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ALKENES FROM ACIDS BY OXIDATIVE DECARBOXYLATION

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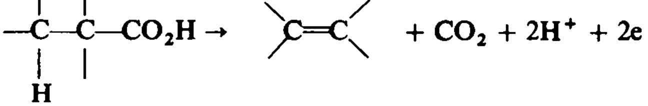
Abstract—Primary and secondary acids can be readily decarboxylated to alkenes by Pb^{IV} tetraacetate in the presence of catalytic amounts of cupric acetate. Terminal alkenes are formed quantitatively from primary acids, but conversions are limited by competitive decarboxylation of acetate. Synthetic procedures can be developed by examination of the effects of acid, Pb^{IV} and catalysts on the rates of decarboxylation and conversions of acids. Unreacted acid is recovered readily from the mixture, and recycling should enable high conversions to alkenes. A convenient preparation of ω-alkenoic acids from dibasic acids, such as 6-heptenoic acid from suberic acid, is described. Secondary acids can be converted to alkenes in high conversions since competitive decarboxylation of acetate is not important. Decarboxylations can be carried out either thermally at 80° or photochemically at 30° with essentially the same results. The latter is the preferred method to employ with heat sensitive compounds.

ACIDS are thermally or photochemically decarboxylated by lead tetraacetate* to a variety of products, depending on their structure.[1] High yields of oxidation products such as alkenes and esters are derived from tertiary and α-benzylic acids with Pb^{IV}. In contrast, primary and secondary acids are only slowly decarboxylated by Pb^{IV} and generally afford poor to mediocre yields of oxidation products. Although *alkanes* are usually the major products in the latter cases, they are not formed in synthetically useful amounts or in high purity.

Earlier, we found that cupric salts catalyzed the decarboxylations of acids by Pb^{IV}. The catalysis is especially marked with primary and secondary acids such as n-valeric, isovaleric and 2-methylbutyric acids. Furthermore, under these conditions alkanes are no longer significant products. In the limited examples which were examined, alkenes were found in excellent yields according to the stoichiometry given in Eq. 1 for valeric acid:

$$CH_3(CH_2)_3CO_2H + Pb^{IV} \xrightarrow{Cu\,X_2} CH_3CH_2CH = CH_2 + CO_2 + Pb^{II} + 2H^+ \quad (1)$$

The replacement of a carboxyl group and introduction of unsaturation as an oxidative process is a synthetically useful objective (Eq. 2). The copper salt catalyzed



$$\underset{H}{-\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-CO_2H \rightarrow \; >C{=}C< \; + CO_2 + 2H^+ + 2e \quad (2)$$

decarboxylation of acids may be applicable in this regard and we have examined

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* Hereafter referred to as Pb^{IV}. Unless required for clarification the coordination around the Pb will not be included. Lead tetraacetate is the Pb^{IV} reagent used in all our studies and carboxylato ligands are implied.

in this report various factors necessary to enhance such a transformation of primary and secondary acids.

RESULTS

Octene-1 *from nonanoic acid*

Experimental variables. A mixture of nonanoic acid and Pb^{IV} (0·10M) was treated with cupric acetate (0·005M) in benzene at 80°. If excess nonanoic acid (0·40M) was employed, octene-1 and CO_2 were formed within approximately 100 min according to the stoichiometry given in Eq. (3). Yields of octene-1 based on Pb^{IV} consumed were virtually quantitative and no significant amounts of other products derived

$$CH_3(CH_2)_7CO_2H + Pb(OAc)_4 \xrightarrow{Cu(OAc)_2} CH_3(CH_2)_5CH{=}CH_2 + CO_2 + Pb(OAc)_2 + 2HOAc \quad (3)$$

from nonanoic acid were found.* The reaction was catalyzed by a variety of bases including lithium acetate and pyridine. For example, in a homogeneous system

TABLE 1. THERMAL DECARBOXYLATION OF NONANOIC ACID WITH Pb^{IV}[a]

Acid[b]	Cu^{II}[c]	Solvent (ml)	Catalyst	Cat.	OAc[d]	Reaction		Octene-1
Pb^{IV}	Pb^{IV}	ØH/ØCl/HOAc		Pb^{IV}	Pb^{IV}	Time (hrs)	Type[e]	(M%)[f]
2·58	0·23	20/0/0	LiOAc	1·04	2·2	2·0	B	91
1·27	0·22	20/0/4	LiOAc	1·01	16·6	1·0	A	43
1·28	0·23	20/0/4	none	—	15·7	3·8	A	42
1·25	0·22	10/10/4	none	—	16·0	0·8	A	42
1·28	0·23	10/10/4	LiOAc	1·03	16·7	0·5	A	44
2·50	0·23	10/10/3	NaOAc	1·11	7·0	1·5	B	45
2·55	0·23	10/10/3	LiOAc	1·04	6·9	0·5	A	62
0·92	0·21	10/10/4	LiOAc	0·95	21·6	0·5	A	42
0·82	0·21	20/0/4	LiOAc	0·95	24·4	1·3	A	44
0·68	0·23	20/0/1	none	—	12·4	30·0	B	38
0·63	0·11	20/0/1	LiOAc	1·00	14·5	3·0	B	56
0·64	0·22	20/0/0·5	LiOAc	1·00	11·4	7·0	B	62
0·64	0·22	20/0/0·5	Li_2CO_3	0·98	10·0	7·0	B	47
0·43	0·22	20/0/1	LiOAc	1·01	21·5	3·0	A	66
0·64	0·11	20/0/0	Pyridine	0·54	6·6	1·0	B	44
0·61	0·22	20/0/0	Pyridine	0·26	7·1	1·7	B	39
0·60	0·11	20/0/0·5	Pyridine	1·04	10·1	0·3	B	65
0·60	0·11	20/0/0·5	Pyridine	2·63	10·0	0·2	B	45

[a] 0·18–0·22M lead tetraacetate (Pb^{IV}) at reflux. [b] Mole/mole. [c] $Cu(OAc)_2 \cdot H_2O$. [d] Total acetate in the system. [e] A = homogeneous, B = heterogeneous. [f] Yield based on non-excess component.

composed of a minor excess of acid, a molar equivalent of lithium acetate reduced the time of reaction from 4 hr to 1 hr. The same reaction with excess Pb^{IV} and less acetic acid was heterogeneous and addition of lithium acetate increased the rate

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* In all our discussions yields were based solely on Pb^{IV} consumed, irrespective of whether the acid or lead tetraacetate was used in excess (unless otherwise specified).

10-fold. Sodium acetate is less soluble in solutions of benzene and acetic acid and was a less effective catalyst (see Table 1).

The rate of reaction was also faster in chlorobenzene than benzene, although yields of octene-1 were not materially altered. Acetic acid was helpful in solubilizing Pb^{IV} nonanoate in these solvents, but suffered from competitive decarboxylation. Thus, when total acetate, including that derived from the Pb^{IV} salt, was increased from 1·0M to 3·0M, the yield of octene-1 was reduced from 91 to 62%. Acetate, introduced as the acid or derived from Pb^{IV} acetate itself, was the single most important deterrent for optimizing yields of octene-1. However, this is not a serious problem if conversion of carboxylic acids is the primary concern since they can be easily recovered from the reaction mixture (*vide infra*).

A reaction employing excess Pb^{IV} was heterogeneous, but it was easily catalyzed by pyridine. The concentration of pyridine was a critical factor in the formation of octene-1. With a small amount of added acetic acid, a molar equivalent of pyridine produced 65% octene-1 in approximately 15 min. However, with 2·6 molar equivalents of pyridine only 45% octene-1 was realized in a similarly rapid reaction. In the absence of a small amount of acetic acid the reaction was considerably more heterogeneous. These data are summarized in Table 1.

The decarboxylation of nonanoic acid by Pb^{IV} can also be induced photolytically at 30° in the absence of acetate or pyridine as catalyst. In the presence of catalytic amounts of cupric acetate the predominant product, octene-1, is contaminated with minor amounts of octane. The latter could easily be eliminated by the addition of small amounts of pyridine. Earlier studies showed that cupric carboxylates in solvents such as benzene are highly dimeric.[2] The dimers are readily dissociated by

TABLE 2. DEPENDENCE OF OCTENE-1 YIELD ON THE RATIO OF NONANOIC ACID/Pb^{IV} BY THERMAL AND PHOTOCHEMICAL METHODS[a]

Acid/Pb^{IV}[b]	Cu(II)[b,c]/Pb^{IV}	Reaction[d]	$\frac{(C_9\ \text{Acid})}{(OAc^-)}$[e]	Octene-1 (M %)[f]
1·00	0·026	Δ	0·247	44
1·03	0·027	hν	0·254	47
1·56	0·026	hν	0·385	60
1·57	0·055	hν	0·382	65
2·07	0·029	Δ	0·510	72
2·13	0·058	Δ	0·519	75
2·11	0·025	hν	0·521	72
2·84	0·051	Δ	0·694	82
3·01	0·052	hν	0·733	87

[a] 0·10M lead tetraacetate, 0·017M pyridine in benzene solvent

[b] Mole/mole.

[c] $Cu(OAc)_2 \cdot H_2O$

[d] Δ = thermal (80°); hν = photolytic (30°, 3500Å).

[e] (OAc^-) = total acetate in system.

[f] Based on Pb^{IV}.

pyridine to monomeric Cu^{II} species which are the actual species responsible for oxidation of alkyl radicals.[3] Results tabulated in Table 2 show that in reactions consisting of equivalent amounts of nonanoic acid, Pb^{IV}, Cu^{II} and pyridine in benzene afford the same yields of octene-1 irrespective of whether they are conducted thermally at 80° or photochemically (3500 Å) at 30°.

Although alkenes have been reported to react with Pb^{IV},[4] under our experimental conditions we could show that octene-1 was not consumed. Thus, lead tetraacetate (0·113M) was catalytically decomposed by lithium acetate (0·216M) in a solution containing 0·163M octene-1 and 0·045M cupric acetate in 4·76 %V acetic acid–benzene at 80° in less than 2 hr. Octene-1 was recovered in greater than 95 % yield. The olefin itself, although not appreciably consumed, had some catalytic effect on the decarboxylation,[5] and reaction with a large excess of octene-1 (0·62M) was complete in less than 40 min. A trace of octenyl acetates was formed.

Although yields of octene-1 based on the Pb^{IV} consumed may have been less than 100 %, it could be shown that yields based on nonanoic acid in these runs were close to quantitative. Nonanoic acid could be recovered from the reaction mixture and together with the octene-1 accounted for the total acid charged as shown in Table 3. Nonanoic acid was analyzed by GLC as the methyl ester.

TABLE 3. RECOVERY OF UNREACTED NONANOIC ACID FROM Pb^{IV} DECARBOXYLATION[a]

Acid charged (mmole)	Octene-1 (mmole)	(%)	Ester formed[b] (mmole)	(%)	Total acid accounted (mmole)	(%)
1·44[c]	—	—	1·39[d]	95·6	1·39[c]	96
2·89	1·83	63·3	1·01	35·0	2·84	98
2·89	1·83	63·3	1·09	37·4	2·92	101
3·02	1·83	60·9	1·20	39·2	2·03	100

[a] A 10 ml aliquot of benzene solution refluxed with 15 ml methanol and 0·2 ml conc sulfuric acid. [b] Methyl nonanoate. [c] Octanoic acid blank. [d] Methyl octanoate.

Acetic acid was a major factor in leading to poor conversion of nonanoic acid, and we conclude that the unaccounted Pb^{IV} was consumed in competitive reactions with acetic acid. This Pb^{IV} deficit is probably due to decarboxylation and acetoxylation of this acid.[6]

5-*Phenylvaleric acid.* Davies[7a] has reported that the lead tetraacetate decarboxylation of 5-phenylvaleric acid in refluxing benzene yielded tetralin (54 %) and n-butylbenzene (4 %), and suggested the intermediacy of the 4-phenylbutyl radical. Earlier, Kochi and Gilliom[7b] had shown that the above radical was derived from 5-phenylvaleryl peroxide and it could be efficiently trapped by Cu(II) species and oxidized to the olefin, 4-phenylbutene-1. The data in Table 4 reveal that in the presence of cupric acetate, a high yield of 4-phenylbutene-1 was obtained from the lead (IV) decarboxylation of 5-phenylvaleric acid in refluxing benzene. Only trace amounts of tetralin and n-butylbenzene could be found. The decarboxylation of this

TABLE 4. CONVERSION OF SELECTED PRIMARY ACIDS TO ALKENES

Carboxylic acid		$Pb^{IV\,a}$	$Cu^{II\,b}$	Solvent (ml)	Temp	Catalyst (M)	Reaction time (hr)	Olefin yield[c]
	M^{m}			ϕH/ϕCl/HOAc				
5-Phenylvaleric	0·24	0·19	0·042	20/0/4	ref.[d]	LiOAc (0·19)	1·0	40[e]
5-Phenylvaleric	0·28	0·21	0·048	20/0/1	ref.	LiOAc (0·21)	1·5	53[e]
5-Phenylvaleric	0·28	0·22	0·050	20/0/0	ref.[f]	none	9·2	65[e]
5-Phenylvaleric	0·28	0·22	0·049	20/0/0	ref.[f]	LiOAc (0·22)	4·6	65[e]
Cyclohexylacetic	0·21	0·10	0·005	0/20/0	30[g]	py[h] (0·017)	1·0	84[i, j]
Cyclohexylacetic	0·21	0·10	0·005	0/20/0	80	py (0·017)	60·0	40[i]
n-Heptanoic	0·21	0·10	0·005	0/20/0	30[g]	py (0·014)	1·0	70[k]
n-Heptanoic	0·21	0·10	0·005	0/20/0	80	py (0·014)	1·5	72[k]
n-Octanoic	0·20	0·10	0·005	0/20/0	30[g]	py (0·015)	1·0	71[l]
n-Octanoic	0·20	0·10	0·005	0/20/0	80	py (0·015)	1·5	68[l]

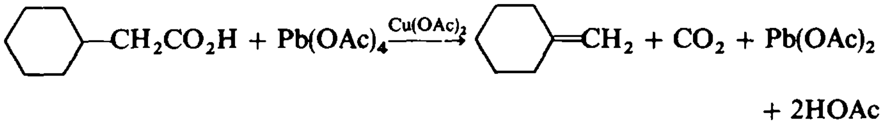
[a] Lead tetraacetate. [b] $Cu(OAc)_2 \cdot H_2O$. [c] Mole %, based on lead (IV) consumed. [d] Reflux. [e] 4-Phenylbutene-1. [f] Heterogeneous reactions, all other homogeneous. [g] Conducted photolytically (3500Å). [h] py = pyridine. [i] Methylenecyclohexane. [j] 0·2 % methylcyclohexane and 2·2 % 1-methylcyclohexene also observed. [k] Hexene-1. [l] Heptene-1. [m] Molarity of carboxylic acid, Pb^{IV} and Cu^{II}.

acid in refluxing bezene was examined with and without added acetic acid and

$$\phi CH_2CH_2CH_2CH_2CO_2H + Pb(OAc)_4 \xrightarrow{Cu(OAc)_2} \phi CH_2CH_2CH{=}CH_2 + CO_2 + Pb(OAc)_2 + 2HOAc \qquad (4)$$

lithium acetate. The reaction in benzene was heterogeneous and required 9·2 hr for complete CO_2 evolution. The reaction time could be halved by the addition of a molar amount of lithium acetate. Although the system was still heterogeneous, no reduction in olefin yield was noticed. Homogeneity and rapid reaction could be attained by adding acetic acid, but acetic acid seriously affected the yield of desired olefin.

The conversion of other primary acids to alkenes, cyclohexylacetic acid to methylenecyclohexane, n-heptanoic acid to hexene-1, n-octanoic acid to heptene-1, are also listed in Table 4. Although some rearranged 1-methylcyclohexene accompanied methylenecyclohexane, neither of the other isomers, norcarane or cycloheptene, were formed. These reactions were best carried out photochemically (see Table 4).

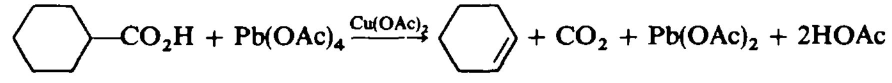


(5)

The procedure was adapted on a preparative scale for the synthesis of ε-heptenoic acid from suberic acid. The latter was converted to its half ethyl ester[8] and decarboxylated directly with Pb^{IV}–Cu^{II} to ethyl ε-heptenoate, which was subsequently saponified. A variety of other terminally unsaturated acids, otherwise rather difficult to obtain, can be easily prepared by this simple procedure. It is also possible to decarboxylate α,ω-dibasic acids directly to the corresponding unsaturated acid by using an excess of acid.[8b]

$$HO_2C(CH_2)_nCO_2H \rightarrow HO_2C(CH_2)_nCO_2Et \rightarrow CH_2{=}CH(CH_2)_{n-2}CO_2H \qquad (6)$$

Cyclohexanecarboxylic acid. The decarboxylation of this secondary acid was examined under a variety of conditions in benzene. At mole ratios of acid to Pb^{IV} of more than 3·5, cyclohexanecarboxylic acid was quantitatively decarboxylated to cyclohexene by 0·20M Pb^{IV} and 0·045M Cu^{II} in benzene at 80° as shown in Table 5. As this ratio was reduced, a slower, heterogeneous system resulted. With excess Pb^{IV}, the mixture was an unstirrable paste. Decarboxylation was exceedingly slow, and the yield of cyclohexene materially reduced.



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If acetic acid was added to a mixture containing only a 25% excess of cyclohexanecarboxylic acid, the reaction was largely homogeneous and good yields of cyclohexene (88–95% based on Pb^{IV}) were obtained. Propionic acid, which is slightly more easily decarboxylated than acetic, created a completely homogeneous system which readily liberated CO_2 and generated equally good yields of cyclohexene. Propionic acid could be used with excess Pb^{IV} to decarboxylate cyclohexanecarboxylic acid rapidly in a homogeneous medium. An 87% conversion of cyclohexanecarboxylic acid to cyclohexene was achieved.

TABLE 5. CYCLOHEXENE FROM DECARBOXYLATION OF CYCLOHEXANECARBOXYLIC ACID BY Pb^{IV}

Pb^{IV}[a] (M)	Acid[b] / Pb^{IV}	Cu^{II}[b,c] / Pb^{IV}	Temp[d]	—Solvent (ml)— ϕH/RCO$_2$H	R =	Reaction Time (hr)	Reaction Type[e]	Cyclohexene Yield[f]
0·26	3·51	0·23	80	15/0	—	0·7	A	98
0·20	3·52	0·23	80	20/0	—	1·0	A	100
0·30	2·36	0·15	80	20/0	—	2·3	B	99
0·33	1·18	0·22	Ref.	20/0	—	6·3	B	90
0·32	0·73	0·22	Ref.	20/0	—	22	D	74[g]
0·31	1·24	0·22	Ref.	20/1	Me	1·2	C	95
0·30	1·29	0·22	Ref.	20/2	Me	1·1	C	88
0·31	1·22	0·22	Ref.	20/1·2	Et	0·7	A	85
0·33	0·69	0·21	Ref.	20/1	Et	1·6	A	87
0·33	0·53	0·21	Ref.	20/1/0·5	Me/Et	8·0	B	92

[a] Lead tetraacetate. [b] Mole/mole. [c] $Cu(OAc)_2 \cdot H_2O$. [d] or reflux. [e] A = heterogeneous, B = homogeneous. C = heterogeneous at reaction completion, D = quite heterogeneous. [f] Mole %, based on non-excess component. [g] incomplete reduction of Pb^{IV}.

Thus, cyclohexanecarboxylic acid can be successfully decarboxylated to cyclohexene under synthetically useful conditions, i.e. with use of excess Pb^{IV} as the expendable component. Competitive decarboxylation of acetic and even propionic acid was not a serious problem. Furthermore, since the rate and ease of carrying out the reaction are quite dependent on the homogeneity of the reaction, primary acids can be utilized as part of the solvent to maintain solubility without seriously jeopardizing the yield of the desired alkene. Prior to workup, excess Pb^{IV} can be destroyed with ethylene glycol to obviate difficulties encountered with hydrolysis of Pb^{IV}. Problems of solubility can be further minimized by working in more dilute solutions. The use of solvents other than benzene is also possible.

A variety of other secondary acids can be readily decarboxylated without interference from the competitive decarboxylation of acetic acid. The results are summarized in Table 6. Cyclobutene could be generated from cyclobutanecarboxylic acid. A mixture of conjugated and unconjugated cyclohexadienes were formed

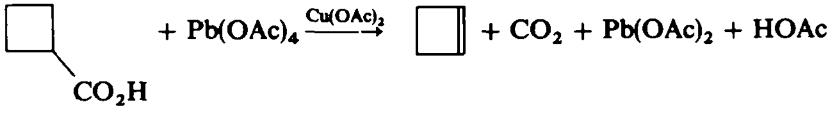
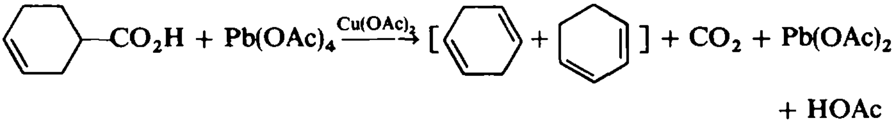


TABLE 6. CONVERSION OF SECONDARY ACIDS TO ALKENES

Carboxylic acid		Pb^{IV}[a]	Cu^{II}[b]	Solvent (ml)	Reaction		M %	Olefin[c]	
		M[m]		ΦH/RCO_2H	Time (hr)	Temp	A	B	A + B
2-Ethylbutyric	0·201	0·231	0·096	20/1	0·8	ref	45[d]	27[e]	72
Cyclo-butanecarboxylic	0·20	0·20	0·044	20/2	0·7	ref	46[f]	1–3[g]	48
Cyclo-butanecarboxylic	0·52	0·10	0·005	25/0	1·0	30[h]	75[f]	<0·1[g]	75
Cyclo-butanecarboxylic	0·52	0·10	0·005	25/0	1·5	80	67[f]	<1[g]	68
Cyclo-butanecarboxylic	0·52	0·10	0·005	20/5	2·0	30[h]	58[f]	—	58
Cyclo-butanecarboxylic	0·52	0·10	0·005	20/5	4·0	80	38[f]	—	38
Cyclo-butanecarboxylic	0·44	0·10	0·005	20/2[n]	1·5	30[h]	77[f]	—	77
Δ^3-Cyclohexenylcarboxylic	0·18	0·21	0·043	20/2	0·3	ref.	18[i]	7[j]	25
Δ^3-Cyclohexenylcarboxylic	0·17	0·20	0·044	20/2[k]	0·5	ref.	38[i]	8[j,l]	64

[a] Lead tetraacetate. [b] $Cu(OAc)_2 \cdot H_2O$. [c] Yields based on non-excess component. [d] *trans*-Pentene-2. [e] *cis*-Pentene-2. [f] Cyclobutene. [g] 1–3 butadiene. [h] Conducted photolytically (3500 Å). [i] 1,4-cyclohexadiene. [j] 1,3-Cyclohexadiene. [k] MeCN/HOAc. [l] 18 % benzene also observed. [m] Molarity of carboxylic acid, Pb^{IV} and Cu^{II}. [n] EtOAc/AcOH.

from Δ^3-cyclohexenecarboxylic acid. The higher apparent yield of the unconjugated isomer may be misleading since further oxidation to benzene occurred.



(8)

DISCUSSION

At concentrations of Cu^{II} acetate as low as 0·005M, it is possible to convert to alkenes most of the alkyl radicals generated from the decarboxylation of primary and secondary acids by Pb^{IV} acetate. Furthermore, Cu^{II} enhances the rate of decarboxylation of these acids by Pb^{IV} and the following chain mechanism can be proposed:

$$RCO_2Pb^{III} \rightarrow R\cdot + CO_2 + Pb^{II} \tag{9}$$

$$R\cdot + Cu^{II} \rightarrow R(-H) + H^+ + Cu^I \tag{10}$$

$$Cu^I + RCO_2Pb^{IV} \rightarrow Cu^{II} + RCO_2Pb^{III} \text{etc.} \tag{11}$$

The formation of alkenes in this system is related to the facile oxidation of primary and secondary alkyl radicals (R·) by Cu^{II} (Eq. 10). The second order rates of these reactions[3] range between 10^8–10^9 1/m-sec and account for the necessity of using only catalytic amounts of Cu species, since reoxidation of Cu^I (Eq. 11) is also fast.[1a] Oxidation of primary alkyl radicals by Cu^{II} in these solvents generates terminal alkenes specifically without further rearrangement of either the position of the double bond or the carbon skeleton.* This method of decarboxylation, thus, offers a specific route to introduction of terminal unsaturation.

$$CH_3(CH_2)_nCH_2\cdot + Cu^{II} \rightarrow CH_3(CH_2)_{n-1}CH{=}CH_2 + Cu^I + H^+ \tag{12}$$

Secondary alkyl radicals are also oxidized by Cu^{II} to alkenes in high yields. If the alkyl radical is unsymmetrical, ambiguity as to the direction of oxidative elimination is possible. Hoffman-type elimination is probably obtained, although sufficient numbers of examples have not yet been examined to establish this point.

We find that the decarboxylation can be carried out equally well by thermal as well as photochemical means. The latter is desired when the products are prone to rearrange or are sensitive to heat. Since the decarboxylation is a rather efficient radical chain reaction, oxygen must be removed carefully. Large-scale reactions are conveniently carried out thermally.

For synthetic purposes, we feel that decarboxylation of acids by Pb^{IV}–Cu^{II} can be adapted to primary acids despite the deleterious effect of acetate. Pb^{IV} acetate is a reasonably available reagent and competitive decarboxylation of acetic acid is not a serious problem. The side products derived from acetate are easily removed and the unreacted primary acid can be recovered without difficulty and recycled. The *conversion* of primary acid to alkene is inversely related to the available acetate in

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* The small amounts of 1-methylcyclohexene from the decarboxylation of cyclohexylacetic acid may result from a *subsequent* rearrangement of methylenecyclohexane.

the reaction mixture, and rises with increasing acid as shown in Fig. 1. When nonanoic acid and Pb^{IV}tetraacetate react in equimolar amounts, an optimum of approximately 45% conversion of nonanoic acid occurs. This value is not significantly altered by use of excess Pb^{IV}. We feel that the ceiling to the conversion is directly related to the metathesis of Pb^{IV} tetraacetate and nonanoic acid. If we assume that the equilibrium

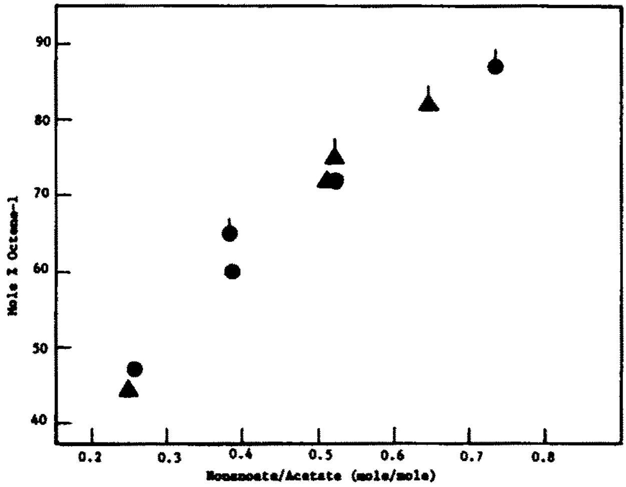
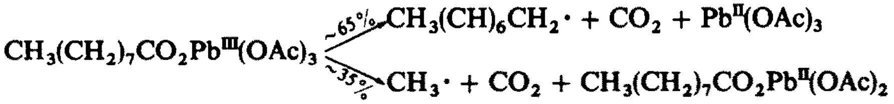


FIG. 1. Effect of nonanoate/acetate ratio on the conversion of nonanoic acid to octene-1, in benzene solution containing 0·10M Pb^{IV}, 2·6 or 5·2% (spiked) Cu^{II}. ▲ thermal (80°); ● photolytic (30°, 3500 Å).

$$RCO_2H + Pb(OAc)_4 \rightleftarrows RCO_2Pb(OAc)_3 + HOAc \qquad (13)$$

$$RCO_2Pb(OAc)_3 + RCO_2H \rightleftarrows (RCO_2)_2Pb(OAc)_2 + HOAc \text{ etc.} \qquad (14)$$

constant for Eq. (13) is 1, then approximately 15% of the groups associated with Pb^{IV} are nonanoato ligands. According to the mechanism given in Eqs (9–11), radicals are generated by fragmentation of a Pb^{III} species. To obtain a conversion of 45% we assume that nonanoato ligands are cleaved about 6 times faster than each acetato ligand.*



$$CH_3(CH_2)_7CO_2Pb^{III}(OAc)_3 \begin{cases} \xrightarrow{\sim 65\%} CH_3(CH)_6CH_2\cdot + CO_2 + Pb^{II}(OAc)_3 \\ \xrightarrow{\sim 35\%} CH_3\cdot + CO_2 + CH_3(CH_2)_7CO_2Pb^{II}(OAc)_2 \end{cases}$$

The rates of cleavage of carboxylato ligands in Pb^{III} intermediates (Eq. 9) are highly dependent on the alkyl radical, and increase in the order: α-benzylic > t-alkyl > sec-alkyl > prim-alkyl > methyl.[1,9] Quantitative values for these rates are difficult to obtain. Qualitatively, this effect can be shown by examining the decarboxylation of acids in the presence of acetic acid. As indicated above, the

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* This assumes, of course, complete and rapid equilibration of ligands, and that mechanism (9)–(11) is essentially correct.

decarboxylation of primary acids is seriously affected by acetic acid, whereas secondary acids can be selectively decarboxylated in the presence of at least 3–4 times excess of acetic acid. Acetic acid can be used as a partial solvent for decarboxylation of tertiary acids and triphenylacetic acid can be quantitatively decarboxylated in acetic acid.[10] We attribute this dependency of the rate of cleavage of carboxylato groups from Pb^{III} species to multibond fragmentation via a transition state* such as $[R \cdots CO_2 \cdots Pb^{III}]$. A similar effect of alkyl groups in the cleavage of t-alkoxy radicals is obtained.[11]

EXPERIMENTAL

Materials. n-Nonanoic acid, n-octanoic acid (Aldrich Chemical Co.), n-heptanoic acid (Matheson, Coleman and Bell), cyclohexane carboxylic acid, propionic acid (Eastman Kodak Co.), cyclobutanecarboxylic acid, suberic acid (Columbia Organic Chemicals Co.), 2-ethylbutyric acid, Δ^3-cyclohexenylcarboxylic acid (K & K Laboratories. Inc.) and cyclohexylacetic acid (Dow Chemical Corp.) were carefully distilled before use. The preparation of 5-phenylvaleric acid is described elsewhere.[7] The purity of these acids was determined by gas chromatographic analysis of the acids and/or their methyl esters.

Benzene, Mallinckrodt analytical reagent, was purified by distillation through a four foot, 22-plate Oldershaw column; *chlorobenzene* and *acetonitrile* (redistilled from P_2O_5) from Matheson, Coleman and Bell; *pyridine*, Reilly Co., redistilled from KOH pellets.

Lead tetraacetate, G. F. Smith Co., recrystallized twice from glacial AcOH containing 3% Ac_2O. Excess AcOH was removed in a vacuum desiccator over KOH. The colorless material indicated 98% $Pb(OAc)_4$ by iodometric titration.

Cupric acetate monohydrate and lithium carbonate were Mallinckrodt analytical reagents; *sodium acetate* (anhyd) and *lithium acetate* dihydrate were supplied by Matheson Coleman and Bell. Anhyd LiOAc was prepared from the dihydrate by heating (>90°) *in vacuo*.

Authentic olefins and other hydrocarbon products were purchased from Columbia Organic and Aldrich Chemical Companies. Possible ester products were independently synthesized from the corresponding alcohols. Authentic cyclobutene was obtained via the decomposition of cyclopropanecarboxaldehyde tosylhydrazone.†

Procedures for decarboxylation. A typical decarboxylation was carried out in the following manner. In a 100 ml volumetric flask was placed $Cu(OAc)_2 \cdot H_2O$ (0·107 g, 0·535 mmole), pyridine (0·110 g, 1·39 mmoles) and heptanoic acid (2·75 g, 21·2 mmoles) and 10–20 ml of solvent (benzene, chlorobenzene). The mixture was stirred magnetically for 30–40 min. To the resulting homogeneous soln was added 97% Pb^{IV} tetraacetate (4·50 g, 9·86 mmoles) and the remainder of the solvent (77–87 ml). The resulting mixture was stirred (in the dark) for an additional hr to effect soln and metathesis of the carboxylic acid with Pb^{IV} acetate.

A 25 ml aliquot was transferred to a 50 ml $\overline{\$}$ round-bottom, one-necked flask equipped with a side arm capped with a rubber septum, a magnetic stirring bar and a spiral microcondenser. The reaction vessel was attached to a Hg-filled eudiometer. The system was purged free of O_2 by sweeping with a slow stream of N_2 introduced via a stainless steel hypodermic needle. The reaction vessel was heated in a thermostatted oil bath, and gas evolution followed volumetrically.

Alternatively, an aliquot was transferred to a cylindrical quartz tube (1 cm diam) which was purged free of O_2 by sweeping with N_2 introduced via a glass capillary and capped with a rubber septum. The solns were photolyzed in a Rayonet photochemical reactor (The Southern N.E. Ultraviolet Co) at 30°. Four 3500 Å region lamps (3050 Å to 4150 Å) arranged in a circular array were employed. Tubes were placed 10 cm from the nearest lamp.

Other thermal reactions were conducted with individually prepared mixtures of components. This was especially true when starting mixtures were heterogeneous at room temp.

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* [a] Undoubtedly, part of the driving force is obtained from the formation of CO_2; [b] In this respect, benzoato should be preferred to acetato since fragmentation of phenyl radicals is quite slow.

† We wish to thank Dr. John Bayless for this sample.

When the reaction was complete, the soln was rinsed into a volumetric cylinder with equal amounts of benzene (or chlorobenzene) and glacial AcOH. Complete reaction was indicated by the cessation of gas evolution and/or the absence of Pb(IV). Aliquots of the benzene soln were washed with water and $NaHCO_3$ aq and dried over Na_2SO_4. The soln was analyzed by quantitative gas chromatography (Aerograph HiFy, hydrogen flame ionization detector) using an internal standard which was previously calibrated against the reaction product. Identification of gas chromatographic peaks was verified by comparing retention times with authentic compounds on at least two columns. Moreover, identification was confirmed by chemical degradation of the reaction product (e.g., hydrogenation).

Cyclobutene was analyzed without workup. The gaseous products trapped within the photolysis tube were analyzed qualitatively for hydrocarbon and then quantitatively after the addition of *cis*-butene-2 as an internal standard. Cyclobutene from the thermal reactions was quantitatively condensed back onto the reaction vessel with a dry ice-isopropanol bath, the reaction vessel capped above the condenser with a rubber septum, warmed to room temp, and the hydrocarbon in the gas and liquid phases analyzed by gas chromatography as described earlier.[1a]

Preparation of ε-heptenoic acid from suberic acid. Suberic acid was converted to its half ethyl ester by equilibrating a mixture of acid with diethyl suberate.[8] A mixture of ethyl hydrogen suberate (121 g, 0·6 mole), pyridine (0·7 mole, 55 g), cupric acetate (0·11 mole, 21 g) and Pb^{IV} acetate (95%, 421 g, 0·95 mole) was stirred with 2 l. benzene. The reaction was flushed with N_2 and carefully warmed to avoid rapid and uncontrollable liberation of CO_2. It was then refluxed for 2 hr and excess ethylene glycol added. The mixture was diluted with water and washed several times with dil nitric or perchloric acid to remove all salts. The benzene was removed after drying. Distillation yielded 33 g ethyl ε-heptenoate boiling at 88–88·5° at 23 mm. Ethyl ε-heptenoate (30 g, 0·19 mole) was added to a soln of 11 g KOH in 300 ml water and 75 ml EtOH. The 2-phase mixture was stirred at room temp until the ester disappeared (72 hr) and then poured into excess water, acidified and extracted with ether. ε-Heptenoic acid (23 g) boiled at 82–84° at 1·5 mm. It was not contaminated with heptanoic acid.

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