The residue was distilled under reduced pressure and the fraction boiling between 100–105° at 22 mm. was collected. By acidifying the carbonate extracts 18 g. of propionylmalonic ester was recovered. Correcting for this recovery the yield was 57% (34 g.) of propionylacetic ester.

In order to prove the identity of the ester it was converted into the corresponding bis-pyrazolone by heating the compound overnight with a slight excess of phenylhydrazine. Ether was then added to the reaction mixture and the white crystalline pyrazolone was separated by filtration and thoroughly washed with ether. The bis-(1-phenyl-3-ethyl-5-pyrazolone) melted with decomposition at 331°, whereas Blaise[9] reports a m. p. of 335°.

**Ethyl Benzoylacetate.**—The benzoylacetic ester was obtained in a manner analogous to that of ethyl propionylacetate. To a solution of one-half mole of the magnesium enolate of malonic ester there was added 75 g. (62 ml., 0.53 mole) of benzoyl chloride dissolved in 75 ml. of dry ether. The reaction mixture was again refluxed for thirty minutes and then worked up and decarboxylated in the same way as described above. From the alkaline washings obtained after the decarboxylation was recovered 25 g. of benzoylmalonic ester. A yield of 34 g. or 44%, after correcting for the recovered benzoylmalonic ester, of ethyl benzoylacetate boiling at 140–145° at 3 mm. was obtained. To prove the identity of the ethyl benzoylacetate it was converted into its copper salt by shaking an ether solution of the ester with a saturated solution of cupric acetate. The copper salt which separated was filtered, washed with water and recrystallized from hot benzene. It melted sharply at 182° which agreed with the m. p. reported by Wislicenus[10] for this compound.

## Summary

1. A method is described for the synthesis of $\beta$-keto esters. It consists in heating acylated malonic esters in the presence of arylsulfonic acids.
2. This desired decomposition takes place if malonic ester is acylated with an aliphatic, aromatic or a half ester acid chloride.
3. It is the most convenient and general method for the production of $\beta$-keto esters.

---

[9] E. E. Blaise, *Compt. rend.*, **132**, 979 (1901).

[10] W. Wislicenus, *Ber.*, **31**, 3151 (1898).

EVANSTON, ILLINOIS RECEIVED MARCH 3, 1945

---

[CONTRIBUTION FROM THE COLGATE-PALMOLIVE-PEET CO., JERSEY CITY, N. J.]

# The Polymerization of Undecylenic Acid

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

Low molecular weight vinyl compounds give high molecular weight polymers in which the ascertaining of the structural relationships and mode of combination of the individual polymer units presents peculiar difficulties. The polymerization of undecylenic acid is an interesting example of the reactivity of an olefinic group in the long chain fatty acid series and the degree of polymerization is sufficiently low to permit the isolation and examination of the structure of the dimeric stage of polymerization.

In 1877 Krafft isolated undecylenic acid from the products of distillation of castor oil. Later, Krafft and Brunner[1] found a solid acid in the distillation residues from castor oil, which was identical with a product they obtained by slow distillation of undecylenic acid. Taking into account the origin of this solid acid, m. p. 29°, and its analysis by combustion, they assigned it the structure $CH_2{=}CH(CH_2)_8COO(CH_2)_{10}COOH$ and called it di-undecylenic acid.

Cann and Amstutz[2] noted that undecylenic acid polymerizes under the influence of boron fluoride and their analytical data indicated that a product with some structural similarities to that postulated by Krafft and Brunner was formed.

We have examined the products of thermal polymerization of undecylenic acid and undecylenic methyl ester and in the dimeric fraction have found no material having the ester structure suggested by Krafft and Brunner. Instead we have found that polymerization proceeds linearly by the direct addition at terminal methylene groups.

Undecylenic acid in the form of the acid, anhydride, methyl ester, or sodium salt,[3] will polymerize at temperatures of 250–325°, to form dimers and higher polymers. When the reaction is allowed to proceed to the point where almost half of the monomer is polymerized, then the approximate composition of the polymerized material is one part of dimer to 2.5 parts of trimer and higher polymer. When polymerization is allowed to proceed further, the yield of dimeric material still remains about the same while the yield of the higher polymer increases.

For convenience, batches of methyl undecylenate were 50% polymerized under pressure of nitrogen gas in a steel bomb at 325° and the product separated by fractional distillation. The dimeric fraction was then further separated into solid and liquid portions by fractional crystallization from methanol.

The solid dimeric ester was shown to be a mixture of an unsaturated and a saturated dicarboxylic ester. The unsaturated dicarboxylic ester proved to be the dimethyl ester of 8-eicosene-1,20-dicarboxylic acid. Upon hydrogenation the latter gave the dimethyl ester of phellogenic acid (eicosane-1,20-dicarboxylic acid) and through periodic acid oxidation of the corresponding dihydroxy derivative, azelaic and brassylic acids were obtained, thus determining the position of the ethylenic linkage. The saturated dicarboxylic ester was not identified, but it appears probable

---

[1] Krafft and Brunner, *Ber.*, **17**, 2985 (1884).

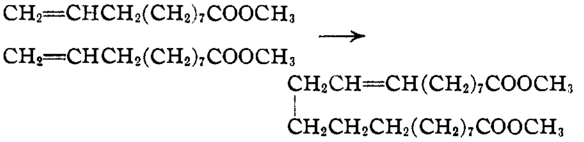
[2] Cann and Amstutz, THIS JOURNAL, **66**, 839 (1944).

[3] J. H. Percy and J. Ross, U. S. Patent 2,341,239 (1944).

that it is an isomeric cyclic compound of the composition $C_{20}H_{38}(COOH)_2$. It was separated from the unsaturated dimer ester by conversion of the latter to the less soluble dihydroxy derivative.

The liquid dimeric ester fraction consists of a more complex mixture. Among the components present, the geometrical isomer of the 8-eicosene-1,20-dicarboxylic ester was isolated and identified through periodic acid splitting of the corresponding dihydroxy derivative and also by conversion to dimethyl phellogenate. Some liquid saturated esters were separated which would appear to be cyclic. There was also a considerable proportion of unsaturated esters which might be expected to be branched chain isomers of eicosene dicarboxylic ester.

From the above it is seen that undecylenic ester can polymerize by terminal addition, two straight 11 carbon chain molecules producing a straight 22 carbon chain molecule. The remaining ethylenic linkage moves from the 10–11 to the 9–10 position, thus



$$\begin{array}{l} CH_2{=}CHCH_2(CH_2)_7COOCH_3 \\ CH_2{=}CHCH_2(CH_2)_7COOCH_3 \end{array} \longrightarrow \begin{array}{l} CH_2CH{=}CH(CH_2)_7COOCH_3 \\ | \\ CH_2CH_2CH_2(CH_2)_7COOCH_3 \end{array}$$

Addition at carbon atoms other than the terminal carbon atom, for example at $C_{10}$ instead of $C_{11}$, would give rise to branched chain olefinic dicarboxylic esters. This undoubtedly does occur and is probably represented by the major part of the liquid isomeric unsaturated dicarboxylic esters, but we have not isolated any individuals from this material to demonstrate any branched chain structure.

Cyclization by intramolecular addition in a structure of the type of 8-eicosene-1,20-dicarboxylic ester would give a saturated cyclic dicarboxylic ester probably with a 5 or 6 carbon ring and, although not identified, such material was shown to be present in the dimeric mixture, the structure of which we have not yet determined.

In the course of this investigation it was found useful to estimate quantitatively the amount of $\alpha,\beta$ dihydroxy compound produced by hydroxylation of olefinic esters. Since this method of analysis has not been applied previously in the field of fat chemistry, the procedure followed for such semi micro determination is described.

Brassylic acid required in this investigation was prepared by a new method which gave increased yields as also does a modified procedure for isolating erucic acid from rape oil.

## Experimental

**Purification of Undecylenic Acid.**—Commercial undecylenic acid (Baker Castor Oil Co., New York) from castor oil was converted to the methyl ester by refluxing twelve hours with four volumes of methanol containing 1% concentrated sulfuric acid. This material was worked up in the usual way and the crude ester was distilled from a Claisen flask and then fractionally distilled through a 100 cm. modified Fenske column. In this way from 6660 g. of crude acid there was obtained 3910 g. of pure ester, b. p. 105.4° at 3.3 mm., refractive index 1.4371 at 25°. This methyl undecylenate and the undecylenic acid derived from it were used throughout this investigation.

**Hydroxylation of Undecylenic Acid.**—Eighteen and four tenths grams of undecylenic acid, b. p. 125.7° at 1.2 mm., was treated with peracetic acid (25 cc. of 30% hydrogen peroxide in 72 cc. acetic acid, heated to 85° for one hour and cooled to room temperature) and warmed to about 85° when the reaction mixture became a clear, homogeneous solution.[4] After standing at room temperature overnight, it was diluted with 600 cc. of water and shaken out several times with ethyl acetate, washed with water, dried with anhydrous magnesium sulfate and the solvent distilled off. The crude residue was saponified with alcoholic caustic potash to eliminate any acetyl derivative. The dihydroxy acid was recovered and washed with a small amount of ether; yield 20.8 g. of white solid, m. p. 84–86.5° (theory 21.8 g.); neutral equivalent, calcd., 218, found, 219. 10,11-Dihydroxyundecanoic acid has a m. p. 85–86°.[5]

**Oxidative Splitting of Dihydroxyundecanoic Acid.**—The above dihydroxy acid was oxidized with periodic acid under predetermined conditions for complete oxidation and the volatile aldehydes examined for acetaldehyde by the method of Shupe.[6] No acetaldehyde was found, proving that the undecylenic acid was substantially free from the 9-undecenoic acid.

**Heat Polymerization of 10-Undecenoic Methyl Ester.**—Five hundred grams of methyl undecylenate was heated in a stainless steel bomb under nitrogen up to 325° and held at this temperature two and one-half hours. The pressure was 400 P. S. I. When cold, the product was removed from the bomb and fractionally distilled from a Claisen flask under vacuum of 0.8 mm. The following fractions were obtained:

| | B. p., °C. at 0.8 mm. | Yield, % | Composition |
|---|---|---|---|
| 1 | 85–103 | 50 | monomer |
| 2 | 195–220 | 14 | dimer |
| 3 | >220 | 36 | higher polymer |

Several bomb runs were made and the total products combined.

The low boiling fraction (monomer) was carefully redistilled and proved to be unchanged methyl undecylenate.

**Examination of Dimeric Ester Fraction.**—The ester boiling 195–220° at 0.8 mm. partially crystallized at room temperature. It was mixed with five volumes of methanol, cooled in ice water and the crystals filtered off. The yield of solid esters was approximately 20% of dimer fraction. From the methanol solution a liquid ester was obtained representing 80% of dimer fraction.

### Solid Dimer Ester

This material was recrystallized three times from methanol in the form of large leaflets which had a m. p. 45.5–46°. Crystallization from other solvents did not change the melting point.

*Anal.* Calcd. for $C_{24}H_{44}O_4$: C, 72.67; H, 11.19; mol. wt., 396; I. V., 64.1. Found: saponification equiv., 197.5; I. V., 58 (Wijs); mol. wt. in benzene, 365; C, 72.6; H, 11.17.

Upon saponification and acidifying, the above ester gave a solid acid which crystallized from ether or acetone and melted at 96–98°.

Upon hydrogenation 3.0 g. of the solid dimeric ester in acetic acid, using platinum oxide catalyst,[7] absorbed 147

---

[4] Scanlan and Swern, THIS JOURNAL, **62**, 2305 (1940).

[5] Hazura and Grassner, *Monatsh.*, **9**, 950 (1888).

[6] Shupe, *J. Assoc. Official Agr. Chem.*, **26**, 249 (1943).

[7] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., p. 452.

cc. of hydrogen at S. T. P. A compound of molecular weight 396 with one double bond would have absorbed 170 cc. of hydrogen. The sparingly soluble hydrogenated ester produced was recrystallized three times from methanol and it melted at 67–68° and weighed 2.0 g.

*Anal.* Calcd. for $C_{24}H_{46}O_4$: C, 72.31; H, 11.63. Found: C, 71.8; H, 11.42.

A portion was saponified and converted to the acid which was crystallized from acetic acid. This acid melted at 125° and had a neutral equivalent of 183.5.

Phellogenic acid melts at 120–122° and the dimethyl ester melts at 68–69°.[8] Mixed melting points of the above hydrogenated acid and ester with phellogenic acid and dimethyl phellogenate showed that these materials were identical.

It is apparent from the above, and subsequent examinations, that the solid dimeric ester is a mixture of saturated and unsaturated esters of the same molecular weight.

**Hydroxylation of Solid Dimer Ester.**—Thirty-four grams of solid dimer ester was treated with peracetic acid (19.5 cc. of 30% hydrogen peroxide in 62 cc. of glacial acetic acid). The product was saponified and the carboxylic acid isolated. This was then extracted twice with one-liter portions of warm ether and there was thus obtained 23.7 g. of acid sparingly soluble in ether, and 9.0 g. of acid readily soluble in ether. Periodic acid oxidation showed that the ether insoluble material was completely dihydroxylated and that the ether soluble acid was not oxidizable under these conditions, hence not hydroxylated and therefore must have been present in the original dimer as a saturated compound.

The dihydroxy acid was crystallized from hot ether or dioxane as fine crystals, m. p. 147–148°.

*Anal.* Calcd. for $C_{22}H_{42}O_6$: C, 65.62; H, 10.51; mol. wt., 402.3. Found: C, 65.56; H, 10.44; neut. equiv., 201.

Upon esterification with methanol containing 1% sulfuric acid, this dihydroxy acid gave a dimethyl ester which was recrystallized from ether as granular crystals, m. p. 98.5–99°; saponification equiv., 213.

*Anal.* Calcd. for $C_{24}H_{46}O_6$: C, 66.92; H, 10.88; mol. wt., 430.4. Found: C, 66.98; H, 10.93.

**Oxidative Splitting of Dihydroxy Solid Dimer Ester.**—Two grams of above pure ester was dissolved in 100 cc. of absolute ethanol and a solution of 2.15 g. of periodic acid ($HIO_4 \cdot 2H_2O$) in a mixture of 20 cc. of ethanol and 6 cc. of water added. Titration of an aliquot showed oxidation complete in forty-five minutes and the reaction mixture was then diluted with 750 cc. of water. Then 4 cc. of concd. HCl and 5 g. of potassium iodide were added, followed by a strong solution of sodium thiosulfate to destroy the liberated iodine. The insoluble oil was shaken out with ether and recovered as a colorless liquid weighing 2.0 g. The extracted aldehydic product was oxidized to the acids directly by warming to 85° for fifteen minutes with peracetic acid (3.2 cc. of 30% hydrogen peroxide in 10.2 cc. of acetic acid). After standing overnight at 40° the reaction of mixture was poured into 300 cc. of water and shaken out with ether. The ether extract was washed alternately with water and ferrous sulfate solution acidified with sulfuric acid to remove peroxides. After removal of the solvent ether, the product was saponified and converted to the acids which were extracted with hot water. The water insoluble acids after recrystallization from ethylene dichloride melted sharply at 112–113°; neut. equiv., 125. This acid was recognized as brassylic acid $(CH_2)_{11}(COOH)_2$, by direct comparison and mixed melting point with an authentic specimen.

After removal of the brassylic acid the water soluble acids were recovered through the lead salt in the usual manner using hydrogen sulfide. A pale yellow solid acid was obtained. This was recrystallized from ethylene dichloride and had m. p. 105.5° and neutral equivalent of 96.3. This was recognized as azelaic acid which has m. p. 106° and neutral equivalent 94. A mixed melting point with a known sample of azelaic acid showed no depression. The *p*-bromophenacyl ester melted at 130° and this was identical with the ester derived from azelaic acid.[9]

**Saturated Solid Dimer.**—From the hydroxylation of the original solid dimer ester, the acid which was readily soluble in ether and which was shown to be not hydroxylated because it could not be oxidized with periodic acid, was purified by recrystallization from acetone as fine needle crystals, m. p. 120–121°; neut. equiv., 181.

*Anal.* Found: C, 70.86; H, 11.42.

Upon esterification it gave a methyl ester which crystallized from methanol as leaflets m. p. 64–65°; saponification equiv., 195.

*Anal.* Found: C, 71.93; H, 11.58.

This ester had no acetal value, iodine value, or bromide bromate value. The purification of this material is difficult and the analyses obtained do not permit of definite conclusions as to the structure.

### Liquid Dimer Ester

After removal of solid dimer ester by crystallizing from methanol, approximately 80% of dimeric material was left as a liquid ester boiling over a range 195–210° (1 mm.) as already described. This liquid ester had an iodine value of 54.3 and was clearly a mixture. Upon hydrogenation of a portion with Adams catalyst, 3.0 g. absorbed 157 cc. of hydrogen at S. T. P.: theory for one double bond, 170 cc. Fractional crystallization of a larger sample of hydrogenated material gave a 15.0% yield of dimethyl phellogenate.

**Hydroxylation of Liquid Dimer Ester.**—Twenty grams of liquid ester was treated with hydrogen peroxide in acetic acid as previously described, de-acetylated by refluxing with methanol containing 1% sulfuric acid and there was obtained 23.1 g. of colorless liquid product. This material was taken up in ether and cooled at 0° for twelve hours when 2.0 g. of crude solid was obtained. The ether solvent was then removed and the thick ester product (20.5 g.) was shaken with petroleum ether (Skellysolve A) and cooled in an ice-bath, when about half the material separated as a soft solid. The solvent was decanted and yielded 8.0 g. of mobile liquid ester which was only 9% oxidizable with periodic acid. By repeated crystallizations of the soft solid from petroleum ether, the product from hydroxylation of the liquid dimer ester was separated into two portions, namely, 55% of a solid hydroxy ester oxidizable by periodic acid, and 45% consisting of a liquid saturated ester not oxidizable by periodic acid.

By fractional crystallization of the lower melting dihydroxy solid ester from ether, there was separated 3.0 g. of pure dihydroxy ester, m. p. 77°, and also 0.5 g. of a less soluble dihydroxy ester, m. p. 99°, which was identical with the dihydroxy ester from the solid dimeric ester described above. Also lower melting material (8.0 g.) not further examined. Analysis of the dihydroxy ester, m. p. 77°, gave the following values:

*Anal.* Calcd. for $C_{24}H_{46}O_6$: C, 66.92; H, 10.88; mol. wt., 430.4. Found: C, 66.98; H, 10.94; sapn. equiv., 216.5.

This ester upon saponification gave an acid m. p. 127° crystallized from aqueous dioxane.

*Anal.* Calcd. for $C_{22}H_{42}O_6$: C, 65.62; H, 10.51; mol. wt., 402.3. Found: C, 65.46; H, 10.67; neut. equiv., 202.0.

**Oxidative Splitting of Dihydroxy Ester, M. p. 77°.**—This was carried out in the same way as the oxidation of the ester m. p. 99°. One and four-tenths grams of solid dihydroxy ester m. p. 77° gave 0.8 g. of water insoluble brassylic acid and 0.6 g. of water soluble azelaic acid, which showed that the two dihydroxy esters, m. p. 77 and 99°, probably are meso and racemic forms derived from the corresponding unsaturated geometrical isomers of 8-eicosene-1,20-dicarboxylic esters.

---

[8] N. L. Drake, H. W. Carhart and R. Mozingo, THIS JOURNAL, 63, 617 (1941). We are indebted to Professor Nathan L. Drake, of the University of Maryland, who kindly supplied us with a known sample of dimethyl phellogenate.

[9] Kelly and Kleff, *ibid.*, 54, 4444 (1932).

### Preparation of Brassylic Acid

Rapeseed oil (420 g.) was converted to methyl esters by treating with boiling methanol (500 ml.) containing 0.75% of caustic soda. The reaction mixture was diluted with water and the fatty esters extracted with petroleum ether and distilled from a Claisen flask. The fraction boiling 170–200° (2 mm.) deposited crystals of methyl arachidate which were filtered off. The liquid esters were saponified with alcoholic caustic potash and, upon cooling, the crystalline potassium salt of erucic acid which separated was filtered off and recrystallized from hot absolute ethanol. The purified potassium salt upon decomposition gave erucic acid which once crystallized from acetone melted at 33°; yield 32% on the rapeseed oil.

13,14-Dihydroxybehenic acid was prepared in theoretical yield by treating 9.0 g. of erucic acid with peracetic acid (6.5 ml. of 30% hydrogen peroxide in 20 ml. of acetic acid) at 92° and standing overnight at 40°. The reaction mixture was poured into water and the solid acid filtered off. Crystallized from ethylene dichloride, it melted at 99°.

The above acid was oxidized by treating 4.0 g. in 500 ml. of ethanol with 3.1 g. of periodic acid for forty minutes. Excess sodium bicarbonate was added and excess periodic acid destroyed with normal sodium arsenite solution. Insoluble sodium salts were filtered off, most of the alcohol removed by distillation, and the residue diluted with water and extracted with ether. The brassylic acid half-aldehyde was separated from pelargonic aldehyde by washing the ether solution with 2% sodium carbonate solution.

Acidification of the sodium carbonate solution yielded 2.8 g. of brassylic half-aldehyde which was oxidized to brassylic acid by peracetic acid in the usual manner. After twice crystallizing from ethylene dichloride, the brassylic acid melted at 113°; yield theoretical.

**Quantitative Semi-micro Determination of $\alpha,\beta$-Dihydroxy Compounds.**—An accurately weighed sample of about 0.1 millimole of dihydroxy compound is dissolved in 5 ml. of 95% pure ethanol in a 200-ml. erlenmeyer flask and 5.0 ml. of periodic acid solution (0.5 g. of periodic acid in 28 ml. of 95% ethanol) is pipetted into the flask, mixed and allowed to stand at room temperature for fifteen to forty-five minutes, the time varying with the compound.

The solution is diluted with 100 ml. of water and approximately 0.5 g. of sodium bicarbonate and 0.5 g. of potassium iodide added in that order. The liberated iodine is titrated with $N/10$ potassium arsenite solution. Titrate similarly a 5.0-ml. sample of the periodic acid solution as a blank. The difference between the two titrations represents the equivalent periodic acid consumed in the oxidation, one atom of oxygen being used per mole of dihydroxy compound oxidized according to the equation

$$\mathrm{RCH(OH)CH(OH)R' + HIO_4 \longrightarrow RCHO + R'CHO + HIO_3 + H_2O}$$

## Summary

1. The thermal polymerization of undecylenic acid and methyl undecylenate has been examined.

2. Linear polymerization has been shown to occur and as evidence the presence of the dimethyl ester of 8-eicosene-1,20-dicarboxylate was shown in the dimeric fraction.

3. Other dimeric esters and higher polymers were shown to be formed but their structure was not elucidated.

Jersey City, New Jersey Received April 18, 1945

---

[Communication No. 1025 from the Kodak Research Laboratories]

# Heats of Polymerization. I. An Isothermal Calorimeter and its Application to Methyl Methacrylate

By L. K. J. Tong and W. O. Kenyon

A knowledge of heats of polymerization is important to a fundamental understanding of the mechanism of polymer-forming processes, but few published quantitative data are available on the subject. Flory[1] has discussed heats of polymerization in his consideration of the mechanism of vinyl polymerizations, but the values used were obtained indirectly. The few direct measurements of heats of polymerization include those of Goldfinger, Josefowitz and Mark,[2] and of Evans and Polanyi.[3] These investigators are not in agreement on the results for methyl methacrylate, giving $\Delta H$ values of $-7.9$ and $-11.6$ kcal./mole, respectively. Houwink[4] has published values for heats of polymerization for several unsaturates, calculated from experimental data on heats of combustion, but a value for methyl methacrylate was not included.

This preliminary paper describes a calorimeter and technique which have been found to be well adapted to the determination of heats of polymerization. Data on methyl methacrylate are presented to illustrate the method. Investigations of other polymerizable systems are expected to be the subjects of future publications.

The present method utilizes the heat evolved from the polymerization reaction to evaporate a liquid which is in equilibrium with its own vapor at its boiling point. Thus the heat given off by the reaction is directly proportional to the amount of material evaporated. The heat of polymerization is calculated from the amount of liquid evaporated and its heat of vaporization. The system is kept at constant temperature by being completely immersed in the boiling vapor. A

---

(1) Flory, *This Journal*, **59**, 241–253 (1937).

(2) Goldfinger, Josefowitz and Mark, *ibid.*, **65**, 1432 (1943).

(3) Evans and Polanyi, *Nature*, **152**, 738 (1943).

(4) Houwink, "Chemie und Technologie der Kunststoffe," Vol. 1, Leipzig, 1940, p. 60.