Isomerization Studies: II. Thermal Alteration of Oleic Acid and Methyl Oleate in the Presence of Mineral Catalysts[1]

A. EISNER[2], P.A. BARR, and T.A. FOGLIA, Eastern Regional Research Center[3], Philadelphia, Pennsylvania 19118

ABSTRACT

A structure analysis has been conducted on the distillable fraction (67-71%) obtained from the clay catalyzed isomerization of methyl oleate and oleic acid. The method of analysis involved the combined use of reductive ozonolysis, urea adduction, and gas liquid chromatography-mass spectrometry. The results of this study indicate that the original unsaturation of the fatty acid is mostly retained, but less than the theoretical amount of hydrogen is absorbed when the products are subjected to low pressure catalytic hydrogenation. These results in conjunction with the gas liquid chromatography-mass spectrometry data suggest that branching of the carbon chain has occurred.

INTRODUCTION

Many methods are available for the dimerization and cyclization of unsaturated fatty acids (1-5). However, little attention has been directed toward the skeletal isomerization of saturated straight chain fatty acids into their isomeric branched chain analogues. A facile method of preparation for these saturated branched chain fatty acids would be extremely important from both a practical and fundamental standpoint. Previously, such skeletal transformations have been achieved by heating an unsaturated fatty acid in the presence of a mineral catalyst (2,3), Lewis acids (4), or water (5). In practice, however, when enoic acids are isomerized in the presence of the above catalysts, dimeric and trimeric species are the major reaction products, and conversions are incomplete. The desired modified isoacids are the minor products. The reaction of both saturated and monounsaturated fatty methyl esters with aluminum chloride also has been reported to result in the isomerization of the carbon chain of normal fatty acids (6,7). This approach, however, also suffers from the disadvantage that dimerization and polymerization are major side reactions. Additionally, the so-called monomer fraction contains considerable amounts of short chain branched fatty acids. The latter are formed from the original fatty acid by a chain cleavage process.

Recently, a series of articles on the thermal isomerization of oleic acid in the presence of a montmorillonite catalyst has appeared (8-11). In addition to a study of the various process parameters for the production of dimer acids from oleic acid, these authors reported a detailed investigation of the structure of the dimer fraction, as well as of the residual monomer fraction (8-10). While the dimer acid fraction had a cyclic structure similar to the dimer acid obtained from the thermal polymerization of polyunsaturated acids (12), the monomeric fraction was composed predominantly of saturated fatty acids of both the normal and branched chain variety. No evidence for the presence of a cyclic monomer, as observed with trienoic acids (13-15), could be detected in these studies (8-10). The above determinations were based mainly upon gas liquid chromatographic (GLC) data obtained from the distilled monomer fraction after hydrogenation and urea fractionation.

As part of a program directed toward the formation of branched saturated fatty acids from their normal chain isomers, we have undertaken a study of the clay catalyzed isomerization of unsaturated fatty acids. This article reports our results on the structure analysis of the monomer fraction obtained from the clay catalyzed isomerization of oleic acid. Our analyses of the distilled monomer are based upon the combined use of reductive ozonolysis, urea fractionation, thin layer chromatography (TLC), GLC, and mass spectrometry.

Materials

Methyl tallowate was prepared by esterification of tallow fatty acid obtained from Wilson-Martin Co., Philadelphia, Pa. No fractionation of this product was made. Oleic acid and methyl oleate (97% and 99% by GLC) were obtained from either Applied Science Laboratories, State College, Pa., or prepared within the laboratory. The clay catalysts made by the acid leaching of subbentonites were obtained from the Georgia Kaolin Co., Elizabeth, N.J. The clays are designated as Clarolite T-60 (pH 5.7) and Clarolite T-300 (pH 3.5). The clays were heated in a vacuum oven for 4 hr at 120 C and used without further treatment. Their residual water content was not determined.

Methods

Clay treatment: Exploratory runs were performed in sealed glass ampules (150 x 20 mm) made from heavy wall glass tubing. The methyl ester (5 g) plus clay (0.25 g, 5 wt %) were placed into the ampule, and, after flushing with nitrogen, the ampule was sealed. The ampules subsequently were heated in a horizontal tube furnace.

Larger scale experiments were carried out in a stainless steel autoclave, 300 ml capacity. In these experiments, the atuoclave was charged with the sample and clay (5 wt %), pressurized with nitrogen (20 psi), and heated by means of an electric heating mantle equipped with a Versatronic potentiometer controller.

Analytical Procedures

Gaseous products were analyzed by IR spectroscopy and mass spectrometry (MS). The gases were bled into an evacuated gas cell and analyzed on a Beckmann IR-8 spectrometer. A gas sample was withdrawn and injected into a gas chromatograph equipped with a Poropak Q column (5 ft x 1/8 in.) which was connected to a Dupont 492 mass spectrometer (MS). A single stage jet separator

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[2]Retired.
[3]ARS, USDA.

TABLE I

Distillation of Monomer Fraction from T-300 Clay Isomerization of Methyl Oleate

Fraction no.	Temperature, C (.1 mm)	Wt. % of distillate	IV
1	56-70	3.3	78.0
2	87-95	6.0	76.4
3	95-99	11.9	75.7
4	97-99	11.9	75.7
5	95-97	12.4	76.5
6	96-98	12.2	77.7
7	96-98	12.7	78.0
8	98	12.2	77.8
9	98-103	12.2	77.1
10	100-	5.2	70.6

TABLE II

Distribution of Products after Clay Isomerization[a]

Clarolite clay	T-60	T-300	T-300
Sample	methyl oleate	Methyl oleate	Oleic acid
Distillate (wt %)	86.9	71.6	67.0
IV (Distillate)	82.7-86.6[b]	70.6-78.0[b]	72.4-79.9[b,c]
Dimer (wt %)	13.1	28.4	33
IV (Dimer)	91.0	75.0	76.9

[a]Samples heated in autoclave for 24 hr at 240 C. Similar results were obtained in duplicate runs carried out with agitation.

[b]Range for various distillate fractions.

[c]For 88% of distillate, remainder contained considerable amount of γ-stearolactone.

was interposed at the interface between the GLC and the mass spectrometer.

Liquid products were examined routinely by IR spectroscopy and GLC. For the latter, the GC was equipped with either SE-30 or OV-17 columns (6 ft x 1/4 in.). The samples obtained from the autoclave experiments were distilled (0.1-0.3 mm) through a spinning band column, and fractions of 3-5 ml were collected until no more distillate was obtainable. These data along with the iodine value (IV) of each fraction are given in Table I. The distillation residue (dimer acid and polymeric materials) was reserved. Each individual fraction was examined by GLC and IR. Structure analyses were performed on selected fractions by ozonolysis-oxidation.

Ozonolysis-Oxidation Procedure

The selected distillate fraction (0.5 g) was dissolved in chloroform (25 ml) and ozone from a Welsbach ozone generator was passed through this solution until ozonization was complete as determined by starch-iodide solution and by TLC. The ozonides were reduced by the addition of zinc dust (0.5 g) and acetic acid (2 ml). The mixture was filtered, solvent was removed in vacuo, and the residual aldehydes were dissolved in acetone (20 ml) and oxidized with aqueous $KMnO_4$ (1 g/10 ml). The precipitated MnO_2 was filtered and washed with acetone, and the filtrates were concentrated in vacuo. The residue was extracted with hexane, the hexane layer was washed with H_2O, dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The acids then were converted to methyl esters by treatment with BF_3 in methanol. The methyl esters were analyzed by GLC on a DEGS column (8 ft x 1/4 in.) and compared with standards.

The methyl esters then were separated with urea into branched and unbranched fractions employing the procedure described by Knight, et al. (16). In a typical fractionation from a 0.44 g sample of methyl esters, there was obtained 0.20 g adduct forming straight chain material and 0.24 g nonadduct forming branched material. Each of these fractions was separated further by preparative TLC on silica gel with a solvent system of hexane-ether (4:1). The newly separated fractions were analyzed by GLC-MS, and comparisons were made with known standards.

RESULTS AND DISCUSSION

Preliminary studies were conducted on methyl tallowate as the starting substrate. Heating these esters in the absence of any additional substances at 180-255 C under reduced pressure (∿1 mm) for 8 hr produced little, if any, changes in the composition of the methyl tallowate, as determined by GLC and TLC. It has been shown that the isomerization and cyclization of unsaturated materials can be induced by heating them in the presence of a catalytic amount of sulfur (14,15) or clays (2,3). We found little change in the overall composition when we heated methyl tallowate with 1% by wt added sulfur under reduced pressure at temperatures varying from 155-235 C. However, IR analysis of this treated material indicated that elaidinization had, indeed, occurred as evidenced by an absorption peak at 970 cm^{-1}.

Heating methyl tallowate at 235 C and 55 mm in the presence of 5% by wt of added Clarolite clay for 12 hr did not produce much significant change in the composition of the ester as noted by GLC. However, when the tallowate ester and clay were heated in a sealed glass tube at 290 C for 24 hr, a considerable change was apparent in the C_{18} unsaturated region of the GLC pattern. IR analysis of this material also showed that extensive elaidinization had occurred. In addition, it was found that the IV of this thermally altered product had increased to 47 as compared to 41 for the starting material. A more detailed analysis of this altered material proved to be exceedingly difficult, because the starting methyl tallowate is a mixture of fatty acids. Therefore, to make a detailed study of the reaction, it was necessary to choose a simpler substrate. Consequently, in all subsequent experiments, either methyl oleate or oleic acid was used as the starting material.

Selected data for the products obtained from the thermal (240 C) alteration of methyl oleate in the presence of the two clays used in this study are given in Table II. It is seen that methyl oleate treated with Clarolite T-60 gave ∿15 wt % more distillate (monomer fraction) than methyl oleate heated with Clarolite T-300. The amount of pot-residue (dimer fraction) was reversed correspondingly. The average iodine value (IV) of the distillate fractions from the T-60 experiment was similar to that of the starting methyl oleate (IV 89.0), while for the T-300 products this value decreased by ∿15%. Also included in Table II are the data obtained when oleic acid was heated in the presence of the T-300 clay. The latter product after thermal treatment was converted to the methyl ester prior to distillation. As shown in Table II, the results obtained for the free acid are similar to those obtained with the methyl ester. The major difference found was that an appreciable amount of γ-lactone was found in the distillate in this experiment. Lactone formation was not unexpected. It is most likely the result of acid catalyzed double bond migration with attendant cyclization of the δ, γ-unsaturated acid (17). The data in Table II in conjunction with GLC analysis of the monomer distillates indicate that the T-300 clay is more active (produced more changes in the methyl oleate) than the T-60 clay. This difference in activity between the two clays is probably due to the difference in pH of the clays, the T-300 being more acidic. Another significant difference is their Al_2O_3 content which is 16.3% for the T-60 clay and 8.7% for the T-300 clay.

Insight as to the nature of the distillate (monomer fraction) obtained from the T-300 clay catalyzed experiments was obtained from hydrogenation experiments. A portion of the distillate (IV, 75) was subjected to low pressure (50 psi) catalytic (PtO_2) hydrogenation at 25 C. Less than the theoretical amount of hydrogen was absorbed

TABLE III

IR Bands of Gas Products from the T-300 Clay Isomerization of Methyl Oleate

$\bar{\gamma}$ (cm^{-1})[a]	Assignment
3800-3600 (m)	H_2O, CO_2
3050 (s)	Alkene
3000-2800 (s)	Alkane
2365 and 2350 (s)	CO_2
2112 and 2100 (w)	Dimethyl ether
1465 (s)	Alkane
1193, 1165, 1156)) (s) 1116, 1102)	Dimethyl ether
1030 (s)	Branched alkane
941 and 918 (s)	Dimethyl ether
720 (w)	Alkane
670 (s)	CO_2

[a](s) = strong, (m) = medium, and (w) = weak.

TABLE IV

Gas Liquid Chromatographic-Mass Specttal Identification of Gaseous Products from the T-300 Clay Isomerization of Methyl Oleate

Peak no.	Retention time[a]	Identity
1	0.06	Acetylene
2	0.32	Propylene
3	0.35	Propane
4	0.45	Dimethyl ether
5	0.65	Isobutane
6	0.76	Butene
7	1.00	Methylene chloride
8	1.04	Pentane
9	1.10	Pentene
10	1.35	Hexane
11	1.40	Hexene
12	1.62	Heptane

[a]Relative retention times to added methylene chloride.

(IV of product, 47), whereas methyl oleate was converted quantitatively to methyl stearate under the same conditions. A second hydrogenation was performed, this time at 500 psi and at 100 C for 6 hr. Again hydrogenation was incomplete (IV product, 34), even under these more forcing reaction conditions. When the monomer fraction (IV, 88) from the T-60 clay catalyzed experiments was subjected to low pressure (50 psi) hydrogenation, incomplete hydrogenation again was observed (IV of product, 24). These results suggest that, in addition to elaidinization of the double bond, increased branching at or adjacent to the double bond had possibly occurred. Support for this assumption can be taken from a study by Kistiakowsky, et al., (18) on the heats of hydrogenation of substituted ethylene derivatives. In that study, it was established that increased branching at the ethylenic linkage decreased the rate of hydrogenation. In the present study, the difficulty in obtaining complete hydrogenation of double bonds together with data to be introduced later indicates the presence of branched olefinic material. The amount of branched material in the distillate was estimated as 55% by urea adduction.

The gaseous products produced in the T-300 clay isomerization of methyl oleate also were analyzed. The observed IR absorptions for this gas sample are listed in Table III. In addition to the characteristic absorption peaks for H_2O, CO_2, CO, and dimethyl ether, the presence of alkenes and branched hydrocarbons are suggested by absorptions at 3050 cm^{-1} and 1030 cm^{-1}, respectively. A more complete compositional analysis of this gas mixture was obtained by the use of GLC-MS. As shown in Table IV, the hydrocarbon component of this gas mixture consisted of a homologous series of isomeric alkanes and alkenes ranging from C_3-C_7. The presence of acetylene and dimethyl ether also was confirmed by this technique. The catalytic formation of petroleum hydrocarbons from fatty acids by decarboxylation and catalytic cracking recently has been described (19,20), and these pathways probably account for hydrocarbons formed in the present study.

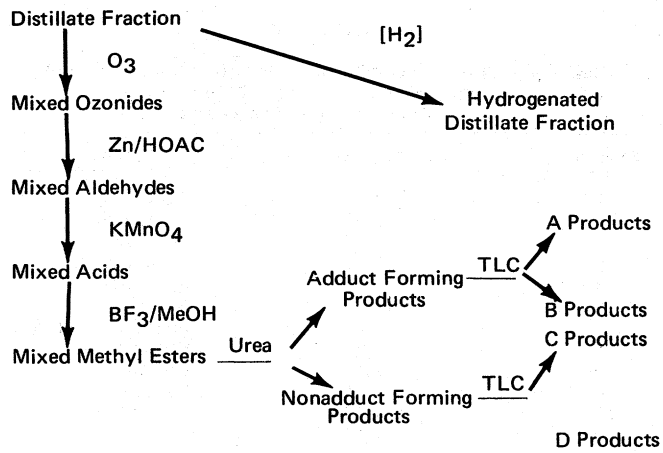
Each of the fractions obtained from the distillation of the monomer fraction was examined by GLC. The earlier fractions (fractions 1-6, Table I) yielded a much different pattern than the starting material, whereas the later fractions (fractions 7-10, Table I) closely resembled the starting material. Certain fractions were selected for a detailed examination and characterization employing the procedure outlined in Scheme I.

For the later fractions (7-10), the ozonolysis procedure plus oxidation proved sufficient for structure analysis. The oxidation products after methylation were analyzed by GLC. Two homologous series were obtained which corresponded to a standard mixture of monobasic (C_4-C_{14}) and dibasic (C_3-C_{14}) normal chain acids. Accordingly, these latter fractions (7-10) are considered to be comprised of a mixture of methyl esters of C_{18} monounsaturated acids with a random distribution of the ethylenic bond along the chain. Presumably, the unsaturated acids are formed by the acid catalyzed migration of the double bond accompanied by elaidinization (21).

The earlier fractions (1-6) had a more complex GLC pattern, and their characterization was more involved (Scheme I). The mixture of oxidation products was complex, and fractionation steps were required. The first of these was the separation of straight chain esters from branched chain esters, according to the ability of the products to form urea adducts. The adduct forming esters (unbranched) comprised 45% of the mixture and the nonadduct forming esters 55%. Further separation of both the adduct forming and nonadduct forming fractions was accomplished by preparative TLC.

In the adduct forming fractions, TLC separated the monoesters (A products) from the diesters (B products). The wt ratio of monoesters to diesters was 2:1. Analysis of the monoester fraction (A fraction) by GLC-MS indicated it to be a homologous series of normal chain methyl esters of chain length varying from C_7-C_{18}. Another GLC peak, tentatively identified as a branched C_{19} methyl ester, also was observed in this fraction. The C_{18} methyl ester which comprised ∿25% of fraction A presumably is formed by disproportionation and hydrogenation as a result of the clay treatment (8-10, 21). The C_{19} methyl ester probably arises from the alkylation of a shorter chain alkenoic acid. In a similar manner, the diester fraction (B products) was demonstrated to be a mixture of normal chain dicarboxylic acids varying in chain length from C_4-C_{14}.

For the nonadduct forming products, the separation by TLC into classes of compounds was not as simple as for the adduct forming products. Two fractions were isolated and designated as C products and D products and the ratio of C to D was 3:1. GLC-MS analysis of the C products indicated that this fraction was a mixture of ketones and methyl esters of branched monocarboxylic acids as also evidenced by IR absorption bands at 1710 and 1740 cm^{-1}, respectively. The ketones were a homologous series ranging from C_7-C_{15} in carbon number, as determined from their observed mass spectral molecular ions (M^+ from 128-226) and fragmentation ions (M^+-C_nH_{2n+1}). The branched acids ranged from C_8-C_{14}, as determined from their molecular ions (M^+ from 158-242) and McLafferty rearrangement ions (M^+-C_nH_{2n}). Ketone formation would result if the unsaturated branched esters of the general formula 1 and 5 (Scheme II) were present in the original distillate. The other components of the C products, the methyl esters of branched monocarboxylic acids, are derived from a mixture of parent branched esters having the general structure 2, Scheme II. Structures 1 and 2 also would account for the

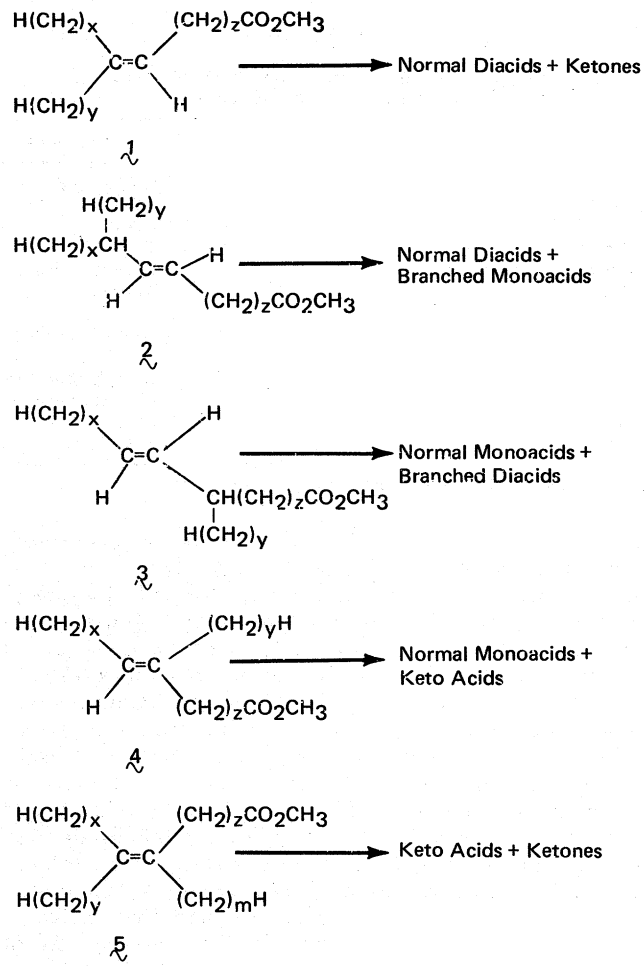


Scheme I

formation of normal diacids in the urea adduct forming fraction B (Scheme I), while structures 3 and 4 would account for the normal chain methyl esters found in fraction A (Scheme I).

The D products proved to be a complex mixture. However, GLC-MS of this fraction, though not definitive, gave strong evidence for the presence of both keto acids and branched chain diacids. The formation of these oxidation products is readily explained if the original distillate contained unsaturated esters of general structures 3 and 4, Scheme II. The complexity of this fraction can be realized if one considers the possibility that one or more of the pendant groups on the ethylenic bond may be branched.

All of the foregoing demonstrates that thermal treatment of long chain monounsaturated fatty acids in the presence of a clay catalyst results in a multitude of reactions, including: elaidinization, isomerization, chain branching, disproportionation, hydrogenation, polymerization, and alkylation. More importantly, the present study shows that under selected conditions the distillable monomer fraction obtained from the clay catalyzed isomerization of methyl oleate retains a large part of the original unsaturation. A portion of this unsaturated ester, however, has been shown to possess a more highly substituted ethylenic linkage than the starting material, and this causes it to be more resistant to hydrogenation.



Scheme II

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C.J. Dooley performed the mass spectrometry described in this article.

REFERENCES

1. Bradley, T.F., and W.B. Johnston, Ind. Eng. Chem. 33:86 (1941).
2. Barrett, F.O., C.G. Goebel, and R.M. Peters, U.S. Pat. 2,793,219 (1957).
3. Barrett, F.O., C.G. Goebel, and R.M. Peters, U.S. Pat. 2,793,220 (1957).
4. Croston, C.B., I.L. Tubb, J.C. Cowan, and H.M. Teeter, JAOCS 29:331 (1952).
5. Goebel, C.G., Ibid. 24:65 (1947).
6. Blanchard, P., R. Perron, and M. Auffret, Bull. Soc. Chim. Fr. 1194 (1968).
7. Paquot, C., R. Perron, and J. Dulieu, Ibid. 1150 (1968).
8. Den Otter, M.J.A.M., Fette Seifen Anstrichm. 72:667 (1970).
9. Den Otter, M.J.A.M., Ibid. 72:875 (1970).
10. Den Otter, M.J.A.M., Ibid. 72:1056 (1970).
11. Heynen, H.W.G., W.H.M.J. Van Opstal, and M.J.A.M. Den Otter, Ibid. 74:677 (1972).
12. Cowan, J.D., JAOCS 39:534 (1962).
13. Friedrich, J.P., and R.E. Beal, Ibid. 39:528 (1962).
14. Nayak, U.R., A.H. Kapadi, and S. Dev, Tetrahedron 26:5071 (1970).
15. Nayak, U.R., A.H. Kapadi, and S. Dev, Ibid. 26:5083 (1970).
16. Knight, H.B., L.P. Witnauer, J.P. Coleman, W.R. Noble, Jr., and D. Swern, Anal. Chem. 24:1331 (1952).
17. Shepherd, I.S., and J.S. Showell, JAOCS 46:479 (1969).
18. Kistiakowsky, G.B., J.R. Ruhoff, H.A. Smith, and W.E. Vaughan, J. Amer. Chem. Soc. 58:137 (1936).
19. Shimoyama, A., and W.D. Johns, Nature Phys. Sci. 232:140 (1971).
20. Waples, D.W., Ibid. 237:63 (1972).
21. Brown, L.H., and R. Swidler, U.S. Pat. 3,065,248 (1962).