Branched Carboxylic Acids from Long-Chain Unsaturated Compounds and Carbon Monoxide at Atmospheric Pressure

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Carbon monoxide at atmospheric pressure adds readily to the double bonds of certain long-chain unsaturated compounds in concentrated sulfuric acid to produce branched carboxylic acids. Unsaturated compounds studied were oleic acid, 10-heneicosenoic acid, oleyl alcohol, methyl ricinoleate, and linoleic acid. A major component from the reactions of the last two compounds is the same.

Infrared spectrophotometry and gas-liquid chromatography have been the major tools employed in determining composition and structure of the products in addition to the usual chemical and physical determinations.

Both the concentration and quantity of sulfuric acid are critically important variables in determining the yields. Water is an essential reactant also and must be available throughout the reaction.

Carbon monoxide has been prepared and utilized in situ by a modification of Koch's (1) method in which the unsaturated compound mixed with formic acid is added to concentrated sulfuric acid or carbon monoxide from a cylinder is passed through sulfuric acid to which the unsaturated compound is added. A method for preparing methyl and butyl esters of carboxylic acids which are difficult to esterify is described.

Reaction mechanisms involving intermediate carboxonium and oxoallenium ions are proposed to account for the products.

Dicarboxylic acids are important intermediates in the preparation of polymers, plasticizers, lubricants, and other functional fluids. At the present time the only commercial methods of preparation of dicarboxylic acids from fat sources are cleavage methods. The most important of these are ozonolysis and alkaline fusion although in the recent past, chromic acid oxidation has also been employed.

One of the inherent drawbacks to a cleavage method is that it may not be sufficiently selective in its point of attack, thereby producing not just two but many products. Aside from the obvious difficulties in cleanly separating complex mixtures on a commercial scale, there is the ever-present problem that all of the cleavage products are not equally valuable and are salable only at unprofitable price levels, if at all. This is self-defeating from the fat-utilization standpoint inasmuch as dicarboxylic acids from nonfat sources are relatively low-priced substances and those prepared from fats must also be low cost to compete effectively.

An approach to which we have been giving considerable thought and attention is one in which the entire fatty molecule is employed. This demands that a) a group be introduced which is readily converted to the carboxyl group (this nitride group is one example), or b) a direct carboxylation technique be utilized. It has been known for some time that carbon monoxide under high pressure in the presence of the Lewis type of catalysts can be used for the direct carboxylation of alkenes and unsaturated fatty materials. The necessity for the use of high pressure and the relatively modest yields are discouraging features to such work. Our interest in carboxylation with carbon monoxide was revived by the interesting reports of Koch and Haaf (1), who showed that a wide variety of unsaturated compounds could be directly carboxylated with carbon monoxide and water at atmospheric or only moderate pressures in the presence of concentrated sulfuric acid, as solvent and reaction medium, a system with which we had worked extensively (2). Although Koch studied numerous alkenes, only two long-chain unsaturated fatty compounds were reported, namely, undecylenic and oleic acids. With the former, carboxylation was reported to give two C₁₂ dicarboxylic acids, and limited characterizing data were supplied. With oleic acid, no characteristics of the products were given. The only statement concerning the reaction of oleic acid with carbon monoxide and water in the presence of concentrated sulfuric acid was that a C₁₀ dicarboxylic acid was formed in good yield.

In this paper is described the direct carboxylation at atmospheric pressure of some unsaturated fatty acids, esters, and alcohols in concentrated sulfuric acid with either gaseous (cylinder) carbon monoxide or by an in situ method which is a modification of that described by Koch, in which formic acid is decomposed to carbon monoxide and water by the concentrated sulfuric acid while the unsaturated component is being added. As shown later in the experimental part, to obtain high carboxylation yields it is necessary to employ ratios of formic acid and sulfuric acid to double bond which are considerably different from those recommended (1). In a formal sense, as illustrated with oleic acid, the molecules of carbon monoxide and water add across a double bond to introduce a carboxyl group as a branch in the chain:

\[
\text{CH}_2 - (\text{CH}_2)_{17} - \text{CH} - (\text{CH}_2)_9 \text{COOH} + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2 - (\text{CH}_2)_{17} - \text{CH} - (\text{CH}_2)_9 \text{COOH} (x + y = 15)
\]

\[
\text{COOH}
\]

\[\text{CH}_2 - (\text{CH}_2)_{17} - \text{CH} - \text{COOH} + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2 - (\text{CH}_2)_{17} - \text{CH} - (\text{CH}_2)_9 \text{COOH} (x + y = 15)
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\text{COOH}
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In addition, we have isolated the reaction products, characterized them by chemical and physical methods, and prepared esters from them. The role of water in obtaining high yields of carboxylated products has also been examined. The infrared spectra of the products have been obtained as an aid in the proof of their structure, and these are also reported. In certain cases gas-liquid chromatography (GLC) has been utilized to indicate that a number of isomers are formed.

**Experimental**

**Starting Materials.** Oleic acid (93%) was prepared from commercial oleic acid by one low-temperature crystallization and fractional distillation. Highly purified (98-99%) oleyl alcohol (3), methyl ricinoleate (4), linoleic acid (5), and 10-hendecenoic acid (6) were prepared by described procedures.

**Preparation of Branched-Chain Carboxylic Acids. Gaseous Carbon Monoxide Method.** Carbon monoxide was passed through 90.4 g. (0.755 mole) of 97.2% sulfuric acid contained in a 500-ml. three-neck flask, using a gas dispersion tube with a coarse teflon cylinder. With stirring 7.1 g. (0.025 mole) of oleic acid were added drop by drop in 16 min. to the sulfuric acid solution, which was saturated with carbon monoxide. Carbon monoxide was allowed to pass through the stirred mixture for a total of 2 hrs. while the temperature was maintained between 9 and 13° with external cooling. At the end of this time the mixture was poured into approximately 300 ml. of a mixture of ice and water. The product was extracted with ether and washed free of sulfuric acid. The ether solution was dried over sodium sulfate and filtered; the ether was then evaporated, yielding 6.4 g. of pale yellow syrup material with an iodine number of 12.9; acid number, 300, and saponification number, 300.

**Preparation of Branched-Chain Carboxylic Acids. Formic Acid Method.** A mixture of 28.3 g. (0.1 mole) of oleic acid and 29.5 g. (0.5 mole) of 98% formic acid in a cylindrical dropping funnel was stirred vigorously and added in 35 min. to 242.2 g. (2.4 moles) of 97.2% sulfuric acid with rapid stirring. A 5-liter flask was used because of copious foaming. The temperature was maintained between 10 and 20° by external cooling. After the reactants were mixed, stirring was continued for an additional 2 hrs. and 25 min. for a total reaction time of 3 hrs. At the end of this time the mixture was poured into approximately 1 liter of a mixture of ice and water and worked up as described above. A yield of 29.8 g. of pale yellow syrup material was obtained with an iodine number of 2.3; acid number, 297, and saponification number, 305.

The reaction product (27.9 g.) was distilled from an alembic flask. Four fractions were taken, two of which were predominantly di-carboxylic acids and were light yellow viscous liquids. One of these fractions b.p. 199-200° (0.45 mm.) weighed 14.5 g. (acid number 325); the other, b.p. 200-201° (0.45 mm.) weighed 3.7 g. (acid number 341). Anal. calcd. for C_{33}H_{54}O_{4}: C, 70.7; H, 11.3; molar refractivity, 102.8. Found: C, 70.6; H, 11.3; molar refractivity, 102.6.

The fraction with an acid number of 325, consisting mainly of carboxystearic acid, was converted to methyl esters by refluxing 13.8 g. with 68 ml. of anhydrous methanol and 5.3 g. (3.9 ml.) of dimethyl sulfate for 42 hrs. The product was worked up by neutralizing the dimethyl sulfate with aqueous sodium carbonate solution in the cold and extracting with ether. In larger preparations, from one-half to two-thirds of the alcohol was distilled off before neutralization and distillation. Distillation of 9.4 g. of the methyl esters from an alembic flask yielded 5.8 g. of a clear, mobile amber liquid, b.p. 146-148° (0.35 mm.); [α]_D^13 = +1.4465. Anal. calcd. for C_{34}H_{54}O: C, 70.7; H, 11.3; molar refractivity, 102.8. Found: C, 70.6; H, 11.3; molar refractivity, 102.6.

The method just described was used in the carboxylation of oleyl alcohol, methyl ricinoleate, and 10-hendecenoic acid. With linoleic acid the quantities of formic acid and sulfuric acid were doubled; otherwise the procedure was the same. After pouring the reaction product obtained by carboxylation of oleyl alcohol into an ice and water mixture, it was necessary to hydrolyze the sulfate ester by boiling. After this the product was worked up as described. In all of the preparations, except the one experiment described above, the crude reaction products were converted directly to methyl esters before distilling.

The dibutyl ester of carboxystearic acid was prepared either by direct esterification or by ester interchange from the dimethyl ester. In direct esterification it was necessary to elevate the boiling point in order to obtain complete reaction. Cymene was used for this purpose, but it made the recovery of the product difficult.

The ester-interchange reaction was carried out in the following way. To 33.5 g. of methyl esters (acid number 6.3) prepared from crude carboxystearic acid (acid number 310) were added 142 ml. of n-butanol with which 0.42 g. of metallic sodium had been reacted, and the mixture was refluxed for 25 hrs. To determine when the interchange was complete, the methanol evolved was removed and measured. For this purpose a 1 x 20-in. fractionating column packed with Raschig rings was used. The product was worked up by pouring the reaction mixture into dilute hydrochloric acid and extracting with ether. After washing the ether layer free of acid, it was dried over sodium sulfate and filtered; the ether was then evaporated, yielding 40.9 g. of crude dibutyl esters with an acid number of 10.7. The acidity of the crude dibutyl esters was neutralized with potassium hydroxide, and the product was vacuum-distilled.

The distilled dibutyl esters of carboxystearic acid obtained by the two methods of preparation had the same properties (Table IV).

**Infrared Spectra.** Infrared spectra were obtained on a Perkin Elmer Model 21 double beam recording spectrophotometer. For general spectra a demountable cell consisting of sodium chloride windows (one window with a moat-type channel) (7), and 0.025 and 0.03 mm. spacers was used since all samples were liquid. Where dilution studies were made, reference to this is made in the text; these spectra were determined with a 0.2-mm. cell.

**Gas-Liquid Chromatography (GLC).** Conventional type of GLC equipment was employed. A four-filament, thermal conductivity cell, and 2-millivolt, 11-in. strip-chart recorder requiring 2 seconds for full-scale pen deflection was used. The column, 8 ft. long by 1/16 in. O.D. and 1/8 in. I.D., was of stainless steel.