

extracted three times with ether. The combined ethereal extracts were washed twice with 100 ml. of 10% sodium hydroxide solution, and then the organic layer was dried and the ether was distilled using an efficient column leaving crude isobornyl chloride which was reconverted to camphene by refluxing for 2 hr. with excess alcoholic sodium ethoxide. Distillation of the alcoholic solution carried over most of the camphene. To the residue was added 20 ml. of water and the distillation was continued until an oil began to steam distil at about 83°. The alcoholic distillate was drowned with a large quantity of water and then extracted thrice with ether. After drying over magnesium sulfate the ethereal solution was distilled yielding 2.08 g. (0.0153 mole, 48%) of fully racemic camphene, b.p. 146–156° (atm.), m.p. 40–51°. The product was carefully sublimed to give pure camphene, m.p. 49–51°, $[\alpha]^{25}_D$ 0.00° (benzene).

Ozonolysis of Racemized Camphene.—The procedure of Harries and Palmén¹¹ was followed exactly with similar results. The dimethylnorcampholide was recrystallized thrice from ether, five times from 1:1 ether-petroleum ether (90–100°) and then was sublimed without change in the

melting point, 94.0–96.5°, previously 96.0–96.5°¹¹ and 95–96°²²; specific activity 21.5 ct./min./mg. BaCO₃; sp. molar activity 1.55×10^7 ct./min./mole dimethylnorcampholide, corrected for "dilution" of camphene.

Analytical Procedure.—Peroxide fusion in a Parr bomb was used. In each case the conversion to barium carbonate and preparation of plates were carried out as described by Calvin, *et al.*²³ The plates were counted using an N-Wood Model K flow counter and a Nuclear Instrument Chemical Co. model 161 scaler with attached Veeder Root register and Precision Scientific Co. timer. The counter was operated at 1400 v., 125 v. above the threshold, under a constant stream of 3–5 bubbles of "Q" gas per sec. The over-all calculated error for molar specific activity is $\pm 4.5\%$.²³

(22) F. W. Semmler, *Ber.*, **42**, 246 (1909).

(23) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 90–92, 118, 283–291.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Decomposition of Organic Acids in the Presence of Lead Tetraacetate*

BY WILLIAM A. MOSHER AND CLIFTON L. KEHR

RECEIVED DECEMBER 8, 1952

Previous workers have shown that lead tetraacetate decomposes in acetic acid to give carbon dioxide, methane, acetoxyacetic acid and methylene diacetate. We have extended this reaction to include a variety of organic acids (formic acid, triphenylacetic acid, trimethylacetic acid, isobutyric acid and isovaleric acid) in a study of the mechanism involved. The products obtained may be readily explained by the following ionic scheme: interchange first occurs between lead tetraacetate and the organic acid present; decomposition of the Pb⁺⁺⁺⁺ salt yields the corresponding Pb⁺⁺ compound, the negative ion of the acid and positive ion such as R-CO-O⁺. This electronically deficient oxygen-containing ion may then decompose to carbon dioxide and a carbonium ion which may stabilize itself by losing a proton to form an olefin, by reacting with solvent anion to form esters, or by abstracting a hydride ion from a molecule of solvent to give rise to a more stable carbonium ion and hydrocarbon gas. No evidence of free radical decomposition was observed.

The decomposition of lead tetraacetate in acetic acid has been reported by Kharasch¹ and co-workers, and a mechanism involving trivalent lead radicals proposed. Previous work² in this Laboratory, however, has suggested that benzpinacolyl alcohol was oxidized by lead tetraacetate in good yield to benzaldehyde and triphenylcarbinol *via* an ionic cleavage reaction involving an electronically deficient oxygen intermediate. In an attempt to determine the generality of ionic reactions of lead tetraacetate, a systematic study has been made of the decomposition of tetravalent lead salts of organic acids of varying structure. Table I presents a concise summary of the conditions and products of the reactions investigated.

A careful study of the products obtained in the above reactions indicated a pronounced mechanistic trend which led us to interpret the reaction from the ionic viewpoint rather than the free radical concept advanced by Kharasch.¹

The oxidation of formic acid³ appeared to be a convenient starting point in the present mechanistic study because this molecule offers to the oxidizing agent only two possible points of attack—the aldehyde function and the hydroxylic function.

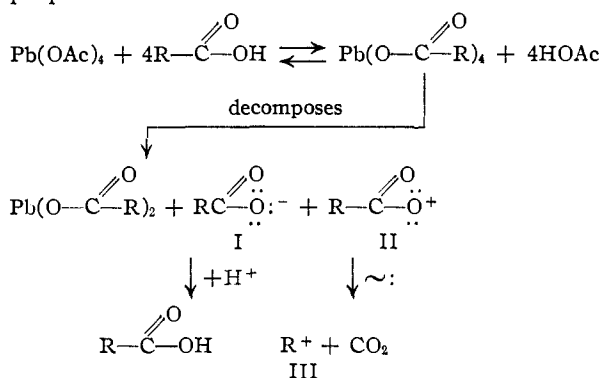
* Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, September, 1952.

(1) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

(2) W. A. Mosher and H. A. Neidig, *THIS JOURNAL*, **72**, 4452 (1950).

(3) J. M. Grosheintz, *ibid.*, **61**, 3379 (1939).

Because it is a well established fact that aldehydes under the conditions employed are stable to lead tetraacetate, it was suspected that the hydroxyl group must be the center of attack by the oxidizing agent. The following generalized mechanism is proposed



There is other evidence⁴ for the rejection of the classical aldehyde theory of oxidation of formic acid.

In support of this mechanism, the tetravalent lead salt of trimethylacetic acid has been prepared and decomposed in trimethylacetic acid solvent. The products obtained from this reaction were nearly identical to those found when lead tetraacetate itself was decomposed under similar con-

(4) Cf. Paul Haas, *Nature*, **167**, 325 (1951).

TABLE I

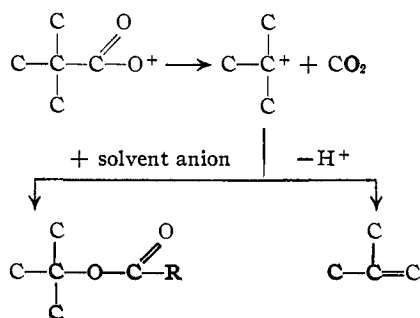
Acid	Conditions and solvent	Carbon dioxide, %	Hydrocarbon, %	Ester, %	Acetic acid, ^a %
Formic	Room temp., 3 hr., acetic acid	96.6
Triphenylacetic	100°, 1 hr., acetic acid	94.1	Triphenylmethyl acetate—95.0 (isolated as carbinol)	...
Trimethylacetic	135–140°, 2 hr., trimethylacetic acid	78.9	1-Butene—4.1 Isobutene—37.8	<i>t</i> -Butyl acetate—2.8 <i>t</i> -Butyl pivalate—3.2	83.0
Isobutyric	135–140°, 1.5 hr., isobutyric acid	66.7	Propane—23.6 Propene—9.1	α -Isobutyroxyisobutyric acid—10.0 Isopropyl acetate—trace Isopropyl isobutyrate—2.7	141.0
Isovaleric	155–160°, 2 hr., isovaleric acid	72.4	<i>n</i> -Butane—8.3 Methane—trace Isobutane—10.7 1-Butene—3.2 2-Butene—5.8 Isobutene—0.2	<i>s</i> -Butyl isovalerate—8.9	126.0
Acetic ^b	120°, ca. 14 hr., acetic acid	42	Methane—30	Methylene diacetate—6 Acetoxyacetic acid—40	...

^a This yield calculated with assumption that the salt precipitate is composed entirely of lead acetate; this is not strictly true as the solvent acid salt precipitates also in small amount, as well as the salt of acyloxy acids. ^b The data included from acetic acid are taken from ref. 1.

ditions in trimethylacetic acid solvent. A similar comparison was made with lead tetraisobutyrate in isobutyric acid and lead tetraacetate in isobutyric acid; again an unmistakable similarity in product distribution was noted. This series of experiments confirms the existence of the reversible equilibrium shown above and indicates that the intermediate compound which gives rise to the isolated products is actually the tetraivalent lead salt of the organic acid solvent employed.

The ease with which the decomposition of the Pb^{++++} salt to give the electronically deficient oxygen intermediate ion II occurs depends on the relative stability of the ion III. In formic acid, the reaction proceeds rapidly at low temperatures because the hydrogen ion liberated is extremely stable. When the group attached to the carboxylic carbon atom was changed from hydrogen to the triphenylmethyl group (triphenylacetic acid), the reaction conditions were more strenuous, but still relatively mild. Triphenylacetic acid oxidations at 100° in glacial acetic acid with lead tetraacetate gave a quantitative yield of carbon dioxide and presumably triphenylmethylcarbonium ion, which stabilizes itself by reaction with the solvent to form the acetate ester of triphenylcarbinol.

By the proposed mechanism trimethylacetic acid yields on oxidation the *t*-butyl carbonium ion and carbon dioxide. The conditions required are



quite drastic in this case and the yields are lower. At the high temperature (135°) employed, the carbonium ion stabilizes itself for the greater part by yielding a hydrogen ion to the solvent to form isobutene, while the reaction to form esters occurs to the extent of only about 6%.

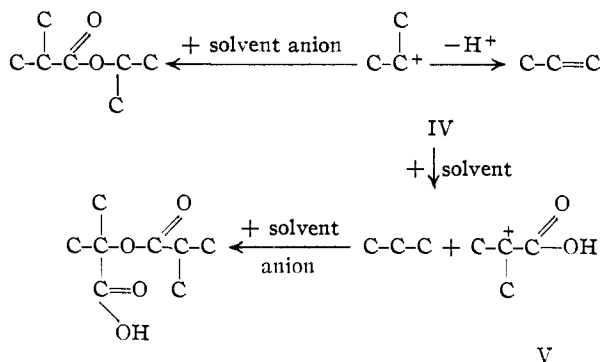
In this reaction there is also formed a small amount of butene-1. This arises undoubtedly from the isomerization of the *t*-butyl carbonium ion. Eltekow⁵ has also found this type of isomerization; he treated *t*-butyl iodide with lead monoxide at elevated temperatures and found that a mixture of isomeric butylenes was generated.

It is important to note that neither isobutane nor hexamethylethane were found as products of this reaction. This indicates the absence of disproportionation and of dimerization, both of which are characteristic of free radical type transformations. McBay⁶ has studied the reaction of the *t*-butyl free radical (produced by high temperature decomposition of ditrimethylacetyl peroxide) in cumene solution and noted no dimerization under these conditions; disproportionation to yield isobutane (58%) and isobutene (42%) was the only observed reaction. This established behavior of the radical and our failure to obtain disproportionation products strengthens the probability of ionic decomposition.

Isobutyric acid and isovaleric acid proved to be exceptionally interesting cases, the former yielding a secondary and the latter a primary (*cf.* acetic acid which also gives a primary carbonium ion) carbonium ion on oxidation with lead tetraacetate. The variety of products obtained from the stabilization of these ions can be explained readily if one takes into consideration both the extreme reactivity (*i.e.*, instability) of these carbonium ions and the availability of tertiary and secondary hydrogen atoms in the solvent molecules.

(5) A. Eltekow, *Ber.*, **13**, 2404 (1880)

(6) H. C. McBay, Ph.D. Dissertation, Univ. of Chicago, 1945.



The isopropyl carbonium ion IV now has a new route of stabilization in that it can react by hydride abstraction with the solvent to form the more stable tertiary carbonium ion V and propane gas. Ion V achieves stabilization by resonance interaction with the carboxyl group and by ultimate reaction with a solvent anion to form α -isobutyroxyisobutyric acid. A third route of stabilization in which the tertiary ion V loses a proton to yield methacrylic acid has been considered; this apparently occurs only to a relatively small extent, and, because of the similar physical properties of the products, could not be detected. Then, too, if methacrylic acid were formed, it would tend to polymerize readily and isolation would be difficult.

The scheme for the isobutyl carbonium ion produced by oxidation of isovaleric acid is more complicated because of the increased possibilities for stabilization.

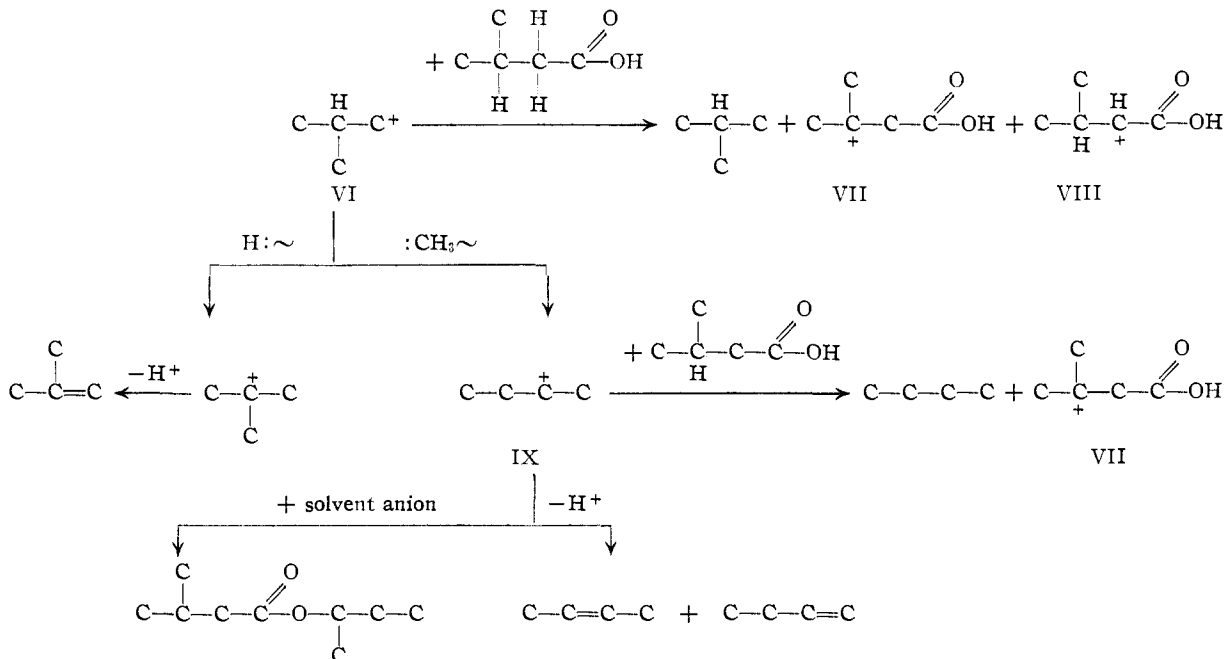
Carbonium ion VI is also capable of undergoing rearrangement by methide ion shift; the two neighboring methyl groups are in a position to stabilize the ion in the transition state by distributing the positive charge over the hydrogen atoms of the methyl groups (hyperconjugation).

The significance of this rearrangement lies in the general observations that free radicals show little or no tendency to rearrange; there is no separation of charge as in the case of ionic structures, and therefore little or no driving force. Compare these results with those obtained in the dehydration of isobutyl alcohol^{7,8} which also yields a mixture of isobutene, butene-2 and butene-1; Konowaloff⁹ found in addition to butene isomers a small amount of isobutane in the dehydration of isobutyl alcohol.

The tendency for the isobutyl carbonium ion VI to undergo hydride shift under the existing conditions is apparently very small; isobutene was present only in trace amounts in the exit gases. This may be due to the inability of the hydrogen atom to adequately diffuse the positive charge in the transition state.

The *s*-butyl carbonium ion IX is also very reactive. Its fate is self-explanatory as shown in the schematic diagram.

The study described above leads one to the conclusion that the decomposition of lead tetraacetate itself is an ionic rather than a free radical phenomenon. This reaction is much slower than that of the other acids previously discussed. There are several reasons for this unusual stability of lead tetraacetate in acetic acid: first, the methyl car-



The primary carbonium ion VI can give rise to isobutane by abstracting hydride ion from the solvent to give the more stable tertiary and secondary ions VII and VIII. These in turn can stabilize themselves by combination with a solvent anion to give the corresponding β - and α -isovaleroxyisovaleric acids.

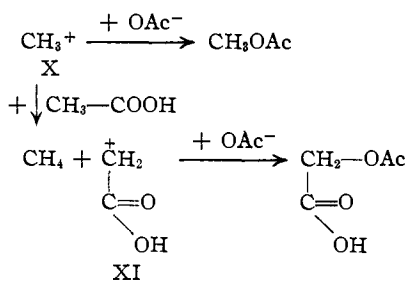
bonium ion is very unstable and, consequently, reluctant to form. Secondly, the temperature is limited to the boiling point of acetic acid. Finally, the carbonium ion formed by the attack of the

(7) W. Ipatiew, *Ber.*, **35**, 1060 (1902).

(8) J. B. Senderens, *Bull. soc. chim. France*, [4] **1**, 692 (1907).

(9) D. Konowaloff, *Ber.*, **13**, 2395 (1880).

methyl carbonium ion on the solvent is only slightly more stable than the methyl carbonium ion itself.



It appears at first glance that there is no decrease in energy content in going from a primary carbonium ion X to another primary carbonium ion XI. There is, however, the possibility in the latter ion of resonance stabilization by interaction of the positive charge with the electrons of the carboxyl group. This stabilization is apparently sufficient to provide the necessary driving force for the reaction.

The ionic concept of the above lead tetraacetate reactions need not be considered completely unique. Criegee¹⁰ and Rigby¹¹ have recently displayed a tendency toward acceptance of the possibility of an ionic mechanism in the cleavage of 1,2-glycols. Furthermore, lead tetraacetate is not the only oxidizing agent capable of reaction with organic acids. Simons¹² has demonstrated that CrO₃ oxidizes triphenylacetic acid to carbon dioxide and triphenylcarbinol, and dimethylphenylacetic acid gives carbon dioxide and acetophenone.

Experimental

Purity of Reagents.—The quality of the organic compounds used is indicated in the following table.

Reagent	M. p., °C.	B. p., °C.	<i>n</i> _D ²⁰
Triphenylacetic acid	262–263 (dec.)
Trimethylacetic acid	163–163.5
Isovaleric acid	175.5–176	1.4033
Isobutyric acid	154–154.5	1.3939
Formic acid	Eastman Kodak "White Label"		
	(98–100%)		
Glacial acetic acid	Baker and Adamson 99.5% glacial		
Lead tetraacetate	Purity >95%; prepared by dissolving red lead in acetic acid at 50°, filtering, and recrystallizing from acetic acid		

Identification of Products.—Triphenylcarbinol was identified by mixed melting point (161.5–162°) with an authentic sample. *t*-Butyl acetate was identified by boiling point (47–48° at 107 mm.), refractive index (*n*_D²⁰ 1.3853) and by preparation of solid derivatives as follows: the acidic component was converted by the method of Hardy¹³ to acetanilide (m.p. and mixed m.p. 113–114°) by reaction of the ester with anilinomagnesium bromide. The alcoholic portion was characterized by refluxing the pure ester for 45 minutes with an equal volume of concd. HCl; the resulting organic layer was separated, dried and distilled through a micro column to yield *t*-butyl chloride (b.p. 50–56°, *n*_D²⁰ 1.3850). This was converted by Grignard reaction with phenyl isocyanate to trimethylacetanilide m.p. 127–128°.

Isopropyl isobutyrate and *s*-butyl isovalerate were identified by the method of Hardy¹³ by reaction with anilinomag-

nesium bromide to give isobutyranilide (m.p. and mixed m.p. 102–103°) and isovaleranilide (m.p. and mixed m.p. 107.5–108°); the alcoholic component was proved by hydrolysis with KOH in diethylene glycol to obtain the alcohol, which was then converted to the 3,5-dinitrobenzoate of isopropyl alcohol (m.p. and mixed m.p. 121–122°) and *s*-butyl alcohol (m.p. and mixed m.p. 75.5–76.0°).

Isopropyl acetate was formed in an amount too small to be derivatized. It was identified only by odor and by boiling range (0.35 g., 70–110°).

The saturated hydrocarbons were identified by mass spectrometric analysis and confirmed by infrared analysis.

The unsaturated compounds were identified by mass spectrometric analysis and by the fact that they were absorbed by passage through pure bromine. In addition, isobutene was further characterized by isolation of the dibromide, which was then hydrolyzed¹⁴ by boiling with water to give isobutyraldehyde (2,4-dinitrophenylhydrazone m.p. and mixed m.p. 185–187°).

α -Isobutyroxyisobutyric acid was identified by neutralization equivalent (found, 168; calcd., 174), by C–H analysis (found: C, 54.94; H, 7.99; calcd.: C, 55.15; H, 8.10) and by mixed melting point 76.5–77.0° with an authentic sample prepared from silver isobutyrate and α -bromoisobutyric acid.

t-Butyl pivalate was identified by odor, boiling range (130–139° at 768 mm.) and refractive index (*n*_D²⁰ 1.3919) (literature b.p. 134–135°, *n*_D²⁰ 1.3920 for *t*-butyl pivalate¹⁵). It was also reacted with anilinomagnesium bromide according to the method of Hardy¹³ to give trimethylacetanilide, m.p. and mixed m.p. 127–128°.

Oxidation of Formic Acid.—Formic acid was found to be readily oxidized quantitatively to CO₂ in a variety of solvents and also in the anhydrous, pure state. No carbon monoxide or hydrogen gas could be detected. A typical run is described here.

To a stirred suspension of 88.8 g. (0.2 mole) of lead tetraacetate in 250 ml. of glacial acetic acid was added dropwise over a period of three hours a solution of 9.7 g. (0.21 mole) of formic acid in 50 ml. of glacial acetic acid. The temperature of the solution rose from 20 to 55° during the addition. When reaction was complete, the solution was refluxed for 10 minutes to drive over the dissolved carbon dioxide. A total of 8.50 g. (96%) of carbon dioxide was trapped in the ascarite tubes provided at the exit end of the condenser.

Oxidation of Triphenylacetic Acid.—To a stirred solution of 10 g. (0.035 mole) of triphenylacetic acid in 150 ml. of glacial acetic acid at 100° was added solid dry lead tetraacetate (15.5 g., 0.035 mole) in small portions from a flask attached to the neck of the reaction vessel by a short length of one-half inch diameter rubber tubing. Addition required one hour. After each addition there was produced in the solution a deep yellow-orange color which faded to a very faint yellow over a period of approximately five minutes. When addition of oxidizing agent was complete, the solution was brought to reflux for about 10 minutes to drive over carbon dioxide. The cooled reaction mixture was then added dropwise with rapid stirring to three volumes of water. The white crystalline precipitate was filtered, washed with water and then dried *in vacuo* at 70°. In this manner 8.56 g. (94.1%) of triphenylcarbinol was obtained; m.p. (crude) 157–159°, after one recrystallization from carbon tetrachloride, 161.5–162°. The ascarite tubes had absorbed 1.45 g. (94.1%) of carbon dioxide.

Oxidation of Trimethylacetic Acid, Isovaleric Acid and Isobutyric Acid.—The oxidations of these acids were carried out under essentially identical conditions.¹⁶ Consequently, the procedure used will be exemplified by discussing only the case of trimethylacetic acid in detail. (See Table I for a summary of results.) The apparatus used consisted of a 500-ml. 3-neck (standard taper) flask equipped with a mercury seal stirrer, a reflux condenser (inside of which was sus-

(14) F. W. L. Evers, H. S. Rothrock, H. M. Woodburn, E. E. Stahly and F. C. Whitmore, *THIS JOURNAL*, **55**, 1136 (1933).

(15) N. C. Cook and W. C. Percival, *ibid.*, **71**, 4142 (1949).

(16) The only variation in procedure involved isolation of the esters from the isobutyric acid oxidation. Because of nearness of their boiling points to those of other main products, separation by distillation was impossible. Consequently, a second run was made, the acids neutralized, the esters extracted with ether, and then isolated by distillation.

(10) R. Criegee, *Ann.*, **560**, 127 (1948).

(11) W. Rigby, *J. Chem. Soc.*, 1907 (1950).

(12) D. M. Simons, Chemistry Department, University of Delaware, Ph.D. Dissertation (1952).

(13) D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

pended a thermometer which dipped into the reaction mixture, and a one-half inch diameter rubber tube to which was attached the flask containing solid lead tetraacetate. To the condenser outlet was fitted a series of three ascarite-filled U-tubes, a gas sampling bulb, and finally a Dry Ice-cooled trap and a sulfuric acid-filled bubble counter.

The trimethylacetic acid (250 g., 2.45 moles) was brought to 135–140° and with rapid stirring the lead tetraacetate (204 g., 0.46 mole) was added portionwise over a period of about two hours. After each addition, a bright greenish-yellow color appeared in the solution and vigorous gas evolution ensued. When the color faded and gas evolution ceased, a new portion of oxidizing agent was added. At the approximate mid-point of the addition of oxidizing agent, the gas sampling bulb was removed from the system and the contents subsequently subjected to mass spectrometric analysis. From the mole per cent. of each constituent present in this gas mixture and the weight of liquid in the Dry Ice trap the yield of each component was calculated: 4.1% 1-butene and 37.8% isobutene were the only hydrocarbon products. A 78.9% yield (15.98 g.) of carbon dioxide was absorbed in the ascarite tubes.

The cooled reaction mixture was poured into 2.5 liters of rapidly stirred anhydrous ether. The ether solution was filtered from the mass of precipitated lead salts and distilled through a 20-plate Whitmore-Lux column filled with Podbielniak Heli-pak packing. After removal of the ether, the products obtained on careful fractionation were *t*-butyl acetate (1.48 g., 2.8%), acetic acid (46.8 g., 83%), *t*-butyl pivalate (2.29 g., 3.2%) and trimethylacetic acid (solvent). The lead salts were dissolved in 200 ml. of glacial acetic acid and saturated with dry HCl gas (ice cooling). After filtration of the lead chloride (126.6 g., 99%), the filtrate was vacuum distilled to yield an additional small amount of trimethylacetic acid. In the case of isobutyric acid, the pot residue of this distillation and the pot residue of the previous distillation were extracted with sodium bicarbonate solution; on reacidification, 5.02 g. (9.6%) of solid α -isobutyroxyisobutyric acid (m.p. and mixed m.p. 76.5–77.0°) was obtained. In the case of isovaleric acid, similar treatment of the pot residues gave 4.9 g. of an oil which could not be made to crystallize; this was probably a mixture of α - and β -isovaleroxyisovaleric acids.

Synthesis of α -Isobutyroxyisobutyric Acid.—To 15.5 g. (0.08 mole) of dry silver isobutyrate was added a solution of 13.0 g. (0.08 mole) of α -bromoisobutyric acid in 45 ml. of isobutyric acid. Upon shaking, heat was produced and the mixture immediately turned yellow. To assure completeness of reaction, the mixture was agitated mechanically overnight. The yellow silver bromide was then filtered and the filtrate vacuum distilled. When all the solvent was removed, a light brown residue (10.32 g., 74%) remained. Upon cooling, the semi-solid mass of acyloxy acid was recrystallized several times from 30–60° petroleum ether (using Dry Ice-bath cooling) to give pure α -isobutyroxyisobutyric acid as colorless plates, m.p. 76.5–77.0°.

Preparation of Lead Tetrapivalate.—The apparatus used for this preparation consisted of a 500-ml. 3-neck flask (standard taper joints) fitted with a "Trubore" stirrer, a thermometer, and a distillation head arranged for vacuum distillation.

The trimethylacetic acid (350 g., 3.5 moles) and lead tetraacetate (177 g., 0.4 mole) were combined in the flask and the pressure reduced to about 40 mm. with continuous stirring. The temperature was then raised until distillation began. Most of the acetic acid came over from 66 to 76°. When a total volume of 107 ml. of distillate was obtained, the acetic acid was completely removed and the boiling temperature started to rise sharply. Upon cooling, the solid lead tetrapivalate was filtered with suction from excess pivalic acid and stored over P₂O₅ in a vacuum desiccator. The snow white product (230 g., 93.8%) on fairly rapid heating between cover glasses on a Fisher-Johns m.p. block gave a melting point of 194–194.1° (dec.). The product was analyzed for lead content (found: Pb, 34.19; calcd., Pb, 33.87) and for C–H (found: C, 38.42; H, 5.6; calcd., C, 39.26; H, 5.93).

Preparation of Lead Tetraisobutyrate.—The same procedure and apparatus were used in this reaction as in the preparation of lead tetrapivalate (above).

At room temperature, 134 g. (0.3 mole) of lead tetraacetate was stirred with 250 g. (2.84 moles) of isobutyric acid. At a pressure of 48 mm., the greater portion of the acetic

acid distilled at a head temperature of 50–60°. The turbid yellow-green residue in the reaction flask was allowed to cool overnight, and the white crystalline solid which had precipitated was filtered and dried over P₂O₅ in a vacuum desiccator. The snow white product (82 g., 49.2%) exhibited m.p. 117–119° (dec.) on moderately rapid heating. Analysis for lead showed 37.38, 37.56%, (calcd., 37.32%).

Decomposition of Lead Tetrapivalate.—The apparatus and conditions for this reaction were similar to those employed in the oxidation of trimethylacetic acid with lead tetraacetate (above) except that no gas sampling bulb was used; no mass spectrometric analysis was performed on the exit gases of this reaction.

To 125 g. (1.22 moles) of trimethylacetic acid heated to 150–155° was added (with stirring) in small portions over a period of two hours 125 g. (0.25 mole) of lead tetrapivalate.

The reaction mixture was poured into two volumes of water and steam distilled until there was no longer any solidification of trimethylacetic acid in the condenser, or until a volume of 1.25 liters of distillate had been obtained. This steam distillate was neutralized with 20% sodium hydroxide and extracted continuously with ether for one week. The ether extract was dried with anhydrous magnesium sulfate and distilled through a 20-plate Whitmore-Lux column filled with Podbielniak Heli-Pak packing. The only product obtained was a cut having b.p. 130–144° and n_D^{20} 1.3970. This was *t*-butyl trimethylacetate (2.95 g., 7.5%).

Upon completion of the steam distillation, solid lead pivalate precipitated out of the solution. This was filtered, and the filtrate permitted to evaporate in the hood. In this manner an additional small amount of lead pivalate was obtained to yield a combined total of 101.9 g. (100.5%).

By acidification of the neutralized and ether-extracted steam distillate, the trimethylacetic acid was recovered. This was distilled to yield 139.3 g. or 14.3 g. (56.5% yield) more than was originally used as a solvent for the reaction.

The Dry Ice trap at the end of the reaction contained 6.9 g. (49.7%) of isobutene. It was distilled into bromine and the dibromide isolated and identified. (The absorption of gas by the bromine was 100%; that is, no saturated gases were present.) The ascarite absorption indicated a yield of 8.73 g. (80.1%) of carbon dioxide.

There was no evidence of isobutane or hexamethylethane as reaction products.

Decomposition of Lead Tetraisobutyrate.—The same apparatus was used for this reaction as in the decomposition of lead tetrapivalate. The general conditions were also the same throughout the reaction.

To a stirred solution of 120 g. (1.38 moles) of isobutyric acid at 145–150° was added in small portions over a period of about three hours 181.5 g. (0.33 mole) of lead tetraisobutyrate. At the end of the reaction, there had collected in the Dry Ice trap 3.89 g. of liquid. This was permitted to distil through six small traps of pure bromine into a second Dry Ice trap. This second trap had condensed 1.77 g. of liquid, which was subjected to infrared analysis. A perfect propane spectrum resulted. Upon destroying the excess bromine with sodium bisulfite solution, the dibromide (1.88 g., 2.8%) was isolated but not identified further. If it is assumed that all of the initially condensed liquid product except that amount corresponding to 1.88 g. of propylene dibromide was propane, a yield of 3.51 g. (24.4%) is indicated. The ascarite had absorbed 8.19 g. (56.8%) carbon dioxide.

The reaction mixture was poured into an equal volume of water and steam distilled. The distillate was treated with 150 ml. of concd. NH₄OH (an excess) and extracted continuously with ether. No esters, however, were isolated upon fractionating the extract. The aqueous reaction mixture remaining behind after steam distillation was treated with 33 g. of concd. H₂SO₄. After filtering the PbSO₄ (when dry, 99.8 g., 99.8%), the filtrate was allowed to concentrate in the hood on a steam-bath. Upon complete evaporation of the water, 7 ml. of an amber oil remained. This was washed well with water, taken up in benzene, dried over anhydrous MgSO₄ and allowed to stand in the hood overnight; 3.25 g. (5.7%) of α -isobutyroxyisobutyric acid was obtained, m.p. and mixed m.p. 76.5–77.0° after recrystallization from petroleum ether (30–60°) at Dry Ice temperatures.

NEWARK, DELAWARE