

On the Mechanism of Ketonic Decarboxylation. Pyrolysis of Calcium Decanoate

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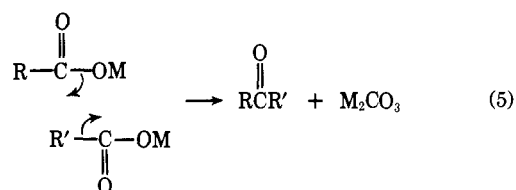
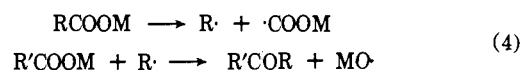
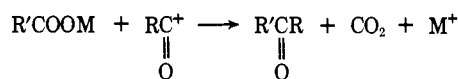
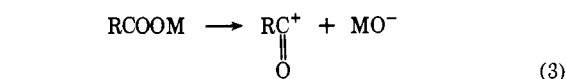
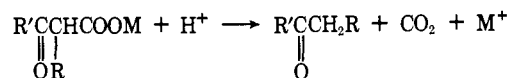
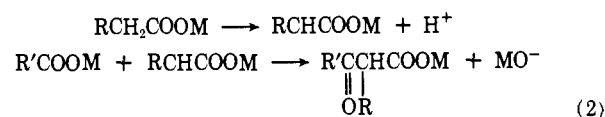
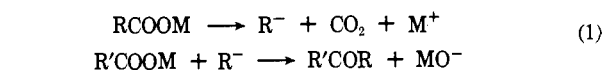
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Abstract: The complex mixtures resulting from pyrolysis of carboxylic acid salts have been analyzed by combined gas chromatography-mass spectrometry with the following results. Pyrolysis of calcium decanoate at 500° produces a homologous series of nonyl ketones, 2-undecanone through 10-nonadecanone; normal alkanes and monoalkenes of nine carbon atoms or less are also produced. Pyrolysis of calcium decanoate deuterated at C-8, C-9, and C-10 indicates that the smaller alkyl groups in the above ketones originate from the portion of the alkyl chain nearest the carbonyl group. When pyrolyzed in the presence of ferric chloride hexahydrate (a chlorine radical donor), calcium decanoate does not produce ketones but yields only normal alkanes and monoalkenes of nine carbon atoms or less. Calcium benzoate gives benzene and diphenyl ketone upon pyrolysis at 500°. The pyrolysis of calcium 2,2-dimethyloctanoate consists of about equal amounts of 2-methyl-1-octene, 2-methyl-2-octene, and 1-hexene. The above data have been interpreted in terms of a free-radical mechanism in which alkyl and acyl radicals act as initiators.

Thermal decomposition of salts of carboxylic acids yields symmetrical ketones.¹ For example, calcium acetate when heated to 350° produces acetone and calcium carbonate.^{1c} Mixtures of salts of two different acids pyrolyze to unsymmetrical ketones in varying yields. Thus, a mixture of benzoate and decanoate salts is converted upon pyrolysis to nonyl phenyl ketone in 50% yield.² In contrast to these straightforward transformations, there are also some anomalous cases which seem to involve a skeletal rearrangement: salts of trimethylacetic acid give a low yield of *tert*-butyl isobutyl ketone (rather than the expected di-*tert*-butyl ketone) under certain pyrolysis conditions.³

In an attempt to study the mechanism of this reaction (known as ketonic decarboxylation), pyrolyses of salt mixtures, one of which is labeled with ¹³C or ¹⁴C in the carbonyl group, were carried out by several authors.⁴ The extent of label retention in the resulting unsymmetrical ketone gave an indication of the source of the carbonyl group. Unfortunately, these data and others⁵⁻⁷ were not conclusive; nevertheless, they formed the basis for proposing various mechanisms involving carbanions^{3,4f,5} (see reactions 1 and 2), carbonium ions^{4b} (see reaction 3), free radicals^{4a,6} (see reaction 4), and a four-center intermediate⁷ (see reaction 5). From the variety of mechanisms reported in the literature, it is obvious that the details of this reaction, even after a century of sporadic work, are still not well understood.

In most of these investigations, the emphasis has been on the yield and nature of the major product as



indicators of the course of the reaction. It was felt that a detailed analysis of *all* the products formed during the pyrolysis of carboxylic acid salts would provide data which could, at least, permit one to rule out some of the previously proposed mechanisms and to support others.

Such a detailed investigation of the complex mixtures produced in these pyrolyses was not an easy task during the times the work discussed above was carried out. Recent advances in instrumental techniques, which now make it possible to identify the components of even quite complex mixtures, prompted a reinvestigation of this problem. In particular, the development of a combined gas chromatograph-mass spectrometer computer system⁸ and various computer-assisted

(1) (a) C. Friedel, *Justus Liebigs Ann. Chem.*, **108**, 122 (1858); (b) H. Limpriht, *ibid.*, **108**, 183 (1858); (c) R. Fittig, *ibid.*, **110**, 17 (1859).

(2) C. Granito and H. P. Schultz, *J. Org. Chem.*, **28**, 879 (1963).

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(4) (a) J. Bell and R. I. Reed, *J. Chem. Soc.*, 1383 (1952); (b) C. C. Lee and J. W. T. Spinks, *J. Org. Chem.*, **18**, 1079 (1953); (c) R. I. Reed, *J. Chem. Soc.*, 4423 (1955); (d) V. D. Nefedov, M. A. Toropova, and I. A. Skulskii, *Zh. Fiz. Khim.*, **29**, 2236 (1955); (e) M. Okubo and R. Goto, *Nippon Kagaku Zasshi*, **81**, 1132 (1960); (f) L. Otvos and L. Noszko, *Tetrahedron Lett.*, 19 (1960).

(5) O. Neunhoeffer and P. Paschke, *Ber. Deut. Chem. Ges. B*, **72**, 919 (1939).

(6) W. A. O'Neill and R. I. Reed, *J. Chem. Soc.*, 3911 (1953).

(7) (a) R. I. Reed and M. B. Thomley, *ibid.*, 3714 (1957); (b) A. M. Rubinshtein and V. I. Yakerson, *Kinet. Katal.*, **2**, 118 (1961).

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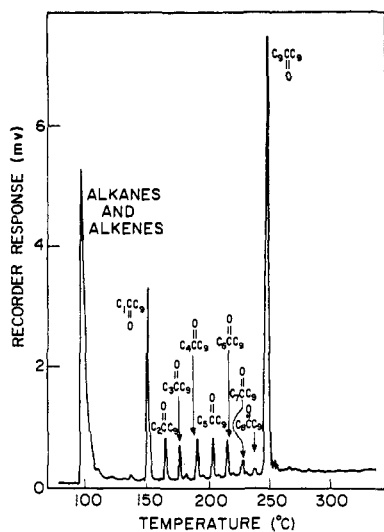


Figure 1. Gas chromatogram resulting from the on-column pyrolysis of 600 μg of calcium decanoate at 500°. The peaks labeled $\text{C}_n\text{C}(=\text{O})\text{C}_9$, $n = 1, 2, \dots, 9$, represent a homologous series of nonyl ketones, 2-undecanone through 10-nonadecanone.

data evaluation techniques⁹ have provided a basis for further work. Most promising for this particular problem was the compatibility of the experiment (the rapid production of volatile products in an inert gas stream) with gas chromatography as a separation technique. In addition, the continuously scanning mass spectrometer, coupled to the computer, is capable of detecting certain characteristics of the product mixture, such as homologous series of compounds and minor components, even if incompletely resolved gas chromatographically.

In an effort to study the products of carboxylate pyrolysis, calcium decanoate, partially deuterated calcium decanoate, calcium pentadecanoate, calcium benzoate, and calcium 2,2-dimethyloctanoate were pyrolyzed under various conditions. The detailed product analyses have led to a working hypothesis which allows one to predict the pyrolytic products of a carboxylate salt. While not definitely establishing the mechanism of ketonic decarboxylation, the results confine it to a much narrower range of possibilities.

Results and Discussion

All pyrolyses were carried out on very small amounts of material (0.1–1.0 mg) and were performed in-line with the gas chromatographic column by techniques described in detail in the Experimental Section.

The gas chromatogram of the 500° pyrolysis products of calcium decanoate (Figure 1) reveals a homologous series of peaks labeled $\text{C}_n\text{C}(=\text{O})\text{C}_9$ where $n = 1, 2, \dots, 9$. The mass spectra of all these peaks show ions at m/e 58, 155, and 170. There is a series of molecular ions observed at m/e 170, 184, 198, . . . 282. The mass spectra corresponding to peaks labeled $\text{C}_1\text{C}(=\text{O})\text{C}_9$ and $\text{C}_9\text{C}(=\text{O})\text{C}_9$ (Figure 1) are identical with those of authentic 2-undecanone and 10-nonadecanone, respectively.^{9b}

The presence of ions at m/e 155, $[\text{CH}_3(\text{CH}_2)_8\text{CO}]^+$, in the spectra of the other members of this series sug-

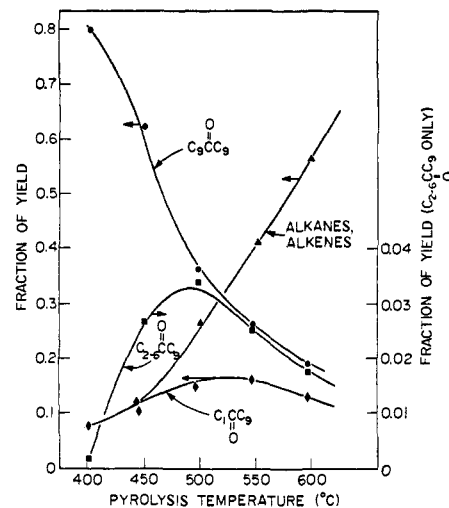


Figure 2. Fraction of total pyrolytic yield of various products vs. pyrolysis temperature. The curve labeled $\text{C}_{2-6}\text{C}(=\text{O})\text{C}_9$ represents the average fractional yield for 3-dodecanone through 7-hexadecanone; it should be read from the right-hand ordinate.

gests that they too are nonyl ketones. The ion at m/e 170 in these spectra results from the McLafferty rearrangement involving the shorter alkyl side chain, leading to $[\text{CH}_3(\text{CH}_2)_8\text{C}(\text{OH})=\text{CH}_2]^+$. The molecular ions, as well as the ions produced by the same rearrangement involving the elimination of the nonyl chain, confirm that the members of this series are ketones of the type C_nCOC_9 where $n = 1, 2, \dots, 9$. The most abundant member, 10-nonadecanone, has an absolute molar yield, relative to calcium decanoate, of 28%.

The peak labeled "alkanes and alkenes" represents a mixture of normal alkanes and monoalkenes of nine carbon atoms or less. This identification is based on characteristic ions (such as m/e 41, 43, 55, 57, . . .) and molecular ions. The compounds shown in Figure 1 are also observed in the pyrolysis of sodium decanoate.

In order to eliminate the possibility that all of the smaller ketones and the hydrocarbons are produced by pyrolysis of the primary product, namely the symmetrical ketone, 10-nonadecanone was pyrolyzed at 500°. To ensure that the ketone actually reached 500° before being swept from the pyrolysis area, it was sealed into a 3-cm length of capillary tubing which was then heated to 500° for 2 min. After cooling, the tube was opened and its contents were analyzed by gas chromatography-mass spectrometry. Approximately half of the ketone was decomposed. The most abundant pyrolysis products were nonane, nonene, and 8-heptadecanone; minor products were 9-octadecanone and 7-hexadecanone. Less than 0.1% of the pyrolytic yield was 2-undecanone, 3-dodecanone, and 4-tridecanone in contrast to the relatively high yield (23%) of these three ketones obtained in the pyrolysis of calcium decanoate. Thus, most of the nonyl ketones must have been produced during the primary pyrolytic reaction rather than by further degradation of 10-nonadecanone.

To allow correlation of this work with other experiments carried out at different pyrolysis temperatures, the relative amounts of the various products as a function of pyrolysis temperature are shown in Figure 2. Eighty per cent of the yield at lower pyrolysis tempera-

(9) (a) R. A. Hites and K. Biemann, *Anal. Chem.*, **42**, 855 (1970); (b) H. S. Hertz, R. A. Hites, and K. Biemann, *ibid.*, **43**, 681 (1971).

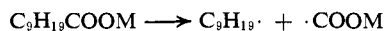
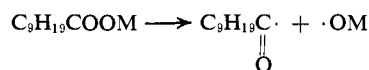
Table I. Deuterium Distribution (in Per Cent of Total) for Calcium Decanoate Deuterated at C-8, C-9, and C-10 and for Several of Its Pyrolysis Products

No. of D atoms	Calcium decanoate ^a	C ₁ CC ₉ O	C ₂ CC ₈ O	C ₃ CC ₇ O	C ₄ CC ₆ O	Calcd ^b	C ₉ CC ₁ O
0	9.9	9.5	11.9	13.0	13.8	1.0	4.1
1	20.2	21.8	23.8	25.0	23.4	4.0	8.1
2	29.8	28.2	28.0	28.0	25.6	10.0	12.7
3	22.2	20.3	19.6	19.0	19.2	16.4	17.2
4	10.9	11.6	9.1	8.0	10.6	20.0	18.3
5	5.4	6.0	4.2	5.0	5.3	18.7	17.5
6	1.9	2.6	3.5	2.0	2.1	14.0	11.6
7						8.8	5.7
8						4.7	2.8
9						2.0	1.3
10						0.7	0.7
Corr coeff		0.99	0.97	0.93	0.96		0.94
Av no. of D atoms	2.3	2.3	2.2	2.1	2.1	4.5	4.0

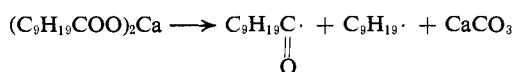
^a Measured as the methyl ester. ^b Calcium decanoate distribution permuted twice to simulate the expected distribution for 10-nonadecanone.

tures (400°) is accounted for by 10-nonadecanone, but as the pyrolysis temperature increases the fraction of alkanes and alkenes approaches 60%.

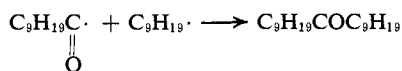
Taking the complete product analysis (Figure 1) and the pyrolysis temperature data (Figure 2) into account, the following working hypothesis is postulated. The first step involves the formation of both alkyl and acyl radicals from the salt



where M is any metal. If M were calcium, for example, these reactions could be combined



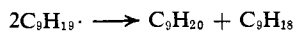
Combination of these two radicals results in the formation of the symmetrical ketone¹⁰



Combination of the inorganic radicals produces the metal carbonate which, depending on the temperature and nature of the metal, may decompose further to the metal oxide and carbon dioxide



Furthermore, the nonyl radicals can also disproportionate¹¹ to nonane and nonene instead of reacting with an acyl radical

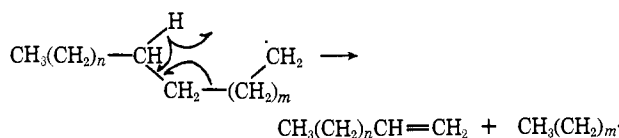


Reactions of this type account for the observed high abundance of alkanes and alkenes (see Figure 1). It is interesting to note that neither octadecane (C₁₈-C₁₈) nor 10,11-eicosanedione (C₉CO-COC₉) is found in the pyrolysis mixture. This indicates that combination of identical radicals is minimal.

(10) Because of the heterogeneous nature of this pyrolysis, these radicals may not be truly free in the gas phase but, rather, they may be trapped in the solid or liquid phase resulting in a "cage" effect.

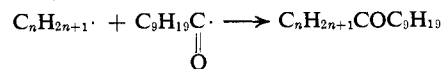
(11) The term disproportionation is not used in the most strict sense of the term.

To investigate the genesis of the series 2-undecanone through 6-pentadecanone (7-hexadecanone, 8-pentadecanone, and 9-octadecanone are also observed in the pyrolytic decomposition of 10-nonadecanone and thus may originate from this primary product), calcium decanoate partially deuterated at C-8, C-9, and C-10 was pyrolyzed. The deuterium distribution of the calcium salt (measured as the methyl ester) and of various products is shown in Table I.¹² The correlations between the distribution for the salt and for 2-undecanone through 5-tetradecanone are high, indicating that the methyl through butyl groups originated from the unlabeled portion of the alkyl chain, namely the section nearest the carbonyl group. Therefore, the smaller alkyl radicals could result from the nonyl radicals by a concerted process of hydrogen rearrangement and β scission which is analogous to a previously suggested process¹³



where $n + m = 5$; n or $m = 0, 1, \dots$. This process must be concerted rather than stepwise because the C₁-C₄ alkyl groups of the lower nonyl ketones contain no deuterium at all (see Table I). If a secondary radical were a long-lived intermediate, β scission on either side of the new radical site would produce both deuterated and undeuterated alkyl radicals.

The smaller alkyl radicals may then either react with nonyl radicals to form the corresponding ketone



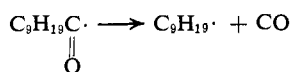
($n = 1, 2, \dots, 6$) or they may disproportionate to give alkanes and alkenes. The smaller radicals (C₁-C₄) could also combine to produce alkanes. The absence of significant amounts of alkanes or alkenes with ten

(12) 6-Pentadecanone is not included in Table I or this discussion because the molecular ions were too weak to allow an accurate determination of the deuterium distribution.

(13) See W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 280-284, and references cited therein.

carbon atoms or more indicates that the large radicals (C_5-C_9) do not combine with each other; however, they may undergo a continued stepwise decomposition to methyl radicals, thus accounting for the relatively high abundance of 2-undecanone and the almost constant abundance of 3-dodecanone through 7-hexadecanone.

The absence of ketones in which both alkyl chains are less than nine carbon atoms long confirms that the nonoyl radical does not decompose to smaller acyl radicals. However, since the increased production of hydrocarbons at higher pyrolysis temperatures is not accompanied by a corresponding increase in smaller ketones, it is probable that the nonoyl radical tends to decompose more readily to the nonyl radical and carbon monoxide as the pyrolysis temperature increases. In



fact, carbon monoxide has been observed as a product of ketonic decarboxylation.³

In order to obtain further support for the hypothesis outlined above, an agent that would react with free radicals at 500° was sought. Ferric chloride was finally selected because of its tendency to act as a source of chlorine radicals¹⁴ and its stability at 500°. Other high-temperature radical traps such as ethyl nitrite,¹⁵ normally used at very low pressures, were rejected for use at atmospheric pressures because of the possibility of induced reactions as well as safety considerations.

Alkyl radicals react in solution with ferric chloride to give alkyl chlorides and ferrous chloride.¹⁴ Since ferric chloride boils well below 400°, it was expected that its copyrolysis with calcium decanoate would result in a gas-phase reaction producing alkyl chlorides rather than ketones. In agreement with earlier reports,¹⁶ pyrolysis of nonyl chloride at 500° showed that alkyl chlorides completely decompose to alkanes, alkenes, and HCl. Thus, while no alkyl chlorides would be detectable, one would observe an increase in the amount of hydrocarbons formed during the copyrolysis if alkyl radicals were indeed present.

It was necessary, of course, to verify that ferric chloride and the nonyl ketones do not react upon copyrolysis. This is indeed the case since copyrolysis of ferric chloride and 10-nonadecanone showed the same gas chromatographic pattern as the pyrolysis of 10-nonadecanone alone. Thus, if a lower yield of ketones were observed, it could not be the result of a reaction of ferric chloride with the pyrolytically formed ketones.

To avoid interactions in the solid or liquid phase, calcium decanoate and ferric chloride were copyrolyzed in separate capillary tubes dropped into the pyrolysis oven at the same time. Several such experiments were performed and in all cases the abundance of ketones was drastically suppressed in comparison to pyrolysis in the absence of ferric chloride. A gas chromatogram resulting from the pyrolysis of 600 μg of calcium decanoate (the same as used for Figure 1) and 3 mg of ferric chloride hexahydrate is shown in Figure 3. The sup-

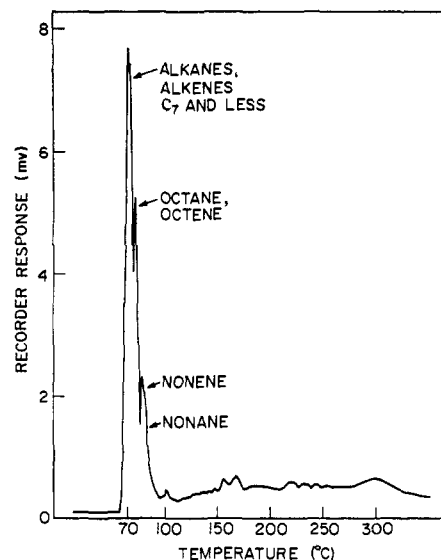


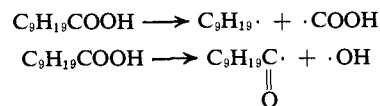
Figure 3. Gas chromatogram resulting from the on-column copyrolysis of 600 μg of calcium decanoate and 3 mg of ferric chloride hexahydrate at 500°. Note the absence of ketones.

pression of the ketones and the increased abundance of alkanes and alkenes are quite apparent from a comparison of Figures 1 and 3.

Although the possibility of induced reactions cannot be completely ruled out, these results imply that the pyrolysis of carboxylic acid salts involves free radicals. Furthermore, the increased abundance of alkanes and alkenes is suggestive of the formation of alkyl radicals during the course of this pyrolysis. Even though these data are not proof of the above hypothesis, they allow one to accept it, at least, for the purpose of predicting the products of similar reactions. Thus, the pyrolytic products of related compounds were examined.

As an example, calcium pentadecanoate was pyrolyzed at 450, 500, and 600°. At all of these temperatures, the homologous series of tetradecyl ketones, $C_nH_{2n+1}COC_{14}H_{29}$, $n = 1, 2, \dots, 14$, is present. Normal alkanes and monoalkenes of 14 carbons or less were also formed. The relative proportions of these compounds approximate those for the pyrolysis of calcium decanoate (Figure 1) and the yield vs. temperature characteristics are similar to those shown in Figure 2.

Next free decanoic acid was pyrolyzed at 500°. The homologous series of nonyl ketones was formed in about the same relative proportions as shown in Figure 1 for the calcium salt. This is in accordance with the above hypothesis if one assumes that the acid also decomposes to alkyl and acyl radicals. The $\cdot COOH$ and $\cdot OH$



radicals would combine to carbonic acid which then decomposes to carbon dioxide and water. This observation is at variance with classical work¹⁷ which states that, except in the presence of catalysts (such as metals or metal oxides), acids do not eliminate carbonic acid to produce ketones; instead they decar-

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(15) E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969).

(16) C. D. Hurd, "Pyrolysis of Organic Compounds," Chemical Catalog Co., New York, N. Y., 1929, pp 125-131.

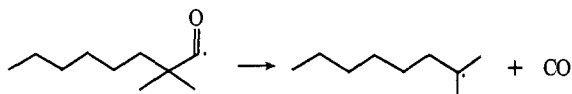
(17) Reference 16, p 330.

boxylate to produce alkanes. It may be that the Vycor tube of the pyrolysis apparatus (see Experimental Section) offers sufficient catalysis to allow the production of ketones.

The pyrolyses of salts of acids lacking hydrogens next to the carboxyl group are reported to produce unsymmetrical ketones or no ketones at all.^{3,5,18} This observation has led some authors^{3,4f,5} to suggest mechanisms involving keto acids as intermediates (see reaction 2). To reinvestigate this question, the salts of two acids lacking α hydrogens, namely calcium benzoate and calcium 2,2-dimethyloctanoate, were pyrolyzed and the products analyzed by gas chromatography and mass spectrometry.

Calcium benzoate when pyrolyzed at 500° produced about equal amounts of benzene and diphenyl ketone in agreement with previous studies.¹⁹ Traces of biphenyl and 9-fluorenone were also observed. All of these products could well result from combinations of phenyl and benzoyl radicals. Obviously, calcium benzoate has no α hydrogens, yet it gives the symmetrical ketone. On the other hand, pyrolysis (at 500°) of calcium 2,2-dimethyloctanoate produces about equal amounts of 1-hexene, 2-methyl-1-octene, and 2-methyl-2-octene.

The fact that calcium benzoate produces the expected ketone but calcium 2,2-dimethyloctanoate yields only alkenes can be attributed to differences in the stability of the proposed free-radical intermediates rather than to differences in α hydrogen composition (neither salt has any). In the case of calcium benzoate, the benzoyl radical would not tend to lose carbon monoxide since the resultant phenyl radical would be energetically unfavorable. The 2,2-dimethyloctanoyl radical has no such stabilizing characteristic. On the contrary, the expulsion of carbon monoxide as a neutral molecule generates a tertiary alkyl radical



This decarbonylation provides the driving force leading to complete decomposition of the acyl radical and thus completely suppresses the formation of ketones. The tertiary radical then stabilizes itself by eliminating a hydrogen radical and forming alkenes, in this case 2-methyl-1-octene and 2-methyl-2-octene. 1-Hexene is formed by elimination of the terminal 3-carbon moiety. There is apparently little disproportionation of these tertiary alkyl radicals since no saturated products are observed.

In summary, the thermal decarboxylation of carboxylic acid salts produces a series of ketones and hydrocarbons. On the basis of the data presented above, the complete set of pyrolytic products for a given saturated monocarboxylic acid salt can now be predicted. One should be careful, however, not to extrapolate these results to the pyrolysates of unsaturated or dicarboxylic acid salts because preliminary examination of calcium 3-decanoate and calcium 1,10-decanedioate indicates that these pyrolytic products are much more diverse and numerous than those resulting from saturated monocarboxylic acid salts.

(18) R. Davis and H. P. Schultz, *J. Org. Chem.*, **27**, 854 (1962).
 (19) E. Peligot, *Justus Liebigs Ann. Chem.*, **12**, 39 (1834).

Experimental Section

The samples were pyrolyzed directly onto the gas chromatographic column using a Hamilton multi-purpose sampling system. This device consists of a 430 mm \times 4 mm i.d. Vycor tube which is divided into three temperature regions. The first section (130 mm), the sample holding area, remains at room temperature; the second section (200 mm), the pyrolysis area, is held at the desired pyrolysis temperature (usually 500°); and the third section, the transition area, is kept at 300°. The end of the Vycor tube is connected to a heated (300°) stainless steel tube (550 mm \times 0.5 mm i.d.) which terminates in a hypodermic needle which can be inserted into the injection port of a gas chromatograph.

In operation, 0.1–1 mg of the sample (in a 5-mm length of capillary tubing, sealed at one end) is placed in the holding area. The needle is inserted through the septum and 30 sec later the carrier gas (helium) is diverted through the tube by switching a three-way valve. After flow equilibrium is established (2 min is allowed) the entire furnace and tube assembly is rotated from the horizontal to the vertical position, dropping the sample into the pyrolysis zone. The salts then melt and decompose. The pyrolytic products are swept immediately onto the gc column which at this stage is at 70 or 100°. This product purge is continued for 90 sec, and the carrier gas is then switched back so that it bypasses the pyrolysis unit. After an additional 30 sec the needle is removed from the septum.

The gas chromatographic column was a 10 ft \times 0.125 in. o.d. stainless steel tube packed with Gas Chrom Q coated with 3% OV-17. The column temperature was programmed from 70 or 100° to 300° at 10°/min. Injector and detector temperatures were 285°. The flow rate of carrier gas through the column and through the pyrolysis tube was 35 ml/min. Thus, residence times in the pyrolysis area were from 2 to 4 sec.

Some comments on the reproducibility of the pyrolysis gas chromatograms are in order. Good reproducibility has been obtained by controlling the carrier gas flow rate, the sample size, and the pyrolysis time. Holding these parameters constant permitted one to obtain good quantitative data such as that shown in Figure 2. However, even large variations in these parameters did not affect the qualitative nature of the chromatograms. For example, the nonyl ketones were always observed in about the same relative amounts as shown in Figure 1. In general, those components which showed the least reproducibility seemed to result from secondary reactions. The small peak at 265° in Figure 1, identified as 10-heneicosanone, was completely absent in many gas chromatograms of this pyrolysate, for example.

The gas chromatograph-mass spectrometer-computer system has been described previously.⁸ The gas chromatograph (Perkin-Elmer Model 990) is interfaced to the mass spectrometer (Hitachi Model RMU-6L) by a 3-cm length of fritted glass tube.²⁰ The mass spectrometer is scanned continuously from m/e 20 to 550 in 4-sec cycles; the data are acquired and partially processed in real time by an IBM 1800 computer.⁸ After final processing the data are output on a computer-controlled microfilming system.²¹ The final microfilm consists of histograms of up to 400 mass spectra and all mass chromatograms.^{9a} Mass spectral data presented below are abbreviated, listing the two most abundant ions in each 14-amu interval.^{9b}

The calcium salts were prepared from calcium hydroxide and the corresponding acid by precipitation and were recrystallized from ethanol.²² The purity of calcium decanoate with respect to other acids was better than 99.8% as determined by gas chromatography (same conditions as above) of the methyl ester prepared from the salt by acidification followed by esterification with diazomethane. The various acids, sodium decanoate, nonyl chloride, and ferric chloride hexahydrate were used as received. 10-Nonadecanone (K & K Laboratories) was recrystallized from ethanol; mp 57–59° (lit.²³ mp 58–59°).

Deuterated Decanoic Acid. 9-Decen-1-ol (2 g) (from K & K Laboratories) in 35 ml of acetone was treated with a mixture of 2.2 g of chromium trioxide, 2 ml of sulfuric acid, and 10 ml of water. After stirring for 1 hr, the mixture was decanted into 10 ml of water

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and extracted with methylene chloride (two 25-ml portions). This extract was washed with water (two 50-ml portions), dried, and concentrated under vacuum. Since gas chromatography of this crude product showed *ca.* 20% 9-decyl 9-decenoate, it was refluxed with 40 ml of 1 *N* sodium hydroxide for 1 hr. The reaction mixture was washed with methylene chloride (two 25-ml portions), adjusted to pH 1–2 by 1 *N* hydrochloric acid, and extracted with methylene chloride (two 25-ml portions). This extract was dried, and the solvent was removed under vacuum giving 1.58 g (72%) of the crude acid.

The acid (0.618 g) in 25 ml of benzene containing 0.2 g of catalyst, tris(triphenylphosphine)rhodium(I) chloride,²⁴ was shaken under deuterium gas for 5 days at atmospheric pressure. The reaction mixture was extracted with 1 *N* sodium hydroxide (two 25-ml portions); the aqueous phase was adjusted to pH 1–2 with 1 *N* hydrochloric acid and extracted with methylene chloride (two 25-ml portions). This extract was dried and the solvent removed under vacuum, giving 0.55 g (89%) of the deuterated acid.

A small portion of the acid was methylated (diazomethane) and the deuterium distribution (shown in Table I) was determined from the mass spectrum of the ester, which showed that the fragments up to and including [(CH₂)₆COOCH₃]⁺ did not contain deuterium. Thus, the deuterium present in the molecule (as deduced from the mass shift of the molecular ion) must have been incorporated on the last three carbon atoms of the aliphatic chain. The abbreviated mass spectrum^{2b} of the methyl ester is: *m/e* 41 (17% relative intensity), 43 (22), 55 (21), 59 (10), 74 (100), 75 (15), 87 (52), 88 (9), 97 (4), 101 (7), 115 (2), 116 (1), 129 (4), 130 (1), 143 (9), 144 (1), 157 (4), 158 (3), 160 (3), 161 (1), 188 (1), 189 (1). (The complete intensity data for the molecular ion region are given in column 2 of Table I.) The purity of the deuterated acid was better than 99% as verified by gas chromatography (same conditions as above) of the methyl ester.

2,2-Dimethyloctanoic Acid. 2,2-Dimethyloctan-1-ol (45.8 g, from K & K Laboratories) in 150 ml of acetone was stirred with 31.9 g of chromium trioxide, 30 ml of sulfuric acid, and 120 ml of water for 2 hr. The reaction mixture was diluted with 700 ml of water and extracted with methylene chloride (two 250-ml portions). The extract was washed with water (two 250-ml portions), dried, and concentrated under vacuum. Gas chromatography showed only traces of ester; therefore, the methylene chloride solution was merely extracted with 1 *N* sodium hydroxide (two 250-ml portions). The aqueous phase was adjusted to pH 1–2 with 1 *N* hydrochloric acid, and extracted with methylene chloride (two 250-ml portions). This extract was dried, and the solvent was removed under vacuum giving 31.8 g (64%) of the acid: exact molecular weight by high-resolution mass spectrometry, 172.1444; calcd for C₁₀H₂₀O₂,

172.1463; nmr (CDCl₃) δ 11.2 (s, 1, COOH), 1.25 (m, 10), 1.20 (s, 6), 0.87 (t, 3, *J* = 5 Hz); abbreviated mass spectrum of the methyl ester (prepared with diazomethane) 41 (38), 43 (55), 55 (21), 57 (58), 69 (12), 71 (51), 85 (38), 87 (23), 102 (100), 103 (6), 111 (4), 115 (9), 127 (21), 129 (8), 157 (3), 186 (1). The base peak at *m/e* 102 (due to the McLafferty rearrangement ion) demonstrates the 2,2-dimethyl substitution. The purity of the acid (by gas chromatography, same conditions as above) was better than 99%.

Calcium 2,2-Dimethyloctanoate. 2,2-Dimethyloctanoic acid (0.5 g) was used to prepare the calcium salt by precipitation with calcium hydroxide.²² A preliminary gas chromatographic–mass spectral experiment showed that the pyrolysate of this salt gave only one poorly shaped gas chromatographic peak. It consisted of at least three compounds, two of which were identified as 2-methyl-1-octene and 2-methyl-2-octene by a comparison of their mass spectra with those of the authentic materials. Since it was difficult to obtain adequate gc resolution for hydrocarbons of nine carbons or less using on-column pyrolysis, a large scale pyrolysis was carried out according to a published procedure.¹⁸ Although the conditions of the large and small scale pyrolyses were quite different, it appears as though the products are the same.

2,2-Dimethyloctanoic acid (10.6 g) was refluxed with 3.24 g of calcium metal (turnings) and 1 ml of ethanolic HCl for 2.5 hr. Upon cooling, the material solidified into a yellow waxy mass. The condenser was set for distillation and the temperature was held at 500° (±50°) for 45 min. The distillate (1.12 g), analyzed by gas chromatography–mass spectrometry, consisted of 39% ethanol, 24% 1-hexene, 14% 2-methyl-1-octene, 21% 2-methyl-2-octene, and 2% ethyl 2,2-dimethyloctanoate. The mass spectra and gas chromatographic retention times (as determined by coinjection) of these compounds were identical with those of authentic material. The observed mass spectra for these five compounds are: ethanol 30 (17), 31 (100), 45 (52), 46 (15); 1-hexene 30 (4), 31 (44), 41 (100), 42 (75), 55 (81), 56 (78), 67 (8), 69 (31), 84 (30); 2-methyl-1-octene 41 (80), 43 (73), 55 (78), 56 (100), 69 (77), 70 (30), 83 (11), 84 (9), 97 (2), 98 (7), 111 (10), 126 (31); 2-methyl-2-octene 39 (28), 41 (90), 55 (65), 56 (92), 69 (100), 70 (42), 83 (13), 84 (18), 97 (2), 98 (3), 111 (5), 126 (61); ethyl 2,2-dimethyloctanoate 41 (51), 43 (88), 56 (28), 57 (82), 69 (25), 71 (78), 85 (59), 88 (43), 98 (3), 101 (5), 116 (100), 117 (12), 127 (35), 129 (10), 143 (4), 155 (3), 171 (2). The ethanol and ethyl ester are artifacts resulting from the ethanolic HCl used as a catalyst.

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Pyrolysis of Lactone Tosylhydrazone Sodium Salts

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Abstract: Preparation and thermal decomposition of five lactone tosylhydrazone salts **1d–5d** are described. The products observed in each case can be accounted for by an intermediate oxycarbene (**1a–5a**) which decomposes according to Scheme I. Apart from electronic state, the intermediates involved appear to be quite similar to those generated in type I photochemical reactions of cyclic ketones.

Several investigations in the past 6 years have focused attention on photochemical transformation of ketones into products which appear to arise through intermediate oxycarbenes.^{1–3} Included among these

transformations have been insertion into the oxygen–hydrogen bond of solvent alcohol to form acetals,¹ addition to double bonds to give cyclopropanes,¹ dimerization,¹ reaction with oxygen to yield an ester

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