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]

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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.

$$RCH_2COOC_2H_5 \xrightarrow{(COOC_2H_5)_2}$$

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

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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).

Experimental

It is important that the reagents and equipment be quite free from water. Distillation of a small portion of ethyl oxalate from the bulk of the material removes the water very effectively. The esters were purchased from the Eastman Kodak Company or prepared from the corresponding fatty acids by direct esterification. The fatty acid ester mixtures were prepared by alcoholysis of the natural glycerides. The alkoxides were prepared from sodium or potassium and the corresponding alcohols, although commercial dry sodium methoxide or 30% solution are suitable. The methyl, ethyl and butyl esters have been used with the corresponding alkoxides. When the alcoholic residues are not the same, some interchange of groups will occur.

General Procedures.—To a solution of 1 mole of the alcohol-free metal alkoxide in 2 moles or more of the oxalate ester was added 1 mole of fatty acid ester. The homogeneous solution was heated at about 50° under reduced pressure (about 100 mm.) while alcohol was continuously removed by distillation. During this process the temperature was gradually increased to about 60°. With the higher fatty acid esters a special fractionating column is not necessary for separation of the alcohol, while a simple indented or packed column is quite suitable in the instance of the lower esters. An alcoholic solution of the metal alkoxide may also be used as condensing agent. In this case the solvent alcohol and the by-product alcohol are then both removed by distillation as the reaction progresses.

When no more alcohol was produced, the reaction product was processed by one of two methods.

A. The reaction product was vigorously stirred at room temperature with an equivalent of glacial acetic acid or sulfuric acid dissolved in a volume of cold water equal to the volume of reaction product. The organic layer was separated, washed with water and dried. The excess oxalate ester was then distilled off under reduced pressure. The residue of α-ethoxalyl ester was then thermally decarbonylated at about 160° under slightly reduced pressure. Reduction of the pressure facilitates removal of carbon monoxide. The residual alkylmalonate was then distilled under reduced pressure. The slight residue which remained consisted of tarry material and ester self-condensation product.

B. The excess oxalate was distilled from the reaction product under reduced pressure (15 mm.). When distillation ceased, the brown, viscous liquid and an equivalent of glacial acetic or sulfuric acid in a volume of water equal to twice the volume of the reaction product were stirred well at about 50–60°, for at room temperature the product becomes extremely viscous. The organic layer was separated either directly or by ether extraction, washed with water, then with saturated sodium bicarbonate solution and finally with water. The α-ethoxalyl-ester was decarbonylated and the alkylmalonic ester distilled as in method A.

Method B has been found to be preferable in most cases since it gives slightly better yields and the separation of ethyl oxalate from the malonic ester is less difficult. Purification by extraction of the α-ethoxalyl ester with potassium carbonate solution producing the potassium salt of the α-ethoxalyl ester is not necessary. It is quite important that moisture be excluded from the reaction in order to prevent hydrolysis of the esters. If a water pump is used as a source of vacuum, a moisture trap should be included in the line to prevent diffusion of water vapor back into the reaction. It has also been found that heating much above 60° during the reaction or above 90° during distillation of the excess oxalate as in method B causes formation of the metal salts of the fatty acids and some decomposition of ethyl oxalate. This lowers the yield and results in incomplete conversion to the condensation products, and the metal soaps formed produce emulsions during the washing process.

This procedure has been applied to fatty acid esters which have 2 hydrogen atoms on the α-carbon atom. Fractional distillation was used to obtain highly purified samples of the products. The saponification equivalents of the alkylmalonic esters listed in the following table and the neutral equivalents of the corresponding acids checked the calculated values to within four parts in one thousand or better. It is important to note that the simple esters of the mixtures of fatty acids which occur naturally in oils such as linseed and soybean oils can be used to prepare the corresponding malonic ester mixtures by this method in yields similar to those given in the following table. The malonic ester mixture derived from soybean oil acids boiled at 185–193° (2 mm.) and the $n^{25}D$ was 1.4552 while that from linseed oil acids boiled at 186–193° (2 mm.) and the $n^{25}D$ was 1.4592. The iodine numbers of these products were in good agreement with calculated values. Table I summarizes the results obtained in the preparation of alkylmalonic esters from fatty acid esters.

TABLE I

ALKYLMALONIC ESTERS, $RCH(COOC_2H_5)_2$, FROM CONDENSATION OF ETHYL OXALATE WITH FATTY ACID ESTERS, $RCH_2COOC_2H_5$

RCH-(COOEt)$_2$ formed: R is	Yield by Method B, %	B. p. (uncor.), °C. (mm.)	$n^{25}D$	M. p. (cor.) RCH(COOH)$_2$, °C.
n-C_2H_5[a]	78.0	88–89 (10)	1.4157	112[h]
n-C_4H_9[b]	91.0	130–133 (17)	1.4218	102[i]
n-C_6H_{13}[c]	89.0	145–148 (15)	1.4270	105[c]
n-C_8H_{17}[d]	90.5	150–153 (7)	1.4315	116[j]
n-$C_{10}H_{21}$[e]	91.0	155–158 (3)	1.4353	120[k]
n-$C_{12}H_{25}$[f]	90.5	170–173 (2.5)	1.4388	119[l]
n-$C_{14}H_{29}$[e]	90.0	182–185 (2)	1.4413	120–121[m]
n-$C_{16}H_{33}$[g]	90.0	196–199 (2)	1.4433	119–120[n]

[a] Conrad, *Ann.*, **204**, 134 (1880).
[b] Adams and Marvel, THIS JOURNAL, **42**, 316 (1920).
[c] Dox, *ibid.*, **46**, 1708 (1924).
[d] Clutterbuck, Raistrick and Rintoul, *Trans. Roy. Soc. (London)*, **B220**, 301 (1931).
[e] Chargaff, *Ber.*, **65**, 752 (1932).
[f] Rothstein, *Bull. soc. chim.*, (5) **2**, 80 (1935).
[g] Guthzeit, *Ann.*, **206**, 357 (1881).
[h] Markownikoff, *ibid.*, **182**, 332 (1876).
[i] Hell and Lumpp, *Ber.*, **17**, 2218 (1884).
[j] Robinson, *J. Chem. Soc.*, **125**, 228 (1924).
[k] Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056 (1941).
[l] *Anal.* Calcd. for $C_{15}H_{28}O_4$: C, 66.1; H, 10.36. Found: C, 66.26; H, 10.20.
[m] Hell and Jordanow, *Ber.*, **24**, 991 (1891).
[n] Hell and Sadomsky, *ibid.*, **24**, 2781 (1891).

Summary

A procedure has been developed for the condensation of oxalate esters with fatty acid esters up to those of stearic acid, and high yields of the corresponding α-ethoxalyl esters have been obtained. These have been thermally decarbonylated to give high yields of alkylmalonic esters. The process is valuable as a general preparative method for alkyl substituted malonic esters.

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