# Oxidation of Alkyl Radicals from Decarboxylation of Acids by Lead(IV) and Copper(II)

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Structural effects on the oxidation of alkyl radicals from decarboxylation of acids by $\mathrm{Pb^{IV}}$ and $\mathrm{Cu^{II}}$ are examined. Cumyl, α- and β-phenylpropyl, β-phenethyl, benzyl, heptenyl, and allyl radicals were generated from the corresponding acids by thermal and photochemical decarboxylation with $\mathrm{Pb^{IV}}$ acetate. Oxidation of radicals by $\mathrm{Pb^{IV}}$ and $\mathrm{Cu^{II}}$ correlate roughly with ionization potentials of the radicals in the gas phase. A variety of tertiary and secondary α-aralkyl radicals are readily oxidized by both oxidants and carbonium ions as intermediates are indicated. $\mathrm{Pb^{IV}}$ is more selective toward benzyl and allyl radicals than $\mathrm{Cu^{II}}$, benzyl radical being particularly slow to be oxidized. Electron-releasing substituents in the aromatic nucleus greatly enhance the ease of oxidation of benzyl radicals, and a large negative Hammett $\rho$ value is indicated for the oxidation. Electron-transfer and ligand-transfer mechanisms are compared in the oxidation of benzyl radicals by $\mathrm{Pb^{IV}}$.

Acids are decarboxylated by $\mathrm{Pb^{IV}}$ acetate[1] *via* a free-radical chain mechanism.[2] The relevant steps in the propagation sequence have been proposed as given in eq 1 and 2. The reaction can be induced thermally or

$$\mathrm{R\cdot + Pb^{IV}O_2CR \longrightarrow [R^+] + Pb^{III}O_2CR} \qquad (1)$$

$$\mathrm{Pb^{III}O_2CR \longrightarrow Pb^{II} + R\cdot + CO_2} \quad \text{etc.} \qquad (2)$$

photochemically.[3] Barring differences in temperature, equivalent results are obtained in these two processes if cognizance is taken of the more efficient initiation and, thus, higher steady-state concentrations of radicals in the latter operation.

With the exception of tertiary alkyl and aralkyl radicals, most alkyl radicals are not efficiently oxidized (eq 1) by $\mathrm{Pb^{IV}}$ and often products derived from other facile free-radical reactions are obtained. Thus, in benzene solutions, alkanes and alkylbenzenes are major products derived from secondary and primary acids and $\mathrm{Pb^{IV}}$ *via* nonoxidative routes. Oxidation products in the form of alkenes and esters are minor.

Various alkyl radicals are oxidized by $\mathrm{Cu^{II}}$ in a second-order process which is close to diffusion controlled.[4] The second-order rate constant for the

$$\mathrm{R\cdot + Cu^{II} \longrightarrow [R^+] + Cu^{I}} \qquad (3)$$

oxidation of tertiary alkyl radicals by $\mathrm{Cu^{II}}$ in glacial acetic acid is $10^9$ l./mole sec. Primary alkyl radicals are oxidized only ten times slower than their tertiary counterpart, and these facile reactions have extraordinarily low activation energies. Alkenes are major products from the oxidation of primary alkyl radicals by $\mathrm{Cu^{II}}$ in glacial acetic acid.

$\mathrm{Cu^{II}}$ carboxylates catalyze the decarboxylation of acids by $\mathrm{Pb^{IV}}$.[2] The catalysis is important with primary acids, less so with secondary acids and practically nil with tertiary acids. The catalysis is related to the efficient scavenging of alkyl radicals by $\mathrm{Cu^{II}}$ (eq 3). Subsequent rapid reoxidation of the $\mathrm{Cu^{I}}$ by $\mathrm{Pb^{IV}}$ regenerates $\mathrm{Pb^{III}}$ and thereby sustains the chain

$$\mathrm{Cu^{I} + Pb^{IV} \longrightarrow Cu^{II} + Pb^{III}} \quad \text{etc.} \qquad (4)$$

process. In the catalytic scheme, eq 3, 4, and 2 replace eq 1 and 2 in the propagation sequence. It follows from this mechanism that primary alkyl radicals are the slowest to react with $\mathrm{Pb^{IV}}$ and tertiary radicals the fastest. This trend is consistent with the relative ionization potentials of alkyl radicals.[5] The mechanism for the catalytic effect further implies that structural variations of the alkyl radical are more important to oxidation by $\mathrm{Pb^{IV}}$ than $\mathrm{Cu^{II}}$. Moreover, we conclude that rates of oxidation of primary and secondary alkyl groups by $\mathrm{Cu^{II}}$ are faster than $\mathrm{Pb^{IV}}$.

The addition of $\mathrm{Cu^{II}}$ obviates the formation of alkanes and alkyl benzenes derived by hydrogen transfer and homolytic substitution of primary and secondary alkyl radicals from $\mathrm{Pb^{IV}}$ decarboxylation. These catalyzed reactions can be utilized synthetically to generate alkenes from primary and secondary acids.[6]

The decarboxylation of acids by $\mathrm{Pb^{IV}}$, thus, offers a convenient and readily available source of alkyl radicals. We wish to utilize this reaction in a comparative study of the oxidation of a variety of alkyl radicals with $\mathrm{Pb^{IV}}$ and $\mathrm{Cu^{II}}$.

## Results and Discussion

The principal products from the oxidation of a series of selected types of alkyl radicals investigated in this study are summarized in Table I. All of these free radicals were generated from the thermolysis of the corresponding carboxylic acid in the presence of lead tetraacetate, with the exception of cumyl radical which for comparison was also generated from cumene by the perester reaction. Each reaction was also examined for copper catalysis. In most cases, photochemical decarboxylation of the same acids with $\mathrm{Pb^{IV}}$ was reexamined at 30° with irradiation at 3500 A. Comparable results with distinctive variations from the thermal decarboxylations were obtained. These results, together with a presentation and discussion of catalysis and inhibition of the decarboxylation, follow in the text for each alkyl radical examined.

**The Oxidation of Cumyl Radicals.**—α,α-Dimethylphenylacetic acid was readily decarboxylated by $\mathrm{Pb^{IV}}$ at 60 or 80° in a 16 vol. % acetic acid–benzene solution. The primary products were cumyl acetate (65%) and α-methylstyrene (13%).[7] The latter is slowly oxidized by $\mathrm{Pb^{IV}}$ to phenylacetone.[8] The rate of decarboxyla-

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[1] Hereafter also referred to as $\mathrm{Pb^{IV}}$. Ligands will be understood to be carboxylato and will not be included, except when it is pertinent to the discussion.

[2] J. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

[3] J. Kochi, J. Bacha, and T. Bethea, III, *ibid.*, **89**, 6538 (1967).

[4] J. Kochi and R. Subramanian, *ibid.*, **87**, 4855 (1965).

[5] R. Taubert and F. Lossing, *ibid.*, **84**, 1523 (1962).

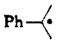
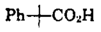
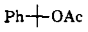
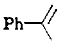
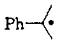
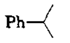
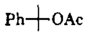
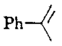
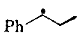
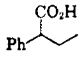
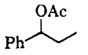
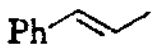
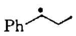
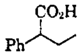
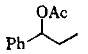
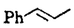
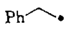
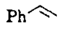
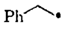
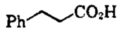
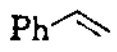
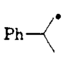
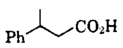
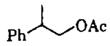
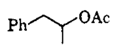
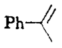
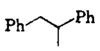
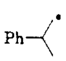
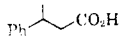
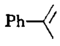
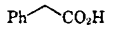
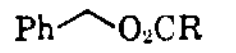
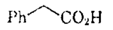
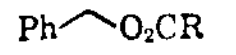
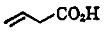
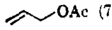
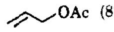
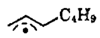
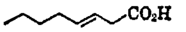
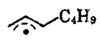
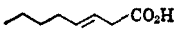
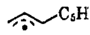
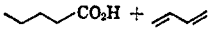
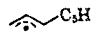
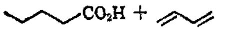
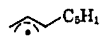
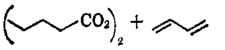
[6] J. Bacha and J. Kochi, *Tetrahedron*, to be published.

[7] All yields are based on moles of products per mole $\mathrm{Pb^{IV}}$, irrespective of stoichiometry.

[8] H. Hock and H. Kropf, *Ber.*, **91**, 1681 (1958).

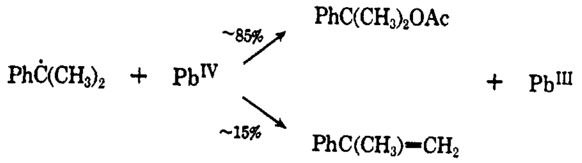
TABLE I

SUMMARY OF OXIDATION OF SELECTED ALKYL RADICALS BY $Pb^{IV}$ AND $Cu^{II}$ IN BENZENE–ACETIC ACID SOLUTIONS[a]

| | | | Products, % yield[b] | |
|---|---|---|---|---|
| Radical | Source | Oxidant | Esters[c] | Hydrocarbons |
|  |  | $PB^{IV}$ |  (74) |  (14) |
|  |  | $Cu^{II}$ |  (54) |  (21) |
|  |  | $Pb^{IV}$ |  (90) |  (5)[d] |
|  |  | $Cu^{II}$ ($Pb^{IV}$) |  (69) |  (18)[d] |
|  |  | $Pb^{IV}$ |  (1) | PhEt (7)<br> (0.2)<br> (22) |
|  |  | $Cu^{II}$ ($Pb^{IV}$) | |  (47) |
|  |  | $Pb^{IV}$ |  (1)<br> (13) |  (1)<br> (13) |
|  |  | $Cu^{II}$ ($Pb^{IV}$) | |  (40) |
| $PhCH_2\cdot$ |  | $Pb^{IV}$ |  (60) | $Ph_2CH_2$ (2)<br> (0.2) |
| $PhCH_2\cdot$ |  | $Cu^{II}$ ($Pb^{IV}$) |  (60) | $Ph_2CH_2$ (1)<br> (1) |
| p-$MeOC_6H_4CH_2\cdot$ | p-$CH_3OC_6H_4CH_2CO_2H$ | $Pb^{IV}$ | p-$MeOC_6H_4CH_2OAc$ (99) | |
| α-Naphthyl $CH_2\cdot$ | α-$C_{10}H_7CH_2CO_2H$ | $Pb^{IV}$ | α-$C_{10}H_7CH_2OAc$ (71) | |
| p-$O_2NC_6H_4CH_2\cdot$ | p-$O_2NC_6H_4CH_2CO_2H$ | $Pb^{IV}$ | p-$O_2NC_6H_4CH_2OAc$ (1) | |
|  |  | $Pb^{IV}$ |  (76) |  (13) |
|  |  | $Cu^{II}$ ($Pb^{IV}$) |  (87) |  (5) |
|  |  | $Pb^{IV}$ | $C_7H_{13}OAc$ (51)[e] | |
|  |  | $Cu^{II}$ ($Pb^{IV}$) | $C_7H_{13}OAc$ (81)[e] | |
|  |  | $Pb^{IV}$ | $C_8H_{15}OAc$[e,f] | |
|  |  | $Cu^{II}$ ($Pb^{IV}$) | $C_8H_{15}OAc$[e,f] | |
|  |  | $Cu^{II}$ | $C_8H_{15}OAc$[e,g] | |

[a] See text for experimental conditions. [b] Yields are based on moles of product per mole $Pb^{IV}$ consumed; for other products see text. [c] In addition to analogous esters derived from carboxylic acid. [d] Mixture of *cis* and *trans* isomers. [e] Mixture of allylic isomers; see text for isomeric distribution under different conditions. [f] See ref 2. [g] See ref 25.

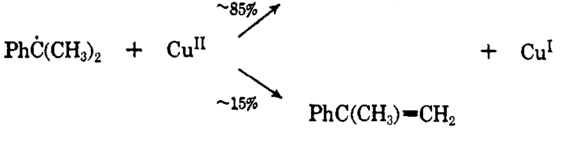
tion was increased threefold by pyridine (2 moles per $Pb^{IV}$) and $Cu^{II}$ acetate (0.2 mole). The yields of products were enhanced but the distribution was largely unchanged. The latter was also insensitive to temperature since a photochemical reaction at 30° produced 78% cumyl acetate and 12% α-methylstyrene.



$$Ph\dot{C}(CH_3)_2 + Pb^{IV} \rightarrow \begin{cases} \xrightarrow{\sim 85\%} PhC(CH_3)_2OAc \\ \xrightarrow{\sim 15\%} PhC(CH_3){=}CH_2 \end{cases} + Pb^{III}$$

Cumyl acetate and α-methylstyrene are also principal products from the oxidation of cumene by *t*-butyl peracetate catalyzed by $Cu^{II}$ acetate at 80°.[9] Under solvent conditions comparable to those employed in the $Pb^{IV}$ decarboxylation of dimethylphenylacetic acid, a 75% material balance could be accounted for as a mixture of cumyl acetate (72%) and α-methylstyrene (28%). The yields of both of these products were adjusted for a side reaction which converted cumyl acetate to α-methylstyrene in the presence of acetic acid.

It has been shown that the perester reaction is a free-radical chain process[10] in which alkoxy radicals abstract hydrogen from cumene. The cumyl radicals are oxidized by $Cu^{II}$ to α-methylstyrene and α-cumylacetate as part of the propagation sequence. The validity of this comparison with $Pb^{IV}$ decarboxylations rests on the assumption that the oxidation of α-cumyl radical by $Cu^{II}$ is the only source of α-methylstyrene.



$$Ph\dot{C}(CH_3)_2 + Cu^{II} \rightarrow \begin{cases} \xrightarrow{\sim 85\%} PhC(CH_3)_2OAc \\ \xrightarrow{\sim 15\%} PhC(CH_3){=}CH_2 \end{cases} + Cu^{I}$$

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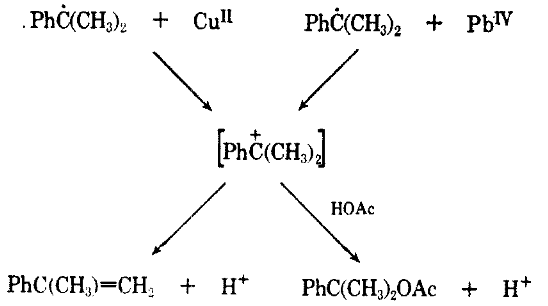
(9) C. Walling and A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963.)

(10) J. Kochi, *Tetrahedron*, **18**, 483 (1962); *J. Am. Chem. Soc.*, **84**, 774 (1962).

However, if abstraction occurs to any significant degree at the $\beta$ position, oxidation of the resulting $\beta$-cumyl radical would be expected to lead to the exclusive production of additional $\alpha$-methylstyrene, since $Cu^{II}$ oxidation of primary radicals generally leads only to olefin. Walling has reported[11] that the chlorination of cumene with *t*-butyl hypochlorite at 40° resulted in 81% $\alpha$ chlorination and 19% $\beta$ chlorination. Since the products of chlorination are determined by a preceding step involving hydrogen abstraction at the cumene side chain by *t*-butoxy radical, exclusive $\alpha$ abstraction does not take place. Thus, some $\alpha$-methylstyrene in the per ester reaction at 81° almost certainly resulted from reaction at the $\beta$ position of cumene.

Despite these and other ambiguities inherent in examining the oxidation of $\alpha$-cumyl radicals derived from $Pb^{IV}$ decarboxylations and $Cu^{II}$ per ester oxidations, certain gross comparisons can be made. It is noteworthy that $Pb^{IV}$ and $Cu^{II}$ oxidize cumyl radicals to a mixture containing approximately the same amounts of cumyl acetate and $\alpha$-methylstyrene. The indistinguishability of these oxidants, in this regard, is consistent with the formulation of a common intermediate. The cumyl cation formed by an electron-transfer reaction can be partitioned to products in a subsequent step independent of the oxidant.



**Oxidation of *sec*-Benzylic Radicals.**—2-Phenylbutyric acid was smoothly decarboxylated by $Pb^{IV}$ in 30 vol. % acetic acid–benzene solutions. After 10 hr at 81° the uncatalyzed reaction yielded 84% 1-phenyl-1-propyl acetate and 4% of a 4:96 mixture of *cis*- and *trans*-$\beta$-methylstyrene.

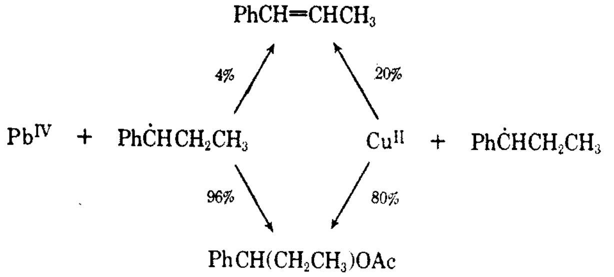
The addition of pyridine enhanced the reaction rate and increased the yield of oxidation products without significantly changing their distribution. After 2.3 hr, the pyridine-catalyzed decarboxylation produced 90% 1-phenyl-1-propyl acetate and a mixture of the above olefins in 5% yield.

Photolytic decarboxylation of 2-phenylbutyric acid at 3500 A and 30° readily produced 92% of the major product $\alpha$-phenylpropyl acetate and (1%) *cis*- and (5%) *trans*-$\beta$-methylstyrene in solutions of 20 vol. % acetic acid–benzene.

In addition to increasing the rate of thermal decarboxylation by a factor of two, $Cu^{II}$ (0.2 mole/mole of $Pb^{IV}$) altered the distribution of products. The yields of *cis*- and *trans*-$\beta$-methylstyrene were enhanced at the expense of the acetate. In 5 hr at 81°, the $Cu^{II}$ reaction yielded 16–19% $\beta$-methylstyrene and 65–74% 1-phenyl-1-propyl acetate. Although minor variations were observed, the distribution of products was essentially independent of $Cu^{II}$ concentration and composition of the benzene–acetic acid solvent system in the range studied.

If both cupric acetate and pyridine were added to the system, extremely rapid decarboxylation took place at 81°. $Pb^{IV}$ was consumed in less than 30 min, and a quantitative yield of $CO_2$ and oxidation products was observed. The distribution of products fell between those observed with $Cu^{II}$ and pyridine individually.

The catalysis of the $Pb^{IV}$ decarboxylation of 2-phenylbutyric acid by $Cu^{II}$ is attributed to the interception of the secondary $\alpha$-phenylpropyl radicals by $Cu^{II}$. According to this interpretation, $Cu^{II}$ in comparison with $Pb^{IV}$ oxidizes secondary $\alpha$-benzylic radicals by promoting alkenes. It is noteworthy that the ratio of *cis*- to *trans*-propenyl benzene is not changed appreciably by temperature or oxidant.



The difference between $Pb^{IV}$ and $Cu^{II}$ oxidation of secondary $\alpha$-aralkyl radicals may be more pronounced than indicated above. For example, the homologous $\alpha$-phenylpentyl radical can be derived from rearrangement of $\epsilon$-phenylpentyl radical in $Cu^{II}$-catalyzed decompositions of bis-$\epsilon$-phenylcaproyl peroxide.[12] Oxidations of such radicals in glacial acetic acid at 50° yielded two to three times as much 1-phenylpentene-1 as 1-phenylpentyl acetate. The apparent inconsistency in the distribution of alkene and ester in $Pb^{IV}$–$Cu^{II}$ decarboxylations *vs.* the decomposition of peroxides by $Cu^{II}$ cited above may result from incomplete exclusion of $Pb^{IV}$ oxidation in the former. The distribution observed then may be the summation of effects by $Pb^{IV}$ and $Cu^{II}$ and reflects only the degree to which both oxidants are involved.

**Oxidation of $\beta$-Aralkyl Radicals.**—The decarboxylation of hydrocinnamic and $\beta$-phenylbutyric acids by $Pb^{IV}$ exhibited characteristics usually associated with primary aliphatic acids. Reactions were slow and products from $\beta$-phenylethyl and $\beta$-phenylpropyl radicals were principally alkanes and alkylbenzenes. Acetic acid used as a partial solvent with benzene underwent significant decarboxylation and yielded toluene and benzyl acetate among other products.[13]

The pyridine-catalyzed decarboxylation of hydrocinnamic acid in 7 vol. % acetic acid–benzene at 81° consumed $Pb^{IV}$ only after 10 hr and yielded ethylbenzene (7%), bibenzyl (22%), toluene (14%), and benzyl acetate (3%) as major products. Only small amounts of oxidative decarboxylation products, styrene (0.2%) and 2-phenylethyl acetate (0.9%), were observed.

A small amount of 1-phenylpropyl acetate (0.8%) was produced from the reaction of styrene and lead tetraacetate.[13b] Similarly, styrene and hydrocinnamic acid with $Pb^{IV}$ in acetic acid solutions afforded 1,4-

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(11) C. Walling and B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).

(12) J. Kochi and R. Gilliom, *ibid.*, **86**, 5251 (1964).

(13) (a) R. Criegee, "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York (1965), p 312 ff; (b) p 288 ff.

diphenylbutyl acetate and 1,4-diphenylbutene-1 probably by the following route.

$$Pb^{III}O_2CCH_2CH_2Ph \longrightarrow Pb^{II} + CO_2 + PhCH_2CH_2\cdot$$

$$PhCH_2CH_2\cdot + PhCH{=}CH_2 \longrightarrow PhCH_2CH_2CH_2\dot{C}HPh$$

$$PhCH_2CH_2CH_2\dot{C}HPh + Pb^{IV} \longrightarrow$$

$$PhCH_2CH_2CH{=}CHPh + PhCH_2CH_2CH(Ph)OAc + Pb^{III} \text{ etc.}$$

The photolytic decarboxylation of hydrocinnamic acid, like the thermal reaction, was relatively slow, and $Pb^{IV}$ was consumed only after 6 hr of irradiation. The major products were ethylbenzene (17%) and bibenzyl (25%) and the oxidation products were produced in lesser amounts (~5%). Toluene, benzyl acetate, methane (10%), and ethane (<1%) resulted from competitive decarboxylation of acetic acid in benzene.[13] *n*-Propylbenzene (3%) probably arose from coupling of methyl and phenylethyl radicals.

$Cu^{II}$ acetate greatly increased (at least a factor of 10) the rate of decarboxylation of hydrocinnamic acid by $Pb^{IV}$. After 5 hr at 81°, the decarboxylation yielded 47% styrene and increased yields of products derived from further reaction of styrene, *i.e.*, β-methylstyrene (1%) and 1-phenylpropyl acetate (3%). The yields of other products were reduced to less than 1% each. The addition of both $Cu^{II}$ and pyridine resulted in rapid decarboxylation (less than 20 min) and produced a similarly high yield of styrene products.

The pyridine-catalyzed decarboxylation of 3-phenylbutyric acid in solutions of 7 vol. % acetic acid in benzene at 81° produced only small amounts of the normal oxidation products, α-methylstyrene (0.7%) and 2-phenyl-1-propyl acetate (9.7%). Toluene (12%), cumene (6%), 2,3-diphenylpropane (13%), benzyl acetate (2%), and 1-phenyl-2-propyl acetate (13%) were the major products. In addition, small amounts (0.4–0.8%) of *n*-propylbenzene, allylbenzene, β-methylstyrene, and α-cumyl acetate were also observed. The rate of reaction was dependent upon pyridine concentration and the composition of the benzene–acetic acid solvent system.

The $Pb^{IV}$ decarboxylation of 3-phenylbutyric acid conducted photolytically at 30° produced the same complex mixture of products observed thermally. All $Pb^{IV}$ was consumed only after 7 hr of irradiation. Cumene (16%) and 1,2-diphenylpropane (13%) and 1-phenyl-1-propyl acetate (11%) were the major products. Normal oxidation products, α-methylstyrene (0.3%) and 2-phenyl-1-propyl acetate (1%), were formed in lesser amounts in addition to *n*-propyl- (0.6%), allyl- (1%), and *sec*-butylbenzenes (3%). The latter is derived from β-phenylpropyl and methyl radicals. Toluene (9%), benzyl acetate (1%), and methane (8–10%) also resulted from the competitive decarboxylation of acetic acid.

When cupric acetate was added to the system (without pyridine), catalysis by a factor of ten was observed. α-Methylstyrene (35–40%) was the main product. The yields of other products observed in the pyridine-catalyzed reaction were reduced to less than 1% each. No β-methylstyrene was produced in the $Cu^{II}$ reaction. The yield of α-methylstyrene was dependent on the composition of the benzene–acetic acid solvent system. When both pyridine and $Cu^{II}$ were added, very rapid decarboxylation took place and α-methylstyrene (43%) was essentially the exclusive product. All of these decarboxylations were complicated by the facile reaction of α-methylstyrene with $Pb^{IV}$ acetate to produce mainly phenylacetone. The loss of α-methylstyrene was most important in the slower decarboxylations.

The rearranged product, 1-phenyl-2-propyl acetate, was generated only in the absence of $Cu^{II}$. *n*-Propylbenzene is the only other product clearly derived from the rearrangement of the β-phenylpropyl moiety. Both cations and radicals are implicated in the decarboxylation mechanism, and, since phenyl migration may occur by both radical and cationic routes, the answer as to which intermediate was involved in rearrangement is not unequivocal.

β-Aralkyl radicals, like other primary alkyl radicals, were only inefficiently oxidized by $Pb^{IV}$, since aralkanes and similar products not related to oxidation were found. Furthermore, like typical primary aliphatic acids, the thermal and photochemical decarboxylations of the parent acid were slow and had short chain lengths. In the presence of $Cu^{II}$, on the other hand, there was catalysis by a factor of five to ten. Only products such as styrene and α-methylstyrene derived from the oxidation of β-phenethyl and β-phenylpropyl radicals, respectively, were observed. It is clear that $Cu^{II}$ is superior to $Pb^{IV}$ in the oxidation of these radicals.

**Oxidation of Benzyl Radicals.**—The decarboxylation of phenylacetic acid by $Pb^{IV}$ proceeded at an unusually slow rate in comparison to other benzylic systems. Its rate of decarboxylation was comparable to that of primary aliphatic acids which were among the slowest acids studied. This anomalous behavior was not due to impurities since careful purification of the acid by several independent methods had no effect.

After 80 hr at 81° in 30 vol. % acetic acid–benzene only 42% $Pb^{IV}$ had disappeared. The products of decarboxylation were benzyl acetate (62%), benzaldehyde (6%), and benzilidene acetate (4%), in addition to minor amounts of toluene (3%), diphenylmethane (2%), and bibenzyl (0.2%). Benzilidene acetate was derived from acetylmandelic acid in a side reaction, and became more important as excess phenylacetic acid was employed. Acetylmandelic acid was quantitatively decarboxylated by $Pb^{IV}$ to benzilidene acetate which partially formed benzaldehyde under the conditions of the reaction.

$$PhCH_2CO_2H \xrightarrow{Pb^{IV}} PhCH(OAc)CO_2H \xrightarrow{Pb^{IV}} PhCH(OAc)_2 + CO_2 \qquad (5)$$

The photolytic decarboxylation at 3500 A of 0.65 *M* phenylacetic acid by 0.068 *M* $Pb^{IV}$ resulted in complete reduction of $Pb^{IV}$ and the production of a high yield (90% material balance) of decarboxylation products in 7 hr at 30°. Benzyl acetate (19%) and benzyl phenylacetate (40%) were the major products. Coupling (bibenzyl, 18%) and aromatic substitution (diphenylmethane, 12%) products were formed in lesser amounts, together with only traces of toluene.

When the photolysis was conducted in 30 vol. % acetic acid in benzene, phenylacetic acid (0.16 *M*) and $Pb^{IV}$ (0.13 *M*) yielded benzyl acetate (20%), bibenzyl (17%), and diphenylmethane (2%), together with 5% ethylbenzene and other products derived from competitive decarboxylation of acetic acid.

Significantly, the addition of $Cu^{II}$ had no effect on the rate of decarboxylation of phenylacetic acid by

$Pb^{IV}$ and only slightly enhanced the yields of *all* the products obtained otherwise. $Cu^{II}$ (5%) also showed little effect on the photochemically induced decarboxylation of phenylacetic acid by $Pb^{IV}$.

These studies indicate that high yields of benzyl radicals are obtained by decarboxylation of the acid and competitive decarboxylation of acetic acid is not a significant factor in the low rates observed. Unlike other primary acids, phenylacetic acid produced very little alkane (toluene) and relatively high yields of dimer (bibenzyl). The latter is not usually an important product from primary acids even under photolytic (3500 A) conditions.

We conclude from the low rates of decarboxylation, high yields of oxidation products, and other studies (see Experimental Section) that the oxidation of benzyl radicals by $Pb^{IV}$ is a relatively slow reaction. The same is also true of $Cu^{II}$ as oxidant. We find both of these conclusions rather surprising, since the ionization potential of benzyl radicals (7.76 ev)[14a] is close to that of *sec*-butyl and 2-pentyl radicals.[14b]

**Oxidation of Substituted Benzyl Radicals.**—Like the parent compound, phenylacetic acid, *p*-chloro- and *p*-nitrophenylacetic acid were also resistant to normal oxidative decarboxylation by lead tetraacetate. In the case of *p*-chlorophenylacetic acid, only 10% of the $Pb^{IV}$ was consumed at 81° in 21 hr. Although *p*-nitrophenylacetic acid eventually consumed all $Pb^{IV}$ (~54 hr), less than 3% of the primary oxidation product, *p*-nitrobenzyl acetate, and no reduction product, *p*-nitrotoluene, could be found. Nitro compounds are known to undergo facile aromatic substitution by free radicals produced in lead tetraacetate reactions.[15] However, no attempt was made to identify such products from these reactions.

In marked contrast, *p*-methoxyphenylacetic acid and α-naphthylacetic acid were readily decarboxylated by $Pb^{IV}$ and produced the anticipated acetates in excellent yields.

The decarboxylation of 0.20 *M* *p*-methoxyphenylacetic acid by 0.10 *M* $Pb^{IV}$ in 17 vol. % acetic acid–benzene was catalyzed by pyridine and cupric ion. Whereas the uncatalyzed reaction was complete in 70–90 min, added pyridine or $Cu^{II}$ acetate reduced the reaction time to 15 and 60 min, respectively. *p*-Methoxybenzyl acetate was formed quantitatively in these reactions.

A small amount of oxygen strongly retarded the decarboxylation of *p*-methoxyphenylacetic acid. After introducing 3 ml of oxygen into the reaction and observing retarded $CO_2$ evolution for 2 hr, the reaction could be flushed free of oxygen with nitrogen and reinitiated at its original rate. This acid is, therefore, decarboxylating by the same radical chain process as its congeners.

α-Naphthylacetic acid (0.20 *M*) was completely decarboxylated by 0.14 *M* $Pb^{IV}$ in 30 vol. % acetic acid–benzene at 80° in approximately 15 hr. α-Naphthylmethyl acetate was found in 70–80% yields and was the only product identified.

The effect of ring substitution on the oxidation of benzyl radicals by $Pb^{IV}$ and $Cu^{II}$ is remarkable. Electron-withdrawing substituents such as *p*-chloro and *p*-nitro retard the oxidation of benzyl radicals to the extent that products of oxidation are not observed in any significant quantities. Benzyl radical itself is only slowly oxidized by $Pb^{IV}$ or $Cu^{II}$ to benzyl acetate.

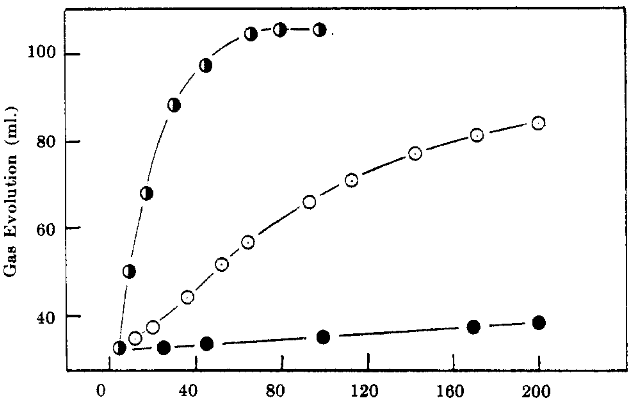
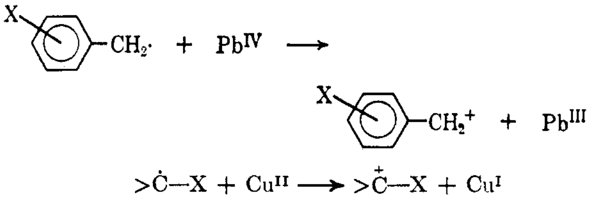


Figure 1.—Relative rates of gas evolution from the thermal (81°) decarboxylation of ● phenylacetic acid, ⊙ α-naphthylacetic acid, and ◑ *p*-methoxyphenylacetic acid.

The presence of electron-releasing groups, such as *p*-methoxy, on the other hand, enhances the rate of oxidation by $Pb^{IV}$ to a degree which is comparable to tertiary alkyl and secondary α-aralkyl radicals. Further extension of the aromatic system to include the α-naphthylmethyl system also has a beneficial effect. The relative rates of oxidative decarboxylation of these acids are shown in Figure 1.

Furthermore, acids such as mandelic, acetylmandelic, and 2-phenylbutyric, which generate benzylic radicals with hydroxy, acetoxy, and alkyl groups in the α position, also readily undergo oxidative decarboxylation with $Pb^{IV}$.

The strong negative polar effect of substituents either in the α or nuclear positions can best be explained in terms of an electron-transfer reaction between the benzyl radical and $Pb^{IV}$ or $Cu^{II}$ (eq 6 and 7). The marked sensitivity of the electron-transfer reactions to positive polar groups has been discussed previously with regard to α substitution on alkyl radicals.[16] Thus, cyano,[17] carbonyl, and halogen groups on the α position of alkyl radicals were found to discourage oxidation by electron-transfer reagents such as $Cu^{II}$ acetate.[4,18] Alkyl and aryl substituents were found generally to facilitate electron-transfer reactions.



(6)

$$>\dot{C}\text{—}X + Cu^{II} \longrightarrow >\overset{+}{C}\text{—}X + Cu^{I} \qquad (7)$$

The same effect of substituents has been observed in the ionization potentials of benzyl radicals.[19] Ionization potentials are linearly correlated with $\sigma^+$ param-

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[14] (a) F. Lossing, K. Ingold, and I. Henderson, *J. Chem. Phys.*, **22**, 621, 1948 (1954); (b) J. de Sousa and F. Lossing, *J. Am. Chem. Soc.*, **81**, 281 (1959).

[15] L. Fieser and F. Chang, *ibid.*, **64**, 2043 (1942); L. Fieser, R. Clapp, and W. Daudt, *ibid.*, **64**, 2052 (1942).

[16] J. Kochi and F. Rust, *ibid.*, **84**, 3946 (1962).

[17] J. Kochi and D. Mog, *ibid.*, **87**, 522 (1965).

[18] The deleterious effect of such substituents has also been observed in the enhanced ionization potential (gas phase) of alkyl radicals which progressively increases with substitution of cyano groups: R. F. Pottie and F. P. Lossing, *ibid.*, **83**, 4737 (1961).

[19] A. Harrison, P. Kebarle, and F. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961).

eters and the $\rho$ value is $-20$! Since heats of formation of benzyl radicals are almost independent of the substituent,[20] the value of $-20$ for $\rho$ can be attributed to the susceptibility of the energy of ion-pair formation in the gas phase to the electronic effect of substituents. Electron-transfer oxidation of benzyl radicals by $Pb^{IV}$ appears to have a similarly high susceptibility to substituent effects since the differences in ionization potential of radicals which are readily oxidized (*p*-methoxybenzyl, 6.8 ev; $\alpha$-naphthylmethyl, 7.3 ev) are not much greater than benzyl (7.7 ev) radicals or those radicals [*p*-chloro, 7.95 ev; *p*-nitro, 8.7 ev (extrapolated)] which are not oxidized.[21]

**Ligand-Transfer Oxidation of Benzyl Radicals. Conversion to Benzyl Chlorides.**—Although electron-transfer reactions are subject to polar substituents, ligand-transfer reactions are relatively insensitive to these factors.[22] Earlier studies showed that acids in the absence of air could be chlorodecarboxylated by chloride salts.[23] This reaction is conducted essentially under the same conditions employed for oxidative decarboxylations by $Pb^{IV}$ and involves a free-radical chain sequence. Alkyl chlorides produced in this manner were considered to arise *via* a ligand-transfer reaction between alkyl radicals and a chloro $Pb^{IV}$ complex (eq 8). In this manner, it is possible to test

$$R\cdot + Pb^{IV}Cl \longrightarrow RCl + Pb^{III} \text{ etc.} \qquad (8)$$

the ease of ligand-transfer oxidation of benzyl radicals by $Pb^{IV}Cl$, in contrast to electron-transfer oxidation with $Pb^{IV}$ carboxylates.

When an equivalent amount of lithium chloride was added to the 0.11 *M* $Pb^{IV}$ reactions of 0.35 *M* phenylacetic, *p*-chlorophenylacetic and *p*-nitrophenylacetic acids in 17 vol. % acetic acid–benzene, rapid decarboxylation (~30 min at 80°) was observed (eq 9).

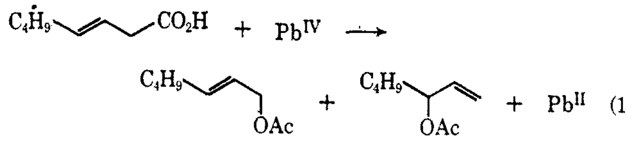
$$ArCH_2CO_2H + Pb^{IV} + Cl^- \longrightarrow ArCH_2Cl + Pb^{II} + H^+ + CO_2 \qquad (9)$$

It was accompanied by the production of excellent yields of the corresponding benzyl chlorides (*p*-nitro, 80%; *p*-chloro, 90–95%; unsubstituted, 90–95%). Thus, while oxidative decarboxylation of these acids was not easily effected by $Pb^{IV}$, chlorodecarboxylation proceeded readily.

The chlorodecarboxylation could also be effected on an incomplete oxidative decarboxylation of phenylacetic acid. Thus, after more than 500 min in the 81° bath, the reaction was removed from the bath, lithium chloride added, and the mixture reflushed with nitrogen. Although a lower yield (80%) of benzyl chloride was realized, there was no apparent difference in the rate of $CO_2$ evolution from an uninterrupted chlorodecarboxylation. Therefore, nothing was formed in the oxidative decarboxylation of phenylacetic acid by $Pb^{IV}$ which inhibited the chlorodecarboxylation.

These results support earlier studies which indicated that benzyl radicals are readily formed by decarboxylation of phenylacetic, *p*-chlorophenylacetic, and *p*-nitrophenylacetic acids with $Pb^{IV}$. High yields of the benzyl chlorides obtained in the chlorodecarboxylation reflect the ease with which these radicals can be oxidized by ligand-transfer processes. It further points up the importance of polar effects in electron-transfer oxidations as they pertain to oxidation of benzyl radicals by $Pb^{IV}$ and $Cu^{II}$.[24]

**Oxidation of Allylic Radicals. 3-Octenoic Acid.**—Oxidative decarboxylation of 0.15 *M* 3-octenoic acid by 0.088 *M* $Pb^{IV}$ in 17 vol. % acetic acid–benzene at 81° yielded as major products a 40:60 mixture of 3-acetoxyheptene-1 (21%) and 1-acetoxyheptene-2 (30%), which were the only products investigated (eq 10).



(10)

While the uncatalyzed decarboxylation was slow (16 hr) with a moderate excess of 3-octenoic acid, the reaction could be accelerated by increasing the acid/$Pb^{IV}$ ratio. The increased rate, however, had no effect on either the yield of heptenyl acetates or the distribution of isomers. This independence of yield and distribution is cited as evidence that the esters are not destroyed either together or preferentially since the acid concentration determines the facility with which the decarboxylation takes place. The less than quantitative yield of $CO_2$ observed in the uncatalyzed reactions suggests that oxidant was lost to nondecarboxylative processes. The good correpondence between $CO_2$ liberated and heptenyl acetate afforded, however, implies that more than 80% of the decarboxylation product was observed as acetates.

Besides causing a moderate (less than twofold) increase in rate of $CO_2$ evolution and reducing the amount of $CO_2$ liberated, the addition of pyridine to the system reduced the yield (30%) and virtually reversed the distribution of heptenyl acetates to a 55:45 mixture of 3 and 1 isomers. As above, the rate of the pyridine reaction was accelerated with increased acid while the yield and distribution of acetates were unaffected. Thus, the observed distribution is probably real and heptenyl acetate products were not consumed.

Cupric acetate had a large catalytic effect on this decarboxylation. Although the uncatalyzed reaction was less than 85% complete in 16 hr, quantitative $CO_2$ was produced with 7% $Cu^{II}$ in 1 hr. Moreover, the yield of $C_7$ acetates was increased to 68% 3-acetoxyheptene-1 and 13% 1-acetoxyheptene-2 (85:15). The addition of 0.0063 *M* $Cu^{II}$ and 0.087 *M* pyridine caused a further increase in rate (20 min) and produced 45% 3-acetoxyheptene-1 and 24% 1-acetoxyheptene-2 (65:35).

The distribution of isomeric heptenyl acetates observed from the decarboxylation of 3-octenoic acid by $Pb^{IV}$ is the same as those mixtures of isomers generated in other allylic systems. Butyl radicals derived from the thermolysis of valeryl peroxide can be trapped by 1,3-butadiene (eq 11). $Cu^{II}$ oxidation of the resulting

(11)

octenyl radicals in benzene–acetic acid produced an 85:15 mixture of 3-acetoxyoctene-1 and 1-acetoxy-

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[20] M. Szwarc, C. Leigh, and A. Sehon, *Proc. Royal Soc.* (London), **A209**, 97 (1951).

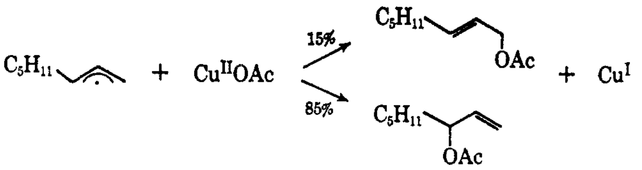
[21] Quantitative differences in rates of oxidation of benzyl radicals are not yet available.

[22] J. Kochi and D. Davis, *Nature*, **202**, 690 (1964).

[23] J. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

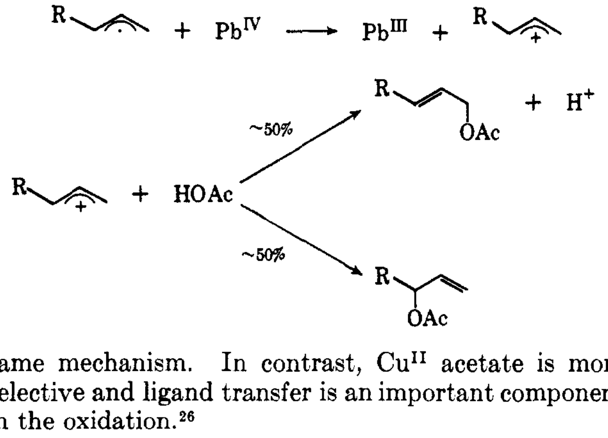
[24] J. Kochi, *Record. Chem. Progr.* (Kresge-Hooker Sci. Lab.), **27**, 207 (1966).

octene-2.[25,26] In the presence of 2 $M$ pyridine, the same reaction yielded a 55:45 mixture of the same octenyl acetates.

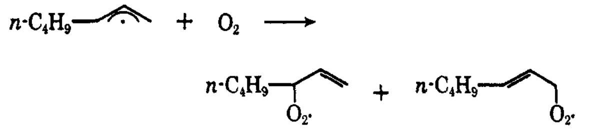


When 1,3-butadiene was added to the $Pb^{IV}$ decarboxylation of valeric acid in benzene, a low yield (5–10%) of a 49:51 mixture of 3-acetoxyoctene-1 and 1-acetoxyoctene-2 was obtained.[2] With $Cu^{II}$ added, the same reaction produced a higher yield of an 85:15 mixture of the same acetates. The addition of pyridine (1.5 $M$) to the $Cu^{II}$–$Pb^{IV}$ system changed the acetate composition to 49:51. The results of the $Pb^{IV}$ system were interpreted as due to oxidation of octenyl radicals formed by the addition of butyl radicals to 1,3-butadiene.[2]

The distribution of heptenyl acetates from the $Cu^{II}$-catalyzed decarboxylation of 3-octenoic acid by $Pb^{IV}$ is virtually identical with the distribution of octenyl acetates from the $Cu^{II}$ oxidation of octenyl radicals from peroxides. The distribution of heptenyl acetates in the uncatalyzed 3-octenoic acid decarboxylation is similar to octenyl acetate distribution from the 1,3-butadiene–valeric acid–$Pb^{IV}$ acetate reaction.[2] Moreover, the direction of the redistribution of the isomeric heptenyl acetates on changing the oxidant from $Cu^{II}$ to $Cu^{II}$ pyridine is the same as that observed for the octenyl acetates in the related systems. These striking parallels are cited as strong evidence for the intermediacy of an allylic heptenyl radical in the $Pb^{IV}$ decarboxylation of 3-octenoic acid. The distribution of isomeric acetates derived by oxidation of the allylic radical intermediate by metallic oxidants has been discussed at length.[25] Suffice it to mention here, we believe that oxidation of allylic radicals by $Pb^{IV}$ generates carbonium ions by an electron-transfer mechanism. $Cu^{II}$ pyridine effects oxidation by the same mechanism. In contrast, $Cu^{II}$ acetate is more selective and ligand transfer is an important component in the oxidation.[26]



Oxygen had no effect on the rate of $CO_2$ evolution from the uncatalyzed 3-octenoic acid decarboxylation. Failure to remove atmospheric oxygen or addition of oxygen to a flushed reaction resulted in the same rate as that of the normal flushed reaction. Added or residual oxygen, however, caused a severe reduction in the heptenyl acetate yield and the appearance of at least five new peaks on the glpc chromatogram, two of which were identified as the allylic alcohols, 3-hydroxyheptene-1 (1.8%) and 1-hydroxyheptene-2 (2.5%). Heptenyl radicals are evidently trapped by oxygen (eq 12),



(12)

and the heptenylperoxy subsequently disproportionates to heptenyl alcohols, as well as ketonic and aldehydic products.

We may explain the anomalous effect, in which oxygen affects the products but not the rate, as due to the slow oxidation of heptenyl radicals by $Pb^{IV}$ and an efficient initiation process (homolysis of $Pb^{IV}$ octenoate). A slow oxidation of heptenyl radicals by $Pb^{IV}$ would encourage dimerization of these radicals and also lead to a short chain process. It would permit the buildup of a sufficiently high concentration of radicals with which oxygen could react without noticeably disturbing the cyclic nature of a chain sequence. A scavenger such as oxygen would be expected to alter drastically the rate of a long radical chain oxidation process with minor effects on products. The opposite, however, is true of a short chain process which is accompanied by a facile initiation reaction.

**Vinylacetic Acid.**—The oxidative decarboxylation of vinylacetic acid was at least five times as rapid as that of 3-octenoic acid under comparable conditions. Although the vinylacetic acid utilized contained 7% crotonic acid, the increased rate cannot be attributed to the impurities, which remained intact throughout.

At 81° in 17% acetic acid–benzene with a moderate excess of vinylacetic acid (0.25 $M$) the decarboxylation by 0.11 $M$ $Pb^{IV}$ produced allyl acetate (70%) along with lesser amounts of allylbenzene (13%) and allyl vinylacetate (6%) in 3.8 hr. In benzene with a large excess of acid (1.9 $M$) the reaction yielded allyl vinylacetate (66%), allylbenzene (13%), and allyl acetate (12%). No propylene or 1,5-hexadiene (diallyl) could be detected in either of these reactions.

Definite catalysis was observed when $Cu^{II}$ (0.010 $M$) was added to the system, and $CO_2$ evolution was complete in 0.5 hr. Moreover, there resulted an over-all increase in ester products (87%) at the expense of allylbenzene (5%).

The photolytic decarboxylation of vinylacetic acid, like phenylacetic acid, was significantly slower than that of other acids (*e.g.*, tertiary acids). The reaction yielded large amounts of what could be considered radical-coupling products.[27] In 17 vol. % acetic acid–benzene with a moderate excess of vinylacetic acid (0.24 $M$), the $Pb^{IV}$ (0.11 $M$) was completely consumed only after 7 hr. The decarboxylation produced 36% diallyl and lesser amounts of allyl acetate (11%), allyl vinylacetate (0.7%), and allylbenzene (3%). Besides methane and ethane which were qualitatively observed, toluene (2%) and butene-1 (3–5%) probably arose *via* competitive decarboxylation of acetic acid and further reaction of methyl and allyl radicals. Only a trace of propylene (<0.5%) could be found.

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(25) J. Kochi and H. Mains, *J. Org. Chem.*, **30**, 1862 (1965).

(26) J. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962).

(27) The dimer derives two alkyl moieties from the acid. All yields of products including dimer are based on *moles* of product per mole of $Pb^{IV}$.

The photolyses conducted in benzene with a large excess of vinylacetic acid (0.81 *M*) consumed the oxidant in 5 hr and afforded a quantitative material balance of allyl products; 55% diallyl, 33% allyl esters, and 10% allylbenzene were observed. These conditions obviously circumvent competitive decarboxylation of acetic acid. No toluene or butene-1 could be detected. The addition of $Cu^{II}$ (5.7 mole %) to the vinylacetic acid photolysis resulted in a large increase in the ester yield (68%), primarily at the expense of the dimer (8%). Allylbenzene (6%) was influenced less.

Oxygen has no effect on either the rate of vinylacetic acid decarboxylation or the yield of allylic products at either 81 or 61°. An unflushed reaction or reactions from which atmospheric oxygen had been removed were equally rapid. No retardation of $CO_2$ evolution or reduction in product yield was observed when oxygen was introduced into a decarboxylating reaction. Moreover, no difference in rate or products was observed in the reactions conducted in a sealed glass bomb under 45 psi of oxygen at either 81 or 61°.

The ineffectiveness of oxygen in altering the course of the vinylacetic acid decarboxylation may be the result of the reversibility of the reaction between allyl radical and oxygen.[28] Allyl radical is known to combine with oxygen less readily than simple alkyl radicals by a factor of $10^8$. According to the calculations of

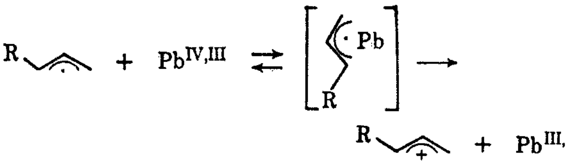
$$R\cdot + O_2 \overset{K_{eq}}{\rightleftharpoons} RO_2\cdot \qquad (13)$$

Benson[28b] at 300°K in the gas phase, $K_{eq} = 10^{13}$ when R is *t*-butyl, while $K_{eq} = 10^5$ when R is allyl (see eq 13). The difference between the behavior of allyl and heptenyl systems toward oxygen is only one of degree. In both cases oxygen does not materially affect the results, although there is evidence of some trapping of heptenyl radicals. These results resemble earlier studies on the oxidation of triphenylmethyl radical which is a similarly delocalized system.[3,28c]

The reaction initiated by light and the nature of the products are strong evidence that the decarboxylation of vinylacetic acid proceeds *via* allyl radicals.[29] Allyl radicals are not efficiently oxidized by $Pb^{IV}$ as indicated by the slow thermal and photolytic decarboxylation and high yields of dimer in the latter process. Despite the sluggish oxidation, allyl radicals generate relatively high yields of oxidation products with $Pb^{IV}$, largely owing to their preference for dimerization over hydrogen abstraction as noted by others.[29b]

In many ways, allyl and heptenyl radicals resemble benzyl radicals in electron-transfer reactions with $Pb^{IV}$. Both are oxidized, albeit slowly, and produce short kinetic chains and slow rates in the decarboxylations of the parent acid by $Pb^{IV}$. Dimerization is preferred to hydrogen abstraction when they are generated photochemically, in contrast to other tertiary alkyl and other α-aralkyl radicals.

Possibly part of this behavior may be attributed to a metastable radical–$Pb^{IV}$ complex similar to allyl[30] and benzyl[31] complexes of transition metal species (eq 14).



(14)

Benzyl lead complexes were presumed intermediates in the metathesis between $Pb^{IV}$ acetate and phenyl benzyl mercury.[32]

The parallel behavior of allylic and benzyl radicals toward $Pb^{IV}$ does not extend to $Cu^{II}$. $Cu^{II}$ is an exceedingly efficient oxidant for allylic radicals of various types and can be efficiently employed in radical chain reactions.[33] $Cu^{II}$, however, like $Pb^{IV}$, is rather indifferent to benzyl radicals. This does not follow from ionization potentials since allyl radicals (8.16 ev) have higher values than benzyl radicals (7.76 ev). Interaction between the $Cu^{II}$ and allyl radicals has been discussed at some length.

## Summary and Conclusions

Examination of a variety of alkyl radicals indicates that $Cu^{II}$ carboxylates are always at least as effective as $Pb^{IV}$ carboxylates despite their widely different oxidation potentials.[34] The efficacy with which $Pb^{IV}$ and $Cu^{II}$ oxidize alkyl radicals diverges sharply as one progresses from trityl and cumyl to tertiary aliphatic and secondary α-aralkyl to secondary aliphatic to primary aliphatic free radicals.

Cumyl radicals are oxidized equally well by $Pb^{IV}$ and $Cu^{II}$ to afford essentially the same mixture of α-methylstyrene and cumyl acetate. $Cu^{II}$ is a slightly better oxidant than $Pb^{IV}$ with secondary α-aralkyl radicals such as α-phenylpropyl, and produces higher yields of alkenes relative to esters. A variety of other secondary α-aralkyl radicals with hydroxy and acetoxy substituents are also readily oxidized by $Pb^{IV}$.

Primary radicals such as β-phenylethyl and β-phenylpropyl radicals are only ineffectively oxidized by $Pb^{IV}$. On the other hand, $Cu^{II}$ affords high yields of alkenes by oxidative elimination.

Both $Cu^{II}$ and $Pb^{IV}$ oxidize benzyl radicals slowly.[35] However, *p*-methoxybenzyl and α-naphthylmethyl radicals are readily oxidized by $Pb^{IV}$. The ligand-transfer oxidation of even such negatively substituted

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(28) (a) Reversible formation of alkylperoxy radicals have been demonstrated for triphenylmethylperoxy radicals: E. Janzen, F. Johnston, and C. Ayers, *J. Am. Chem. Soc.*, **89**, 1176 (1967). Reversibility as an explanation for the absence of an oxygen effect has been given previously.[3] (b) S. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965). (c) So far, the only acids which have not been affected by oxygen during $Pb^{IV}$ decarboxylation are those which generate extensively delocalized radicals. The latter are also those which produce thermodynamically less stable alkylperoxy radicals.

(29) (a) The formation of allylic products *via* other processes not involving allylic radicals is discounted from our studies with decarboxylation of primary acids by $Pb^{IV}$ in the presence of butadiene.[3] (b) J. McNesby and A. Gordon, *J. Am. Chem. Soc.*, **79**, 825 (1957); D. James and G. Troughton, *Chem. Comm.*, 94 (1965).

(30) M. Green and P. Nagy, *Advan. Organometallic Chem.*, **2**, 325 (1964)

(31) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); J. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965).

(32) R. Criegee, P. Dimroth, and R. Schempf, *Ber.*, **90**, 1337 (1957).

(33) J. Kochi, *Science*, **155**, 415 (1967); L. Boguslavskaya, *Russ. Chem. Rev.*, **34**, 503 (1965).

(34) Oxidation potentials in acetic acid are not known for $Cu^{II}$ or $Pb^{IV}$ acetate. We estimate the former as 0.7 ev and the latter to be at least 1.5 ev ($Pb^{IV}$–$Pb^{III}$).

(35) In this context, "slowness" and "fastness" are highly *qualitative* comparisons since these studies are obviously not interpretable in quantitative terms. There are a number of facile competing reactions in radical chain processes such as this, and minor changes in rates of reaction may have pronounced effects on yields of products. Such is particularly true in our discussion of the effects of oxygen on the allylic and benzylic systems. Nonetheless, we feel that *qualitative* discussions of rates of oxidation of radicals are valid.

radicals as *p*-nitrobenzyl and *p*-chlorobenzyl is facile with $ClPb^{IV}$.

Allyl and heptenyl radicals are slow to react with $Pb^{IV}$. $Cu^{II}$, in contrast, is an effective scavenger of all allylic radicals and these oxidations compare with earlier studies of allyl radicals in Cu-catalyzed reactions of peroxides.

There is a rough correlation between ease of oxidation and the ionization potential of the radical in the gas phase. The oxidations of tertiary, benzylic, and allylic radicals are best explained by an electron transfer mechanism which yields carbonium ions as intermediates. Products are derived from subsequent partitioning of the carbonium ion by elimination or solvation. The facile oxidation of primary alkyl and allyl radicals by $Cu^{II}$ involves a combination of factors which may not be directly related to carbonium ions, *per se*. The latter has been discussed in $Cu^{II}$ oxidation of allylic radicals and is under further study with primary alkyl radicals.

## Experimental Section

**Materials. Acids.**—Carboxylic acids were obtained as commercial samples and subsequently purified by crystallization and/or distillation. 3-Phenylbutyric acid, mp 40–41.5°, *meso*-2,3-diphenylsuccinic acid, mp 244° dec, crotonic acid, mp 71–72°, *o*-hydroxyphenylacetic acid, mp 146–147°, and *n*-octanoic acid, bp 105–107° (2 mm), were from the Aldrich Chemical Co. $\alpha,\alpha$-Dimethylphenylacetic acid, mp 78°, and *p*-methoxyphenylacetic acid, mp 86–87°, were from Columbia Organic Chemicals Co. 2-Phenylbutyric acid, bp 135° (2 mm), mp 42–44°, hydrocinnamic acid, mp 48°, and DL-mandelic acid were from the Eastman Kodak Co. *p*-Nitrophenylacetic acid, mp 151–152°, was supplied by Interchem Organic Chemicals Co. $\alpha$-Naphthylacetic acid, mp 133°, 3-octenoic acid, bp 103° (2 mm), and 2-octenoic acid were purchased from the City Chemical Co. Phenylacetic acid, mp 76°, was from K & K Laboratories, Aldrich and Eastman Kodak. Vinylacetic acid, bp 163–165°, was from K & K Laboratories, Columbia, and Peninsular Chem Research, Inc.

Acetylmandelic acid was prepared by acetylating mandelic acid in acetic anhydride:[36a] mp 79.5–81°. *p*-Chlorophenylacetic acid was obtained from hydrolysis of *p*-chlorobenzonitrile in aqueous acetic acid with sulfuric acid catalyst.[36b]

Di-*t*-butyl peroxide was donated by the Shell Chemical Co. *m*-Chloroperbenzoic acid, 85% by titration, was donated by the FMC Corp. *t*-Butyl peracetate (a 75% solution in benzene) was purchased from the Lucidol Division of Wallace and Tiernan Corp. Redistillation of the perester *in vacuo*, bp 33–34° (1.2 mm), yielded material that was 95% pure by titration.

**Esters.**—2-Phenyl-1-propyl acetate, bp 78° (1.7 mm) $n^{25}$D 1.4934, 1-phenyl-2-propyl acetate, bp 81° (1.9 mm), $n^{25}$D 1.4880, 1-phenyl-1-propyl acetate, bp 78° (1.8 mm), *p*-methoxybenzyl acetate, bp 120–121° (2 mm), *n*-heptyl acetate, *n*-octyl acetate, and benzhydryl acetate, bp 128–132° (1.0 mm), mp 41°, were all prepared from the alcohol and acetyl chloride with pyridine as catalyst. $\alpha$-Naphthylcarbinyl acetate was prepared from 1-chloromethyl naphthalene and potassium acetate in refluxing glacial acetic acid:[37] bp 132° (1.4 mm). Cumyl acetate was prepared by the per ester reaction of cumene and *t*-butyl peracetate in benzene acetic acid solution with cupric acetate, bp 80° (2 mm).[9] Cyclopropyl acetate was made from methylcyclopropyl ketone and *m*-chloroperbenzoic acid:[38] Benzilidene diacetate was prepared from benzaldehyde and acetic anhydride with boron trifluoride etherate catalyst:[39] bp 116–117° (3.5 mm), mp 43–46°.

Dihydrocoumarin was from K & K Laboratories. Coumaran-2-one was prepared from *o*-hydroxyphenylacetic acid by heating to its melting point:[40] bp 98° at 2.7 (mm). It was also prepared in solution with *p*-toluenesulfonic acid catalyst. It crystallized to a low melting solid (lit. mp 49 and 28.5°, dimorphous).[41] Dicumene was prepared from the thermolysis of *t*-butyl peracetate in cumene:[9] mp 115–116°.

**Procedure.**—Lead tetraacetate was described previously.[2] Analysis and procedures for carrying out thermal and photochemical oxidative decarboxylations of acids with $Pb^{IV}$ were also described in detail.

The chlorodecarboxylation reactions[23] were conducted in a manner identical with that described for oxidative decarboxylation, except that a weighed amount of lithium chloride was added to the system as the last component prior to sweeping with an inert gas.

**Per Ester Reaction with Cumene.**—Oxidation of cumene with *t*-butyl peracetate was investigated under various conditions which simulated the decarboxylation of $\alpha,\alpha$-dimethylphenylacetic acid by $Pb^{IV}$. Reactions are summarized in Table II.

**Phenylacetic Acid.**—Since the oxidative decarboxylation of phenylacetic acid by $Pb^{IV}$ was unexpectedly slow, we investigated the reaction in detail, particularly with respect to catalysis and the notion that inhibitors were generated during the course of reaction. Acid from different suppliers and recrystallized and sublimed acid exhibited identical behavior, and the reluctance to decarboxylate was not the result of the presence of an inhibiting impurity. Moreover, the acid employed gave good neutralization equivalents and sharp melting points. The methyl and ethyl esters of the acid gave only one sharp peak by glpc analysis.

The decarboxylation was subject to acetate, pyridine, and triethylamine catalysis. The effectiveness of these species in promoting $Pb^{IV}$ reduction and acid decarboxylation is recorded in Table III.

Although the uncatalyzed reaction with low acid concentration failed to react completely in 80 hr, the $Pb^{IV}$ consumed effected a good yield (73%) of benzylic products. The reaction with a large excess of phenylacetic acid was complete in less than 50 hr, but a lower yield (56%) of products was observed. Although added $Cu^{II}$ did not increase the rate of the reaction, it effected an increase in product yield. The pyridine reaction was more rapid, but produced the lowest yield of benzylic products.

As indicated by the results of the blank reactions, pyridine also catalyzed the reduction of $Pb^{IV}$ in the absence of phenylacetic acid *via* decarboxylation of acetic acid. The reaction produced, besides methane and ethane, considerable toluene and benzyl acetate. Thus, the results of the pyridine-catalyzed decarboxylation of phenylacetic acid in benzene–acetic acid must be treated cautiously.

The increase in the yield of benzaldehyde when oxygen was added to the system was accompanied by the inhibition of $CO_2$ evolution. Such an effect can be interpreted as the result of oxygen trapping of benzyl radicals. Intermediate peroxy radicals would be expected to disproportionate. Benzyl alcohol so formed would be oxidized by $Pb^{IV}$ to benzaldehyde.

$$2C_6H_5CH_2\cdot \xrightarrow{O_2} 2C_6H_5CH_2O_2\cdot \longrightarrow C_6H_5CHO + C_6H_5CH_2OH + O_2$$

The results of the reactions to which triethylamine was added indicate that this amine was more than 20 times as effective a catalyst as pyridine. The variations in product distribution with triethylamine concentrations were minor. However, the yield of bibenzyl (dimer) appeared to increase with rate, *i.e.*, with increasing amine concentrations, at the expense of benzyl acetate. If the increased rate is interpreted as an effect on an initiation reaction which produced a higher concentration of benzyl radicals that are not effectively oxidized by $Pb^{IV}$ then the increased yield of bibenzyl might be interpreted as stemming from a greater probability of radical dimerization.

Although $Cu^{II}$–pyridine was a much more effective catalyst than pyridine alone, the addition of cupric acetate to the triethylamine system had little effect on the rate of the already rapid reaction. An increase in the yield of benzyl acetate, however, was found with added cupric acetate.

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(36) (a) E. Kaiser and F. Carson, *J. Am. Chem. Soc.*, **86**, 2922 (1964). (b) Preparative procedure adapted to method of A. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1951, p 723.

(37) R. Manske and A. Ledingham, *Can. J. Res.*, **17B**, 14 (1939).

(38) R. Sauers and R. Ubersox, *J. Org. Chem.*, **30**, 3939 (1965).

(39) E. Man, J. Sanderson, and C. Hauser, *J. Am. Chem. Soc.*, **72**, 847 (1950).

(40) R. Elderfield, Ed., "Heterocyclic Compounds," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1951, p 3; A. Katrikzky and J. M. Lagowski, "Heterocyclic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 190.

(41) "Chemistry of Carbon Compounds," Vol. IVA, E. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1951, p 180.

TABLE II

COPPER-CATALYZED REACTION OF CUMENE AND *t*-BUTYL PERACETATE[a]

| Cumene/TBPA$^b$ | Cu$^{II}$/TBPA$^b$ | Solvent PhH/HOAc, ml | Products$^c$ | | | | Composition | |
|---|---|---|---|---|---|---|---|---|
| | | | α-Cumyl$^d$ | | | | | |
| | | | acetate | alcohol | α-Methylstyrene | Material balance | Olefin | Alcohol + acetate |
| 17.3 | 0.079 | 0/20 | 9 | 3 | 39 | 51 | 76 | 24 |
| 17.2 | 0.077 | 5/15 | 22 | 5 | 33 | 60 | 55 | 45 |
| 17.2 | 0.077 | 10/10 | 40 | 4 | 22 | 66 | 33 | 67 |
| 17.6 | 0.078 | 15/5 | 48 | 6 | 21 | 75 | 28 | 72 |
| 17.3$^e$ | 0.076 | 20/0 | 14 | 3 | 19 | 36 | 53 | 47 |
| 8.6 | 0.038 | 10/10 | 38 | 3 | 17 | 58 | 29 | 71 |
| 8.6 | 0.077 | 10/10 | 37 | 2 | 19 | 58 | 33 | 67 |
| 17.5$^f$ | 0.079 | 10/10 | 35 | 4 | 29 | 68 | 43 | 57 |
| 17.4$^g$ | 0.079 | 10/10 | 38 | 4 | 25 | 67 | 37 | 63 |

[a] 0.19 *M* *t*-butyl peracetate (TBPA) and 15 ml of cumene in indicated solvent at 81°. [b] Mole/mole. [c] Yields tabulated in mole % *vs*. TBPA. [d] α,α-Dimethylbenzyl. [e] Heterogeneous system, all others homogenous. [f] Millimoles of pyridine/millimoles of Cu$^{II}$ = 24. [g] Millimoles of pyridine/millimoles of Cu$^{II}$ = 47.

TABLE III

CATALYSIS AND PRODUCTS OF DECARBOXYLATION OF PHENYLACETIC ACID BY Pb$^{IV}$ [a,b]

| Acid/LTA$^c$ | Additive/LTA$^c$ | Solvent, ml $C_6H_6$/HOAc | Reacn time, hr | Pb$^{IV}$ consumed,$^d$ mole % | Products$^d$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $CO_2$ | $C_6H_5CH_3$ | $(C_6H_5)_2CH_2$ | $(C_6H_5CH_2)_2$ | $C_6H_5CHO$ | $C_6H_5CH_2OAc$ |
| 1.21 | | 20/10 | 80 | 42 | | 2.8 | 1.6 | 0.2 | 6.6 | 61.6 |
| 2.68 | | 25/5 | 46 | 62 | >26 | | | | | |
| 9.51 | | 30/0 | <50 | 100 | >45 | <1 | 0.4 | 1.0 | 1.9 | 19$^f$ |
| 9.51 | *e* | 30/0 | <50 | 100 | >52 | <1 | 0.9 | 0.9 | 2.1 | 19$^f$ |
| 1.20 | 1.2$^g$ | 20/10 | 68 | 71 | 45 | | | | 2.5 | 55 |
| 1.18 | 2.1$^g$ | 20/10 | 68 | 77 | | | | | 4.0 | 42 |
| 0$^k$ | 3.2$^h$ | 20/10 | 4.3 | 46 | <38 | 16 | | | | 17 |
| 1.36 | 2.9$^h$ | 25/9 | 4.3 | 72 | 45 | 0.8 | 0.5 | 0.6 | 4.4 | 25 |
| 2.06 | 3.2$^h$ | 20/5 | <17 | 100 | 23 | | | | | |
| 1.2 | 1.3$^{h,i}$ | 20/10 | 7.2 | 100 | 70 | | | | 0.5 | 46 |
| 1.2 | 2.8$^{h,i}$ | 15/10 | 2.7 | 100 | 85 | | | | 3.9 | 45 |
| 1.2 | 2.8$^{h,e}$ | 15/10 | 1.3 | 100 | 90 | | | | 0.5 | 45 |
| 1.2 | 2.8$^{e,h,l}$ | 15/10 | 6.8 | 100 | 53 | | | | 10.2 | 27 |
| 1.2 | 0.8$^j$ | 20/10 | 3.5 | 100 | 61 | 1.7 | 0.4 | 1.8 | 1.9 | 37 |
| 1.2 | 1.6$^j$ | 20/10 | 2.3 | 100 | 53 | 1.8 | 0.4 | 2.6 | 3.1 | 30 |
| 1.2 | 1.6$^{i,j}$ | 20/10 | 1.9 | 100 | 70 | 0.4 | 0.2 | 2.5 | 1.5 | 39 |
| 1.2 | 2.4$^j$ | 20/10 | 1.0 | 100 | 63 | 1.7 | 0.5 | 4.2 | 1.6 | 31 |

[a] 0.15–0.18 *M* Pb$^{IV}$ acetate. [b] 81°. [c] Mole/mole. [d] Moles/mole of Pb$^{IV}$. [e] $Cu(OAc)_2 \cdot H_2O/Pb(OAc)_4$ = 0.48. [f] 34–39% benzyl phenylacetate also observed. [g] LiOAc. [h] Pyridine. [i] $Cu(OAc)_2 \cdot H_2O/Pb(OAc)_4$ = 0.24. [j] Triethylamine. [k] No $C_6H_5CH_2CO_2H$, *i.e.*, HOAc decarboxylation. [l] 5% $O_2$ added.

The rate of phenylacetic acid decarboxylation, as measured by time for cessation of gas evolution, was dependent on the amount of *both* Cu$^{II}$ and pyridine added to the system. While pyridine alone was less effective in promoting reaction, Cu$^{II}$ alone was quite ineffective. Although the yield of major products among the Cu$^{II}$–pyridine reactions was essentially invariant, a significant increase in benzyl acetate yield over the straight pyridine reaction was observed. The yield in either system, however, represented only a fraction of the $CO_2$ liberated.

Although lithium acetate catalyzed the decarboxylation of phenylacetic acid, the reaction was independent of the amount of the acetate added. The yields of benzaldehyde and benzyl acetate were comparable to that found in the uncatalyzed reaction.

When the solutions from several decarboxylations that went to completion were examined for unreacted phenylacetic acid by converting the acid to its ethyl ester and analyzing for ester by glpc, the acid found in all but one case was greater than the excess of acid to Pb$^{IV}$ in the reaction. Therefore, phenylacetic acid and Pb$^{IV}$ did not react stoichiometrically; some Pb$^{IV}$ must have been consumed in other ways. Moreover, of the acid initially present in the system only 65% could be accounted for as unreacted acid or as benzyl products.

The possibility that benzyl radicals or cations were consumed by reactions with pyridine itself was rendered doubtful when neither benzylpyridines nor N-benzylpyridinium species could be detected by glpc and nmr analysis,[42] respectively.

To test the possibility that destruction of products was responsible for the low yields of benzyl fragments, the integrity of benzaldehyde and bibenzyl under the reaction conditions and the reactivity of benzyl acetate with lead tetraacetate were examined. Of the bibenzyl added to an uncatalyzed decarboxylation, 97% was recovered unchanged. Since it was normally observed only as a minor product, the near quantitative recovery firmly established the chemical integrity of bibenzyl in the reaction. Of the benzaldehyde added to the uncatalyzed and pyridine-catalyzed reactions, greater than 85% was recovered in both cases. If the benzaldehyde normally observed was taken into account, only 12–16% of the added benzaldehyde could have been consumed. If the 3–7% benzaldehyde normally observed as product of the decarboxlation represented 85% of the total formed, less than 1% of product of further oxidation of benzaldehyde could be formed. It is not surprising then, that *no* benzoic acid could be found among the products. Although not consumed to any great extent, the addition of either benzaldehyde or bibenzyl resulted in parallel increases in rate and yields of benzyl acetate.

It is possible that benzaldehyde was formed from benzilidene diacetate generated by two routes: (a) α-acetoxylation of phenylacetic acid followed by decarboxylation and (b) acetoxylation of benzyl acetate.

When benzyl acetate was added to the pyridine-catalyzed decomposition of lead tetraacetate in benzene–acetic acid, it was completely recovered along with the amount of benzyl acetate formed in the reaction. The copper-catalyzed reaction of benzyl acetate and *t*-butyl peracetate is known to produce benzylidine diacetate.[43]

The formation of acetylmandelic acid is analogous to the forma-

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[42] R. Lyle, *Chem. Eng. News*, **44**, No. 2, 72 (1966).

[43] G. Sosnovsky and N. Yang, *J. Org. Chem.*, **25**, 899 (1960).

tion of acetoxyacetic acid, the major product from the reaction of acetic acid with lead tetraacetate.[44] Moreover, α esterification of isobutyric acid has also been observed.[45]

Benzylidene diacetate is quite stable to acidic conditions, less than 8% being converted to benzaldehyde in dilute refluxing sulfuric acid after 1 hr. Refluxing 2% KOH, however, smoothly converted a benzene solution to benzaldehyde. Although quantitative glpc analysis could not be carried out owing to partial decomposition, it was identified qualitatively on several glpc columns.

The lead tetraacetate decarboxylations of acetylmandelic acid indicated that it was smoothly converted to a mixture of benzaldehyde and benzylidene diacetate under *uncatalyzed* conditions. While 10% phenylacetic acid significantly retarded the decarboxylation, acetylmandelic acid still reacted readily in its presence. This strongly suggests that any acetylmandelic acid formed in the reaction of phenylacetic acid would be readily decarboxylated. The analysis was performed by quantitatively determining benzaldehyde and then reanalyzing for benzaldehyde after base treatment. The increase in benzaldehyde observed after base treatment was coincident with the loss of the glpc peak attributed to benzilidene diacetate.

Benzylidene diacetate was observed as a significant product from the phenylacetic acid decarboxylations. It was identified qualitatively by glpc and quantitatively by the increase in benzaldehyde upon basic hydrolysis of pyridine-catalyzed reactions. With excess $Pb^{IV}$, increased yields of diacetate were observed, along with parallel increases in the yield of benzyl acetate, the latter undoubtedly resulting from the reaction of excess $Pb^{IV}$ with solvent.

The implication of the α hydrogens in the formation of benzaldehyde *via* acetylmandelic acid raised the question of their importance in possible chain termination processes, *i.e.*, by dimerization of the intermediate α-carboxybenzyl radicals to 2,3-diphenylsuccinic acid. The latter is easily bisdecarboxylated under these conditions to stilbene,[46] as is 2,3-diphenylpropionic acid from the mixed coupling with benzyl radicals.

Although stilbene was partially (27%) consumed when added to a pyridine-catalyzed phenylacetic acid decarboxylation, 30–40% stilbene was observed from separate reactions to which *meso*-2,3-diphenylsuccinic acid was added. Even when as little as 1% 2,3-diphenylsuccinic acid was added, stilbene was readily observed as a product by glpc analysis. Since *no* stilbene was observed from any normal phenylacetic acid decarboxylation, it is unlikely that either of the termination processes is important.

Phenolic materials inhibit the decarboxylation of acids by lead tetraacetate, and since phenylacetic acid behaved as if it were inhibiting its own decarboxylation, the effect of possible phenolic materials generated in the system was investigated. The formation of coumaran-2-one and the phenyl ester ($PhO_2CCH_2OAc$) and their possible role as inhibitors were also considered in analogy with the work of Starnes[47] on the decarboxylation of triarylpropionic acids with lead tetraacetate.

Phenyl esters, however, were stable in the pyridine–phenylacetic acid–lead tetraacetate system and had no effect on the decarboxylation. The addition of small amounts (1–3%) of coumaran-2-one or *o*-hydroxyphenylacetic acid to a pyridine-catalyzed decarboxylation of phenylacetic acid at 81° caused rapid evolution of $CO_2$ rather than inhibition. Since the amount of gas liberated was proportional to the amount of either component added, it is suggested that the consumption of additive was responsible for the observed effect.

An excess (30%) of *o*-hydroxyphenylacetic acid reacted with $Pb^{IV}$ at room temperature without the evolution of $CO_2$ in a manner which suggests preferential reaction with the phenolic function. Simple mixing of the components in benzene–acetic acid (20 ml:10 ml) was sufficient to produce the red color characteristic of the reaction of phenols with lead tetraacetate.[13] Moreover, the $Pb^{IV}$ was consumed in 1–2 hr.

While they may still account for unidentified benzylic products, the experiments with *o*-hydroxyphenylacetic acid and coumaran-2-one suggest that neither could be responsible for any inhibition of the phenylacetic acid decarboxylation. Furthermore, if produced, they most certainly would be consumed by further oxidation.

To test the effect of products, possible products and model compounds on a lead tetraacetate reaction, benzene solutions of the components were added to a model system which consisted of a pyridine-catalyzed decarboxylation of isobutyric acid at 81° (Table IV). While phenylacetic acid itself retarded the reaction, the observed products from phenylacetic acid decarboxylation had no effect. Small amounts of coumaran-2-one and *o*-hydroxyphenylacetic acid had the effect described above, while neither the homologous lactone, dihydrocoumarin, nor tetralin had any effect. *o*-Cresol retarded the rate of $CO_2$ evolution in proportion to the amount added.

TABLE IV

EFFECT OF ADDITIVES ON ISOBUTYRIC ACID DECARBOXYLATION AT 81°[a]

| Additive | Mole % relative to $Pb^{IV}$ | Effect on gas evolution[b] |
|---|---|---|
| Phenylacetic acid | 9 | B |
| Acetic acid | 5 | A |
| Benzyl acetate | 62 | A |
| Benzaldehyde | 31 | A |
| Bibenzyl | 5 | A |
| Coumaran-2-one | 2.3 | C |
| Coumaran-2-one | 1.1 | C |
| Coumaran-2-one | 1.8 | C |
| *o*-Hydroxyphenylacetic acid | 1.1 | C |
| *o*-Hydroxyphenylacetic acid | 1.1 | C |
| Phenyl acetate | 2.1 | A |
| Phenyl acetate | 10 | A |
| Phenol | 0.8 | B |
| *o*-Cresol | 0.24 | B |
| *o*-Cresol | 0.48 | B |
| *o*-Cresol | 1.2 | B |
| *o*-Cresol | 5.9 | B |
| Phenylacetone | 3.0 | D |
| Dihydrocoumarin | 1.7 | A |
| Tetralin | 1.4 | A |

[a] 0.17 *M* lead tetraacetate in benzene; isobutyric acid/LTA (moles/mole) = 12, pyridine/LTA (moles/mole) = 36. [b] A = no effect, B = retardation, C = rapid acceleration followed by resumption of original rate, D = apparent acceleration.

**Registry No.**—2-Phenyl-1-propyl acetate, 10402-52-5; 1-phenyl-2-propyl acetate, 2114-33-2; 1-phenyl-1-propyl acetate, 2114-29-6; *p*-methoxybenzyl acetate, 104-21-2; benzhydryl acetate, 954-67-6; cumene, 98-82-8; *t*-butyl peracetate, 107-71-1; phenylacetic acid, 103-82-2; isobutyric acid, 79-31-2; lead(IV), 15158-12-0; copper(II), 15158-11-9.

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