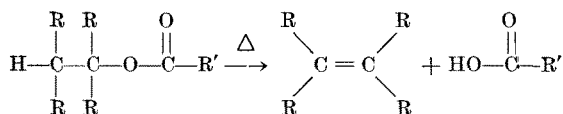


# Synthesis and Purification of Fatty Acids by The Pyrolysis of Esters<sup>1,2</sup>

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WHEN AN ESTER containing a  $\beta$ -hydrogen in the alkyl portion is heated to a high temperature, a cleavage usually takes place to form an olefin and an acid. This reaction has been used for a long time (7) to prepare



simple olefins, particularly those that were not sensitive to acid catalyzed rearrangements. It was recently reported however that if carbonization were avoided, this reaction could also be used for the synthesis of strained olefins (1). Thus 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene, was prepared in a 92% yield by the pyrolysis of a diacetate (3) while the decomposition of the corresponding quaternary ammonium hydroxide gave only *o*-xylene (8). Since the pyrolysis of esters is such an excellent method for the synthesis of unsaturated compounds, it appeared likely that pyrolysis should also be useful for the synthesis of acids. For this reason a research program was initiated to determine in which cases the pyrolysis of esters was superior in some respects to the conventional hydrolysis for the preparation of acids or their derivatives.

Although titration of the liberated acid has often been used to determine the extent of pyrolysis, very little has been published about the use of this reaction for the preparation of acids. Ratchford, Rehberg, and Fisher prepared acrylic and methacrylic acids in high yields by the pyrolysis of the corresponding esters (10, 11). Halbig developed a synthesis of formic acid which involved the pyrolysis of *tert*-amyl formate (6).

<sup>1</sup> Paper No. 6 in a series on the pyrolysis of esters; previous paper in this series, *J. Org. Chem.*, **21**, 328 (1956).

<sup>2</sup> This paper was awarded the first Fatty Acid Producers' Research Award administered by the American Oil Chemists' Society. Presentation of the award, consisting of a scroll plus \$500, was made before the fall meeting of the American Oil Chemists' Society, Oct. 11, 1955, Philadelphia, Pa.

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A survey was made to determine in which syntheses or processes a chemist proceeds from an ester to an acid. The purification of fatty acids appeared to be the most common use of this step (5). Although naturally occurring fatty acids, which contain an even number of carbon atoms, differ in boiling point by 25-30°, separation or purification by vacuum distillation requires a careful fractionation through a highly efficient column. This difficulty is due to the fact that the acids are associated in the liquid state, probably as dimers, and the mixed dimers would have boiling points intermediate between those of the simple dimers. However, if the fatty acids are converted to the corresponding ethyl esters, which do not associate as dimers, the fractionation is much easier. The ethyl esters also can be conveniently prepared directly from fat by an ester interchange (alcoholysis). The regeneration of the acid from the ester always has been the most tedious step in the procedure. The laboratory procedure involves the basic hydrolysis of the water-insoluble ester, acidification of the reaction mixture, and extraction of the acid, followed by distillation or recrystallization. A commercial process uses an acid-catalyzed hydrolysis under high pressure and temperature. It seemed likely that pyrolysis of the ethyl esters would be much easier in many cases than the conventional hydrolysis and would therefore simplify the separation or purification of the fatty acids.

A series of ethyl esters of fatty acids, caproic through stearic, was pyrolyzed by the dropping of the liquid esters through a Vycor tube packed with glass helices at 520-560°. The optimum conditions for these pyrolyses are given in Table I.

The yields of acids, based on unrecovered ester, were 86 to 90%. With the lower molecular weight esters, ethyl caproate and ethyl caprylate, virtually complete pyrolysis took place at 560° with substantially no other decomposition. However with the higher molecular weight esters considerable decomposition occurred at 560°, reducing the yield to 70 to 80%. If the pyrolysis temperature were lowered to

TABLE I  
Pyrolysis of Ethyl Esters

Ethyl Ester	Amount Pyrolyzed, G.	Boiling Point of Ester °C. mm.	<i>n</i> <sub>D</sub> <sup>20</sup> of Ester	Temp. of Furnace, °C.	Time of Pyrolysis Min.	Amount of Crude Pyrolysate G.	Amount of Acid G.	Boiling Point of Acid °C. mm.	<i>n</i> <sub>D</sub> <sup>20</sup> of Acid	Melting Point of Acid, °C.	Conversion to Acid, %	Amount of Recovered Ester, G.	Yield of Acid, Based on Unrecovered Material, %
Caproate.....	102.6	81 39	1.4047	560	80	73 <sup>a</sup>	72.4	125 33	1.4142	.....	89	1.2	90
Caprylate.....	197.6	102 20	1.4153	560	150	156 <sup>b</sup>	146	114 16	1.4256	.....	88	1.6	89
Laurate.....	103.6	106-106.5	1.5	1.4292	530	86.8 <sup>c</sup>	71.8 <sup>d</sup>	123-124 0.8	.....	44-46	79	10.1	87
Myristate.....	95.4	112 <sup>e</sup>	0.5	1.4337	540	79.2 <sup>f</sup>	67.9 <sup>g</sup>	121 0.2	.....	.....	79	6.5	86
Palmitate.....	89.2	113-120 <sup>h</sup>	0.2	1.4381	520	78.9 <sup>c</sup>	65.5 <sup>i</sup>	139-140 0.05	.....	62-64	80	5.1	86
Stearate.....	96	143 <sup>j</sup>	0.3	.....	540	83.1 <sup>c</sup>	69.5 <sup>k</sup>	140-145 0.05	.....	65-67	79	6.9	86
Glutarate.....	105	95 2.0	1.4222	560	120	81.1	79.0	.....	.....	96-97	94	.....	94
$\beta$ -Ethoxypropionate.....	46.6	65 14	1.4044	500	60	38 <sup>b,l</sup>	17.3	113 14	1.4189	.....	47	12	62
2,4,6-Trimethylbenzoate.....	10.4	72-74 0.5	1.4980	540	30	.....	7.78	.....	.....	145-149	88	.....	88

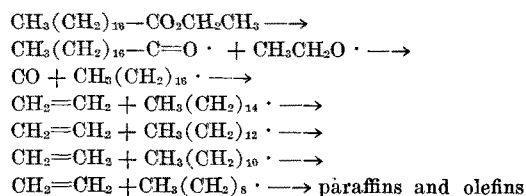
<sup>a</sup> Slightly yellow; trace of charring. <sup>b</sup> Water-white; no charring. <sup>c</sup> White solid; very little charring. <sup>d</sup> Residue in pot and 12-in. Vigreux column was dissolved in 20 ml. of petroleum ether (60-80°), treated with charcoal, and cooled in dry ice to produce 2.75 g. of lauric acid, m.p. 44-44.5°. <sup>e</sup> M.p. 12°. <sup>f</sup> Negligible amount of charring. <sup>g</sup> Residue in pot and 12-in. Vigreux column was dissolved in benzene, extracted with dilute sodium hydroxide; aqueous extracts were acidified with dilute sulfuric acid to yield 2.6 g. of myristic acid. <sup>h</sup> M.p. 24°. <sup>i</sup> Treatment of residue in pot and 12-in. Vigreux column as in g gave 2.9 g. of palmitic acid, m.p. 58-62°. <sup>j</sup> M.p. 31-32.5°. <sup>k</sup> Treatment of residue in pot and 12-in. Vigreux column as in d gave 5.5 g. of stearic acid, m.p. 66-67°. <sup>l</sup> Trace of hydroquinone added and mixture fractionated through 10-in. helix-packed column.

520–540°, the amount of acid obtained remained nearly unchanged, but some of the starting ester was recovered, increasing the yield, based on unrecovered material, to 86 to 87%.

In order to calibrate our procedure as well as to compare the pyrolysis of ethyl stearate with the basic hydrolysis, this ester was saponified with potassium hydroxide, and the crude acid was distilled through the same column that was used in working up the pyrolysate of ethyl stearate. Under these conditions a 92% yield of stearic acid was obtained, compared with 86% yield obtained by pyrolysis. Even though the pyrolysis procedure gives a slightly lower yield, it is superior to saponification in several respects.

1. No reagents or solvents are necessary.
2. Much less time is required to carry out the reaction and purification.
3. The apparatus is well adapted for the preparation of large amounts of acids.

The decomposition that occurred during the pyrolysis of the fatty acid esters at higher temperatures was very probably a free radical cleavage; depolymerization could then occur according to the following scheme:



Some decomposition undoubtedly proceeds through an acyloxy free radical as well.

When ethyl stearate was pyrolyzed at 600°, 37% of the material was lost as noncondensable gases, and a 22% yield of stearic acid was obtained. (Very little carbon dioxide was formed.) If these noncondensable gases were passed through a bromine trap, two moles of ethylene dibromine were obtained for every mole of ester pyrolyzed. One must conclude that some of the acid fragments depolymerized to produce several molecules of ethylene. This free radical decomposition is quite serious, on a percentage basis, for the esters of high molecular weight acids, but it can be neglected for the esters of low molecular weight acids since there are many more ester groups per unit weight of ester. At the lower temperatures this decomposition is not serious, and good material balances are obtained, even with ethyl stearate.

It was reasoned that this pyrolytic method should have special utility for the preparation of water-soluble acids. Glutaric acid is obtained as a by-product in the preparation of adipic acid and is conveniently separated as its ester. The free acid is regenerated by basic hydrolysis. However the high solubility of glutaric acid in water makes the isolation very tedious. If, on the other hand, the diethyl glutarate were dropped through the pyrolysis tube at 560°, a 94% yield of glutaric acid was obtained. This pyrolysis is undoubtedly the method of choice for the preparation of glutaric acid. Thus other water-soluble acids, especially dicarboxylic acids, probably could be best prepared by the pyrolysis of their esters.

In an extension of this method to other polyfunctional compounds, the pyrolysis of ethyl  $\beta$ -ethoxypropionate was studied. In this case the ester is more readily available than the acid since the ester is pre-

pared by the addition of alcohol to ethyl acrylate. When the ethyl  $\beta$ -ethoxypropionate was pyrolyzed at 560°, the principal products were acrylic acid, ethyl alcohol, and ethylene; very little  $\beta$ -ethoxypropionic acid was formed. (The amounts of alcohol and acrylic acid were determined by the use of infrared absorption.) If the temperature of pyrolysis were lowered to 500°, less acrylic acid was formed and a 47% conversion to  $\beta$ -ethoxypropionic acid was realized. Under these milder conditions 26% of the original ester was recovered so that the yield, based on unrecovered ester, was 62%. If still milder conditions were employed, presumably a higher yield of  $\beta$ -ethoxypropionic acid would be obtained.

Since it was shown that steric hindrance has little effect on the pyrolysis of esters (2), it seemed logical that pyrolysis would be useful for the preparation of sterically hindered acids. Ethyl 2,4,6-trimethylbenzoate is almost completely resistant to basic hydrolysis. Newman (9) found that this ester could be hydrolyzed by dissolving it in 100% sulfuric acid and pouring this solution into water. The ethyl 2,4,6-trimethylbenzoate was prepared in a 50% yield by the reaction of mesitylmagnesium bromide with ethyl chloroformate. Brown and Kornblum (4) used a similar procedure to prepare ethyl pivalate and 2,2-dimethylbutanoate from *tert*-butyl chloride and *tert*-amyl chloride, respectively. When 10 g. of the hindered ester were pyrolyzed at 540°, an 88% yield of the 2,4,6-trimethylbenzoic acid was obtained. It appears that pyrolysis is the preferred method to obtain a sterically hindered acid from the corresponding ester. It is significant that the high yield of acid was obtained with only a small amount of ester. Thus, if a solid acid is obtained from the pyrolysis, this method can be easily adapted to small runs.

The saving of time and material makes the pyrolysis preferable to the basic hydrolysis for the production of many acids from the corresponding esters. Pyrolysis is particularly well suited for the synthesis of water-soluble or sterically hindered acids.

The extension of the pyrolytic procedure to the synthesis of other acid derivatives will be reported later.

#### Experimental <sup>4</sup>

Typical pyrolyses of the esters are listed below. In several cases the product was identified by infrared absorption, and the purity of the acid was determined by titration with standard base.

*Pyrolysis of Ethyl Caproate.* At the rate of approximately 1 g. per minute 102.6 g. (0.71 mole) of ethyl caproate were added dropwise to a vertical Vycor combustion tube, packed with 1/8-in. glass helices and externally heated at 560°, as described by Bailey and Golden (1). The tube was continuously flushed out with a slow stream of oxygen-free nitrogen to minimize oxidation and charring. The pyrolysate was collected in a 300-ml. side-arm flask, and cooled in a dry ice-methyl cellosolve bath. The side arm of this flask was connected to a series of three traps, which were also cooled in a dry ice bath. An Ascarite tube was connected to the end trap to detect any carbon dioxide that might be liberated by decarboxylation of the acid during pyrolysis of the ester. The slightly yellow pyrolysate, 78 g., was distilled through a 10-in., helix-packed column to yield 1.2 g. of unchanged

<sup>4</sup> All melting points are corrected. The authors are grateful to Kathryn Gerdeman and Joseph Wenograd for the infrared absorption spectra.

ethyl caproate and 72.4 g. (89%) of caproic acid.

The yield of caproic acid, based on unrecovered ester, was 90%. The gain in weight of the Ascarite tube was less than 0.1 g.

**Pyrolysis of Ethyl Stearate at 600°.** When 55.6 g. of ethyl stearate were pyrolyzed in the same apparatus at 600°, the pyrolysate was condensed in a series of five traps that were cooled in a dry ice-methyl cellosolve bath to obtain 34.9 g. of condensable material. Distillation of the crude liquid pyrolysate through a 12-in. Vigreux column yielded 10.9 g. (22%) of stearic acid, m. p. 59–63°, plus a large amount of low boiling liquids. The gain in weight of the Ascarite tube was less than 0.4 g.

The gaseous pyrolysate that did not condense in the dry ice traps was passed through a solution of 150 g. of bromine in 1,000 ml. of carbon tetrachloride. The carbon tetrachloride solution was washed with a 5% sodium sulfite solution until the brown color disappeared and then with 100 ml. of water. After it was dried over calcium chloride, the solution was distilled through a 10-in., helix-packed column to yield 60.2 g. of ethylene dibromide, b. p. 122–130°,  $n_D^{25}$  1.5370 [reported (12) b. p. 130°,  $n_D^{25}$  1.5379]. If one were to assume that each molecule of ethyl stearate would liberate only one molecule of ethylene, only 33.4 g. of ethylene dibromide would be expected.

**Saponification of Ethyl Stearate.** A mixture of 100 g. (0.32 mole) of ethyl stearate, 200 ml. of water, 1,300 ml. of ethyl alcohol, and 35.8 g. (0.64 mole) of potassium hydroxide was heated under reflux for 5 hrs. (although 30 min. may have been sufficient). After 500 ml. of water had been added and 1,200 ml. of ethyl alcohol had been removed by distillation, the residue was acidified with dilute sulfuric acid. The reaction mixture was then extracted with three 250-ml. portions of a benzene-ether mixture, and the combined extracts were dried over anhydrous magnesium sulfate. After the solvents were removed by evaporation, the residue was distilled through a 12-in. Vigreux column to yield 79.5 g. of stearic acid, b. p. 153–161° (0.02 mm.), m. p. 66.5–70°. The residue in the pot and column was recrystallized from a water-dioxane mixture to give an additional 4.7 g. of stearic acid, m. p. 68–69.5°. The total yield of stearic acid was 84.2 g. (92%).

**Ethyl 2, 4, 6-Trimethylbenzoate.** To a 1-liter, three-necked flask containing 9.19 g. of magnesium and

20 ml. of ether was added dropwise a solution of 75.6 g. (0.38 mole) of bromomesitylene in 100 ml. of anhydrous ether. After the reaction mixture had been heated under reflux for 24 hrs., approximately one-fourth of the magnesium remained unreacted. Over a period of 30 min. 70 g. (0.68 mole) of freshly distilled ethyl chloroformate were added to the Grignard solution. After the reaction mixture had been heated for an additional 24 hrs., dilute sulfuric acid was added until two layers separated. The aqueous layer was extracted with two 50-ml. portions of ether, and the combined ether layers were washed successively with 50 ml. of 1N sodium hydroxide, two 50-ml. portions of a 5% potassium bicarbonate solution, and two 50 ml. portions of water. The ether solution was dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residue was fractionated through a 10-in., helix-packed column to yield 35.7 g. (50%) of ethyl 2,4,6-trimethylbenzoate.

**Pyrolysis of Ethyl 2, 4, 6-Trimethylbenzoate.** When 10.4 g. of ethyl 2,4,6-trimethylbenzoate were pyrolyzed by the same procedure, considerable charring occurred. The brown pyrolysate was dissolved in 150 ml. of ether, and this ether solution was extracted with three 25-ml. portions of 1N sodium hydroxide. The combined extracts were cooled in an ice bath and acidified with concentrated sulfuric acid. The resulting solid was removed by filtration and dried over night under vacuum to yield 7.78 g. (88%) of 2, 4, 6-trimethylbenzoic acid.

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## Report of Cellulose Yield Committee—1955-1956

GIVEN below are the checked yield analyses obtained on samples sent out during the year to 10 laboratories. During this period three samples were sent out three times during the season. Two samples were made up of second-cut linters and one hull fiber.

Very good checked analyses were obtained, as shown by the above table. It is recommended that this work be continued, that is, samples sent out at least three times a year to all laboratories equipped to run cellulose yield analyses.

Lab. No.	No. of Tests	A Linter	B Linter	C Fiber	Over-all Avg. for the year
1.....	3	78.0	72.3	71.2	73.9
2.....	3	78.5	72.7	71.0	74.1
3.....	3	77.5	72.1	70.2	73.3
4.....	3	78.8	73.0	71.8	74.6
5.....	3	77.7	72.7	71.5	74.0
6.....	3	78.8	72.3	69.6	73.6
7.....	3	78.0	72.0	70.0	73.3
9.....	3	78.1	72.1	70.8	73.7
10.....	3	78.2	72.3	70.7	73.7
11.....	3	76.6	72.3	70.7	73.2
Average.....		78.0	72.4	70.8	73.7

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