Oxidations with Lead(IV). I. Mechanism of the Decarboxylation of Pentanoic Acids

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Oxidative decarboxylations of n-valeric, isovaleric, and 2-methylbutyric acids with lead tetraacetate in benzene solutions have been examined at 81°. The rates of decomposition are enhanced by pyridine or valeryl peroxide. The decarboxylations are strongly inhibited by oxygen. A free-radical chain mechanism is proposed which includes butyl radicals as transient, and Pb(III) species as metastable intermediates. The mediation of copper salts in an efficient catalytic reaction is described. Short chain lengths in the thermal and pyridine-induced reactions and long chains in the copper salt catalyzed reactions are mainly due to the difference in the efficiency with which butyl radicals are oxidized by Pb(IV) and Cu(II) oxidants, respectively. Chain lengths are also a function of the alkyl moiety, generally being longer with secondary and higher alkyl groups than with primary alkyl groups as a consequence of more facile chain transfer (eq. 16 and 17). The products derived from the thermal as well as the pyridine-induced reactions are butanes, butenes, butyl esters, and butylbenzenes, while only butenes are formed in the presence of catalytic amounts of copper salts. Oxidation of butyl radicals by Pb(IV), quasi-homolytic aromatic substitution with butyl radicals, and the trapping of butyl radicals with butadiene and oxygen are delineated. The selective decarboxylation of secondary and more highly branched carboxylic acids in glacial acetic acid is discussed.

Introduction

Lead tetraacetate is used as a reagent for the oxidative decarboxylation of aliphatic carboxylic acids and bisdecarboxylation of 1,2-dicarboxylic acids.[1,2] Lead(IV) carboxylate is converted to lead(II), carbon dioxide, and products of oxidation of the alkyl moiety. The relative ease of decarboxylation of various carboxylic acids, RCO_2H, and isolation of products characteristic of a carbonium intermediate derived from R, led Mosher and Kehr[3] to formulate a direct 2-equiv. process. Direct formation of Pb(II) salt and an acyloxonium intermediate I, which underwent subsequent decarboxylation, was postulated. They adduced no evidence for free radicals and attributed the formation of alkanes to hydride-transfer processes.[4]

$$RCO_2Pb^{IV} \longrightarrow \underset{\text{I}}{RCO_2^+} + Pb^{II} \qquad (1)$$

The decomposition of lead tetraacetate itself in glacial acetic acid has been studied and found to be accelerated by sodium acetate.[5,6] Both investigators concluded that the decomposition proceeded *via* 1-equiv. changes and implicated Pb(III) as an intermediate. Significantly, the reaction catalyzed by sodium acetate gave no conspicuous amounts of carbon dioxide or methane.

Oxidative bisdecarboxylation is also induced by bases such as pyridine and trialkylamines.[7,8] Corey and Casanova found that pyridine does not affect the products of decarboxylation. The possibility of a cationic intermediate was further strengthened by the isolation of rearranged benzhydryl phenyl ketone from α,β,β-triphenyl-β-hydroxypropionic acid. Partially racemized *exo*-2-norbornyl acetate obtained from optically active *endo*- and *exo*-norbornane-2-carboxylic acids was attributed to intermediary 2-norbornyl cations.

There is no doubt that the oxidative decarboxylation of aliphatic acids by lead(IV) acetate to alkenes, alkyl acetates, and related products involves carbonium ion intermediates (or a transition state of cationic character). Furthermore, the facile oxidation of some acids, particularly formic acid, may involve a direct 2-equiv. change from Pb(IV) to Pb(II).[3,9]

$$HCO_2Pb^{IV} \longrightarrow Pb^{II} + H^+ + CO_2 \qquad (2)$$

It is not clear, however, that all or even most decarboxylations proceed *via* such a mechanism. The 1-equiv. process, in essence given by eq. 3 and 4, could not be obviated. A clear selection between the two diverse mechanisms has not been forthcoming.[1,8]

$$RCO_2Pb^{IV} \longrightarrow Pb^{III} + R\cdot + CO_2 \qquad (3)$$

$$R\cdot + Pb^{III} \longrightarrow Pb^{II} + \text{oxidation products} \qquad (4)$$

The products derived from the related oxidative cleavage and cyclization[10,11] of alcohols by lead(IV) acetate are symptomatic of free radicals as intermediates. Cyclic ethers formed in a number of cases have been

(1) W. H. Starnes, *J. Am. Chem. Soc.*, **86**, 5603 (1964).
(2) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1340 (1960); J. Kazan and F. D. Greene, *J. Org. Chem.*, **28**, 2965 (1963).
(3) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953); **82**, 5342 (1960); W. A. Mosher, C. L. Kehr, and L. W. Wright, *J. Org. Chem.*, **26**, 1044 (1961).
(4) No consistent attempt will be made to include all the coordination around the Pb atom, except where it is pertinent to the discussion. Pb(IV) can show tetrahedral, octahedral, and, suppposedly, dodecahedral coordination.
(5) M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).
(6) D. Benson, L. H. Sutcliffe, and J. Walkley, *J. Am. Chem. Soc.*, **81**, 4488 (1959).
(7) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).
(8) E. J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963).
(9) (a) Facile 2-equiv. oxidation of formate has been reported by J. Halpern and S. M. Taylor, *Discussions Faraday Soc.*, **29**, 174 (1960); (b) G. Büchi, R. E. Erickson, and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961).
(10) S. Moon and J. Lodge, *J. Org. Chem.*, **29**, 3453 (1964); R. E. Partch, *ibid.*, **28**, 276 (1963); J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.*, 107 (1953); R. Criegee, *et al.*, *Ann.*, **599**, B1 (1956); H. B. Henbest, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **53**, 146 (1956); R. M. Moriarty and K. Kapadia, *Tetrahedron Letters*, 1165 (1964); 465 (1965).
(11) K. Heusler and J. Kalvoda, *ibid.*, 1001 (1964); V. M. Micovic, *et al.*, *ibid.*, 2091 (1963); Tetrahedron, **20**, 2279 (1964).

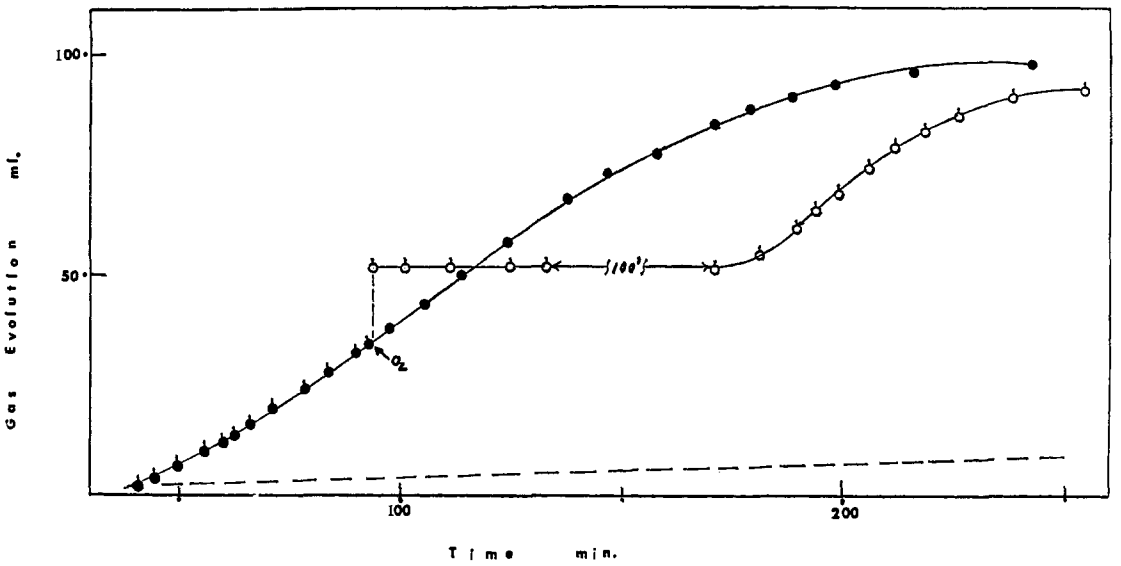


Figure 1. Decomposition of valeric acid with 0.2 *M* lead(IV) acetate: in benzene at 81° (– – – –); catalysis by pyridine (●); inhibition by oxygen (ȯ).

interpreted[12] as arising *via* free alkoxy radicals. These are known to undergo intramolecular 1,5-hydrogen

$$ROPb^{IV} \longrightarrow Pb^{III} + RO\cdot \text{ etc.} \quad (5)$$

abstraction.[13,14] Fragmentation and cyclization are also characteristic of alkoxy radicals. However, similar behavior patterns have also been evinced *via* heterolytic "oxonium" routes.[15]

Results

The thermal decomposition of 0.25 *M* lead(IV) acetate in benzene solutions containing excess (2.1 *M*) carboxylic acid is relatively slow, and the rate is dependent on the acid. In the absence of oxygen, lead(IV) acetate and 2-methylbutyric acid in refluxing benzene solutions are decomposed in less than 10 hr. Under equivalent conditions *n*-valeric and isovaleric acids require more than 48 hr. for complete reaction. Lead tetraacetate alone under similar conditions is reasonably stable. Decomposition in glacial acetic acid is not appreciable until the refluxing temperature (120°) is attained.

Catalysis and Inhibition. The decomposition of lead(IV) acetate and *n*-valeric acid in the presence of 1.4 *M* pyridine is completed in slightly more than 3 hr. at 81° as shown in Figure 1. The onset of decomposition is characterized by an induction period which is proportional to the amount of oxygen present.[16,17] If no precaution is exercised to remove oxygen from the system, the decomposition is interminably reluctant. Similarly if oxygen is added to the reaction at an intermediate juncture, the decomposition is interrupted instantaneously. It remains inhibited for a relatively long period (2 hr. with 0.5 mequiv. of O_2). It then resumes at a rate similar to that before inhibition (Figure 1). The inhibition can be removed sooner if oxygen is purged by flushing with an inert gas.

The decomposition of lead(IV) acetate in the presence of isovaleric acid behaves in much the same manner as that described for *n*-valeric acid. The decarboxylation of 2-methylbutyric acid by lead(IV) acetate in benzene is three to four times faster than that of either *n*- or isovaleric acid. In the presence of pyridine it is roughly twice as fast (measured as time for half-decomposition). The pyridine-induced decarboxylation of 2-methylbutyric acid is inhibited by oxygen much like its primary acid counterparts. The rate of decarboxylation of 2-methylbutyric acid by lead(IV) acetate is accelerated in a remarkable manner by divaleryl peroxide as shown in Figure 2. At most a minor induction period follows the addition of the peroxide.

Products of Decomposition. The decarboxylation of carboxylic acids by acetate yields lead(II) carboxylates and carbon dioxide in stoichiometric amounts[18] together with products derived from the alkyl moiety. In general, four types of compounds have been identified as products derived from the butyl moiety: butane,

(12) (a) D. Hauser, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1883 (1964); (b) D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *ibid.*, **47**, 1961 (1964); (c) K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, **3**, 525 (1964).

(13) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963); C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

(14) (a) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); (b) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(15) (a) E. J. Corey and R. W. White, *ibid.*, **80**, 6686 (1958); (b) P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 85 (1961); **80**, 4954 (1958); (c) R. A. Sneen and N. P. Matheny, *ibid.*, **86**, 5503 (1964).

(16) (a) An induction period and the variable nature of lead(IV) acetate decompositions were noted early [(b) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *ibid.*, **64**, 2052 (1942)], but apparently unheeded or overlooked by many subsequent investigators. (c) In two examples,[1,8] oxygen was reported to be without effect on the products.

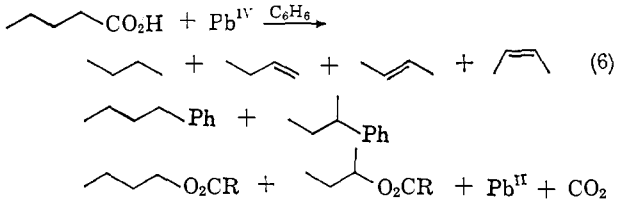
(17) (a) The acetate-induced decompositions appear to proceed readily under mild conditions with no apparent attempt to remove oxygen; (b) A. C. Cope, C. H. Park, and P. Scheiner, *J. Am. Chem. Soc.*, **84**, 4682 (1962).

(18) (a) All yields are based on Pb(IV), mole per mole, with no regard to whether the product is derived by oxidation or reduction. (b) Acidic[8] and basic products were removed in the work-up and not investigated further. Incomplete material balance is attributed to these products, and the competitive fragmentation of acetate, especially with valeric and isovaleric acids.[19]

(19) Selective fragmentation applies especially to decarboxylations in glacial acetic acid of secondary, tertiary, or similarly highly branched carboxylic acids. Decarboxylation of primary acids have only been studied in the acid itself as solvent,[8,16b] or, as in this study, in benzene solutions containing an excess of primary acid. The degree to which selective decarboxylation of primary acids such as valeric and isovaleric acids compared to acetic acid occurs has, thus, not been fully assessed. Even under our conditions the less than quantitative material balance on the butyl moieties from valeric and isovaleric acids is probably indicative of such competition.

butene, butyl esters, and butylbenzene. The relative amounts of each of these products depend mainly on the nature of the alkyl group. In the following sections only products derived from the butyl fragment will be presented. These are indicated by eq. 6–8.

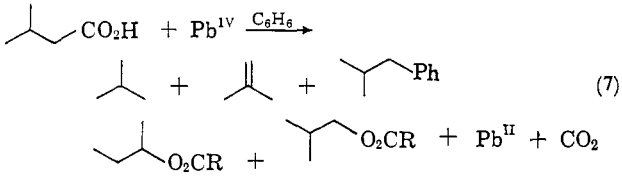
n-Valeric acid and lead(IV) acetate in benzene yield 25% *n*-butane, 2% butene-1, 0.7% *trans*-butene-2, and 0.4% *cis*-butene-2 (relative molar composition: 86, 8.5, 3.5, 2.0, respectively). *n*-Butylbenzene is formed in 20% yield together with 0.6% *sec*-butylbenzene. No isobutyl- or *t*-butylbenzene is formed. Among ester products there are *sec*-butyl valerate (8%), *n*-butyl valerate (2%), *sec*-butyl acetate (2%), and *n*-butyl acetate (0.3%).



(6)

In the presence of pyridine, the yields of butane (9%), butene-1 (1.3%), *trans*-butene-2 (0.5%), and *cis*-butene-2 (0.3%) (relative proportion: 74, 18, 5, 3, respectively) are diminished, together with *n*-butylbenzene (11%) and traces (~0.1%) of *sec*-butylbenzene. The yields of esters are unchanged: *sec*-butyl valerate (8%), *n*-butyl valerate (2%), *sec*-butyl acetate (3%), and *n*-butyl acetate (0.4%). The yields of products derived from the butyl fragment depend somewhat on oxygen and are lower when oxygen is used to inhibit the decomposition.

Isovaleric acid and lead(IV) acetate in benzene yield 38% isobutane and only insignificant amounts (<0.3%) of isomeric butenes (isobutylene, butene-1, and *trans*- and *cis*-butene-2). Isobutylbenzene (11%) is also the sole butylbenzene isomer found in significant amounts. Isobutyl isovalerate (2%) is the principal ester component together with small amounts of *sec*-butyl isovalerate (0.3%), traces (0.1%) of isobutyl acetate, and some higher boiling unidentified esters.



(7)

In the presence of pyridine, isobutane is formed in 35% yield contaminated with a small amount (1%) of isobutylene. No significant amounts of butene-1 or *cis*- and *trans*-butene-2 are detected. Isobutylbenzene is found in approximately the same amounts (10%) as in the absence of pyridine, together with such minor ester products as isobutyl isovalerate (2%), *sec*-butyl isovalerate (0.3%), and isobutyl acetate (0.2%).

2-Methylbutyric acid is easily decomposed by lead(IV) acetate in benzene to *n*-butane (15%), butene-1 (14%), *trans*-butene-2 (11%), and *cis*-butene-2 (5%) in a molar ratio: 34, 31, 24, and 11, respectively. In addition, reasonably high yields of *sec*-butyl 2-methylbutyrate (35%) and *sec*-butyl acetate (20%) are formed.

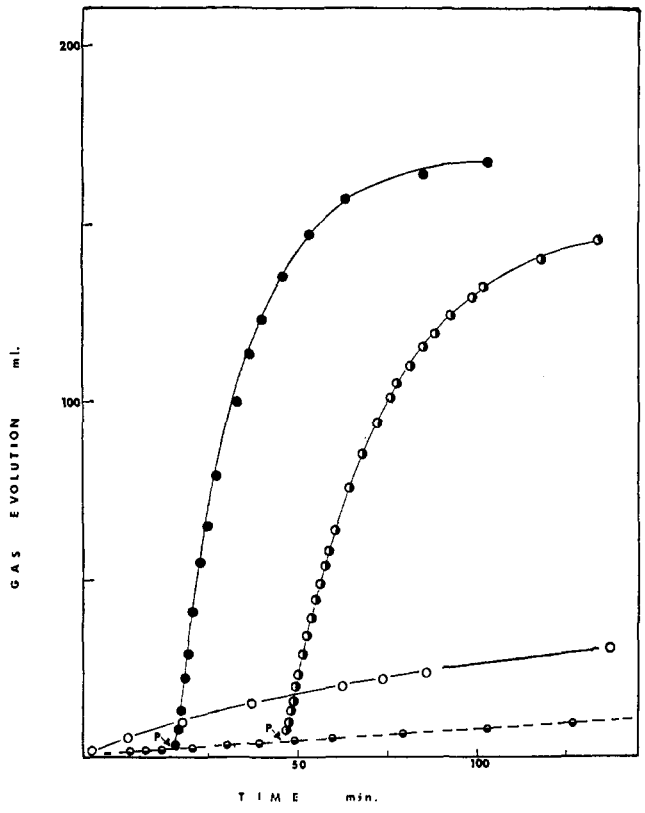
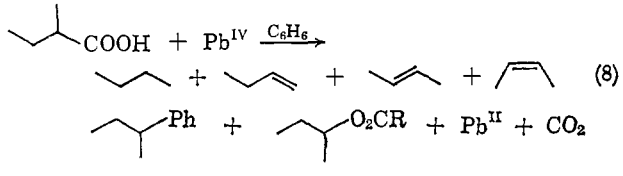


Figure 2. Divaleryl peroxide induced decarboxylation of 2.1 *M* 2-methylbutyric acid with 0.25 *M* lead(IV) acetate in benzene at 81°: ◒, no peroxide; ○, no lead(IV) acetate, 0.037 *M* peroxide; ●, 0.037 *M* peroxide; ◑, 0.013 *M* peroxide; P = point of peroxide addition.

sec-Butylbenzene uncontaminated with any of the isomeric aralkanes is formed in 10% yield together with a higher boiling hydrocarbon of undetermined structure (~1%).



(8)

A similar reaction in the presence of pyridine affords butane (9%), butene-1 (12%), *trans*-butene-2 (13%), and *cis*-butene-2 (6.5%) in a molar proportion: 22, 29, 33, and 16, respectively. *sec*-Butyl 2-methylbutyrate (28%) and acetate (16%) and *sec*-butylbenzene (7%) are also found in diminished yields. The pyridine-induced decomposition in acetonitrile gives substantially comparable results: butane (12%), butene-1 (10%), *trans*-butene-2 (10%), *cis*-butene-2 (6%) (relative proportions: 32, 27, 26, and 5), and *sec*-butyl 2-methylbutyrate (38%) and acetate (10%). No other products are evident.

The products from the valeryl peroxide initiated decarboxylation of 2-methylbutyric acid are substantially the same as those obtained with or without pyridine. Valeryl peroxide alone under these conditions slowly (Figure 2) yields butane, carbon dioxide, valeric acid, and *n*-butylbenzene. From the standpoint of products, its effect appears to be merely additive. The presence of peroxide does not materially affect the yields of products derived from 2-methylbutyric acid. Thus, decarboxylation initiated by 5 mole % valeryl

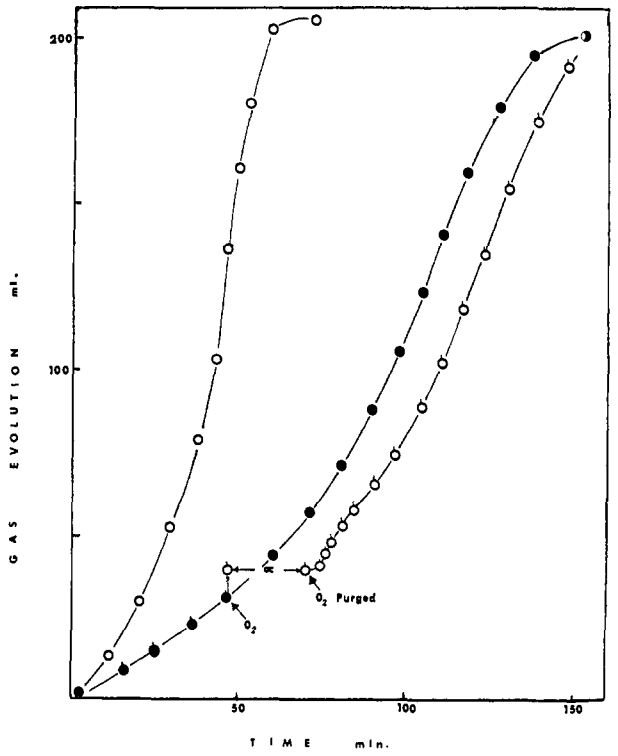


Figure 3. Copper salt catalysis in the decarboxylation of 2.1 *M* *n*-valeric acid with 0.25 *M* lead(IV) acetate in the absence of pyridine: O, 0.097 *M* copper(II) acetate; ●, 0.045 *M* copper(II) acetate; ȯ, inhibition by oxygen.

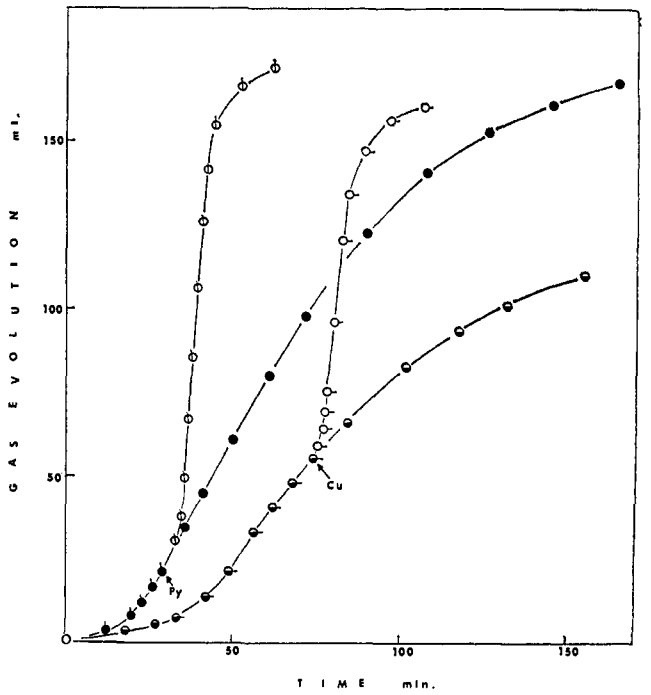


Figure 4. Decarboxylation of 2.1 *M* 2-methylbutyric acid: ⊖, catalysis by 1.4 *M* pyridine and ⊖-, 0.0084 *M* copper(I) acetate; ●, catalysis by 0.093 *M* copper(II) acetate and ⦶, 1.4 *M* pyridine.

peroxide yields *sec*-butyl acetate (14%) and 2-methylbutyrate (43%), and *sec*-butyl- (7%) and *n*-butylbenzene (0.8%), together with *n*-butane (26%), butene-1 (12%), *trans*-butene-2 (12%), and *cis*-butene-2 (7%).

In those reactions in which oxygen is used to inhibit the reaction, the yields of butenes, butane, esters, and *sec*-butylbenzene are diminished in proportion to the amount of oxygen added. These products can be almost completely eliminated in the presence of excess oxygen. In separate experiments, 2-methylbutyric acid, pyridine, and lead(IV) acetate dissolved in benzene are added to a thick-walled glass reactor and magnetically stirred slowly. The vessel is charged with 40 p.s.i.g. of oxygen and heated at 81° for 48 hr. Except for the high oxygen pressure, the reaction is otherwise the same as those described above. Only small amounts of butane (1%), butenes (0.3%), and *sec*-butyl esters (<0.01%), roughly in the same relative proportion as that obtained in the absence of oxygen, is formed. The major products are methyl ethyl ketone (14–20%) and *sec*-butyl alcohol (3–5%) and some as yet unaccounted fragments.

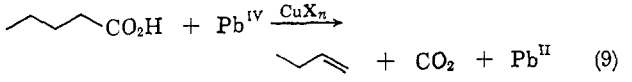
Decarboxylations Catalyzed by Copper Salts. The decomposition of lead(IV) acetate and valeric acid in benzene at 81° is also catalyzed by copper salts in the absence of pyridine, provided oxygen is scrupulously removed. The reaction shows a certain autocatalytic behavior seen in Figure 3. If oxygen (1 mequiv.) is added to the decomposition in progress, the reaction ceases abruptly. It remains dormant for prolonged periods (the inhibition has been allowed to go for as long as 12 hr.). Unlike the reaction induced by pyridine, it is not resuscitated until the oxygen is deliberately removed. The added oxygen (0.5 mequiv.) is purged from the inhibited reaction after 2 hr. by removing the reaction vessel from the bath, cooling to 10°, and flushing with argon for 5 min. When the flask is reimmersed into the bath (total elapsed time, 14 min.), the reaction proceeds on the same course as that preceding its inhibition (Figure 3). At the low levels of copper catalysts employed, no apparent difference is detected between Cu(I) and Cu(II) salts (see, however, Discussion).

The effect of copper salt as catalyst in the decarboxylation of 2-methylbutyric acid is not as marked as that derived from *n*- or isovaleric acid (Figure 4). In the catalyzed reactions of 2-methylbutyric acid, the induction periods are shorter, and the decompositions are less sensitive to degassing procedures compared to those of either primary acid. The secondary acid also differs from *n*-valeric or isovaleric acid in that a copper salt reaction deliberately inhibited by oxygen will reinitiate itself in the absence of pyridine after a relatively short (several hours) inhibition period.

Copper salts and pyridine conjunctively catalyze the decomposition of lead(IV) acetate and valeric acid at an extraordinary rate. If either copper salt [Cu(I) or Cu(II)] is added to a pyridine-induced reaction or, conversely, pyridine is added to a copper-catalyzed reaction, there is a marked increase in rate of gas evolution as shown in Figures 4 and 5. This strongly catalyzed decomposition can be arrested with oxygen. However, the inhibition period is shorter than that for pyridine alone. The reaction resumes abruptly and spontaneously after the oxygen is consumed by the reaction.

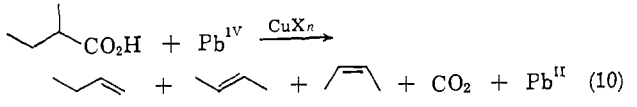
In the presence of copper salts, the butyl moiety derived from *n*-valeric, 2-methylbutyric, or isovaleric acid is quantitatively converted to butenes according

to eq. 9–11. Excellent yields (70–80%) of butene-1 are formed from *n*-valeric acid and lead(IV) acetate in the presence of copper salts, together with only minor amounts of *trans*-butene-2 (3%) and *cis*-butene-2 (2%) (relative amounts: 93, 3.7, 3.3, respectively).



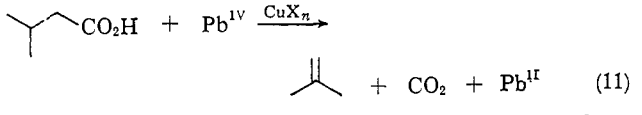
No *n*-butane and only insignificant amounts of butylbenzene and esters are apparent.

A virtually quantitative yield of butenes is obtained from 2-methylbutyric acid and copper salts (0.08–0.03 *M*) in benzene or acetonitrile (heterogeneous). The relative distribution of butene-1, *trans*-butene-2, and *cis*-butene-2 is 51:26:23 in benzene and 51:28:21 in acetonitrile. Except for a small amount of *n*-butane (1%) found in acetonitrile [0.091 *M* Cu(II)] and small amounts of *sec*-butyl 2-methylbutyrate



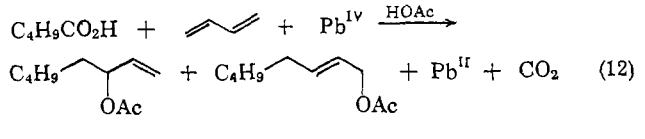
and acetate, no butane, butylbenzene, or other products are otherwise apparent. If copper salts are added at a midpoint of a pyridine-induced reaction, the products consist of half of each type of reaction (thermal and copper catalyzed). Only butenes are formed by the converse addition and both reactions are marked by increased rate.

In the decarboxylation of isovaleric acid, isobutyl isovalerate persists (0.3%) even at 0.08 *M* copper(II) isovalerate. Isobutylbenzene and isobutane are nonexistent at concentrations of copper salt as high as 0.03 *M*. The dominant product under these conditions is isobutylene (40–70%). An increase in rate accompanies the addition of copper salts to the decomposing solution of lead(IV) acetate, isovaleric acid, and pyridine at an inter-



mediate point. A mixture of products is derived from the thermal (pyridine) and copper-catalyzed processes, indicative of two successive reactions. The converse addition (pyridine to copper catalyzed) only affords products (alkenes) derived from the copper reactions. Except for a marked increase in rate there is no other apparent change.

Valeric acid and butadiene with lead(IV) acetate in acetic acid or acetic acid–benzene solutions afford a mixture of octenyl acetates in 5–10% yield. The mixture consists of 48–51% 3-acetoxyoctene-1 and 52–49% 1-acetoxyoctene-2 among other high boiling esters.[20] In the presence of catalytic amounts (0.014 *M*) of copper acetate, much higher yields (40–50%) of octenyl acetates are obtained. The composition is 85% 3-acetoxyoctene-1 and 15% 1-acetoxyoctene-2.



(20) *Cf.* R. Criegee, *Ann.*, **481**, 263 (1930); T. Posternak and H. Friedli, *Helv. Chim. Acta*, **36**, 25 (1953).

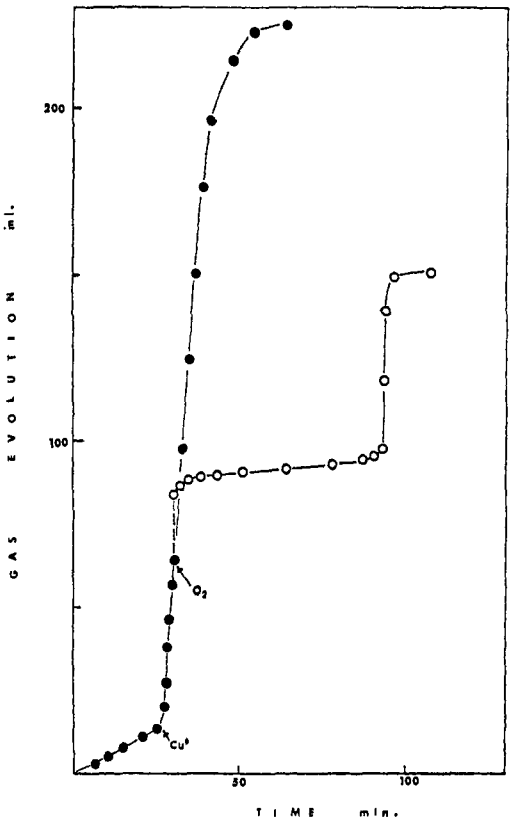


Figure 5. Decarboxylation of 2.1 *M* *n*-valeric acid with 0.25 *M* lead(IV) acetate and 1.4 *M* pyridine: ●, catalysis by 0.0084 *M* copper(I) acetate; ○, inhibition by oxygen.

The addition of pyridine (1.5 *M*) to the latter reaction alters the composition of the octenyl acetate mixture (20–30%) to 49% 3-acetoxyoctene-1 and 51% 3-acetoxyoctene-2.

Discussion

An insight into the mechanism of the decarboxylation of acids by lead(IV) acetate is lent from the rate studies, catalysis and inhibition, coupled with extensive product analyses. Oxygen or a weak molecular complex thereof is responsible for inhibition by oxygen, since it can be removed simply by sweeping with an inert gas. Oxygen is undoubtedly destroying free radicals produced in the reaction.[21] However, adventitious oxygen alone is not responsible for the initial induction period. The rate after oxygen is removed from the inhibited reaction is more akin to that just before inhibition than that at the beginning of the reaction itself (Figures 3 and 5). The large enhancement in rate of decarboxylation by divaleryl peroxide is additional evidence for a free-radical reaction.

Mosher and Kehr[3] reported that the decarboxylation of formic acid occurred readily at room temperature. Pivalic and triphenylacetic were more readily decom-

(21) The mechanism by which oxygen inhibits the reaction has not yet been completely resolved. An important function is to trap butyl radicals since methyl ethyl ketone and *sec*-butyl alcohol are products of the oxygen runs, albeit in low yields (*vide infra*). The fate of the remainder of the butyl moiety is in doubt. *n*-Butyl and isobutyl radicals are also probably converted to the aldehydes and alcohols and in the subsequent work-up usually lost. Pb(III) species may also react with oxygen or the alkylperoxy radicals. No or little change in gas volume (see figures) during the inhibition is due to the liberation of one carbon dioxide with each butyl radical and ensuant consumption of one oxygen.

posed than isovaleric or acetic acid. They related the relative ease of decarboxylations of acids to the cationic stability of the species resulting from the loss of carbon dioxide: H > tertiary > secondary > primary. In earlier studies[1–7,17] no specific effort was made to remove oxygen from the system. Refluxing solvent was employed in many studies. It fortuitously served to remove oxygen from the reaction medium. However, since the decomposition of Pb(IV) is quite sensitive to oxygen, earlier kinetic investigations in which no attempt was made to remove this ubiquitous adulterant cannot be compared directly.

We feel that the accumulated evidence favors a free-radical chain mechanism for the decomposition of Pb(IV) under these conditions. Lead(III) is implicated as an intermediate in the following manner.[4]

Pre-equilibration

$$Pb^{IV}(OAc)_4 + nRCO_2H \rightleftharpoons \underset{IIa}{Pb^{IV}(OAc)_{4-n}(O_2CR)_n} + nHOAc \quad (13)$$

$$IIa + mPy \rightleftharpoons \underset{IIb}{Pb^{IV}(OAc)_{4-n}(O_2CR)_nPy_m} \quad (14)$$

Initiation

$$II(a,b) \longrightarrow Pb^{III} + R\cdot + CO_2 \quad (15)$$

Propagation

$$RCO_2Pb^{III} \longrightarrow Pb^{II} + R\cdot + CO_2 \quad (16)$$

$$R\cdot + Pb^{IV} \longrightarrow R^+ \text{(alkene, ester)} + Pb^{III} \text{ etc.} \quad (17)$$

Termination

$$R\cdot + Pb^{III} \longrightarrow R^+ \text{ (alkene, ester)} + Pb^{II} \quad (18)$$

$$R\cdot \text{ (radical reactions)} \xrightarrow{HS} RH + S\cdot \text{ (disprop., recomb., etc.)} \quad (19)$$

HS = solvent; n = 1, 2, 3, 4,

In the following discussion each step will be examined in greater detail.

The *initiation* depends on the homolysis of a Pb(IV) species to Pb(III), carbon dioxide, and an alkyl radical.[22] In general, lead tetraacetate or similar species such as IIa are relatively stable and at 80° undergo homolysis rather slowly. However, the formation of pyridine complexes such as IIb can labilize Pb(IV) to undergo more facile homolysis.[23] Acetate *probably* has a similar effect in labilizing lead(IV) acetate as an hexaacetatoplumbate(IV) species IIIa.

$$Pb^{IV}(OAc)_4 + 2OAc^- \rightleftharpoons \underset{IIIa}{Pb^{IV}(OAc)_6^{-2}} \quad (20a)$$

In addition to its role as a ligand in a Pb(IV) complex such as IIb, pyridine may also function as base catalyst for the pre-equilibrative exchange of carboxylate ligands (eq. 13). It is not known how fast or to what extent ligand exchange between acetato and carboxylate groups occurs under these conditions. Some evidence points to a fast exchange similar to that found with acetato groups in glacial acetic acid.[24]

This concept involving catalysis of Pb(IV) decarboxylation by pyridine is subject to experimental validation. A variety of nucleophilic reagents other than pyridine and nitrogen bases are available. If the mechanism postulated is tenable, other highly coordinated Pb(IV) species IIIb formed as in eq. 20b are possible, and general catalysis by nucleophiles should be obtained. Indeed, it has been found that

$$Pb^{IV}(O_2CR)_4 + nB^-: \rightleftharpoons \underset{IIIb}{Pb^{IV}(O_2CR)_4B_n^{-n}} \quad (20b)$$

acetate and halides as well as cyanide and thiocyanate as anions initiate rapid decomposition of Pb(IV) esters.[25] Under these conditions, acetate salts promote facile oxidative decarboxylation. The products from the reaction of Pb(IV) esters and halides are alkyl halides; halodecarboxylation of acids by this method is a useful synthetic method for the preparation of alkyl chlorides.[25b] When cyanides are used as nucleophilic initiators, decarboxylation yields alkyl cyanides as products. Similar substitutive decarboxylations are presumably obtainable with other nucleophiles such as azide and thiocyanate salts.[25c]

The selective decarboxylation[19] of a carboxylic acid in preference to acetic acid is a consequence of the fragmentation of carboxylatolead species. These are involved in the propagation step (16) and, to a lesser extent, in the initiation steps (13, 14). Such homolyses

(22) It has been commonly assumed[3,5–8] that a Pb(IV) ester such as II and III decomposes directly. The possibility of a bimolecular reaction involving hydrogen (or electron) transfer cannot yet be ruled out, *e.g.*

$$RCO_2H + AcOPb^{IV} \longrightarrow [RCO_2\cdots H\cdots AcOPb] \longrightarrow R\cdot + CO_2 + (HOAcPb^{III})^+ \text{ etc.} \quad (13a)$$

(23) (a) Pyridine contributes to the formation of a moderately efficient initiator. Reactions inhibited by oxygen will reinitiate themselves in the presence of pyridine. It does not appear to affect the nature of the products. (b) Until such species as IIb [*cf.* J. P. Fackler, *J. Am. Chem. Soc.*, **84**, 24 (1962); **86**, 5132 (1964); *Inorg. Chem.*, **1**, 266 (1963)] are actually isolated and examined, pyridine assistance in the homolysis is speculative. The labilization by coordination of Pb(IV) toward homolysis is not known. However, increased polarization interaction in the Pb–N bond compared to Pb–O or the formation of anionic complexes would reduce the positive charge in the vicinity of the Pb atom and may lead to an oxidation–reduction reaction: R. S. Nyholm and M. L. Tobe, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963). An effect of ligands from a similar point of view in the related Sn and Hg systems has been expressed by R. E. Dessy, *et al.* [*J. Am. Chem. Soc.*, **85**, 1812 (1963); **86**, 28 (1964)], though 1-equiv. changes are not involved.

Pyridine catalysis can also be partially operative through a species such as III or $Pb^{IV}(OAc)_5^-$ and related species

$$Pb(OAc)_4 + RCO_2H \rightleftharpoons Pb(OAc)_4(HO_2CR)^{25}$$

$$Py + Pb(OAc)_4(HO_2CR) \rightleftharpoons PyH^+ + Pb(OAc)_4(O_2CR)^- \rightleftharpoons AcO^- + IIa \text{ etc.}$$

The effect of bases such as pyridine and triethylamine is more profound than simply that of providing acetate for III and related ions. Addition of lithium acetate up to 3 *M* to lead(IV) acetate in glacial acetic acid causes a minor hypsochromic shift in the ultraviolet absorption spectrum (shoulder, 280 mμ). Small amounts of triethylamine, however, cause a marked shift and in much greater proportion relative to its concentration. Pyridine could not be examined owing to its cutoff at 290 mμ.

(24) (a) The selective decarboxylations observed[3,17b] in glacial acetic acid can be so accounted (see, however, footnote[19] and *vide infra*). Furthermore, the propagation step (16) requires a carboxylatolead(III) complex, unless it too[22] is bimolecular, *i.e.*

$$RCO_2H + Pb^{III} \longrightarrow R\cdot + CO_2 + (HPb^{II})^+ \quad (16a)$$

(b) L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960); (c) E. A. Evans, J. L. Huston, and T. H. Norris, *J. Am. Chem. Soc.*, 74, 4985 (1952); (d) *cf.* also G. B. Bachman and J. W. Wittman, *J. Org. Chem.*, **28**, 66 (1963).

(25) (a) J. D. Bacha and J. K. Kochi, unpublished results. (b) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965). (c) Substitutive decarboxylation of acids promoted by lead(IV) acetate and a variety of anionic species is under investigation.

of Pb(IV) and Pb(III) esters probably involve simultaneous two-bond cleavages to generate Pb(III) and Pb(II), carbon dioxide, and alkyl radicals directly, rather than a simple homolysis to an acyloxy radical intermediate.[26] This postulate invokes the stability of the incipient alkyl radical as a driving force for the homolysis.

Multibond cleavages have been discussed by Bartlett and co-workers[27] as they pertain to the homolysis of peresters. Szwarc[28] has presented an interesting thermochemical argument. He relates the one-bond *vs.* multibond rupture of diacyl peroxides to the thermodynamic stability of the resultant alkyl radicals. Peroxides derived from primary carboxylic acids such as acetic, propionic, and *n*-butyric acids were considered to thermolyze to two acyloxy radicals. Those constituted from secondary and more highly substituted moieties such as isopropyl, benzyl, trityl, etc., underwent multibond rupture. His conclusion with regard to diacetyl peroxide, however, has been recently challenged by Goldstein.[29] The importance of solvation to account for the difference has not been assessed.[30] Nonetheless, it is clear that diacetyl peroxide decomposes more slowly than secondary, tertiary, and more highly substituted diacyl peroxides. The stability of the incipient alkyl radicals plays a major role in affecting the rate of decomposition: CH_3 < primary < secondary < tertiary, etc. The energetics of acyloxy rupture have only been estimated, but the relative rates of cleavage of *t*-alkoxy radicals can be measured. Methyl fragmentation is at least a factor of 10^2 slower than other alkyl radicals.[14b] Applied to the homolysis of Pb(IV) esters, this is certainly a minimum value since the activation energy of the former process is particularly low (~4–5 kcal./mole).[31] A similar order is found in transfer reactions which yield alkyl radicals.[32]

The *propagation* of the free-radical chain reaction is dependent on the efficiency of steps 16 and 17. Pb(III) compounds are unknown,[33] and it is not unreasonable to expect these species to decompose to the stable Pb(II) ester and free radicals (eq. 16, 16a). Pb(III) as metastable intermediates have been speculatively postulated earlier[5] to disproportionate. Recently, Wang, *et al.*,[34] reduced triethyllead(IV) cation by one-electron reductants such as Ti(III) and biscyclopentadienyliron(II) to the hypothetical triethyllead(III). The latter spontaneously yielded Pb(II) and ethyl radical.

$$(C_2H_5)_3Pb^{III} \longrightarrow (C_2H_5)_2Pb^{II} + C_2H_5\cdot \qquad (21)$$

The reduction (eq. 17) of Pb(IV) by alkyl radicals formed in the disproportionation step 16 is without direct precedent. However, lead(IV) acetate is reduced by

$$R\cdot + Pb^{IV} \longrightarrow [R^+] + Pb^{III} \qquad (22)$$

Ce(III), diphenylpicrylhydrazyl, and Co(II) in 1-equiv. processes.[35] The reduction of triethyllead(IV) by Ti(III), Fe(II), and V(II) compounds is probably analogous.[34] Sn(III), the Vth period analog of Pb(III), has recently been formulated as an intermediate in radical chain reductions and additions with trialkyltin hydrides.[36]

The general concept of oxidation of a free radical by a metal salt has ample chemical support,[37] especially with respect to Cu(II) and Fe(III) compounds. The reduction potential of Pb(IV)–Pb(III) is unknown. It is difficult to compare it to either the Cu(II) or Fe(III) couple, especially in nonaqueous solutions. Chemically, however, certain qualitative estimates of Pb(IV) as a 1-equiv. oxidant can be made. Butenes and butyl esters derived from pentanoic acids are products of oxidation, and butanes are products of reduction. There is no longer any doubt that alkyl radicals and not alkylcarbonium ions are the primary intermediates in these reactions. We postulate that butanes arise from butyl radicals by either direct chain transfer from hydrogen donors (eq. 19), or reduction[31b] to carbanionic intermediates followed by protonation, or both. We strongly disfavor hydride transfer to a butyl cation as a route to butane.[3,38]

n-Valeric and isovaleric acids decarboxylate at a relatively slow rate compared to 2-methylbutyric acid. The chain length associated with the decomposition of secondary and tertiary acids is undoubtedly longer than that involved with primary acids.[39] Moreover, the formation of sizable yields of *n*-butane and isobutane indicate that oxidation of primary alkyl radicals by Pb(IV) occurs less readily than *sec*-butyl radicals. The latter also yields less butane and more butenes. From *sec*-butyl radicals high yields of butyl esters coincide with favorable formation of butenes. This is consistent with low yields of both butyl esters and butenes from primary radicals. The ease of oxidation of alkyl radicals obtained qualitatively in this manner

(26) (a) Starnes[1] has also made a case against acyloxy radicals as intermediates, and considers participation as a driving force. (b) However, in unusual cases oxidations without decarboxylation have been reported (ref. 1, footnotes 11, 12, 13) in aliphatic systems. However, ionic acyloxylations as an alternative route to Pb(IV) decompositions should be considered (see ref. 53, *vide infra*).

(27) P. D. Bartlett and R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1764 (1960).

(28) M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publication, New York, N. Y., 1962, p. 153 ff.

(29) M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964).

(30) *Cf.* C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

(31) (a) A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957); (b) J. K. Kochi and P. Mocadlo, *ibid.*, **30**, 1134 (1965).

(32) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p. 108 ff.

(33) Electron spin resonance studies are in progress.

(34) C. H. Wang, H. G. Pars, and P. L. Levins, *Tetrahedron Letters*, 687 (1964).

(35) (a) L. H. Sutcliffe and J. Walkley, *Nature*, **178**, 999 (1956); (b) D. Benson, *et al.*, *Discussions Faraday Soc.*, **29**, 60 (1960); (c) *Trans. Faraday Soc.*, **56**, 246 (1960).

(36) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964); H. G. Kuivila, "Advances in Organometallic Chemistry," F. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964.

(37) (a) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962); (b) C. H. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc.* (London), **A239**, 214 (1957); (c) E. Collinson, F. S. Dainton, *et al.*, *Discussions Faraday Soc.*, **29**, 188 (1960); (d) H. E. De La Mare, J. Kochi, and F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963); (e) J. K. Kochi, *ibid.*, **85**, 1958 (1963); (f) F. Minisci, *Gazz. chim. ital.*, **89**, 1910, 1943, 1202, 2428, 2440 (1959), and later papers.

(38) We could find no evidence of rearrangement[3] in the butane fraction. Thus, isovaleric acid gave only isobutane. Butane and normal butenes observed by Mosher and Kehr[3] under more drastic conditions may have arisen from methyl addition to propylene formed from the cleavage of isobutyl radicals, or difficulty in mass spectral analysis of such a mixture.

(39) The formation of alkane formally involves no reduction of Pb(IV). Mechanistically, however, Pb(IV) will be affected by its mode of formation. If solvent is involved as a hydrogen donor and subsequently oxidized, Pb(IV) will be converted to Pb(II). However, if butyl radicals are reduced by Pb(III) or less likely Pb(II), or if the solvent radicals derived above are not oxidized, no change in Pb(IV) equivalence is obtained by alkane formation. In our studies, oxidation of solvent (carboxylic acid) will not have been noticed because of work-up procedures. For this reason, the over-all yield[18] must be interpreted with caution.

can be compared to the values of the ionization potential of alkyl radicals. The latter increase in the order[40]: tertiary < secondary < primary; for example, *n*-butyl (199 kcal./mole), isobutyl (197 kcal./mole), *sec*-butyl (182 kcal./mole), and *t*-butyl (169 kcal./mole). Of the two steps involved in the propagation sequence, the oxidation (eq. 17) of alkyl radicals by Pb(IV) is rate-limiting, particularly with primary alkyl moieties.

It can be argued that esters, alkanes, alkenes, and alkylbenzenes do not all arise from alkyl radicals but from different intermediates and *via* different mechanisms. The generally high yields of esters from secondary and tertiary acids in contrast to high yields of alkanes and alkylbenzenes from primary acids may be due to simultaneous and competing 2-equiv. and 1-equiv. processes, respectively. Such a dualism cannot be operative in these systems. The decarboxylation of the secondary as well as the primary acids is strongly inhibited by oxygen, though the inhibition *period* is shorter with the former. Esters as products from the secondary acid can be virtually eliminated in the presence of oxygen. For example, the formation of methyl ethyl ketone and *sec*-butyl alcohol is in accord with the interception of *sec*-butyl radicals with oxygen and subsequent decomposition of the *sec*-butylperoxy radical. The partial pressure of oxygen in benzene at

$$CH_3CH_2CHCH_3 + O_2 \longrightarrow CH_2CH_2\underset{\underset{O_2\cdot}{|}}{C}HCH_3$$

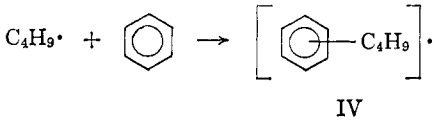
$$CH_3CH_2\underset{\underset{O_2\cdot}{|}}{C}HCH_3 \longrightarrow CH_3CH_2COCH_3 + CH_3CH_2CH(OH)CH_3, \text{ etc.}$$

81° is undoubtedly low. Product yield alone is not a reliable measure of the presence of butyl radicals, since even under high oxygen pressure butane is a minor but significant product. Furthermore, it is extremely unlikely that a simple transposition of a methyl group from the β- or γ-position to the α-position of butyric acid would effect such a drastic change in mechanism from a 1-equiv. to a 2-equiv. process. Moreover, as a general principle, *yields* of products cannot be truly diagnostic of a free-radical chain mechanism of any sizable chain length. The termination process could make only a relatively minor contribution to the over-all yield. The *rate* of reaction, on the other hand, is highly dependent on the termination process(es). Thus, the lack of any noticeable difference in yields of products from the oxidative decarboxylation of norbornane-2-carboxylic acid[8] in the presence of oxygen could be interpreted as due to a long kinetic chain (*i.e.*, facile oxidation (eq. 17) of the 2-norbornyl radical by Pb(IV) to the stable carbonium ion).

Extensive rearrangement of the butyl moiety is observed among butenes and butyl esters as products of oxidation. In addition to butene-1, *trans*- and *cis*-butene-2 is formed from *n*-valeric acid. No significant amount of carbon rearrangement is observed in the butene fraction from isovaleric acid. Similarly, the *n*-butyl moiety yielded small but significant amounts of *sec*-butyl esters. Even smaller amounts of *sec*-butyl ester were obtained from the isobutyl moiety. Other investigators[3,8,41] have noted rearrangement of the alkyl moiety in the ester fraction. The *sec*-butyl moiety from 2-methylbutyric acid is partitioned between acetate and 2-methylbutyrate as esters roughly in proportion to the mole fraction of acetate and 2-methylbutyrate in the medium.

Electron transfer rather than ligand transfer appears to be the predominant path to ester and alkene formation in the oxidation step (17). Corey and Casanova[8] concluded that 2-norbornyl cations were formed from lead(IV) acetate and both *endo*- and *exo*-norbornane-2-carboxylic acids.[42] In addition to the Pb(IV) oxidation of an alkyl radical, step 18 in the *termination* mechanism involves Pb(III) as an oxidant. The extent to which this mode contributes to the products will depend on the chain length of the reaction. The relative importance of electron transfer and ligand transfer with Pb(III) as an oxidant is not necessarily related to oxidations with Pb(IV).

The *butylbenzenes* derived from decarboxylations in benzene as solvent are unique in the retention of the structural integrity of the butyl moiety. No rearrangement was observed with *sec*-butyl or isobutyl fragments. Less than 3% *sec*-butylbenzene contaminated the *n*-butylbenzene derived from *n*-valeric acid. These results are in marked contrast to the extensive rearrangement of primary alkyl groups commonly observed in electrophilic substitutions.[43] We postulate that alkylbenzenes are derived from a free-radical intermediate IV, which is oxidized further by lead.[44] Such a process has been discussed[45] with respect to



(23)

IV

$$IV + Pb^{IV,III} \longrightarrow C_4H_9C_6H_5 + H^+ + Pb^{III,II} \quad (24)$$

Cu(II). Aromatic compounds have been previously acetoxylated and methylated in the nucleus with lead tetraacetate.[46] The former has been accomplished with compounds like polycyclic aromatics and aryl ethers which are susceptible to electrophilic substitution.[47–49] The latter is operative with aromatics such as polynitrobenzenes and chlorobenzene which are

(40) (a) R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1525 (1962). (b) Ionization potentials are reported only for the gas phase. Solvation will undoubtedly modify these values, but probably not the relative values. (c) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(41) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963).

(42) However, they attributed partial retention of optical activity in the norbornyl acetate product to the intervention of classical and bridged carbonium ions. We do not feel their study of a solvent effect is sufficient to eliminate the possibility that unrearranged product can arise *via* a ligand-transfer oxidation of the norbornyl radical, especially in view of the exceedingly rapid rearrangement of the norbornyl cation recently observed by M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5860 (1964). Clearly, more work is required to resolve this interesting dichotomy.

(43) R. M. Roberts, *Chem. Eng. News*, **43**, [4] 96 (1965).

(44) Nothing is implied about whether IV is a π- or σ-complex. Further studies are in progress.

(45) J. K. Kochi and R. D. Gilliom, *J. Am. Chem. Soc.*, **86**, 5251 (1964).

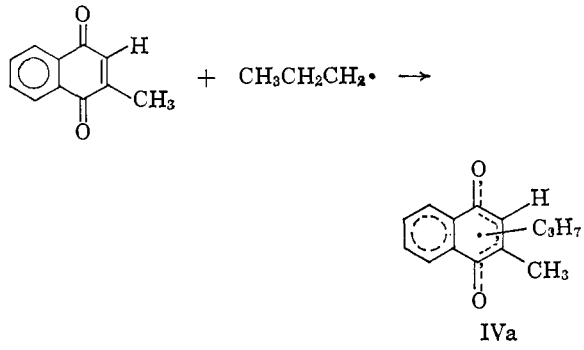
(46) R. Criegee, *Angew. Chem.*, **70**, 173 (1958); "Newer Methods of Preparative Organic Chemistry," Vol. 2, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, p. 368 ff.

(47) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 1893, 2542 (1938); **61**, 1565 (1939); L. F. Fieser and S. T. Putnam, *ibid.*, **69**, 1038, 1041 (1947); K. H. Meyer, *Ann.*, **379**, 73 (1911).

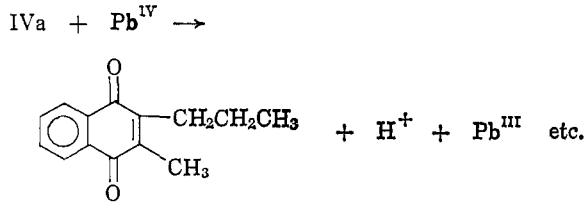
(48) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1404 (1955); H. E. Barron, *et al.*, *Chem. Ind.* (London), 76 (1954).

(49) P. B. D. DeLaMare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 160 ff.

much less prone to cationic substitution but undergo homolytic substitution relatively easily.[50,51] Nuclear acetoxylation of aromatic compounds presumably proceeds *via* an ionic mechanism.[52,53] Methylation, alkylation, and arylation probably occur *via* free-radical processes such as eq. 23, 24, etc. The latter mechanism can be applied with slight modification to the facile alkylation of quinones discovered by Fieser and Chang.[54,55] Significantly, no rearrangement of alkyl groups was observed; for example



(25)



(26)

Lower yields of products obtained from decarboxylations induced by pyridine are probably due to alkylation of pyridine[50a] and subsequent loss during work-up.

Catalysis by Copper Salts. Copper salts are particularly effective oxidants of alkyl radicals.[37] The bimolecular reaction between *n*-butyl radicals and Cu(II) in glacial acetic acid is more than 10^4 times faster than hydrogen abstraction reactions. Butyl radical has been studied with such active hydrogen donors as chloroform, aldehydes, and allylic ethers.[56] Butene-1 is formed quantitatively from *n*-butyl radical, isobutylene from isobutyl radical, and a nearly statistical mixture of butene-1, *trans*-butene-2, and *cis*-butene-2 from *sec*-butyl radical.[37e] The foregoing results obtained with radicals produced from peroxides are the same as those obtained in the present study from lead(IV) carboxylates. The catalysis by copper salts is consistent with the mechanism presented in eq. 13–19 if one considers the relatively slow and inefficient oxidation of *n*-butyl and isobutyl radicals by Pb(IV). This rate-limiting oxidation is superseded by the efficient oxidation (eq. 27) by Cu(II). It operates in conjunction with the fast reoxidation (eq. 28) of Cu(I) by Pb(IV). The absence of the usual products formed during Pb(IV) oxidation is also in accord with the high efficiency of Cu(II) as a radical scavenger.[37d] The complete interception of all alkyl radicals by Cu(II)

$$C_4H_9\cdot + Cu^{II} \longrightarrow C_4H_8 + H^+ + Cu^I \quad (27)$$

$$Cu^I + Pb^{IV} \longrightarrow Cu^{II} + Pb^{III} \text{ etc.} \quad (28)$$

is shown even with the *sec*-butyl radical which is reasonably prone to oxidation by Pb(IV).

Although quantitative estimates are not yet available, the chain length of the free-radical process (eq. 27, 28, and 16) in the presence of copper salts is long. It is a consequence of bypassing the inefficient oxidation (eq. 17) by Pb(IV). This is shown qualitatively by the copper-catalyzed decomposition of Pb(IV) in the absence of pyridine. Initiation under these conditions is relatively slow. Nonetheless, after a short buildup time, the copper-catalyzed reaction proceeds at a rapid clip (*e.g.*, Figures 3 and 4), although it is exceedingly sensitive to inhibition by oxygen.

The validity of the mechanism of the copper-catalyzed reactions proposed in the propagation sequence (eq. 27, 28, and 16) is supported by the spontaneous reduction of lead(IV) esters by copper(I) acetate. In acetic acid, acetonitrile–acetic acid mixtures, or benzene solutions, lead(IV) acetate and 2-methylbutyric acid react rapidly at 25° with copper(I) acetate or copper(II) acetate–copper metal combination to yield a mixture of butene-1, *trans*-butene-2, and *cis*-butene-2 in a relative molar proportion 46–50, 26–30, and 24–26, respectively. The yields of combined butenes in the stoichiometric reactions are low (10–20%) compared to the catalytic reaction described previously. The complementary reaction is given by eq. 29. *n*-Valeric acid yields butene-1 (3–5%) and isovaleric acid yields isobutylene

$$Pb(O_2CR)_4 + 2Cu^I \longrightarrow Pb(O_2CR)_2 + 2Cu^{II}O_2CR \quad (29)$$

(2–4%) together with small amounts of methane derived from the acetic acid. With these primary acids reduction of Pb(IV) to Pb(II) without decarboxylation is the principal course (eq. 29). The low yields of butenes obtained in this manner are mainly due to the high instantaneous concentration of Cu(I), in contrast to the low steady-state concentration of this species in the catalytic reaction. Under such circumstances, the competitive diversion of the Pb(III) intermediates by reduction (eq. 30) obviates the formation of butyl radicals by fragmentation.[57] The higher yields of butenes from the secondary (2-methylbutyric) acid compared to the primary (*n*-valeric or isovaleric) acids probably reflect the more facile fragmentation (eq. 16) of the corresponding carboxylatolead(III) species. This is consistent with the selectivity discussed earlier.

$$Pb^{III}(O_2CR)_3 + Cu^I \longrightarrow Pb^{II}(O_2CR)_2 + Cu^{II}O_2CR \quad (30)$$

Trapping the Butyl Radical with Butadiene. Butyl radicals produced in the decomposition of valeryl

(50) (a) D. H. Hey, J. M. Stirling, and G. W. Williams, *J. Chem. Soc.*, 2747 (1954); 3963 (1955); (b) D. I. Davies, *ibid.*, 2351 (1963); (c) J. W. Cornforth and E. Cookson, *ibid.*, 1085 (1952).

(51) (a) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960, p. 45, 99 ff; (b) B. R. Knowles, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

(52) (a) D. R. Harvey and R. O. C. Norman, *ibid.*, 4860 (1964). (b) Side-chain acetoxylation is a free-radical process: G. W. K. Cavill and D. H. Solomon, *ibid.*, 3943 (1954); D. I. Davies, *ibid.*, 2352 (1963).

(53) Acid catalyses in acetoxylation and glycol cleavage have been interpreted as diagnostic of ionic reactions (*i.e.*, Pb(IV)–Pb(II) by direct 2-equiv. change): R. P. Bell and W. A. Waters, *ibid.*, 1696 (1958); H. B. Henbest, D. N. Jones, and G. P. Slater, *ibid.*, 4472 (1961). Rearrangement is also observed: K. Alder, F. H. Flock, and H. Wirtz, *Ber.*, **91**, 609 (1958).

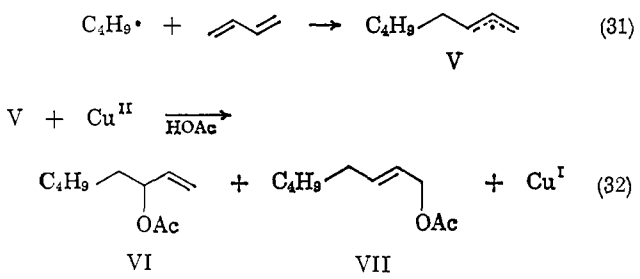
(54) L. F. Fieser and F. C. Chang, *J. Am. Chem. Soc.*, 64, 2043 (1942).

(55) "Promoters" used by Fieser can be construed as compounds which are easily decarboxylated or oxidized by Pb(IV) to Pb(III). Better yields would probably be obtained under oxygen-free conditions.

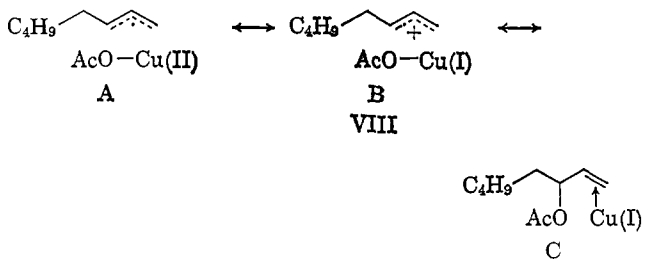
(56) J. K. Kochi and R. V. Subramanian, to be published.

(57) The *ca.* 50° temperature difference may also be important in determining the relative rates of fragmentation (eq. 16) compared to reduction (eq. 30), provided the activation energy difference (eq. 29, 30) for the primary is larger than that of the secondary system.

peroxide can be trapped with 1,3-butadiene.[37e] In the presence of copper salts the resultant octenyl radicals V have been oxidized to a mixture of isomeric allylic acetates. 3-Acetoxyoctene-1 (VI) and 1-acetoxyoctene-2 (VII) have been obtained in a relative proportion of 85:15 in benzene and acetic acid solutions.[58] In the presence of 2 *M* pyridine, the same reaction yielded

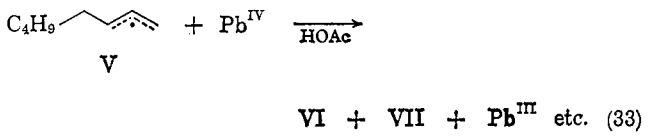


the octenyl acetates in a relative proportion: VI (55) and VII (45).[58] The formation of *identical mixtures* of octenyl acetates from the decomposition of valeric acid, butadiene, and lead(IV) acetate indicates that similar intermediates are involved in both reactions.[58] The oxidation of allylic radicals by copper(II) acetate has been described as proceeding *via* a transition state VIII, which has electron-transfer and ligand-transfer



components.[59] Complexing the Cu(II) oxidant with pyridine, phenanthroline, and acetonitrile decreases the contribution from VIIIC, and electron-transfer oxidation is essentially obtained.[58,59]

The formation of octenyl acetates VI and VII in equimolar amounts, albeit in low yields, from lead(IV) acetate is consistent with an electron-transfer oxidation discussed earlier with alkyl radicals. This reaction is also marked by the formation of higher telomers, $C_4H_9(C_4H_6)_nOAc$, owing to the inefficient oxidation (eq. 33) by Pb(IV).



Conclusions

The decarboxylation of the pentanoic acids by lead(IV) acetate in benzene solutions is a free-radical chain reaction, based on rate studies, oxygen inhibition, and copper salt and peroxide catalysis, together with product analysis. Alkyl radicals and Pb(III) species are principal and vital intermediates. Butyl radicals are oxidized by Pb(IV) and Pb(III) to esters and alkenes much less efficiently than they are oxidized by Cu(II) to alkenes. Owing to inefficient oxidation by Pb(IV), butyl radicals competitively form butanes by hydrogen abstraction and butylbenzenes by a quasi-homolytic substitution, and are trapped by butadiene and oxygen. In general, decarboxylation of secondary and more highly branched carboxylic acids are less susceptible to oxygen inhibition than primary acids owing to the more efficient initiation (eq. 15) and oxidation steps (eq. 17). Butenes are formed in excellent yields from decarboxylations carried out in the presence of copper salts.

Experimental

Materials. n-Valeric, isovaleric, and *2-methylbutyric acids* (Eastman Kodak reagent grade) were redistilled before use. Each was converted to its methyl ester by treatment with methanol and sulfuric acid catalyst and analyzed by gas chromatography. Both *n*-valeric acid and isovaleric acid were greater than 99% isomerically pure. However, 2-methylbutyric acid was contaminated with isovaleric acid (7%) which could not be separated by distillation. The presence of the isovaleric acid impurity in the 2-methylbutyric acid was corrected for in the final analysis.

Authentic *esters* were prepared from the acid chloride and the alcohols in ether with pyridine as catalyst. *n*-Valeryl, isovaleryl, and 2-methylbutyryl chlorides were Eastman Kodak reagent grade and redistilled through a 4-ft. glass-helix-packed column. The latter acid chlorides were not separated by distillation and each contained the other as impurity. *sec*-Butyl, isobutyl, and *n*-butyl alcohols (Eastman reagent grade) were treated with each of the acid chlorides and the nine esters separately characterized by gas chromatography. *t*-Butyl isovalerate was synthesized as described.[60]

Isobutyl and *sec-butylbenzene* were Eastman reagent grades; *cumene* and *t-butylbenzene*, Phillips Petroleum Co. research grade. *Butadiene-1,3* was from Phillips Petroleum Co., pure grade, distilled twice and dried over calcium chloride; glacial *acetic acid*, DuPont Co. reagent; *benzene*, Mallinckrodt analytical reagent; *acetonitrile*, Matheson Coleman and Bell, redistilled from phosphorus pentoxide; *pyridine*, Reilly Co. redistilled twice from potassium hydroxide.

Lead tetraacetate, G. F. Smith Co., was recrystallized twice from glacial acetic acid containing 3% acetic anhydride, sucked dry in a Büchner funnel, and dried in a vacuum desiccator over potassium hydroxide. It was used as a free-flowing colorless crystalline solid and care was exercized to avoid exposure to moisture and light. Analysis by iodometric titration[5] indicated 98% $Pb(OAc)_4$. *Cupric acetate* hydrate $Cu(OAc)_2 \cdot H_2O$ was Mallinckrodt analytical reagent grade; *3-acetoxyoctene-1* and *1-acetoxyoctene-2* were characterized with authentic samples.[58]

Oxidative Decarboxylation of Valeric Acid with Lead(IV) Acetate. General Procedure. Into a 50-ml. round-bottom $^{14}/_{20}$ ₮ flask equipped with a short 8-mm. side arm was added 4 ml. (3.76 g.) of valeric acid, 2.0 g. (4.5 mequiv.) of lead(IV) acetate, and 15 ml. of benzene. It was attached with a glass capillary tubing *via* a three-way stopcock to a mercury-filled eudiometer. A rubber septum was placed over the side arm and a

(58) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, 30, 1862 (1965).
(59) J. K. Kochi, *J. Am. Chem. Soc.*, 84, 774, 2785, 3271 (1962).
(60) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 144.

hypodermic needle inserted, through which a slow stream of argon or prepurified nitrogen was passed. In this manner, the solution, the free space, and the gas buret were thoroughly purged of oxygen. The vessel was placed in a constant temperature bath (81 ± 0.5°) and stirred magnetically. Gas evolution was followed volumetrically. Gas evolution is a reasonable measure of the rate of these reactions since supersaturation is a minor problem. High reproducibility is limited more by conditions than measurements. It is sufficient to point out certain pertinent features of the decompositions.

When the reaction was complete, the reaction vessel was placed in an ice bath followed by a Dry Ice bath and the evolved gases were transferred back quantitatively. The reaction vessel was capped with a rubber septum, and the hydrocarbons in the gas and liquid phases were analyzed by gas chromatography. Finally a marker was added, and the total amounts of hydrocarbons were determined by the internal standard method. Butane and butenes were analyzed on a 10-ft. Dowtherm A–firebrick column (isobutane, 7.9 min.; *n*-butane, 10.5 min.; isobutylene and butene-1, 13.4 min.; *trans*-butene-2, 19.2 min.; *cis*-butene-2, 22.4 min.) and a 15-ft. silver nitrate–benzyl cyanide–firebrick column (isobutane, 6.4 min.; *n*-butane, 8.3 min.; *trans*-butene-2, 17.0 min.; isobutylene, 17.8 min.; butene-1, 23.4 min.; *cis*-butene-2, 28.6 min.).

The benzene solution was washed with excess water and dilute perchloric acid and sodium carbonate solution and dried over sodium sulfate. It was analyzed by gas chromatography (Aerograph HiFy, hydrogen flame ionization detector) with (A) diethylene glycol succinate–firebrick, (B) carbowax 4M–Bentone–Chromosorb P, and (C) dodecyl phthalate–HMDS–Chromosorb P columns. Column C was used to separate *sec*-butyl acetate (17.1), isobutyl acetate (20.0), and *n*-butyl acetate (27.4). Column A was used to resolve isobutylbenzene (34.3), *sec*-butylbenzene (35.7), *t*-butylbenzene (36.4), and *n*-butylbenzene (49.4). Column B separated the esters: *sec*-butyl acetate (10.5) and *sec*-butyl 2-methylbutyrate (23.7), *sec*-butyl isovalerate (27.5) and isobutyl isovalerate (30.6); *sec*-butyl valerate (38) and *n*-butyl valerate (62.4). Column B was also used to separate the butylbenzenes, and column A the esters.

Esters were analyzed quantitatively with ethyl butyrate as an internal standard. Total ester was also determined by saponification and agreed with the gas chromatographic results within 5%. The butylbenzenes were analyzed with ethylbenzene as an internal standard. They were the only outstanding components after the reaction mixture was subjected to Claisen's alkali for 2 hr. at 40°. Qualitative identification was effected by examination of the infrared spectrum of samples isolated by gas chromatography.

Reactions conducted with pyridine were allowed to equilibrate in the bath for periods from 30 min. to 2 hr. with no apparent difference. To start decarboxylation, pyridine was injected into the reaction mixture with a hypodermic syringe. The reactions with copper(II) acetate as catalyst were run by first dissolving copper(II) acetate (150–350 mg.) in the pure acid (4 ml.) with gentle warming and swirling, then diluting with benzene followed by lead(IV) acetate. These solutions were quickly flushed to prevent extraneous oxidation. The products from the reaction degassed by the standard freeze–thaw technique were the same as those obtained from flushing with inert gas.

Valeric Acid and Butadiene with Lead(IV) Acetate. 1,3-Butadiene was bubbled through the solution until it was saturated, and an atmosphere of pressure was maintained over the reaction during decomposition of lead(IV) acetate. Alternatively, butadiene was condensed into the chilled reaction mixture and the decompositions carried out in sealed glass bombs at 80°. Although yields of octenyl acetates were higher under the latter conditions, the composition of the mixture represented by 3-acetoxyoctene-1 and 1-acetoxyoctene-2 was invariant. The composition of the octenyl acetate is characteristic of the metal salt employed as oxidant, whether it be lead(IV), copper(II), or copper(II)–pyridine complex. Butane and butene fractions were not characterized. The octenyl acetates were analyzed by gas chromatography; diethylene glycol succinate–firebrick: 3-acetoxyoctene-1 (20) and 1-acetoxyoctene-2 (39) with ethyl 2-ethylhexanoate (16) as marker. They were characterized by comparison with authentic samples.

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