

Isomerization Studies: III. Decarbonylation of Oleoyl Chloride Preparation of C₁₉ Dicarboxylic Acids

4054

P.A. BARR, T.A. FOGLIA, and I. SCHMELTZ¹, Eastern Regional Research Center, ARS, USDA, Philadelphia, Pennsylvania 19118

ABSTRACT

Mixtures of isomeric C₁₇ diene hydrocarbons were obtained when oleoyl chloride was decarbonylated in the presence of a transition metal catalyst. The choice of catalyst determined the composition of diene mixture produced. Diene mixtures were characterized as a mixture of conjugated and 1,4- dienes, or as a mixture of isolated double bond dienes. Carboxylation of the conjugated C₁₇ diene by hydroformylation-oxidation procedure gave a C₁₈ monocarboxylic acid as the major product, whereas with nonconjugated C₁₇ diene, the major product was a C₁₉ dicarboxylic acid. Application of the Koch carboxylation procedure to C₁₇ diene mixtures gave a C₁₉ dicarboxylic acid mixture as the major product. This latter acid mixture was structurally different from diacids obtained from the hydroformylation-oxidation procedure.

INTRODUCTION

Considerable effort is being directed toward the development of methods for conversion of linear saturated fatty acids into their isomeric branched chain analogues (1). This interest is derived from the fact that branched chain carboxylic acids in general do not resemble their straight chain counterparts in physical properties and to a lesser degree in their chemical properties. The introduction of branching into the fatty acid hydrocarbon chain, aside from affording a new variety of fat derivatives, also may impart improved physical and chemical properties, thus expanding commercial utility of fatty acids and their derivatives.

In a prior study (2), we reported methods for the preparation of liquid branched saturated fatty acids from their normal chain counterparts. This transformation was accomplished by either a 2- or 3-step process. The intermediate in both procedures was an isomeric mixture of monoenes possessing one less carbon atom than the starting acid. Subsequent carbonylation of the monoene mixture yielded the α -branched chain fatty acid. The acids prepared in that

study were all liquids, and initial testing results indicated that these acids exhibited improved physical properties such as lower freezing points, improved pour points, and good oxidative stability.

The present study was undertaken to expand the scope of the above study to include unsaturated fatty acids (oleic acid), with the intention of preparing branched C₁₉ dicarboxylic acids from the anticipated diene mixtures. These C₁₉ dicarboxylic acids, unlike the carboxystearic acids prepared in other studies (3), should contain a minimum number of terminal carboxy functions.

EXPERIMENTAL PROCEDURES

Materials

Oleic acid was obtained by the fractionation of Groco 5L oleic acid (A. Gross & Co., Newark, NJ). Oleoyl chloride was prepared from oleic acid by reaction with oxalyl chloride employing the procedure of Bosshard, et al. (4). Oleoyl chloride thus prepared was used without further purification. PdCl₂, RhCl₃, and 5% Rh/Al₂O₃ were obtained from Englehardt Industries Inc. (Cataret, NJ) or Pfaltz and Bauer (Flushing, NY) and were used as received.

Gas liquid chromatographic (GLC) analyses of diene mixtures were carried out on stainless steel columns (6 ft x 1/4 in.) packed with 10% Carbowax on Chromosorb W, 60-80 mesh. The hydroformylated and carboxylated products were analyzed on columns (6 ft x 1 in.) packed with 10% UCW-98 on Chromosorb W, 60-80 mesh. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 237-B grating spectrophotometer. Acid numbers were determined by official AOCS method (5). Mass spectra were obtained on a Dupont 21-492 double focusing instrument operating at an ionization potential of 70 eV. Samples were introduced by either a batch inlet system or by direct probe. The position of unsaturation in diene mixtures was determined by an ozonolysis-oxidation procedure described previously (6).

Decarbonylation of oleoyl chloride. The procedure used for decarbonylation of oleoyl chloride was similar to that described previously for stearyl chloride (2). The mole ratio of oleoyl chloride to metal catalyst was 150:1 (acid

¹Present address: Naylor Dana Institute for Disease Prevention, 2 East End Avenue, New York, NY 10021.

TABLE I
Decarbonylation of Oleoyl Chloride

Catalyst	C ₁₇ diene mixture	Boiling point	Infrared bands	GLC relative retention times ^a	Ultraviolet data
PdCl ₂	H(CH ₂) _x CH=CH-CH ₂ -CH=CH(CH ₂) _y H <i>1a</i> (x+y=12)	106-110 C ^b	980 cm ⁻¹ (s) 960 cm ⁻¹ (m) 940 cm ⁻¹ (w)	<i>1a</i> 11.6 (45%) 10.9 (s) ^d	λ_{\max} 214 ϵ_{\max} 320
	H(CH ₂) _x CH=CH-CH=CH(CH ₂) _y H <i>1b</i> (x+y=13)				
RhCl ₃	H(CH ₂) _x CH=CH(CH ₂) _y CH=CH(CH ₂) _z H <i>2</i> (x+y+z=13)	98-102 C ^b	960 cm ⁻¹ (s) 910 cm ⁻¹ (w)	12.25	λ_{\max} 230 ϵ_{\max} 351

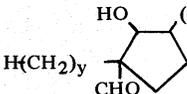
^aRelative to air peak. GLC = gas liquid chromatography.

^bAt 0.15 Torr.

^c() = Strong (s), medium (m), weak (w).

^dShoulder.

TABLE II
Carboxylated Products from C₁₇ Dienes

Diene	Carboxylation procedure	Products	(%) Composition ^a	Acid number ^c
1a + 1b	Hydroformylation oxidation	$\text{H}(\text{CH}_2)_x-\underset{\text{R-CO}}{\text{CH}}-(\text{CH}_2)_y\text{H}$	70	143 (197.5)
		R=H 3a; R=OH 3b (x+y=16)		
		$\text{H}(\text{CH}_2)_x-\underset{\text{R-CO}}{\text{CH}}-(\text{CH}_2)_y-\underset{\text{R-CO}}{\text{CH}}-(\text{CH}_2)_z\text{H}$	12	
		R=H 4a; R=OH 4b (x+y+z=15)		
			18	
		5a (x+y=13)		
2	Hydroformylation oxidation	$\text{H}(\text{CH}_2)_x-\underset{\text{R-CO}}{\text{CH}}-(\text{CH}_2)_y-\underset{\text{R-CO}}{\text{CH}}-(\text{CH}_2)_z\text{H}$	75 ^b , 60	188 ^d , 248 ^e
		R=H 6a; R=OH 6b (x+y+z=15)		
		C ₃₄ H ₆₉ CO(R)	25 ^b , 40	84 ^d
		R=H 7a; R=OH 7b		
2	Koch	$\text{H}-(\text{CH}_2)_x-\underset{\text{CO}_2\text{H}}{\text{C}}-(\text{CH}_2)_y-\underset{\text{CO}_2\text{H}}{\text{C}}-(\text{CH}_2)_z\text{H}$	70 ^b	235 (342)
		8 (x+y+z+m+n=15)		
		branched lactone	10	
		9		

^aBased on wt after distillation.

^bAcid chromatographed on Silica Gel.

^c() = Theoretical values.

^dValues for distilled products after oxidation.

^eValues for chromatographed acids.

chloride:metal) for both catalytic systems, RhCl₃ and PdCl₂. Reaction was judged complete when gas evolution ceased or when IR showed the absence of the acyl chloride absorption band (1800 cm⁻¹). Residual catalyst was recovered by filtration through Celite. Crude diene mixtures then were distilled in vacuo to give pure C₁₇ dienes as colorless liquids. The bp and spectroscopic data for the 2 diene mixtures obtained are given in Table I.

Hydroformylation-oxidation procedure. The hydroformylation-oxidation procedure used has been described previously (7). GLC analysis of the crude hydroformylated product indicated that hydroformylation was complete by the absence of the starting dienes.

Distillation of formyl products obtained from the diene mixture 1a and 1b, as illustrated in Table I, yielded a monoformyl derivative 3a, shown in Table II, with a bp of 124 C (0.04 Torr, 70%), a diformyl derivative 4a (Table II) with bp of 150 C (0.06 Torr, 12%), and a nondistillable hydroxyformyl derivative 5a (Table II) (18%).

The crude hydroformylation product obtained from diene mixture 2 (Table I) gave a diformyl derivative 6a (Table II) with bp of 152-160 C (0.1 Torr, 60%) and a residue which after chromatography on Florisil tentatively was identified as a monoformyl dimer derivative 7a (Table II) (40%). GLC analyses of these various fractions and residues were carried out on the carbomethoxy derivatives. The latter were prepared by oxidation with KMnO₄ and air of the formyl compounds by the procedure of Frankel (7) followed by methylation with diazomethane (Table II).

Carboxylation by Koch procedure. Formic acid (48.5 g,

1.05 mole) and diene mixture 2 (Table I) (23.6 g, 0.1 mole) were added dropwise over a period of 30 min to cold (0 C) stirred sulfuric acid (950 g, 98%). After 3 hr at 0 C, the mixture was poured onto 2 kg ice and extracted with 200 ml ether 3 times. Combined ether layers were washed with water until neutral, dried over anhydrous MgSO₄, and the solvent was removed in vacuo to give the crude acid mixture as a viscous amber oil (33.8 g, acid number 235.7). The product 8 (Table II) was purified by chromatography on silica gel (acid number 305.6, theoretical 342).

Characterization of 5a (Scheme 1). After purification by column chromatography on Florisil, 5a exhibited the following IR bands: 3500, OH; 2690, HC=O; 1720, C=O; and 1170 cm⁻¹, C-O. Reduction of 5a with lithium aluminum hydride gave diol 10 (Scheme I) with IR of 3400 and 1050 cm⁻¹. Reaction of 10 with acetic anhydride gave the diacetoxyl derivative 12 (Scheme I) with IR of 1740, C=O, and 1240 cm⁻¹.

Reaction of 5a (Scheme I) with acetic anhydride produced the monoacetoxyl aldehyde 11 (Scheme I) with the following IR absorptions: 2600 and 1720 cm⁻¹, CHO; and 1740 and 1240 cm⁻¹, acetate.

RESULTS AND DISCUSSION

Decarbonylation

When heated to 200 C in the presence of a catalytic quantity of either RhCl₃ or PdCl₂, oleoyl chloride was quantitatively decarbonylated to a C₁₇ diene mixture, carbon monoxide, and hydrogen chloride. With all other re-

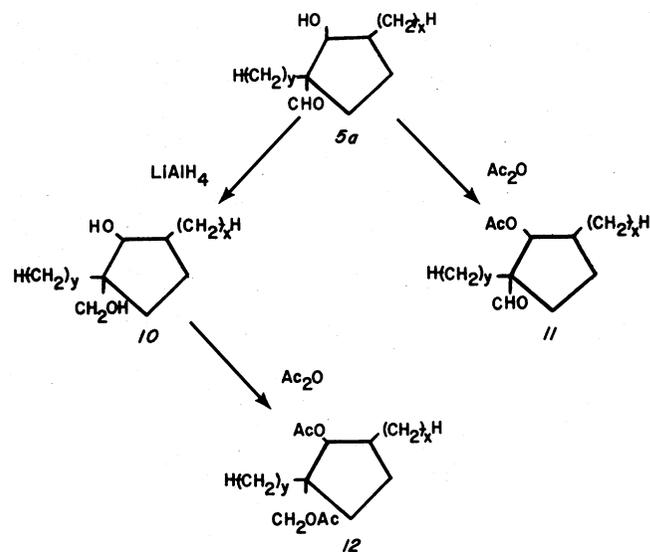
action parameters remaining constant, the structural composition of the diene mixture obtained was found to be dependent upon the particular catalyst used for the decarbonylation reaction. When PdCl_2 was used as the catalyst, diene mixture 1 (Table I) was obtained, and was mainly a mixture of 1,3- and 1,4-dienes, structures 1a and 1b (Table I). In contrast, diene mixture 2 (Table I) containing only isolated double bonds was obtained from the RhCl_3 catalyzed decarbonylation of oleoyl chloride. This assignment of structural composition for the diene mixtures was made on the basis of the following spectroscopic and chemical data (Table I). The mass spectra of diene mixtures 1 and 2 (Table I) were very similar, both giving molecular ions at m/e of 236, in agreement with the empirical formula of $\text{C}_{17}\text{H}_{32}$. IR analysis of dienes 1 and 2 (Table I), however, showed major differences in the 800-1000 cm^{-1} region. Diene mixture 1 (Table I) had a strong absorption band at 980 cm^{-1} and bands of lesser intensity at 960 and 940 cm^{-1} , while diene 2 (Table I) had a strong absorption at 960 cm^{-1} and a weak band at 910 cm^{-1} . The 960 cm^{-1} band observed in the spectra of both dienes was characteristic for an isolated *trans* double bond, while the shifting of this band to higher frequency (980 cm^{-1}) in diene 1 (Table I) was attributed to the presence of a conjugated diene structure (8). Evidence from GLC and ultraviolet (UV) data substantiated the above conclusions.

Diene 2 (Table I) eluted from the gas chromatograph as a single symmetrical peak with a retention time of 12.25. Its UV maximum and extinction coefficient (Table I) were values expected for an isolated double bond structure. Diene mixture 1 (Table I) run under identical conditions gave a more complicated GLC pattern. Two major peaks (1a and 1b), eluted with retention times of 11.6 and 14.0, respectively. Individual components were isolated by preparative GLC and subjected to UV analysis. Diene 1b (Table I) had a λ_{max} at 234 nm and an ϵ_{max} of 24,400, data which were consistent with a conjugated diene structure. In contrast, diene 1a (Table I) had a λ_{max} at 214 nm and ϵ_{max} of 320, data which were consistent with an isolated double bond structure. Quantitative measurements indicated that diene 1 (Table I) was comprised of 45% of 1a (Table I) and 55% of conjugated diene 1b (Table I).

Double Bond Position Analysis

Positions of unsaturation in diene mixtures 1 and 2 (Table I) were determined by reductive ozonolysis followed by oxidation and esterification (6). The resulting methyl esters were then analyzed by GLC. From diene mixture 2 (Table I), a homologous series of linear monobasic acids from C_6 to C_{13} , and a linear homologous series of dibasic acids from C_5 to C_{10} were obtained. The major monobasic acid was C_9 (60%), which indicated that the Δ^9 unsaturation inherent to oleoyl chloride, for the most part, was unaffected by the decarbonylation catalyst. The major dibasic acids were C_6 to C_8 (ca. 90%), thus demonstrating that the newly introduced double bond was centered mainly at the Δ^1 , Δ^2 , and Δ^3 positions of the hydrocarbon chain. This result was in excellent agreement with results obtained previously from the decarbonylation of saturated acid chlorides (2). From the above, we concluded that diene mixture 2 (Table I) was comprised chiefly of 2 isomers, namely $\Delta^{1,8}$ - and $\Delta^{2,8}$ -heptadecadiene.

For diene mixture 1 (Table I) only a single homologous series of linear monobasic acids ranging from C_5 to C_{15} was obtained on ozonolysis. Because our method (6) of analysis was sensitive to dibasic acids of 4 carbon atoms or greater and monobasic acids of C_5 or larger, we assumed that the only dibasic acids formed were C_2 and C_3 . The presence of the conjugated diene 1b (Table I) has been previously demonstrated and yielded a C_2 dibasic acid fraction upon ozonolysis-oxidation. The nonconjugated diene 1a (Table I)



SCHEME I

Chemical Characterization of 5a

must be of the classical 1,4- diene structure, because ozonolysis-oxidation would have yielded a C_3 dibasic acid. The distribution of the monobasic acids was statistical, thus indicating that the double bonds in 1 were randomly distributed within the internal positions of the hydrocarbon chain.

Introduction of Carboxyl Groups

Reincorporation of the carboxylic acid function into diene mixtures 1 and 2 (Table I) was accomplished by either a hydroformylation-oxidation procedure (7) or the Koch procedure (9). Because the Koch carboxylation procedure was carried out in strong acid media and proceeded through the intermediary of carbo-cations (10), double bond isomerization occurred prior to carboxylation. Accordingly, the nature of the starting diene mixture was unimportant, because any C_{17} diene would have yielded the same product mixture. In contrast, the hydroformylation-oxidation procedure used in this study introduced the carboxy groups at those positions previously occupied by the internal double bonds (7). In view of the above, diene mixture 2 (Table I) was carboxylated by both procedures, while the highly conjugated diene mixture 1 (Table I) was carboxylated only by the hydroformylation-oxidation procedure. Products obtained from the carboxylation of dienes 1 and 2 are listed in Table II.

Hydroformylation Procedure

Hydroformylation of diene mixture 1 (Table I) was carried out using a modification of the procedure developed by Frankel, et al., (2). Distillation of the crude formyl product gave the distillable monoformal and diformal derivatives 3a and 4a (Table II) and the nondistillable hydroxyformyl derivative 5a (Table II). The monoformal product 3a (Table II) was subsequently oxidized to the corresponding acid 3b (Table II) and esterified with diazomethane. GLC analysis of the methyl ester mixture results in essentially one peak with a retention time similar to that of C_{18} branched acids prepared in previous studies from stearic acid (2). Mass spectra of the methyl ester of 3b (Table II) gave a molecular ion at m/e 298 and a fragmentation pattern characteristic of an α -branched fatty methyl ester (7) with a carbo-methoxy group randomly distributed along a C_{17} hydrocarbon backbone. Diformal derivative 4a (Table II) was similarly oxidized and esterified. IR spectra of the methyl esters of 3b and 4b (Table II) were identical with the ex-

ception that the diester derivative exhibited a stronger 1740 cm^{-1} ester band relative to the 2900 cm^{-1} carbon-hydrogen band. Mass spectrum of the methyl ester of *4b* (Table II) gave a molecular ion at m/e 356. A comparison of the fragmentation pattern of *4b* (Table II) with the mass spectral data reported for methyl carboxystearate confirmed the structure of *4b* as a dicarboxy derivative (11). Hydroxyformyl derivative *5a* (Scheme I), after purification on a Florisil chromatography column, was identified from the chemical reactions shown in Scheme I. Reduction of *5a* with lithium aluminum hydride yielded the dihydroxy derivative *10* (Scheme I), which on reaction with acetic anhydride yielded the diacetate *12* (Scheme I). Alternatively, *5a* was reacted with acetic anhydride to yield the monoacetoxymethyl derivative *11* (Scheme I). Mass spectra of *10* and *12* had molecular ions at m/e of 298 and 382, respectively, and fragmentation patterns characteristic of cyclic 1,3 diols and 1,3 diacetates. Formation of hydroxyformyl derivative *5a* most probably arose by the internal aldol cyclization of *4a* (Table II) during distillation (E.N. Frankel, personal communication, 1975). The predominant formation of *3a* (Table II) over the expected diformyl compound *4a* probably occurred from the 1,4 addition of hydrogen and formyl groups followed by hydrogenation of the resulting α,β -unsaturated aldehyde. This propensity of conjugated diene systems to undergo monohydroformylation preferentially also has been observed by Frankel when he attempted to hydroformylate conjugated linoleate (12).

Diene mixture 2 (Table I), containing only isolated double bonds, readily underwent hydroformylation to give as the major distillable product the diformyl derivative *6a* (Table II) and the nondistillable monoformyl adduct *7a* (Table II). Mixture *6a* was oxidized to the diacid *6b* (Table II), and the methyl ester of the latter was analyzed by GLC and mass spectrometry. Comparison of GLC retention time and mass spectral fragmentation ions of esters of *4b* and *6b* (Table II) indicated that they were essentially identical. Close examination of the mass spectra of *4b* and *6b* revealed that *6b* contained a higher percentage of terminal carboxy function. This was to be expected, because diene 2 was shown to contain a high percentage of terminal unsaturation. The yield of C_{19} dicarboxylic acid *6b* was improved considerably when the crude hydroformylation product was not distilled (Table II). The residue *7a* could not be assigned a definitive structure; however, from elemental analysis, IR and mass spectral analyses, it appeared to be a monoformyl dimer of diene mixture 2.

Koch Carboxylation

Diene mixture 2 (Table I) also was carboxylated with formic acid in sulfuric acid by the Koch procedure as modified by Roe and Swern (9). The crude acid mixture *8* (Table II) obtained from this reaction had an acid number of 235, well below theoretical. Following purification by

column chromatography, the acid number rose to 305.6 (calculated 342). A byproduct isolated from this reaction tentatively was assigned a lactone structure from its IR spectrum (1780 cm^{-1}). Lactone formation was not unexpected in view of the fact that oleic acid readily underwent lactonization in the presence of strong acid catalysis (13).

Diacid mixture *8* (Table II) was esterified by diazomethane and analyzed by GLC and mass spectrometry. The observed molecular ion for the methyl esters of *8* was at m/e 356 indicating that acids *8* were isomeric with acids *4b* and *6b* (Table II). However, relative retention times of the methyl esters of *8* were shorter than those observed for the methyl esters of *4b* and *6b*. It has been demonstrated previously (2) that the Koch carboxylation of alkenes yields α,α -disubstituted carboxylic acids. In view of this and the GLC data obtained for acids *8*, we conclude that both carboxy functions of diacids *8* are of the trialkyl acetic acid type.

As anticipated, all of the C_{19} diacids prepared in the present study were obtained as clear mobile liquids. As shown in Table II, acid numbers of the crude mixtures were significantly lower than the theoretical values. After purification of the acids by either chromatography or distillation, acid numbers approached the theoretical, although yields decreased slightly.

ACKNOWLEDGMENTS

E.N. Frankel provided constructive comments in the preparation of this manuscript, and C.J. Dooley performed mass spectral analyses.

REFERENCES

- den Otter, M.J.A.M., *Fette Seifen Anstrichm.* 72:667 (1970).
- Foglia, T.A., I. Schmeltz, and P.A. Barr, *Tetrahedron* 30:11 (1974).
- Pryde, E.H., E.N. Frankel, and J.C. Cowan, *JAOCS* 49:451 (1972).
- Bosshard, H.H., R. Mory, M. Schmid, and H. Zollinger, *Helv. Chem. Acta* 42:1653 (1959).
- AOCS, "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third Edition, AOCS, Champaign, IL, 1964 (revised to 1972), Method Te-1a-64.
- Eisner, A., P.A. Barr, and T.A. Foglia, *JAOCS* 51:381 (1974).
- Frankel, E.N., *Ibid.* 48:248 (1971).
- Williams, D.H., and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill, London, England, 1966, p. 53.
- Roe, E.T., and D. Swern, *JAOCS* 37:661 (1960).
- Kell, D.R., and F.J. McQuillin, *J. Chem. Soc. Perkin Trans. I*:2096 (1972).
- Frankel, E.N., S. Metlin, W.R. Rohwedder, and I. Wender, *JAOCS* 46:133 (1969).
- Frankel, E.N., F.L. Thomas, and W.K. Rohwedder, *Ind. Eng. Chem. Prod. Res. Develop.* 12:47 (1973).
- Shepherd, I.S., and J.S. Showell, *JAOCS* 46:479 (1969).