ISOMERIZATION STUDIES—I

CONVERSION OF LINEAR ACIDS INTO THEIR ISOMERIC BRANCHED-CHAIN ANALOGUES[a]

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T. A. FOGLIA,* I. SCHMELTZ and P. A. BARR
Eastern Regional Research Center,† Philadelphia, Pennsylvania 19118

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Eastern Regional Research Center,† Philadelphia, Pennsylvania 19118

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Abstract – The transformation of linear saturated carboxylic acid chlorides (i.e., stearoyl chloride) into mixtures of isomeric, highly branched acids, each having the same molecular weight as the starting material, was investigated. The fatty acid backbone was modified in either a two or three step process generally with excellent overall yield. In both procedures, the first step was catalytic decarbonylation of the acid chloride, which yielded a hydrocarbon monoene mixture having one less carbon atom than the starting acid. The monoene mixtures were reconverted to the branched acid derivatives by either the Koch reaction or the hydroformylation oxidative procedure. Products were designated as either di- or trisubstituted carboxylic acids, on the basis of mass spectroscopic and GLC data.

The skeletal isomerization of linear fatty acids into their isomeric branched chain analogs has been the subject of considerable interest.[1] Generally, such transformations have been achieved by heating an unsaturated fatty acid in the presence of water, mineral acids, or clays.[1,2] The resulting isomerized fatty acids, which are isolated by distillation, still retain unsaturation but show some loss in iodine number. Subsequent hydrogenation of these isomerized enoic acids followed by removal of the starting acids by low-temperature crystallization yields the saturated liquid isomerized fatty acids.

The above thermal isomerization reactions have been successful when the starting fatty acids are either mono or dienoic acids, typically commercial oleic and tall oil acids. With the dienoic fatty acids skeletal reorganizations or dimerization can be induced by simple heat treatment at 300°.[1] On the other hand, appreciable isomerization and dimerization of monounsaturated acids and their esters only proceeds under the influence of a catalyst. Many catalysts have been used for this latter isomerization process, the more important of which are acidic and basic mineral clays.[2] Previously, when the above enoic acids have been directly isomerized to their skeletal reorganized derivatives, the dimeric and trimeric species as well as the original starting acids, have always accompanied the formation of the desired modified "isoacids". In practice, the latter have always been the minor products of these reactions and the former species have been the major reaction products.[1]

To date, no successful attempt has been reported on the preparation of isomerized saturated fatty acids from saturated linear fatty acids. It is the purpose of this report to describe our studies which are directed towards the preparation of alkyl branched saturated fatty acids from their straight chain counterparts (i.e., stearic acid). Our procedure, although not a true isomerization method, involved the catalytic decarbonylation of a fatty acid chloride to a monoene having one less C atom than the starting acid chloride. The monoene then was reconstituted into the branched acid derivative by one of two carboxylation procedures.

EXPERIMENTAL

Materials. Stearoyl chloride was prepared from stearic acid by reaction with oxalyl chloride by the procedure of Bosshardt.[3] The purified acid chloride had b.p. 161–63°, 0·5 Torr. GLC analysis of the corresponding methyl esters indicated that the composition was: stearate 94%; palmitate 6%.

Similarly, the acid chlorides of hydrogenated tallow acids were prepared. This material had a b.p. range of 145–160°, 1·0 Torr. GLC analysis of the methyl esters gave the following composition: C_{18}, 63%; C_{16}, 34%; C_{14}, 3%.

$PdCl_2$, $RhCl_3$, and 5% Rh/Al_2O_3 were obtained from Englehardt Industries Inc‡ and all other reagents were from commercial suppliers and were used as received.

GLC analyses were performed on a Hewlett Packard Model 810 gas chromtograph. IR spectra were recorded on a Perkin Elmer Model 237-B grating spectrophotometer. Mass spectra were obtained on a DuPont Model-492 spectrometer. Acid numbers, saponification, and iodine values were determined by official AOCS methods.

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[a]Presented at 1972 Spring AOCS Meeting in Los Angeles.

†Agricultural Research Service, U.S. Department of Agriculture.

‡Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Decarbonylation of stearoyl chloride. Stearoyl chloride (125 g, 0·40 mole) and $PdCl_2$ (107 mg, 0·6 mmole) were placed into a flask equipped with a thermometer, magnetic stirrer, and condenser connected to a gas bubble counter. The stirred mixture then was heated to an internal temp of 185° and gas evolution commenced. After 1·5 hr at 185° the evolution of gases ceased. The IR spectral analysis of the crude mixture confirmed the absence of acyl chloride. The residual catalyst was removed by filtration to give the crude monoenes **2a** as an amber liquid. Distillation through a spinning band column gave the pure monoenes with b.p. 86–89° (0·10 Torr) in 98% yield (C_{17}, 94%; C_{15}, 6%).

Decarbonylation of tallowyl chlorides. Hydrogenated tallow acid chlorides (100 g, 0·33 mole) and $PdCl_2$ (177 mg, 1·0 mmole) were heated at 200° for 2 hr at which time gas evolution ceased. The crude monoene mixture, after removal of catalyst, was distilled on a spinning band column to give a 95% yield of monoene mixture (C_{17}, 64%; C_{15}, 34%; C_{13}, 2%) with b.p. 65–90° (0·05 Torr).

Carboxylation procedures—Koch method. Formic acid (48 g, 1·0 mole) and the heptadecenes **2a** (47·6 g, 0·20 mole) were added dropwise over a period of 0·5 hr to cold (0°) stirred H_2SO_4 (870 g, 98%). After 3 hr at 0° the mixture was poured onto ice (2 kg) and extracted with ether (3 × 200 ml). The organic layers were washed with H_2O, until the washings were neutral, dried over anhyd $MgSO_4$, and the solvent removed *in vacuo* to give the crude acid mixture of **3** and **4** as an amber liquid (54·2 g, acid number 151). Distillation of this material yielded a colorless liquid with b.p. 170–176° (0·35 Torr) having an acid number of 180. Alternatively this material could be purified by chromatography on silica gel, which gave acids with an acid number of 177. The GLC patterns of the methyl esters of the crude and purified acid mixtures were essentially identical. Other pertinent data are summarized in Table 1.

Hydroformylation-oxidation procedure. We used a modification of the method developed by Frankel *et al.*[4] Into a 1 liter stainless steel autoclave were placed the heptadecenes **2a** (42·8 g, 0·18 mole), triphenylphosphine (1·3 g, 3% wt of olefin), 5% Rh metal on Al_2O_3 (1·7 g, 0·2% Rh wt of olefin) and toluene (50 ml). The reactor was sealed, flushed with N_2 gas, and charged with synthesis gas (500 psi, 1:1 $CO:H_2$). The reactor was heated to and maintained at 125° until the pressure stabilized (420 psi). The reactor was cooled, vented, the mixture filtered through celite, and the solvent removed *in vacuo* to leave a brown oil (49 g). GLC of this oil indicated a 96% conversion to the mixed octadecylaldehydes **5a**. Distillation yielded the pure aldehydes (b.p. 122–129° at 0·15 Torr, 93% yield).

The aldehydes were oxidized with $KMnO_4$ and air by the procedure of Frankel.[5] The yield of mixed branched acids **6a** (acid number 171) was quantitative. GLC (Table 2), IR, and mass spectroscopy (Table 3) of the methyl esters of **6a** confirmed these acids as C_{18} branched.

Table 2. GLC retention times of methyl esters

Acid structure	Relative retention time
3	0·75
4a and **4b**	0·80
6	0·81
8c and **8d**	0·83
8b	0·87
8a	0·90
Methyl stearate	1·00

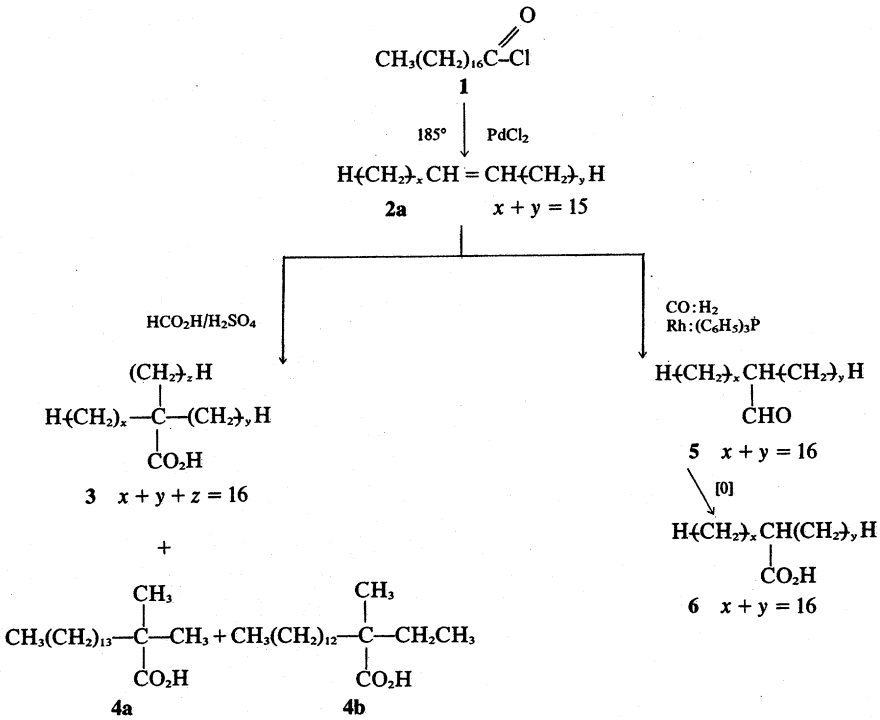
RESULTS AND DISCUSSION

The procedure we used to prepare branched chain saturated fatty acids from their linear counterparts is illustrated in Scheme 1 using stearoyl chloride as a prototype. The initial step of this reaction sequence was the catalytic decarbonylation of the fatty acid chloride using palladium chloride as the catalyst. The transition metal catalyzed decarbonylation of acyl halides and aldehydes has been recently reviewed by Tsuji.[6] With acyl halides as starting materials, the products of the above reaction were shown to be monoenes, having one less carbon atom than the starting acyl chloride, plus carbon monoxide and hydrogen chloride. When stearoyl chloride (**1**) was heated to 185° in the presence of palladium chloride, the evolution of carbon monoxide and hydrogen chloride was observed. The residual product from this reaction, in quantitative yield, was confirmed, as heptadecene mixture **2a** from the following spectroscopic and chemical data. The molecular weight of **2a**, by mass spectrometry, was 238 and agreed with the molecular

Table 1. Characteristics of branched acids

Starting acid	Decarbonylation catalyst	Carboxylation procedure	% Yield[a]	Acid no.	Sapon. no.	Iodine no.	Freezing point °C
Stearic	$PdCl_2$	Koch	91	151[b]	157	8	−23
Stearic	$PdCl_2$	Koch	55[c]	180	182	<1	−29
Stearic	$PdCl_2$	Koch	63[d]	177	183	3·5	−28
Stearic	$PdCl_2$	Hydroformylation	93	171	170	3·0	−10
Stearic	$RhCl_3$	Hydroformylation	88	165	153	1·0	+6
Tallow	$PdCl_2$	Koch	90	138	137	10	−24
Tallow	$PdCl_2$	Hydroformylation	88	148	147	12	−26

[a] Yield based on acid chloride.
[b] Theo. for stearic acid 197·5.
[c] Distilled acids.
[d] Chromatographed acids.



SCHEME 1

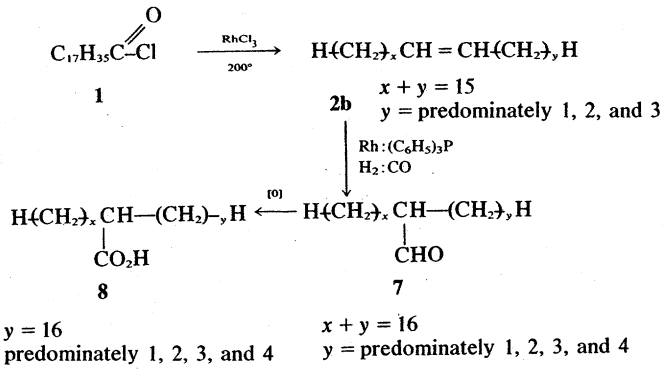
Table 3. Relative ion intensities[a] of methyl esters

m/e	3	4	6	8c & d	8b	8a
57	100	71	33	37	26	27
69	34	26	29	26	21	19
71	58	42	14	15	12	10
83	17	14	17	15	12	11
85	39	29		13		
87			100	100	67	29
88		—	32			100
101	73	20	24	10		44
102		100	27		100	36
116	—	97	24	64	43	18
130	28	12	25	51	22	12
144	33		29	13	10	
158	25		23	9		
172	20		19			
186	16		20			
200	14	—	16			
214	13		15			
228	12		11	9		
239	35	25	9			
242	11		9	13		
256			—	11		
269	—		4			
298	4	9	38	21	32	39

[a]Normalized intensity.

formula of $C_{17}H_{34}$. The IR spectrum of monoene **2a**, aside from the expected carbon-hydrogen absorptions, was characterized by an intense band at 975 cm^{-1} indicative of a *trans* substituted olefin. Comparison of **2a** with *cis* and *trans*-9-octadecene standards by argentation TLC confirmed that monoene **2a** had > 95% of its double bonds in the *trans* geometry. To determine the position of the unsaturation, monoene **2a** was subjected to reductive ozonolysis followed by GLC analysis of the resulting aldehyde mixture. A homologous series of linear aldehydes was found and ranged from C_5 to C_{15} in about equal concentrations. These data showed that the unsaturation in **2a** was randomly distributed within the internal positions of the carbon chain with no evidence of terminal unsaturation. This experiment also indicated that no branching of the hydrocarbon backbone had occurred. In contrast, when the above decarbonylation reaction was carried out with rhodium trichloride catalyst a different heptadecene mixture (**2b**) was obtained (Scheme 2). This olefin (**2b**) was a 50:50 mixture of *cis* and *trans* isomers. Reductive ozonolysis of **2b** showed that a large proportion of its double bond was located at the penultimate positions of the carbon chain (≈75% at C_2 and C_3). Much of the remainder has its double bond at C_3. Again, little if any branching of the carbon chain was observed. A more detailed study of the decarbonylation reaction with various transition metal catalysts is in progress.

The carboxylic acid function was reincorporated into heptadecenes **2a** and **2b** by either the Koch method[7] or the hydroformylation-oxidation procedure.[4] Since the Koch carboxylation procedure is



SCHEME 2

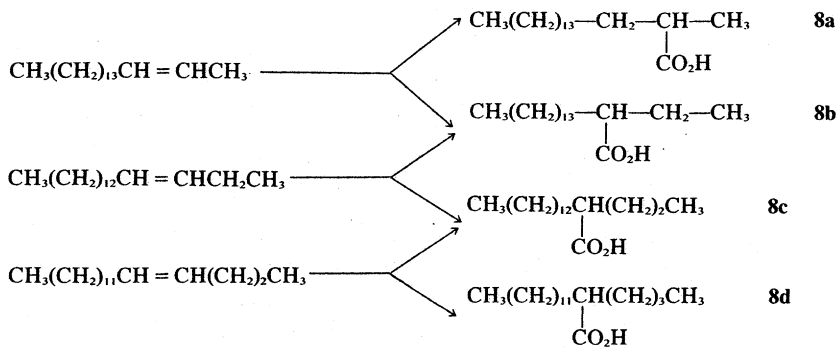
carried out in strong acid media and proceeds through the intermediary of carbocations,[8] olefin isomerization (both double bond and alkyl migration) occurs prior to carboxylation. This leads to a mixture of di- and trialkylacetic acids regardless of the original structure of the starting olefin.[8,9] With the hydroformylation oxidative procedure used in this study, the formyl groups were introduced at those positions originally occupied by the double bonds,[4] and since no branching of the C_{17} carbon chain occurred, only dialkylacetic acids were produced. In view of the above, monoene **2a** was carboxylated by both procedures (Scheme 1), while **2b** was carboxylated only by the hydroformylation-oxidation method (Scheme 2).

Utilizing the procedure of Swern *et al.*[7] heptadecene **2a** was carboxylated with formic acid in sulfuric acid. The crude acid mixture from this reaction had an acid number of 151. Purification of this acid by either distillation or chromatography gave a liquid acid mixture with an acid number of 180. Esterification of this liquid with diazomethane gave the corresponding methyl esters. Analysis of the esters by GLC indicated that this "isoacid" mixture was composed of two types of branched acids (structures **3** and **4** Scheme 1) in ratio of 3:2. At this point we should mention that the acid mixture of **3** and **4** could not be totally esterified by conventional techniques even after prolonged reaction times.[10] These esterification resistant acids were separated from the esters by column chromatography on Florisil and, after esterification with diazomethane, were shown by GLC to be predominantly the branched acids **3**. The individual methyl esters of acids **3** and **4** were isolated by GLC and analyzed by mass spectroscopy. The molecular ions for the methyl esters of acids **3** and **4** were observed at m/e 298 which is the expected molecular ion for a methyl "isostearate". Thus we concluded that both acids are isomeric mixtures of C_{18} carboxylic acids.

Alternatively, monoene **2a** was carboxylated using the procedure of Frankel.[4] Reaction of **2a** with synthesis gas ($CO:H_2$, 1:1) in the presence of a rhodium-triphenylphosphine catalyst gave aldehyde mixture **5** in > 95% yield. Mixture **5** was oxidized to the corresponding acid mixture **6** in quantitative yield. Acid mixture **6** was readily methylated by conventional methods.[10] GLC analysis of the ester mixture gave essentially one component with a retention time (Table 2) similar to that of acids **4**. As has been demonstrated, the formyl groups were incorporated at the positions previously occupied by the double bond and this led to the formation of dialkylacetic acids **6** since monoene **2a** was shown to be linear.

Monoene **2b**, from the rhodiumtrichloride decarbonylation, also was hydroformylated and oxidized to give acid mixture **8**. Since the olefinic bonds of **2b** were centered mainly at the 2, 3, and 4 positions of the C_{17} chain, acid mixture **8** was composed chiefly of the 2, 3, 4, and 5-carboxyheptadecanes **8a** to **8d** (Scheme 3). This view was confirmed because GLC analysis of the methyl esters of this acid mixture produced three distinct peaks. The three components were isolated by GLC, and mass spectrometry gave molecular ions of 298 for each, indicating they were isomeric with methyl stearate. Retention times of these branched esters were not similar to those of the esters of acids **3**, **4**, or **6** (Table 2).

Insight as to the structure of the branched acids prepared in this study could be obtained from a comparison of mass spectral fragmentation ions of the methyl esters of the various acids (Table 3) along with relative GLC retention times. It is generally recognized that the methyl esters of iso- and anteiso-acids have smaller retention times than those of the normal chain isomers. It has also been shown that the retention time decreases in a regular manner with displacement of the methoxycarbonyl group from the end towards the middle of the chain.[11] Table 2 gives the GLC retention times, relative to methyl stearate, for the methyl esters of the various acids. Retention times of the Koch acids **3** were lowest, while the acids **8a** through **8d** were highest, while acids **4** and **6** had intermediate retention times.



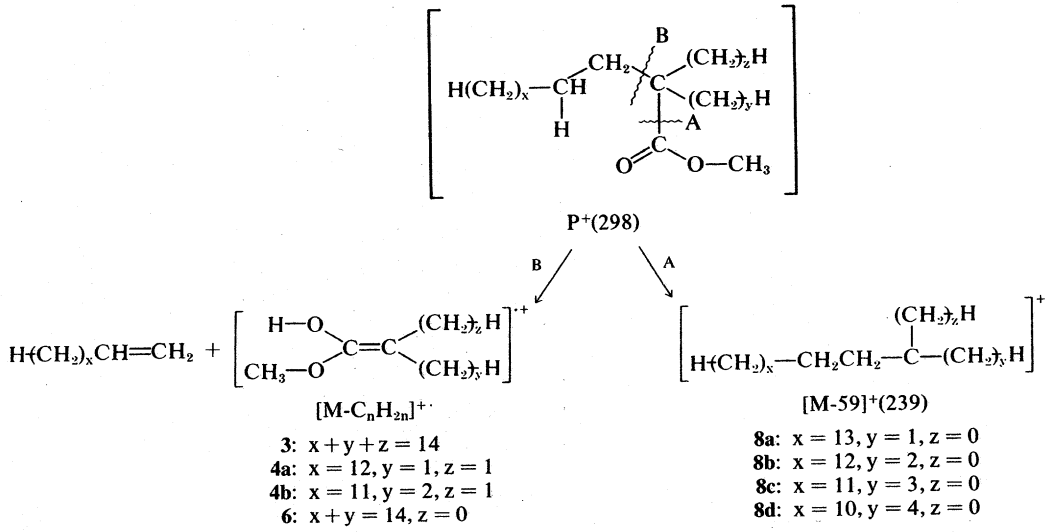
SCHEME 3

In view of the above, it would appear that acids **8** have their carbomethoxy function at the penultimate positions of the hydrocarbon chain while acids **3** are more symmetrically substituted. Acids **4** and **6**, with similar retention times, should have similar structures with the carbomethoxy group located at the remaining positions of the hydrocarbon chain. These conclusions are valid, however only if dialkyl acetic acid structures are considered and trialkylacetic acids are neglected, as discussed below.

Aside from those ions arising from the characteristic paraffin and olefinic peaks (57, 71, 85, 101, and so forth) the mass spectra of methyl esters of **3**, **4**, **6**, and **8a** to **8d** are dominated by fragmentation at the carbomethoxy substituted carbon atom. Scheme 4 shows that two types of cleavage processes predominate, simple cleavage at A (loss of carbomethoxy) to give a $[M\text{-}59]^+$ ion (239) and McLafferty rearrangement (path B) via an available γ-hydrogen atom to a $[M\text{–}C_nH_{2n}]^+$ ion.

It is this latter fragmentation pathway which allows for the assignment of the position of the carbomethoxy function along the hydrocarbon chain. First, let us consider the fragmentation course of the methyl esters of acid **6**. The method of synthesis established that acids **6** are dialkyl acetic acids. In the mass spectrum of the acids **6** a strong parent ion (P^+ 298) is observed. More importantly, the spectrum of **6** is characterized by a homologous series of ions corresponding to $[M\text{–}C_nH_{2n}]^+$ (88, 102, 116, . . . , 242). The intensities of these ions are of similar magnitude thus indicating that the carbomethoxy group is randomly located along the C_{17} hydrocarbon chain.[4,9]

The spectra of acids **8a** to **8d** also gave evidence of a prominent parent ion. However, from the spectra of the individual methyl esters, isolated by GLC, the following conclusions were drawn. The slowest eluting component (**8a**) has its base peak ion at m/e of 88. This ion arises via cleavage at B Scheme 4, with $z = 0$ and $y = 1$. Accordingly, the structure of this methyl ester is 2-carbomethoxy heptadecane (**8a**). This structure would be compat-



SCHEME 4

ible with the fact that, of all the acids prepared in this study, **8a** has the highest GLC retention time. The mass spectrum of compound **8b** had its base peak at m/e 102 which by McLafferty rearrangement establishes its structure as 3-carbomethoxyheptadecane. The third isolated component was ascertained to be a mixture of acids since the mass spectrum had major ion pairs at m/e 116, 130 and 242, 256. These ions are expected from a mixture of 4- and 5-carbomethoxyheptadecane (**8c** and **8d**). That these acids are indeed dialkyl acids and not isomeric trialkyl derivatives is concluded from their method of synthesis. The above mass spectral data are in agreement with the GLC retention times because as the carbomethoxy group moves towards the end of the heptadecane chain, the relative retention time should approach that of methyl stearate. Also, since **8c** and **8d** have slightly higher retention times than **6**, the carbomethoxy group in **6** must be located more centrally (7, 8, 9 positions) that in **8c** and **8d**.

For the Koch type acids **3** and **4** it is immediately apparent from Table 3 that cleavage to the $[M-59]^+$ ion is more prominent than for acids **6** and **8**. Cleavage at A (Scheme 4) would be favored by acid structures **3** and **4** if the residual carbocation had a tertiary structure. The trialkyl structures of **3** and **4** were confirmed by analysis of their McLafferty fragmentation ions. For acids **4**, two prominent ions are observed at m/e 102 (100%) and 116 (97%). These ions can arise from acid structures **8b** and **8c**. GLC retention data, however, show that acids **4** cannot be identical with acids **8**. Accordingly, the most probable structures for acids **4** are the isomeric trialkyl structures **4a** and **4b** (Scheme 1). This conclusion confirms a recent report that tertiary structures such as **4a** and **4b** are also the major acids formed when 1-octene is carboxylated via the Koch procedure.[8] In the present study acids **4** are found to comprise 40% of the crude acid product. It has yet to be explained why these acid structures are formed preferentially. Aside from the large P^+-59 ion the acids **3** display a homologous series of $[M-C_nH_{2n}]^+$ ions as do acids of structure **6**. Acids **3**, however, have lower GLC retention times than acids **6** and cannot therefore have a dialkyl structure. Since they do give a large $[M-59]^+$ ion, they apparently have trialkyl structures (Scheme 1). Alternatively, this tertiary branching might be located at carbon atoms β or γ to the carbomethoxy function; this also would account for the low GLC retention times and resistance to total esterification of these acids, but, would not be compatible with the prominent P^+-59 ion observed.

All of the acid mixtures prepared in this were obtained as liquids having the physica chemical properties listed in Table 1. The fre points ranged from + 6 to − 30° with the Koch acids having the best low temperature prope Table 1 also shows data for branched acids de when the above reactions are applied to h genated tallow fatty acids. We expect the t acids, which are composed mainly of C_{16} ar acids, to significantly lower the freezing poi the branched acid mixtures. When the Koch p dure was used, the freezing point of the res branched tallow acids were not significantly than that of the branched stearic acid. How with the hydroformylation procedure, fre point was lowered 15°.

As can be seen in Table 1 the acid numbe the crude acid mixtures were significantly than predicted theoretical values. After purific of the acids by simple distillation or chro graphy, the acid numbers approached the retical. In spite of these low acid number freezing points of the purified acids were n preciably different from the crude acid mix Saponification numbers for all mixtures prepa general, paralleled the acid numbers, and the i values ranged from a low of 1 to a high of 12. iodine values indicate that these acids should good oxidative stability. The physical propert the various acid mixtures are being studied completely.

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