

Recrystallization of the dark yellow residue from ether and again from carbon tetrachloride yielded white needles, identified as *trans*-4,4'-dimethylstilbene, m.p. 177–179° (lit.³⁰ m.p. 180°).

V.p.c. of the distillate on a 0.25 in. × 8 ft. column, 20% QF-1 on Gas-Chrom R (Aerograph, A-90-P; injector, 185°; column, 128°; He flow, 60 cc./min.) indicated that about 85% of this material consisted of two high-boiling components, retention times 39 and 47 min., respectively. A small impurity, manifested as a shoulder on the trace of the longer retention time product was presumably a bromide. Treatment of the distillate with 2 *N* ethanolic silver nitrate removed this impurity. The impurity could also be cleanly separated on capillary v.p.c. (see below). The high-boiling components were trapped separately and identified *via* n.m.r. spectroscopy (see Table I). The *syn* isomer had the shorter retention time.

Anal. Calcd. for C₁₄H₂₀ (188.31): C, 89.29; H, 10.70. Found: C, 89.34; H, 10.88.

Other cyclopropanes synthesized *via* reaction 1 above were prepared as just described, with the following exceptions. Addition to propene was carried out at –50°, and additions to isopropylethylene, 1-butene, and *trans*-butene were carried out at –10°. Because all other cyclopropanes had shorter retention times than the *t*-butyl isomers, the bromide impurity did not interfere with v.p.c. isolation. Boiling points, yields, and analyses are collected in Table V. The 1-aryl-2-ethylcyclopropanes and 1-aryl-2,3-*trans*-dimethylcyclopropane have been described previously.² All preparative v.p.c. was done on the QF-1 column described above. Under the indicated conditions,

TABLE V
CYCLOPROPANES FROM 1-ALKENES AND
p-METHYLBENZAL BROMIDE

Olefin	B.p., °C. (mm.)	Yield, %	Calcd., %		Found, %	
			C	H	C	H
Propene	37 (0.4)	37	90.35	9.65	90.41	9.89
Isopropyl- ethylene	45–50 (0.5)	48	89.59	10.41	89.41	10.44
<i>t</i> -Butyl- ethylene	62 (0.5)	28	89.29	10.70	89.34	10.88

(30) "Chemistry of Carbon Compounds," Vol. III^B, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1956, p. 1145. The *trans* stereochemistry is supported by the strongly deshielded vinyl protons observable in the n.m.r. of this material, ca. τ 3; compare "High Resolution NMR Spectra Catalog," Vol. I, N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Ed., Varian Associates, Palo Alto, Calif., 1962, Spectra 305, 306.

syn-cyclopropanes had shorter retention times than their *anti* isomers.

Competition Experiments.—The procedure was similar to the synthetic procedure described above, except that mixtures of *trans*-butene and the requisite olefin were employed. All competitions were carried out with 0.4–0.5 g. of bromide or iodide starting material at –10°. Enough alkyllithium was added to achieve excess. *syn/anti* ratios and product ratios were determined on undistilled product by v.p.c. on a 150-ft. Apiezon L gelay column (Barber-Colman, Series 5000 chromatograph). The flame ionization detector was calibrated with mixtures of purified cyclopropanes. Relative rates were derived from the standard expression: $K_2/K_1 = (P_1/P_2)(O_2/O_1)$, where P_1/P_2 is the cyclopropane product ratio and O_2/O_1 represents the mole ratio of starting olefins. Olefin was present in at least 20-fold excess.

Authenticity of observed v.p.c. product ratios was established by spectral examination of trapped products and by control experiments which established that spurious products were not contributing to v.p.c. traces at cyclopropane retention times. In addition, product ratios generally showed good agreement whether obtained from separation on QF-1 or Apiezon L capillary v.p.c.

Controls. Product Stability.—Mixtures of purified adducts (*t*-butyl series) showed no change in composition on rechromatography. *syn-anti* ratios of prepared mixtures were unaltered by treatment with excess alkyllithium reagents. Product ratios were also identical whether stoichiometrically sufficient, insufficient, or excess alkyllithium was employed.

Isomerization of *syn*- to *anti*-1-*p*-Tolyl-2-butylcyclopropane.—A mixture of *syn*- and *anti*-cyclopropanes, 35 mg., trapped from the QF-1 column, was sealed into an ampoule with 1.2 ml. of 2 *N* potassium *t*-butoxide in dimethyl sulfoxide. The ampoule was kept in an oil bath at 102° for 23 hr. The ampoule was broken into water (30 ml.), and the resulting liquid was extracted three times with 10-ml. portions of ether. Combined ether was dried and stripped. V.p.c. of the residue showed only one product, identical in retention time with *anti*-1-*p*-tolyl-2-*t*-butylcyclopropane. Trapping of this material and comparison of n.m.r. spectra verified this identity. Similar isomerization of pure *syn*-cyclopropane also led only to *anti* product. Isomerizations in the isopropyl adduct series, starting from pure *syn*-1-*p*-tolyl-2-isopropylcyclopropane, gave 90% *anti*-cyclopropane after 3 days. Equilibrium may not have been reached, however.

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Formation of Alkyl Halides from Acids by Decarboxylation with Lead(IV) Acetate and Halide Salts

JAY K. KOCHI

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

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Halide salts induce the rapid decarboxylation of Pb^{IV} esters. Alkyl halides, particularly chlorides, are formed in excellent yields. This method of halodecarboxylation offers a convenient synthesis of alkyl halides from carboxylic acids. Unlike the classic Hunsdiecker reaction, it is applicable to secondary and tertiary acids. Cyclobutyl and neopentyl moieties are converted to the corresponding chlorides with no rearrangement. Decarboxylation by this method is strongly inhibited by oxygen. A free-radical mechanism is proposed which includes alkyl radicals and Pb^{III} species as intermediates. Halodecarboxylation with halide is compared with oxidative decarboxylation conducted with pyridine or acetate under comparable conditions. Similarities in the mechanisms of the two reactions are discussed with respect to electron transfer and ligand transfer in the propagation steps. Halodecarboxylation of Pb^{IV} esters with halide salts is also compared with the photochemically induced and thermal reactions with halogen (iodine).

Lead tetraacetate can be conveniently employed to effect decarboxylations of acids. The products of oxidation are generally alkenes and esters.¹ For example,

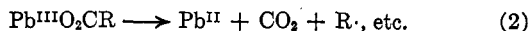
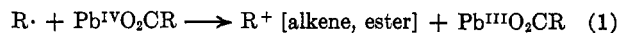
(1) For leading references, see W. H. Starnes, *J. Am. Chem. Soc.*, **86**, 5603 (1964); R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. 2, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, p. 368 ff; W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

α -methylbutyric acid is converted to a mixture of butenes and *sec*-butyl acetate and α -methylbutyrate.² Cyclohexanecarboxylic acid is oxidized to cyclohexene and cyclohexyl acetate and cyclohexanecarboxylate. Predominantly *exo*-norbornyl acetate has been ob-

(2) J. K. Kochi, *ibid.*, **87**, 1811 (1965).

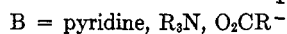
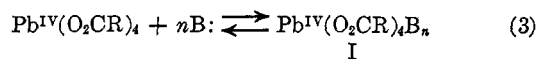
tained from both *endo*- and *exo*-norbornane-2-carboxylic acid.³

Oxidative decarboxylations of valeric, isovaleric, and α -methylbutyric acids are inhibited by oxygen and promoted by valeryl peroxide.² Free alkyl radicals have been shown to be prime and vital intermediates in these reactions. A radical-chain mechanism has been proposed, which includes Pb^{III} species as metastable intermediates. The relevant sequence of *propagation* steps in the chain sequence² is given by eq. 1 and 2.⁴ Skeletal rearrangement and racemization of alkyl



moieties have been observed, and carbonium ions have been postulated as intermediates (*cf.* eq. 1).¹⁻³

In benzene solutions the decarboxylation is induced by acetate salts as well as bases such as pyridine and trialkylamines.⁵ The catalysis by these nucleophilic reagents has been attributed to the formation of highly coordinated Pb^{IV} species such as I.² It has



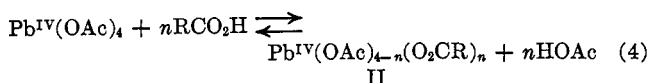
been suggested that complexes such as I are more labile to homolysis than the parent Pb^{IV} esters.² Initiation of the free-radical chain process is facilitated in this manner.

This speculation is subject to experimental validation. A variety of nucleophilic reagents other than nitrogen bases and carboxylate anions are available. If the mechanism postulated previously is tenable, general catalysis by nucleophiles should be obtained.

Indeed, it has been found that halides, as well as thiocyanate and cyanide as anions, initiate rapid decomposition of Pb^{IV} esters. The products from the reaction of Pb^{IV} esters and halides are alkyl halides, which in most cases are formed in excellent yields. *Halodecarboxylation* of acids by this method appears to be a useful synthetic method for the preparation of alkyl halides, particularly chlorides. In this paper, we are primarily concerned with delineating the mechanism of the reaction of Pb^{IV} esters with halide salts as it pertains generally to the decarboxylation of Pb^{IV} esters. Though representative conditions for the reaction have been explored, optimum qualifications for the synthesis of alkyl halides by decarboxylation of acids have not been scrutinized.

Results

Lead tetraacetate is insoluble in benzene. Its solubility is enhanced greatly by many carboxylic acids, probably by metathesis (eq. 4) to form mixed esters such as II.⁶ Pb^{IV} esters are readily hydrolyzed and,



(3) E. J. Corey and J. Casanova, *J. Am. Chem. Soc.*, **85**, 165 (1963).

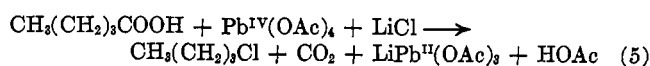
(4) No consistent attempt will be made to include all the coordination around the Pb atom, except when it is pertinent to the discussion. Pb^{IV} can show tetrahedral, octahedral, and, supposedly, dodecahedral coordination.

(5) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

(6) *Cf.* (a) E. A. Evans, J. L. Huston, and T. H. Norris, *J. Am. Chem. Soc.*, **74**, 4985 (1952); (b) see also G. B. Bachman and J. W. Wittman, *J. Org. Chem.*, **28**, 65 (1963).

unless extreme care is exercised to maintain anhydrous conditions, benzene solutions acquire a light yellow coloration. The latter is minimized by the addition of excess acid.

Except in specific examples, benzene solutions of Pb^{IV} esters such as II are moderately stable at reflux temperatures. If lithium chloride is added, a rapid evolution of carbon dioxide ensues, even though the solubility of the salt in this medium is low. For example, a 1.7 *M* solution of valeric acid and 0.4 *M* Pb^{IV} acetate at 81° requires greater than 48 hr. for complete decomposition. The addition of 105 mole % of LiCl causes rapid decomposition, and the decarboxylation is complete within 30 min. One mole of carbon dioxide is liberated. *n*-Butyl chloride is formed in 90–95% yield together with methyl chloride (4%) and butene-1 (<1%).⁷ Pb^{II} salts (acetate and valerate) are also formed, but they have not been determined quantitatively. The stoichiometry of the reaction given by eq. 5 is suggested.



The completion of the reaction is characterized by a change in color from yellow to completely colorless. This provides a sensitive method of determining the presence of unreacted Pb^{IV} species (partially hydrolyzed), since the latter even in low concentrations lend a yellow cast to the reaction mixture. In many cases the completed reaction mixture is heterogeneous owing to precipitated Pb^{II} salts. If excess acid is used, the latter can be kept in solution. Extra acid can be replaced with acetic acid if the acid to be decarboxylated is secondary or tertiary (*vide infra*).

The decomposition is sensitive to oxygen. If this contaminant is not removed by sweeping the reaction mixture with an inert gas, the decomposition is much slower. Moreover, the decarboxylation of valeric acid induced by chloride ion can be interrupted instantaneously by deliberate addition of oxygen. The inhibition is not easily removed until the oxygen is purged from the system. The yield of butyl chloride is slightly diminished under these conditions.

The success of the halodecarboxylation is dependent on the amount and the nature of ionic halide added. Although LiCl has limited solubility in benzene, the addition of more than a stoichiometric amount causes a progressive lowering of the yields of butyl chloride (Table I). Optimum conditions require 1 equiv. of LiCl/mole of Pb^{IV} acetate employed. If 4 equiv. is used, the yield of alkyl chloride from valeric acid is nil and copious amounts of chlorine are released. If less than 1 equiv. of LiCl is employed, the reaction proceeds smoothly until the chloride is consumed and stops. The utilization of chloride under these conditions to effect chlorodecarboxylation of valeric acid is >95%. Once the chloride is consumed, the decomposition of the remaining Pb^{IV} ester proceeds at the slower rate characteristic of oxidative decarboxylation. Butane is formed from valeric acid in the latter case, but in runs employing an excess of LiCl no significant amounts of butane are produced (butene-1 is often found in trace amounts).

(7) Unless specified otherwise, all yields are based on Pb^{IV} acetate.

TABLE I
CHLORODECARBOXYLATION OF VALERIC ACID WITH
CHLORIDE SALTS^a

Valeric acid, mequiv.	Chloride, mequiv. ^b	Methyl chloride, % ^c	Butyl chloride, % ^c	Butene-1, %
39.6	10.4 LiCl	1.5	71	...
39.6	4.8 LiCl	1.0	96	...
19.6	20.4 LiCl	0	4 ^d	...
19.6	10.4 LiCl	2.5	63	...
19.6	4.8 LiCl	3.7	93	0.6
19.6	2.2 LiCl	3.3	94 ^e	2 ^e
9.2	4.8 LiCl	...	87	...
4.6	10.4 LiCl	10	56	f
4.9	4.8 LiCl	...	68	...
19.6	6.9 NaCl	...	97	...
9.8	6.9 KCl	...	85	...
19.6	9.3 CaCl ₂	1.5	74	0.7
19.6	9.1 CuCl ₂	1.8	40	15
19.6	4.5 (CH ₃) ₄ NCl	9.2	63	3
19.6 ^g	8.1 LiCl	...	84	...
19.6 ^h	7.5 LiCl	6	71	1
19.6 ⁱ	7.2 LiCl	...	79	...

^a In benzene (10 ml.) and 4.5 mequiv. of Pb^{IV} acetate at 81°. ^b Based on chloride. ^c Yield based on Pb^{IV} acetate, unless stated otherwise. ^d Traces of chlorobenzene in addition to large indeterminate amounts of chlorine. ^e Butane. ^f Traces of chlorobenzene. All yields are based on g.l.p.c. analyses. ^g 50:50 v./v. hexane-benzene. ^h Acetonitrile. ⁱ Inhibited by oxygen.

Among chlorides examined, the soluble tetramethylammonium chloride affords the lowest yield of butyl chloride. The highly insoluble potassium and sodium chlorides give the best yields. The latter salts require longer heating for complete reaction than lithium chloride, owing largely to insolubility. The surface of the crystals of LiCl immersed in a benzene solution of Pb^{IV} ester acquire a yellow color even at room temperature. Similarly, a solution of tetramethylammonium chloride and Pb^{IV} ester is yellow. Chlorine can be detected with a moist starch-iodide paper held over the solution. The highly insoluble KCl and NaCl do not show any appreciable change in this manner, and the stoichiometric ratios of chloride to Pb^{IV} ester are not a critical problem. A large flocculent mass of precipitate is formed both with calcium and cupric chlorides. The latter mixture is especially intractable, and stirring becomes difficult. A relatively high yield of butene-1 is formed under these conditions.

The conversion of Pb^{IV} acetate to butyl chloride increases with the amount of valeric acid charged. At a 9:1 mole ratio of acid to Pb^{IV} acetate an almost quantitative yield of butyl chloride is formed. The side product, methyl chloride from acetate, is minimum (<1%) under these conditions. At a 1:1 mole ratio the yield of butyl chloride falls to 68% and methyl chloride increases to 10%. If high conversion of the acid is required, it is possible to use excess Pb^{IV} acetate in conjunction with acetic acid. Though methyl chloride can be easily separated, the problem is compounded by the competitive formation of chlorine.

Pb^{IV} acetate with acetic acid and LiCl in benzene is decomposed to methyl chloride in poor yields (40-60%). Chlorine is a major side product which disappears during the course of the reaction by reacting with acetic acid, methyl chloride (methylene chloride), and benzene. Chlorobenzene is formed as a minor side product (1-3%) from the latter. Its yield gener-

ally increases with chloride content of the reaction mixture, and is most important with acetic and primary acids.

The importance of chlorine in these side reactions diminishes as one proceeds from acetic to primary acids and disappears with secondary and tertiary acids. For these reasons, it is preferable to recycle the recovered primary acid to obtain maximum utilization of the acid. For synthetic purposes, however, recycling is inconvenient and excess Pb^{IV} acetate can be employed. In such cases a relatively mild chlorine scavenger such as isohexane should also be added to minimize further chlorination of the product.

In addition to benzene as solvent, acetonitrile and hexane-benzene mixtures can be used. The effect of solvent has not been examined, and it appears that there are potentially a variety of others available. No particular precaution is exercised to remove adventitious moisture from the solvents or reagents. A high yield of *n*-butyl chloride obtained in benzene was not lowered significantly when a small amount of water was accidentally added.

The accompanying methyl chloride and chlorobenzene serve as convenient internal monitors for qualitatively evaluating the rates of chlorodecarboxylation of various acids. The relative order of rates obtained in this manner is methyl << primary < secondary, tertiary. In general, the yields of alkyl chlorides from secondary and tertiary acids are excellent (Table II). Competition from the decarboxylation of acetic acid and the chlorination of benzene is insignificant. Pb^{IV} acetate, α -methylbutyric acid, and LiCl added in stoichiometric amounts afford *sec*-butyl chloride in approximately 90% yield. Similar high yields are obtained with cyclohexanecarboxylic acid. Small amounts of acetic acid added to keep some of the Pb^{II} salts in

TABLE II
ALKYL CHLORIDES FROM DECARBOXYLATION OF ACIDS
WITH Pb^{IV} ACETATE AND LITHIUM CHLORIDE^a

Carboxylic acid (mequiv.)	Methyl chloride,		Alkyl chloride	Yield, % ^b
	LiCl, mequiv.	% ^b		
Acetic (70)	10.1	55	c	...
α -Methylbutyric (39)	10.3	0	<i>sec</i> -Butyl	94
α -Methylbutyric ^d (4.5)	4.7	4.4	<i>sec</i> -Butyl	89
α -Methylbutyric ^d (4.5)	4.7	3.7	<i>sec</i> -Butyl	87
Isovaleric (19)	7.7	3.2	Isobutyl	77
Isovaleric (19)	4.8	...	Isobutyl	99
Isobutyric (11)	6.2	<0.1	Isopropyl	98
β,β -Dimethylbutyric (7.7)	6.2	5	Neopentyl	86
β,β -Dimethylbutyric (7.9)	6.3	6.5	Neopentyl	92
Cyclobutanecarboxylic (11)	6.2	0.7	Cyclobutyl	100
Cyclobutanecarboxylic ^e (10)	6.7	...	Cyclobutyl	75
Pivalic (9.5)	6.3	0	<i>t</i> -Butyl ^f	69
Pivalic (14)	4.7	0	<i>t</i> -Butyl ^g	65
Pivalic ^h (4.9)	4.7	1.6	<i>t</i> -Butyl ⁱ	58
Pivalic ^j (5.3)	5.5	1.6	<i>t</i> -Butyl ^k	65
α,α -Dimethylbutyric (17)	6.6	0	<i>t</i> -Amyl ^l	91
Cyclohexanecarboxylic (15)	6.4	0	Cyclohexyl	100
Cyclohexanecarboxylic ^f (4.6)	4.7	...	Cyclohexyl	92
Allylacetic (9.8)	6.9	...	4-Chlorobutene-1	~2 ^m
Benzoic (13)	6.7	58	Chlorobenzene	8

^a In benzene (10 ml.) and 4.5 mequiv. of Pb^{IV} acetate at 81°. ^b Based on Pb^{IV} acetate. ^c 2% methylene chloride, 3% chlorobenzene, and indeterminate amounts of chlorine. ^d 16 mequiv. of HOAc and 5 mequiv. of water were also added. ^e In acetonitrile solvent. ^f In addition to 7% isobutylene. ^g 6.5% isobutylene. ^h 33 mequiv. of HOAc was also added. ⁱ 1.3% isobutylene. ^j 16 mequiv. of HOAc was also added. ^k 2.3% isobutylene. ^l Approximately 2% each of 2-methylbutene-1 and 2-methylbutene-2 were also formed. ^m Other products were unidentified.

solution do not decrease the yields of cyclohexyl and *sec*-butyl chlorides materially.

Tertiary acids such as pivalic and α,α -dimethylbutyric form the corresponding chlorides in good yields. Small amounts of isobutylene and 2-methylbutenes, respectively, accompany the tertiary chlorides. They probably result from the subsequent dehydrochlorination of the products.

Among the acids examined no evidence for rearrangement of the alkyl moiety has been found. Thus, β,β -dimethylbutyric acid affords only neopentyl chloride. No *t*-amyl chloride or 2-methylbutenes can be found. Similarly, cyclobutanecarboxylic acid gives excellent yields of cyclobutyl chloride, and no cyclopropylmethyl or allylcarbinyl chloride can be detected.

Benzoic acid gives only poor yields of chlorobenzene. Methyl chloride is the principal product. Other aromatic acids are being examined. The unsaturated allylacetic acid produces only traces of allylcarbinyl chloride. No cyclobutyl or cyclopropylmethyl chloride is apparent. The principal course of this reaction has not yet been elucidated.

Decarboxylation to alkyl bromides and iodides can also be effected with bromide and iodide salts. Isobutyric acid and LiBr afford isobutyl bromide in 50–60% yields. The formation of bromine is apparent in the initial stages, and during the course of the reaction it disappears. Large amounts of iodine are produced from Pb^{IV} acetate and KI and the yields of isopropyl iodide are low. The latter is not surprising in view of the iodometric procedure for the analysis of Pb^{IV} acetate. In these reactions, no attempt was made to protect the mixture from extraneous light.

Discussion

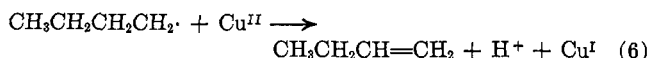
The reduction of Pb^{IV} esters to Pb^{II} esters and alkyl chlorides is induced by halide salts in a remarkable manner. The effect of these salts is more pronounced than that by pyridine or lithium acetate. They compare with cyanide and thiocyanate in their effectiveness. Iodide qualitatively reacts faster than bromide, and bromide faster than chloride. The rates are not significantly different to merit further comment at this stage, especially because of differences in solubility. If one considers that salts [except (CH₃)₄NCl] are rather insoluble in benzene, the facile reactions are all the more remarkable. Kinetic studies under these conditions are difficult to interpret and are of limited value.

Though pyridine, acetate, halides, thiocyanate, and cyanide as nucleophiles all effect rapid decarboxylation of Pb^{IV} esters, they do not lead to the same products. Pyridine and acetate effect oxidative decarboxylation. The halides⁸ cause halodecarboxylation. The products from the decomposition induced by thiocyanate and cyanide have not yet been examined.

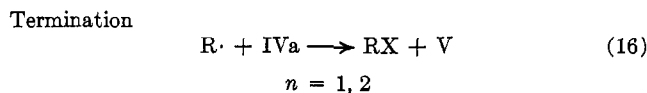
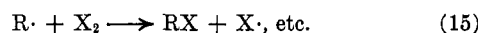
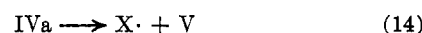
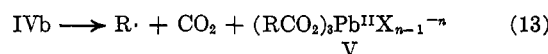
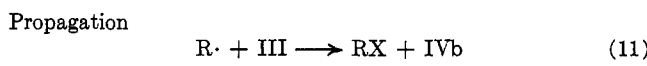
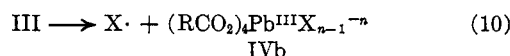
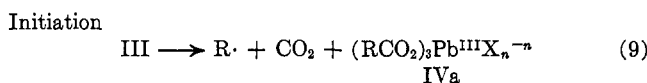
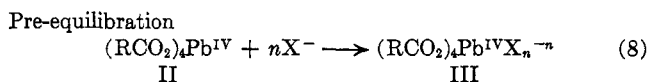
It is clear that all of these nucleophiles cause decarboxylation of the carboxylate moiety since copious amounts of carbon dioxide are evolved. In a series of acids the ease of decarboxylation can be determined by following the loss of carbon dioxide. The same order of reactivity is found for both oxidative and

halodecarboxylation. It is benzoic < acetic < primary < secondary, tertiary acids.

Both oxidative decarboxylation and halodecarboxylation are sensitive to oxygen and are easily inhibited by this ubiquitous adulterant. It has been shown that free alkyl radicals are the prime intermediates in the former reaction. Free radicals also appear to be principal intermediates when metal halides are employed. Thus, butane as a minor product from valeric acid, Pb^{IV} acetate, and LiCl is derived from butyl radical by hydrogen abstraction from solvent. As expected, it is formed in the largest amount when a deficit of chloride is added. The yield of butene-1, usually found in trace amounts, is greatly enhanced when cupric chloride is employed in a highly heterogeneous system.⁹ Butyl radicals are known to be readily oxidized by cupric carboxylates to butene-1.¹⁰



Except for the addition of halide salt and shorter time for reaction, the halodecarboxylation is conducted under essentially the same conditions as those for oxidative decarboxylation. We propose that halodecarboxylation proceeds *via* a free-radical chain mechanism.¹¹ The sequence of reactions presented in eq. 8–16 is similar to that proposed for oxidative decarboxylation. In addition to free alkyl radicals, Pb^{III} species are considered as metastable intermediates.¹²

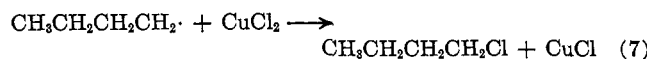


The radical-chain decarboxylation is *initiated* by homolysis of a Pb^{IV} species II and greatly promoted by the more labile complex III (*i.e.*, I, B = X⁻ = halide). The lability of complexes such as III is con-

(9) Butyl radicals are generally oxidized preferentially to butyl chloride by a mixture of cupric acetate and chloride. However, under conditions in which cupric chloride is insoluble, and in the presence of excess valeric acid (which yields benzene-soluble cupric salts), the oxidation of butyl radicals by cupric chloride may be relatively slow.

(10) H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).

(11) Of the halide salts examined, only cupric chloride presents the dual possibility that butyl chloride is formed from butyl radical by oxidation with cupric chloride as well as Pb^{IV} esters (*vide infra*).



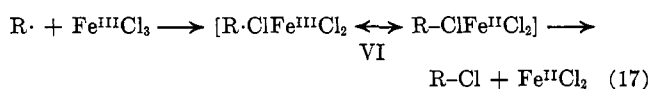
(12) Pb^{III} species as intermediates in Pb^{IV} acetate oxidations has been discussed.

(8) Fluoride salts are under investigation.

sistent with the effect of acetate and pyridine in oxidative decarboxylations and of cyanide and thiocyanate as discussed earlier.

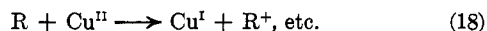
The *propagation* sequence suggested by eq. 11 and 13 is similar to that proposed for oxidative decarboxylation (eq. 1 and 2). The selectivity in the decarboxylation of acids is obtained in the fragmentation step (13). It is considered to occur by two-bond cleavage of a Pb^{III} ester to generate an alkyl radical, carbon dioxide, and Pb^{II} salts simultaneously. Such a multibond cleavage which derives part of its driving force from the stability of the alkyl radical has been delineated.² The ease of formation of the radical generally follows the order: phenyl < methyl < primary alkyl < secondary and tertiary alkyl. It parallels the order obtained in decarboxylations of Pb^{IV} esters.

The pertinent difference between the mechanism for oxidative decarboxylation and halodecarboxylation is attributable primarily to the complexation of the *oxidation step* (11). We propose that the halogen-containing Pb^{IV} species such as III function as *ligand-transfer* oxidants. Ligand transfer as a mode of oxidation of alkyl radicals by metal halides (eq. 17), especially ferric and cupric halides, has received extensive documentation.¹³



In a ligand-transfer process the direct transference of an atom or radical moderates the development of changes in the transition state such as VI (eq. 17). Rearrangement of the alkyl radical is not commonly observed. Thus, cyclobutyl and neopentyl radicals are converted by ligand-transfer oxidation with cupric chloride to cyclobutyl and neopentyl chlorides largely without rearrangement.¹⁴

An alternative mode of oxidation of an alkyl radical has been described as *electron transfer*.¹⁵ Cyclobutyl and neopentyl radicals undergo facile oxidation by electron transfer with cupric acetate to produce a mixture of extensively rearranged products.^{14,15}



The concepts of *electron transfer* and *ligand transfer* can be employed to reconcile the two decarboxylative methods by a single unifying mechanism. Free alkyl radicals are postulated as important intermediates in both reactions. In *halodecarboxylations* the chain sequence involves a *ligand-transfer* oxidation of the alkyl radical (eq. 11). In *oxidative decarboxylations*, Pb^{IV} esters such as II effect oxidation of alkyl radicals by *electron transfer* (eq. 1). The latter involves the formation of carbonium ions which undergo subsequent rearrangement, elimination, or solvation. Thus, butyl, isobutyl, cyclobutyl, neopentyl, and 2-norbornyl groups all afford products of rearrangement during oxidative decarboxylation. Ligand transfer with the halogen-containing Pb^{IV} oxidant III produces only neopentyl and cyclobutyl chlorides from their parent acids by halodecarboxylation. However, a variety of other

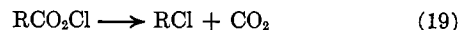
acids, which contain alkyl groups more prone to rearrange cationically, should be examined before the charge requirements on the alkyl moiety in the transition state can be fully established in halodecarboxylations. Nonetheless, there is no doubt that free radicals generated in this reaction are not oxidized to carbonium ions of the type encountered in oxidative decarboxylations.

The formation of alkyl chlorides is favored over esters even in the presence of 1 equiv. of halide and excess carboxylic acid. If the mechanism as postulated is operative and two modes of oxidation of the intermediary alkyl radicals are involved, the results imply that one (*viz.*, ligand transfer) proceeds more readily than the other.¹⁶

Among other metal systems examined, ligand transfer involving chloride and bromide is usually faster than the corresponding electron-transfer process. Quantitative results for both reactions are not yet available. Both reactions are facile with cupric oxidants.¹⁷ For example, the oxidation of butyl radical to butene-1 by cupric acetate is estimated to have a second-order rate constant of 10^7 – 10^8 l./mole sec. at 40° . The ligand-transfer rate is at least as fast. Ferric oxidants provide facile reaction as halides,¹⁸ but are rather ineffective as electron-transfer agents.¹⁹

Pb^{IV} esters, on this basis, resemble Fe^{III} species. They oxidize normal alkyl radicals comparatively slowly to alkenes and esters. Electron-transfer oxidation of alkyl radicals by Pb^{IV} esters is synthetically practical only with the more easily oxidized secondary and tertiary alkyl moieties.² Moreover, alkanes are often by-products from a competing hydrogen-transfer reaction even with secondary radicals. It is not unlikely that ligand-transfer oxidation of alkyl radicals by Pb^{IV} species III is much faster than electron-transfer oxidation by Pb^{IV} species II. In this manner, the high yields of alkyl chlorides can be explained within the scope of a common mechanism.

Attractive as it appears, there are alternatives to a common mechanism for oxidative decarboxylation and halodecarboxylation. Probably the most important of these involve acyl hypohalites as intermediates, which are known to decarboxylate readily to



alkyl chlorides.²⁰ Direct isolation of most acyl hypohalites has not been possible; they have been postulated as intermediates in the Hunsdiecker reaction²¹ and the reaction of peroxides with halide salts.²² Under conditions of halodecarboxylation with Pb^{IV} esters, reactions such as 20–22 can be written.

(16) J. K. Kochi and D. M. Mog, *ibid.*, **87**, 522 (1965).

(17) R. V. Subramanian, unpublished results.

(18) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **58**, 1212 (1962); J. Betts, F. S. Dainton, and K. J. Ivin, *ibid.*, **58**, 1203 (1962).

(19) Cf. W. Cooper and W. H. T. Davison, *J. Chem. Soc.*, 1180 (1952), and M. S. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1322 (1958), with ref. 10.

(20) W. Bockmuller and F. W. Hoffman, *Ann.*, 165 (1935); see also M. Anbar and D. Ginsberg, *Chem. Rev.*, **54**, 965 (1954).

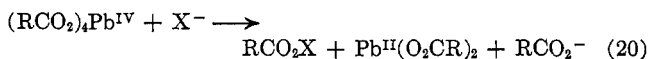
(21) (a) R. G. Johnson and R. K. Ingham, *ibid.*, **56**, 219 (1956); (b) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957); (c) S. J. Cristol and W. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961); **27**, 2711 (1962); (d) J. A. Davis, *et al.*, *ibid.*, **30**, 415 (1965).

(22) J. K. Kochi, B. M. Graybill, and M. Kurz, *J. Am. Chem. Soc.*, **86**, 5257 (1964); J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).

(13) (a) C. H. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957); (b) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); **84**, 2124 (1962); (c) J. Kumamoto, H. DeLaMare, and F. F. Rust, *ibid.*, **82**, 1935 (1960).

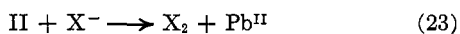
(14) J. Kochi and H. Mains, unpublished results.

(15) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).



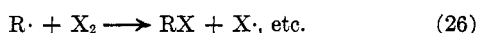
A mechanism involving reaction 21 followed by 19 is discounted since it does not account for oxygen inhibition. The role of halogen and halogen atoms as key intermediates is more difficult to dismiss. There is no doubt that chlorine is formed when chloride is added to a solution of Pb^{IV} ester in benzene. It is the principal product from valeric acid when excess LiCl is used and little chlorodecarboxylation is obtained. The reaction of Pb^{IV} acetate and LiCl produces appreciable amounts of chlorine, whereas the more easily decarboxylated acids give little indication of being adversely affected by chlorine production. A decrease in yield of alkyl halide and concomitant increase in halogen follows the sequence: $\text{I} > \text{Br} > \text{Cl}$. Iodine production is quantitative from Pb^{IV} acetate and KI .²³

Chlorine disappears by chlorination of the acid, benzene, or even the alkyl chloride (*vide supra*). The formation of bromine in the early stages of the reaction is easily seen, and it disappears by bromination of the acid. Iodine once formed is largely unreacted. Halogen, thus, appears to be a side product which is formed by reactions such as 10 and 12, or an ionic reaction such as 23. The importance of such reactions is prob-



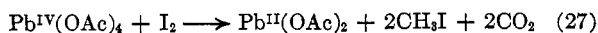
ably related to the oxidation potential and nucleophilicity of X^- (*vide infra*).²⁴

A chain sequence involving chlorine and chlorine atom as chain carriers can be constructed (eq. 24–26).



However, we find that chlorine has a deleterious effect on the halodecarboxylation of cyclohexanecarboxylic acid. Only low yields of cyclohexyl chloride were produced when chlorine was bubbled through a solution of Pb^{IV} acetate, cyclohexanecarboxylic acid, and LiCl in refluxing benzene. The Pb^{IV} -catalyzed decarboxylation of acids with chlorine was not achieved, and the principal product was chlorobenzene. The effect of light was not examined.

In many respects, the halodecarboxylation conducted with halide salts is similar to the reaction using *halogen* (iodine).²⁵ The latter is induced photochemically and the stoichiometry has been given as eq. 27. Barton



and Serebryakov²⁵ postulated acyl hypoiodites as intermediates. Although iodine is the reagent, a Hunsdiecker mechanism cannot be operative since Pb^{IV} is reduced to Pb^{II} . The need for irradiation is suggestive of a radical-chain process such as 24–26, with the photodissociation of iodine as the initiating step.

(23) R. C. Hockett and W. S. McClenahan, *J. Am. Chem. Soc.*, **61**, 1667 (1939).

(24) Cf. J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962); J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).

(25) D. H. R. Barton and E. P. Serebryakov, *Proc. Chem. Soc.*, 309 (1962); *J. Chem. Soc.*, 2438 (1965).

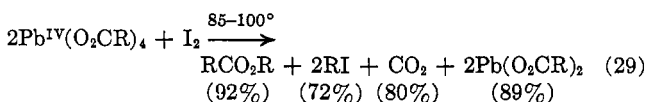
The mechanisms presented in eq. 8–16 and eq. 24–26 are not necessarily incompatible. They are complementary in that some common steps and intermediates occur. In the *halogen* reaction the importance of hypoiodite as intermediate may be related to eq. 24. The reduction of Pb^{IV} species is probably more likely to occur with I than Cl owing to the lower ionization potential of the former.²⁶ Furthermore, *halides* destroy hypohalites (eq. 28). The *halogen* reaction, therefore,



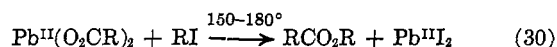
is more likely to lead to decarboxylation of this intermediate (eq. 19).

The same principle can be applied to explain the low yields of alkyl iodides in the *halide* reaction. The chain sequence requires that homolysis of a Pb^{IV} species III liberates an alkyl radical (eq. 9) rather than an halogen atom. With iodide salts, the latter may be a significant competing reaction.

A simultaneous formation of ester and alkyl iodide has recently been reported by Bachman and Wittman.^{6b} The distribution between ester and alkyl iodide is a function of temperature. At 85–105° and without deliberate irradiation, Pb^{IV} palmitate reacted according to eq. 29. At higher temperatures (150–180°), alkyl



iodides were converted to esters by a further reaction (30). Though they disfavored a free-radical process,



pentadecane ($\text{R}-\text{H}$, 0.19 mole/mole of acid) was found when the reaction was conducted with a deficit of iodine ($\text{Pb}^{\text{IV}}/\text{I}_2 = 4$). No dimeric hydrocarbon could be detected.

Superficially, it appears that ester and alkyl iodide can be formed by common oxidative processes as discussed earlier. Such an explanation is unlikely, however, since palmitic acid (being a primary acid) is expected to produce ester by oxidative decarboxylation only poorly.²⁷ Until additional studies are completed, further comparisons are unfruitful.

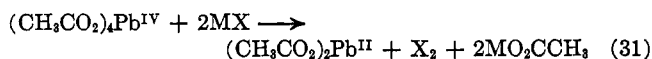
Conclusions.—The decarboxylation of Pb^{IV} esters is induced by a variety of nucleophilic reagents. Halides produce alkyl halides (halodecarboxylation) in contrast to ester by acetate and pyridine (oxidative decarboxylation). Both reactions show similar acid selectivities and behavior toward oxygen inhibition. A common radical-chain mechanism can be written which includes alkyl radicals and Pb^{III} species as intermediates. According to this proposal, the difference arises mainly in the nature of the propagation step: alkyl radicals are oxidized by *electron transfer* in oxidative decarboxylation and by *ligand transfer* in halodecarboxylation.

Halodecarboxylation of an acid with Pb^{IV} acetate yields the corresponding alkyl halide and carbon di-

(26) If such an explanation were correct, it would predict that the reaction reported by Barton and Serebryakov²⁵ would be less effective with chlorine.

(27) Such a statement is based on the difficulty of oxidizing (eq. 1) a primary radical by Pb^{IV} species such as II. However, in the presence of iodine other Pb^{IV} or even Pb^{III} species capable of such oxidation may be present.

oxide as principal products (*cf.* eq. 5), and halogen as the major side product from a reaction such as eq. 31.



We postulate that propagation steps 11 and 13 constitute the major chain sequence by which alkyl halides are formed. The formation of halogen occurs by a series of related reactions such as 12 and 14. The relative importance of alkyl halides and halogens as products is dependent on the pool of available halide, the halogen being formed in higher amounts with increasing halide. The effect of increased halide is to enhance the (average) value of n in the haloacetato-Pb^{IV} complexes III. These higher halo-Pb^{IV} complexes may very well favor halogen formation (*via* eq. 12 and 14) at the expense of alkyl halide (*via* eq. 11 and 13).

Halodecarboxylations can also be effected with halogen (iodine) and Pb^{IV} esters. These photochemically and thermally induced reactions can be considered to involve similar and complementary reactions to those with halide (chloride). Chloride is synthetically useful in the halide reaction, and iodine is efficacious in the halogen reaction. It is possible to explain each qualitatively on the basis of the most desirable halogen moiety in the propagation steps.

Experimental Section

Materials.—*n*-Valeric, isovaleric, and α -methylbutyric acids were prepared as described previously. Pivalic acid (Enjay Chemical Co.), isobutyric acid (Fisher Certified), allylacetic acid (Peninsular ChemResearch), cyclobutanecarboxylic acid (K and K Laboratories), and cyclohexanecarboxylic acid (Eastman Organic Chemicals) were used after undergoing purification. α,α -Dimethylbutyric (b.p. 186–187°) and β,β -dimethylbutyric acids (b.p. 182–182.5°) were made by carbonation of the Grignard reagents from *t*-amyl chloride and neopentyl chloride, respectively. Every acid was redistilled and converted to its methyl ester with diazomethane and analyzed by gas chromatography for isomeric impurities.

Lead tetraacetate was prepared as described previously. Lithium chloride and lithium bromide (Mallinckrodt, Analyzed Reagent), tetramethylammonium chloride, (Eastman Organic Chemical, dried *in vacuo*), and benzene (Mallinckrodt Analyzed Reagent) were used as supplied.

n-Butyl, isobutyl, *sec*-butyl, and *t*-butyl chlorides were from Eastman Organic Chemicals. Neopentyl chloride (from gas phase photochlorination of neopentane) was kindly provided by Dr. L. Friedman. *t*-Amyl chloride was prepared from *t*-amyl alcohol and HCl. Cyclohexyl chloride and isopropyl chloride,

and iodide were also from Eastman Organic Chemicals. Cyclobutyl, allylcarbonyl, and cyclopropylmethyl chlorides were an authentic mixture kindly provided by Mr. J. Bayless.

General Procedure.—A weighed amount (2.0 g., 4.5 mequiv.) of Pb^{IV} acetate was added to a solution of carboxylic acid in benzene (10 ml.) in an apparatus described earlier. The mixture was stirred at room temperature until homogeneous. If anhydrous, the resulting solution was colorless. A weighed amount of halide salt was added and the mixture was immediately flushed with nitrogen or argon. The surface of the salt at room temperature rapidly achieved a yellow coloration with LiCl and CrCl₂. For facile decarboxylation, it was necessary to flush the solution carefully to remove oxygen. A freeze-thaw degassing was time consuming and did not yield results significantly different. The mixture was placed in a constant-temperature oil bath (81 ± 0.3°) and the rate of gas evolution was followed volumetrically. The induction period was very short and gas evolution followed apace.

In many cases the completed reaction consisted of a clear colorless solution and a colorless amorphous solid or second phase. Alkyl chloride did not seem to be occluded in this mass since simple decantation of the solution was sufficient to obtain the product. The solution was extracted with dilute aqueous perchloric acid, followed by a sodium carbonate wash, and dried over sodium sulfate.

The clear, colorless solution was analyzed by gas chromatography using an internal standard method. Isomeric halides were used as markers. No attempt was made to isolate the products in synthetic amounts. Infrared spectra were taken of samples of alkyl halide obtained by gas chromatography to authenticate the product. However, usually two gas chromatographic columns were used to check purity.

Neopentyl chloride and *t*-amyl chloride were resolved on a 15-ft. didecylphthalate on Chromosorb W-Bentone-HMDS column (neopentyl chloride, 16.5 min.; *t*-amyl chloride, 20.0 min.). Allylcarbonyl chloride (16.5 min.), cyclobutyl chloride (19.0 min.), and cyclopropylcarbonyl chloride (27.5 min.) were resolved on a 10-ft. Carbowax 400M on firebrick column. The isomeric butyl chlorides were easily separated on a didecyl phthalate or diethylene glycol succinate column.

Chlorobenzene (22.5 min.) and cyclohexyl chloride (29.0 min.) were separated on a 8-ft. SF-96 (silicone) on firebrick column at 120°. Methyl chloride was analyzed on a 15-ft. α -chloronaphthalene on firebrick column at room temperature. Ethyl chloride was used as an internal standard. The other gases, carbon dioxide, butane, and butenes, were separated on a 15-ft. Dowtherm (silicone) on firebrick column at 10° as described previously.

In order to check the yields of halides, the benzene solutions were heated with methanolic KOH in sealed tubes at 100°. The liberated chloride was analyzed by Volhard titration and gave results within 5% of the gas chromatographic values.

Acknowledgment.—The author wishes to thank the National Science Foundation for a generous grant which supported this work.