ml. of ethanol was heated under reflux for twenty hours. To the mixture was added 400 ml. of 12 *N* sodium hydroxide solution, and heating on the steam-bath was continued for seventy-two hours. The solid was taken up in 3 liters of hot water, and the clear solution was acidified with concentrated hydrochloric acid. The precipitate of 1,13-tridecanedicarboxylic acid was collected, dried and recrystallized from acetone–petroleum ether to give 127 g. (93%) of the desired product, m. p. 113–114° (lit. 115°).

ω-Carbethoxyaliphatic Acids.—The ω-carbethoxyaliphatic acids containing eleven to seventeen carbon atoms were prepared by a modification of the "Organic Syntheses" method[5] for ethyl hydrogen sebacate. The preparation of ethyl hydrogen brassylate will illustrate the procedure.

A mixture of 122 g. (0.5 mole) of brassylic acid, 86 g. (0.29 mole) of diethyl brassylate, 35 ml. of di-*n*-butyl ether and 12.5 ml. of concentrated hydrochloric acid was heated under reflux for one-half hour and then 30.0 ml. of 95% ethanol was added, and heating was continued for two hours. An additional 10 ml. of 95% ethanol was added, the mixture was boiled under reflux for another two hours, and finally the water and dibutyl ether were distilled under vacuum. The remaining hot liquid was poured into 1.5 liters of petroleum ether, allowed to stand at 20° for one hour and the precipitated brassylic acid (26 g.) was removed by filtrations. The petroleum ether filtrate was placed in a 4-liter separatory funnel and extracted with two 1-liter portions of water each containing 0.4 mole of sodium carbonate. The petroleum ether solution was evaporated, and the residue was distilled to yield 96 g. of diethyl brassylate. The combined aqueous extracts were acidified with concentrated hydrochloric acid and extracted with three 200-ml. portions of ether. After drying over magnesium sulfate, the ether solution was evaporated, and the ethyl hydrogen brassylate was distilled in vacuum. The ω-carbethoxy acids together with their boiling points, melting points and analyses are presented in Table III.

The separation of the monoesters from the diesters of the acids containing more than fourteen carbon atoms by extraction of the petroleum ether solutions with aqueous sodium or potassium carbonate was unsatisfactory because of the troublesome emulsions which formed. In these cases the monoester was best separated by fractional distillation followed by recrystallization from methanol. The yields of the desired monoesters were usually about 60%.

The ω-carbethoxy acid chlorides were obtained in 90 to 100% yields by the use of thionyl chloride; and the lower members of the series were distilled in vacuum (Table III). Those derived from the fourteen, fifteen, sixteen and seventeen-carbon acids were used directly without distillation.

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(9) Perkins and Cruz, THIS JOURNAL, **49**, 1070 (1927); Flaschentrager, *Z. physiol. Chem.*, **192**, 245 (1930); Smith, *Chemistry & Industry*, 461 (1938).

(10) Hydrogen bromide from a tank or that generated by the reaction of bromine with tetraline was satisfactory. In one run in which the hydrogen bromide was generated by burning hydrogen in bromine vapor the only product isolated was 10-bromoundecylic acid (m. p. 34–35°) even though peroxide was initially present.

(11) Wojcik and Adkins, THIS JOURNAL, **55**, 4939 (1933).

TABLE III

ω-CARBETHOXYALIPHATIC ACIDS, $C_2H_5OOC(CH_2)_nCOOH$

					Analyses, %				Acid chloride $C_2H_5OOC(CH_2)_nCOCl$	
					Calcd.		Found			
n	Empirical formula	B. p., °C.	Mm.	M. p., °C.	C	H	C	H	B. p., °C.	Mm.
8	$C_{12}H_{22}O_4$	158–160	1							
9	$C_{13}H_{24}O_4$	176–178	3	43–44	63.91	9.80	64.03	9.76	137–140	2
10	$C_{14}H_{26}O_4$	182–184	1	49–50	65.08	10.14	64.89	10.01	147–150	3
11	$C_{15}H_{28}O_4$	191–193	2	56–57	66.14	10.36	66.21	10.57	157–159	2
12	$C_{16}H_{30}O_4$	198–200	2	60–61	67.10	10.56	67.21	10.47	185–190	5
13	$C_{17}H_{32}O_4$	185–187	1	64–65	67.96	10.74	67.89	10.55		
14	$C_{18}H_{34}O_4$	220–223	3	65–66	68.75	10.90	68.69	11.12		
15	$C_{19}H_{36}O_4$	196–200	0.5	67–68	69.47	11.05	69.35	10.79		

Long-chain Ketonic Acids.—The following preparation of 12-ketotriacontanoic acid is typical of the method employed in the preparation of the long-chain ketonic acids (Table IV).

A solution of 110 g. (0.33 mole) of octadecyl bromide,[12] b. p. 182–183° (2.5 mm.), m. p. 28.5°; in 400 ml. of anhydrous ether was added in the usual way to 15 g. of magnesium turnings in 100 ml. of ether. Titration[13] of the resulting Grignard solution showed it to be 0.58 molar (about 85% yield).

In a 1-liter, three-necked flask provided with a stirrer, reflux condenser and dropping funnel, were placed 38 g. (0.27 mole) of freshly-fused, powdered zinc chloride and 100 ml. of anhydrous ether. To this was added (by means of a 100-ml. pipet) 470 ml. (0.27 mole) of the octadecylmagnesium bromide solution. After the initial reaction, the mixture was stirred and heated for two hours during which time ether was allowed to distill until the volume had been reduced to about 300 ml. With continued stirring a solution of 54 g. (0.20 mole) of ω-carbethoxyundecanoyl chloride in 100 ml. of dry benzene was added during fifteen minutes. The viscous mixture was stirred and heated under reflux for three hours and then hydrolyzed with 500 ml. of 2 *N* hydrochloric acid solution. One liter of hot benzene was added. The aqueous layer was separated, and the warm benzene solution was washed with 400 ml. of hot dilute hydrochloric acid and two 400-ml. portions of hot (60–70°) water. The benzene solution was evaporated to about 100 ml., treated with 30 ml. of 12 *N* sodium hydroxide solution and 50 ml. of ethanol and digested on the steam-bath for two hours during which time most of the remaining solvent evaporated. The resulting white solid was thoroughly washed by suspension in two 500-ml. portions of warm benzene, air-dried, and then washed by suspension in two 500-ml. portions of water. Finally it was suspended in 500 ml. of 2 *N* hydrochloric acid solution and digested on the steam-bath for two hours. The 12-ketotriacontanoic acid was collected, air-dried and recrystallized from benzene.

TABLE IV

KETONIC ACIDS, $CH_3(CH_2)_{17}CO(CH_2)_nCOOH$

				Analyses, %			
				Calcd.		Found	
n	Empirical formula	Yield, %	M. p., °C.	C	H	C	H
8	$C_{28}H_{54}O_3$	77	100	76.65	12.40	76.70	12.04
9	$C_{29}H_{56}O_3$	92	101–101.5	76.93	12.47	76.90	12.14
10	$C_{30}H_{58}O_3$	79	102	77.19	12.53	76.90	12.43
11	$C_{31}H_{60}O_3$	89	103	77.44	12.58	77.35	12.77
12	$C_{32}H_{62}O_3$	76	105–105.5	77.69	12.63	77.90	12.77
13	$C_{33}H_{64}O_3$	83	105–105.5	77.89	12.68	77.78	12.55
14	$C_{34}H_{66}O_3$	77	106–106.5	78.09	12.72	78.02	13.00
15	$C_{35}H_{68}O_3$	80	106–106.5	78.29	12.77	78.39	12.58

Clemmensen Reduction of the Ketonic Acids.[4e]—Amalgamated zinc was prepared by stirring for ten minutes 600 g. of mossy zinc in a solution of 30 g. of mercuric chloride and 30 ml. of concentrated hydrochloric acid in 600 ml. of water. The zinc was then washed successively with two 400-ml. portions of water, two 300-ml. portions of 95% ethanol and two 200-ml. portions of absolute ethanol.

A mixture of 73 g. (0.15 mole) of 13-ketohentriacontanoic acid and 600 g. of amalgamated zinc in 1500 ml. of absolute alcohol was saturated with dry hydrogen chloride and boiled under reflux for twenty-four hours. There was considerable foaming at first, and for this reason it was necessary to conduct the reaction in a large flask (at least 5-liter capacity). The mixture was again thoroughly saturated with dry hydrogen chloride and heated under reflux for an additional thirty hours. The hot liquid was poured into 5 liters of water whereupon the crude ethyl hentriacontanoate solidified. The product was taken up in 1 liter of warm benzene (which had first been used to wash the reaction flask and unreacted zinc), and the benzene solution was washed with 500 ml. of hot, dilute hydrochloric acid, two 500-ml. portions of hot water, then dried over magnesium sulfate and filtered hot. The benzene solution was evaporated to a small volume and the residue was taken up in 500 ml. of hot acetone. After cooling the mixture to 0°, the ethyl hentriacontanoate was collected on a filter and recrystallized once again from acetone.

This procedure is typical for the preparation of the esters shown in Table II. The yields ranged from 85 to 95%.

Reduction of the Esters to Alcohols.—The reductions were carried out essentially as described by Francis, Collins and Piper[2a] except that sodium sand was used in place of sodium wire. The yields of the crude alcohols averaged about 50 to 60% which is considerably lower than reported by the British workers.[2a] The crude alcohols were sublimed in vacuum (1 mm., bath temperature 200 to 250°) and then recrystallized from petroleum ether to give the samples reported in Table I.

***n*-Nonacosyl Alcohol From ω-Acetoxyundecanoyl Chloride and Octadecylzinc Chloride.**—A mixture of 335 g. (1.25 mole) of ω-bromoundecanoic acid, 475 g. of anhydrous sodium acetate and 700 ml. of glacial acetic acid was boiled under reflux for eight hours. Most of the acetic acid (about 500 ml.) was removed by distillation in vacuum, and 2 liters of water was added to the solid residue. After shaking, two layers formed. The non-aqueous layer was separated and the water solution was extracted with two 200-ml. portions of ether. The combined ether and non-aqueous layer was dried over magnesium sulfate, the ether removed and the residual product distilled in vacuum to yield 218 g. (72%) of ω-acetoxyundecanoic acid[8a]; b. p. 180–182° (1.5 mm.); m. p. 35–36°.

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 64.11; H, 9.63.

A mixture of 49 g. (0.20 mole) of ω-acetoxyundecanoic acid and 30 ml. of thionyl chloride was allowed to stand at room temperature overnight and then heated for one hour on the steam-bath. The excess thionyl chloride was evaporated, and the ω-acetoxyundecanoyl chloride was distilled in vacuum. It boiled at 149–150° (2 mm.). The yield was 51 g. (97%).

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(12) Reid, Ruhoff and Burnett, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 246.

(13) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

To a preparation of octadecylzinc chloride made from 0.24 mole of octadecylmagnesium bromide and 0.3 mole of zinc chloride in a total of 500 ml. of ether was added 50 g. (0.19 mole) of ω-acetoxyundecanoyl chloride in 50 ml. of ether during fifteen minutes. While the mixture was stirred and heated, the ether was allowed to distill until the reaction mass became viscous. Then 250 ml. of dry benzene was added, and the mixture was stirred and boiled under reflux for one hour. Hydrolysis was effected by the very slow addition of 150 ml. of 2 *N* hydrochloric acid. The benzene layer was separated, washed with two 300-ml. portions of hot (70–75°) water; dried over magnesium sulfate, filtered hot and cooled to 0°. The crystalline 11-keto-1-nonacosyl acetate was collected on a filter and recrystallized from a benzene–acetone mixture. The yield was 80 g. (88%), and the melting point, 75.0–75.5°, was unchanged after recrystallization from petroleum ether.

Anal. Calcd. for $C_{31}H_{60}O_3$: C, 77.51; H, 12.50. Found: C, 77.45; H, 12.61.

The 11-keto-1-nonacosyl acetate, 71 g. (0.148 mole) was reduced by the Clemmensen method in the same manner as described above for the ketonic acids. The resulting crude nonacosyl alcohol was dissolved in 800 ml. of hot benzene and the solution was washed with 400 ml. of hot, dilute hydrochloric acid and twice with 400-ml. portions of hot water. After drying the solution over magnesium sulfate, it was filtered hot and evaporated to about 150 ml.; 150 ml. of acetone was added and the mixture cooled to −10°. The product was collected on a filter and recrystallized twice from petroleum ether (700 ml.). The yield of pure nonacosyl alcohol was 50 g. (80%) and its melting point, 83.8°, was identical with that of the sample prepared by reduction of ethyl nonacosanoate (Table I).

Melting Points.—The melting points of the alcohols (Table I) and the esters (Table II) were determined in capillary tubes essentially as described by Francis and Collins.[14] A Bureau of Standards tested thermometer was used on which 2.5 cm. of scale corresponded to 1°. The bath temperature was raised at a rate of 0.1° per five minutes.

Summary

An improved method has been developed for the preparation of the ethyl esters of long-chain acids containing twenty-eight to thirty-five carbon atoms.

A new method is described for the direct preparation of long-chain alcohols.

The ethyl esters of the acids and the primary alcohols containing twenty-nine, thirty-one, thirty-three and thirty-five carbon atoms are described for the first time.

(14) Francis and Collins, *J. Chem. Soc.*, 137 (1936).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF GENERAL MILLS, INC.]

Synthesis of Alkylmalonic Esters by Oxalate Condensations[1,2]

BY DON E. FLOYD AND SIDNEY E. MILLER

Condensations of the Claisen type between ethyl oxalate and esters of fatty acids producing α-ethoxalyl esters were first carried out by Wislicenus.[3,4] Since then the reaction has been used many times.

By removal of the alcohol formed in the reaction, McElvain and co-workers[5,6] forced ester self-condensations and obtained high yields of the β-ketoesters. Wallingford and others[7] applied this principle to the condensation of ethyl carbonate with other esters to produce yields of 10–86% of alkylmalonic esters.

Hauser and Hudson[8] give ninety-nine references in their monograph (The Acetoacetic Ester Condensation and Certain Related Reactions), but do not mention the condensation of ethyl oxalate with aliphatic esters higher than butyric. Although the preparations of the α-ethoxalyl derivatives of a variety of esters have been reported,[9,10,11] the reaction has not been applied to fatty acid esters under forcing conditions.

In the present study it was found that removing by-product alcohol in Claisen condensations involving ethyl oxalate and adjusting the relative amounts of ethyl oxalate to fatty acid ester in these reactions makes it possible to obtain excellent yields of α-ethoxalyl esters.

When the alcohol formed in the reaction is removed by distillation and the molar ratio of oxalate to other ester is 1:1, about 75–80% of the product is the α-ethoxalyl ester and the remainder is the self-condensation product of the fatty ester. When the molar ratio of oxalate to fatty ester is 2:1, the yield of α-ethoxalyl ester may exceed 90%. Higher ratios will improve the yield slightly. The yield is also higher with fatty acid esters of higher molecular weight, since the lower esters condense with themselves more readily. Ethyl oxalate gives higher yields in these reactions than does ethyl carbonate. This may be because the sodium alkoxides are much more soluble in ethyl oxalate than in ethyl carbonate or because the addition products are more soluble. The condensation, therefore, has value as a general preparative method for the higher alkylmalonic esters, since the α-ethoxalyl esters can be thermally decarbonylated to give high yields of alkylmalonic esters.

$$\mathrm{RCH_2COOC_2H_5} \xrightarrow{(\mathrm{COOC_2H_5})_2} \mathrm{RCH(COOC_2H_5)COCOOC_2H_5} \xrightarrow{-\mathrm{CO}} \mathrm{RCH(COOC_2H_5)_2}$$

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(1) Paper No. 77, Journal Series, Research Department, General Mills, Inc.

(2) Presented at the spring, 1947, meeting of the American Chemical Society at Atlantic City.

(3) Wislicenus, *Ber.*, **19**, 3225 (1886).

(4) Wislicenus, *ibid.*, **20**, 591 (1887).

(5) McElvain, THIS JOURNAL, **51**, 3124 (1929).

(6) Briese and McElvain, *ibid.*, **55**, 1697 (1933).

(7) Wallingford, Homeyer and Jones, *ibid.*, **63**, 2056 (1941).

(8) Hauser and Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, p. 266.

(9) Wislicenus, *Ber.*, **27**, 1091 (1894).

(10) Adickes and Andresen, *Ann.*, **55**, 41 (1943).

(11) Fieser and Hershberg, THIS JOURNAL, **57**, 1851 (1935).